Nickel/Bis(oxazoline)-Catalyzed Asymmetric Kumada Reactions of Alkyl Electrophiles: Cross-Couplings of Racemic α-Bromoketones

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Supporting Information

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I. General Information

The following reagents were purchased and used without further purification: PhMgBr (3.0 M in Et₂O; Aldrich), 3,4-(methylenedioxy)phenylmagnesium bromide (1.0 M in toluene/THF, Aldrich), i-PrMgCl (2.0 M in Et₂O; Aldrich), NiCl₂·glyme (Strem), 1,2-dimethoxyethane (Fluka), and (R)-1 (Aldrich). (S)-1 was prepared according to a literature procedure.¹

HPLC analyses were carried out on an Agilent 1100 series system with Daicel CHIRALCEL ® columns or Daicel CHIRALPAK® columns (internal diameter 4.6 mm, column length 250 mm, particle size 5 µ).

All reactions were carried out in oven-dried glassware under an atmosphere of argon.

II. Preparation of α-Bromoketones

**General Procedure:** Bromine (10.0 mmol) was added to a solution of the ketone (10.0 mmol) in Et₂O (25 mL). The solution was stirred for 30 min (until the color of the solution changed from red to light-yellow). Then, the reaction was quenched with water (10 mL), and the mixture was diluted with Et₂O (25 mL). The organic layer was washed with a saturated solution of aqueous NaHCO₃ (30 mL), a saturated solution of aqueous Na₂S₂O₃ (30 mL), and brine (30 mL), and then it was dried over MgSO₄, filtered, and concentrated. The α-bromoketone was purified by flash chromatography on silica gel.

The yields have not been optimized.

2-Bromo-1-(3-chlorophenyl)propan-1-one [34911-51-8]. This compound was prepared according to the General Procedure from 1-(3-chlorophenyl)propan-1-one (1.69 g, 10.0 mmol). The product was obtained as a colorless oil (eluted with 30% CH₂Cl₂ in hexanes; 2.42 g, 94% yield).

¹H NMR (CDCl₃, 500 MHz) δ 7.99 (s, 1H), 7.90 (d, J = 8.0 Hz, 1H), 7.57 (d, J = 8.0 Hz, 1H), 7.44 (d, J = 8.0 Hz, 1H), 5.22 (q, J = 7.0 Hz, 1H), 1.90 (d, J = 7.0 Hz, 3H).

1-(4-(Benzyloxy)phenyl)-2-bromopropan-1-one [35081-45-9]. This compound was prepared according to the General Procedure from 1-(4-(benzyloxy)phenyl)propan-1-one (2.40 g, 10.0 mmol). The product was obtained as a crystalline white solid (eluted with 50% CH₂Cl₂ in hexanes; 3.0 g, 94% yield).

¹H NMR (CDCl₃, 500 MHz) δ 8.01 (d, J = 9.0 Hz, 2H), 7.44-7.39 (m, 4H), 7.37-7.33 (m, 1H), 7.03 (d, J = 9.0 Hz, 2H), 5.26 (q, J = 7.0 Hz, 1H), 5.15 (s, 2H), 1.89 (d, J = 7.0 Hz, 3H).
1-(Benzo[d][1,3]dioxol-5-yl)-2-bromopropan-1-one [52190-28-0]. This compound was prepared according to the General Procedure from 3,4-methylenedioxypropiophenone (1.78 g, 10.0 mmol). The product was obtained as a white solid (eluted with 50% CH₂Cl₂ in hexanes; 2.13 g, 82% yield).

\[ ^1H \text{ NMR (CDCl}_3, 500 \text{ MHz}) \delta 7.64 (d, J = 8.0 \text{ Hz}, 1H), 7.49 (s, 1H), 6.87 (d, J = 8.0 \text{ Hz}, 1H), 6.07 (s, 2H), 5.21 (q, J = 7.0 \text{ Hz}, 1H), 1.88 (d, J = 7.0 \text{ Hz}, 3H). \]

4-Azido-2-bromo-1-phenylbutan-1-one [950819-68-8]. This compound was prepared according to the General Procedure from 4-azido-1-phenylbutan-1-one (1.37 g, 7.30 mmol). The product was obtained as a colorless oil (eluted with 50% CH₂Cl₂ in hexanes; 1.81 g, 95% yield).

\[ ^1H \text{ NMR (CDCl}_3, 500 \text{ MHz}) \delta 8.03 (d, J = 8.0 \text{ Hz}, 2H), 7.62 (q, J = 8.0 \text{ Hz}, 1H), 7.51 (t, J = 8.0 \text{ Hz}, 2H), 5.32 (dd, J = 7.0, 6.0 \text{ Hz}, 1H), 3.64-3.60 (m, 2H), 2.40-2.35 (m, 2H). \]

3-Bromo-4-oxo-4-phenylbutyl acetate [139518-45-9]. This compound was prepared according to the General Procedure from 4-oxo-4-phenylbutyl acetate (1.70 g, 8.30 mmol). The product was obtained as a colorless oil (eluted with CH₂Cl₂; 2.23 g, 95% yield).

\[ ^1H \text{ NMR (CDCl}_3, 500 \text{ MHz}) \delta 8.04 (d, J = 8.0 \text{ Hz}, 2H), 7.61 (t, J = 8.0 \text{ Hz}, 1H), 7.51 (t, J = 8.0 \text{ Hz}, 2H), 5.28 (dd, J = 8.0, 6.0 \text{ Hz}, 1H), 4.30-4.27 (m, 2H), 2.58-2.53 (m, 1H), 2.46-2.43 (m, 1H), 2.05 (s, 3H). \]

2-Bromopentan-3-one [815-52-1]. Bromine (1.04 mL, 20.0 mmol) was added to a solution of pentan-3-one (1.72 g, 20.0 mmol) in Et₂O (50 mL). The solution was stirred for 30 min (until the
color of the solution changed from dark-red to light-yellow). Then, the reaction was quenched with water (20 mL), and the mixture was diluted with Et₂O (50 mL). The organic layer was washed with a saturated solution of aqueous NaHCO₃ (60 mL), a saturated solution of aqueous Na₂S₂O₃ (60 mL), and brine (60 mL), and then it was dried over sodium sulfate, filtered, and concentrated. The α-bromoketone was purified by flash chromatography on silica gel (eluted with 20% CH₂Cl₂ in hexanes), which afforded a colorless oil (2.97 g, 90% yield).

¹H NMR (CDCl₃, 500 MHz) δ 4.41 (q, J = 7.0 Hz, 1H), 2.90-2.83 (m, 1H), 2.63-2.57 (m, 1H), 1.76 (d, J = 7.0 Hz, 3H), 0.60 (t, J = 7.0 Hz, 3H).

3-Bromo-1-diazobutan-2-one [91226-68-5]. THF (50 mL) and 2-bromopropanoyl bromide (5.30 mL, 50.0 mmol) were added to a 250-mL round-bottom flask. The resulting solution was cooled to 0 °C, and then a solution of (trimethylsilyl)diazomethane in hexanes (2.0 M; 50 mL, 100 mmol) was added over 10 min. The solution was stirred for 3 h at room temperature, and then it was concentrated by rotary evaporation. The residue was purified by flash chromatography on silica gel (eluted with 30→50% EtOAc in hexanes), which afforded a colorless oil (7.26 g, 82% yield).

¹H NMR (CDCl₃, 500 MHz) δ 5.71 (s, 1H), 4.35 (q, J = 6.0 Hz, 1H), 1.81 (d, J = 6.0 Hz, 3H).

3-Bromo-1-phenylbutan-2-one [29412-73-5].² Benzene (100 mL), Rh₂(O₂CCF₃) (10 mg, 0.015 mmol), and anhydrous K₂CO₃ (5.00 g, 14.0 mmol) were added to a 250-mL round-bottom flask, and the resulting solution was stirred at room temperature for 5 min. Then, a solution of 3-bromo-1-diazobutan-2-one (1.24 g, 7.0 mmol) in benzene (50 mL) was added dropwise over 30 min via syringe pump. The resulting reaction mixture was stirred at room temperature for 2 h, and then it was concentrated by rotary evaporation. The residue was purified by flash chromatography on silica gel (eluted with 10→30% CH₂Cl₂ in hexanes), which afforded the desired product as a yellow oil (1.79 g, 95% yield).

**1H NMR (CDCl$_3$, 500 MHz)** δ 7.34 (t, $J = 7.0$ Hz, 2H), 7.30 (t, $J = 7.0$ Hz, 1H), 7.25 (d, $J = 7.0$ Hz, 2H), 4.50 (q, $J = 7.0$ Hz, 1H), 4.04 (d, $J = 15.5$ Hz, 1H), 3.99 (d, $J = 15.5$ Hz, 1H), 1.72 (d, $J = 7.0$ Hz, 3H).

**3-Bromo-1-cyclohexylbutan-2-one.** Cyclohexane (90 mL) and Rh$_2$(O$_2$CCF$_3$) (19.7 mg, 0.030 mmol) were added to a 200-mL round-bottom flask. The resulting solution was heated to 80 °C, and then a solution of 3-bromo-1-diazobutan-2-one (531 mg, 3.0 mmol) in cyclohexane (10 mL) was added dropwise over 30 min via syringe pump. The resulting reaction mixture was stirred for 4 h at 80 °C, and then it was concentrated by rotary evaporation. The residue was purified by flash chromatography on silica gel (eluted with 20% CH$_2$Cl$_2$ in hexanes), which afforded the desired product as a colorless oil (560 mg, 80% yield).

**1H NMR (CDCl$_3$, 500 MHz)** δ 4.33 (q, $J = 7.0$ Hz, 1H), 2.60 (dd, $J = 16.5$, 7.0 Hz, 1H), 2.50 (dd, $J = 16.5$, 7.0 Hz, 1H), 1.89-1.86 (m, 1H), 1.69 (d, $J = 7.0$ Hz, 3H), 1.73-1.63 (m, 5H), 1.29-1.24 (m, 2H), 1.17-1.12 (m, 1H), 0.98-0.95 (m, 2H);

**13C NMR (CDCl$_3$, 75 MHz)** δ 204.0, 48.2, 46.5, 34.0, 33.3, 33.1, 26.3, 26.24, 26.20, 20.1;
IR (film) 2924, 1717, 1446, 1376, 1356, 1110, 1021, 957, 896 cm$^{-1}$;
LRMS (EI) calcd for C$_{10}$H$_{17}$BrO (M) 232, found 232.

**3-Bromo-1-cyclohexylpentan-2-one.** This compound was prepared according to the General Procedure from 3-bromo-1-diazopentan-2-one (955 mg, 5.00 mmol). The product was obtained as a colorless oil (eluted with 20% CH$_2$Cl$_2$ in hexanes; 1.03 g, 84% yield).

**1H NMR (CDCl$_3$, 500 MHz)** δ 4.14 (dd, $J = 8.0$, 6.5 Hz, 1H), 2.53 (d, $J = 7.0$ Hz, 2H), 2.05-2.00 (m, 1H), 1.95-1.84 (m, 2H), 1.69-1.62 (m, 5H), 1.31-1.23 (m, 2H), 1.16-1.10 (m, 1H), 1.00 (t, $J = 7.0$ Hz, 3H), 0.98-0.91 (m, 2H);

**13C NMR (CDCl$_3$, 75 MHz)** δ 203.8, 56.1, 46.9, 33.9, 33.3, 33.1, 26.9, 26.4, 26.3, 26.2, 12.2;
IR (film) 2923, 1717, 1653, 1559, 1506, 1456, 1224 cm$^{-1}$;
LRMS (EI) calcd for C$_{11}$H$_{19}$BrO (M) 246, found 246.

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2-Bromo-4-methylpentan-3-one [29583-93-5]. A solution of LiHMDS in THF (1.06 M; 2.0 mL, 2.1 mmol) was added by syringe into a 100-mL round-bottom flask. The solution was cooled to −78 °C, and 2-methylpentan-3-one (2.0 g, 20 mmol) was added over 5 min. After the addition was complete, the reaction mixture was allowed to warm to 0 °C for 10 min. Next, it was cooled to −78 °C, and bromine (1.03 mL, 20.0 mmol) was added dropwise over 10 min. After the addition was complete, the reaction mixture was stirred for 2 min, and then it was poured into a saturated aqueous NaHCO₃ solution (40 mL) and extracted with ether (3×50 mL). The combined organic layers were successively washed with water (50 mL), a saturated aqueous Na₂S₂O₃ solution (50 mL), and brine (50 mL). The solution was dried over MgSO₄, filtered, and concentrated via rotary evaporation. The residue was purified by flash chromatography on silica gel (eluted with 15→40% CH₂Cl₂ in hexanes), which furnished a colorless oil (2.57 g, 72%).

¹H NMR (CDCl₃, 500 MHz) δ 4.55 (q, J = 7.0 Hz, 1H), 3.12-3.08 (m, 1H), 1.74 (d, J = 7.0 Hz, 3H), 1.70 (d, J = 7.0 Hz, 3H), 1.40 (d, J = 7.0 Hz, 3H).

