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# Supporting Information

# A New Anthraquinoid Ligand for the Iron-catalyzed Hydrosilylation of Carbonyl Compounds at Room Temperature: New Insights and Kinetics.

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#### 1. General procedures of laboratory

All experiments were performed under an inert atmosphere of N<sub>2</sub> using standard Schlenk techniques or a glovebox. Deuterated solvents were degassed and dried over activated molecular sieves prior to use. DMSO was dried by distillation from anhydrous CaH<sub>2</sub> and then stored over activated 4Å molecular sieves. 2-(2-aminoethyl)pyridine was distilled from KOH under reduced pressure before use. 1-Chloroanthraquinone was purchased from Aldrich and used as received. THF and hexane were dried and degassed in a Solvent Purification System. Fe(HMDS)<sub>2</sub> was synthesized by a method previously described in literature.<sup>1</sup> LiHMDS and FeCl<sub>2</sub> were purchased from ABCR and used as received. All hydrosilanes employed in the catalytic runs were purchased from Acros and used without further purification. All ketones and aldehydes used for catalysis were purified and dried by standard methodologies prior to use. Triethylamine was distilled from CaH<sub>2</sub>, degassed and stored over activated 4Å molecular sieves. NMR spectra were measured in a Bruker Avance III HD 500 spectrometer. IR spectra were recorded in a FT-IR Bruker Alpha spectrometer. Elemental analyses (EA) were performed on a Elementar vario EL cube in the CHN mode.

Mass spectra were acquired using a mass spectrometer Orbitrap Thermo Fisher Scientific (ExactiveTM, Thermo Fisher Scientific, Bremen, Germany) using an electrospray interface (ESI) (HESI-II, Thermo Fisher Scientific, San Jose, CA, USA). The ESI parameters for the spectrometric detection, were as follows: spray voltage, 4 kV; sheath gas (N2, >95%), 35 (adimensional); auxiliary gas (N2, >95%), 10 (adimensional); skimmer voltage, 18 V; capillary voltage, 35 V; tube lens voltage, 95 V; heater temperature, 305 °C; capillary temperature, 300 °C. The mass spectra were acquired employing two alternating acquisition functions: (1) full MS, ESI+, without fragmentation (the higher collisional dissociation (HCD) collision cell was switched off), mass resolving power = 25 000 full width at half maximum (FWHM); scan time = 0.25 s, (2) full MS, ESI- using the aforementioned settings, (3) all-ions fragmentation (AIF), ESI+, with fragmentation (HCD on, collision energy 30 eV), mass resolving power = 10000 FWHM; scan time = 0.10 s, and (4) AIF, ESI- using the settings explained for (3).

#### 2. Synthesis and Characterization data for ligand 2 and Iron(II) complexes

2.1. Synthesis and analytical data for ligand 2



Ligand 2 was synthesized by modification of a method previously described in the literature.<sup>2</sup> To a pre-heated solution of 1-chloroanthraquinone (2 g, 8.1 mmol) in dry DMSO (20 mL), 2-(2-aminoethyl)pyridine (2 mL, 16.7 mmol) was added and the resulting solution stirred at 150 °C for 15 minutes. The solution was then poured into cold water (200 mL) and the red precipitate was filtered out and washed with water. The pure product was obtained as a red powder after flash chromatography on silica gel using EtOAc/Hexanes (1:1) as eluent. Yield: 1.34 g (50%). Suitable crystals for X-ray diffraction were grown by layering a solution of 2 in dichloromethane with hexane. M.p. 124.8 °C. <sup>1</sup>H-NMR (500.13 MHz, CDCl<sub>3</sub>): δ (ppm) 10.89 (1H, bs, NH), 8.63 (1H, d, J = 4.2 Hz, H-21), 8.29 (1H, dd, J = 1.5 Hz, 7.5 Hz, H-8), 8.25 (1H, dd, J = 1.5 Hz, 9 Hz, H-5), 7.78 (1H, ddd, J = 1.5 Hz, 7.2 Hz, 7.5 Hz, H-7), 7.72 (1H, ddd, J = 1.8 Hz, 7.5 Hz, 7.5 Hz, H-6), 7.67 (1H, dd, J = 1.8 Hz, 7.5 Hz, H-19), 7.62 (1H, dd, J = 1.5 Hz, 7.5 Hz, H-4), 7.56 (1H, dd, m, H-3), 7.25 (2H, m, H-18, H-20), 3.82 (2H, q, J = 6.9 Hz, H-16), 3.25 (2H, t, J = 6.9 Hz, H-15). <sup>13</sup>C-NMR (150.92 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) 185.0 (CO, C9), 183.9 (CO, C10), 158.8 (C17), 151.3 (C1), 149.7 (C21), 136.3 (C19), 135.3 (C3), 135.0 (C12), 134.7 (C14), 133.9 (C7), 133.0 (C6), 132.9 (C11), 126.7 (C8), 126.7 (C5), 123.6 (C19), 121.8 (C18), 117.9 (C2), 115.8 (C4), 113.1 (C13), 42.8 (C16), 37.8 (C15). <sup>15</sup>N NMR (500.13 MHz, CDCl<sub>3</sub>, via gHMBC): δ -489.1, -315.9 ppm. IR (KBr): v (cm<sup>-1</sup>) 3272w, 3077w, 2933w, 1663s, 1626s, 1589s, 1568s, 1511s, 1474m, 1407m, 1366m, 1310m, 1268s, 1167m, 1072m, 987m, 708s.

