Light-Induced Enantioselective Hydrogenation Using Chiral Derivatives of Casey's Iron Cyclopentadienone Catalyst

Supporting Information

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I. Control experiments

V.1. Racemization of 1-phenylethanol

Three control experiments were carried out to check for racemization of the product alcohol 1-phenylethanol under the reaction conditions.

V.1.1) 1-Phenylethanol [34.0 μL, 0.28 mmol, 1.0 eq, 93 % *ee (R)* by GC] and dodecane (68.0 μL) were dissolved in toluene (1.0 mL) in a glass autoclave under a stream of argon. A GC-sample was taken before the iron complex **7** (15 mg, 37 μmol, 13 mol%) was added as a solid. The reaction vessel was purged with hydrogen. Under 5 bar hydrogen pressure, the reaction mixture was irradiated in a Rayonet RPR-100 at λ_{max}=350 nm for 2 hours and then stirred for 72 hours without irradiation. Subsequent GC-analysis showed no appreciable conversion of 1-phenylethanol, the *ee* had decreased to 85% *(R)*.

V.1.2) 1-Phenylethanol [4.8 μL, 40.0 μmol, 0.67 eq., 94 % *ee (R)* by GC], acetophenone (7.0 μL, 60.0 μmol, 1.0 eq) and dodecane (20.0 μL) were dissolved in toluene (1.0 mL) in a glass autoclave under a stream of argon. A GC-sample was taken before the iron complex **7** (5.8 mg, 14.0 μmol, 0.23 eq) was added as a solid. The reaction mixture was purged three times with 6 bar H_2.The glass autoclave was filled with 5 bar hydrogen and irradiated in a Rayonet RPR-100 at λ_{max}=350 nm for 2.5 h and then stirred for 21.5 h without irradiation. GC-analysis showed full conversion of acetophenone to racemic 1-phenylethanol. The *ee* value of 34% *(R)* obtained for the product alcohol 1-phenylethanol is in agreement with minor racemization (without product racemization, 38% *ee (R)* were expected for full conversion of acetophenone to racemic 1-phenylethanol).

V.1.3) 1-Phenylethanol [5.3 μL, 44.0 μmol, 1.0 eq., 98 % *ee (R)* by GC] and dodecane (6.0 μL) were dissolved in toluene (1.0 mL) in a glass autoclave under a stream of argon. A GC-sample was taken (showing 4.6 % acetophenone present as an impurity) before iron complex **7** (2.0 mg, 5.0 μmol, 11 mol%) was added as a solid. The reaction vessel was purged three times with argon. Under 5 bar argon pressure, the reaction mixture was irradiated in a Rayonet RPR-100 at λ_{max}=350 nm for 3 hours and then stirred for 21 hours without irradiation. GC-analysis showed 7 %

conversion of 1-phenylethanol to acetophenone, and an *ee* of 83% *(R)* for the remaining alcohol.

V.2. Blank experiment in the absence of iron catalyst

Acetophenone (35.0 µl, 0.30 mmol) and dodecane as GC-Standard (68.0 µl, 0.30 mmol) were dissolved in toluene (1.0 mL) in a glass autoclave under a stream of inert gas. No catalyst was added. The reaction mixture was irradiated in a Rayonet RPR-100 at λ_{max}=350 nm for 2 hours under H_2 pressure (5 bar) and then stirred for 20 hours under the same pressure without irradiation. No conversion of acetophenone could be detected by GC-analysis.