4-Bromo-2-methylhexan-3-one. A solution of LiHMDS in THF (1.06 M; 2.0 mL, 2.1 mmol) was added by syringe into a 100-mL round-bottom flask. The solution was cooled to −78 °C, and 2-methylhexan-3-one (2.28 g, 20.0 mmol) was added over 5 min. After the addition was complete, the reaction mixture was allowed to warm to 0 °C for 10 min. Next, it was cooled to −78 °C, and bromine (1.03 mL, 20.0 mmol) was added dropwise over 10 min. After the addition was complete, the reaction mixture was stirred for 2 min, and then it was poured into a saturated aqueous NaHCO₃ solution (40 mL) and extracted with ether (3×50 mL). The combined organic layers were successively washed with water (50 mL), a saturated aqueous Na₂S₂O₃ solution (50 mL), and brine (50 mL). The solution was dried over MgSO₄, filtered, and concentrated via rotary evaporation. The residue was purified by flash chromatography on silica gel (eluted with CH₂Cl₂), which furnished a colorless oil (2.32 g, 60%).

¹H NMR (CDCl₃, 500 MHz) δ 4.30 (t, J = 6.5 Hz, 1H), 3.04-2.98 (m, 1H), 2.07-2.04 (m, 1H), 1.95-1.91 (m, 1H), 1.15 (d, J = 6.5 Hz, 3H), 1.11 (d, J = 6.5 Hz, 3H), 0.98 (t, J = 7.5 Hz, 3H);

¹³C NMR (CDCl₃, 75 MHz) δ 207.8, 53.5, 38.2, 26.8, 19.5, 18.8, 12.2;

IR (film) 2972, 1717, 1457, 1383, 1126, 1032, 914, 835, 802 cm⁻¹;

LRMS (EI) calcd for C₇H₁₄BrO (M+H) 193, found 193.
III. Preparation of Ligand 2

\[
\text{(4R,4'R)-2,2'-(2,3-dihydro-1H-phenalene-2,2-diyl)bis(4-phenyl-4,5-dihydrooxazole).}
\]

Bis((R)-4-phenyl-4,5-dihydrooxazol-2-yl)methane (918 mg, 3.00 mmol; prepared from the condensation of (R)-2-phenylglycinol with diethyl malonimidate dihydrochloride according to a reported procedure\(^4\)) and anhydrous THF (45 mL) were added to a 100-mL round-bottom flask equipped with a stir bar. The resulting solution was cooled to 0 °C, and NaH (216 mg, 9.00 mmol) was added in 5 portions over 5 min. The reaction mixture was stirred for 30 min at 0 °C, and then a solution of 1,8-bis(bromomethyl)naphthalene (1.04 g, 3.3 mmol) in THF (10 mL) was added over 2 min. The solution was stirred at room temperature for 4 h and then at 50 °C for an additional 2 h. Next, the reaction was quenched by the addition of a saturated aqueous NH\(_4\)Cl solution (50 mL). The mixture was extracted with CH\(_2\)Cl\(_2\) (3 × 50 mL), and then the organic layers were combined, dried over anhydrous MgSO\(_4\), and filtered. The filtrate was concentrated by rotary evaporation, and the residue was purified by flash chromatography on silica gel (eluted with 20% EtOAc in hexanes), which afforded the desired product as a white solid (1.13 g, 82% yield).

\[
\alpha^{\text{D}}_{\text{D}} = +4.2 \text{ (c = 1.0, CHCl}_3).\]

\(^1\)H NMR (CDCl\(_3\), 500 MHz) \(\delta 7.75 \text{ (d, } J = 8.0 \text{ Hz, 2H)}, 7.41 \text{ (t, } J = 8.0 \text{ Hz, 2H)}, 7.36 \text{ (d, } J = 8.0 \text{ Hz, 2H)}, 7.17-7.13 \text{ (m, 6H)}, 6.74 \text{ (d, } J = 6.5 \text{ Hz, 4H)}, 5.17 \text{ (t, } J = 10.0 \text{ Hz, 2H)}, 4.61 \text{ (t, } J = 10.0 \text{ Hz, 2H)}, 4.00 \text{ (t, } J = 10.0 \text{ Hz, 2H)}, 3.94 \text{ (d, } J = 15.5 \text{ Hz, 2H)}, 3.84 \text{ (d, } J = 15.5 \text{ Hz, 2H});

\(^13\)C NMR (CDCl\(_3\), 75 MHz) \(\delta 168.1, 142.1, 133.3, 132.7, 128.5, 127.3, 126.4, 126.30, 126.26, 125.9, 124.9, 75.5, 69.4, 42.7, 37.8;

IR (film) 3030, 2900, 1751, 1653, 1493, 1455, 1356, 1218, 1178, 1029, 755, 699 cm\(^{-1}\);

LRMS (ESI) calcd for C\(_{31}\)H\(_{27}\)N\(_2\)O\(_2\) (M+H) 459.2, found 459.2.

\((4S,4'S)-2,2'-(2,3-dihydro-1H-phenalene-2,2-diyl)bis(4-phenyl-4,5-dihydrooxazole) was also prepared according to this procedure: [\(\alpha\)]\text{D}_{\text{D}} = -4.2 \text{ (c = 1.0, CHCl}_3).\]

IV. Asymmetric Kumada Cross-Couplings (Tables 1 and 2)

**General Procedure A** (for commercially available Grignard reagents). A 20-mL vial equipped with a stir bar was capped with a septum and taped. The vial was purged with argon for 2 min. 1,2-Dimethoxyethane (8 mL) was added by syringe, and then the vial was cooled to −20 °C and a solution of the Grignard reagent (a solution in Et₂O is preferred; 1.1 mmol) was added. The solution was stirred at −20 °C for 10 min, and then it was cooled to −60 °C.

(R,R)-2,2′-Isopropylidene-bis(4-phenyl-2-oxazoline) ((R)-1; 30.0 mg, 0.090 mmol) and NiCl₂·glyme (15.3 mg, 0.070 mmol) were added to a 4.0-mL vial equipped with a stir bar. The vial was capped with a septum, taped, and gently purged with argon for 1 min. 1,2-Dimethoxyethane (2.0 mL) was added, and this solution of the catalyst was stirred at room temperature for 5 min. Next, the α-bromoketone (1.0 mmol) was added. The mixture was stirred at room temperature for 5 min, and then the resulting homogeneous dark-pink solution was added dropwise over 3 min to the −60 °C solution of the Grignard reagent. The resulting yellow solution was stirred at −60 °C for 16 h (if the ArMgX is electron-rich, then the reaction was run for 32 h). Next, the reaction was quenched with ethanol (2 mL), and the resulting mixture was filtered through a Büchner funnel that contained a bed of silica gel (height: 3.0 cm). The silica gel was washed with additional Et₂O (40 mL), and then the combined filtrates were concentrated by rotary evaporation. The resulting residue was purified by flash chromatography on silica gel.

**General Procedure B** (for Grignard reagents prepared in situ; the second paragraph is the same as for General Procedure A). A 20-mL vial equipped with a stir bar was capped with a septum and taped. The vial was purged with argon for 2 min, and then 1,2-dimethoxyethane (8 mL) was added by syringe, followed by the aryl iodide (1.10 mmol). The solution was cooled to −20 °C, and a solution of i-PrMgCl (2.0 M solution in Et₂O; 0.55 mL, 1.1 mmol) was added over 1.0 min. The resulting mixture was stirred at −20 °C for 16 h (if the ArMgX is electron-poor ArI and 2.0 h for electron-rich ArI), and then it was cooled to −60 °C.

(R,R)-2,2′-Isopropylidene-bis(4-phenyl-2-oxazoline) ((R)-1; 30.0 mg, 0.090 mmol) and NiCl₂·glyme (15.3 mg, 0.070 mmol) were added to a 4.0-mL vial equipped with a stir bar. The vial was capped with a septum, taped, and gently purged with argon for 1 min. 1,2-Dimethoxyethane (2.0 mL) was added, and this solution of the catalyst was stirred at room temperature for 5 min. Next, the α-bromoketone (1.0 mmol) was added. The mixture was stirred at room temperature for 5 min, and then the resulting homogeneous dark-pink solution was added dropwise over 3 min to the −60 °C solution of the Grignard reagent. The resulting yellow solution was stirred at −60 °C for 16 h (if the ArMgX is electron-rich, then the reaction was run for 32 h). Next, the reaction was quenched with ethanol (2 mL), and the resulting mixture was filtered through a Büchner funnel that contained a bed of silica gel (height: 3.0 cm). The silica gel was washed with additional Et₂O (40 mL), and then the combined filtrates were

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concentrated by rotary evaporation. The resulting residue was purified by flash chromatography on silica gel.

\[
\begin{align*}
\text{(S)-1,2-Diphenylpropan-1-one (Table 1, entry 1) [145673-71-8].} & \quad \text{The title compound was prepared according to General Procedure A with 2-bromo-1-phenylpropan-1-one (213 mg, 1.00 mmol) and PhMgBr (3.0 M in Et}_2\text{O; 0.37 mL, 1.1 mmol). After purification by flash chromatography (eluted with 30\%\rightarrow70\% CH}_2\text{Cl}_2 in hexanes), the title compound was isolated as a colorless oil (168 mg, 80\% yield) with 92\% ee (HPLC analysis of the product: Daicel CHIRALCEL OJ-H column; solvent system: 1\% i-PrOH in hexanes; 1.0 mL/min; retention times: 17.4 min (minor), 20.0 min (major)).} \\
\ \ \ \ \ \ \ \ [\alpha]^{22}_D = +175 (c = 1.0, CHCl}_3).
\end{align*}
\]

The second run was performed with (S)-1. The product was isolated as a colorless oil (172 mg, 82\% yield) with 92\% ee.

\[
\begin{align*}
^1\text{H NMR (CDCl}_3, 500 MHz) \delta 7.93 \text{ (d, } J = 8.0 \text{ Hz, 2H), 7.45 \text{ (t, } J = 8.0 \text{ Hz, 1H), 7.36 \text{ (t, } J = 8.0 \text{ Hz, 2H), 7.27-7.25 \text{ (m, 4H), 7.19-7.17 \text{ (m, 1H), 4.67 \text{ (q, } J = 7.0 \text{ Hz, 1H), 1.51 \text{ (d, } J = 7.0 \text{ Hz, 3H); }}}
\end{align*}
\]

\[
\begin{align*}
^{13}\text{C NMR (CDCl}_3, 75 MHz) \delta 200.5, 141.6, 136.6, 133.0, 129.2, 128.9, 128.6, 127.9, 127.1, 48.1, 19.7.
\end{align*}
\]

The spectral data are in agreement with literature data.\(^5\)

\[
\begin{align*}
\text{(S)-Ethyl 2-(1-oxo-1-phenylpropan-2-yl)benzoate (Table 1, entry 2).} & \quad \text{The title compound was prepared according to General Procedure B with 2-bromo-1-phenylpropan-1-one (213 mg, 1.00 mmol) and ethyl 2-iodobenzoate (304 mg, 1.10 mmol). After purification by flash chromatography (eluted with 30\%\rightarrow60\% CH}_2\text{Cl}_2 in hexanes), the title compound was isolated as a colorless oil (228 mg, 81\% yield) with 80\% ee (HPLC analysis of the product: Daicel CHIRALPAK AD-H column; solvent system: 2\% i-PrOH in hexanes; 1.0 mL/min; retention times: 9.1 min (minor), 13.1 min (major)).} \\
\ \ \ \ \ \ \ \ [\alpha]^{22}_D = +185 (c = 1.0, CHCl}_3).
\end{align*}
\]

The second run was performed with (S)-1. The product was isolated as a colorless oil (214 mg, 76% yield) with 80% ee.

\[ \text{H NMR (CDCl}_3, 500 \text{ MHz}) \delta 7.98 \text{ (d, } J = 8.0 \text{ Hz, 2H), 7.94 \text{ (d, } J = 8.0 \text{ Hz, 1H), 7.45 \text{ (t, } J = 8.0 \text{ Hz, 1H), 7.40-7.35 \text{ (m, 3H), 7.27-7.22 \text{ (m, 2H), 5.83 \text{ (q, } J = 7.0 \text{ Hz, 1H), 4.16 \text{ (q, } J = 7.0 \text{ Hz, 2H), 1.52 \text{ (d, } J = 7.0 \text{ Hz, 3H), 1.42 \text{ (t, } J = 7.0 \text{ Hz, 3H);}}}

\]

\[ \text{C NMR (CDCl}_3, 75 \text{ MHz}) \delta 201.1, 167.8, 142.9, 136.6, 132.8, 132.6, 131.2, 128.9, 128.6, 126.8, 61.4, 43.8, 19.2, 14.4; \]

IR (film) 2979, 1713, 1684, 1597, 1448, 1266, 1085, 1057, 952, 703 cm\(^{-1}\);

LRMS (ESI) calcd for C\(_{18}\)H\(_{19}\)O\(_3\) (M+H) 283.1, found 283.1.

