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Iron-catalyzed chemoselective hydride transfer reactions.

Sébastien Coufourier,^a Daouda Ndiaye,^{a,b} Quentin Gaignard Gaillard,^a Léo Bettoni,^a Nicolas Joly,^{a,c} Mbaye Diagne Mbaye,^{a,b} Albert Poater,^c Sylvain Gaillard,^a Jean-Luc Renaud.*^a

^a Normandie Univ., LCMT, ENSICAEN, UNICAEN, CNRS, 6 boulevard du Maréchal Juin, 14050 Caen, France

^b Université Assane Seck de Ziguinchor, BP 523, Ziguinchor, Sénégal

^c Departament de Química, Institut de Química Computacional i Catàlisi (IQCC), University of Girona, c/ M^a Aurèlia Capmany 69, 17003 Girona, Catalonia, Spain

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ABSTRACT

A Diaminocyclopentadienone iron tricarbonyl complex has been applied in chemoselective hydrogen transfer reductions. This bifunctional iron complex demonstrated a broad applicability in mild conditions in various reactions, such as reduction of aldehydes over ketones, reductive alkylation of various functionalized amines with functionalized aldehydes and reduction of α,β -unsaturated ketones into the corresponding saturated ketones. A broad range of functionalized substrates has been isolated in excellent yields with this practical procedure.

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1. Introduction

Reduction reactions are a prominent process in organic synthesis, both from an academic and an industrial point of view.¹⁻⁸ Metal-catalyzed syntheses of amines and alcohols have been developed to prevent the use of stoichiometric amount of borohydrides or aluminum hydrides, and consequently to diminish the environmental impact.⁹⁻¹⁴ These procedures reside in hydrogenation and transfer hydrogenation (with *isopropanol* or formic acid) and involve platinum complexes,⁹⁻¹⁰ and more recently first-row transition metals.¹¹⁻¹⁴ Hydrogenation is the most atom economical approach, but requires hydrogen gas handling and consequently implies some safety issues. Hydrogen transfer (TH) is an alternative pathway and a more practical tool in the presence of alcohols, formic acid or formates as advantageous hydride donors.

The control of the chemoselectivity, which allows the differentiation of functional groups, is a key factor in organic synthesis and in fine chemistry. Indeed, it may shorten the syntheses as tedious protection/deprotection steps can be then avoided.¹⁵⁻¹⁶ While the discrimination between two different functions (i.e. alkene vs. carbonyl) can appear manageable, this is much more problematical when the two reactive functions belong to the same class. Catalytic chemoselective reductions of carbonyl functions over alkenes or alkynes, or alkenes over carbonyl functions have been described in literature with the presence of noble metals or earth-abundant metals.¹⁷⁻¹⁹ But the chemoselective reduction of aldehydes in the presence of ketones

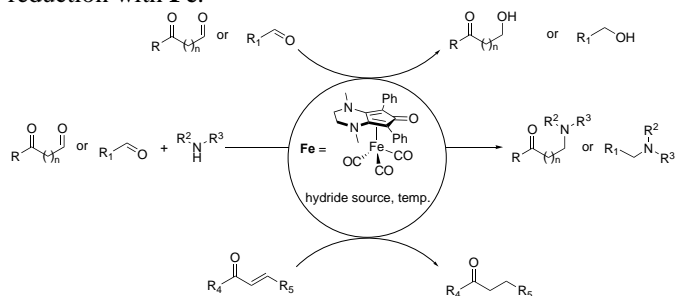
has been underexamined.^{18b, 20-24} Dupau described in 2015 a general $[\text{Ru}(\text{diamine})(\text{diphosphine})(\text{carboxylate})_2]$ complex-catalyzed hydrogenation of aldehydes in the presence of ketones.²¹ More recently, very few examples of such chemoselective reduction have been reported with a phosphine-containing iron complex,^{22a} a pincer-type ligand containing Earth-abundant metal complexes (Fe ,^{22b-d} Co ,²³ Mn ²⁴) or a triaminocyclopentadienyl ancillary ligand.²⁵ Albeit these works showed the feasibility with Earth-abundant metal complexes, the scope was rather limited to some non-functionalized aromatic carbonyl derivatives.

Iron-catalyzed transfer hydrogenation has received some attention in the last ten years as a practical method for carbonyl and imine reduction, including some enantioselective processes.^{22-23, 26-30}

Among the iron complexes, the bifunctional cyclopentadienone iron carbonyl complexes presented several advantages.²⁸ These pre-catalysts are easily synthesized, robust, and stable and have been used in several hydrogenation reactions, transfer hydrogenation, reductive aminations and alkylations.²⁸⁻³⁰ However, with the exception of the hydrogenation of α,β -unsaturated aldehydes into allylic alcohols, no chemoselective reductions has been described up to date with cyclopentadienone iron carbonyl complexes. Following our ongoing interest in hydrogenation and hydrogen autotransfer technology,³¹⁻³² we report a general chemoselective hydride transfer reduction of aldehydes over ketones, of enones into saturated ketones and a chemoselective reductive alkylation of amines with aldehydes,

catalyzed by the diaminocyclopentadienone iron carbonyl complex **Fe** (Figure 1).

Scheme 1. Layout of the chemoselective hydride transfer reduction with **Fe**.



2. Results and Discussion

First, the reduction of 4-methoxybenzaldehyde in the presence of formic acid derivatives was chosen as a model reaction to optimize the reaction conditions (Table 1). Various parameters such as the temperature, the reaction time and the hydrogen donor were scrutinized in this set of reactions (Table 1). The active species was generated in situ from the air-stable **Fe** pre-catalyst, through the addition of trimethylamine oxide (Me_3NO).³³⁻³⁴

Table 1: Optimization of the reaction conditions for aldehyde reduction.^[a]

Entry	HCO_2X	Fe (mol%)	Me_3NO (mol%)	T (°C)	Time (h)	Conv. (%) ^[b]
1	HCO_2H	2	2.5	80	24	-
2	HCO_2NH_4	2	2.5	80	24	-
3	HCO_2Na	2	2.5	80	24	100
4	HCO_2K	2	2.5	80	24	100
5	-	2	2.5	80	24	-
6	HCO_2K	-	-	80	24	-
7	$\text{HCO}_2\text{K}^{[c]}$	2	2.5	80	24	33
8	HCO_2K	2	2.5	80	16	100
9	HCO_2K	1	1.25	80	16	30
10	HCO_2K	2	2.5	60	16	100
11	HCO_2K	2	2.5	45	16	73
12	HCO_2K	2	2.5	45	24	100 (99%) ^[d]

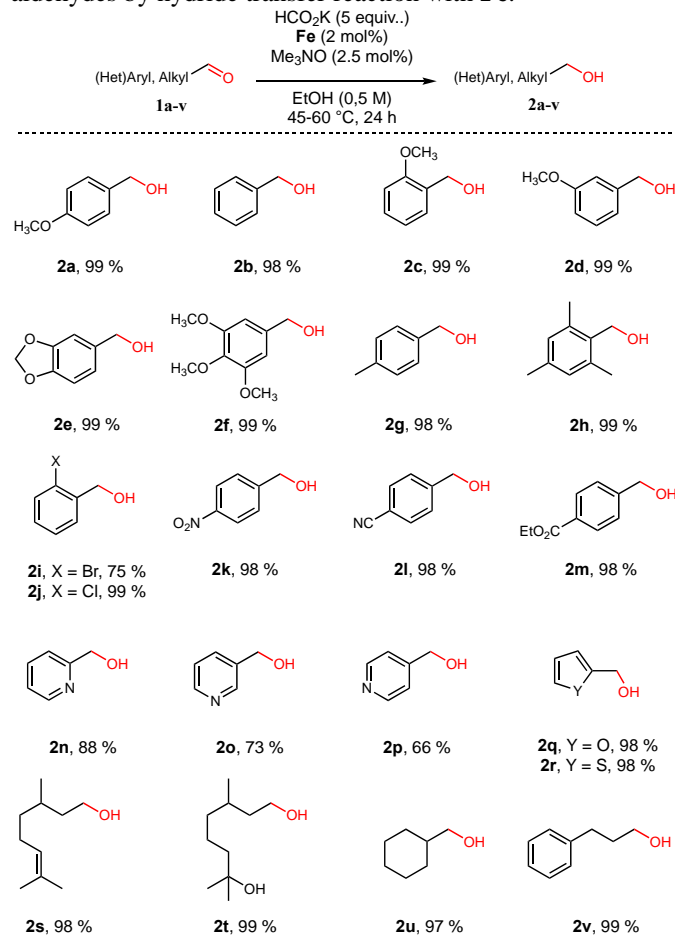
^[a] General conditions: HCO_2X (5 mmol, 5 equiv.), 4-methoxybenzaldehyde (1 mmol), pre-catalyst **Fe** (2 mol %), Me_3NO (2.5 mol %), ethanol (2 mL).^[b] Determined by $^1\text{H-NMR}$ spectroscopy. ^[c] 3 equivalents. ^[d] Isolated yield

No reaction was observed initially when formic acid or ammonium formate was used (Entries 1-2, Table 1), while sodium and potassium formate led to complete conversion within 24 h at 80 °C (Entries 3-4, Table 1). For solubility issues in ethanol, potassium formate was used for this study. Whereas alcohols can be a source of hydrogen in basic conditions in the presence of diaminocyclopentadienone iron tricarbonyl complexes,^{19d} ethanol did not act as hydride donor in these

conditions as no reduction was observed without formate (Entry 5, Table 1). In the absence of iron complex, no reduction occurred as well (Entry 6, Table 1). Decreasing the amount of formate (from 5 to 3 equivalents) or the catalyst loading led to lower conversions (entries 7 and 9, Table 1). Shortening the reaction time from 24 to 16 h did not impede the activity and the alcohol was isolated in full conversion (entries 4 and 8, table 1). Finally, the optimized conditions were the following ones: 1 mmol of aldehyde in the presence of 5 equivalents of potassium formate, 2 mol % of iron complex **Fe**, 2.5 mol % of Me_3NO in 2 mL of ethanol at 45-60 °C. In these conditions, the 4-methoxybenzyl alcohol was isolated in 99 % yield.

These conditions were applied to explore the scope of the hydrogen transfer reduction of aromatic and aliphatic aldehydes **1** (Scheme 2). A variety of substituted benzaldehydes **1a-m** were initially introduced in this reduction. The corresponding alcohols **2a-m** were prepared in excellent yields (75-99 %, Scheme 2). Other reducible functions such as nitro group, esters, nitrile, remained untouched (compounds **2k-m**). Halides were not reduced as well (**2i-j**) and no hydrogenolysis of ethers was noticed (**2a, 2c-f**). Heteroaromatic aldehydes, such as pyridine carboxaldehydes **1n-p**, thiophene carboxaldehyde **1r** or furfural **1p**, can be also used. The corresponding alcohols **2n-r** have been synthesized in 66-98 % yield (Scheme 2). The lower yields with the pyridine derivatives **2n-p** might be due to a possible coordination of the pyridine to the 16-electron deficient iron centre.³⁵ Extension to the reduction of aliphatic aldehydes **1s-v** was also explored and the corresponding alcohols **2s-v** were obtained in excellent yields (97-99 %, Scheme 2).

