Supporting Information

Iridium/f-Ampha-Catalyzed Asymmetric Hydrogenation of Aromatic α-Keto Esters

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1. General remarks

All reactions and manipulations which are sensitive to moisture or air were performed in an argon-filled glove box or using standard Schlenk techniques. Anhydrous i-PrOH, MeOH, DCM, THF, Dioxane, EtOAc and MeCN purchased from J&K were treated with argon before used; anhydrous toluene was prepared by treating the commercially available toluene with Na and benzophenone. Unless otherwise noted, commercially available chemicals are used without purification. [Ir(COD)Cl]$_2$ was prepared according to the literature$^{1-2}$. $^1$H, $^{13}$C and $^{19}$F NMR spectra were recorded with a Bruker ADVANCE III (400 MHz) spectrometer with CDCl$_3$ as the solvent and tetramethylsilane (TMS) as the internal standard. Chemical shifts are reported in parts per million (ppm, $\delta$ scale) downfield from TMS at 0.00 ppm and referenced to the CDCl$_3$ at 7.26 ppm (for $^1$H NMR) or 77.0 ppm (for $^{13}$C NMR). Data are reported as: multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constant in hertz (Hz) and signal area integration in natural numbers. $^{13}$C NMR and $^{19}$F NMR analyses were run with decoupling. HPLC analyses were performed by Agilent 1260 HPLC using Daicel chiral columns.

2. General procedure for the preparation of substrate compounds

![Scheme S1. General procedure for the preparation of substrates 1a,1b,1c,1e, 1j, 1m,1n,1p,1r.](image)

Step 1$^3$: A mixture of substituted acetophenone SM-1 (40 mmol) and selenium dioxide (6.7 g, 60 mmol) in dry pyridine (20 mL) was stirred at 100 °C under a nitrogen atmosphere for 15 h and then cooled in an ice bath. 4Å molecular sieves (0.24 g) and methanol (29 mL) were then added, and the reaction mixture was stirred for additional 10 min. After thionyl chloride (15 mL) was added dropwise over 1 h, the mixture was stirred for another 16 h at room temperature. A mixture of perchloric acid (5 mL, 70%), acetonitrile (100 mL) and deionized water (10 mL) were poured into the flask, and the mixture was stirred for 24 h. The mixture was neutralized with saturated sodium bicarbonate, filtrated. The resulting aqueous phase was extracted with ethyl acetate (100 mL×3). The combined organic layers were washed with brine, dried over anhydrous Na$_2$SO$_4$, and concentrated under reduced pressure. The residue was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 10:1) to afford the a-keto esters SM-2.

Step 2: To a solution of a-keto esters SM-2 (5 mmol) in $^t$PrOH (10 mL), catalytic amount 'BuOLi was added, the mixture was concentrated after stirred at room temperature for 1 hour, and purified by column chromatography (Petrokeum Ether/EtOAc = 10:1) to afford 1.
Scheme S2. General procedure for the preparation of substrates If, Ig, Ih, II, Io, lq.

To a suspension solution of SM-3 (8.2 mmol) and AlCl₃ (8.2 mmol) in dry DCM, isopropyl 2-chloro-2-oxoacetate was added dropwise at 0 °C. After this reaction mixture was stirred at room temperature for 4 h, 6.6 mL hydrochloric acid (6.6 mL, 5 % wt) was added slowly. The organic phase was washed with water, and dried with Na₂SO₄. After removal of the volatiles, the crude product was purified by column chromatography (petroleum ether/ethyl acetate = 10:1).

**isopropyl 2-(2-chlorophenyl)-2-oxoacetate (1a)**

![chemical structure](image)

Light yellow oil, 47% yield for two steps. ¹H NMR (400 MHz, Chloroform-d) δ 7.78 (dd, J = 7.7, 1.7 Hz, 1H), 7.55 (ddd, J = 8.1, 7.3, 1.7 Hz, 1H), 7.50 – 7.37 (m, 2H), 5.28 (hept, J = 6.3 Hz, 1H), 1.41 (d, J = 6.3 Hz, 6H). ¹³C NMR (101 MHz, CDCl₃) δ 186.94, 162.74, 134.20, 133.75, 133.48, 131.65, 130.50, 127.23, 71.09, 21.49. HRMS m/z: Calcd for [C₁₁H₁₁ClO₃+H]⁺: 227.0466. Found: 227.0469.

**isopropyl 2-(4-chlorophenyl)-2-oxoacetate (1b)**

![chemical structure](image)

Light yellow oil, 52% yield for two steps. ¹H NMR (400 MHz, Chloroform-d) δ 8.02 – 7.94 (m, 2H), 7.56 – 7.46 (m, 2H), 5.33 (hept, J = 6.3 Hz, 1H), 1.42 (d, J = 6.3 Hz, 6H). ¹³C NMR (101 MHz, CDCl₃) δ 185.21, 163.00, 141.51, 131.35, 130.97, 129.29, 70.95, 21.71. HRMS m/z: Calcd for [C₁₁H₁₁ClO₃+H]⁺: 227.0464. Found: 227.0469.

**isopropyl 2-(3-chlorophenyl)-2-oxoacetate (1c)**

![chemical structure](image)

Light yellow oil, 37% yield for two steps. ¹H NMR (400 MHz, Chloroform-d) δ 8.02 (t, J = 1.9 Hz, 1H), 7.91 (ddd, J = 7.8, 1.6, 1.1 Hz, 1H), 7.64 (ddd, J = 8.0, 2.1, 1.1 Hz, 1H), 7.48 (t, J = 7.9 Hz, 1H), 5.34 (hept, J = 6.3 Hz, 1H), 1.44 (d, J = 6.3 Hz, 6H). ¹³C NMR (101 MHz, CDCl₃) δ 185.15, 162.78, 135.24, 134.70, 134.13, 130.20, 129.81, 128.16, 71.10, 21.71. HRMS m/z: Calcd for [C₁₁H₁₁ClO₃+Na]⁺: 249.0285. Found: 245.0289.

**isopropyl 2-oxo-2-phenylacetate (1d)**

![chemical structure](image)
Light yellow oil, 92% yield for two steps. $^1$H NMR (400 MHz, Chloroform-$d$) $\delta$ 8.05 – 7.97 (m, 2H), 7.68 (ddt, $J$ = 7.8, 7.0, 1.3 Hz, 1H), 7.58 – 7.48 (m, 2H), 5.35 (hept, $J$ = 6.3 Hz, 1H), 1.43 (d, $J$ = 6.3 Hz, 6H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 186.73, 163.64, 134.82, 132.52, 129.96, 128.89, 70.70, 21.74. HRMS $m/z$: Calcd for [C$_{11}$H$_{12}$O$_3$+Na]$^+$: 215.0671. Found: 211.0679.

**isopropyl 2-oxo-2-(m-tolyl)acetate (1e)**

Light yellow oil, 48% yield for two steps. $^1$H NMR (400 MHz, Chloroform-$d$) $\delta$ 7.80 (dd, $J$ = 9.3, 1.8 Hz, 2H), 7.48 (d, $J$ = 7.6 Hz, 1H), 7.41 (t, $J$ = 7.6 Hz, 1H), 5.35 (hept, $J$ = 6.3 Hz, 1H), 2.44 (s, 3H), 1.43 (d, $J$ = 6.3 Hz, 6H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 186.97, 163.80, 138.83, 135.67, 132.51, 130.22, 128.76, 127.30, 70.60, 21.74, 21.30. HRMS $m/z$: Calcd for [C$_{12}$H$_{14}$O$_3$+H]$^+$: 207.1010. Found: 207.1016.