(S)-2-(3-Bromophenyl)-1-phenylpropan-1-one (Table 1, entry 3). The title compound was prepared according to General Procedure B with 2-bromo-1-phenylpropan-1-one (213 mg, 1.00 mmol) and 1-bromo-3-iodobenzene (311 mg, 1.10 mmol). After purification by flash chromatography (eluted with 10→30% CH\(_2\)_Cl\(_2\) in hexanes), the title compound was isolated as a colorless oil (220 mg, 76% yield) with 91% ee (HPLC analysis of the product: Daicel CHIRALPAK OJ-H column; solvent system: 2% i-PrOH in hexanes; 1.0 mL/min; retention times: 12.1 min (minor), 13.6 min (major)).

\[ \alpha^{22}_D = +137 \text{ (c = 1.0, CHCl}_3\). \]

The second run was performed with (S)-1. The product was isolated as a colorless oil (217 mg, 75% yield) with 94% ee.

\[ \text{H NMR (CDCl}_3, 500 \text{ MHz}) \delta 7.94 \text{ (d, } J = 8.0 \text{ Hz, 2H), 7.50 \text{ (t, } J = 8.0 \text{ Hz, 1H), 7.45 \text{ (s, } 1H), 7.41 \text{ (t, } J = 8.0 \text{ Hz, 2H), 7.34 \text{ (d, } J = 8.0 \text{ Hz, 1H), 7.21 \text{ (d, } J = 7.5 \text{ Hz, 1H), 7.16 \text{ (t, } J = 8.0 \text{ Hz, 1H), 4.66 \text{ (q, } J = 7.0 \text{ Hz, 1H), 1.52 \text{ (d, } J = 7.0 \text{ Hz, 3H);}}}

\]

\[ \text{C NMR (CDCl}_3, 75 \text{ MHz}) \delta 199.8, 143.7, 136.2, 133.2, 130.9, 130.6, 130.2, 128.9, 128.7, 126.5, 123.0, 47.4, 19.6; \]

IR (film) 3060, 2977, 1683, 1594, 1567, 1448, 1340, 1219, 1075, 954, 781, 693 cm\(^{-1}\);

LRMS (ESI) calcd for C\(_{15}\)H\(_{12}\)BrO (M–H) 287.0, found 287.0.
(S)-3-(1-Oxo-1-phenylpropan-2-yl)benzonitrile (Table 1, entry 4). The title compound was prepared according to General Procedure B with 2-bromo-1-phenylpropan-1-one (213 mg, 1.00 mmol) and 3-iodobenzonitrile (252 mg, 1.10 mmol). After purification by flash chromatography (eluted with 30→70% CH$_2$Cl$_2$ in hexanes), the title compound was isolated as a colorless oil (210 mg, 89% yield) with 95% ee (HPLC analysis of the product: Daicel CHIRALCEL OD-H column; solvent system: 5% i-PrOH in hexanes; 1.0 mL/min; retention times: 12.3 min (major), 15.4 min (minor)).

$\left[\alpha\right]_{D}^{22} = +117$ (c = 1.0, CHCl$_3$).

The second run was performed with (S)-1. The product was isolated as a colorless oil (219 mg, 93% yield) with 95% ee.

$^1$H NMR (CDCl$_3$, 500 MHz) δ 7.91 (d, $J$ = 8.0 Hz, 2H), 7.60 (s, 1H), 7.54–7.48 (m, 3H), 7.43–7.24 (m, 3H), 4.73 (q, $J$ = 7.0 Hz, 1H), 1.53 (d, $J$ = 7.0 Hz, 3H);

$^{13}$C NMR (CDCl$_3$, 75 MHz) δ 199.4, 142.7, 135.8, 133.4, 132.5, 131.5, 130.7, 129.8, 128.8, 128.7, 118.7, 112.9, 46.9, 19.4;

IR (film) 3524, 2978, 2230, 1684, 1596, 1582, 1448, 1338, 1207, 958, 796, 729, 691 cm$^{-1}$;

LRMS (ESI) calcd for C$_{16}$H$_{12}$NO (M–H) 234.1, found 234.1.

(S)-2-(3-Methoxyphenyl)-1-phenylpropan-1-one (Table 1, entry 5) [1126519-12-7]. The title compound was prepared according to General Procedure B with 2-bromo-1-phenylpropan-1-one (213 mg, 1.00 mmol) and 1-iodo-3-methoxybenzene (257 mg, 1.10 mmol). After purification by flash chromatography (eluted with 30→60% CH$_2$Cl$_2$ in hexanes), the title compound was isolated as a colorless oil (180 mg, 75% yield) with 92% ee (HPLC analysis of the product: Daicel CHIRALPAK OD-H column; solvent system: 1% i-PrOH in hexanes; 1.0 mL/min; retention times: 8.2 min (major), 10.3 min (minor)).

$\left[\alpha\right]_{D}^{22} = +162$ (c = 1.0, CHCl$_3$).

The second run was performed with (S)-1. The product was isolated as a colorless oil (185 mg, 77% yield) with 92% ee.
(S)-Phenyl-2-(4-(trifluoromethyl)phenyl)propan-1-one (Table 1, entry 6). The title compound was prepared according to General Procedure B with 2-bromo-1-phenylpropan-1-one (213 mg, 1.00 mmol) and 1-iodo-4-(trifluoromethyl)benzene (299 mg, 1.10 mmol). After purification by flash chromatography (eluted with 10→30% CH₂Cl₂ in hexanes), the title compound was isolated as a colorless oil (228 mg, 82% yield) with 94% ee (HPLC analysis of the product: Daicel CHIRALPAK OJ-H column; solvent system: 2% i-PrOH in hexanes; 1.0 mL/min; retention times: 8.4 min (minor), 9.4 min (major)).

\[ [\alpha]_{D}^{22} = +120 \ (c = 1.0, \text{CHCl}_3). \]

The second run was performed with (S)-1. The product was isolated as a colorless oil (239 mg, 86% yield) with 94% ee.

\( ^{1} \text{H NMR (CDCl}_3, 500 MHz) \delta 7.95 (d, J = 8.0 \text{ Hz}, 2\text{H}), 7.56 (d, J = 8.5 \text{ Hz}, 2\text{H}), 7.53 (t, J = 8.0 \text{ Hz}, 1\text{H}), 7.43-7.41 (m, 4\text{H}), 4.78 (q, J = 7.0 \text{ Hz}, 1\text{H}), 1.56 (d, J = 7.0 \text{ Hz}, 3\text{H}); \)

\( ^{13} \text{C NMR (CDCl}_3, 75 MHz) \delta 199.8, 145.5, 136.2, 133.4, 128.9, 128.8, 128.3, 126.0, 47.6, 19.6; \)

IR (film) 2981, 1687, 1618, 1597, 1449, 1325, 1123, 1070, 952, 846, 699 cm\(^{-1}\);

LRMS (ESI) calcd for C\(_{16}\)H\(_{12}\)F\(_3\)O (M–H) 277.1, found 277.1.
(S)-Ethyl 4-(1-oxo-1-phenylpropan-2-yl)benzoate (Table 1, entry 7). The title compound was prepared according to General Procedure B with 2-bromo-1-phenylpropan-1-one (213 mg, 1.00 mmol) and ethyl 4-iodobenzoate (304 mg, 1.10 mmol). After purification by flash chromatography (eluted with 30→60% CH$_2$Cl$_2$ in hexanes), the title compound was isolated as a colorless oil (257 mg, 91% yield) with 95% ee (HPLC analysis of the product: Daicel CHIRALPAK AD-H column; solvent system: 2% i-PrOH in hexanes; 1.0 mL/min; retention times: 23.1 min (major), 24.9 min (minor)). 

[α]$^2_D$ = +168 (c = 1.0, CHCl$_3$).

The second run was performed with (S)-1. The product was isolated as a colorless oil (255 mg, 90% yield) with 94% ee.

$^1$H NMR (CDCl$_3$, 500 MHz) δ 7.95 (d, J = 8.0 Hz, 2H), 7.90 (d, J = 8.0 Hz, 2H), 7.47 (t, J = 8.0 Hz, 1H), 7.36 (t, J = 8.0 Hz, 2H), 7.34 (d, J = 8.0 Hz, 2H), 4.72 (q, J = 7.0 Hz, 1H), 4.32 (q, J = 7.0 Hz, 2H), 1.53 (d, J = 7.0 Hz, 3H), 1.34 (t, J = 7.0 Hz, 3H);

$^{13}$C NMR (CDCl$_3$, 75 MHz) δ 199.9, 166.5, 146.8, 136.4, 133.3, 130.5, 129.4, 129.0, 128.8, 128.0, 61.2, 48.0, 19.6, 14.5;

IR (film) 3532, 2980, 1716, 1686, 1608, 1448, 1416, 1367, 1277, 1180, 1106, 1021, 952, 859, 769, 702 cm$^{-1}$;

LRMS (ESI) calcd for C$_{18}$H$_{19}$O$_3$ (M+H) 283.1, found 283.1.

(S)-2-(4-Iodophenyl)-1-phenylpropan-1-one (Table 1, entry 8). The title compound was prepared according to General Procedure B with 2-bromo-1-phenylpropan-1-one (213 mg, 1.00 mmol) and 1,4-diiodobenzene (363 mg, 1.10 mmol). After purification by flash chromatography (eluted with 10→30% CH$_2$Cl$_2$ in hexanes), the title compound was isolated as a colorless oil (280 mg, 83% yield) with 93% ee (HPLC analysis of the product: Daicel CHIRALPAK OJ-H column; solvent system: 2% i-PrOH in hexanes; 1.0 mL/min; retention times: 13.3 min (minor), 14.3 min (major)).
The second run was performed with (S)-1. The product was isolated as a colorless oil (279 mg, 83% yield) with 95% ee.

$^1$H NMR (CDCl$_3$, 500 MHz) $\delta$ 7.93 (d, $J = 8.0$ Hz, 2H), 7.62 (d, $J = 8.5$ Hz, 2H), 7.51 (t, $J = 8.0$ Hz, 1H), 7.40 (t, $J = 8.0$ Hz, 2H), 7.05 (d, $J = 8.5$ Hz, 2H), 4.65 (q, $J = 7.0$ Hz, 1H), 1.52 (d, $J = 7.0$ Hz, 3H);

$^{13}$C NMR (CDCl$_3$, 75 MHz) $\delta$ 200.0, 141.4, 138.3, 136.4, 133.3, 130.1, 129.0, 128.9, 128.7, 106.6, 1003, 952, 909, 814, 701 cm$^{-1}$;

IR (film) 2976, 1901, 1683, 1596, 1581, 1484, 1448, 1401, 1338, 1220, 1066, 1003, 952, 909, 814, 701 cm$^{-1}$;

LRMS (ESI) calcd for C$_{15}$H$_{14}$IO (M+H) 337.0, found 337.0.

The second run was performed with (S)-1. The product was isolated as a colorless oil (192 mg, 80% yield) with 91% ee.

$^1$H NMR (CDCl$_3$, 500 MHz) $\delta$ 7.93 (d, $J = 8.0$ Hz, 2H), 7.45 (t, $J = 8.0$ Hz, 1H), 7.36 (t, $J = 8.0$ Hz, 2H), 7.18 (d, $J = 8.0$ Hz, 2H), 6.81 (d, $J = 8.0$ Hz, 2H), 4.62 (q, $J = 7.0$ Hz, 1H), 1.48 (d, $J = 7.0$ Hz, 3H);

$^{13}$C NMR (CDCl$_3$, 75 MHz) $\delta$ 200.8, 158.7, 136.7, 133.7, 133.0, 129.0, 128.7, 114.6, 55.4, 47.2, 19.8.

The spectral data are in agreement with literature data.$^5$
(S)-2-(3-Chloro-4-fluorophenyl)-1-phenylpropan-1-one (Table 1, entry 10). The title compound was prepared according to General Procedure B with 2-bromo-1-phenylpropan-1-one (213 mg, 1.00 mmol) and 2-chloro-1-fluoro-4-iodobenzene (282 mg, 1.10 mmol). After purification by flash chromatography (eluted with 10→20% CH$_2$Cl$_2$ in hexanes), the title compound was isolated as a colorless oil (194 mg, 74% yield) with 95% ee (HPLC analysis of the product: Daicel CHIRALPAK OJ-H column; solvent system: 2% i-PrOH in hexanes; 1.0 mL/min; retention times: 12.0 min (minor), 13.4 min (major)).

[α]$^2_D = +127$ (c = 1.0, CHCl$_3$).

The second run was performed with (S)-1. The product was isolated as a colorless oil (205 mg, 78% yield) with 95% ee.

$^1$H NMR (CDCl$_3$, 500 MHz) δ 7.91 (d, $J = 8.0$ Hz, 2H), 7.50 (t, $J = 8.0$ Hz, 1H), 7.40 (t, $J = 8.0$ Hz, 2H), 7.32 (dd, $J = 7.0$, 2.0 Hz, 1H), 7.15-7.12 (m, 1H), 7.04 (t, $J = 7.0$ Hz, 1H), 4.65 (q, $J = 7.0$ Hz, 1H), 1.50 (d, $J = 7.0$ Hz, 3H);

$^{13}$C NMR (CDCl$_3$, 75 MHz) δ 199.8, 158.9, 155.6, 138.5, 136.1, 133.4, 130.0, 128.9, 127.8, 121.4 (d, $J = 18$ Hz), 117.0 (d, $J = 21$ Hz), 46.6, 19.7;

IR (film) 3062, 2979, 1684, 1596, 1500, 1448, 1249, 1065, 955, 750, 688, 605 cm$^{-1}$;

LRMS (ESI) calcd for C$_{15}$H$_{13}$ClFO (M+H) 263.0, found 263.0.