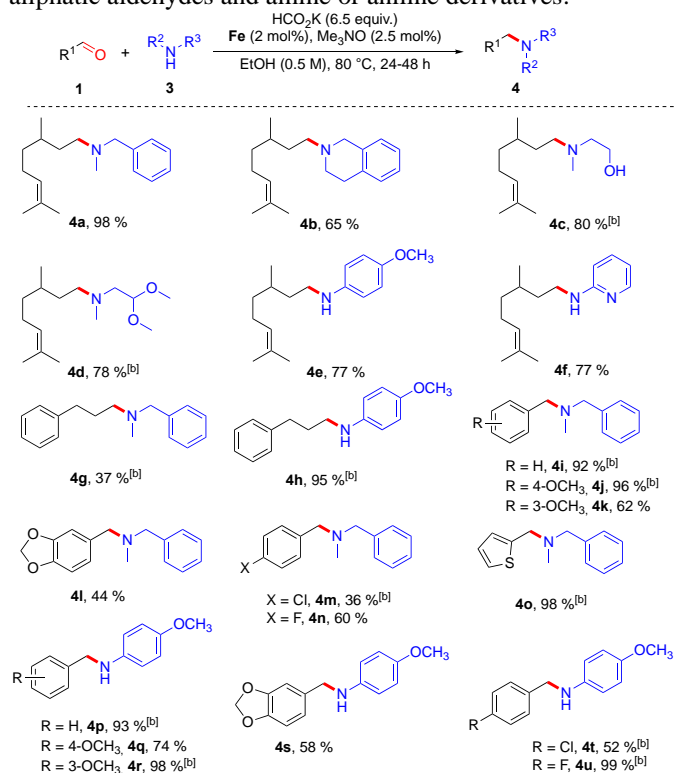
Scheme 2. Reduction of (hetero)aromatic and aliphatic aldehydes by hydride transfer reaction with **Fe**.^[a]



^[a] General conditions: HCO₂K (5 mmol, 5 equiv.), aldehyde **1** (1 mmol), pre-catalyst **Fe** (2 mol %), Me₃NO (2.5 mol %), ethanol (2 mL) at 45 °C for 24 h. ^[b] 60 °C.

Having established a simple protocol for the reduction of aldehydes, we thought to extend this work to the synthesis of substituted amines. We have already demonstrated that cyclopentadienone iron complexes were able to catalyze the reductive alkylation of amines with aldehydes and ketones under hydrogen pressure.³² After a rapid optimization of the reaction conditions, we found that **Fe** catalyzed the reductive alkylation of *N*-methyl benzylamine **3a** with citronellal **1s** in the presence of 6.5 equivalents of potassium formate at 80 °C (Table S2 in ESI). The alkylated amine **4a** was obtained in 98 % yield (Scheme 3 and Table S2). Both aromatic and aliphatic amines **3b-f** can be engaged in this reaction without impeding the catalytic activities. Thus, tetrahydroisoquinoline **3b**, functionalized *N*-methyl amines **3c-d**, anisidine **3e** and even the 2-aminopyridine **3f** were engaged with citronellal **1s** and the corresponding alkylated amines **4b-f** were isolated in 65 to 80 % yields (Scheme 3). To showcase the efficiency of this catalytic system, *N*-methylethanolamine **3c** and *N*-(methyl)amino acetaldehyde dimethyl acetal **3d** were alkylated with citronellal **1s** leading to **4c** and **4d** in 80 and 78 % yields, respectively (Scheme 3). The synthesis of amine **4f** in 77 % is quite remarkable as 2-aminopyridine **3f** is not often used in reductive amination. Other benzaldehydes **1a-b, d, r, w-x** (the last two having halide atoms in para position) or aliphatic aldehyde, such as 3-phenylpropanal **1v**, could be used with benzylamine **3a** or aniline **3e**. The corresponding alkylated amines **4g-u** have been prepared in 37 to 98 % yield (Scheme 3). Ether function on **4h** and **4p-u**, halide substituent on **4m-n** and **4t-u** were tolerated as well as heteroaromatic ring (**4o**) and *N*-benzyl anisidine derivatives **4p-u** were isolated in 52-98 % (Scheme 3).

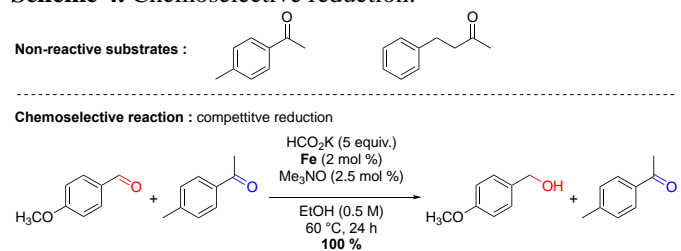
Scheme 3. Reductive amination between aromatic and aliphatic aldehydes and amine or aniline derivatives.^[a]



^[a] General conditions: HCO₂X (6.5 mmol, 6.5 equiv.), aldehyde **1** (1 mmol), amine **3** (2 mmol), pre-catalyst **Fe** (2 mol %), Me₃NO (2.5 mol %), ethanol (2 mL), 80 °C, 24 h. ^[b] 48 h.

In the same reaction conditions, no reduction or no reductive amination of aliphatic or aromatic ketones was noticed. In a competition reaction, when 4-methoxybenzaldehyde **1a** and 4-methyl acetophenone were engaged in reduction, 4-methoxybenzyl alcohol **2a** was isolated in full conversion and 97 % yield, when the ketone remained non-reactive (Scheme 4).

Scheme 4. Chemoselective reduction.

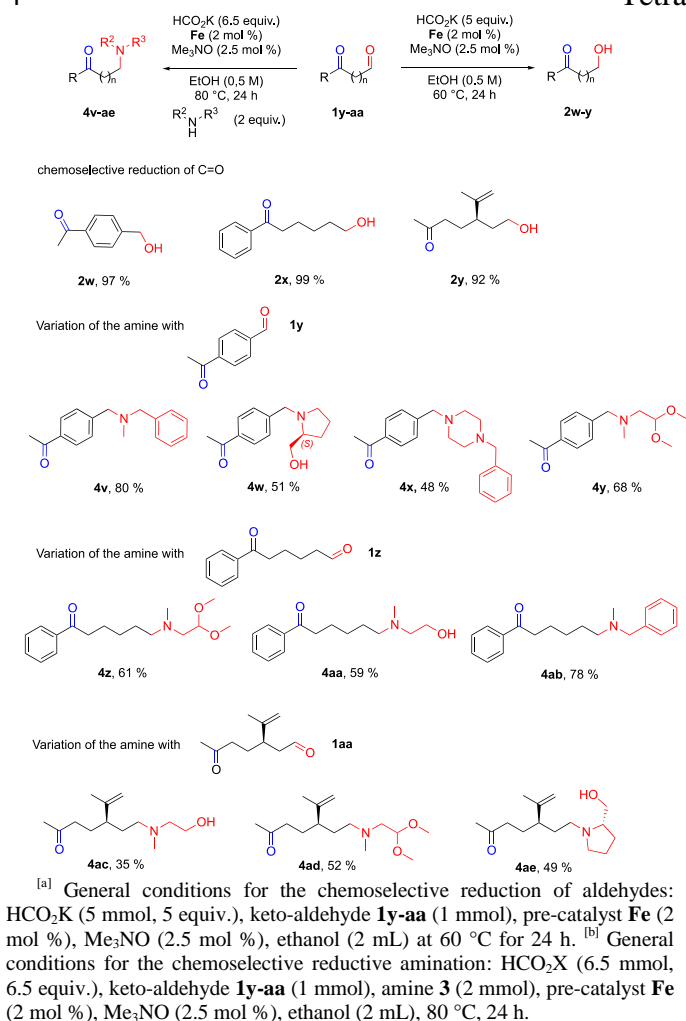


^[a] General conditions: HCO₂K (5 mmol, 5 equiv.), aldehyde **1a** (1 mmol), 4-methylacetophenone (1 mmol), pre-catalyst **Fe** (2 mol %), Me₃NO (2.5 mol %), ethanol (2 mL) at 60 °C for 24 h.

As the development of chemoselective reaction is crucial in organic chemistry and because complete selectivity for aldehydes toward ketones is still not fully explored,²⁵ we undertook some hydrogenation and reductive amination of ketoaldehydes (Scheme 5). As reported in scheme 5, for this study, three keto-aldehydes **1y-aa**, being representative of the different classes of carbonyl compounds, were introduced in reduction and reductive alkylation of amines. The iron-catalyzed reduction of keto-aldehydes **1y-aa** at 60 °C in the presence of potassium formate provided exclusively the keto-alcohols **2w-y** in excellent yields (92-99 %). Whatever the aromatic or aliphatic carbonyl function, the aldehyde was chemoselectively reduced.

To emphasize the benefit of the chemoselective hydrogen transfer methodology, we turned our attention to the reductive alkylation of amines with keto-aldehydes **1y-aa**. Quite surprisingly, no report to date has appeared on the catalytic chemoselective reductive amination with aldehydes under hydrogen transfer conditions, while amines are important compounds in organic chemistry, chemical industry and biological processes, as well. Remarkably, the same trend was observed in the reductive alkylation with amines. The functionalized amino-ketones **4v-ae** were synthesized in 35-80% yield from keto-aldehydes **1y-aa**. Neither reduction nor reductive amination of the ketone was detected by ¹H-NMR analysis of the crude mixture. With 4-acetylbenzaldehyde **1y**, alkylated amines **4v-y** were obtained in 48-80% yield (Scheme 5). Non protected alcohol, acetal and benzyl function were tolerated. The same conclusions could be drawn starting with 6-oxo-6-phenyl-hexanal **1z** and the corresponding amines **4z-ab** were produced in 59-78% yield (Scheme 5). With the more challenging 3(*R*)-(propen-2'-yl)-6-oxo-heptanal **1aa**, containing two aliphatic carbonyl function, highly functionalized aminoketones **4ac-ae** were synthesized in mild conditions in modest yields but with a complete control of the chemoselectivity. The sole other products were the remaining starting materials (Scheme 5).

Scheme 5. Fe-Catalyzed chemoselective reduction and reductive alkylation of amines.

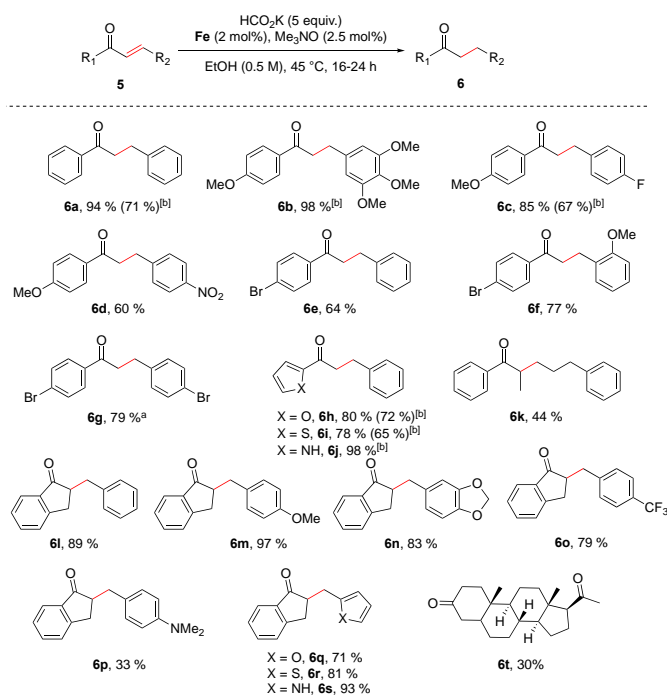


Chemoselective hydrogenation of unsaturated carbonyl functions, leading either to allylic alcohols or saturated ketones, has been already reported with noble metal-based complexes.¹⁷ Recently, some Earth-abundant metal complexes have been described to reduce selectively α,β -unsaturated aldehydes into allylic alcohols,¹⁸ and enones into the corresponding saturated ketones.¹⁹ In iron chemistry, the first chemoselective reduction of α,β -unsaturated ketones into the corresponding saturated ones was reported by Bianchini with the iron hydride complex [P₄FeH(H₂)]BPh₄ (with P₄ = P(CH₂CH₂PPh₃)₃) in cyclopentanol as hydrogen donor.³⁶ More recently, Bhanage used a combination of FeSO₄ and ethylenediaminetetraacetic acid disodium dihydrate (EDTANa₂·2H₂O) in water at 100 °C under 27.5 bar of hydrogen.³⁷ As the discrimination of various carbonyl functions was feasible with the iron complex **Fe**, we thought to widen this work to the chemoselective reduction of α,β -unsaturated carbonyl derivatives.