#### 2.2. Synthesis and analytical data for complex $Fe(2)_2$



A solution of Fe(HMDS)<sub>2</sub> (34.4 mg, 0.091 mmol) in THF (12 mL) was added to a solution of 2 (60 mg, 0.183 mmol) in THF (8 mL). The resulting solution was stirred overnight at room temperature and then all the volatiles were removed under reduced pressure. The dark solid was dissolved in THF (10 mL), layered with hexane (10 mL) and kept at -20 °C for 24 hours to yield the pure product as dark blue crystals. Yield: 48.5 mg (75%). X-ray diffraction suitable crystals were grown from layering with npentane a THF solution of complex  $Fe(2)_2$  at room temperature. Complex  $Fe(2)_2$  can be alternatively synthesized using FeCl<sub>2</sub> as iron(II) precursor. Thus, a solution of LiHMDS (26.8 mg, 0.152 mmol) in THF (5 mL) was added to a solution of 2 (50 mg, 0.152) mmol) in THF (12 mL). The resulting blue solution, was poured upon a suspension of FeCl<sub>2</sub> (9.6 mg, 0.076 mmol) in THF (5 mL) with triethylamine (42 µL, 0.304 mmol) and the mixture was stirred overnight. After removing all the volatiles under vacuum, dichloromethane was added in order to dissolve  $Fe(2)_2$  and remove LiCl by filtration. Then, dichloromethane was removed under reduced pressure and the product purified as described above. Elemental analysis: calcd (%) for C42H30FeN4O4: C, 70.99; H, 4.26; N, 7.88; found: C, 70.60; H, 4.64; N, 7.42. <sup>1</sup>H-NMR (500.13 MHz, THF-d<sub>8</sub>): δ (ppm) 57.32 ( $W_{1/2}$  = 298 Hz, bs), 32.39 ( $W_{1/2}$  = 242 Hz, bs), 20.86 ( $W_{1/2}$  = 112 Hz, bs), 18.48  $(W_{1/2} = 213 \text{ Hz, bs}), 9.67 (W_{1/2} = 77 \text{ Hz, s}), -17.64 (W_{1/2} = 157 \text{ Hz, bs}), -21.20 (W_{1/2} = 157 \text{ Hz}), -21.20 (W_{1/2} = 157$ 337 Hz, bs), -43.58 ( $W_{1/2}$  = 1955 Hz, s). ESI-MS: calcd (m/z) for C<sub>42</sub>H<sub>30</sub>FeN<sub>4</sub>O<sub>4</sub><sup>+</sup>: 710.16110; found: 710.16465 [M]<sup>+</sup>. IR (THF solution): υ (cm<sup>-1</sup>) 2924w, 2854w, 1643m, 1579m, 1518m, 1486m, 1444m, 1411m, 1347m, 1307m, 1256m, 1230m, 1160w, 1092w, 1070w, 1001w, 917w, 775w, 711w.