(S)-2-(3,4-(Methylenedioxy)phenyl)-1-phenylpropan-1-one (Table 1, entry 11). The title compound was prepared according to General Procedure A with 2-bromo-1-phenylpropan-1-one (213 mg, 1.00 mmol) and 3,4-(methylenedioxy)phenylmagnesium bromide (1.0 M in toluene/THF, Aldrich; 1.1 mL, 1.1 mmol). After purification by flash chromatography (eluted with 30→70% CH$_2$Cl$_2$ in hexanes), the title compound was isolated as a white solid (193 mg, 76% yield) with 92% ee (HPLC analysis of the product: Daicel CHIRALCEL AD-H column; solvent system: 2% i-PrOH in hexanes; 1.0 mL/min; retention times: 13.5 min (major), 14.4 min (minor)).

[α]$^2_D = +178$ (c = 1.0, CHCl$_3$).
The second run was performed with (S)-1. The product was isolated as a colorless oil (188 mg, 74% yield) with 93% ee.

$^1$H NMR (CDCl$_3$, 500 MHz) $\delta$ 7.95 (d, $J = 8.0$ Hz, 2H), 7.49 (t, $J = 8.0$ Hz, 1H), 7.39 (t, $J = 8.0$ Hz, 2H), 6.77 (s, 1H), 6.75–6.71 (m, 2H), 5.90 (d, $J = 8.0$ Hz, 2H), 4.60 (q, $J = 7.0$ Hz, 1H), 1.49 (d, $J = 7.0$ Hz, 3H);

$^{13}$C NMR (CDCl$_3$, 75 MHz) $\delta$ 200.4, 148.2, 146.6, 136.5, 135.3, 132.9, 128.9, 128.6, 121.2, 108.8, 108.2, 101.2, 47.5, 19.7;

IR (film) 2975, 1682, 1596, 1503, 1485, 1447, 1247, 1039, 956, 805, 695 cm$^{-1}$;

LRMS (ESI) calcd for C$_{16}$H$_{15}$O$_3$ (M+H) 255.1, found 255.1.

(S)-2-(2-Methylbenzofuran-5-yl)-1-phenylpropan-1-one (Table 1, entry 12). The title compound was prepared according to General Procedure B with 2-bromo-1-phenylpropan-1-one (213 mg, 1.00 mmol) and 5-iodo-2-methylbenzofuran (284 mg, 1.10 mmol). After purification by flash chromatography (eluted with 20–50% CH$_2$Cl$_2$ in hexanes), the title compound was isolated as a colorless oil (232 mg, 88% yield) with 92% ee (HPLC analysis of the product: Daicel CHIRALPAK AD-H column; solvent system: 2% i-PrOH in hexanes; 1.0 mL/min; retention times: 9.9 min (major), 13.7 min (minor)).

$[\alpha]^{22}_D = +191$ (c = 1.0, CHCl$_3$).

The second run was performed with (S)-1. The product was isolated as a colorless oil (224 mg, 85% yield) with 90% ee.

$^1$H NMR (CDCl$_3$, 500 MHz) $\delta$ 7.96 (d, $J = 8.0$ Hz, 2H), 7.45 (t, $J = 8.0$ Hz, 1H), 7.36 (t, $J = 8.0$ Hz, 2H), 7.30 (d, $J = 8.5$ Hz, 1H), 7.25 (s, 1H), 7.12 (dd, $J = 8.5$, 2.0 Hz, 1H), 6.29 (s, 1H), 4.74 (q, $J = 7.0$ Hz, 1H), 2.41 (s, 3H), 1.55 (d, $J = 7.0$ Hz, 3H);

$^{13}$C NMR (CDCl$_3$, 75 MHz) $\delta$ 200.8, 156.2, 153.9, 136.6, 135.9, 132.8, 129.9, 128.9, 128.5, 123.0, 119.2, 111.1, 47.9, 20.1, 14.1;

IR (film) 2976, 2930, 1682, 1597, 1471, 1448, 1258, 1191, 957, 805, 737, 699, 608 cm$^{-1}$;

LRMS (ESI) calcd for C$_{18}$H$_{17}$O$_2$ (M+H) 265.1, found 265.1.
(S)-tert-Butyl 5-(1-oxo-1-phenylpropan-2-yl)-1H-indole-1-carboxylate (Table 1, entry 13). The title compound was prepared according to General Procedure B with 2-bromo-1-phenylpropan-1-one (213 mg, 1.00 mmol) and tert-butyl 5-iodo-1H-indole-1-carboxylate (377 mg, 1.10 mmol). After purification by flash chromatography (eluted with 20→50% CH₂Cl₂ in hexanes), the title compound was isolated as a colorless oil (258 mg, 74% yield) with 92% ee (HPLC analysis of the product: Daicel CHIRALPAK AD-H column; solvent system: 2% i-PrOH in hexanes; 1.0 mL/min; retention times: 10.2 min (major), 12.5 min (minor)).

\[\alpha\] \(22^\circ_D = +107\ (c = 1.0, \text{CHCl}_3)\).

The second run was performed with (S)-1. The product was isolated as a colorless oil (253 mg, 72% yield) with 90% ee.

\(^1\)H NMR (CDCl₃, 500 MHz) δ 8.05-8.03 (m, 1H), 7.95 (d, \(J = 8.0\) Hz, 2H), 7.54-7.52 (m, 1H), 7.45-7.40 (m, 2H), 7.33 (t, \(J = 8.0\) Hz, 2H), 7.21 (d, \(J = 8.5\) Hz, 1H), 6.47 (d, \(J = 4.0\) Hz, 1H), 4.75 (q, \(J = 7.0\) Hz), 1.62 (s, 9H), 1.55 (d, \(J = 7.0\) Hz, 3H);

\(^{13}\)C NMR (CDCl₃, 75 MHz) δ 200.8, 149.9, 136.7, 136.2, 132.9, 131.4, 129.0, 128.7, 126.6, 124.3, 120.1, 115.9, 107.4, 84.0, 48.1, 43.9, 28.4, 20.1;

IR (film) 2978, 1732, 1682, 1469, 1372, 1257, 1162, 1024, 958, 910, 732 cm⁻¹;

LRMS (ESI) calcd for C₂₂H₂₀NO₃ (M–H) 348.2, found 348.2.

(S)-1-(2-Fluorophenyl)-2-phenylpropan-1-one (Table 2, entry 1) [1126519-22-9]. The title compound was prepared according to General Procedure A with 2-bromo-1-(2-fluorophenyl)propan-1-one (230 mg, 1.00 mmol) and PhMgBr (3.0 M in Et₂O; 0.37 mL, 1.1 mmol). After purification by flash chromatography (eluted with 20→50% CH₂Cl₂ in hexanes), the title compound was isolated as a colorless oil (200 mg, 88% yield) with 72% ee (HPLC analysis of the product: Daicel CHIRALCEL OJ-H column; solvent system: 2% i-PrOH in hexanes; 1.0 mL/min; retention times: 12.0 min (minor), 16.0 min (major)).

\[\alpha\] \(22^\circ_D = +170\ (c = 1.0, \text{CHCl}_3)\).

The second run was performed with (S)-1. The product was isolated as a colorless oil (205 mg, 90% yield) with 72% ee.

\(\text{S-17}\)
\[ \text{H NMR (CDCl}_3, 500 \text{ MHz)} \delta 7.75 (d, J = 8.0 \text{ Hz, 1H}), 7.43-7.38 (m, 1H), 7.29-7.27 (m, 4H), 7.22-7.18 (m, 1H), 7.15 (d, J = 8.0 \text{ Hz, 1H}), 7.02 (dd, J = 8.0, 12.0 \text{ Hz, 1H}), 4.65 (q, J = 7.0 \text{ Hz, 1H}), 1.56 (d, J = 7.0 \text{ Hz, 3H}); \]

\[ \text{C NMR (CDCl}_3, 75 \text{ MHz)} \delta 199.5, 160.7, 140.2, 134.6, 130.7, 128.4, 128.0, 126.8, 125.9, 124.1, 116.3, 51.8. \]

The spectral data are in agreement with literature data.\(^5\)

(S)-1-(3-Chlorophenyl)-2-phenylpropan-1-one (Table 2, entry 2). The title compound was prepared according to General Procedure A with 2-bromo-1-(3-chlorophenyl)propan-1-one (176 mg, 1.00 mmol) and PhMgBr (3.0 M in Et\(_2\)O; 0.37 mL, 1.1 mmol). After purification by flash chromatography (eluted with 20→40% CH\(_2\)Cl\(_2\) in hexanes), the title compound was isolated as a colorless oil (174 mg, 71% yield) with 80% ee (HPLC analysis of the product: Daicel CHIRALCEL OJ-H column; solvent system: 3% i-PrOH in hexanes; 1.0 mL/min; retention times: 9.4 min (minor), 12.5 min (major)).

\[ [\alpha]^{22}_D = +138 \text{ (c = 1.0, CHCl}_3). \]

The second run was performed with (S)-1. The product was isolated as a colorless oil (177 mg, 72% yield) with 80% ee.

\[ \text{H NMR (CDCl}_3, 500 \text{ MHz)} \delta 7.93 (s, 1H), 7.80 (d, J = 8.0 \text{ Hz, 1H}), 7.45-7.43 (m, 1H), 7.32-7.21 (m, 6H), 4.62 (q, J = 13.5, 7.0 \text{ Hz, 1H}), 1.53 (d, J = 7.0 \text{ Hz, 3H}); \]

\[ \text{C NMR (CDCl}_3, 75 \text{ MHz)} \delta 199.2, 141.1, 138.2, 135.0, 132.9, 130.0, 129.3, 129.0, 127.9, 127.3, 127.0, 48.3, 19.6; \]

IR (film) 2978, 1686, 1571, 1450, 1420, 1215, 1076, 782, 728, 700 cm\(^{-1}\);

LRMS (ESI) calcd for C\(_{15}\)H\(_{14}\)ClO (M+H) 245.0, found 245.0.

(S)-1-(3-Methoxyphenyl)-2-phenylpropan-1-one (Table 2, entry 3). The title compound was prepared according to General Procedure A with 2-bromo-1-(3-methoxyphenyl)propan-1-one (243 mg, 1.00 mmol) and PhMgBr (3.0 M in Et\(_2\)O; 0.37 mL, 1.1 mmol). After purification by flash chromatography (eluted with 30→60% CH\(_2\)Cl\(_2\) in hexanes), the title compound was isolated as a colorless oil (187 mg, 78% yield) with 92% ee (HPLC analysis of the product: Daicel
CHIRALPAK AD-H column; solvent system: 2% i-PrOH in hexanes; 1.0 mL/min; retention times: 8.4 min (major), 9.9 min (minor)).

$[\alpha]^{22}_D = +136$ (c = 1.0, CHCl$_3$).

The second run was performed with (S)-1. The product was isolated as a colorless oil (201 mg, 84% yield) with 92% ee.

$^1$H NMR (CDCl$_3$, 500 MHz) $\delta$ 7.53 (d, $J = 8.0$ Hz, 1H), 7.49-7.48 (m, 1H), 7.30-7.27 (m, 5H), 7.22-7.19 (m, 1H), 7.03-7.01 (dd, $J = 8.0$, 2.5 Hz, 1H), 4.66 (q, $J = 7.0$ Hz, 1H), 3.80 (s, 3H), 1.53 (d, $J = 7.0$ Hz, 3H);

$^{13}$C NMR (CDCl$_3$, 75 MHz) $\delta$ 200.3, 159.9, 141.7, 138.0, 129.6, 129.2, 127.9, 127.1, 121.6, 119.5, 113.2, 55.5, 48.2, 19.7;

IR (film) 2931, 1683, 1584, 1452, 1403, 745, 701 cm$^{-1}$;

LRMS (ESI) calcd for C$_{16}$H$_{17}$O$_2$ (M+H) 241.1, found 241.1.

(S)-1-(4-Bromophenyl)-2-phenylpropan-1-one (Table 2, entry 4). The title compound was prepared according to General Procedure A with 2-bromo-1-(4-bromophenyl)propan-1-one (292 mg, 1.00 mmol) and PhMgBr (3.0 M in Et$_2$O; 0.37 mL, 1.1 mmol). After purification by flash chromatography (eluted with 20→50% CH$_2$Cl$_2$ in hexanes), the title compound was isolated as a colorless oil (240 mg, 83% yield) with 80% ee (HPLC analysis of the product: Daicel CHIRALCEL OJ-H column; solvent system: 2% i-PrOH in hexanes; 1.0 mL/min; retention times: 9.6 min (minor), 14.0 min (major)).

$[\alpha]^{22}_D = +46$ (c = 1.0, CHCl$_3$).

The second run was performed with (S)-1. The product was isolated as a colorless oil (225 mg, 77% yield) with 80% ee.