Substituted chalcone derivatives were first evaluated. Worth to note is the unselective hydrogenation process with **5a**. A mixture of saturated ketone, allylic alcohol and saturated alcohol was observed in a ratio depending on the reaction conditions (hydrogen pressure and temperature). In sharp contrast, the alkene was selectively reduced under transfer hydrogenation in basic conditions (Scheme 6). Both electron-donating and electron-withdrawing substituents on the aromatic rings were tolerated and the corresponding ketones **6a-g** were produced in 60-98 % yield. To illustrate the interest of the chemoselective transfer hydrogenation, **6b**, bearing methoxy groups, was synthesized in 98 % yields when **6d** having a nitro group was

isolated in 60 % yield. No reduction of Csp²-Br bond was noticed in these conditions. Heteroaromatic chalcone type compounds, such as 2-thiophenyl **5i** and 2-furfuryl ketones **5h**, furnished the saturated ketones **6h-i** in 78-80 %. The unprotected pyrrole compound **6j** was prepared in an excellent 98 % yield. To emphasize the versatility of this methodology and to demonstrate its interest in synthesis, the scope was broadened to trisubstituted unsaturated ketones **5k-t**. Again, whatever the nature of the substituent on the aromatic ring, the presence of heterocyclic moiety, the ketones **6k-t** were obtained in 30-97 % yield. The reduction of progesterone **5t** provided not only chemoselectively but also diastereoselectively **6t** in 30 % yield. The sole other product was the remaining starting material.

Scheme 6. Chemoselective C=C bond reduction of α,β -unsaturated ketones.



[^a] General conditions: HCO₂K (5 mmol, 5 equiv.), enone **5** (1 mmol), pre-catalyst **Fe** (2 mol %), Me₃NO (2.5 mol %), ethanol (2 mL) at 45 °C for 24 h. [^b] 16 h.

3. Conclusion

We have described a general and easy-to-perform catalytic system for the chemoselective reduction of aldehydes and α,β -unsaturated ketones, and a chemoselective reductive alkylation of amines. These results highlighted the versatility of the bifunctional phosphine-free iron complex. The combination of diaminocyclopentadienone iron tricarbonyl complex (2 mol %) and potassium formate allowed the reduction of a variety of aliphatic and aromatic aldehydes (over ketones), of enones into ketones and the reductive amination of aldehydes (over ketones) with functionalized amines. This procedure is, up to date, one of the most general technology for a chemoselective hydrogen transfer methodology with an earth abundant metal-based complex.

4. Experimental section

General Considerations: All reactions were carried out using the Schlenk technics under an atmosphere of dry Argon. Water was degassed prior to use by bubbling argon gas directly in the solvent. Other solvents were purchased from Carlo Erba and degassed prior to use by freeze-pump thaw procedure (3 times).

NMR spectra were recorded on a 400 MHz and 500 MHz Bruker spectrometer. Proton (^1H) NMR information is given in the following format: multiplicity: s, singlet; d, doublet; t, triplet; q, quartet; quint, quintuplet; sept, septet; m, multiplet), coupling constant(s) (J) in Hertz (Hz), number of protons. The prefix *app* is occasionally applied when the true signal multiplicity was unresolved and *br* indicates the signal in question broadened. Carbon NMR spectra are reported in ppm (δ) relative to CDCl_3 (δ 77.16) unless noted otherwise. HRMS analyses were performed by LCMT analytical services. Neutral activated aluminium oxide was purchased from Alfa Aesar (Brockmann Grade I, 58 Angstroms, -60 Mesh Powder, S.A. 150 m^2/g) and from Merck (Grade I, 90 Angstroms, 70-230 Mesh ASTM). Basic aluminium oxide was purchased from Alfa Aesar (Brockmann Grade I, 58 Angstroms, -60 Mesh Powder, S.A. 150 m^2/g). NMR solvents were filtered through a pad of basic alumina for NMR analysis of iron complexes.

4.1. 6-oxo-6-phenylhexanal (**1z**)²⁵

In a 100 mL roundbottom flask equipped with a stirring bar, 2-phenylcyclohexene (3.18 mL, 20 mmol) was solubilized in dry methylene chloride (50 mL) and cooled down to 0 °C with an ice bath. mCPBA (50% wt) (7.6 g, 22 mmol) was added slowly by portion over 10 min. The reaction was stirred for 1 h at 0 °C and then quenched by a saturated aqueous solution of NaHCO_3 (20 mL). The organic phase was separated and the aqueous phase was extracted twice with dichloromethane (2 \times 20 mL). The organic phases were combined, dried over MgSO_4 , filtered, and concentrated under vacuum. The crude product was purified by flash column chromatography on silica (pentane/Et₂O 95:5), and the pure epoxide intermediate was then directly engaged in the next step. The epoxide intermediate was solubilized in a 1/1 mixture of THF/H₂O (30 mL). Sodium periodate (30 mmol, 1.5 equiv, 6.41 g) was added, and the reaction was stirred at room temperature for 18 h. The mixture was extracted with dichloromethane (3 \times 20 mL), and the organic layers were dried over Na_2SO_4 , filtered, and concentrated under vacuum. The crude product was purified by flash column chromatography on silica (eluent: pentane/Et₂O [8:2]) and the pure ketoaldehyde **1z** was obtained as a white solid (1.81 g, 48%). ^1H NMR (500 MHz, CDCl_3) δ : 9.78 (1H, s), 7.94 (2H, d, J = 7.5 Hz), 7.56 (1H, t, J = 6.7 Hz), 7.46 (2H, t, J = 7.4 Hz), 3.00 (2H, t, J = 6.8 Hz), 2.51 (1H, t, J = 6.7 Hz), 2.42 (1H, t, J = 7 Hz), 1.81-1.72 (1H, m) ppm. ^{13}C NMR (125 MHz, CDCl_3) δ : 199.9, 179.2, 136.9, 133.1, 128.6 (2C), 128.1 (2C), 38.1, 33.8, 24.3, 23.6 ppm.

4.2. (R)-6-oxo-3-(prop-1-en-2-yl)heptanal (**1aa**)²⁵

To a round-bottom flask was added a magnetic stir-bar, sodium periodate (1.00 g, 4.7 mmol) and water (3 mL). The mixture was stirred for 10 minutes, then THF (6 mL) and (-)-limonene oxide (357 mg, 2.3 mmol) were added and stirred overnight. Upon reaction completion, the iodate salts were filtered off and washed with Et₂O creating two distinct layers. The aqueous layer was extracted (x3) with Et₂O. The combined organic extracts were washed with water and brine, dried over MgSO_4 , filtered, and concentrated *in vacuo*. Ketoaldehyde **1aa** was obtained as a colorless liquid (275 mg, 70 %) after purification by flash column chromatography on silica (eluent: pentane/Et₂O [7:3] to [1:1]). ^1H NMR (500 MHz, CDCl_3) δ : 9.67 (1H, t, J = 2.3 Hz), 4.84-4.82 (1H, m), 4.78-4.76 (1H, m), 2.71-2.65 (1H, m), 2.45 (2H, ddd, J = 8.8, 7.5, 2.3 Hz), 2.39 (2H, t, J = 7.5 Hz), 2.13 (3H, s), 1.76-1.69 (1H, m), 1.66-1.56 (4H, m) ppm. ^{13}C NMR (125 MHz, CDCl_3) δ : 208.3, 201.9, 145.1, 113.4, 47.5, 40.9, 40.8, 30.1, 26.4, 18.4 ppm.

General procedure A for chemoselective reduction of aldehydes or C=C bond by hydrogen transfer reaction. In a

dried flamed Schlenk tube under argon, aldehyde or enone (1 equiv.) and potassium formate (5 equiv.) were added in ethanol (0.5 M) followed by the addition of the iron complex **Fe** (2 mol%) and trimethylamine *N*-oxide (2.5 mol%). The mixture was heated at 45-60 °C for 24 h. After cooling-down to room temperature, the reaction mixture was hydrolyzed with a saturated aqueous solution of sodium bicarbonate and extracted three times with ethyl acetate. The organic phase was dried over MgSO_4 , filtrated and the solvent evaporated *in vacuo* to give the crude product, which was purified by flash chromatography.

4.3. (4-methoxyphenyl)methanol (**2a**)³⁸

Following the general procedure A, starting from 4'-methoxybenzaldehyde (61 μL , 0.5 mmol), potassium formate (170 mg, 2.5 mmol), **Fe** (5 mg, 0.01 mmol) and Me_3NO (1 mg, 0.0126 mmol) at 45 °C, alcohol **2a** was obtained as a colorless oil (68 mg, 99 %) after purification by flash column chromatography on silica (eluent: pentane/AcOEt [8:2]). ^1H NMR (500 MHz, CDCl_3) δ : 7.30 (2H, d, J = 8.3 Hz), 6.90 (2H, d, J = 8.3 Hz), 4.62 (2H, s), 3.81 (3H, s) (OH signal not observed) ppm. ^{13}C NMR (125 MHz, CDCl_3) δ : 159.2, 133.1, 128.7, 114.0, 65.1, 55.3 ppm.

4.4. Benzyl alcohol (**2b**)³⁸

Following the general procedure A, starting from benzaldehyde (51 μL , 0.5 mmol), potassium formate (210 mg, 2.5 mmol), **Fe** (5 mg, 0.01 mmol) and Me_3NO (1 mg, 0.0126 mmol) at 45 °C, alcohol **2b** was obtained as a colorless oil (53 mg, 98 %) after purification by flash column chromatography on silica (eluent: pentane/AcOEt [8:2]). ^1H NMR (500 MHz, CDCl_3) δ : 7.37 (4H, d, J = 4.4 Hz), 7.33-7.29 (1H, m), 4.70 (2H, s), 1.70 (1H, s) ppm. ^{13}C NMR (125 MHz, CDCl_3) δ : 140.9, 128.6, 127.7, 127.0, 65.4 ppm.

4.5. (2-methoxyphenyl)methanol (**2c**)³⁸

Following the general procedure A, starting from 2-methoxybenzaldehyde (68 mg, 0.5 mmol), potassium formate (210 mg, 2.5 mmol), **Fe** (5 mg, 0.01 mmol) and Me_3NO (1 mg, 0.0126 mmol) at 45 °C, alcohol **2c** was obtained as a colorless oil (68 mg, 99 %) after purification by flash column chromatography on silica (eluent: pentane/AcOEt [9:1] then [7:3]). ^1H NMR (500 MHz, CDCl_3) δ : 7.30-7.26 (2H, m), 6.95 (1H, t, J = 7.4 Hz), 6.90 (1H, d, J = 8.0 Hz), 4.69 (2H, d, J = 5.0 Hz), 3.88 (3H, s), 2.30 (1H, s) ppm. ^{13}C NMR (125 MHz, CDCl_3) δ : 157.5, 129.0, 128.8, 120.7, 110.2, 62.3, 55.3 ppm.

