Supporting Information

Synthesis and Catalytic Activity of (3,4-Diphenylcyclopentadienone)Iron Tricarbonyl Compounds in Transfer Hydrogenations and Dehydrogenations

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**General Methods.** Compound 3 was prepared according to the literature procedure. All commercially available chemicals and anhydrous solvents were used as received, and all reactions were done under an atmosphere of nitrogen unless otherwise noted. Reagent grade isopropanol and acetone (for the transfer hydrogenations and dehydrogenations) were degassed by bubbling $\text{N}_2$ through them for at least 15 minutes prior to use, but no attempt was made to remove residual water. NMR spectra were recorded at rt (approx. 22 °C) unless otherwise noted on a Bruker Avance 400 MHz FT-NMR spectrometer. $^{13}$C NMR spectra (100 MHz) were all proton decoupled. Chemical shifts are reported in parts per million (ppm) downfield from tetramethylsilane (TMS) with reference to TMS for $^1$H NMR and $^{13}$C NMR spectra. Multiplicities are abbreviated as follows: singlet (s), doublet (d), triplet (t), quartet (q), quintet (quint), sextet (sext), septet (sept), multiplet (m), and broad (br). IR spectra were collected on a Nicolet IR200 attenuated total reflectance FT-IR spectrometer and only diagnostic peaks are given. IR bands are given in cm$^{-1}$ and peak intensities correspond to weak (w), medium (m), strong (s), and broad (br). High resolution mass spectrometry data were collected at the Johns Hopkins University Mass Spectrometry Facility.

Analytical thin-layer chromatography (TLC) was performed using silica gel 60 F254 precoated plates (0.25 mm thickness) with a fluorescent indicator. Visualization was performed with UV light. Flash column chromatography was performed using silica gel 60 (230-400 mesh). Gas chromatograms were collected on a Thermo Scientific Trace 1300 gas chromatograph with an Al 1310 autosampler and an FID. A TR-5 (5% phenyl methylpolysiloxane) column (30 m length x 0.25 mm ID x 0.25 μm film thickness) was used under the following method conditions: 110 °C for 5 min, ramp 20 °C/min to 250 °C, hold at 250 °C for 2 min. The carrier gas was helium, used at a constant flow rate of 1 mL/min. A sample volume of 1 μL was added to the 300 °C injector at a 30:1 split ratio, and the FID temperature was 250 °C. Retention times (4.7 min for acetophenone, 4.5 min for 1-phenylethanol, 7.6 min for 4-phenyl-2-butanol, 7.4 min for 4-phenyl-2-butanone, 11.2 min for N-benzylideneaniline, 11.5 min for N-benzyllamine, and 9.0 min for biphenyl) were determined using pure samples.

**Synthesis of Iron Compounds**

**Scheme S1. Synthesis of 4.**

(2,3,4,5-Tetraphenylcyclopentadienone)iron tricarbonyl (4).\(^{S2}\) A solution of 2,3,4,5-tetraphenylcyclopentadienone\(^{S3}\) 8a (3.0 g, 7.8 mmol) and iron pentacarbonyl (2.0 mL, 3.0 g 15 mmol) in 35 mL degassed toluene in a thick-walled round-bottom flask with a PTFE screw cap was heated to 140 °C for 24 h. After cooling to rt, the volatiles were evaporated under reduced pressure and the crude product was purified by flash chromatography (CH$_2$Cl$_2$ followed by 98.5% CH$_2$Cl$_2$/1.5% MTBE) to afford 2.11 g (51%) of 4 as a yellow powder. $R_f$ = 0.33 (98.5% CH$_2$Cl$_2$/1.5% MTBE). $^1$H NMR (400 MHz, CDCl$_3$, ppm): δ 7.57–7.54 (m, 4H), 7.25–7.21 (m, 8H), 7.18–7.12 (m, 8H). $^{13}$C NMR (100 MHz, CDCl$_3$, ppm): δ 208.6, 169.8, 131.9, 130.9, 130.3, 130.0, 128.7, 128.1, 128.1, 127.9, 104.1, 82.6. IR (neat): 3058 (w), 2057 (s), 2010 (s), 1988 (s), 1640 (s). HR-MS (FAB): calculated for [M+H]$^+$ 525.07893, found 525.07897.
Scheme S2. Synthesis of 5.