$^1$H NMR (CDCl$_3$, 500 MHz) $\delta$ 7.77 (d, $J = 8.5$ Hz, 2H), 7.49 (d, $J = 8.5$ Hz, 2H), 7.29-7.17 (m, 5H), 4.58 (q, $J = 7.0$ Hz, 1H), 1.50 (d, $J = 7.0$ Hz, 3H);

$^{13}$C NMR (CDCl$_3$, 75 MHz) $\delta$ 199.3, 141.3, 135.2, 131.9, 130.5, 129.3, 128.1, 127.8, 127.2, 48.2, 19.6;

IR (film) 2976, 1684, 1584, 1456, 1395, 1217, 1070, 950, 753, 700 cm$^{-1}$;

LRMS (ESI) calcd for C$_{15}$H$_{14}$BrO (M+H) 289.0, found 289.0.
(S)-1-(4-(Benzyloxy)phenyl)-2-phenylpropan-1-one (Table 2, entry 5). The title compound was prepared according to General Procedure A with 1-(4-(benzyloxy)phenyl)-2-bromopropan-1-one (319 mg, 1.00 mmol) and PhMgBr (3.0 M in Et₂O; 0.37 mL, 1.1 mmol). After purification by flash chromatography (eluted with 30→60% CH₂Cl₂ in hexanes), the title compound was isolated as a white solid (253 mg, 80% yield) with 90% ee (HPLC analysis of the product: Daicel CHIRALPAK AS-H column; solvent system: 20% i-PrOH in hexanes; 0.9 mL/min; retention times: 9.3 min (minor), 10.6 min (major)).

[α]²²_D = +89 (c = 1.0, CHCl₃).

The second run was performed with (S)-1. The product was isolated as a white solid (254 mg, 80% yield) with 90% ee.

¹H NMR (CDCl₃, 500 MHz) δ 7.92 (d, J = 9.0 Hz, 2H), 7.37-7.31 (m, 5H), 7.27-7.25 (m, 4H), 7.21-7.18 (m, 1H), 6.90 (d, J = 9.0 Hz, 2H), 5.05 (s, 2H), 4.62 (q, J = 7.0 Hz, 1H), 1.49 (d, J = 7.0 Hz, 3H);

¹³C NMR (CDCl₃, 75 MHz) δ 198.8, 162.4, 141.9, 136.2, 131.1, 129.6, 129.0, 128.7, 128.2, 127.5, 126.8, 114.5, 70.0, 47.5, 19.6;

IR (film) 2982, 1668, 1602, 1509, 1453, 1258, 1178, 1039, 907, 846, 794, 756, 701, 645, 563 cm⁻¹; LRMS (ESI) calcd for C₂₂H₂₁O₂ (M+H) 317.1, found 317.1.

(S)-1-(3,4-(Methylenedioxy)phenyl)-2-phenylpropan-1-one (Table 2, entry 6). The title compound was prepared according to General Procedure A with 1-(3,4-(methylenedioxy)phenyl)-2-bromopropan-1-one (257 mg, 1.00 mmol) and PhMgBr (3.0 M in Et₂O; 0.37 mL, 1.1 mmol). After purification by flash chromatography (eluted with 30→60% CH₂Cl₂ in hexanes), the title compound was isolated as a colorless oil (190 mg, 75% yield) with 90% ee (HPLC analysis of the product: Daicel CHIRALPAK AD-H column; solvent system: 2% i-PrOH in hexanes; 1.0 mL/min; retention times: 14.5 min (major), 16.0 min (minor)).

[α]²²_D = +181 (c = 1.0, CHCl₃).

The second run was performed with (S)-1. The product was isolated as a colorless oil (195 mg, 77% yield) with 91% ee.

¹H NMR (CDCl₃, 500 MHz) δ 7.55 (dd, J = 8.0, 1.5 Hz, 1H), 7.41 (d, J = 1.5 Hz, 1H), 7.29-7.23 (m, 4H), 7.20-7.16 (m, 1H), 6.74 (d, J = 8.0 Hz, 1H), 5.97 (s, 2H), 4.57 (q, J = 7.0 Hz, 1H), 1.48 (d, J = 7.0 Hz, 3H);
\[^{13}\text{C} \text{NMR} (\text{CDCl}_3, 75 \text{ MHz}) \delta 198.5, 151.6, 148.2, 141.9, 131.3, 129.1, 127.8, 127.0, 125.2, 108.7, 107.9, 101.9, 47.7, 19.8; \]
\[\text{IR (film)} 2973, 1664, 1600, 1503, 1451, 1258, 1116, 1037, 931, 882, 790, 702 \text{ cm}^{-1}; \]
\[\text{LRMS (ESI) calcd for } C_{16}H_{15}O_3 (M+H) 255.1, \text{ found } 255.1. \]

(S)-2-Phenyl-1-(thiophen-2-yl)propan-1-one (Table 2, entry 7) [1126519-27-4]. The title compound was prepared according to General Procedure A with 2-bromo-1-(thiophen-2-yl)propan-1-one (219 mg, 1.00 mmol) and PhMgBr (3.0 M in Et\(_2\)O; 0.37 mL, 1.1 mmol). After purification by flash chromatography (eluted with 30→60% CH\(_2\)Cl\(_2\) in hexanes), the title compound was isolated as a colorless oil (197 mg, 91% yield) with 88% ee (HPLC analysis of the product: Daicel CHIRALPAK OD-H column; solvent system: 1% i-PrOH in hexanes; 1.0 mL/min; retention times: 8.2 min (major), 9.8 min (minor)).
\[\alpha\]D\(^{22}\) = +140 (c = 1.0, CHCl\(_3\)).
The second run was performed with (S)-1. The product was isolated as a colorless oil (195 mg, 90% yield) with 86% ee.
\[^{1}\text{H} \text{NMR} (\text{CDCl}_3, 500 \text{ MHz}) \delta 7.66 (d, J = 4.0 \text{ Hz}, 1H), 7.53 (d, J = 4.0 \text{ Hz}, 1H), 7.34-7.28 (m, 4H), 7.23-7.19 (m, 1H), 7.01 (t, J = 4.0 \text{ Hz}, 1H), 4.51 (q, J = 7.0 \text{ Hz}, 1H), 1.53 (d, J = 7.0 \text{ Hz}, 3H). \]
\[^{13}\text{C} \text{NMR} (\text{CDCl}_3, 75 \text{ MHz}) \delta 193.4, 143.8, 141.4, 133.8, 132.6, 129.1, 128.2, 127.9, 127.2, 49.4, 19.3. \]
The spectral data are in agreement with literature data.\(^5\)

(S)-1,2-Diphenylbutan-1-one (Table 2, entry 8) [175274-19-8]. The title compound was prepared according to General Procedure A with 2-bromo-1-phenylbutan-1-one (227 mg, 1.00 mmol) and PhMgBr (3.0 M in Et\(_2\)O; 0.37 mL, 1.1 mmol). After purification by flash chromatography (eluted with 30→60% CH\(_2\)Cl\(_2\) in hexanes), the title compound was isolated as a colorless oil (170 mg, 76% yield) with 90% ee (HPLC analysis of the product: Daicel CHIRALPAK OD-H column; solvent system: 1% i-PrOH in hexanes; 1.0 mL/min; retention times: 5.4 min (major), 6.1 min (minor)).
\[\alpha\]D\(^{22}\) = +162 (c = 1.0, CHCl\(_3\)).
The second run was performed with (S)-1. The product was isolated as a colorless oil (172 mg, 77% yield) with 90% ee.
1H NMR (CDCl₃, 500 MHz) δ 7.94 (d, J = 8.0 Hz, 2H), 7.46 (t, J = 8.0 Hz, 1H), 7.37 (t, J = 8.0 Hz, 2H), 7.28-7.24 (m, 4H), 7.20-7.16 (m, 1H), 4.42 (t, J = 7.0 Hz, 1H), 2.21-2.15 (m, 1H), 1.87-1.81 (m, 1H), 0.88 (t, J = 7.0 Hz, 3H);

13C NMR (CDCl₃, 75 MHz) δ 200.3, 139.8, 137.1, 133.0, 129.0, 128.8, 128.7, 128.4, 127.1, 55.6, 27.3, 12.5.

The spectral data are in agreement with literature data.²

(S)-4-Chloro-1,2-diphenylbutan-1-one (Table 2, entry 9) [1126519-20-7]. The title compound was prepared according to General Procedure A with 2-bromo-4-chloro-1-phenylbutan-1-one (262 mg, 1.00 mmol) and PhMgBr (3.0 M in Et₂O; 0.37 mL, 1.1 mmol). After purification by flash chromatography (eluted with 30→60% CH₂Cl₂ in hexanes), the title compound was isolated as a colorless oil (186 mg, 72% yield) with 85% ee (HPLC analysis of the product: Daicel CHIRALCEL OJ-H column; solvent system: 1% i-PrOH in hexanes; 1.0 mL/min; retention times: 17.0 min (minor), 18.1 min (major)).

[α]²²l = +172 (c = 1.0, CHCl₃).

The second run was performed with (S)-1. The product was isolated as a colorless oil (192 mg, 74% yield) with 86% ee.

1H NMR (CDCl₃, 500 MHz) δ 7.97 (d, J = 8.0 Hz, 2H), 7.50 (t, J = 8.0 Hz, 1H), 7.40 (t, J = 8.0 Hz, 2H), 7.34-7.31 (m, 4H), 7.25-7.22 (m, 1H), 4.45 (dd, J = 6.5, 7.0 Hz, 1H), 3.63-3.58 (m, 1H), 3.47-3.41 (m, 1H), 2.63-2.58 (m, 1H), 2.35-2.27 (m, 1H);

13C NMR (CDCl₃, 75 MHz) δ 199.2, 138.3, 136.5, 133.3, 129.4, 129.0, 128.8, 128.5, 127.7, 50.3, 43.3, 36.2.

The spectral data are in agreement with literature data.²

(S)-4-Azido-1,2-diphenylbutan-1-one (Table 2, entry 10). The title compound was prepared according to General Procedure A with 4-azido-2-bromo-1-phenylbutan-1-one (268 mg, 1.00 mmol) and PhMgBr (3.0 M in Et₂O; 0.37 mL, 1.1 mmol). After purification by flash chromatography (eluted with 30→60% CH₂Cl₂ in hexanes), the title compound was isolated as a colorless oil (196 mg, 74% yield) with 80% ee (HPLC analysis of the product: Daicel CHIRALPAK AS-H column; solvent system: 15% i-PrOH in hexanes; 1.0 mL/min; retention times: 5.7 min (major), 6.0 min (minor)).
[α]_D^{22} = +67 (c = 1.0, CHCl₃).

The second run was performed with (S)-1. The product was isolated as a colorless oil (186 mg, 70% yield) with 80% ee.

¹H NMR (CDCl₃, 500 MHz) δ 7.94 (d, J = 8.0 Hz, 2H), 7.47 (t, J = 8.0 Hz, 1H), 7.37 (t, J = 8.0 Hz, 2H), 7.30-7.27 (m, 4H), 7.22-7.20 (m, 1H), 4.71 (t, J = 7.0 Hz, 1H), 3.35-3.30 (m, 1H), 3.24-3.18 (m, 1H), 2.43-2.38 (m, 1H), 2.10-2.05 (m, 1H);

¹³C NMR (CDCl₃, 75 MHz) δ 199.0, 138.5, 136.5, 133.3, 129.4, 129.0, 128.8, 128.5, 127.6, 50.5, 49.5, 32.9;

IR (film) 2932, 2096, 1683, 1597, 1493, 1448, 1264, 983, 756, 697 cm⁻¹;

LRMS (ESI) calcd for C₁₆H₁₆N₃O (M+H) 266.1, found 266.1.

(S)-4-Oxo-3,4-diphenylbutyl acetate (Table 2, entry 11). The title compound was prepared according to General Procedure A with 3-bromo-4-oxo-4-phenylbutyl acetate (285 mg, 1.00 mmol) and PhMgBr (3.0 M in Et₂O; 0.37 mL, 1.1 mmol). After purification by flash chromatography (eluted with 20–40% CH₂Cl₂ in hexanes), the title compound was isolated as a colorless oil (214 mg, 76% yield) with 85% ee (HPLC analysis of the product: Daicel CHIRALPAK AS-H column; solvent system: 10% i-PrOH in hexanes; 1.0 mL/min; retention times: 9.6 min (major), 10.8 min (minor)).

[α]_D^{22} = +57 (c = 0.50, CHCl₃).

The second run was performed with (S)-1. The product was isolated as a colorless oil (200 mg, 71% yield) with 85% ee.

¹H NMR (CDCl₃, 500 MHz) δ 7.94 (d, J = 8.0 Hz, 2H), 7.47 (t, J = 8.0 Hz, 1H), 7.37 (t, J = 8.0 Hz, 2H), 7.28-7.26 (m, 4H), 7.21-7.18 (m, 1H), 4.68 (t, J = 7.0 Hz, 1H), 4.08-4.05 (m, 1H), 3.99-3.97 (m, 1H), 2.53-2.49 (m, 1H), 2.16-2.11 (m, 1H), 1.99 (s, 3H);

¹³C NMR (CDCl₃, 75 MHz) δ 199.0, 171.2, 138.5, 136.5, 133.3, 129.4, 129.0, 128.8, 128.5, 127.6, 50.4, 32.8, 21.2;

IR (film) 2960, 1734, 1684, 1597, 1576, 1491, 1447, 1363, 1235, 1037, 756, 697 cm⁻¹;

LRMS (ESI) calcd for C₁₈H₁₉N₃O (M+H) 283.1, found 283.1.