II. NMR Experiments

In a glovebox, single crystals of complex *ent*-**8a** (10.4 mg, 14 µmol) were dissolved in d_8-toluene (0.55 mL). The sample was sealed and examined by ^{1}H- and ^{31}P-NMR-spectroscopy (Figure S1 and Figure S4). The sample was transferred to a glass autoclave under a stream of argon, and the autoclave was sealed and purged with argon (14 bar) and three times hydrogen (14 bar). The solution was irradiated at λ_{max}=350 nm under hydrogen pressure with magnetic stirring for 1.5 h, after which a slight colour change from yellow to orange could be observed. The sample was transferred to an NMR-tube (septum sealed under argon atmosphere) through a syringe filter. ^{1}H and ^{31}P-NMR-spectra were obtained immediately afterwards. Figure S2 shows the ^{1}H-NMR-spectrum obtained after 1.5 h of irradiation under hydrogen pressure, Figure S3 shows a magnified view of the hydride region. The two doublets in the upper, ^{31}P-coupled ^{1}H-NMR-spectrum collapsed to singlets when the spectrum was recorded with ^{31}P-decoupling (O2P= 208.0 ppm, lower spectrum in Figure S3). Figure S5 shows the ^{31}P-{^{1}H}-NMR-spectrum when the proton-decoupling offset (O2P) was set to 4.8 ppm. Despite this decoupling pulse, two doublets (δ = 208.8 and 207.2 ppm respectively) could be observed. The spectrum in Figure S5 also shows the signals characteristic for the parent complex *ent*-**8a** (δ = 195.5 ppm) and the free phosphoramidite *ent*-**9a** (δ = 149.2 ppm), indicating that the phosphoramidite ligand can dissociate from the iron complex under the reaction conditions. Phosphoramidite dissociation prior to hydrogen uptake offers an explanation for the formation of

achiral hydride **6** (as observed in the ^{1}H-NMR-spectrum, Figure S3, δ = -11.68 ppm). When the ^{1}H-decoupling pulse was applied in the hydride region (O2P= -12.67 ppm), the signals at δ = 208.8 and 207.2 ppm collapsed to singlets (Figure S6). This confirms that the phosphorus atoms giving rise to these signals couple to hydrides. The signal for the parent dicarbonylphosphoramidite complex *ent*-**8a** (δ = 195.5 ppm) could not be observed in this experiment, possibly due to proton coupling.