(2,5-Dimethyl-3,4-diphenylcyclopentadienone)iron tricarbonyl (5). A solution of 2,5-dimethyl-3,4-diphenylcyclopentadienone dimer 8b (2.0 g, 3.8 mmol of dimer which dissociates into 7.6 mmol of the monomer) and iron pentacarbonyl (2.0 mL, 3.0 g, 15 mmol) in 35 mL degassed toluene in a thick-walled round-bottom flask with a PTFE screw cap was heated to 140 °C for 24 h. After cooling to rt, the volatiles were evaporated under reduced pressure and the crude product was purified by flash chromatography (1:1 hexanes/CH₂Cl₂ followed by 1:1 hexanes/ethyl acetate) to afford 2.3 g (75%) of 5 as a yellow powder. R₅ = 0.0 (1:1 hexanes/CH₂Cl₂); R₅ = 0.34 (1:1 hexanes/ethyl acetate). ¹H NMR (400 MHz, CDCl₃, ppm): δ 7.28–7.23 (m, 10H), 1.90 (s, 6H). ¹³C NMR (100 MHz, CDCl₃, ppm): δ 208.8, 171.3, 131.1, 129.9, 128.8, 128.3, 104.2, 80.4, 10.3. IR (neat): 3060 (w), 2051 (m), 1997 (s), 1976 (s), 1641 (s). HR-MS (FAB): calculated for [M+H]+ 401.04763, found 401.04769.


(2,5-Diethyl-3,4-diphenylcyclopentadienone)iron tricarbonyl (6). A solution of 2,5-diethyl-3,4-diphenylcyclopentadienone 8c (2.0 g, 6.9 mmol) and iron pentacarbonyl (1.8 mL, 2.7 g, 13.7 mmol) in 32 mL degassed toluene in a thick-walled round-bottom flask with a PTFE screw cap was heated to 140 °C for 24 h. After cooling to rt, the volatiles were evaporated under reduced pressure and the crude product was purified by flash chromatography (1:1 hexanes/CH₂Cl₂ followed by 3:1 hexanes/ethyl acetate) to afford 2.1 g (71%) of 6 as a yellow powder. R₅ = 0.0 (1:1 hexanes/CH₂Cl₂); R₅ = 0.35 (3:1 hexanes/ethyl acetate). ¹H NMR (400 MHz, CDCl₃, ppm): δ 7.28–7.21 (m, 10H), 2.35 (dq, J = 14.4 and 7.6 Hz, 2H), 2.18 (dq, J = 14.4 and 7.6 Hz, 2H), 1.19 (t, J = 7.6 Hz, 6H). ¹³C NMR (100 MHz, CDCl₃, ppm): δ 209.1, 171.6, 131.1, 130.1, 128.6, 128.2, 104.6, 87.1, 18.1, 15.0. IR (neat): 2957 (w), 2055 (s), 2007 (s), 1981 (s), 1641 (s). HR-MS (FAB): calculated for [M+H]+ 429.07893, found 429.07975.

Multistep synthesis of [2,5-bis(3,5-dimethylphenyl)-3,4-diphenylcyclopentadienone]iron tricarbonyl (7)

Scheme S4. Synthesis of ketone 12.
5,5’-(2-Isocyano-2-tosylpropane-1,3-diyl)bis(1,3-dimethylbenzene) (11). To a stirred solution of p-toluenesulfonylmethyl isocyanide (TosMIC, 10) (2.87 g, 14.7 mmol), 3,5-dimethylbenzyl bromide 9 (6.00 g, 30.1 mmol), and tetrabutylammonium iodide (543 mg, 1.47 mmol) in 36 mL CH₂Cl₂ in air was slowly added 60 mL of 40% aqueous NaOH. After stirring for 18 h at 850 rpm, the yellow solution was diluted with 30 mL water and the organic layer was removed. The aqueous layer was extracted with 2 x 50 mL CH₂Cl₂. The combined organic layers were washed with 50 mL water, 50 mL brine, dried over sodium sulfate, filtered, and evaporated under reduced pressure to a yellow oil that solidified upon standing. (This material could be used directly in the next step, but purifying at this stage simplified later purifications.) The yellow solid was purified by flash chromatography (92% hexanes/8% ethyl acetate) to afford 6.24 g (98%) of 11 as a pale yellow oil that solidified into a white solid upon standing. R<sub>f</sub> = 0.29 (92% hexanes/8% ethyl acetate).<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, ppm): δ 7.80 (d, J = 8.4 Hz, 2H), 7.32 (d, J = 8.0 Hz, 2H), 6.88 (s, 2H), 6.69 (s, 4H), 3.24 (d, J = 14.0 Hz, 2H), 3.12 (d, J = 14.0 Hz, 2H), 2.45 (s, 3H), 2.22 (s, 12H).<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, ppm): δ 166.3, 146.0, 137.8, 132.3, 131.3, 130.8, 129.6, 129.5, 128.7, 81.9, 39.5, 21.7, 21.2. IR (neat): 2918 (m), 2112 (m), 1604 (m), 1325 (m), 1151 (s). The molecular ion was not observed by HR-MS (FAB), most likely due to decomposition in the spectrometer.