V. Asymmetric Kumada Cross-Couplings (Table 3)

General Procedure C (for commercially available Grignard reagents). A 20-mL vial equipped with a stir bar was capped with a septum and taped. The vial was purged with argon for 2 min. 1,2-Dimethoxyethane (8 mL) and a solution of the Grignard reagent (1.2 mmol) were
added in turn by syringe. The solution was stirred at room temperature for 2 min, and then it was cooled to −40 °C.

Ligand (R)-2 (44.0 mg, 0.09 mmol) and NiCl₂-glyme (15.3 mg, 0.070 mmol) were added to a 4.0-mL vial equipped with a stir bar. The vial was capped with a septum, taped, and gently purged with argon for 1 min. 1,2-Dimethoxyethane (2.0 mL) was added, and this solution of the catalyst was stirred at room temperature for 5 min. Next, the α-bromoketone (1.0 mmol) was added. The mixture was stirred at room temperature for 5 min, and then the resulting homogeneous dark-pink solution was added dropwise over 3 min to the −40 °C solution of the Grignard reagent. The resulting yellow solution was stirred at −40 °C for 48 h. Next, the reaction was quenched with ethanol (2 mL), and the resulting mixture was filtered through a Büchner funnel that contained a bed of silica gel (height: 3.0 cm). The silica gel was washed with additional Et₂O (40 mL), and then the combined filtrates were concentrated by rotary evaporation. The resulting residue was purified by flash chromatography on silica gel.

**General Procedure D** (for Grignard reagents prepared in situ; the second paragraph is the same as for General Procedure A). A 20-mL vial equipped with a stir bar was capped with a septum and taped. The vial was purged with argon for 2 min, and then 1,2-dimethoxyethane (8 mL) was added by syringe, followed by the aryl iodide (1.20 mmol). The solution was cooled to −20 °C, and a solution of i-PrMgCl (2.0 M solution in Et₂O; 0.60 mL, 1.2 mmol) was added over 1.0 min. The resulting mixture was stirred at −20 °C (30 min for electron-poor ArI and 2.0 h for electron-rich ArI), and then it was cooled to −40 °C.

Ligand (R)-2 (44.0 mg, 0.09 mmol) and NiCl₂-glyme (15.3 mg, 0.070 mmol) were added to a 4.0-mL vial equipped with a stir bar. The vial was capped with a septum, taped, and gently purged with argon for 1 min. 1,2-Dimethoxyethane (2.0 mL) was added, and this solution of the catalyst was stirred at room temperature for 5 min. Next, the α-bromoketone (1.0 mmol) was added. The mixture was stirred at room temperature for 5 min, and then the resulting homogeneous dark-pink solution was added dropwise over 3 min to the −40 °C solution of the Grignard reagent. The resulting yellow solution was stirred at −40 °C for 48 h. Next, the reaction was quenched with ethanol (2 mL), and the resulting mixture was filtered through a Büchner funnel that contained a bed of silica gel (height: 3.0 cm). The silica gel was washed with additional Et₂O (40 mL), and then the combined filtrates were concentrated by rotary evaporation. The resulting residue was purified by flash chromatography on silica gel.

**OMe**

(R)-2-Phenylpentan-3-one [103130-61-6] (Table 3, entry 1). The title compound was prepared according to General Procedure C with 2-bromopentan-3-one (165 mg, 1.00 mmol) and
PhMgBr (3.0 M solution in Et\textsubscript{2}O; 0.40 mL, 1.2 mmol). After purification by flash chromatography (eluted with 20→70% CH\textsubscript{2}Cl\textsubscript{2} in hexanes), the title compound was isolated as a colorless oil (146 mg, 90% yield) with 73% ee (HPLC analysis of the product: Daicel CHIRALPAK OD-H column; solvent system: 1% i-PrOH in hexanes; 1.0 mL/min; retention times: 4.3 min (minor), 5.2 min (major)).

\[\alpha\]\textsuperscript{22}_D = -47 (c = 1.0, CHCl\textsubscript{3}).

The second run was performed with (S)-2. The product was isolated as a colorless oil (145 mg, 90% yield) with 73% ee

\(^1\)H NMR (CDCl\textsubscript{3}, 500 MHz) \(\delta\) 7.35 (t, \(J = 8.0\) Hz, 2H), 7.27-7.25 (m, 1H), 7.22 (d, \(J = 8.0\) Hz, 2H), 3.77 (q, \(J = 7.0\) Hz, 1H), 2.45-2.33 (m, 2H), 1.40 (d, \(J = 7.0\) Hz, 3H), 0.96 (t, \(J = 7.0\) Hz, 3H).

The spectral data are in agreement with literature data.\(^6\)

(R)-1,3-Diphenylbutan-2-one (Table 3, entry 2). The title compound was prepared according to General Procedure C with 3-bromo-1-phenylbutan-2-one (227 mg, 1.00 mmol) and PhMgBr (3.0 M solution in Et\textsubscript{2}O; 0.40 mL, 1.2 mmol). After purification by flash chromatography (eluted with 20→70% CH\textsubscript{2}Cl\textsubscript{2} in hexanes), the title compound was isolated as a colorless oil (170 mg, 76% yield) with 85% ee (HPLC analysis of the product: Daicel CHIRALCEL OD-H column; solvent system: 1% i-PrOH in hexanes; 1.0 mL/min; retention times: 5.6 min (minor), 6.1 min (major)).

\[\alpha\]\textsuperscript{22}_D = -94 (c = 1.0, CHCl\textsubscript{3}).

The second run was performed with (S)-2. The product was isolated as a colorless oil (160 mg, 72% yield) with 85% ee.

\(^1\)H NMR (CDCl\textsubscript{3}, 500 MHz) \(\delta\) 7.36-7.19 (m, 8H), 7.05 (d, \(J = 8.0\) Hz, 2H), 3.85 (q, \(J = 7.0\) Hz, 1H), 3.62 (s, 2H), 1.37 (d, \(J = 8.0\) Hz, 3H);

\(^{13}\)C NMR (CDCl\textsubscript{3}, 75 MHz) \(\delta\) 208.3, 140.6, 134.5, 129.6, 129.2, 128.8, 128.3, 127.4, 127.1, 52.3, 48.2, 17.9;

IR (film) 2917, 1717, 1635, 1540, 1495, 1456, 1029, 698 cm\textsuperscript{-1};

LRMS (ESI) calcd for C\textsubscript{16}H\textsubscript{17}O (M+H) 225.1, found 225.1.

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(R)-3-(4-Chlorophenyl)-1-phenylbutan-2-one (Table 3, entry 3). The title compound was prepared according to General Procedure D with 3-bromo-1-phenylbutan-2-one (227 mg, 1.00 mmol) and 1-chloro-4-iodobenzene (286 mg, 1.20 mmol). After purification by flash chromatography (eluted with 20→70% CH₂Cl₂ in hexanes), the title compound was isolated as a colorless oil (212 mg, 82% yield) with 90% ee (HPLC analysis of the product: Daicel CHIRALCEL AD-H column; solvent system: 1% i-PrOH in hexanes; 1.0 mL/min; retention times: 6.82 min (minor), 7.45 min (major)).

\[ \alpha \] D₂₂ = −98 (c = 1.0, CHCl₃).

The second run was performed with (S)-2. The product was isolated as a colorless oil (212 mg, 82% yield) with 90% ee.

¹H NMR (CDCl₃, 500 MHz) δ 7.30 (d, J = 8.0 Hz, 2H), 7.28-7.24 (m, 3H), 7.11 (d, J = 8.0 Hz, 2H), 7.05 (d, J = 7.0 Hz, 2H), 3.83 (q, J = 7.0 Hz, 1H), 3.63 (d, J = 14.0 Hz, 1H), 3.62 (d, J = 14.0 Hz, 1H), 1.34 (d, J = 7.0 Hz, 3H);

¹³C NMR (CDCl₃, 75 MHz) δ 207.9, 139.0, 134.1, 130.1, 129.64, 129.60, 129.3, 128.9, 127.2, 51.4, 48.4, 17.9;

IR (film) 2976, 1716, 1491, 1408, 1330, 1092, 1014, 830, 697 cm⁻¹;

LRMS (ESI) calcd for C₁₆H₁₅O (M–Cl) 223.0, found 223.0.

(R)-Ethyl 4-(3-oxo-4-phenylbutan-2-yl)benzoate (Table 3, entry 4). The title compound was prepared according to General Procedure D with 3-bromo-1-phenylbutan-2-one (227 mg, 1.00 mmol) and ethyl 4-iodobenzoate (332 mg, 1.20 mmol). After purification by flash chromatography (eluted with 20→100% CH₂Cl₂ in hexanes), the title compound was isolated as a colorless oil (233 mg, 79% yield) with 81% ee (HPLC analysis of the product: Daicel CHIRALPAK AS-H column; solvent system: 1% i-PrOH in hexanes; 1.0 mL/min; retention times: 9.21 min (minor), 9.73 min (major)).

\[ \alpha \] D₂₂ = −73 (c = 1.0, CHCl₃).
The second run was performed with (S)-2. The product was isolated as a colorless oil (231 mg, 78% yield) with 81% ee.

$^1$H NMR (CDCl$_3$, 500 MHz) $\delta$ 8.01 (d, $J = 8.0$ Hz, 2H), 7.26-7.22 (m, 5H), 7.03 (d, $J = 8.0$ Hz, 2H), 4.37 (q, $J = 7.0$ Hz, 2H), 3.92 (q, $J = 7.0$ Hz, 1H), 3.62 (s, 2H), 1.40 (t, $J = 7.0$ Hz, 3H), 1.37 (d, $J = 7.0$ Hz, 3H);

$^{13}$C NMR (CDCl$_3$, 75 MHz) $\delta$ 207.6, 166.5, 145.6, 134.1, 130.5, 129.73, 129.66, 128.9, 128.2, 127.2, 61.3, 52.1, 48.6, 17.9, 14.6;

IR (film) 2978, 1717, 1684, 1653, 1521, 1456, 1276, 1107, 1020, 699 cm$^{-1}$;

LRMS (ESI) calcd for C$_{19}$H$_{20}$O$_3$ (M) 296.1, found 296.1.

The title compound was prepared according to General Procedure D with 3-bromo-1-phenylbutan-2-one (227 mg, 1.00 mmol) and 1-iodo-4-methoxybenzene (280 mg, 1.20 mmol). After purification by flash chromatography (eluted with 20→100% CH$_2$Cl$_2$ in hexanes), the title compound was isolated as a colorless oil (185 mg, 73% yield) with 90% ee (HPLC analysis of the product: Daicel CHIRALCEL OD-H column; solvent system: 1% i-PrOH in hexanes; 1.0 mL/min; retention times: 9.0 min (minor), 10.1 min (major)).

$[\alpha]_{D}^{22} = -96$ (c = 1.0, CHCl$_3$).

The second run was performed with (S)-2. The product was isolated as a colorless oil (182 mg, 72% yield) with 90% ee.

$^1$H NMR (CDCl$_3$, 500 MHz) $\delta$ 7.27-7.18 (m, 3H), 7.11 (d, $J = 8.0$ Hz, 2H), 7.05 (d, $J = 8.0$ Hz, 2H), 6.87 (d, $J = 8.0$ Hz, 2H), 3.81 (s, 3H), 3.78 (q, $J = 7.0$ Hz, 1H), 3.62 (s, 2H), 1.33 (d, $J = 7.0$ Hz, 3H);

$^{13}$C NMR (CDCl$_3$, 75 MHz) $\delta$ 208.5, 159.0, 134.7, 132.6, 129.7, 129.3, 128.8, 127.0, 114.6, 55.5, 51.4, 48.1, 17.9;

IR (film) 2940, 1717, 1669, 1616, 1559, 1472, 667 cm$^{-1}$;

LRMS (ESI) calcd for C$_{17}$H$_{19}$O$_2$ (M+H) 255.1, found 255.1.
(R)-1-Cyclohexyl-3-phenylbutan-2-one (Table 3, entry 6). The title compound was prepared according to General Procedure C with 3-bromo-1-cyclohexylbutan-2-one (233 mg, 1.0 mmol) and PhMgBr (3.0 M solution in Et₂O; 0.40 mL, 1.2 mmol). After purification by flash chromatography (eluted with 20→100% CH₂Cl₂ in hexanes), the title compound was isolated as a colorless oil (165 mg, 72% yield) with 85% ee (HPLC analysis of the product: Daicel CHIRALPAK AD-H column; solvent system: 1% i-PrOH in hexanes; 1.0 mL/min; retention times: 6.0 min (minor), 6.95 min (major)).

\[ [\alpha]^{22}_D = -118 \text{ (c = 1.0, CHCl}_3) \].

The second run was performed with (S)-2. The product was isolated as a colorless oil (172 mg, 75% yield) with 85% ee.