**isopropyl 2-oxo-2-(o-tolyl)acetate (1f)**

Light yellow oil, 48% yield for two steps. $^1$H NMR (400 MHz, Chloroform-$d$) $\delta$ 7.70 (dd, $J$ = 7.8, 1.4 Hz, 2H), 7.51 (td, $J$ = 7.6, 1.4 Hz, 1H), 7.34 (td, $J$ = 8.3, 7.7, 1.3 Hz, 2H), 5.32 (hept, $J$ = 6.3 Hz, 1H), 2.63 (s, 3H), 1.42 (d, $J$ = 6.3 Hz, 6H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 189.04, 164.37, 141.36, 133.61, 132.36, 132.24, 131.26, 125.90, 70.53, 21.70, 21.52. HRMS $m/z$: Calcd for [C$_{12}$H$_{14}$O$_3$+Na]$^+$: 229.0835. Found: 229.0835.

**isopropyl 2-(4-isopropylphenyl)-2-oxoacetate (1g)**

Light yellow oil, 39% yield for two steps. $^1$H NMR (400 MHz, Chloroform-$d$) $\delta$ 7.98 – 7.90 (m, 2H), 7.42 – 7.34 (m, 2H), 5.34 (hept, $J$ = 6.3 Hz, 1H), 3.00 (hept, $J$ = 6.9 Hz, 1H), 1.42 (d, $J$ = 6.3 Hz, 6H), 1.29 (d, $J$ = 6.9 Hz, 6H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 186.42, 163.88, 156.73, 130.40, 130.25, 127.06, 70.49, 34.47, 23.54, 21.74. HRMS $m/z$: Calcd for [C$_{14}$H$_{18}$O$_3$+H]$^+$: 235.1322. Found: 235.1329.

**isopropyl 2-(4-ethylphenyl)-2-oxoacetate (1h)**
Light yellow oil, 41% yield for two steps. $^1$H NMR (400 MHz, Chloroform-$d$) $\delta$ 7.97 – 7.89 (m, 2H), 7.38 – 7.31 (m, 2H), 5.34 (hept, $J = 6.3$ Hz, 1H), 2.74 (q, $J = 7.6$ Hz, 2H), 1.41 (s, 6H), 1.28 (t, $J = 7.6$ Hz, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 186.43, 163.87, 152.21, 130.28, 130.19, 128.45, 70.50, 29.16, 21.74, 15.05. HRMS $m/z$: Calcd for [C$_{13}$H$_{16}$O$_3$+H]$^+$: 221.1166. Found: 221.1172.

**isopropyl 2-(4-methoxyphenyl)-2-oxoacetate (1i)**

Light yellow oil, 43% yield for two steps. $^1$H NMR (400 MHz, Chloroform-$d$) $\delta$ 8.04 – 7.96 (m, 2H), 7.04 – 6.95 (m, 2H), 5.32 (hept, $J = 6.3$ Hz, 1H), 3.91 (s, 3H), 1.42 (d, $J = 6.2$ Hz, 6H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 185.23, 164.93, 163.97, 132.49, 125.57, 114.23, 70.43, 55.65, 21.75. HRMS $m/z$: Calcd for [C$_{12}$H$_{14}$O$_4$+H]$^+$: 223.0959. Found: 223.0965.

**isopropyl 2-(3,5-dimethylphenyl)-2-oxoacetate (1j)**

Light yellow oil, 47% yield for two steps. $^1$H NMR (400 MHz, Chloroform-$d$) $\delta$ 7.64 – 7.57 (m, 1H), 7.18 – 7.10 (m, 2H), 5.32 (hept, $J = 6.3$ Hz, 1H), 2.61 (s, 3H), 2.40 (s, 3H), 1.42 (d, $J = 6.3$ Hz, 6H), 133.28, 132.75, 128.48, 126.63, 70.34, 21.71, 21.68, 21.63. HRMS $m/z$: Calcd for [C$_{13}$H$_{16}$O$_3$+Na]$^+$: 243.0984. Found: 243.0992.

**isopropyl 2-(3,5-dimethylphenyl)-2-oxoacetate (1k)**

Light yellow oil, 47% yield for two steps. $^1$H NMR (400 MHz, Chloroform-$d$) $\delta$ 7.52 – 7.46 (m, 1H), 7.35 – 7.28 (m, 1H), 7.21 (d, $J = 7.8$ Hz, 1H), 5.39 – 5.28 (m, 1H), 2.58 (s, 3H), 2.38 (s, 3H), 1.43 (d, $J = 6.3$ Hz, 6H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 189.20, 164.50, 138.23, 135.51, 134.45, 132.69, 132.27, 131.11, 70.43, 21.69, 21.01, 20.84. HRMS $m/z$: Calcd for [C$_{13}$H$_{16}$O$_3$+H]$^+$: 221.1165. Found: 221.1172.

**isopropyl 2-(2-methoxy-5-methylphenyl)-2-oxoacetate (1l)**
Light yellow oil, 35% yield for two steps. $^1$H NMR (400 MHz, Chloroform-$d$) $\delta$ 7.69 (d, $J$ = 2.4 Hz, 1H), 7.43 – 7.35 (m, 1H), 6.89 (d, $J$ = 8.5 Hz, 1H), 5.25 (hept, $J$ = 6.3 Hz, 1H), 3.85 (s, 3H), 2.34 (s, 3H), 2.19 (s, 6H), 1.39 (d, $J$ = 6.3 Hz, 6H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 186.99, 165.04, 158.34, 136.93, 130.80, 130.72, 122.44, 111.89, 69.77, 55.86, 21.70, 20.24. HRMS $m/z$: Calcd for [C$_{13}$H$_{16}$O$_4$+H]$^+$: 237.1115. Found: 237.1121.

**isopropyl 2-(4-bromophenyl)-2-oxoacetate (1m)$^4$**

Light yellow oil, 61% yield for two steps. $^1$H NMR (400 MHz, Chloroform-$d$) $\delta$ 7.93 – 7.84 (m, 2H), 7.72 – 7.63 (m, 2H), 5.32 (hept, $J$ = 6.3 Hz, 1H), 1.42 (d, $J$ = 6.3 Hz, 6H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 185.42, 162.95, 132.28, 131.58, 131.37, 130.40, 70.96, 21.71. HRMS $m/z$: Calcd for [C$_{11}$H$_{11}$O$_3$Br+H]$^+$: 270.9956. Found: 270.9964.

**isopropyl 2-(4-fluorophenyl)-2-oxoacetate (1n)$^4$**

Light yellow oil, 45% yield for two steps. $^1$H NMR (400 MHz, Chloroform-$d$) $\delta$ 8.13 – 8.03 (m, 2H), 7.21 (t, $J$ = 8.6 Hz, 2H), 5.34 (hept, $J$ = 6.3 Hz, 1H), 1.43 (d, $J$ = 6.3 Hz, 6H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 184.87, 166.75 (d, $J$ = 259.6 Hz), 163.20, 132.86 (d, $J$ = 10.1 Hz), 116.36, 116.14, 70.87, 21.72. $^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$ -101.41. HRMS $m/z$: Calcd for [C$_{11}$H$_{11}$FO$_3$+H]$^+$: 211.0760. Found: 211.0765.

**isopropyl 2-(benzo[d][1,3]dioxol-5-yl)-2-oxoacetate (1o)**

A white solid, $^1$H NMR (400 MHz, Chloroform-$d$) $\delta$ 7.60 (dd, $J$ = 8.2, 1.7 Hz, 1H), 7.48 (d, $J$ = 1.7 Hz, 1H), 6.91 (d, $J$ = 8.2 Hz, 1H), 6.10 (s, 2H), 5.31 (hept, $J$ = 6.3 Hz, 1H), 1.42 (d, $J$ = 6.3 Hz, 6H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 184.89, 163.79, 153.44, 148.49, 127.71, 127.29, 108.67, 108.31, 102.23, 70.58, 21.73. HRMS $m/z$: Calcd for [C$_{12}$H$_{12}$O$_5$+H]$^+$: 237.0751. Found: 237.0757.