1,3-Bis(3,5-dimethylphenyl)propan-2-one (12). To a stirred solution/suspension of 11 (6.24 g, 14.5 mmol) in 22 mL of Et₂O and 8 mL CH₂Cl₂ at rt in air was slowly added concentrated aqueous HCl (1.5 mL, 18 mmol). After 15 min, 18 mL of aqueous 1M NaOH was added and the reaction solution was extracted with 2 x 25 mL MTBE. The combined organic layers were washed with 50 mL aqueous 1M NaOH, 50 mL water, 50 mL brine, were dried over sodium sulfate, filtered, and evaporated under reduced pressure to a pale yellow oil. Purification of the oil by flash chromatography (95% hexanes/5% ethyl acetate) afforded 3.12 g (81%) of 12 as a white solid. R<sub>f</sub> = 0.32 (95% hexanes/5% ethyl acetate).<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, ppm): δ 6.89 (s, 2H), 6.75 (s, 4H), 3.62 (s, 4H), 2.28 (s, 12H).<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, ppm): δ 206.4, 138.2, 133.9, 128.7, 127.4, 49.0, 21.3. IR (neat): 3019 (w), 2915 (w), 1702 (s), 1601 (m). HR-MS (FAB): calculated for [M+H]<sup>+</sup> 267.17452, found 267.17489.


2,5-Bis(3,5-dimethylphenyl)-3,4-diphenylcyclopentadienone (13). To a solution of 12 (3.00 g, 11.3 mmol) and benzil (2.37 g, 11.3 mmol) in 17 mL of 100% ethanol at 75 °C in air was slowly added a solution of potassium hydroxide (335 mg, 5.97 mmol) in 1.7 mL of 100% ethanol. The dark purple reaction stirred at reflux for 30 minutes. The reaction mixture was cooled to rt and then in an ice/salt bath. The purple crystals were collected by suction filtration and washed with 3 x 7mL cold 95% ethanol to afford 4.16 g (84%) of 13. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, ppm): δ 7.25–7.21 (m, 2H), 7.18–7.14 (m, 4H), 6.94–6.92 (m, 4H), 6.85 (s, 2H), 6.84 (s, 4H), 2.18 (s, 12H).<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, ppm): δ 200.8, 154.2, 137.3, 133.3, 130.6, 129.3, 129.2, 128.3, 127.9, 127.9, 125.4, 21.3. IR (neat): 3030 (w), 2912 (w), 1705 (s), 1601 (s). HR-MS (FAB): calculated for M+ 440.21402, found 440.21452.

![Scheme S6](image)

[2,5-Bis(3,5-dimethylphenyl)-3,4-diphenylcyclopentadienone]iron tricarbonyl (7). A solution of 13 (1.0 g, 2.3 mmol) and iron pentacarbonyl (0.60 mL, 0.89 g, 4.6 mmol) in 20 mL degassed toluene in a thick-walled round-bottom flask with a PTFE screw cap was heated to 140 °C for 24 h. After cooling to rt, the volatiles were evaporated under reduced pressure and the crude product was purified by flash chromatography (90% hexanes/10% ethyl acetate) to afford a solid that was suspended in hexanes at 0 °C and was collected by suction filtration. The solid was washed with 3 x 4 mL of 0 °C hexanes and 0.99 g (75%) of 7 as a brownish-yellow solid was collected. R = 0.31 (90% hexanes/10% ethyl acetate). 1H NMR (400 MHz, CDCl$_3$, ppm): δ 7.26–7.20 (m, 2H), 7.18–7.13 (m, 12H), 6.87 (s, 2H), 2.18 (s, 12H). 13C NMR (100 MHz, CDCl$_3$, ppm): δ 208.8, 170.0, 137.3, 131.9, 130.6, 130.2, 129.6, 128.5, 128.2, 127.9, 104.0, 82.8, 21.3. IR (neat): 2915 (w), 2080 (s), 2011 (s), 1982 (s), 1739 (m), 1642 (s). HR-MS (FAB): calculated for [M+H]$^+$ 581.14153, found 581.14176.