\(^1\)H NMR (CDCl₃, 500 MHz) \( \delta 7.32 \text{ (t, } J = 8.0 \text{ Hz, 2H), 7.26-7.23 \text{ (m, 1H), 7.20 (d, } J = 8.0 \text{ Hz, 2H), 3.71 \text{ (q, } J = 7.0 \text{ Hz, 1H), 2.24-2.16 \text{ (m, 2H), 1.79-1.77 \text{ (m, 1H), 1.63-1.57 \text{ (m, 4H), 1.49 (d, } J = 13.0 \text{ Hz, 1H), 1.36 (d, } J = 7.0 \text{ Hz, 3H), 1.26-1.18 \text{ (m, 2H), 1.09-1.04 \text{ (m, 1H), 0.88-0.81 \text{ (m, 1H), 0.71-0.67 \text{ (m, 1H);}} \)

\(^13\)C NMR (CDCl₃, 75 MHz) \( \delta 210.5, 140.5, 128.8, 127.9, 127.0, 53.4, 48.7, 33.6, 33.2, 32.8, 26.2, 26.1, 25.9, 17.3; \)

IR (film) 2923, 1713, 1493, 1448, 1374, 1069, 1029, 956, 760, 701 cm⁻¹;

LRMS (ESI) calcd for C₁₆H₂₃O (M+H) 231.1, found 231.1.

(R)-3-(3-Bromophenyl)-1-cyclohexylpentan-2-one (Table 3, entry 7). The title compound was prepared according to General Procedure D with 3-bromo-1-cyclohexylpentan-2-one (247 mg, 1.00 mmol) and 1-bromo-3-iodobenzene (338 mg, 1.20 mmol). After purification by flash chromatography (eluted with 20→100% CH₂Cl₂ in hexanes), the title compound was isolated as a colorless oil (252 mg, 70% yield) with 78% ee (HPLC analysis of the product: Daicel CHIRALPAK AD-H column; solvent system: 1% i-PrOH in hexanes; 1.0 mL/min; retention times: 5.68 min (minor), 6.25 min (major)).

\[ [\alpha]^{22}_D = -76 \text{ (c = 1.0, CHCl}_3) \].

The second run was performed with (S)-2. The product was isolated as a colorless oil (223 mg, 69% yield) with 78% ee
\[ ^1H \text{NMR (CDCl}_3, 500 \text{ MHz}) \delta 7.39 \text{ (d, } J = 8.0 \text{ Hz, 1H), 7.36 \text{ (s, 1H), 7.19 \text{ (t, } J = 8.0 \text{ Hz, 1H), 7.12 \text{ (d, } J = 8.0 \text{ Hz, 1H), 3.45 \text{ (t, } J = 7.0 \text{ Hz, 1H), 2.26-2.17 \text{ (m, 2H), 2.05-1.99 \text{ (m, 1H), 1.81-1.76 \text{ (m, 1H), 1.69-1.58 \text{ (m, 5H), 1.54 \text{ (d, } J = 12.0 \text{ Hz, 1H), 1.27-1.17 \text{ (m, 2H), 1.10-1.05 \text{ (m, 1H), 0.88-0.83 \text{ (m, 1H), 0.82 \text{ (t, } J = 7.0 \text{ Hz, 3H), 0.75-0.67 \text{ (m, 1H); ^13C \text{NMR (CDCl}_3, 75 \text{ MHz}) \delta 209.7, 141.4, 131.6, 130.49, 130.47, 127.1, 123.0, 60.9, 50.1, 33.7, 33.4, 33.1, 26.4, 26.3, 26.2, 25.6, 12.3; IR (film) 2923, 1715, 1559, 1473, 1448, 1072, 781 \text{ cm}^{-1}; LRMS (ESI) calcd for C_{17}H_{23}O (M–Br) 243.1, found 243.1.} \]

(R)-2-Methyl-4-phenylpentan-3-one [107656-30-4: (S) isomer] (Table 3, entry 8). The title compound was prepared according to General Procedure C with 2-bromo-4-methylpentan-3-one (179 mg, 1.00 mmol) and PhMgBr (3.0 M solution in Et₂O; 0.40 mL, 1.2 mmol). After purification by flash chromatography (eluted with 20→70% CH₂Cl₂ in hexanes), the title compound was isolated as a colorless oil (146 mg, 83% yield) with 84% ee (HPLC analysis of the product: Daicel CHIRALPAK OD-H column; solvent system: 1% i-PrOH in hexanes; 1.0 mL/min; retention times: 4.6 min (minor), 5.6 min (major)).

[α]$_D^{22}$ = −232 (c = 1.0, CHCl₃).

The second run was performed with (S)-2. The product was isolated as a colorless oil (144 mg, 82% yield) with 84% ee.

\[ ^1H \text{NMR (CDCl}_3, 500 \text{ MHz}) \delta 7.33 \text{ (t, } J = 6.5 \text{ Hz, 2H), 7.26-7.21 \text{ (m, 3H), 3.92 \text{ (q, } J = 7.0 \text{ Hz, 1H), 2.70-2.67 \text{ (m, 1H), 1.38 \text{ (d, } J = 7.0 \text{ Hz, 3H), 1.09 \text{ (d, } J = 7.0 \text{ Hz, 3H), 0.91 \text{ (d, } J = 7.0 \text{ Hz, 3H); ^13C \text{NMR (CDCl}_3, 75 \text{ MHz}) \delta 214.9, 141.0, 129.0, 128.2, 127.2, 51.3, 39.4, 19.5, 18.5, 18.4.} \]

The spectral data are in agreement with literature data.\(^7\)

(R)-2-(3,4-(Methylenedioxy)phenyl)-4-methylpentan-3-one (Table 3, entry 9). The title compound was prepared according to General Procedure C with 2-bromo-4-methylpentan-3-one (179 mg, 1.00 mmol) and PhMgBr (3.0 M solution in Et₂O; 0.40 mL, 1.2 mmol). After purification by flash chromatography (eluted with 20→70% CH₂Cl₂ in hexanes), the title compound was isolated as a colorless oil (146 mg, 83% yield) with 84% ee (HPLC analysis of the product: Daicel CHIRALPAK OD-H column; solvent system: 1% i-PrOH in hexanes; 1.0 mL/min; retention times: 4.6 min (minor), 5.6 min (major)).

[α]$_D^{22}$ = −232 (c = 1.0, CHCl₃).

The second run was performed with (S)-2. The product was isolated as a colorless oil (144 mg, 82% yield) with 84% ee.

\[ ^1H \text{NMR (CDCl}_3, 500 \text{ MHz}) \delta 7.33 \text{ (t, } J = 6.5 \text{ Hz, 2H), 7.26-7.21 \text{ (m, 3H), 3.92 \text{ (q, } J = 7.0 \text{ Hz, 1H), 2.70-2.67 \text{ (m, 1H), 1.38 \text{ (d, } J = 7.0 \text{ Hz, 3H), 1.09 \text{ (d, } J = 7.0 \text{ Hz, 3H), 0.91 \text{ (d, } J = 7.0 \text{ Hz, 3H); ^13C \text{NMR (CDCl}_3, 75 \text{ MHz}) \delta 214.9, 141.0, 129.0, 128.2, 127.2, 51.3, 39.4, 19.5, 18.5, 18.4.} \]

The spectral data are in agreement with literature data.\(^7\)

one (179 mg, 1.00 mmol) and 3,4-(methylenedioxy)phenylmagnesium bromide (1.0 M in toluene/THF, Aldrich; 1.20 mL, 1.2 mmol). After purification by flash chromatography (eluted with 30→100% CH₂Cl₂ in hexanes), the title compound was isolated as a colorless oil (162 mg, 74% yield) with 83% ee (HPLC analysis of the product: Daicel CHIRALPAK AS-H column; solvent system: 1% i-PrOH in hexanes; 1.0 mL/min; retention times: 7.1 min (minor), 7.8 min (major)).

\[ \alpha \]^{22}_D = -157 (c = 1.0, CHCl₃).

The second run was performed with (S)-2. The product was isolated as a colorless oil (167 mg, 76% yield) with 83% ee.

\(^1\)H NMR (CDCl₃, 500 MHz) \( \delta \) 6.74 (d, \( J = 8.0 \) Hz, 1H), 6.70 (d, \( J = 1.5 \) Hz, 1H), 6.66 (dd, \( J = 8.0 \), 1.5 Hz, 1H), 5.93 (s, 2H), 3.83 (q, \( J = 7.0 \) Hz, 1H), 2.71-2.68 (m, 1H), 1.32 (d, \( J = 7.0 \) Hz, 3H), 1.07 (d, \( J = 8.0 \) Hz, 3H), 0.92 (d, \( J = 8.0 \) Hz, 3H);

\(^{13}\)C NMR (CDCl₃, 75 MHz) \( \delta \) 214.9, 148.2, 146.7, 134.7, 121.4, 108.7, 108.4, 101.3, 50.8, 39.3, 19.4, 18.5, 18.4;

IR (film) 2972, 1710, 1505, 1486, 1440, 1247, 1040, 1017, 937, 909, 814, 635 cm⁻¹;
LRMS (ESI) calcd for C₁₃H₁₇O₃ (M+H) 221.1, found 221.1.

(R)-Ethyl 4-(5-methyl-4-oxohexan-3-yl)benzoate (Table 3, entry 10). The title compound was prepared according to General Procedure D with 4-bromo-2-methylhexan-3-one (193 mg, 1.00 mmol) and ethyl 4-iodobenzoate (332 mg, 1.20 mmol). After purification by flash chromatography (eluted with 30→100% CH₂Cl₂ in hexanes), the title compound was isolated as a colorless oil (212 mg, 81% yield) with 80% ee (HPLC analysis of the product: Daicel CHIRALCEL AD-H column; solvent system: 1% i-PrOH in hexanes; 1.0 mL/min; retention times: 8.56 min (minor), 9.55 min (major)).

\[ \alpha \]^{22}_D = -136 (c = 1.0, CHCl₃).

The second run was performed with (S)-2. The product was isolated as a colorless oil (199 mg, 76% yield) with 79% ee.

\(^1\)H NMR (CDCl₃, 500 MHz) \( \delta \) 7.99 (d, \( J = 6.5 \) Hz, 2H), 7.30 (d, \( J = 6.5 \) Hz, 2H), 4.37 (q, \( J = 7.0 \) Hz, 2H), 3.77 (t, \( J = 7.0 \) Hz, 1H), 2.65-2.62 (m, 1H), 2.09-2.03 (m, 1H), 1.72-1.66 (m, 1H), 1.39 (t, \( J = 7.0 \) Hz, 3H), 1.08 (d, \( J = 3.0 \) Hz, 3H), 0.92 (d, \( J = 3.0 \) Hz, 3H), 0.83 (t, \( J = 3.0 \) Hz, 3H);

\(^{13}\)C NMR (CDCl₃, 75 MHz) \( \delta \) 213.8, 166.6, 144.5, 130.2, 129.6, 128.6, 61.2, 59.1, 40.6, 26.3, 18.9, 18.3, 14.6, 12.4;
VI. Functionalization of the Cross-Coupling Products (eq 2 and 3)

(1S,2S)-1,2-Diphenylpropan-1-ol (eq 2) [89103-72-0]. A solution of lithium aluminum hydride (1.0 M in hexanes; 0.60 mL, 0.60 mmol) was added over 2 min to a −78 °C solution of (S)-1,2-diphenylpropan-1-one (105 mg, 0.50 mmol; 92% ee) in THF (2.0 mL) in a 10-mL round-bottom flask under argon. The reaction mixture was allowed to warm to 0 °C over 2 h, and then it was stirred at 0 °C for 2 h. Next, water (0.5 mL) was added dropwise to the reaction mixture at 0 °C to quench the reaction. Aqueous HCl (1.0 N; 5.0 mL) was added, and the mixture was extracted with EtOAc (3×5 mL). The combined organic extracts were dried over MgSO₄, filtered, and concentrated. The residue was purified by flash chromatography on silica gel, which afforded the alcohol as a white solid (97 mg, 91% yield; >20 : 1 dr, 92% ee (HPLC analysis of the product: Daicel CHIRALPAK AD-H column; solvent system: 5% i-PrOH in hexanes; 1.0 mL/min; retention times: 12.4 min (major), 13.6 min (minor)))

\[ \alpha \] = −60 (c = 1.0, CHCl₃).

¹H NMR (CDCl₃, 500 MHz) δ 7.38–7.26 (m, 10H), 4.66 (d, J = 8.5 Hz, 1H), 3.05–2.99 (m, 1H), 1.84 (s, 1H), 1.08 (d, J = 7.0 Hz, 3H).

The relative stereochemistry was determined by comparison of the ¹H NMR data with reported values.⁸

(1S,2S)-N-Benzyl-1,2-diphenylpropan-1-amine (eq 3). Benzylamine (59.0 mg, 0.550 mmol) and Et₃N (210 µL, 1.50 mmol) were added to a −78 °C solution of (S)-1,2-diphenylpropan-1-one (105 mg, 0.50 mmol; 92% ee) in THF (2.5 mL) in a 10-mL round-bottom flask. Then, a solution of TiCl₄ in CH₂Cl₂ (1.0 M; 0.50 mL, 0.50 mmol) was added over 3 min. The reaction mixture was stirred at −78 °C for 5 min, and then it was allowed to warm to −20 °C and stirred for 1 h. Next, a solution of NaBH(OAc)₃ (0.530 g, 5.0 mmol) in AcOH (1.5 mL) was added to the reaction

mixture over 3 min. The resulting mixture was stirred at −20 °C for 4 h and then at 0 °C for 15 h. Next, water (5 mL) was added to the 0 °C reaction mixture to quench the reaction. Then, aqueous NaOH (6.0 N) was added to adjust the pH to 11. The resulting solution was extracted with EtOAc (3×15 mL), and the combined organic layers were dried over MgSO₄, filtered, and concentrated. The residue was purified by flash chromatography on silica gel, which afforded the product as a white solid (115 mg, 76% yield; 10:1 dr, 92% ee).