**isopropyl 2-(naphthalen-1-yl)-2-oxoacetate (1p)$^4$**
A yellow oil, $^1$H NMR (400 MHz, Chloroform-$d$) $\delta$ 8.17 – 8.07 (m, 2H), 7.79 – 7.72 (m, 2H), 7.66 (d, $J = 7.5$ Hz, 2H), 7.51 (dd, $J = 8.3$, 6.5 Hz, 2H), 7.46 (d, $J = 7.1$ Hz, 1H), 5.37 (hept, $J = 6.3$ Hz, 1H), 1.46 (d, $J = 6.2$ Hz, 6H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 186.22, 163.63, 147.51, 139.51, 131.30, 130.57, 129.04, 128.62, 127.51, 127.35, 70.68, 21.76.

**isopropyl 2-oxo-2-(thiophen-2-yl)acetate (1q)$^i$**

A red oil, $^1$H NMR (400 MHz, Chloroform-$d$) $\delta$ 8.12 (dd, $J = 3.9$, 1.2 Hz, 1H), 7.83 (dd, $J = 4.9$, 1.2 Hz, 1H), 7.21 (dd, $J = 4.9$, 3.9 Hz, 1H), 5.29 (hept, $J = 6.3$ Hz, 1H), 1.43 (d, $J = 6.3$ Hz, 6H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 176.83, 161.34, 139.14, 137.30, 137.04, 128.61, 71.14, 21.66. HRMS $m/z$: Calcd for [C$_9$H$_{10}$O$_3$S+H]$^+$: 199.0418. Found: 199.0423.

**isopropyl 2-(naphthalen-2-yl)-2-oxoacetate (1r)$^i$**

A yellow oil, $^1$H NMR (500 MHz, Chloroform-$d$) $\delta$ 8.58 – 8.53 (m, 1H), 8.06 (dd, $J = 8.6$, 1.8 Hz, 1H), 7.99 (dd, $J = 8.2$, 1.1 Hz, 1H), 7.98 – 7.88 (m, 2H), 7.67 (dddd, $J = 8.2$, 6.8, 1.3 Hz, 1H), 7.60 (ddd, $J = 8.2$, 6.9, 1.3 Hz, 1H), 5.42 (hept, $J = 6.3$ Hz, 1H), 1.48 (d, $J = 6.3$ Hz, 6H). $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 186.66, 163.72, 136.34, 133.37, 132.30, 129.99, 129.88, 129.54, 128.95, 127.94, 127.16, 124.00, 70.76, 21.80.
3. Reaction condition optimization using f-amphol as ligand

![Chemical Structure]

**Table 1: Reaction Conditions Optimization**

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<th>Base</th>
<th>Conv. (%)</th>
<th>Ee (%)</th>
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</table>

* Reaction conditions: 0.2 mmol substrate, 0.05 mol% [Ir(COD)Cl]₂, 0.1 mol% ligand, 1.0 mL solvent, reaction time 16 h. * Determined by ¹H NMR analysis. ** Determined by HPLC analysis.

4. Asymmetric hydrogenation of α-keto esters

**General procedure with S/C = 1000:**

In an argon-filled glove box, a 4.0 mL vial was charged with the metal precursor [Ir(COD)Cl]₂ (3.4 mg, 5.0×10⁻³ mmol), f-ampha (7.9 mg, 10.5×10⁻³ mmol) and anhydrous ΡrOH (1.0 mL). The mixture was stirred for 1.0 h at 25°C, giving an orange red solution as a stock solution. The resulting solution (20 μL) and a solution of tBuONa in ΡrOH (200 μL, c = 0.010 mmol/mL) transferred by syringes into a 5.0 mL vial charged with α-keto esters (0.20 mmol) in 1.0 mL anhydrous ΡrOH. The vial was transferred to an autoclave, which was then pressurized with 10 atm of H₂ and stirred at room temperature for 1 h. The hydrogen gas was released slowly in a well-ventilated hood and the solution was concentrated. The crude product was purified with flash chromatography. Enatiomeric excess was analyzed by chiral HPLC on a chiral stationary phase.

**Preparation of racemic samples:**

All the racemic samples were prepared by the reduction of α-keto esters with NaBH₄ in methanol. This method causes a partial transesterification in some cases, giving a methyl ester product.
isopropyl (S)-2-(2-chlorophenyl)-2-hydroxyacetate (2a)\(^6\)

![Structure of isopropyl (S)-2-(2-chlorophenyl)-2-hydroxyacetate (2a)](image)

White solid (44 mg), >99% conv., 96% yield, 79.2% ee. The enantiomeric excess was determined by HPLC on Chiracel OD-H column, 210 nm, 27 °C, n-hexane: i-PrOH = 95:5; flow 1.0 mL/min; \(t_{R1} = 7.8\) min, \(t_{R2} = 9.1\) min.

\(^1\)H NMR (400 MHz, Chloroform-\(d\)) \(\delta\) 7.45 – 7.35 (m, 2H), 7.33 – 7.22 (m, 2H), 5.53 (s, 1H), 5.10 (hept, \(J = 6.3\) Hz, 1H), 3.70 (s, 1H), 1.28 (d, \(J = 6.3\) Hz, 3H), 1.13 (d, \(J = 6.2\) Hz, 3H). \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 172.73, 136.34, 133.57, 129.88, 129.59, 128.69, 127.05, 70.50, 70.42, 21.62, 21.39. HRMS m/z: Calcd for [C\(_{11}\)H\(_{13}\)ClO\(_3\)+Na]\(^+\): 251.0439. Found: 251.0445.

isopropyl (S)-2-(4-chlorophenyl)-2-hydroxyacetate (2b)\(^6\)

White solid (43 mg), >99% conv., 94% yield, 91.6% ee. The enantiomeric excess was determined by HPLC on Chiracel OD-H column, 210 nm, 27 °C, n-hexane: i-PrOH = 95:5; flow 1.0 mL/min; \(t_{R1} = 5.9\) min, \(t_{R2} = 6.4\) min.

\(^1\)H NMR (400 MHz, Chloroform-\(d\)) \(\delta\) 7.42 – 7.30 (m, 4H), 5.15 – 5.01 (m, 2H), 3.60 (d, \(J = 5.4\) Hz, 1H), 1.30 (d, \(J = 6.3\) Hz, 3H), 1.13 (d, \(J = 6.3\) Hz, 3H). \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 172.84, 137.01, 134.12, 128.65, 127.79, 72.19, 70.51, 21.70, 21.42. HRMS m/z: Calcd for [C\(_{11}\)H\(_{13}\)ClO\(_3\)+Na]\(^+\): 251.0438. Found: 251.0445.

isopropyl (S)-2-(3-chlorophenyl)-2-hydroxyacetate (2c)\(^4\)

White solid (41), >99% conv., 90% yield, 87.6% ee. The enantiomeric excess was determined by HPLC on Chiracel OD-H column, 210 nm, 27 °C, n-hexane: i-PrOH = 95:5; flow 1.0 mL/min; \(t_{R1} = 6.1\) min, \(t_{R2} = 7.1\) min.