Acetophenone transfer hydrogenation reactions (Figure 2).

Scheme S7. Acetophenone transfer reductions with 3–7.

![Scheme S7](image)

Reaction procedure. A round-bottom flask under N$_2$ was charged with acetophenone (1.20 g, 10 mmol), biphenyl (386 mg, 2.5 mmol) and 20 mL of degassed isopropanol. A 100 μL aliquot of this solution was removed, diluted to 1.5 mL with acetone, and was analyzed by gas chromatography to provide a reference for acetophenone relative to biphenyl (the internal standard) at t = 0. (Cyclopentadienone)iron tricarbonyl compound (0.2 mmol) and anhydrous trimethylamine N-oxide (15 mg, 0.2 mmol) were added to the flask and it was submerged in an 80 °C oil bath. Aliquots (200 μL) were removed at 0.5 h, 1.5 h, 3 h, 6 h, 24 h, 30 h, 48 h, and 72 h. Each aliquot was diluted with 1 mL of hexanes, added to a Pasteur pipet half full of silica gel, and was eluted with 4 mL 1:1 hexanes/ethyl acetate. TLC showed this eluent readily eluted acetophenone, 1-phenylethanol, and biphenyl. A sample of the eluted solution was analyzed by gas chromatography. Conversion was determined based on how much acetophenone had been consumed compared to the amount of acetophenone in the t = 0 chromatogram relative to the internal standard (biphenyl). Each reaction was run at least twice and the average conversions (typically off by no more than ± 5%) were used. Importantly, the trends for each catalyst were consistent.

Calibration curves and GC yield. To determine the GC yield of 1-phenylethanol in the acetophenone transfer hydrogenation reactions, two calibration curves were made: one correlating acetophenone to biphenyl and one correlating 1-phenylethanol to biphenyl. The acetophenone/biphenyl curve was made by mixing known quantities of an acetophenone solution in acetone (0.03309M) and a biphenyl solution in acetone (0.2579M) in the following acetophenone/biphenyl molar ratios: 4:1, 2:1, 1:1, and 1:4. These solutions were analyzed by gas chromatography and a plot was made that correlated the moles of acetophenone (relative to
biphenyl) to the peak area of acetophenone (relative to biphenyl). The equation from the line fit to the data \((R^2 = 0.9998)\) was \(y = 1.538x - 0.0355\), where \(y\) = moles of acetophenone (relative to biphenyl), and \(x\) = peak area of acetophenone (relative to biphenyl). The same thing was done to make a 1-phenylethanol/biphenyl calibration curve using the same biphenyl in acetone solution and a 0.03317M solution of 1-phenylethanol in acetone. The equation from the line fit to the data \((R^2 = 0.9999)\) was \(y = 1.589x + 0.0076\), where \(y\) = moles of 1-phenylethanol (relative to biphenyl), and \(x\) = peak area of 1-phenylethanol (relative to biphenyl). The acetophenone and biphenyl peak areas from the \(t = 0\) solution described in the “Reaction Procedure” above were converted into the relative moles of acetophenone using the acetophenone equation. This value was the initial moles of acetophenone in the reaction. To determine the GC yield of 1-phenylethanol (i.e. the moles of 1-phenylethanol formed relative to the initial moles of acetophenone), the peak area of 1-phenylethanol relative to the peak area of biphenyl at a given time was converted into moles of 1-phenylethanol using the 1-phenylethanol equation. This value for 1-phenylethanol moles was divided by the initial moles of acetophenone (determined as described above) to get a GC yield. For all the iron catalysts used in this study, the GC yield of 1-phenylethanol was almost identical to the conversions of acetophenone, suggesting no other by-products were forming during the reaction.