4.6. (3-methoxyphenyl)methanol (**2d**)³⁸

Following the general procedure A, starting from 3-methoxybenzaldehyde (61 μL , 0.5 mmol), potassium formate (210 mg, 2.5 mmol), **Fe** (5 mg, 0.01 mmol) and Me_3NO (1 mg, 0.0126 mmol) at 60 °C, alcohol **2d** was obtained as a colorless liquid (68 mg, 99 %) after purification by flash column chromatography on silica (eluent: pentane/AcOEt [9:1]). ^1H NMR (500 MHz, CDCl_3) δ : 7.29 (1H, t, J = 7.9 Hz), 6.94 (2H, d, J = 7.2 Hz), 6.84 (1H, d, J = 8.3 Hz), 4.68 (2H, s), 3.82 (3H, s), 1.66 (1H, s) ppm. ^{13}C NMR (125 MHz, CDCl_3) δ : 159.9, 142.5, 129.6, 119.1, 113.3, 112.3, 65.3, 55.3 ppm.

4.7. Piperonyl alcohol (**2e**)³⁸

Following the general procedure A, starting from piperonal (75 mg, 0.5 mmol), potassium formate (210 mg, 2.5 mmol), **Fe** (5 mg, 0.01 mmol) and Me_3NO (1 mg, 0.0126 mmol) at 45 °C, alcohol **2e** was obtained as a white solid (75 mg, 99 %) after purification by flash column chromatography on silica (eluent:

pentane/AcOEt [8:2]). ¹H NMR (500 MHz, CDCl₃) δ: 6.88 (1H, s), 6.80 (2H, q, *J* = 7.9 Hz), 5.96 (2H, s), 4.59 (2H, s) (OH signal not observed) ppm. ¹³C NMR (125 MHz, CDCl₃) δ: 147.9, 147.1, 134.9, 120.5, 108.2, 107.9, 101.0, 65.3 ppm.

4.8. (3,4,5-trimethoxyphenyl)methanol (**2f**)³⁸

Following the general procedure A, starting from (3,4,5-trimethoxy)benzaldehyde (98 mg, 0.5 mmol), potassium formate (210 mg, 2.5 mmol), **Fe** (5 mg, 0.01 mmol) and Me₃NO (1 mg, 0.0126 mmol) at 45 °C, alcohol **2f** was obtained as a thick colorless oil (98 mg, 99 %) purification by flash column chromatography on silica (eluent: pentane/AcOEt [8:2]). ¹H NMR (500 MHz, CDCl₃) δ: 6.60 (2H, s), 4.64 (2H, s), 3.87 (6H, s), 3.84 (3H, s), 1.72 (1H, s) ppm. ¹³C NMR (125 MHz, CDCl₃) δ: 153.4, 137.3, 136.6, 103.8, 65.6, 60.9, 56.1 ppm.

4.9. *p*-tolylmethanol (**2g**)³⁸

Following the general procedure A, starting from 4-methylbenzaldehyde (59 μL, 0.5 mmol), potassium formate (210 mg, 2.5 mmol), **Fe** (5 mg, 0.01 mmol) and Me₃NO (1 mg, 0.0126 mmol) at 60 °C, alcohol **2g** was obtained as a white solid (60 mg, 98 %) purification by flash column chromatography on silica (eluent: pentane/AcOEt [8:2]). ¹H NMR (500 MHz, CDCl₃) δ: 7.19 (2H, d, *J* = 7.6 Hz), 7.10 (2H, d, *J* = 7.6 Hz), 4.58 (2H, s), 2.28 (3H, s) (OH signal not observed) ppm. ¹³C NMR (125 MHz, CDCl₃) δ: 137.9, 137.4, 129.3, 127.1, 65.3, 21.2 ppm.

4.10. (2,4,6-trimethylphenyl)methanol (**2h**)³⁸

Following the general procedure A, starting from (2,4,6-trimethyl)benzaldehyde (74 μL, 0.5 mmol), potassium formate (210 mg, 2.5 mmol), **Fe** (5 mg, 0.01 mmol) and Me₃NO (1 mg, 0.0126 mmol) at 60 °C, alcohol **2h** was obtained as a white solid (74 mg, 99 %) purification by flash column chromatography on silica (eluent: pentane/AcOEt [8:2]). ¹H NMR (500 MHz, CDCl₃) δ: 6.87 (2H, s), 4.71 (2H, s), 2.40 (6H, s), 2.27 (3H, s), 1.18 (1H, s) ppm. ¹³C NMR (125 MHz, CDCl₃) δ: 137.8, 137.3, 133.7, 129.2, 59.2, 21.0, 19.4 ppm.

4.11. (2-bromophenyl)methanol (**2i**)³⁸

Following the general procedure A, starting from 2-bromobenzaldehyde (58 μL, 0.5 mmol), potassium formate (170 mg, 2.5 mmol), **Fe** (5 mg, 0.01 mmol) and Me₃NO (1 mg, 0.0126 mmol) at 60 °C, alcohol **2i** was obtained as a white powder (70 mg, 75 %) after purification by flash column chromatography on silica (eluent: pentane/AcOEt [7:3]). ¹H NMR (500 MHz, CDCl₃) δ: 7.55 (1H, d, *J* = 7.6 Hz), 7.48 (1H, d, *J* = 7.6 Hz), 7.34 (1H, t, *J* = 7.6 Hz), 7.17 (1H, t, *J* = 7.6 Hz), 4.76 (2H, d, *J* = 5.8 Hz), 1.97 (1H, t, *J* = 5.8 Hz) ppm. ¹³C NMR (125 MHz, CDCl₃) δ: 139.7, 132.6, 129.2, 128.9, 127.7, 122.6, 65.1 ppm.

4.12. (2-chlorophenyl)methanol (**2j**)³⁸

Following the general procedure A, starting from 2-chlorobenzaldehyde (56 μL, 0.5 mmol), potassium formate (210 mg, 2.5 mmol), **Fe** (5 mg, 0.01 mmol) and Me₃NO (1 mg, 0.0126 mmol) at 60 °C, alcohol **2j** was obtained as a white powder (93 mg, 99 %) after purification by flash column chromatography on silica (eluent: pentane/AcOEt [7:3]). ¹H NMR (500 MHz, CDCl₃) δ: 7.48 (1H, d, *J* = 7.4 Hz), 7.37 (1H, d, *J* = 7.4 Hz), 7.29 (1H, t, *J* = 7.4 Hz), 7.24 (1H, t, *J* = 7.4 Hz), 4.79 (2H, d, *J* = 6.2 Hz), 1.93 (1H, t, *J* = 6.2 Hz) ppm. ¹³C NMR (125 MHz, CDCl₃) δ: 138.2, 132.8, 129.4, 128.9, 128.8, 127.1, 62.9 ppm.

4.13. (4-nitrophenyl)methanol (**2k**)³⁸

Following the general procedure A, starting from 4-nitrobenzaldehyde (75 mg, 0.5 mmol), potassium formate (210 mg, 2.5 mmol), **Fe** (5 mg, 0.01 mmol) and Me₃NO (1 mg, 0.0126 mmol) at 45 °C, alcohol **2k** was obtained as a yellow powder (75 mg, 98 %) after purification by flash column chromatography on silica (eluent: pentane/AcOEt [7:3]). ¹H NMR (500 MHz, CDCl₃) δ: 8.22 (2H, d, *J* = 8.4 Hz), 7.54 (2H, d, *J* = 8.4 Hz), 4.84 (2H, d, *J* = 5.6 Hz), 1.91 (1H, t, *J* = 5.6 Hz) ppm. ¹³C NMR (125 MHz, CDCl₃) δ: 148.1, 147.3, 127.0, 123.8, 64.1 ppm.

4.14. (4-cyanophenyl)methanol (**2l**)³⁸

Following the general procedure A, starting from 4-cyanobenzaldehyde (65 mg, 0.5 mmol), potassium formate (210 mg, 2.5 mmol), **Fe** (5 mg, 0.01 mmol) and Me₃NO (1 mg, 0.0126 mmol) at 45 °C, alcohol **2l** was obtained as a white powder (65 mg, 98 %) after purification by flash column chromatography on silica (eluent: pentane/AcOEt [7:3]). ¹H NMR (500 MHz, CDCl₃) δ: 7.65 (2H, d, *J* = 8.0 Hz), 7.48 (2H, d, *J* = 8.0 Hz), 4.79 (2H, d, *J* = 3.3 Hz), 1.94 (1H, s) ppm. ¹³C NMR (125 MHz, CDCl₃) δ: 146.1, 132.4, 127.0, 118.9, 111.2, 64.3 ppm.

4.15. ethyl 4-(hydroxymethyl)benzoate (**2m**)³⁸

Following the general procedure A, starting from methyl 4-formylbenzoate (82 mg, 0.5 mmol), potassium formate (210 mg, 2.5 mmol), **Fe** (5 mg, 0.01 mmol) and Me₃NO (1 mg, 0.0126 mmol) at 60 °C, alcohol **1m** was obtained as a colorless oil (88 mg, 98 %) after purification by flash column chromatography on silica (eluent: pentane/Et₂O [1:1]). ¹H NMR (500 MHz, CDCl₃) δ: 8.04 (2H, d, *J* = 8.3 Hz), 7.43 (1H, d, *J* = 8.3 Hz), 4.78 (2H, d, *J* = 4.7 Hz), 4.38 (2H, q, *J* = 7.1 Hz), 1.81 (1H, t, *J* = 5.2 Hz), 1.40 (3H, t, *J* = 7.1 Hz) ppm. ¹³C NMR (125 MHz, CDCl₃) δ: 166.5, 145.8, 129.8, 129.7, 126.5, 64.8, 61.0, 14.4 ppm.

4.16. Pyridin-2-ylmethanol (**2n**)³⁸

Following the general procedure A, starting from 2-pyridinecarboxaldehyde (48 μL, 0.5 mmol), potassium formate (210 mg, 2.5 mmol), **Fe** (5 mg, 0.01 mmol) and Me₃NO (1 mg, 0.0126 mmol) at 60 °C, alcohol **2n** was obtained as a colorless oil (48 mg, 88 %) after purification by flash column chromatography on silica (eluent: AcOEt to AcOEt/MeOH [95:5]). ¹H NMR (500 MHz, CDCl₃) δ: 8.55 (1H, d, *J* = 4.7 Hz), 7.68 (1H, t, *J* = 7.8 Hz), 7.25 (1H, d, *J* = 7.8 Hz), 7.20 (1H, t, *J* = 4.7 Hz), 4.76 (2H, s), 3.95 (1H, s) ppm. ¹³C NMR (125 MHz, CDCl₃) δ: 159.0, 148.5, 136.7, 122.4, 120.5, 64.1 ppm.

4.17. Pyridin-3-ylmethanol (**2o**)³⁸

Following the general procedure A, starting from 3-pyridinecarboxaldehyde (47 μL, 0.5 mmol), potassium formate (210 mg, 2.5 mmol), **Fe** (9 mg, 0.01 mmol) and Me₃NO (1 mg, 0.0126 mmol) at 60 °C, alcohol **1o** was obtained as a colorless oil (40 mg, 73 %) after purification by flash column chromatography on silica (eluent: AcOEt to AcOEt/MeOH [95:5]). ¹H NMR (500 MHz, CDCl₃) δ: 8.55 (1H, s), 8.50 (1H, d, *J* = 3.8 Hz), 7.73 (1H, d, *J* = 7.7 Hz), 7.29 (1H, dd, *J* = 7.5, 5.0 Hz), 4.73 (2H, s) (OH signal not observed) ppm. ¹³C NMR (125 MHz, CDCl₃) δ: 148.8, 148.4, 136.4, 134.9, 123.6, 62.6 ppm.