\(^1\)H NMR (400 MHz, Chloroform-\(d\)) \(\delta\) 7.46 (dq, \(J = 1.6, 1.0\) Hz, 1H), 7.40 – 7.27 (m, 3H), 5.17 – 5.02 (m, 2H), 3.59 (dd, \(J = 5.8, 1.4\) Hz, 1H), 1.32 (d, \(J = 6.2\) Hz, 3H), 1.15 (d, \(J = 6.2\) Hz, 3H). \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 172.66, 140.43, 134.41, 129.72, 128.64, 126.60, 124.59, 72.19, 70.64, 21.70, 21.42. HRMS m/z: Calcd for [C\(_{11}\)H\(_{13}\)ClO\(_3\)+Na]\(^+\): 251.0439. Found: 251.0445.

isopropyl (S)-2-hydroxy-2-phenylacetate (2d)\(^6\)
White solid (38 mg), >99% conv., 98% yield, The enantiomeric excess was determined by HPLC on Chiracel OD-H column, 210 nm, 27 °C, n-hexane: i-PrOH = 95:5; flow 1.0 mL/min; t_{R1} = 6.4 min, t_{R2} = 11.2 min.

\[ ^1H \text{ NMR (400 MHz, Chloroform-}d\) \delta 7.48 - 7.27 (m, 5H), 5.18 - 5.02 (m, 2H), 3.54 (d, J = 6.0 Hz, 1H), 1.31 (d, J = 6.3 Hz, 3H), 1.13 (d, J = 6.2 Hz, 3H). \]

\[ ^13C \text{ NMR (101 MHz, CDCl}_3\) \delta 173.22, 138.57, 128.49, 128.28, 126.43, 72.91, 70.16, 21.71, 21.40. \]


**isopropyl (S)-2-hydroxy-2-(m-tolyl)acetate (2e)**

Colorless oil (40 mg), >99% conv., 96% yield, 93.6% ee. The enantiomeric excess was determined by HPLC on Chiracel OD-H column, 210 nm, 27 °C, n-hexane: i-PrOH = 95:5; flow 1.0 mL/min; t_{R1} = 5.9 min, t_{R2} = 10.3 min.

\[ ^1H \text{ NMR (400 MHz, Chloroform-}d\) \delta 7.31 - 7.17 (m, 3H), 7.15 (s, 1H), 5.16 - 5.02 (m, 2H), 3.52 (d, J = 5.9 Hz, 1H), 2.37 (s, 3H), 1.30 (d, J = 6.3 Hz, 3H), 1.14 (d, J = 6.2 Hz, 3H). \]

\[ ^13C \text{ NMR (101 MHz, CDCl}_3\) \delta 173.30, 138.47, 138.21, 129.05, 128.38, 127.06, 123.58, 72.94, 70.09, 21.73, 21.42. \]

HRMS m/z: Calcd for [C_{12}H_{16}O_3+Na]^+: 231.0985. Found: 231.0992.

**isopropyl (S)-2-hydroxy-2-(o-tolyl)acetate (2f)**

Colorless oil (40 mg), >99% conv., 96% yield, 85.6% ee. The enantiomeric excess was determined by HPLC on Chiracel OD-H column, 210 nm, 27 °C, n-hexane: i-PrOH = 95:5; flow 1.0 mL/min; t_{R1} = 6.9 min, t_{R2} = 8.4 min.

\[ ^1H \text{ NMR (400 MHz, Chloroform-}d\) \delta 7.31 (dd, J = 7.3, 1.9 Hz, 1H), 7.28 - 7.16 (m, 3H), 5.35 (d, J = 5.3 Hz, 1H), 5.10 (hept, J = 6.2 Hz, 1H), 3.50 (d, J = 5.3 Hz, 1H), 2.46 (s, 3H), 1.29 (d, J = 6.3 Hz, 3H), 1.13 (d, J = 6.2 Hz, 3H). \]

\[ ^13C \text{ NMR (101 MHz, CDCl}_3\) \delta 173.74, 136.90, 136.36, 130.72, 128.27, 126.55, 126.18, 70.41, 70.10, 21.71, 21.43, 19.32. \]

HRMS m/z: Calcd for [C_{12}H_{16}O_3+Na]^+: 231.0990. Found: 231.0992.

**isopropyl (S)-2-hydroxy-2-(4-isopropylphenyl)acetate (2g)**
White oil (47 mg), >99% conv., 99% yield, 97.6% ee. The enantiomeric excess was determined by HPLC on Chiracel OD-H column, 210 nm, 27 °C, n-hexane: i-PrOH = 95:5; flow 1.0 mL/min; t_R1 = 5.4 min, t_R2 = 6.2 min.

^1^H NMR (400 MHz, Chloroform-d) δ 7.39 – 7.32 (m, 2H), 7.32 – 7.18 (m, 2H), 5.16 – 5.02 (m, 2H), 3.48 (d, J = 6.2 Hz, 1H), 2.92 (hept, J = 6.9 Hz, 1H), 1.31 (d, J = 6.2 Hz, 3H), 1.26 (d, J = 6.9 Hz, 6H), 1.16 (d, J = 6.3 Hz, 3H). ^13^C NMR (101 MHz, CDCl_3) δ 173.34, 148.99, 135.95, 126.60, 126.39, 72.78, 70.04, 33.84, 23.94, 21.74, 21.47. HRMS m/z: Calcd for [C_{14}H_{20}O_3]+: 259.1299. Found: 259.1305.

**isopropyl (S)-2-(4-ethylphenyl)-2-hydroxyacetate (2h)**

White solid (42 mg), >99% conv., 95% yield. The enantiomeric excess was determined by HPLC on Chiracel OD-H column, 210 nm, 27 °C, n-hexane: i-PrOH = 95:5; flow 1.0 mL/min; t_R1 = 5.7 min, t_R2 = 7.7 min.

^1^H NMR (400 MHz, Chloroform-d) δ 7.34 (d, J = 8.1 Hz, 2H), 7.21 (d, J = 8.1 Hz, 2H), 5.09 (dp, J = 12.5, 6.3 Hz, 2H), 3.46 (d, J = 6.1 Hz, 1H), 2.67 (q, J = 7.6 Hz, 2H), 1.30 (d, J = 6.3 Hz, 3H), 1.25 (t, J = 7.6 Hz, 3H), 1.15 (d, J = 6.2 Hz, 3H). ^13^C NMR (101 MHz, CDCl_3) δ 173.37, 144.39, 135.84, 128.02, 126.41, 72.78, 70.06, 28.57, 21.73, 21.45, 15.49. HRMS m/z: Calcd for [C_{13}H_{18}O_3]+: 245.1142. Found: 245.1148.

**isopropyl (S)-2-hydroxy-2-(4-methoxyphenyl)acetate (2i)**

White solid (43 mg), >99% conv., 96% yield. The enantiomeric excess was determined by HPLC on Chiracel OD-H column, 210 nm, 27 °C, n-hexane: i-PrOH = 95:5; flow 1.0 mL/min; t_R1 = 8.6 min, t_R2 = 14.8 min.

^1^H NMR (400 MHz, Chloroform-d) δ 7.34 (d, J = 8.7 Hz, 2H), 6.89 (d, J = 8.8 Hz, 2H), 5.17 – 5.00 (m, 2H), 3.81 (s, 3H), 3.59 (s, 1H), 1.29 (s, 3H), 1.13 (d, J = 6.3 Hz, 3H). ^13^C NMR (101 MHz, CDCl_3) δ 173.41, 159.57, 130.80, 127.93, 127.75, 113.90, 72.53, 69.98, 55.25, 21.70, 21.43. HRMS m/z: Calcd for [C_{12}H_{16}O_4]+: 247.0933. Found: 247.0941.

**isopropyl (S)-2-(3,5-dimethylphenyl)-2-hydroxyacetate (2j)**
White solid (42 mg), >99% conv., 95% yield, The enantiomeric excess was determined by HPLC on Chiracel OD-H column, 210 nm, 27 °C, n-hexane: i-PrOH = 95:5; flow 1.0 mL/min; $t_{R1}$ = 6.2 min, $t_{R2}$ = 8.4 min.

$^1$H NMR (400 MHz, Chloroform-$d$) $\delta$ 7.17 (d, $J = 8.3$ Hz, 1H), 7.06 – 6.98 (m, 2H), 5.30 (d, $J = 3.8$ Hz, 1H), 5.10 (hept, $J = 6.0$ Hz, 1H), 3.41 (d, $J = 5.0$ Hz, 1H), 2.42 (s, 3H), 2.33 (s, 3H), 1.29 (d, $J = 6.3$ Hz, 3H), 1.15 (d, $J = 6.2$ Hz, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 173.89, 137.99, 136.19, 133.99, 131.53, 126.85, 126.54, 70.32, 70.00, 21.72, 21.47, 21.07, 19.21. HRMS $m/z$: Calcd for [C$_{13}$H$_{18}$O$_3$+Na]$^+$: 245.1141. Found: 245.1148.