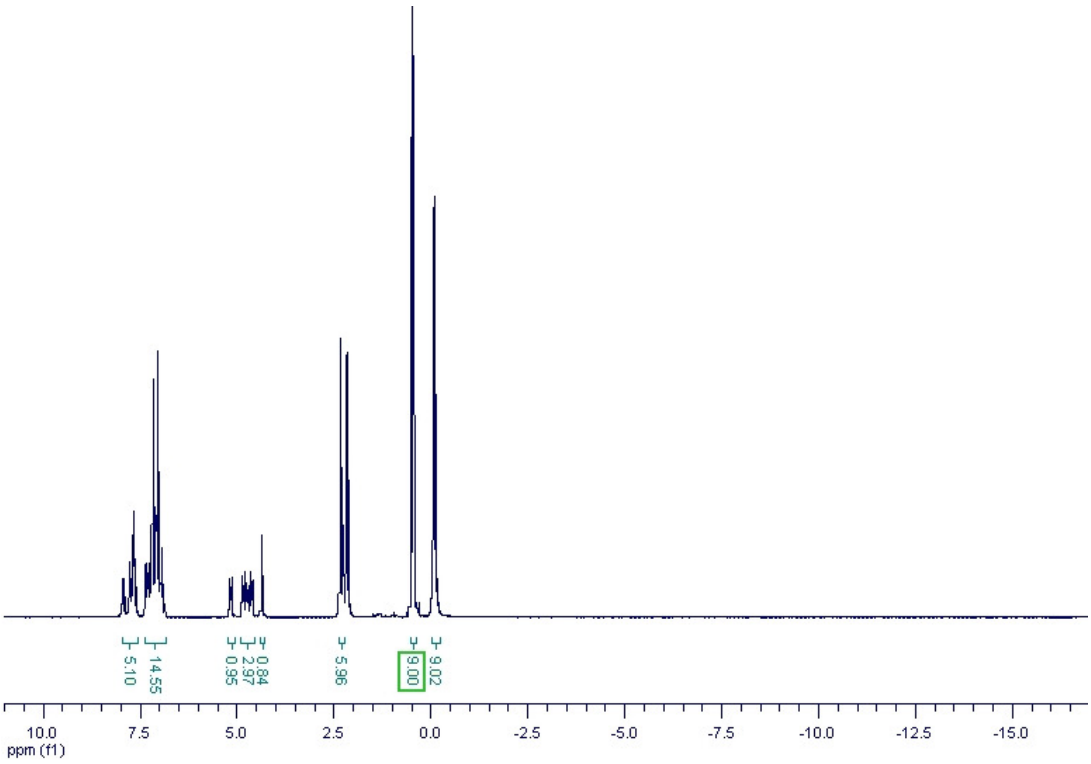

Figure S1: ^{1}H-NMR-spectrum of *ent*-8a in d_8-toluene (co-crystallized residual dichloromethane at δ = 4.34 ppm) prior to irradiation under hydrogen pressure.

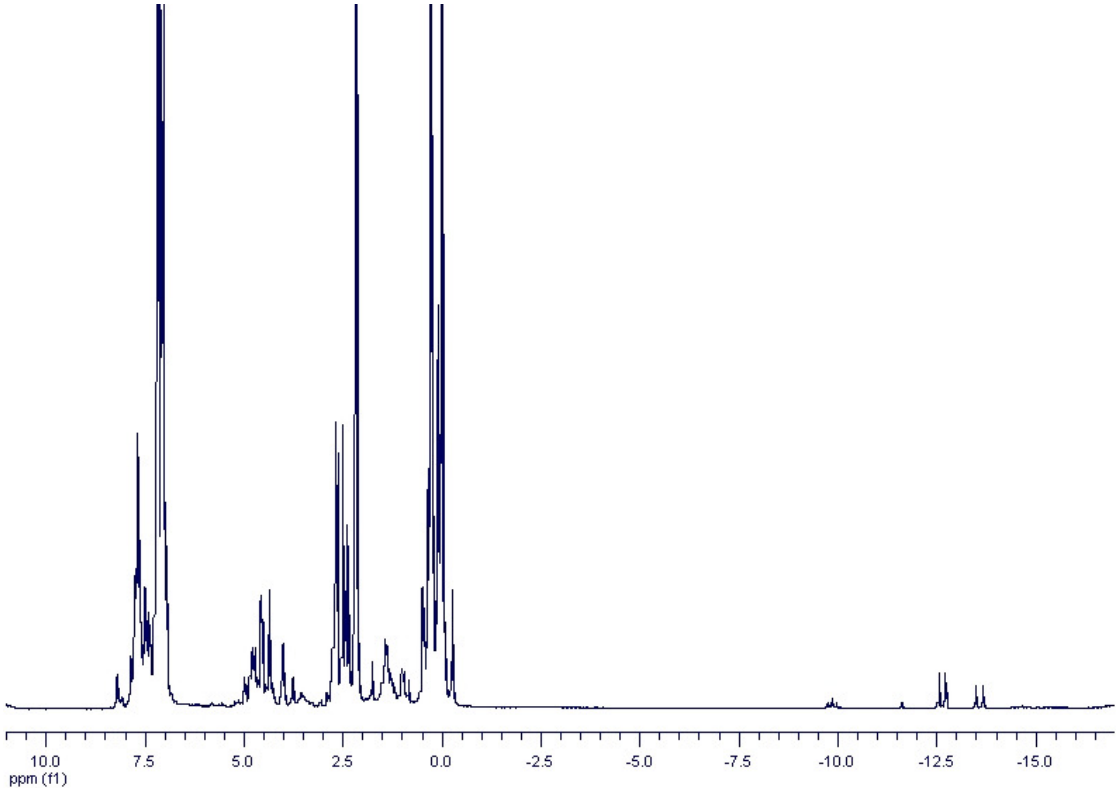

Figure S2: ^{1}H-NMR-spectrum of *ent*-8a in d_8-toluene after 1.5 h irradiation under hydrogen pressure. The region from δ = -9.0 to -15 ppm shows the presence of hydride species (see Figure S3 for magnified view).