**General transfer hydrogenation procedure (Table 1)**

**Scheme S8. Transfer reductions with 3 and 7.**

A round-bottom flask under N\(_2\) was charged with ketone or aldehyde (2.5 mmol), biphenyl (96 mg, 0.63 mmol) and 5 mL of degassed isopropanol. A 100 \(\mu\)L aliquot of this solution was removed, diluted to 1.5 mL with acetone, and was analyzed by gas chromatography to provide a reference for the amount of ketone or aldehyde relative to biphenyl (the internal standard) at \(t = 0\). Compound 3 or 7 (0.05 mmol) and anhydrous trimethylamine N-oxide (4 mg, 0.05 mmol) were added to the flask and it was submerged in an 80 °C oil bath. After 24h, a 200 \(\mu\)L aliquot was removed. It was diluted with 1 mL of hexanes, added to a Pasteur pipet half full of silica gel, and was eluted with 4 mL 1:1 hexanes/ethyl acetate. TLC showed this eluent readily eluted all the reactants, products, and biphenyl. A 1.5 mL sample of the eluted solution was analyzed by gas chromatography, and the remaining eluted solution was evaporated under reduced pressure and the residue was analyzed by \(^1\)H NMR spectroscopy (CDCl\(_3\)). Conversion was determined by GC based on how much ketone/aldehyde had been consumed compared to the amount of ketone/aldehyde in the \(t = 0\) chromatogram relative to the internal standard (biphenyl). Yield of alcohol (which matched GC conversions for all the compounds in Table S1) was determined by comparing the amount of alcohol product formed to the total amount of both ketone/aldehyde and alcohol using integration values in the \(^1\)H NMR spectrum.
4-Phenyl-2-butanol transfer dehydrogenation reactions (Figure 3).

Scheme S9. 4-Phenyl-2-butanol transfer oxidations with 3–7.

**Reaction procedure.** A round-bottom flask under N₂ was charged with 4-phenyl-2-butanol (1.50 g, 10 mmol), biphenyl (386 mg, 2.5 mmol) and 20 mL of degassed acetone. A 100 μL aliquot of this solution was removed, diluted to 1.5 mL with acetone, and was analyzed by gas chromatography to provide a reference for 4-phenyl-2-butanol relative to biphenyl (the internal standard) at t = 0. (Cyclopentadienone)iron tricarbonyl compound (0.25 mmol) and anhydrous trimethylamine N-oxide (19 mg, 0.25 mmol) were added to the flask and it was submerged in a 60 °C oil bath. Aliquots (200 μL) were removed at 0.5 h, 1.5 h, 3 h, 6 h, 24 h, 30 h, 48 h, and 72 h. Each aliquot was diluted with 1 mL of hexanes, added to a Pasteur pipet half full of silica gel, and was eluted with 4 mL 1:1 hexanes/ethyl acetate. TLC showed this eluent readily eluted 4-phenyl-2-butanol, 4-phenyl-2-butanone, and biphenyl. A sample of the eluted solution was analyzed by gas chromatography. Conversion was determined based on how much 4-phenyl-2-butanol had been consumed compared to the amount of 4-phenyl-2-butanol in the t = 0 chromatogram relative to the internal standard (biphenyl). Each reaction was run at least twice and the average conversions (typically off by no more than ± 5%) were used. Importantly, the trends for each catalyst were consistent.

**Calibration curves and GC yield.** To determine the GC yield of 4-phenyl-2-butanone in the 4-phenyl-2-butanol transfer dehydrogenation reactions, two calibration curves were made: one correlating 4-phenyl-2-butanol to biphenyl and one correlating 4-phenyl-2-butanol to biphenyl. The 4-phenyl-2-butanol/biphenyl curve was made by mixing known quantities of a 4-phenyl-2-butanol solution in acetone (0.03257M) and a biphenyl solution in acetone (0.2579M) in the following 4-phenyl-2-butanol/biphenyl molar ratios: 4:1, 2:1, 1:1, and 1:4. These solutions were analyzed by gas chromatography and a plot was made that correlated the moles of 4-phenyl-2-butanol (relative to biphenyl) to the peak area of 4-phenyl-2-butanol in acetone solution and a 0.03402M solution of 4-phenyl-2-butanone in acetone. The equation from the line fit to the data (R² = 0.9996) was y = 1.292x – 0.0062, where y = moles of 4-phenyl-2-butanol (relative to biphenyl), and x = peak area of 4-phenyl-2-butanol (relative to biphenyl). The same thing was done to make a 4-phenyl-2-butanone/biphenyl calibration curve using the same biphenyl in acetone solution and a 0.03402M solution of 4-phenyl-2-butanone in acetone. The equation from the line fit to the data (R² = 0.9993) was y = 1.415x – 0.076, where y = moles of 4-phenyl-2-butanone (relative to biphenyl), and x = peak area of 4-phenyl-2-butanone (relative to biphenyl). The 4-phenyl-2-butanol and biphenyl peak areas from the t = 0 solution described in the “Reaction Procedure” above were converted into the relative moles of 4-phenyl-2-butanol using the 4-phenyl-2-butanol equation. This value was the initial moles of 4-phenyl-2-butanol in the reaction. To determine the GC yield of 4-phenyl-2-butanone (i.e. the moles of 4-phenyl-2-butanone formed relative to the initial moles of 4-phenyl-2-butanol), the peak area of 4-phenyl-2-butanone relative to the peak area of biphenyl at a given time was converted into moles of 4-phenyl-2-butanone using the 4-phenyl-2-butanone equation. This value for 4-phenyl-2-butanone moles was divided by the initial moles of 4-phenyl-2-butanol (determined as described above) to get a GC yield. For all the iron catalysts used in this study, the GC yield of 4-phenyl-2-butanone was almost identical to the conversions of 4-phenyl-2-butanol, suggesting no other by-products were forming during the reaction.
**General transfer dehydrogenation procedure (Table 2)**