**isopropyl (S)-2-hydroxy-2-(2-methoxy-5-methylphenyl)acetate (2k)**

White solid (42 mg), 90% conv., 88% yield, The enantiomeric excess was determined by HPLC on Chiracel OD-H column, 210 nm, 27 °C, n-hexane: i-PrOH = 95:5; flow 1.0 mL/min; $t_{R1}$ = 7.7 min, $t_{R2}$ = 8.5 min.

$^1$H NMR (400 MHz, Chloroform-$d$) $\delta$ 7.16 – 7.03 (m, 2H), 6.80 (d, $J = 8.2$ Hz, 1H), 5.19 (d, $J = 6.6$ Hz, 1H), 5.11 (h, $J = 6.3$ Hz, 1H), 3.81 (s, 3H), 3.58 (d, $J = 6.9$ Hz, 1H), 2.30 (s, 3H), 1.26 (d, $J = 6.3$ Hz, 3H), 1.16 (d, $J = 6.3$ Hz, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 173.39, 155.01, 130.23, 130.06, 129.98, 126.94, 110.95, 70.51, 69.44, 55.52, 21.70, 21.46, 20.44. HRMS $m/z$: Calcd for [C$_{13}$H$_{18}$O$_4$+Na]$^+$: 261.1090. Found: 261.1097.

**isopropyl (S)-2-(4-bromophenyl)-2-hydroxyacetate (2l)**

White solid (42 mg), >99% conv., 91.2% ee. The enantiomeric excess was determined by HPLC on Chiracel OD-H column, 210 nm, 27 °C, n-hexane: i-PrOH = 95:5; flow 1.0 mL/min; $t_{R1}$ = 6.2 min, $t_{R2}$ = 6.7 min.

$^1$H NMR (400 MHz, Chloroform-$d$) $\delta$ 7.50 (d, $J = 8.5$ Hz, 2H), 7.33 (d, $J = 8.4$ Hz, 2H), 5.13 – 5.04 (m, 2H), 3.60 (d, $J = 5.5$ Hz, 1H), 1.29 (s, 3H), 1.13 (d, $J = 6.2$ Hz, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 172.76, 137.53, 131.59, 128.12, 122.30, 72.24, 70.54, 21.70, 21.43. HRMS $m/z$: Calcd for [C$_{11}$H$_{13}$BrO$_3$+Na]$^+$: 294.9934 Found: 294.9940.

**isopropyl (S)-2-(4-fluorophenyl)-2-hydroxyacetate (2m)**

White solid (42 mg), >99% conv., 97% yield, The enantiomeric excess was determined by HPLC on Chiracel OD-H column, 210 nm, 27 °C, n-hexane: i-PrOH = 95:5; flow 1.0 mL/min; $t_{R1}$ = 6.2 min, $t_{R2}$ = 6.7 min.

$^1$H NMR (400 MHz, Chloroform-$d$) $\delta$ 7.50 (d, $J = 8.5$ Hz, 2H), 7.33 (d, $J = 8.4$ Hz, 2H), 5.13 – 5.04 (m, 2H), 3.60 (d, $J = 5.5$ Hz, 1H), 1.29 (s, 3H), 1.13 (d, $J = 6.2$ Hz, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 172.76, 137.53, 131.59, 128.12, 122.30, 72.24, 70.54, 21.70, 21.43. HRMS $m/z$: Calcd for [C$_{11}$H$_{13}$BrO$_3$+Na]$^+$: 294.9934 Found: 294.9940.
White solid (40 mg), >99% conv., 94% yield, 97.0% ee. The enantiomeric excess was determined by HPLC on Chiracel OD-H column, 210 nm, 27 °C, n-hexane: i-PrOH = 95:5; flow 1.0 mL/min; t_R1 = 6.2 min, t_R2 = 6.7 min.

^1^H NMR (400 MHz, Chloroform-d) δ 7.44 – 7.34 (m, 2H), 7.09 – 6.97 (m, 2H), 5.18 – 4.98 (m, 2H), 3.60 (s, 1H), 1.27 (d, J = 6.3 Hz, 3H), 1.10 (d, J = 6.2 Hz, 3H). ^1^3^C NMR (101 MHz, CDCl_3) δ 173.04, 162.66 (d, J = 247.4 Hz), 134.35 (d, J = 3.0 Hz), 128.17 (d, J = 8.1 Hz), 115.38 (d, J = 21.2 Hz), 72.22, 70.33, 21.67, 21.39. ^1^9^F NMR (376 MHz, CDCl_3) δ -113.98. HRMS m/z: Calcd for [C_{11}H_{13}O_F+Na]^+: 235.0734. Found: 235.0741.

**isopropyl (S)-2-(benzo[d][1,3]dioxol-5-yl)-2-hydroxyacetate (2n)**

White solid (46 mg), >99% conv., 97% yield, 91.8% ee. The enantiomeric excess was determined by HPLC on Chiracel OD-H column, 210 nm, 27 °C, n-hexane: i-PrOH = 95:5; flow 1.0 mL/min; t_R1 = 9.1 min, t_R2 = 11.7 min.

^1^H NMR (400 MHz, Chloroform-d) δ 6.91 (dq, J = 3.1, 1.8 Hz, 2H), 6.80 (d, J = 8.4 Hz, 1H), 5.16 – 5.00 (m, 2H), 3.47 (dd, J = 5.8, 3.8 Hz, 1H), 1.29 (s, 3H), 1.16 (d, J = 6.2 Hz, 3H). ^1^3^C NMR (101 MHz, CDCl_3) δ 173.21, 147.80, 147.61, 132.48, 120.24, 108.22, 106.88, 101.16, 72.65, 70.21, 21.71, 21.46. HRMS m/z: Calcd for [C_{12}H_{14}O_5+Na]^+: 261.0732. Found: 261.0733.

**isopropyl (S)-2-hydroxy-2-(naphthalen-1-yl)acetate (2o)**

White solid (44 mg), 94% conv., 90% yield, 86.1% ee. The enantiomeric excess was determined by HPLC on Chiracel OD-H column, 210 nm, 27 °C, n-hexane: i-PrOH = 95:5; flow 1.0 mL/min; t_R1 = 14.2 min, t_R2 = 15.3 min.

^1^H NMR (500 MHz, Chloroform-d) δ 8.17 (dd, J = 8.5, 1.2 Hz, 1H), 7.88 – 7.81 (m, 2H), 7.55 – 7.42 (m, 4H), 5.77 (d, J = 4.0 Hz, 1H), 5.09 (hept, J = 6.3 Hz, 1H), 3.62 (d, J = 5.0 Hz, 1H), 1.23 (d, J = 6.2 Hz, 3H), 0.99 (d, J = 6.2 Hz, 3H). ^1^3^C NMR (126 MHz, CDCl_3) δ 173.76, 134.35, 134.02, 131.10, 129.30, 128.73, 126.39, 125.83, 125.62, 125.20, 123.85, 71.41, 70.31, 21.68, 21.37.

**isopropyl (R)-2-hydroxy-2-(thiophen-2-yl)acetate (2p)**
Yellow solid (37 mg), 92% yield, 74.7% ee. The enantiomeric excess was determined by HPLC on Chiracel OD-H column, 210 nm, 27 °C, n-hexane: i-PrOH = 95:5; flow 1.0 mL/min; \( t_{R1} = 5.9 \) min, \( t_{R2} = 8.3 \) min.

\( \text{H NMR (400 MHz, Chloroform-}d\text{)} \delta 7.29 (dd, \( J = 5.1, 1.3 \) Hz, 1H), 7.12 (dt, \( J = 3.6, 1.1 \) Hz, 1H), 7.00 (dd, \( J = 5.1, 3.5 \) Hz, 1H), 5.38 (d, \( J = 6.5 \) Hz, 1H), 5.15 (hept, \( J = 6.3 \) Hz, 1H), 3.64 – 3.56 (m, 1H), 1.34 (d, \( J = 6.2 \) Hz, 3H), 1.24 (d, \( J = 6.3 \) Hz, 3H).