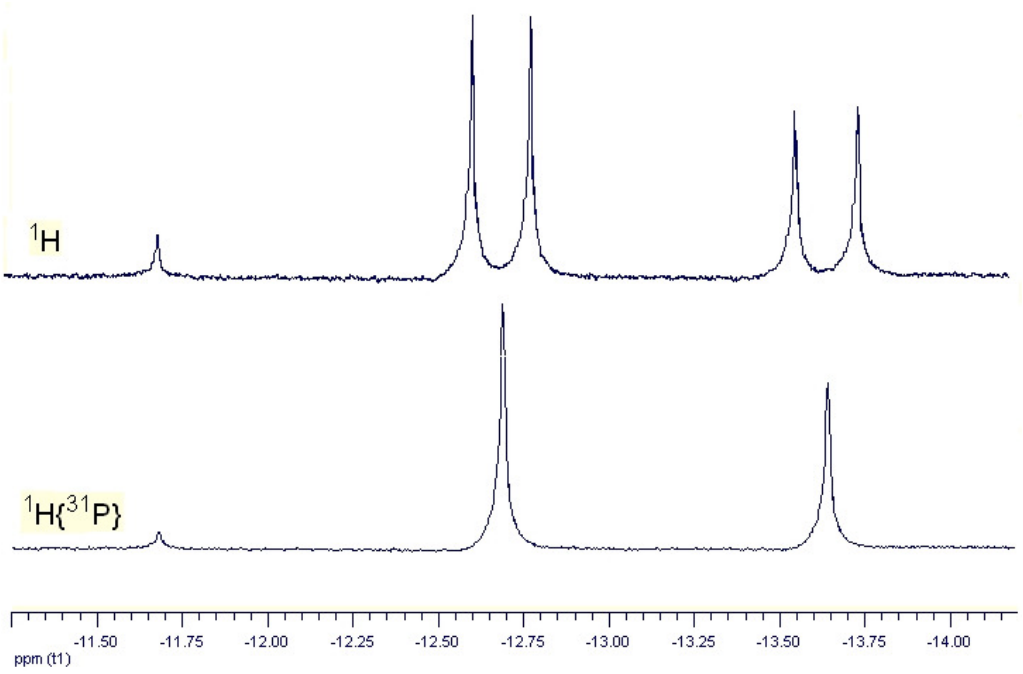

Figure S3: Magnified view of the hydride region of the ^{1}H-NMR-spectra (upper: ^{31}P-coupled, lower: ^{31}P-decoupled, O2P= 208.0 ppm) of complex *ent*-8a after 1.5 h irradiation under hydrogen pressure. Comparison of the spectra shows that the doublets at δ = -12.69 ppm and -13.64 ppm arise from coupling to phosphorus.