#### 2.3. Preparation of complex [Fe(1)<sub>2</sub>·{(EtO)<sub>2</sub>MeSiH}<sub>2</sub>]



 $[Fe(1)_{2} \cdot \{(EtO)_{2}MeSiH\}_{2}]$   $C_{50}H_{54}FeN_{4}O_{8}Si_{2}$ MW = 951.00 g/mol

Complex Fe(1)<sub>2</sub> was prepared as previously reported.<sup>3</sup> Inside the glovebox, complex Fe(1)<sub>2</sub> (25 mg, 0.037 mmol) was dissolved in THF (5 mL) and then (EtO)<sub>2</sub>MeSiH (12.1  $\mu$ L, 0.073 mmol) was added and the solution stirred at room temperature for 72 hours. Then hexane (20 mL) was added to precipitate the product, which was collected by filtration. In order to follow the reaction progress by <sup>1</sup>H-NMR, Fe(1)<sub>2</sub> (10 mg, 0.015 mmol) was dissolved in THF-*d*<sub>8</sub> (0.6 mL) and put inside a NMR sample tube equipped with a J. Young valve. Then (EtO)<sub>2</sub>MeSiH (4.84  $\mu$ L, 0.030 mmol) was added and the resulting mixture was shaken periodically and monitored by <sup>1</sup>H-NMR until complete conversion was reached, after 2 days. A color shift from dark blue to brown can also be observed during the transformation of Fe(1)<sub>2</sub> into [Fe(1)<sub>2</sub>· {(EtO)<sub>2</sub>MeSiH}<sub>2</sub>]. <sup>1</sup>H-NMR (500.13 MHz, THF-*d*<sub>8</sub>):  $\delta$  (ppm) 95.00 (*W*<sub>1/2</sub> = 2553 Hz, bs), 74.44 (*W*<sub>1/2</sub> = 1115 Hz, bs), 42.61 (*W*<sub>1/2</sub> = 329 Hz, bs), 27.82 (*W*<sub>1/2</sub> = 291 Hz, bs), 25.07 (*W*<sub>1/2</sub> = 1532 Hz, bs), 19.55 (*W*<sub>1/2</sub> = 157 Hz, bs), -2.44 (*W*<sub>1/2</sub> = 617 Hz, bs), -12.78 (*W*<sub>1/2</sub> = 186 Hz, bs), -39.35 (*W*<sub>1/2</sub> = 278 Hz, bs), -56.15 (*W*<sub>1/2</sub> = 617 Hz, bs). ESI-MS: calcd (*m/z*) for C<sub>50</sub>H<sub>54</sub>FeN<sub>4</sub>O<sub>8</sub>Si<sub>2</sub><sup>+</sup>: 950.2830; found: 950.28919 [M]<sup>+</sup>.

# **3.** General procedures for catalytic hydrosilylation of carbonyl compounds experiments

## 3.1. General procedure for fixed time reactions

Inside the glovebox, compound  $Fe(2)_2$  (0.25-0.50 mol%) was dissolved in THF (2 mL) inside a small vial. The corresponding silane (0.63 mmol) was then added to the solution, followed by the carbonyl substrate (0.56 mmol), and the vial was sealed. The resulting mixture was stirred at room temperature during the times indicated in Tables 2 or 3 and then the reaction was quenched by adding HCl(aq) 1M (2 mL) and stirred for 30 minutes to ensure the complete hydrolysis of the silylether product. The mixture was then taken to ph 7 by adding NaOH(aq) 5M and the organic products extracted with ethyl acetate (3x15 mL). The organic layers were dried using anhydrous Na<sub>2</sub>SO<sub>4</sub>, filtered and concentrated by rotatory evaporation. Isolated products were obtained after column chromatography in silica gel using ethyl acetate/hexane or dichloromethane as eluent.

## **3.2. General procedure for NMR monitored reactions**

Compound Fe(2)<sub>2</sub> (0.05-0.50 mol%) was put inside a J. Young screw-capped NMR sample tube and dissolved in THF- $d_8$  (1 mL). The corresponding silane (0.63 mmol) was then added to the solution, followed by the carbonyl substrate (0.56 mmol), and the tube was sealed. The sample tube was shaken to ensure the homogeneity of the mixture and then placed inside the NMR spectrometer, where remained for the entire duration of the monitoring.

Quantitative NMR acquisition parameters: <sup>1</sup>H NMR determination of product conversion was carried out by comparing signals arising from both carbonyl substrate and product. The standard acquisition parameters were one-dimensional pulse sequence which includes a 30° flip angle (Bruker zg30), recycle time (D1 = 30 s), time domain (TD = 64k), number of scans (NS = 1), acquisition time (AQ = 2.97 s), transmitter (frequency) offset (O1P = 8.0 ppm), and spectral width (SW = 22.0 ppm).