\( \text{C NMR (101 MHz, CDCl}_{3}\text{)} \delta 172.00, 141.70, 126.88, 125.54, 125.14, 70.65, 69.17, 21.73, 21.47. \text{HRMS } m/z: \text{ Calcd for } [C_{9}H_{12}SO_{3}+Na]^{+}: 223.0399. \text{ Found: 223.0399.}

isopropyl (S)-2-hydroxy-2-(naphthalen-2-yl)acetate (2q)

White solid (49 mg), >99% conv., 99% yield, 78.1% ee. The enantiomeric excess was determined by HPLC on Chiracel OD-H column, 210 nm, 27 °C, n-hexane: i-PrOH = 95:5; flow 1.0 mL/min; \( t_{R1} = 9.9 \) min, \( t_{R2} = 11.7 \) min.

\( \text{H NMR (400 MHz, Chloroform-}d\text{)} \delta 7.93 (d, \( J = 1.7 \) Hz, 1H), 7.87 (dd, \( J = 9.4, 5.5 \) Hz, 3H), 7.57 – 7.47 (m, 3H), 5.31 (d, \( J = 5.4 \) Hz, 1H), 5.11 (hept, \( J = 6.3 \) Hz, 1H), 3.63 (d, \( J = 5.8 \) Hz, 1H), 1.32 (d, \( J = 6.3 \) Hz, 3H), 1.11 (d, \( J = 6.2 \) Hz, 3H).

\( \text{C NMR (101 MHz, CDCl}_{3}\text{)} \delta 173.24, 135.92, 133.24, 133.19, 128.32, 128.14, 127.68, 126.26, 126.24, 125.76, 124.11, 73.04, 70.36, 21.73, 21.44.
5. NMR spectra of substrates compounds

![NMR spectra of substrates compounds](image-url)
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6. NMR spectra of products
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2o

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7. HPLC chromatography

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Acq. Operator : SYSTEM
Acq. Instrument : 1260
Injection Date : 3/15/2017 0:17:47
Injection : 1
Method : D:\chemlst\DATA\gxx\9-1 2017-03-14 18-15-03\GXX-S.M (Sequence Method)
Last changed : 3/14/2017 18:15:02 by SYSTEM
Additional Info : Peak(s) manually integrated

Area Percent Report

Sorted By : Signal
Multiplier : 1.0000
Dilution : 1.0000
Use Multiplier & Dilution Factor with ISTDs

Signal 1: DAD1 C, Sig=210.4 Ref=off

Peak RetTime Type Width Area Height Area %
---|---------|------------|-----------|-------------|---------------|
1 5.894 BB 0.1180 3584.17383 464.82129 50.5300
2 10.252 BB 0.2278 3588.98999 238.28192 49.4700
Totals: 7093.16382 703.10321

*** End of Report ***
Acq. Operator : SYSTEM  Seq. Line : 22
Acq. Instrument : 1260  Location : P2-D4
Injection Date : 3/15/2017 3:18:02  Inj : 1
Inj Volume : 1.000 μl
Method : D:\Chem32\DATA\agp\1-2017-03-14 18-15-02\88X-5.8 (Sequence Method)
Last changed : 3/14/2017 18:15:02 by SYSTEM
Additional Info : Peak(s) manually integrated

---

Area Percent Report
---

Sorted By : Signal
Multiplier : 1.0000
Dilution : 1.0000
Use Multiplier & Dilution Factor with ISTDs

Signal 1: DAD1 C, Sig=210.4 Ref=off

<table>
<thead>
<tr>
<th>Peak RetTime</th>
<th>Type</th>
<th>Width</th>
<th>Area</th>
<th>Height</th>
<th>Area</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>[min]</td>
<td>[μAU]</td>
<td>[μAU/s]</td>
<td>[μAU]</td>
</tr>
<tr>
<td>1</td>
<td>5.920</td>
<td>0.130</td>
<td>1.377</td>
<td>464</td>
<td>1755</td>
</tr>
<tr>
<td>2</td>
<td>10.442</td>
<td>0.236</td>
<td>458.0</td>
<td>29665</td>
<td>29.93</td>
</tr>
</tbody>
</table>

Totals : 1.4252464 1785.0298

---

*** End of Report ***
**Area Percent Report**

Sorted By: Signal  
Multiplier: 1.0000  
Dilution: 1.0000  
Use Multiplier & Dilution Factor with ISTDs

**Signal 1: DAD1 C, Sig=2104 Ref=off**

<table>
<thead>
<tr>
<th>RetTime</th>
<th>Width</th>
<th>Area</th>
<th>Height</th>
<th>Area%</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>6.909</td>
<td>0.1428</td>
<td>2612.70074</td>
<td>85.44299</td>
</tr>
<tr>
<td>2</td>
<td>8.352</td>
<td>0.1923</td>
<td>2638.39551</td>
<td>228.70086</td>
</tr>
</tbody>
</table>

Totals: 5251.10425 534.14305  

***End of Report***
Area Percent Report

Sorted By: Signal
Multiplier: 1.0000
Dilution: 1.0000
Use Multiplier & Dilution Factor with ISTDs

Signal 1: DAD3 C, Sig-210,4 Ref-off

<table>
<thead>
<tr>
<th>Peak</th>
<th>RetTime</th>
<th>Width</th>
<th>Area</th>
<th>Height</th>
<th>Area %</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>5.400</td>
<td>0.1201</td>
<td>2416.54810</td>
<td>335.3322</td>
<td>49.5225</td>
</tr>
<tr>
<td>2</td>
<td>6.210</td>
<td>0.1436</td>
<td>2425.21499</td>
<td>281.45435</td>
<td>50.00005</td>
</tr>
</tbody>
</table>

Totals: 4841.66399 616.78757

*** End of Report ***
**Area Percent Report**

Sorted By: Signal
Multiplier: 1.0000
Dilution: 1.0000
Use Multiplier & Dilution Factor with ISTDs

**Signal 1: DAM1 C, Sig-218, 4 Ref-off**

<table>
<thead>
<tr>
<th>#</th>
<th>RetTime [min]</th>
<th>Width [min]</th>
<th>Area [mAU*μs]</th>
<th>Height [mAU]</th>
<th>Area %</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>5.488</td>
<td>0.1232</td>
<td>4878.49752</td>
<td>659.10056</td>
<td>98.7716</td>
</tr>
<tr>
<td>2</td>
<td>6.352</td>
<td>0.1518</td>
<td>685.7245</td>
<td>6.64851</td>
<td>1.2284</td>
</tr>
</tbody>
</table>

Totals: 4931.02997 665.75846

*** End of Report ***
Area Percent Report

Sorted By : Signal
Multiplier : 1.0000
Dilution : 1.0000
Use Multiplier & Dilution Factor with ISTDs

Signal 1: DAD1 C, Sig-210,4 Ref-off

```
<table>
<thead>
<tr>
<th>#</th>
<th>RetTime</th>
<th>Peak Type</th>
<th>Width</th>
<th>Area [min]</th>
<th>Height [min]</th>
<th>[mAU]</th>
<th>[mAU*s]</th>
<th>[%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>5.711</td>
<td>MF</td>
<td>0.1237</td>
<td>2974.48340</td>
<td>408.04231</td>
<td>49.1202</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>7.737</td>
<td>BU</td>
<td>0.1062</td>
<td>9981.89711</td>
<td>204.85322</td>
<td>50.8798</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
```

Totals : 6055.52051 685.67453

*** End of Report ***
Area Percent Report

Signal 1: DA01 C, Sig=220, Ref-off

Peak RetTime Type Width Area Height Area %

<p>| | | | | | | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>8.56</td>
<td>0.19</td>
<td>3571.36</td>
<td>3574.32</td>
<td>328.17</td>
<td>49.78</td>
</tr>
<tr>
<td>2</td>
<td>14.62</td>
<td>0.35</td>
<td>4106.89</td>
<td>4936.81</td>
<td>179.64</td>
<td>50.21</td>
</tr>
</tbody>
</table>