**Scheme S10. Transfer dehydrogenations with 3 and 7.**

A round-bottom flask under N₂ was charged with alcohol (2.5 mmol), biphenyl (96 mg, 0.63 mmol) and 5 mL of degassed acetone. A 100 µL aliquot of this solution was removed, diluted to 1.5 mL with acetone, and was analyzed by gas chromatography to provide a reference for the amount of alcohol relative to biphenyl (the internal standard) at t = 0. Compound 3 or 7 (0.063 mmol) and anhydrous trimethylamine N-oxide (5 mg, 0.063 mmol) were added to the flask and it was submerged in a 60 °C oil bath. After 24h, a 200 µL aliquot was removed. It was diluted with 1 mL of hexanes, added to a Pasteur pipet half full of silica gel, and was eluted with 4 mL 1:1 hexanes/ethyl acetate. TLC showed this eluent readily eluted all the reactants, products, and biphenyl. A 1.5 mL sample of the eluted solution was analyzed by gas chromatography, and the remaining eluted solution was evaporated under reduced pressure and the residue was analyzed by ¹H NMR spectroscopy (CDCl₃). Conversion was determined by GC based on how much alcohol had been consumed compared to the amount of alcohol in the t = 0 chromatogram relative to the internal standard (biphenyl). Yield of carbonyl compound (which matched GC conversions for all the compounds in Table S1) was determined by comparing the amount of carbonyl product formed to the total amount of both alcohol and carbonyl compound using integration values in the ¹H NMR spectrum.

**Product inhibition experiments (Figures 4 and 5)**

**Scheme S11. Product inhibition in transfer reductions with 3 and 7.**

**General procedure for testing product inhibition in acetophenone transfer hydrogenations.** A round-bottom flask under N₂ was charged with acetophenone (1.20 g, 10 mmol), 1-phenylethanol (1.22 g, 10 mmol), biphenyl (386 mg, 2.5 mmol), and 19 mL of degassed isopropanol. A 100 µL aliquot of this solution was removed, diluted to 1.5 mL with acetone, and was analyzed by gas chromatography to provide a reference for acetophenone relative to biphenyl (the internal standard) at t = 0. Compound 3 or 7 (0.2 mmol) and anhydrous trimethylamine N-oxide (15 mg, 0.2 mmol) were added to the flask and it was submerged in an 80 °C oil bath. Aliquots (200 µL) were removed at 0.5 h, 1.5 h, 3 h, 6 h, 24 h, 30 h, 48 h, and 72 h. Each aliquot was diluted with 1 mL of hexanes, added to a Pasteur pipet half full of silica gel, and was eluted with 4 mL 1:1 hexanes/ethyl acetate. TLC showed this eluent readily eluted acetophenone, 1-phenylethanol, and biphenyl. A sample of the eluted solution was analyzed by gas chromatography. Conversion was determined based on how much acetophenone had been consumed compared to the amount of acetophenone in the t = 0 chromatogram relative to the internal standard (biphenyl).
Scheme S12. Product inhibition in transfer dehydrogenations with 3 and 7.