Figure S1. <sup>1</sup>H-NMR (500.13 MHz, CDCl<sub>3</sub>) spectrum of 2.



Figure S2. Expanded <sup>1</sup>H-NMR (500.13 MHz, CDCl<sub>3</sub>) spectrum of 2.



Figure S4. <sup>13</sup>C-NMR (150.92 MHz, CDCl<sub>3</sub>) and DEPT-135 spectra of 2.



Figure S5. Expanded <sup>13</sup>C-NMR (150.92 MHz, CDCl<sub>3</sub>) and DEPT-135 spectra of 2.



Figure S6. HMQC spectrum of 2.



Figure S7. Expanded HMQC spectrum of 2.



Figure S8. HMBC spectrum of 2.



Figure S9. Expanded HMBC spectrum of 2.



**Figure S10**. <sup>1</sup>H-NMR (500.13 MHz, THF-*d*<sub>8</sub>) spectrum of Fe(**2**)<sub>2</sub>.





**Figure S12**. <sup>1</sup>H-NMR (500.13 MHz, THF-*d*<sub>8</sub>) spectra showing the transformation of  $Fe(1)_2$  into  $[Fe(1)_2 \cdot \{(EtO)_2MeSiH\}_2]$ . A: Spectrum of complex  $Fe(1)_2$ ; B:  $Fe(1)_2 + (EtO)_2MeSiH$  (1 equiv.) after 24 hours; C:  $Fe(1)_2 + (EtO)_2MeSiH$  (2 equiv.) after 24 hours; D:  $Fe(1)_2 + (EtO)_2MeSiH$  (2 equiv.) after 48 hours.



Figure S13. IR (KBr) spectrum of 2.



Figure S14. IR (THF solution) spectrum of Fe(2)<sub>2</sub>.



Figure S15. Full ESI(+)-MS spectrum of Fe(2)<sub>2</sub>.



Figure S16. Expanded ESI(+)-MS spectrum for isotopic cluster of complex  $Fe(2)_2$ . Measured spectrum at the top and simulated spectrum at the bottom.



Figure S17. Full ESI(+)-MS spectrum of  $[Fe(1)_2 \cdot \{(EtO)_2 MeSiH\}_2]$ .



Figure S18. Expanded ESI(+)-MS spectrum for isotopic cluster of complex  $[Fe(1)_2 \cdot \{(EtO)_2MeSiH\}_2]$ . Measured spectrum at the top and simulated spectrum at the bottom.

Compound	2
Chem. form.	$C_{21}H_{16}N_2O_2$
Form. weight	328.36
Cryst. system	Monoclinic
Space group	$P2_{1}/c$
<i>a</i> (Å)	10.7345(4)
<i>b</i> (Å)	7.9738(3)
<i>c</i> (Å)	18.3724(8)
α (°)	90
β (°)	96.220(2)
γ (°)	90
V (Å <sup>3</sup> )	1563.32(11)
Z	4
GOF <sup>a</sup>	1.020
R <sub>int</sub>	0.091
$R_1 b / wR^2 c [I > 2\sigma(I)]$	0.0498 / 0.1169
$R_1 b / wR^2 c$ (all data)	0.0844 / 0.1317
$[a] S = [\sum w(F_0^2 - F_c^2)^2 / (N_{obs} - N_{param})]^{1/2}$	
[b] $R_1 = \sum   F_0  -  F_c   / \sum  F_0 $	
[c] wR <sub>2</sub> = $[\sum w(F_0^2 - F_c^2)^2 / \sum wF_0^2]^{1/2}$	
w = $1/[\sigma^2(F_0^2) + (aP)^2 + bP]$ where P = $(max(F_0^2, 0) + 2Fc^2)/3$	