4.18. Pyridin-4-ylmethanol (**2p**)³⁸

Following the general procedure A, starting from 4-pyridinecarboxaldehyde (47 μL, 0.5 mmol), potassium formate (210 mg, 2.5 mmol), **Fe** (5 mg, 0.01 mmol) and Me₃NO (1 mg, 0.0126 mmol) at 60 °C, alcohol **2p** was obtained as a white powder (36 mg, 66 %) after purification by flash column

chromatography on silica (eluent: AcOEt to AcOEt/MeOH [9:1]). ^1H NMR (500 MHz, CDCl_3) δ : 8.49 (2H, d, $J = 4.8$ Hz), 7.29 (2H, d, $J = 4.8$ Hz), 4.74 (2H, s) (OH signal not observed) ppm. ^{13}C NMR (125 MHz, CDCl_3) δ : 150.8, 149.5, 121.2, 63.1 ppm.

4.19. Thiophen-2-ylmethanol (**2q**)³⁸

Following the general procedure A, starting from 2-thiophenecarboxaldehyde (47 μL , 0.5 mmol), potassium formate (210 mg, 2.5 mmol), **Fe** (5 mg, 0.01 mmol) and Me_3NO (1 mg, 0.0126 mmol) at 60 °C, alcohol **2q** was obtained as a colorless oil (56 mg, 98 %) after purification by flash column chromatography on silica (eluent: pentane/AcOEt [7:3]). ^1H NMR (500 MHz, CDCl_3) δ : 7.29 (1H, d, $J = 5.0$ Hz), 7.02 (1H, s), 6.98 (1H, t, $J = 4.0$ Hz), 4.84 (2H, s), 1.83 (1H, s) ppm. ^{13}C NMR (125 MHz, CDCl_3) δ : 144.0, 126.9, 126.7, 126.5, 60.1 ppm.

4.20. Furan-2-ylmethanol (**2r**)³⁸

Following the general procedure A, starting from furfural (41 μL , 0.5 mmol), potassium formate (210 mg, 2.5 mmol), **Fe** (5 mg, 0.01 mmol) and Me_3NO (1 mg, 0.0126 mmol) at 60 °C, alcohol **2r** was obtained as a yellow oil (48 mg, 98 %) after purification by flash column chromatography on silica (eluent: pentane/AcOEt [7:3]). ^1H NMR (500 MHz, CDCl_3) δ : 7.40 (1H, dd, $J = 1.9, 0.8$ Hz), 6.34 (1H, dd, $J = 3.2, 1.9$ Hz), 6.30 (1H, d, $J = 3.2$ Hz), 4.61 (2H, s), 1.76 (1H, s) ppm. ^{13}C NMR (125 MHz, CDCl_3) δ : 153.9, 142.6, 110.4, 107.8, 57.5 ppm.

4.21. Citronellol (**2s**)³⁸

Following the general procedure A, starting from citronellal (90 μL , 0.5 mmol), potassium formate (210 mg, 2.5 mmol), **Fe** (5 mg, 0.01 mmol) and Me_3NO (1 mg, 0.0126 mmol) at 60 °C, alcohol **2s** was obtained as a colorless oil (77 mg, 99 %) without purification. ^1H NMR (500 MHz, CDCl_3) δ : 5.09 (1H, app t, $J = 7.2$ Hz), 3.67-3.55 (2H, m), 2.00-1.82 (2H, m), 1.62 (3H, s), 1.60-1.45 (5H, m), 1.38-1.22 (2H, m), 1.19-1.06 (2H, m), 0.90 (3H, d, $J = 7.2$ Hz) ppm. ^{13}C NMR (125 MHz, CDCl_3) δ : 131.3, 124.7, 61.2, 39.9, 37.2, 29.2, 25.7, 25.5, 19.5, 17.7 ppm.

4.22. 3,7-dimethyloctane-1,7-diol (**2t**)³⁸

Following the general procedure A, starting from 7-hydroxycitronellal (93 μL , 0.5 mmol), potassium formate (210 mg, 2.5 mmol), **Fe** (5 mg, 0.01 mmol) and Me_3NO (1 mg, 0.0126 mmol) at 60 °C, diol **2t** was obtained as a thick colorless oil (86 mg, 99 %) without purification. ^1H NMR (500 MHz, CDCl_3) δ : 3.73-3.64 (2H, m), 1.64-1.57 (2H, m), 1.44-1.31 (8H, m), 1.21 (6H, s), 1.17-1.13 (1H, m), 0.90 (3H, d, $J = 6.6$ Hz) ppm. ^{13}C NMR (125 MHz, CDCl_3) δ : 71.1, 61.2, 44.1, 39.9, 37.6, 29.5, 29.4, 29.2, 21.7, 19.6 ppm.

4.23. Cyclohexylmethanol (**2u**)³⁸

Following the general procedure A, starting from cyclohexane carboxaldehyde (60 μL , 0.5 mmol), potassium formate (210 mg, 2.5 mmol), **Fe** (5 mg, 0.01 mmol) and Me_3NO (1 mg, 0.0126 mmol) at 60 °C, alcohol **2u** was obtained as a clear yellow oil (55 mg, 97 %) without purification. ^1H NMR (500 MHz, CDCl_3) δ : 3.44 (2H, d, $J = 6.4$ Hz), 1.76-1.72 (4H, m), 1.69-1.66 (1H, m), 1.51-1.43 (1H, m), 1.27-1.14 (3H, m), 0.97-0.88 (2H, m) (OH signal not observed) ppm. ^{13}C NMR (125 MHz, CDCl_3) δ : 68.8, 40.5, 29.6, 26.6, 25.8 ppm.

4.24. 3-phenylpropan-1-ol (**2v**)³⁸

Following the general procedure A, starting from 3-phenylpropanal (66 μL , 0.5 mmol), potassium formate (210 mg, 2.5 mmol), **Fe** (5 mg, 0.01 mmol) and Me_3NO (1 mg, 0.0126 mmol) at 60 °C, alcohol **2v** was obtained as a colorless oil (67 mg, 99 %) after purification by flash column chromatography on silica (eluent: pentane/AcOEt [9:1] to [7:3]). ^1H NMR (500 MHz, CDCl_3) δ : 7.31-7.28 (2H, m), 7.22-7.18 (3H, m), 3.69 (2H, app t, $J = 6.1$ Hz), 2.72 (2H, app t, $J = 6.1$ Hz), 1.93-1.88 (2H, m), 1.25 (1H, s) ppm. ^{13}C NMR (125 MHz, CDCl_3) δ : 141.8, 128.5, 128.4, 126.9, 62.3, 34.2, 32.1 ppm.

4.25. 1-(4-(hydroxymethyl)phenyl)ethan-1-one (**2w**)³⁹

Following the general procedure A, starting from (4-acetyl)benzaldehyde (73 mg, 0.5 mmol), potassium formate (210 mg, 2.5 mmol), **Fe** (5 mg, 0.01 mmol) and Me_3NO (1 mg, 0.0126 mmol) at 60 °C, alcohol **2w** was obtained as a white solid (73 mg, 97 %) after purification by flash column chromatography on silica (eluent: pentane/AcOEt [1:1]). ^1H NMR (500 MHz, CDCl_3) δ : 7.96 (2H, d, $J = 7.7$ Hz), 7.46 (2H, d, $J = 7.7$ Hz), 4.78 (2H, s), 2.61 (3H, s), 1.84 (1H, s) ppm. ^{13}C NMR (125 MHz, CDCl_3) δ : 197.9, 146.2, 136.4, 128.7, 126.6, 64.7, 26.7 ppm.

4.26. 6-hydroxy-1-phenylhex-1-one (**2x**)⁴⁰

Following the general procedure A, starting from ketoaldehyde **1z** (95 mg, 0.5 mmol), potassium formate (210 mg, 2.5 mmol), **Fe** (5 mg, 0.01 mmol) and Me_3NO (1 mg, 0.0126 mmol) at 60 °C, alcohol **2x** was obtained as a yellow oil (40 mg, 42 %) after purification by flash column chromatography on silica (eluent: pentane/AcOEt [8:2]). ^1H NMR (500 MHz, CDCl_3) δ : 7.97 (2H, d, $J = 7.7$ Hz), 7.55 (1H, t, $J = 7.3$ Hz), 7.45 (2H, t, $J = 7.4$ Hz), 3.66 (2H, t, $J = 6.2$ Hz), 2.99 (2H, t, $J = 7.2$ Hz), 1.77 (2H, quint, $J = 7.5$ Hz), 1.62 (2H, quint, $J = 7.2$ Hz), 1.46 (2H, quint, $J = 7.5$ Hz) ppm. ^{13}C NMR (125 MHz, CDCl_3) δ : 200.4, 137.0, 133.0, 128.6, 128.1, 62.7, 38.5, 32.5, 25.5, 23.9 ppm.

4.27. (R)-5-(2-hydroxyethyl)-6-methylhept-6-en-2-one (**2y**)⁴¹

Following the general procedure A, starting from ketoaldehyde **1aa** (84 mg, 0.5 mmol), potassium formate (210 mg, 2.5 mmol), **Fe** (5 mg, 0.01 mmol) and Me_3NO (1 mg, 0.0126 mmol) at 60 °C, alcohol **2y** was obtained as a colorless oil (78 mg, 92 %) after purification by flash column chromatography on silica (eluent: pentane/AcOEt [7:3] to [1:1]). ^1H NMR (500 MHz, CDCl_3) δ : 4.80 (1H, s), 4.74 (1H, s), 3.64-3.58 (2H, m), 2.36 (2H, t, $J = 7.5$ Hz), 2.22-2.17 (1H, m), 2.12 (3H, s), 1.70-1.55 (7H, m), 1.46 (1H, s) ppm. ^{13}C NMR (125 MHz, CDCl_3) δ : 209.1, 146.7, 112.9, 61.3, 43.6, 41.4, 36.1, 30.1, 26.6, 17.5 ppm.

General procedure B for reductive amination by hydrogen transfer reaction. In a flamed dried Schlenk under an argon atmosphere containing a stirring bar was charged the aldehyde (1 equiv.), amine (2 equiv.), potassium formate (6.5 equiv.), iron complex (2 mol%) and trimethylamine N-oxide (2.5 mol%) in ethanol (1 mL). The reaction mixture was heated at 80 °C for 24-48 h. After cooling-down to room temperature, the reaction mixture was quenched with a saturated aqueous solution of NaHCO_3 and the organic layer was extracted twice with AcOEt and washed with water. Combined organic layer was dried over MgSO_4 and concentrated under reduced pressure to afford the crude product that was purified by silica gel column chromatography.

4.28. N-benzyl-N,3,7-trimethyloct-6-en-1-amine (**4a**)²⁵

Following the general procedure B, starting from citronellal (91 μL , 0.5 mmol), N-methylbenzylamine (150 μL , 1 mmol), **Fe** (5

mg, 0.01 mmol), Me₃NO (1 mg, 0.0126 mmol) and potassium formate (273 mg, 3.25 mmol) for 16 h at 80 °C, the corresponding amine **4a** was obtained as a yellow oil (127 mg, 98 %) after purification by flash column chromatography on silica (eluent: CH₂Cl₂/MeOH [99:1]). ¹H NMR (500 MHz, CDCl₃) δ: 7.31 (4H, d, *J* = 4.4 Hz), 7.26-7.22 (1H, m), 5.09 (1H, t, *J* = 7.1 Hz), 3.48 (2H, q, *J* = 13.0 Hz), 2.39 (2H, t, *J* = 7.5 Hz), 2.18 (3H, s), 2.04-1.90 (2H, m), 1.68 (3H, s), 1.60 (3H, s), 1.58-1.55 (1H, m), 1.50-1.46 (1H, m), 1.34-1.29 (2H, m), 1.19-1.11 (1H, m), 0.87 (3H, d, *J* = 6.6 Hz) ppm. ¹³C NMR (125 MHz, CDCl₃) δ: 139.3, 131.1, 129.1, 128.2, 126.9, 124.9, 62.4, 55.6, 42.3, 37.3, 34.4, 30.9, 25.8, 25.5, 19.7, 17.7 ppm.