General procedure for testing product inhibition in 4-phenyl-2-butanol transfer dehydrogenations. A round-bottom flask under N₂ was charged with 4-phenyl-2-butanol (1.50 g, 10 mmol), 4-phenyl-2-butanone (1.48 g, 10 mmol), biphenyl (386 mg, 2.5 mmol) and 18.5 mL of degassed acetone. A 100 μL aliquot of this solution was removed, diluted to 1.5 mL with acetone, and was analyzed by gas chromatography to provide a reference for 4-phenyl-2-butanol relative to biphenyl (the internal standard) at t = 0. Compound 3 or 7 (0.25 mmol) and anhydrous trimethylamine N-oxide (19 mg, 0.25 mmol) were added to the flask and it was submerged in a 60 °C oil bath. Aliquots (200 μL) were removed at 0.5 h, 1.5 h, 3 h, 6 h, 24 h, 30 h, 48 h, and 72 h. Each aliquot was diluted with 1 mL of hexanes, added to a Pasteur pipet half full of silica gel, and was eluted with 4 mL 1:1 hexanes/ethyl acetate. TLC showed this eluent readily eluted 4-phenyl-2-butanol, 4-phenyl-2-butanone, and biphenyl. A sample of the eluted solution was analyzed by gas chromatography. Conversion was determined based on how much 4-phenyl-2-butanol had been consumed compared to the amount of 4-phenyl-2-butanol in the t = 0 chromatogram relative to the internal standard (biphenyl).

Monitoring iron compound 7 by NMR spectroscopy (Scheme 4)


Formation of proposed iron hydride 8. A solution of iron compound 7 (10 mg, 0.017 mmol) and anhydrous trimethylamine N-oxide (1.3 mg, 0.017 mmol) in 0.6 mL of degassed toluene-d₈ and 0.6 mL of degassed isopropanol in a round-bottom flask under N₂ was placed in an 80 °C oil bath. After 10 min, 0.7 mL of the solution was removed and placed in a screw-cap NMR tube under N₂. A ¹H NMR spectrum at rt showed a diagnostic peak at –10.72 ppm.

Monitoring iron compound 7 during acetophenone transfer reduction. A solution of acetophenone (60 mg, 0.50 mmol), iron compound 7 (15 mg, 0.025 mmol), and anhydrous trimethylamine N-oxide (2 mg, 0.025 mmol) in 0.5 mL of degassed toluene-d₈ and 0.5 mL of degassed isopropanol in a round-bottom flask under N₂ was placed in an 80 °C oil bath. After 15 min, 0.7 mL of the solution was removed and placed in a screw-cap NMR tube under N₂. A ¹H NMR spectrum taken at rt showed the diagnostic peak at –10.72 ppm. The sample was heated to 70 °C, and a ¹H NMR spectrum taken at 70 °C still showed a peak at –10.72 ppm, and peaks corresponding to 1-phenylethanol (δ 4.69 ppm (q, J = 6.0 Hz, 1H), 1.34 ppm (d, J = 6.0 Hz, 3H)) were also present.

Monitoring iron compound 7 during 4-phenyl-2-butanol transfer dehydrogenation. A solution of 4-phenyl-2-butanol (75 mg, 0.5 mmol), iron compound 7 (15 mg, 0.025 mmol), and anhydrous trimethylamine N-oxide (2 mg, 0.025 mmol) in 1 mL degassed acetone-d₆ in a round-bottom flask under N₂ was placed in a 60 °C oil bath. After 30 min, 0.7 mL of the solution was placed
in a screw-cap NMR tube under N₂. A ¹H NMR spectrum taken at rt showed a small, broad peak at –4.65 ppm. The sample was heated to 50 °C and a ¹H NMR spectrum taken at 50 °C showed very small peaks at –4.87 ppm and –10.82 ppm. Additionally, peaks corresponding to 4-phenyl-2-butanone (overlapping multiplet at 2.82 ppm and singlet at 2.09 ppm) and isopropanol-d₆ (3.89 ppm) were also present.

*N-Benzyldieneaniline transfer hydrogenation reactions (Figure 6).*


**Reaction procedure.** A round-bottom flask under N₂ was charged with *N*-benzyldieneaniline (1.18 g, 10 mmol), biphenyl (386 mg, 2.5 mmol) and 20 mL of degassed isopropanol. A 100 μL aliquot of this solution was removed, diluted to 1.5 mL with a cetone, and was analyzed by gas chromatography to provide a reference for *N*-benzyldieneaniline relative to biphenyl (the internal standard) at t = 0. (Cyclopentadienone)iron tricarbonyl compound (0.2 mmol) and anhydrous trimethylamine-N-oxide (15 mg, 0.2 mmol) were added to the flask and it was submerged in an 80 °C oil bath. Aliquots (200 μL) were removed at 0.5 h, 1.5 h, 3 h, 4 h or 6 h, 24 h, 30 h, 48 h, and 72 h. Each aliquot was diluted with 1 mL of hexanes, added to a Pasteur pipet half full of silica gel, and was eluted with 4 mL 1:1 hexanes/ethyl acetate. TLC showed this eluent readily eluted *N*-benzyldieneaniline, *N*-benzylaniline, and biphenyl. A sample of the eluted solution was analyzed by gas chromatography. Conversion was determined based on how much *N*-benzyldieneaniline had been consumed compared to the amount of *N*-benzyldieneaniline in the t = 0 chromatogram relative to the internal standard (biphenyl). Each reaction was run at least twice and the average conversions (typically off by no more than ± 5%) were used. Importantly, the trends for each catalyst were consistent.