 Table S1. Crystallographic data and structure refinement details of 2

Bond angles for 2 (°)
N1 C1 C2 121.07(13)
N1 C1 C13 120.84(13)
C2 C1 C13 118.08(13)
C5 C6 C7 120.44(13)
O1 C9 C13 123.03(12)
O1 C9 C12 118.35(13)
C13 C9 C12 118.61(12)
O2 C10 C11 121.31(13)
O2 C10 C14 120.51(14)
C11 C10 C14 118.18(13)
C5 C11 C12 119.59(14)
C5 C11 C10 120.33(14)
C12 C11 C10 120.06(12)
C8 C12 C11 119.57(12)
C8 C12 C9 118.63(13)
C11 C12 C9 121.79(13)
C14 C13 C1 118.84(13)
C14 C13 C9 120.12(12)
C1 C13 C9 121.02(13)
C13 C14 C10 121.22(13)
N1 C15 C16 114.19(12)
C17 C16 C15 109.82(12)
N2 C17 C18 122.70(12)
N2 C17 C16 115.79(13)
C19 C20 C21 118.31(13)
N2 C21 C20 124.17(15)
C1 N1 C15 124.89(13)
C21 N2 C17 116.82(13)

 Table S2. Bond distances and angles for 2



Figure S19. X-Ray diffraction structure of 2 showing  $\pi$ -stacking arrangements.



Figure S20. Intramolecular hydrogen bond between NH and C=O (quinone) in 2.

Compound	$Fe(2)_2$	
Chem. form.	$C_{44}H_{34}FeN_4O_{4.50}$	
Form. weight	746.60	
Cryst. system	Monoclinic	
Space group	$P2_{1}/c$	
<i>a</i> (Å)	15.547(2)	
<i>b</i> (Å)	14.268(1)	
<i>c</i> (Å)	17.633(2)	
α (°)	90	
β (°)	115.42(1)	
γ (°)	90	
V (Å <sup>3</sup> )	3532.7(7)	
Z	4	
GOF a	0.854	
R <sub>int</sub>	0.155	
$R_1 b / wR^2 c [I > 2\sigma(I)]$	0.0639 / 0.1134	
$R_1 b / wR^2 c$ (all data)	0.1544 / 0.1418	
[a] S = $[\sum w(F_0^2 - F_c^2)^2 / (N_{obs} - N_{param})]^{1/2}$		
[b] $R_1 = \sum   F_0  -  F_c   / \sum  F_0 $		
[c] wR <sub>2</sub> = $[\sum w(F_0^2 - F_c^2)^2 / \sum wF_0^2]^{1/2}$		
w = $1/[\sigma^2(F_0^2) + (aP)^2 + bP]$ where P = $(max(F_0^2, 0) + 2Fc^2)/3$		

Table S3. Crystallographic data and structure refinement details of  $Fe(2)_2$ 

**Table S4.** Bond distances and angles for  $Fe(2)_2$ 

0

C17 C18 1.379(6)	C9 C10 C11 119.6(5)
C18 H18 0.9500	C12 C11 C10 121.1(5)
C18 C19 1.383(7)	C11 C12 C13 123.2(5)
C19 H19 0.9500	N1 C13 C12 122.2(4)
C19 C20 1.375(7)	N1 C13 C14 122.6(4)
C20 H20 0.9500	C12 C13 C14 115.2(4)
C20 C21 1.397(6)	C1 C14 C9 119.2(4)
C21 H21 0.9500	C1 C14 C13 121.4(4)
O3 C22 1.262(5)	C9 C14 C13 119.0(4)
O4 C29 1.236(5)	N1 C15 C16 112.8(4)
N3 C34 1.340(6)	C17 C16 C15 112.4(5)
N3 C36 1.474(6)	N2 C17 C16 116.6(4)
N4 C38 1.352(6)	N2 C17 C18 121.5(5)
N4 C42 1.350(6)	C18 C17 C16 121.9(5)
C22 C23 1.491(7)	C17 C18 C19 120.1(5)
C22 C35 1.421(7)	C20 C19 C18 119.2(5)
C23 C24 1.393(7)	C19 C20 C21 118.3(5)
C23 C28 1.410(6)	N2 C21 C20 122.4(5)
C24 H24 0.9500	C22 O3 Fe1 128.6(3)
C24 C25 1.383(8)	C34 N3 Fe1 122.8(3)
C25 H25 0.9500	C34 N3 C36 114.9(4)
C25 C26 1.389(7)	C36 N3 Fe1 119.1(3)
C26 H26 0.9500	C38 N4 Fe1 120.4(3)
C26 C27 1.380(8)	C38 N4 C42 117.9(4)
C27 H27 0.9500	C42 N4 Fe1 121.0(3)
C27 C28 1.384(8)	O3 C22 C23 116.4(4)
C28 C29 1.480(7)	O3 C22 C35 124.8(5)
C29 C30 1.475(7)	C35 C22 C23 118.7(4)
C30 C31 1.379(7)	C24 C23 C22 120.3(4)
C30 C35 1.434(6)	C24 C23 C28 118.2(5)
C31 H31 0.9500	C28 C23 C22 121.5(5)
C31 C32 1.387(7)	C25 C24 C23 121.6(5)
C32 H32 0.9500	C24 C25 C26 119.5(6)
C32 C33 1.359(7)	C27 C26 C25 119.8(6)
C33 H33 0.9500	C26 C27 C28 121.0(5)
C33 C34 1.452(7)	C23 C28 C29 118.9(5)
C34 C35 1.456(7)	C27 C28 C23 119.8(5)
C36 H36A 0.9900	C27 C28 C29 121.4(4)
C36 H36B 0.9900	O4 C29 C28 120.5(5)
C36 C37 1.531(6)	O4 C29 C30 122.1(5)
C37 H37A 0.9900	C30 C29 C28 117.2(4)
C37 H37B 0.9900	C31 C30 C29 117.2(4)
C37 C38 1.509(6)	C31 C30 C35 121.0(5)
C38 C39 1.373(7)	C35 C30 C29 121.7(4)