4.29. 2-(3,7-dimethyloct-6-en-1-yl)-1,2,3,4-tetrahydroisoquinoline (**4b**)²⁵

Following the general procedure B, starting from citronellal (91 μL, 0.5 mmol), 1,2,3,4-tetrahydroisoquinoline (126 μL, 1 mmol), **Fe** (5 mg, 0.01 mmol), Me₃NO (1 mg, 0.0126 mmol) and potassium formate (273 mg, 3.25 mmol) for 24 h at 80 °C, the corresponding amine **4b** was obtained as a yellow oil (88 mg, 65 %) after purification by flash column chromatography on silica (eluent: pentane/AcOEt [95:5] to [90:10]). ¹H NMR (500 MHz, CDCl₃) δ: 7.12-7.08 (3H, m), 7.03-7.01 (1H, m), 5.11 (1H, t, *J* = 7.1 Hz), 3.62 (2H, s), 2.91 (2H, t, *J* = 5.9 Hz), 2.73 (2H, td, *J* = 6.0, 3.0 Hz), 2.52 (2H, dt, *J* = 9.5, 5.6 Hz), 2.06-1.93 (2H, m), 1.69 (3H, s), 1.67-1.63 (1H, m), 1.61 (3H, s), 1.55-1.48 (1H, m), 1.45-1.33 (2H, m), 1.29-1.17 (1H, m), 0.93 (3H, d, *J* = 6.6 Hz) ppm. ¹³C NMR (125 MHz, CDCl₃) δ: 135.0, 134.4, 131.2, 128.7, 126.6, 126.1, 126.6, 124.9, 56.6, 56.4, 51.1, 37.3, 34.3, 31.2, 29.2, 25.7, 25.5, 19.8, 17.7 ppm.

4.30. 2-(*N*-methyl-*N*-3,7-dimethyloct-6-enyl)amino)ethanol (**4c**)

Following the general procedure B, starting from citronellal (90 μL, 0.5 mmol), *N*-methylethanolamine (61.2 μL, 1 mmol), **Fe** (5 mg, 0.01 mmol), Me₃NO (1 mg, 0.0126 mmol) and potassium formate (273 mg, 3.25 mmol) for 48 h at 80 °C, the corresponding amine **4c** was obtained as a colorless oil (85 mg, 80 %) after purification by flash column chromatography on silica (eluent: CH₂Cl₂/MeOH [90:10] to [70:30]). *n*_{max} (liquid film) 3353, 2922, 2853, 2799, 1455, 1376, 1042, 937, 878, 821 cm⁻¹. ¹H NMR (500 MHz, CDCl₃) δ: 5.08 (1H, t, *J* = 7.0 Hz), 3.64 (2H, t, *J* = 5.2 Hz), 2.61 (2H, t, *J* = 5.2 Hz), 2.53-2.50 (2H, m), 2.33 (3H, s), 2.04-1.90 (2H, m), 1.68 (3H, s), 1.60 (3H, s), 1.58-1.51 (1H, m), 1.50-1.42 (1H, m), 1.37-1.29 (2H, m), 1.28-1.25 (1H, m), 1.20-1.13 (1H, m), 0.89 (3H, d, *J* = 6.5 Hz) ppm. ¹³C NMR (125 MHz, CDCl₃) δ: 131.4, 124.6, 59.0, 58.0, 55.8, 41.5, 37.1, 33.7, 30.6, 25.7, 25.6, 19.6, 17.7 ppm. HRMS: MH⁺, found: 214.2168. C₁₃H₂₈NO requires 214.2171.

4.31. (2,2 dimethoxyethyl)(3,7 dimethyloct-6-en-1-yl)methylamine (**4d**)²⁵

Following the general procedure B, starting from citronellal (90 μL, 0.5 mmol), *N*-methylaminoacetaldehyde dimethyl acetal (99 μL, 1 mmol), **Fe** (5 mg, 0.01 mmol), Me₃NO (1 mg, 0.0126 mmol) and potassium formate (273 mg, 3.25 mmol) for 48 h at 80 °C, the corresponding amine **4d** was obtained as a yellow oil (100 mg, 78 %) after purification by flash column chromatography on silica (eluent: Pentane/Et₂O [90:10] to [70:30]). ¹H NMR (500 MHz, CDCl₃) δ: 5.09 (1H, t, *J* = 7.0 Hz), 4.49 (1H, t, *J* = 5.0 Hz), 3.36 (6H, s), 2.54-2.47 (2H, m), 2.46-2.39 (2H, m), 2.29 (3H, s), 2.04-1.88 (2H, m), 1.67 (3H, s), 1.59 (3H, s), 1.56-1.48 (1H, m), 1.46-1.38 (1H, m), 1.36-1.25 (2H, m), 1.19-1.12 (1H, m), 0.88 (3H, d, *J* = 6.6 Hz) ppm. ¹³C NMR (125

MHz, CDCl₃) δ: 131.1, 124.9, 102.8, 58.9, 56.6, 53.3, 43.3, 37.3, 34.0, 30.9, 25.7, 25.5, 19.7, 17.7 ppm.

4.32. *N*-(3,7-dimethyloct-6-en-1-yl)-4-methoxyaniline (**4e**)^{32a}

Following the general procedure B, starting from citronellal (91 μL, 0.5 mmol), *p*-anisidine (123 mg, 1 mmol), **Fe** (5 mg, 0.01 mmol), Me₃NO (1 mg, 0.0126 mmol) and potassium formate (273 mg, 3.25 mmol) for 16 h at 80 °C, the corresponding amine **4e** was obtained as a yellow oil (101 mg, 77 %) after purification by flash column chromatography on silica (eluent: pentane/AcOEt [95:5] to [90:10]). ¹H NMR (500 MHz, CDCl₃) δ: 6.78 (2H, d, *J* = 8.6 Hz), 6.58 (2H, d, *J* = 8.6 Hz), 5.10 (1H, t, *J* = 6.6 Hz), 3.75 (3H, s), 3.37 (1H, s), 3.13-3.05 (2H, m), 2.05-1.93 (2H, m), 1.69 (3H, s), 1.67-1.54 (5H, m), 1.46-1.34 (2H, m), 1.26-1.17 (1H, m), 0.94 (3H, d, *J* = 6.5 Hz) ppm. ¹³C NMR (125 MHz, CDCl₃) δ: 151.9, 142.8, 131.4, 124.7, 114.9, 114.1, 55.9, 43.0, 37.1, 36.8, 30.5, 25.8, 25.5, 19.6, 17.7 ppm.

4.33. *N*-(3,7-dimethyloct-6-enyl)pyridin-2-amine (**4f**)

Following the general procedure B, starting from citronellal (90 μL, 0.5 mmol), 2-aminopyridine (94 mg, 1 mmol), **Fe** (5 mg, 0.01 mmol), Me₃NO (1 mg, 0.0126 mmol) and potassium formate (273 mg, 3.25 mmol) for 48 h at 80 °C, the corresponding amine **4f** was obtained as a yellow oil (114 mg, 98 %) after purification by flash column chromatography on silica (eluent: CH₂Cl₂/MeOH [95:5]). *n*_{max} (liquid film) 3340, 3210, 2960, 2915, 2856, 2042, 1980, 1605, 1570, 1488, 1443, 1377, 1324, 1288, 1152, 1056, 988, 829, 770, 736, 700, 521 cm⁻¹. ¹H NMR (500 MHz, CDCl₃) δ: 8.05 (1H, d, *J* = 4.9 Hz), 7.42 (1H, t, *J* = 7.7 Hz), 6.64 (1H, t, *J* = 6.1 Hz), 6.50 (1H, d, *J* = 8.3 Hz), 5.09 (1H, t, *J* = 6.8 Hz), 4.44 (1H, br s (NH)), 3.72-3.63 (2H, m), 2.04-1.91 (2H, m), 1.68 (3H, s), 1.60 (3H, s), 1.58-1.53 (1H, m), 1.41-1.30 (2H, m), 1.26-1.24 (1H, m), 1.20-1.13 (1H, m), 0.90 (3H, d, *J* = 6.5 Hz) ppm. ¹³C NMR (125 MHz, CDCl₃) δ: 158.4, 148.1, 137.8, 131.3, 124.7, 114.1, 108.6, 61.2, 40.0, 37.2, 29.2, 25.7, 25.5, 19.5, 17.7 ppm. HRMS: MH⁺, found: 233.2016. C₁₅H₂₅N₂ requires 233.2018.

4.34. *N*-benzyl-*N*-methyl-3-phenylpropan-1-amine (**4g**)^{32b}

Following the general procedure B, starting from hydrocinnamaldehyde (66 μL, 0.5 mmol), *N*-methylbenzylamine (150 μL, 1 mmol), **Fe** (5 mg, 0.01 mmol), Me₃NO (1 mg, 0.0126 mmol) and potassium formate (273 mg, 3.25 mmol) for 48 h at 80 °C, the corresponding amine **4g** was obtained as a colorless oil (44 mg, 37 %) after purification by flash column chromatography on silica (eluent: pentane/AcOEt [95:5] to [90:10]). ¹H NMR (500 MHz, CDCl₃) δ: 7.24 (3H, d, *J* = 4.2 Hz), 7.19 (4H, m), 7.10 (3H, d, *J* = 7.2 Hz), 3.41 (2H, s), 2.57 (2H, t, *J* = 7.8 Hz), 2.35 (2H, t, *J* = 7.8 Hz), 2.12 (3H, s), 1.77 (2H, quint, *J* = 7.8 Hz) ppm. ¹³C NMR (125 MHz, CDCl₃) δ: 142.5, 139.3, 129.2, 129.1, 128.5, 128.4, 128.3, 128.2, 126.9, 126.7, 62.3, 56.9, 42.2, 33.6, 29.2 ppm.

4.35. 4-methoxy-*N*-(3-phenylpropyl)aniline (**4h**)⁴²

Following the general procedure B, starting from hydrocinnamaldehyde (66 μL, 0.5 mmol), *p*-anisidine (123 mg, 1 mmol), **Fe** (5 mg, 0.01 mmol), Me₃NO (1 mg, 0.0126 mmol) and potassium formate (273 mg, 3.25 mmol) for 48 h at 80 °C, the corresponding amine **4h** was obtained as a yellow oil (115 mg, 95 %) after purification by flash column chromatography on silica (eluent: pentane/AcOEt [95:5] to [90:10]). ¹H NMR (500 MHz, CDCl₃) δ: 7.30 (2H, t, *J* = 7.4 Hz), 7.22 (3H, d, *J* = 6.3 Hz), 6.79 (2H, d, *J* = 8.5 Hz), 6.56 (2H, d, *J* = 8.5 Hz), 3.76 (3H, s), 3.12 (2H, t, *J* = 7.1 Hz), 2.74 (2H, t, *J* = 7.1 Hz), 1.95 (2H,

quint., $J = 7.1$ Hz) (NH signal not observed) ppm. ^{13}C NMR (125 MHz, CDCl_3) δ : 152.0, 142.7, 141.8, 128.5, 128.4, 126.9, 114.9, 114.1, 55.9, 44.5, 33.5, 31.2 ppm.