**Calibration curves and GC yield.** To determine the GC yield of *N*-benzylaniline in the *N*-benzyldieneaniline transfer hydrogenation reactions, two calibration curves were made: one correlating *N*-benzyldieneaniline to biphenyl and one correlating *N*-benzylaniline to biphenyl. The *N*-benzyldieneaniline/biphenyl curve was made by mixing known quantities of an *N*-benzyldieneaniline solution in acetone (0.03292M) and a biphenyl solution in acetone (0.2579M) in the following *N*-benzyldieneaniline/biphenyl molar ratios: 4:1, 2:1, 1:1, and 1:4. These solutions were analyzed by gas chromatography and a plot was made that correlated the moles of *N*-benzyldieneaniline (relative to biphenyl) to the peak area of *N*-benzyldieneaniline (relative to biphenyl). The equation from the line fit to the data (R² = 0.9985) was y = 1.1055x – 0.0868, where y = moles of *N*-benzyldieneaniline (relative to biphenyl), and x = peak area of *N*-benzyldieneaniline (relative to biphenyl). The same thing was done to make an *N*-benzylaniline/biphenyl calibration curve using the same biphenyl in acetone solution and a 0.03250M solution of *N*-benzylaniline in acetone. The equation from the line fit to the data (R² = 0.9995) was y = 1.0806x – 0.011, where y = moles of *N*-benzylaniline (relative to biphenyl), and x = peak area of *N*-benzylaniline (relative to biphenyl). The *N*-benzyldieneaniline and biphenyl peak areas from the t = 0 solution described in the “Reaction Procedure” above were converted into the relative moles of *N*-benzyldieneaniline using the *N*-benzyldieneaniline equation. This value was the initial moles of *N*-benzyldieneaniline in the reaction. To determine the GC yield of *N*-benzylaniline (i.e. the moles of *N*-benzylaniline formed relative to the initial moles of *N*-benzyldieneaniline), the peak area of *N*-benzylaniline relative to the peak area of biphenyl at a given time was converted into moles of *N*-benzylaniline.
using the $N$-benzylaniline equation. This value for $N$-benzylaniline moles was divided by the initial moles of $N$-benzylideneaniline (determined as described above) to get a GC yield. For all the iron catalysts used in this study, the GC yield of $N$-benzylaniline was almost identical to the conversions of $N$-benzylideneaniline, suggesting no other by-products were forming during the reaction.

References


Figure S1. $^1$H NMR spectrum (400 MHz, CDCl$_3$) of 4
Figure S2. $^{13}$C NMR spectrum (100 MHz, CDCl$_3$) of 4
Figure S3. $^1$H NMR spectrum (400 MHz, CDCl$_3$) of 5
Figure S4. $^{13}$C NMR spectrum (100 MHz, CDCl$_3$) of 5
Figure S5. $^1$H NMR spectrum (400 MHz, CDCl$_3$) of 6
Figure S6. $^{13}$C NMR spectrum (100 MHz, CDCl$_3$) of 6
Figure S7. $^1\text{H}$ NMR spectrum (400 MHz, CDCl$_3$) of 11
Figure S8. $^{13}$C NMR spectrum (100 MHz, CDCl$_3$) of 11
Figure S9. $^1$H NMR spectrum (400 MHz, CDCl$_3$) of 12
Figure S10. $^{13}$C NMR spectrum (100 MHz, CDCl$_3$) of 12
Figure S11. $^1$H NMR spectrum (400 MHz, CDCl$_3$) of 13
Figure S12 $^{13}$C NMR spectrum (100 MHz, CDCl$_3$) of 13
Figure S13. $^1\text{H}$ NMR spectrum (400 MHz, CDCl$_3$) of 7
Figure S14. $^{13}$C NMR spectrum (100 MHz, CDCl$_3$) of 7