[α]²º = −29 (c = 1.0, CHCl₃).

HPLC analysis of the product: Daicel CHIRALPAK AD-H column; solvent system: 5% i-PrOH in hexanes; 1.0 mL/min; retention times: 4.58 (syn, major), 5.16 min (anti, major), 5.68 (syn, minor), 6.39 min (anti, minor).

¹H NMR (CDCl₃, 500 MHz) δ 7.38-7.15 (m, 13H), 6.94 (d, J = 6.5 Hz, 2H), 3.60 (d, J = 10.0 Hz, 1H), 3.54 (d, J = 14 Hz, 1H), 3.28 (d, J = 10.0 Hz, 1H), 2.94-2.87 (m, 1H), 0.94 (d, J = 7.0 Hz, 3H);
¹³C NMR (CDCl₃, 75 MHz) δ 145.4, 141.1, 139.3, 129.4, 129.2, 128.9, 128.8, 128.6, 128.4, 127.9, 127.4, 127.3, 68.5, 51.9, 47.9, 20.6;
IR (film) 3017, 1683, 1600, 1493, 1452, 1222, 1103, 1028, 952, 757, 698 cm⁻¹;
LRMS (ESI) calcd for C₂₂H₂₄N (M+H) 302.2, found 302.2.

(1S,2S)-1,2-Diphenylpropan-1-amine. To determine the relative stereochemistry, the benzyl group was removed. Pd(OH)₂ on carbon (10 weight percent; 55.0 mg, 0.040 mmol) was added to a solution of (1S,2S)-N-benzyl-1,2-diphenylpropan-1-amine (60 mg, 0.20 mmol) in methanol (2 mL). Then, ammonium formate (320 mg, 5.0 mmol) was added in a single portion, and the reaction mixture was stirred for 4 h at 60 °C. Next, Et₃N (0.40 mL) was added, and the mixture was stirred for 10 min. The reaction mixture was then filtered through a bed of Celite. The Celite was rinsed thoroughly with 1% Et₃N in methanol, and the combined filtrates were concentrated. The residue was purified by flash chromatography on silica gel (2%MeOH/98% CH₂Cl₂/0.5% Et₃N), which furnished the title compound as a white solid (36.0 mg, 75% yield).

¹H NMR (CD₃OD, 500 MHz) δ 7.40-7.05 (m, 10H), 4.24 (d, J = 10.5 Hz, 1H), 3.16-3.08 (m, 3H), 0.87 (d, J = 7.0 Hz, 3H).

The relative stereochemistry was determined by comparing this ¹H NMR data with reported data.⁹

VII. Assignment of Absolute Configuration

Table 1, entry 1. The optical rotation of the product generated in the presence of (R)-1 was measured: \([\alpha]^{21}_D = +175\) (c = 1.00, CHCl₃; 92% ee).

(S) isomer: Lit.⁵ \([\alpha]^{22}_D = +190\) (c = 1.08, CHCl₃; 96% ee); Lit.¹⁰ \([\alpha]^{19}_D = +196\) (c = 1.10, CHCl₃).

Table 3, entry 1. The optical rotation of the product generated in the presence of (R)-2 was measured: \([\alpha]^{21}_D = -47.2\) (c = 1.00, CHCl₃; 73% ee).

(R) isomer: Lit.¹¹ \([\alpha]^{25}_D = -76\) (c = 1.2, CHCl₃; 95% ee).

Table 3, entry 8. \(m\)-Chloroperoxybenzoic acid (70% purity; 621 mg, 2.50 mmol) and NaHCO₃ (210 mg, 2.50 mmol) were added in turn to a solution of 2-methyl-4-phenylpentan-3-one (88.2 mg, 0.50 mmol; generated in the presence of (R)-2; 84% ee) in CH₂Cl₂ (4.0 mL) in a 10-mL round-bottom flask. The reaction mixture was stirred at room temperature for 6 h. Then, the solution was diluted with Et₂O (20 mL), washed with saturated aqueous NaHCO₃ (15 mL), dried over Na₂SO₄ and filtered. The filtrate was concentrated, and the residue was purified by flash chromatography on silica gel (eluted with 20→60% CH₂Cl₂ in hexanes), which afforded the desired ester as a colorless oil (96 mg, 73% yield).

The ester (48.0 mg, 0.250 mmol), NaOH (150 mg in 1.0 mL of H₂O), THF (2.0 mL), and MeOH (2.0 mL) were added in turn to a 10-mL round-bottom flask. The resulting mixture was stirred at room temperature for 6 h. Then, the reaction was quenched by the addition of HCl (1.0 N; 10 mL), and the mixture was diluted with CHCl₃ (10 mL). The organic layer was washed with brine (10 mL), dried over Na₂SO₄ and filtered. The filtrate was concentrated, and the residue

was purified by flash chromatography on silica gel (eluted with 50→100% CH₂Cl₂ in hexanes), which afforded (R)-1-phenylethanol as a colorless oil (24.0 mg, 80% yield). \([\alpha]^{22}_{D} = +36 \text{ (c = 0.50, MeOH; 84% ee)}\); authentic (R)-1-phenylethanol obtained from Aldrich: \([\alpha]^{22}_{D} +46 \text{ (c = 0.50, MeOH; 99% ee)}\).

**Table 2, entry 5.** A crystal structure of the product generated in the presence of (R)-1 was obtained. The absolute configuration of (S)-1-(4-(benzylxy)phenyl)-2-phenylpropan-1-one was determined by X-ray crystallography with Cu radiation.
Table 1. Crystal data and structure refinement for d09024.

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Table 2. Atomic coordinates ($x \times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for d09024. $U(eq)$ is defined as one third of the trace of the orthogonalized $U^0$ tensor.

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Table 3. Bond lengths [Å] and angles [°] for d09024.

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C(19)-H(19) 0.9500
C(20)-C(21) 1.389(3)
C(20)-H(20) 0.9500
C(21)-H(21) 0.9500
C(22)-H(22A) 0.9800
C(22)-H(22B) 0.9800
C(22)-H(22C) 0.9800

C(8)-O(1)-C(1) 117.30(13)
O(1)-C(1)-H(1A) 109.6
O(1)-C(1)-H(1B) 109.6
C(2)-C(1)-H(1A) 109.6
C(2)-C(1)-H(1B) 109.6
H(1A)-C(1)-H(1B) 108.1
C(7)-C(2)-C(3) 118.97(16)
C(7)-C(2)-C(1) 123.44(15)
C(3)-C(2)-C(1) 117.60(15)
C(4)-C(3)-C(2) 120.43(17)
C(4)-C(3)-H(3) 119.8
C(2)-C(3)-H(3) 119.8
C(3)-C(4)-C(5) 120.58(16)
C(3)-C(4)-H(4) 119.7
C(5)-C(4)-H(4) 119.7
C(4)-C(5)-C(6) 119.26(17)
C(4)-C(5)-H(5) 120.4
C(6)-C(5)-H(5) 120.4
C(7)-C(6)-C(5) 120.59(17)
C(7)-C(6)-H(6) 119.7
C(5)-C(6)-H(6) 119.7
C(6)-C(7)-C(2) 120.16(16)
C(6)-C(7)-H(7) 119.9
C(2)-C(7)-H(7) 119.9
O(1)-C(8)-C(9) 124.35(15)
O(1)-C(8)-C(13) 115.89(15)
C(9)-C(8)-C(13)  119.75(16)
C(10)-C(9)-C(8)  119.48(15)
C(10)-C(9)-H(9)  120.3
C(8)-C(9)-H(9)  120.3
C(9)-C(10)-C(11)  121.59(16)
C(9)-C(10)-H(10)  119.2
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C(16)-C(15)-C(14)  112.08(15)
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C(22)-C(15)-H(15)  107.6
C(14)-C(15)-H(15)  107.6
C(21)-C(16)-C(17)  118.45(18)
C(21)-C(16)-C(15)  122.75(16)
C(17)-C(16)-C(15)  118.81(16)
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C(17)-C(18)-H(18)  119.9
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C(20)-C(21)-H(21)  119.5
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C(15)-C(22)-H(22B)  109.5
H(22A)-C(22)-H(22B)  109.5
C(15)-C(22)-H(22C)  109.5
H(22A)-C(22)-H(22C)  109.5
H(22B)-C(22)-H(22C)  109.5

Symmetry transformations used to generate equivalent atoms:
Table 4. Anisotropic displacement parameters (Å² x 10³) for d09024. The anisotropic displacement factor exponent takes the form: \(-2\pi^2 [ h^2 a^{*2} U^{11} + ... + 2 h k a^{*} b^{*} U^{12} ]\)

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Table 5. Hydrogen coordinates ($x \times 10^4$) and isotropic displacement parameters ($Å^2 \times 10^{-3}$) for d09024.

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<th>z</th>
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VIII. Kinetics Studies

General procedure. A 20-mL vial equipped with a stir bar was charged with 1,2-dimethoxyethane (8.5 mL) and dodecane (23 µL, 0.10** mmol). The solution was cooled to −20 °C, and PhMgBr was added. The mixture was stirred until it was homogeneous, and then it was cooled to −60 °C.

A 4.0-mL vial was charged with NiCl₂-glyme, ligand 1, and 1,2-dimethoxyethane (1.5 mL). The solution was stirred for 5.0 min, and then 2-bromo-1-phenylpropan-1-one was added. The solution was stirred for 3.0 min, and then this homogeneous pink solution was added over 2-3 min to the −60 °C solution of the Grignard reagent. An aliquot (0.2 mL) of the reaction mixture was removed after 5 min, 10 min, 15 min, 20 min, 30 min, 45 min, 60 min, 90 min, 120 min, 3.0 h, 4.0 h, and 6.0 h (quenched with EtOH). The amount of product was determined by GC analysis (calibrated with dodecane as the internal standard). The initial rate was measured by plotting the conversion for the first 30% of the reaction.

Order in the catalyst:

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<th>[Ni(II)/1]_{initial} (mM)⁴</th>
<th>k_{obs} (M/h)</th>
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⁴Reactions were run with [electrophile]_{initial} = 0.010 M and [PhMgBr]_{initial} = 0.012 M.

Figure S1.

Order of the catalyst
Order in the electrophile:

**Table S2.** Observed Initial Rates.

<table>
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<th>[electrophile]$_{\text{initial}}$ (mM)$^a$</th>
<th>$k_{\text{obs}}$ (M/h)</th>
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<td>0</td>
</tr>
<tr>
<td>5.0</td>
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<tr>
<td>20</td>
<td>0.37</td>
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<td>30</td>
<td>0.38</td>
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</table>

$^a$ Reactions were run with [catalyst]$_{\text{initial}} = 0.50$ mM and [PhMgBr]$_{\text{initial}} = 0.012$ M.

**Figure S2.**

Order of the Electrophile

Order in the Grignard reagent:

**Table S3.** Observed Initial Rates.

<table>
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<th>[PhMgBr]$_{\text{initial}}$ (mM)$^a$</th>
<th>$k_{\text{obs}}$ (M/h)</th>
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</thead>
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<td>7.5</td>
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<tr>
<td>10</td>
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<td>0.68</td>
</tr>
<tr>
<td>20</td>
<td>0.85</td>
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</table>

$^a$ Reactions were run with [catalyst]$_{\text{initial}} = 0.50$ mM and [electrophile]$_{\text{initial}} = 0.010$ M.
Figure S3.

Order of the nucleophile

\[ y = 0.1045x \]
\[ r^2 = 0.991 \]
Table 1, entry 1

Me

Ph

Ph
Table 1, entry 4

![Chemical Structure]

Table contents and parameters...
Table 1, entry 6

![Chemical Structure]

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<tr>
<th>C02</th>
<th>Me</th>
<th>CF3</th>
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</thead>
</table>

ACQUISITION

Sample 8 2000 of d1-15C19 Me

SAMPLE 9 6-2
Table 1, entry 7

\[
\text{Ph} - \text{O} - \text{COEt}
\]
Table 1, entry 9

Ome

Ph

Me

O
Table 1, Entry 10

![Structural diagram]
Table 1, entry II

[Chemical structure diagram]

Acquisition: 1H-NMR, 600.13 MHz, 200 Hz, 499.74 MHz, 19F-NMR
Sample: 3,001 mg
Solvent: CCl4, CH2Cl2, CDCl3
Dilution: 1:20,000
Data: Dec 8, 2008, Cat. A, V1

[Data table]

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Note: The table above has been truncated for brevity.
### Table 2: Entry 5

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**Notes:**
- Table 2 provides the chemical structures and properties for the compounds under study.
- The structures are represented using standard chemical shorthand.
- Additional details are provided in the footnotes.
Table 2, Entry 7

![Chemical Structure Image]
Table 3, entry 2

![Chemical Structure]

DEG A VP

0-11-14-3
Table 3, entry 4

\[
\text{CO}^2\text{Et} \\
\begin{array}{c}
\text{Ph} \\
\text{Me}
\end{array}
\]
Table 3: Entry 9

\[
\begin{align*}
\text{Me} & \quad \text{Me} \\
\text{O} & \quad \text{Me} \\
\text{N} & \quad \text{Me}
\end{align*}
\]