4.36. *N*-benzyl-*N*-methyl-1-phenylmethanamine (**4i**)^{32c}

Following the general procedure B, starting from benzaldehyde (51 μL , 0.5 mmol), *N*-methylbenzylamine (150 μL , 1 mmol), **Fe** (5 mg, 0.01 mmol), Me_3NO (1 mg, 0.0126 mmol) and potassium formate (273 mg, 3.25 mmol) for 48 h at 80 °C, the corresponding amine **4i** was obtained as a yellow oil (97 mg, 92 %) after purification by flash column chromatography on silica (eluent: pentane/AcOEt [97:3]). ^1H NMR (500 MHz, CDCl_3) δ : 7.37 (4H, d, $J = 7.4$ Hz), 7.32 (4H, t, $J = 7.4$ Hz), 7.25 (2H, t, $J = 7.4$ Hz), 3.53 (4H, s), 2.19 (3H, s) ppm. ^{13}C NMR (125 MHz, CDCl_3) δ : 139.4, 128.9, 128.2, 126.9, 61.9, 42.3 ppm.

4.37. *N*-benzyl-1-(4-methoxyphenyl)-*N*-methylmethanamine (**4j**)^{32c}

Following the general procedure B, starting from *p*-anisaldehyde (61 μL , 0.5 mmol), *N*-methylbenzylamine (150 μL , 1 mmol), **Fe** (5 mg, 0.01 mmol), Me_3NO (1 mg, 0.0126 mmol) and potassium formate (273 mg, 3.25 mmol) for 48 h at 80 °C, the corresponding amine **4j** was obtained as a yellow oil (116 mg, 96 %) after purification by flash column chromatography on silica (eluent: pentane/AcOEt [95:5] to [90:10]). ^1H NMR (500 MHz, CDCl_3) δ : 7.28-7.15 (7H, m), 6.80 (2H, t, $J = 5.7$ Hz), 3.73 (3H, s), 3.42 (2H, s), 3.39 (2H, s), 2.09 (3H, s) ppm. ^{13}C NMR (125 MHz, CDCl_3) δ : 158.7, 139.4, 131.4, 130.1, 128.9, 128.2, 126.9, 113.6, 61.7, 61.3, 55.3, 42.1 ppm.

4.38. *N*-benzyl-1-(3-methoxyphenyl)-*N*-methylmethanamine (**4k**)^{32c}

Following the general procedure B, starting from *m*-anisaldehyde (61 μL , 0.5 mmol), *N*-methylbenzylamine (150 μL , 1 mmol), **Fe** (5 mg, 0.01 mmol), Me_3NO (1 mg, 0.0126 mmol) and potassium formate (273 mg, 3.25 mmol) for 24 h at 80 °C, the corresponding amine **4k** was obtained as a yellow oil (75 mg, 62 %) after purification by flash column chromatography on silica (eluent: pentane/AcOEt [95:5] to [90:10]). ^1H NMR (500 MHz, CDCl_3) δ : 7.29 (2H, d, $J = 7.6$ Hz), 7.24 (2H, t, $J = 7.4$ Hz), 7.17-7.13 (2H, m), 6.88 (1H, s), 6.87 (1H, d, $J = 8.2$ Hz), 6.71 (1H, d, $J = 8.2$ Hz), 3.73 (3H, s), 3.44 (2H, s), 3.42 (2H, s), 2.11 (3H, s) ppm. ^{13}C NMR (125 MHz, CDCl_3) δ : 159.7, 141.1, 139.4, 129.2, 128.9, 128.3, 126.9, 121.3, 114.4, 112.5, 61.9, 61.9, 55.2, 42.4 ppm.

4.39. 1-(benzo[d][1,3]dioxol-5-yl)-*N*-benzyl-*N*-methylmethanamine (**4l**)³⁸

Following the general procedure B, starting from piperonal (75 mg, 0.5 mmol), *N*-methylbenzylamine (150 μL , 1 mmol), **Fe** (5 mg, 0.01 mmol), Me_3NO (1 mg, 0.0126 mmol) and potassium formate (273 mg, 3.25 mmol) for 24 h at 80 °C, the corresponding amine **4l** was obtained as a yellow oil (55 mg, 44 %) after purification by flash column chromatography on silica (eluent: pentane/AcOEt [95:5] to [90:10]). ^1H NMR (500 MHz, CDCl_3) δ : 7.36-7.31 (4H, m), 7.26-7.23 (1H, m), 6.91 (1H, s), 6.77 (2H, q, $J = 7.9$ Hz), 5.9 (2H, s), 3.51 (2H, s), 3.43 (2H, s), 2.17 (2H, s) ppm. ^{13}C NMR (125 MHz, CDCl_3) δ : 147.7, 146.5, 139.4, 133.4, 128.9, 128.3, 126.9, 121.9, 109.3, 107.9, 100.9, 61.8, 61.6, 42.1 ppm.

4.40. *N*-benzyl-1-(4-chlorophenyl)-*N*-methylmethanamine (**4m**)

Following the general procedure B, starting from 4-chlorobenzaldehyde (70 mg, 0.5 mmol), *N*-methylbenzylamine (150 μL , 1 mmol), **Fe** (5 mg, 0.01 mmol), Me_3NO (1 mg, 0.0126 mmol) and potassium formate (273 mg, 3.25 mmol) for 48 h at 80 °C, the corresponding amine **4m** was obtained as a yellow oil (44 mg, 36 %) after purification by flash column chromatography on silica (eluent: pentane/AcOEt [95:5] to [90:10]). n_{max} (liquid film) 3028, 2924, 2840, 2786, 1598, 1490, 1452, 1406, 1364, 1284, 1263, 1240, 1192, 1132, 1088, 1025, 1015, 979, 939, 908, 867, 838, 799, 737, 697, 671, 634, 611, 536, 488, 456 cm^{-1} . ^1H NMR (500 MHz, CDCl_3) δ : 7.32-7.21 (10H, m), 3.48 (2H, s), 3.45 (2H, s), 2.14 (3H, s) ppm. ^{13}C NMR (125 MHz, CDCl_3) δ : 139.1, 137.9, 132.6, 130.2, 128.9, 128.4, 128.3, 127.1, 61.9, 61.1, 42.2 ppm. HRMS: MH^+ , found: 246.1052. $\text{C}_{15}\text{H}_{17}\text{NCl}$ requires 246.1050.

4.41. *N*-benzyl-1-(4-fluorophenyl)-*N*-methylmethanamine (**4n**)³⁸

Following the general procedure B, starting from 4-fluorobenzaldehyde (54 μL , 0.5 mmol), *N*-methylbenzylamine (150 μL , 1 mmol), **Fe** (5 mg, 0.01 mmol), Me_3NO (1 mg, 0.0126 mmol) and potassium formate (273 mg, 3.25 mmol) for 24 h at 80 °C, the corresponding amine **4n** was obtained as a yellow oil (69 mg, 60 %) after purification by flash column chromatography on silica (eluent: pentane/AcOEt [95:5] to [90:10]). ^1H NMR (500 MHz, CDCl_3) δ : 7.28-7.23 (6H, m), 7.18-7.16 (1H, m), 6.92 (2H, t, $J = 8.3$ Hz), 3.43 (2H, s), 3.40 (2H, s), 2.09 (3H, s) ppm. ^{13}C NMR (125 MHz, CDCl_3) δ : 162.9, 161.0, 139.2, 135.1, 130.4, 130.3, 128.9, 128.3, 127.0, 115.1, 114.9, 61.9, 61.1, 42.2 ppm. ^{19}F NMR (500 MHz, CDCl_3) δ : -116.16 ppm.

4.42. *N*-benzyl-*N*-methyl-1-(thiophen-2-yl)methanamine (**4o**)

Following the general procedure B, starting from 2-thiophenecarboxaldehyde (47 μL , 0.5 mmol), *N*-methylbenzylamine (150 μL , 1 mmol), **Fe** (5 mg, 0.01 mmol), Me_3NO (1 mg, 0.0126 mmol) and potassium formate (273 mg, 3.25 mmol) for 48 h at 80 °C, the corresponding amine **4o** was obtained as a yellow oil (107 mg, 98 %) after purification by flash column chromatography on silica (eluent: pentane/AcOEt [95:5] to [90:10]); n_{max} (liquid film) 3027, 2924, 2837, 2785, 1495, 1452, 1418, 1366, 1340, 1277, 1263, 1222, 1168, 1130, 1075, 1023, 973, 908, 863, 820, 736, 694, 606, 502, 479 cm^{-1} . ^1H NMR (500 MHz, CDCl_3) δ : 7.27 (2H, d, $J = 7.5$ Hz), 7.22 (2H, t, $J = 7.4$ Hz), 7.16-7.13 (2H, m), 6.85-6.84 (1H, m), 6.83 (1H, s), 3.66 (2H, s), 3.44 (2H, s), 2.15 (3H, s) ppm. ^{13}C NMR (125 MHz, CDCl_3) δ : 142.9, 139.0, 128.9, 128.3, 127.0, 126.4, 126.7, 124.9, 61.1, 56.1, 42.2 ppm. HRMS: MH^+ , found: 218.1009. $\text{C}_{13}\text{H}_{16}\text{NS}$ requires 218.1003.

4.43. *N*-benzyl-4-methoxyaniline (**4p**)⁴³

Following the general procedure B, starting from benzaldehyde (51 μL , 0.5 mmol), *p*-anisidine (123 mg, 1 mmol), **Fe** (5 mg, 0.01 mmol), Me_3NO (1 mg, 0.0126 mmol) and potassium formate (273 mg, 3.25 mmol) for 48 h at 80 °C, the corresponding amine **4p** was obtained as a yellow powder (99 mg, 93 %) after purification by flash column chromatography on silica (eluent: pentane/AcOEt [95:5] to [90:10]). ^1H NMR (500 MHz, CDCl_3) δ : 7.37 (2H, t, $J = 7.2$ Hz), 7.34 (2H, t, $J = 7.2$ Hz), 7.27 (1H, t, $J = 7.2$ Hz), 6.78 (2H, d, $J = 8.6$ Hz), 6.62 (2H, d, $J = 8.6$ Hz), 4.29 (2H, s), 3.75 (3H, s) (NH signal not observed) ppm. ^{13}C NMR (125 MHz, CDCl_3) δ : 152.3, 142.5, 139.7, 128.6, 127.6, 127.2, 114.9, 114.2, 55.9, 49.3 ppm.

4.44. 4-methoxy-*N*-(4-methoxybenzyl)aniline (**4q**)⁴³

Following the general procedure B, starting from *p*-anisaldehyde (61 μ L, 0.5 mmol), *p*-anisidine (123 mg, 1 mmol), **Fe** (5 mg, 0.01 mmol), Me_3NO (1 mg, 0.0126 mmol) and potassium formate (273 mg, 3.25 mmol) for 24 h at 80 °C, the corresponding amine **4q** was obtained as a white powder (90 mg, 74 %) after purification by flash column chromatography on silica (eluent: pentane/AcOEt [95:5] to [90:10]). ^1H NMR (500 MHz, CDCl_3) δ : 7.29 (2H, d, $J = 8.4$ Hz), 6.88 (2H, d, $J = 8.4$ Hz), 6.78 (2H, d, $J = 8.7$ Hz), 6.62 (2H, d, $J = 8.7$ Hz), 4.21 (2H, s), 3.80 (3H, s), 3.74 (3H, s) (NH signal not observed) ppm. ^{13}C NMR (125 MHz, CDCl_3) δ : 158.9, 152.3, 131.6, 128.9, 122.1, 114.9, 114.3, 114.0, 55.9, 55.3, 48.8 ppm.