C39 H39 0.9500	C30 C31 C32 120.0(5)
C39 C40 1.390(7)	C33 C32 C31 121.5(5)
C40 H40 0.9500	C32 C33 C34 122.5(5)
C40 C41 1.382(7)	N3 C34 C33 122.1(5)
C41 H41 0.9500	N3 C34 C35 122.5(4)
C41 C42 1.389(7)	C33 C34 C35 115.4(4)
C42 H42 0.9500	C22 C35 C30 119.2(5)



Figure S21. Variable temperature SQUID magnetization data for  $Fe(2)_2$ . Data are corrected for underlying diamagnetism.



**Figure S22**. Initial rate as a function of concentration of pre-catalyst  $Fe(2)_2$  using  $(EtO)_2MeSiH$  as reducing agent. The concentrations assayed were 0.56 mM (0.05 mol %), 1.12 mM (0.1 mol %), 2.8 mM (0.25 mol %) and 5.6 mM (0.5 mol %).



**Figure S23**. Ln(initial rate) as a function of Ln(concentration) of catalyst using (EtO)<sub>2</sub>MeSiH as reducing agent. The concentrations assayed were 0.56 mM (0.05 mol %), 1.12 mM (0.1 mol %), 2.8 mM (0.25 mol %) and 5.6 mM (0.5 mol %).



**Figure S24**. Initial rate as a function of concentration of pre-catalyst  $Fe(2)_2$  using Ph<sub>2</sub>SiH<sub>2</sub> as reducing agent. The concentrations assayed were 0.56 mM (0.05 mol %), 1.12 mM (0.1 mol %), 2.8 mM (0.25 mol %) and 5.6 mM (0.5 mol %).



Figure S25. Ln(initial rate) as a function of Ln(concentration) of catalyst using  $Ph_2SiH_2$  as reducing agent. The concentrations assayed were 0.56 mM (0.05 mol %), 1.12 mM (0.1 mol %), 2.8 mM (0.25 mol %) and 5.6 mM (0.5 mol %).



**Figure S26.** Section of the <sup>1</sup>H, <sup>15</sup>N gHMBC 2D NMR spectrum acquired in a 500 MHz spectrometer for a 30 mM sample of ligand **2** at room temperature in CDCl<sub>3</sub>. Chemical shifts are referred to NH<sub>3</sub>. The data set were acquired with 160-F1 series and a preparation delay optimized for a 7 Hz coupling constant. The number of scans were 80. The gradient ratio was calculated according to the  $\gamma$  values and set to 70:30:50.1.



**Figure S27.** Effect of the addition of substoichiometric amounts of trimethylphosphine on the reaction rate of the transfer hydrogenation of acetophenone catalyzed by  $Fe(2)_2$ .



**Figure S28**. <sup>1</sup>H-NMR spectrum of the reaction crude (entry 1, Table 1). The singlet at 2.4 ppm (3H) corresponds to the methyl group in the unconverted acetophenone and the doublet at 1.3 ppm (3H) corresponds to the methyl group of the 1-phenylethanol product. The signals marked with asterisks correspond to ethyl acetate remaining from work-up.



**Figure S29**. <sup>1</sup>H-NMR spectrum of isolated 1-phenylethanol obtained from the reaction run given in entry 7 of Table 1.

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