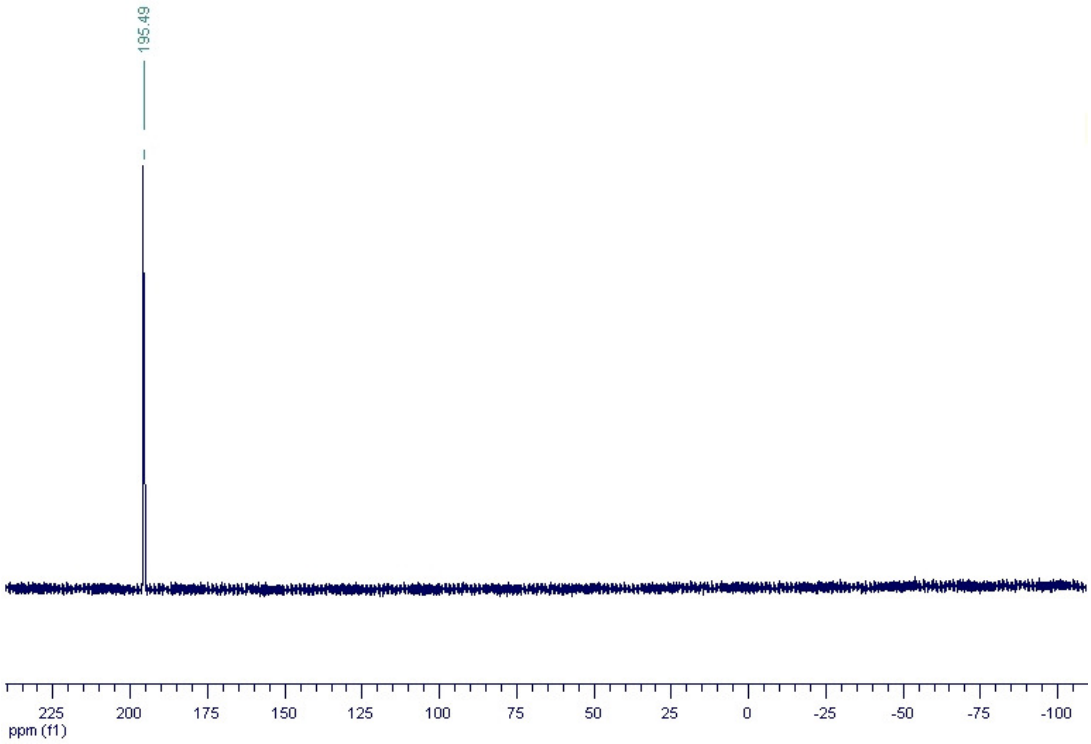

Figure S4: ^{31}P-{^{1}H}-NMR-spectrum (O2P= 4.8 ppm) of *ent*-8a in d_8-toluene prior to irradiation under hydrogen pressure.