Totals: 8178.22 507.81 56

*** End of Report ***
Acq. Operator : SYSTEM  Seq. Line : 19
Acq. Instrument : 1260  Location : P2-D1
Injection Date : 3/15/2017 2:00:47  Inj. : 1
[n] Volume : 1.000 μl
Method : D:\chemlab\DATA\gxs\9-2 01 2017-03-14 18-15-01\GSS-X.s.N (Sequence Method)
Last changed : 3/14/2017 18:15:02 by SYSTEM
Additional Info : Peak(s) manually integrated

Area Percent Report

Sorted By : Signal
Multiplier : 1.0000
Dilution : 1.0000
Use Multiplier & Dilution Factor with ISTDs

Signal 1: DAD1 C, Sig-210,4 Ref-off

<table>
<thead>
<tr>
<th>Peak</th>
<th>RetTime</th>
<th>Width</th>
<th>Area</th>
<th>Height</th>
<th>Area</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>8.391</td>
<td>0.1846</td>
<td>5128.1377</td>
<td>448.6244</td>
<td>97.8620</td>
</tr>
<tr>
<td>2</td>
<td>14.178</td>
<td>0.3351</td>
<td>1164.0244</td>
<td>528.087</td>
<td>2.1380</td>
</tr>
</tbody>
</table>

Totals : 5444.54013 453.90605

*** End of Report ***
Acq. Operator : SYSTEM
Acq. Instrument : 1260
Injection Date : 3/14/2017 19:34:20
Inj : 1
Inj Volume : 1.000 µl
Method : D:\Chem32\DATA\ggx\9-1 2017-03-14 18-15-013\SSK-5.M (Sequence Method)
Last changed : 3/14/2017 18:15:02 by SYSTEM
Additional Info : Peak(s) manually integrated

Area Percent Report

Sorted By : Signal
Multiplier : 1.0000
Dilution : 1.0000
Use Multiplier & Dilution Factor with ISTDs

Signal 1: DAD1 C, Sig=210.4 Ref-off

<table>
<thead>
<tr>
<th>Peak RetTime Type Width</th>
<th>Area</th>
<th>Height</th>
<th>Area %</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 6.195 min 8.103 min</td>
<td>9957.25537</td>
<td>786.9059</td>
<td>49.8927</td>
</tr>
<tr>
<td>2 8.422 min 8.209 min</td>
<td>9982.6798</td>
<td>844.21732</td>
<td>50.1073</td>
</tr>
</tbody>
</table>

Totals : 1.19401e4 1191.12241

*** End of Report ***

68
Area Percent Report

Sorted By : Signal
Multiplier : 1.0000
Dilution : 1.0000
Use Multiplier & Dilution Factor with ISTDs

Signal 1: DAD1 C, Sig=210,4 Ref=off

<table>
<thead>
<tr>
<th>Peak RetTime Type</th>
<th>Width</th>
<th>Height</th>
<th>Area</th>
<th>Area %</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>[min]</td>
<td>[mAU]</td>
<td>[mAU^2]</td>
<td></td>
</tr>
<tr>
<td>------------------</td>
<td>-------</td>
<td>--------</td>
<td>----------</td>
<td>--------</td>
</tr>
<tr>
<td>1</td>
<td>6.235</td>
<td>6922.53662</td>
<td>810.69971</td>
<td>93.3834</td>
</tr>
<tr>
<td>2</td>
<td>8.517</td>
<td>490.49265</td>
<td>39.51351</td>
<td>6.6166</td>
</tr>
</tbody>
</table>

Totals : 7413.02927 850.21321

*** End of Report ***
Acq. Operator : SYSTEM
Acq. Instrument : 1260
Injection Date : 3/24/2017 3:25:14
Inj Volume : 1.000 μl
Method : D:\Chem32\DATA\gxx\13-1-7 2017-03-23 23-05-46\GGX-5.M (Sequence Method)
Last changed : 3/23/2017 23:05:46 by SYSTEM
Additional Info : Peak(s) manually integrated.

Area Percent Report

Sorted By  : Signal
Multiplier  : 1.0000
Dilution  : 1.0000
Use Multiplier & Dilution Factor with ISTDs

Signal 1: DAD1, Sig=230,4 Ref=360,100

Peak RetTime Type Width Area Height Area %
#   [min]  [min]  [μAU*s]  [μAU]  
 1  7.181 MF  0.1525  3033.78027  331.52954  50.2766 
 2  9.088 BD  0.2044  3000.39600  226.72795  49.7234

Totals : 6034.17627 558.25749

*** End of Report ***
Area Percent Report

Sorted By: Signal
Multiplier: 1.0000
Dilution: 1.0000
Use Multiplier & Dilution Factor with ISTDs

Signal 1: DAD1 C, Sig=210,4 Ref=off

<table>
<thead>
<tr>
<th>Peak RetTime Type</th>
<th>Width</th>
<th>Area</th>
<th>Height</th>
<th>Area %</th>
</tr>
</thead>
<tbody>
<tr>
<td>#</td>
<td>[min]</td>
<td>[min]</td>
<td>[mAU's]</td>
<td>[mAU]</td>
</tr>
<tr>
<td>1</td>
<td>7.734</td>
<td>0.1862</td>
<td>4284.19238</td>
<td>383.39209</td>
</tr>
<tr>
<td>2</td>
<td>8.555</td>
<td>0.2162</td>
<td>4418.19580</td>
<td>340.55148</td>
</tr>
</tbody>
</table>

Totals: 8702.38818 723.94357

*** End of Report ***
**Chemical Structure**

![Chemical Structure Image]

**Textual Representation**

**Signal 1**: DAD1 C, Sig-210.4 Ref-off

<table>
<thead>
<tr>
<th>Peak Retime</th>
<th>Width</th>
<th>Area</th>
<th>Height</th>
<th>Area %</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>7.573</td>
<td>3538.62324</td>
<td>327.16706</td>
<td>68.3497</td>
</tr>
<tr>
<td>2</td>
<td>8.371</td>
<td>3638.70398</td>
<td>126.38110</td>
<td>31.6503</td>
</tr>
</tbody>
</table>

Totals: 5177.52722 453.54877

---

**Area Percent Report**

- **Sorted By**: Signal
- **Multiplier**: 1.00000
- **Dilution**: 1.00000
- Use Multiplier & Dilution Factor with ISIDs

---

***End of Report***
Acq. Operator : SYSTEM  Seq. Line :  7
Acq. Instrument : 1280  Location :  P2-F6
Injection Date : 3/13/2017 16:16:47  Inj : 1
Method : D:\Chem32\DATA\ggx\7-2 2017-03-13 13-40-14\GGX-5.M (Sequence Method)
Last changed : 3/13/2017 13:40:14 by SYSTEM
Additional Info : Peak(s) manually integrated

---

**Area Percent Report**

---

Sorted By : Signal
Multiplier : 1.0000
Dilution : 1.0000
Use Multiplier & Dilution Factor with ISTDs

**Signal 1 : DAD1 C, Sig=210,4 Ref=off**

<table>
<thead>
<tr>
<th>Peak RetTime Type</th>
<th>Width</th>
<th>Area</th>
<th>Height</th>
<th>Area %</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>[min]</td>
<td>[mAU]</td>
<td>[mAU]</td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>6.185</td>
<td>0.133</td>
<td>2905.469</td>
<td>368.00174</td>
</tr>
<tr>
<td>2</td>
<td>6.657</td>
<td>0.145</td>
<td>2919.58032</td>
<td>335.09683</td>
</tr>
</tbody>
</table>

Totals : 5825.04956 703.18857

---

*** End of Report ***
Acq. Operator  : SYSTEM  Seq. line  : 23
Acq. Instrument : 1260  Location  : P2-D5
Injection Date  : 3/15/2017 3:43:45  Inj  : 1
Inj Volume  : 1.000 µl
Method  : D:\Chem2\DATA\ggs\8-1 2017-03-14 18-15-02\66X-5.M (Sequence Method)
Last changed  : 3/14/2017 18:15:02 by SYSTEM
Additional Info : Peaks manually integrated