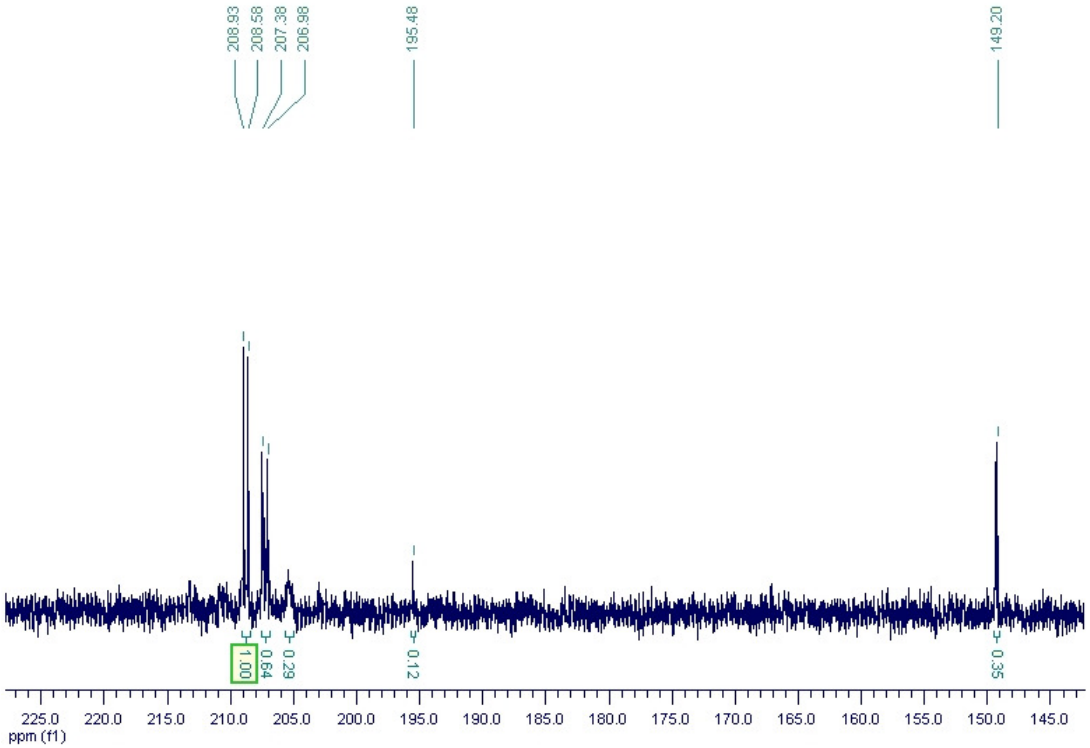

Figure S5: Relevant region of the ^{31}P-{^{1}H}-NMR-spectrum of *ent*-8a in d_8-toluene after 1.5 h irradiation under hydrogen pressure; the proton decoupling pulse was applied at O2P= 4.8 ppm.

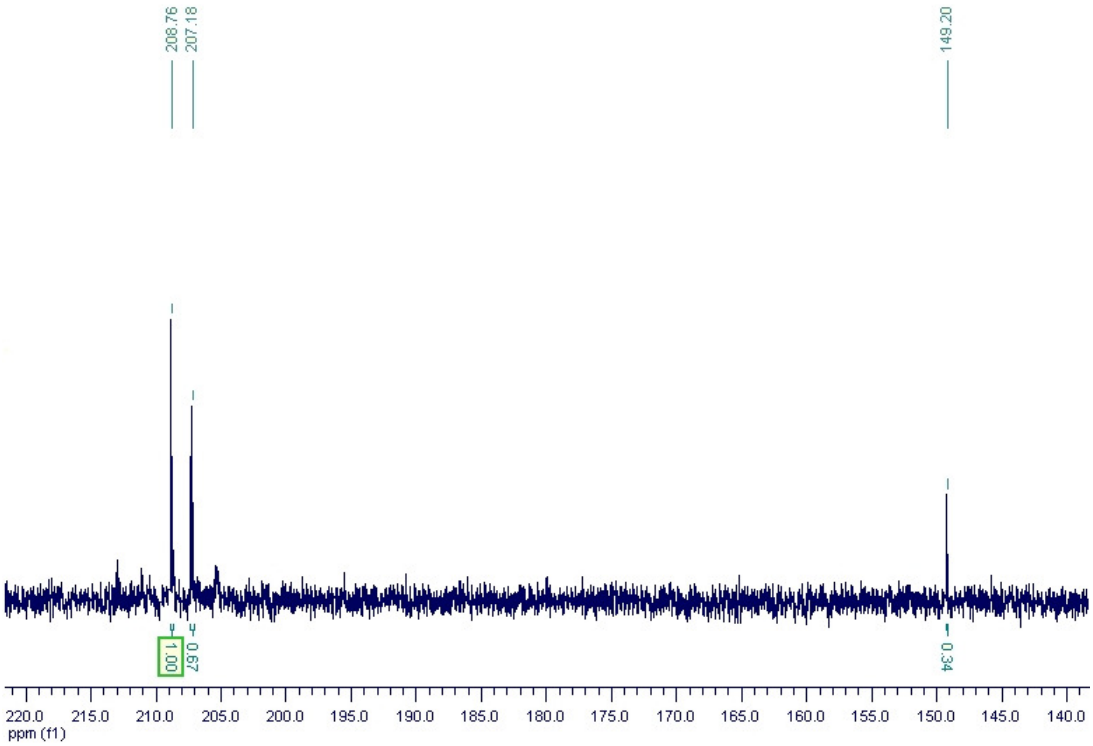

Figure S6: Relevant region of the ^{31}P-{^{1}H}-NMR-spectrum of *ent*-8a in d_8-toluene after 1.5 h irradiation under hydrogen pressure; the proton decoupling pulse was applied in the hydride region (O2P= -12.67 ppm). The resonance at δ = 149.2 ppm corresponds to the free *MonoPhos*™-ligand, δ = 208.8 and 207.2 ppm to diastereomeric hydrides. The broad signal at 205.0 ppm is attributed to hydrides containing two P-ligands undergoing rapid exchange at room temperature, either di-*MonoPhos*™-hydrides or dimers thereof.