---

Signal 1: DAU1 C, Sig-z20,4 Hef-off

Peak RetTime Type Width Area Height Area
#  [min]  [min]  [nAU's]  [nAU]  [%]
---|------|------|---------|---|---|
1  6.343 VM  0.341R  1.0642/7e4  1290.94727  95.6354
2  6.850 VM  0.1409  485.78392  57.47088  4.3646

Totals : 1.11284e4  1308.41814

---

*** End of Report ***
Area Percent Report

Sorted By : Signal
Multiplier : 1.0000
Dilution : 1.0000
Use Multiplier & Dilution Factor with ISTDs

Signal 1: DAD1 C, Sig=210.4 Ref-off

<table>
<thead>
<tr>
<th>#</th>
<th>RetTime</th>
<th>Type</th>
<th>Width</th>
<th>Area</th>
<th>Height</th>
<th>Area %</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>5.932</td>
<td>MF</td>
<td>0.1325</td>
<td>3794.08660</td>
<td>477.23677</td>
<td>56.0113</td>
</tr>
<tr>
<td>2</td>
<td>6.789</td>
<td>VB</td>
<td>0.1503</td>
<td>3752.35034</td>
<td>380.37491</td>
<td>49.9887</td>
</tr>
</tbody>
</table>

Totals : 7586.41895 857.60577

*** End of Report ***
reaction for 16 h

---

Acq. Operator : SYSTEM
Acq. Instrument : 1260
Injection Date : 3/11/2017 18:51:22
Inj Volume : 1.000 µl
Method : D:\Chem32\DATA\agga\7-2 2017-03-13 13-40-14\agga-5.4 (Sequence Method)
Last changed : 3/11/2017 13:40:34 by SYSTEM
Additional Info : Peak(s) manually integrated

---

Area Percent Report

---

Sorted By : Signal
Multiplier : 1.0000
Dilution : 1.0000
Use Multiplier & Dilution Factor with IS/IDs

Signal 1: DAD1 C, Sig=210.4 Ref=off

Peak RetTime Type Width Area Height Area %
--------|------|--------|--------|--------|
1 5.759 Min 0.1078 3621.28271 516.79048 88.10048
2 6.513 Min 0.1289 839.28748 79.33147 19.80432

Totals : 4520.57019 596.83665

---

*** End of Report ***

---
Area Percent Report

Sorted By: Signal
Multiplier: 1.0000
Dilution: 1.0000
Use Multiplier & Dilution Factor with ISTDs

Signal 1: DAD1 A, Sig-210,4 Ref-off

<table>
<thead>
<tr>
<th>#</th>
<th>RetTime</th>
<th>Width</th>
<th>Area</th>
<th>Height</th>
<th>Area</th>
<th>%</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>14.195</td>
<td>0.3849</td>
<td>5.8420e4</td>
<td>2375.36597</td>
<td>49.6598</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>15.310</td>
<td>0.4228</td>
<td>5.9220e4</td>
<td>2181.21021</td>
<td>50.3402</td>
<td></td>
</tr>
</tbody>
</table>

Totals: 1.17641e5 4556.57617

*** End of Report ***
**Signal 1: DAD1c, Sig=210.4 Ref=off**

<table>
<thead>
<tr>
<th>#</th>
<th>RetTime</th>
<th>Width</th>
<th>Area</th>
<th>Height</th>
<th>Area %</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>14.350</td>
<td>0.3576</td>
<td>784.16967</td>
<td>33.93178</td>
<td>6.9278</td>
</tr>
<tr>
<td>2</td>
<td>15.446</td>
<td>0.3913</td>
<td>1.05349e4</td>
<td>418.99063</td>
<td>93.0722</td>
</tr>
</tbody>
</table>

Totals: 1.13191e4 452.92241

*** End of Report ***
Acq. Operator : SYSTEM
Acq. Instrument : 1260
Injection Date : 3/24/2017 3:50:59
Inj : 1
Method : D:\Chem32\DATA\ggs\13-1-7 2017-03-23 23:05-46\80X-5.M (Sequence Method)
Last changed : 3/24/2017 23:05:46 by SYSTEM
Additional Info : Peak(s) manually integrated

Area Percent Report

Sorted By : Signal
Multiplier : 1.0000
Dilution : 1.0000
Use Multiplier & Dilution Factor with ISTDs

Signal 1: DAD1 C, Sig-210,4 Ref-off

Peak RetTime Type Width Area Height Area
[ min ] [ min ] [ nMU*s ] [ nMUs ] %
---|--------|--------|----------|----------|
1  5.940  0.1322  2812.63628  833.47835  49.8129
2  8.252  0.1850  2814.67390  237.52841  50.1871

Totals :  5647.00928  591.40656

*** End of Report ***
Area Percent Report

Sorted By: Signal
Multiplier: 1.0000
Dilution: 1.0000
Use Multiplier & Dilution Factor with ISTDs

Signal 1: DAD1 A, Sig=210,4 Ref-off

<table>
<thead>
<tr>
<th>Peak RetTime</th>
<th>Type</th>
<th>Width</th>
<th>Area</th>
<th>Height</th>
<th>Area %</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>DB</td>
<td>0.2390</td>
<td>1.6148e4</td>
<td>1032.5756</td>
<td>49.945</td>
</tr>
<tr>
<td>2</td>
<td>MF</td>
<td>0.3890</td>
<td>1.0186e4</td>
<td>884.48088</td>
<td>50.055</td>
</tr>
</tbody>
</table>

Totals: 3.23346e4 1937.06244

*** End of Report ***
**Area Percent Report**

**Sorted By** : Signal
Multiplier : 1.0000
Dilution : 1.0000

Use Multiplier & Dilution Factor with ISTDs

**Signal 1: DAD1 A, Sig=210.4 Ref-off**

<table>
<thead>
<tr>
<th>#</th>
<th>RetTime</th>
<th>Type</th>
<th>Width</th>
<th>Area</th>
<th>Height</th>
<th>Area</th>
<th>%</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>9.937</td>
<td>V8 R</td>
<td>0.2414</td>
<td>2.73200E4</td>
<td>1755.95349</td>
<td>89.0723</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>11.743</td>
<td>BB</td>
<td>0.2813</td>
<td>3351.72192</td>
<td>185.07556</td>
<td>10.9277</td>
<td></td>
</tr>
</tbody>
</table>

Totals : 3.067E4 1941.02905

*** End of Report ***
8. Computational Details

DFT calculations were carried out by using Gaussian 16 package. Geometric structures of all species in gas phase were optimized with M06-L functional. The Lanl2DZ basis set was employed for Ir and Fe with polarization functions added for Ir ($f = 0.938$), and Fe ($f = 2.462$). All electron 6-31G* basis set was used in describing all other main-group atoms. On the basis of the gas-phase optimized geometries, the solvation effect of $i$-PrOH was incorporated with the PCM solvent model at the level of M06-L/6-311++G** theory. The 3D molecular structures were generated by using CYL-view.

![Fig. S1](image1.png)

**Fig. S1.** Optimized geometries with selected structural parameters (distances in Å) for the $I_{Up}$ and $I_{Dn}$. The solvation corrected relative free energies ($\Delta G_{sol}$) are shown in kcal/mol. Unimportant hydrogen atoms are not shown for clarity as well as in Fig. S2.

![TS(S) (0.0), TS(R) (4.8), TS(R)1 (6.1), TS(R)2 (10.3)](image2.png)

**Fig. S2.** Optimized geometries for the transition states for hydride transfer.
9. References


5. Isopropyl 2-oxo-2-phenylacetate (1d) was prepared from methyl 2-oxo-2-phenylacetate purchased from Energy Chemical.


14. CYLview, 1.0b; Legault, C. Y., Université de Sherbrooke, 2009 (http://www.cylview.org).