4.45. 4-methoxy-*N*-(3-methoxybenzyl)aniline (**4r**)⁴³

Following the general procedure B, starting from *m*-anisaldehyde (61 μ L, 0.5 mmol), *p*-anisidine (123 mg, 1 mmol), **Fe** (5 mg, 0.01 mmol), Me_3NO (1 mg, 0.0126 mmol) and potassium formate (273 mg, 3.25 mmol) for 48 h at 80 °C, the corresponding amine **4r** was obtained as a white powder (119 mg, 98 %) after purification by flash column chromatography on silica (eluent: pentane/AcOEt [95:5] to [90:10]). ^1H NMR (500 MHz, CDCl_3) δ : 7.58 (1H, t, $J = 7.8$ Hz), 7.28 (1H, d, $J = 7.8$ Hz), 7.26 (1H, s), 7.13 (1H, d, $J = 8.7$ Hz), 7.10 (2H, d, $J = 8.7$ Hz), 6.93 (2H, d, $J = 8.7$ Hz), 4.58 (2H, s), 4.12 (3H, s), 4.06 (3H, s) (NH signal not observed) ppm. ^{13}C NMR (125 MHz, CDCl_3) δ : 159.9, 152.2, 142.4, 141.4, 129.6, 119.8, 114.9, 114.1, 113.0, 112.6, 55.8, 55.2, 49.2 ppm.

4.46. *N*-(benzo[d][1,3]dioxol-5-ylmethyl)-4-methoxyaniline (**4s**)

Following the general procedure B, starting from piperonal (75 mg, 0.5 mmol), *p*-anisidine (123 mg, 1 mmol), **Fe** (5 mg, 0.01 mmol), Me_3NO (1 mg, 0.0126 mmol) and potassium formate (273 mg, 3.25 mmol) for 24 h at 80 °C, the corresponding amine **4s** was obtained as a white powder (75 mg, 58 %) after purification by flash column chromatography on silica (eluent: pentane/AcOEt [95:5] to [90:10]); n_{max} (liquid film) 3385, 2923, 2853, 1732, 1625, 1511, 1460, 1440, 1405, 1373, 1291, 1233, 1180, 1119, 1097, 1079, 1032, 925, 879, 815, 783, 746, 612, 571, 510 cm^{-1} . ^1H NMR (500 MHz, CDCl_3) δ : 6.87 (1H, s), 6.83 (1H, d, $J = 8.2$ Hz), 6.79-6.76 (3H, m), 6.60 (2H, d, $J = 8.8$ Hz), 5.94 (2H, s), 4.19 (2H, s), 3.74 (3H, s) (NH signal not observed) ppm. ^{13}C NMR (125 MHz, CDCl_3) δ : 152.3, 147.9, 146.7, 142.4, 133.7, 120.6, 114.9, 114.2, 108.3, 108.1, 101.0, 55.9, 49.1 ppm. HRMS: MH^+ , found: 257.1051. $\text{C}_{15}\text{H}_{16}\text{NO}_3$ requires 257.1052.

4.47. *N*-(4-chlorobenzyl)-4-methoxyaniline (**4t**)⁴³

Following the general procedure B, starting from 4-chlorobenzaldehyde (70 mg, 0.5 mmol), *p*-anisidine (123 mg, 1 mmol), **Fe** (5 mg, 0.01 mmol), Me_3NO (1 mg, 0.0126 mmol) and potassium formate (273 mg, 3.25 mmol) for 48 h at 80 °C, the corresponding amine **4t** was obtained as a white solid (64 mg, 52 %) after purification by flash column chromatography on silica (eluent: pentane/AcOEt [95:5] to [90:10]). ^1H NMR (500 MHz, CDCl_3) δ : 7.31 (4H, s), 6.79 (2H, d, $J = 8.7$ Hz), 6.59 (2H, d, $J = 8.7$ Hz), 4.27 (2H, s), 3.75 (3H, s) (NH signal not observed) ppm. ^{13}C NMR (125 MHz, CDCl_3) δ : 152.4, 142.1, 138.3, 132.8, 128.8, 128.8, 114.9, 114.2, 55.8, 48.6 ppm.

4.48. *N*-(4-fluorobenzyl)-4-methoxyaniline (**4u**)⁴³

Following the general procedure B, starting from 4-fluorobenzaldehyde (54 μ L, 0.5 mmol), *p*-anisidine (123 mg, 1 mmol), **Fe** (5 mg, 0.01 mmol), Me_3NO (1 mg, 0.0126 mmol) and potassium formate (273 mg, 3.25 mmol) for 48 h at 80 °C, the corresponding amine **4u** was obtained as a yellow powder (114

mg, 99 %) after purification by flash column chromatography on silica (eluent: pentane/AcOEt [95:5] to [90:10]). ^1H NMR (500 MHz, CDCl_3) δ : 7.34 (2H, t, $J = 4.1$ Hz), 7.03 (2H, t, $J = 8.4$ Hz), 6.79 (2H, d, $J = 8.4$ Hz), 6.60 (2H, d, $J = 8.2$ Hz), 4.26 (2H, s), 3.75 (3H, s) (NH signal not observed) ppm. ^{13}C NMR (125 MHz, CDCl_3) δ : 163.0, 161.1, 152.4, 142.3, 135.4, 135.4, 129.1, 129.0, 115.5, 115.3, 114.9, 114.2, 55.8, 48.6 ppm. ^{19}F NMR (500 MHz, CDCl_3) δ : -115.71 ppm.

4.49. 1-(4-((benzyl(methyl)amino)methyl)phenyl)ethan-1-one (**4v**)²⁵

Following the general procedure B, starting from 4-acetylbenzaldehyde (75 mg, 0.5 mmol), *N*-benzylmethylamine (80 μ L, 1 mmol), **Fe** (5 mg, 0.01 mmol), Me_3NO (1 mg, 0.0126 mmol) and potassium formate (273 mg, 3.25 mmol) for 24 h at 80 °C, the corresponding amine **4v** was obtained as a colorless oil (101 mg, 80 %) after purification by flash column chromatography on silica (eluent: pentane/Et₂O [8:2]). ^1H NMR (500 MHz, CDCl_3) δ : 7.81 (2H, d, $J = 8.7$ Hz), 7.35 (2H, d, $J = 8.7$ Hz), 7.29-7.14 (5H, m), 3.49 (2H, s), 3.45 (2H, s), 2.51 (3H, s), 2.08 (3H, s) ppm. ^{13}C NMR (125 MHz, CDCl_3) δ : 197.9, 145.3, 139.0, 136.1, 128.9, 128.8, 128.4, 128.3, 127.2, 62.1, 61.4, 42.4, 26.7 ppm.

4.50. (*S*)-1-(4-((2-(hydroxymethyl)pyrrolidin-1-yl)methyl)phenyl)ethan-1-one (**4w**)²⁵

Following the general procedure B, starting from 4-acetylbenzaldehyde (75 mg, 0.5 mmol), *L*-prolinol (100 μ L, 1 mmol), **Fe** (5 mg, 0.01 mmol), Me_3NO (1 mg, 0.0126 mmol) and potassium formate (273 mg, 3.25 mmol) for 24 h at 80 °C, the corresponding amine **4w** was obtained as a colorless oil (60 mg, 51 %) after purification by flash column chromatography on silica (eluent: $\text{CH}_2\text{Cl}_2/\text{MeOH}$ [98:2]). ^1H NMR (500 MHz, CDCl_3) δ : 7.92 (2H, d, $J = 8.0$ Hz), 7.41 (2H, d, $J = 8.0$ Hz), 4.08 (1H, d, $J = 13.8$ Hz), 3.66 (1H, dd, $J = 10.5$; 3.1 Hz), 3.44 (2H, t, $J = 13.2$ Hz), 2.99-2.94 (1H, m), 2.79-2.73 (1H, m), 2.69-2.61 (1H, m), 2.60 (3H, s), 2.28 (1H, q, $J = 8.0$ Hz), 1.99-1.90 (1H, m), 1.89-1.81 (1H, m), 1.77-1.67 (2H, m) ppm. ^{13}C NMR (125 MHz, CDCl_3) δ : 197.8, 145.1, 136.1, 128.7, 128.5, 64.5, 61.8, 58.3, 54.6, 27.6, 26.6, 23.5 ppm.

4.51. 1-(4-((4-benzylpiperazin-1-yl)methyl)phenyl)ethan-1-one (**4x**)

Following the general procedure B, starting from 4-acetylbenzaldehyde (75 mg, 0.5 mmol), benzylpiperazine (210 μ L, 1 mmol), **Fe** (5 mg, 0.01 mmol), Me_3NO (1 mg, 0.0126 mmol) and potassium formate (273 mg, 3.25 mmol) for 24 h at 80 °C, the corresponding amine **4x** was obtained as a yellow solid (75 mg, 48 %) after purification by flash column chromatography on silica (eluent: $\text{CH}_2\text{Cl}_2/\text{MeOH}$ [98:2]). ^1H NMR (500 MHz, CDCl_3) δ : 7.90 (2H, d, $J = 8.3$ Hz), 7.42 (2H, d, $J = 8.2$ Hz), 7.31-7.28 (5H, m), 3.55 (2H, s), 3.52 (2H, s), 2.58 (3H, s), 2.56 - 2.41 (8H, br. s) ppm. ^{13}C NMR (125 MHz, CDCl_3) δ : 197.9, 136.1, 129.26, 129.2, 128.4, 128.2, 127.1, 126.7, 63.1, 62.6, 53.2, 53.0, 26.7 ppm. HRMS: MH^+ , found: 309.1971. $\text{C}_{20}\text{H}_{25}\text{N}_2\text{O}$ requires 309.1967.

4.52. 1-(4-(((2,2-dimethoxyethyl)(methyl)amino)methyl)phenyl)ethan-1-one (**4y**)²⁵

Following the general procedure B, starting from 4-acetylbenzaldehyde (75 mg, 0.5 mmol), *N*-methylaminoacetaldehyde dimethyl acetal (99 μ L, 1 mmol), **Fe** (5 mg, 0.01 mmol), Me_3NO (1 mg, 0.0126 mmol) and potassium formate (273 mg, 3.25 mmol) for 24 h at 80 °C, the

corresponding amine **4y** was obtained as a light yellow oil (85 mg, 68 %) after purification by flash column chromatography on silica (eluent: pentane/Et₂O [1:1]). ¹H NMR (500 MHz, CDCl₃) δ: 7.91 (2H, d, *J* = 8.3 Hz), 7.42 (2H, d, *J* = 8.3 Hz), 4.51 (1H, t, *J* = 5.0 Hz), 3.61 (2H, s), 3.32 (6H, s), 2.58 (3H, s), 2.54 (2H, d, *J* = 5.0 Hz), 2.28 (3H, s). ¹³C NMR (125 MHz, CDCl₃) δ: 197.9, 136.0, 128.9, 128.5, 126.5, 102.8, 62.4, 58.5, 53.3, 43.2, 26.6 ppm.

4.53. 6-((2,2-dimethoxyethyl)(methylamino)-1-phenylhexan-1-one (**4z**)²⁵

Following the general procedure B, starting from ketoaldehyde **1z** (95 mg, 0.5 mmol), *N*-methylaminoacetaldehyde dimethyl acetal (99 μL, 1 mmol), **Fe** (5 mg, 0.01 mmol), Me₃NO (1 mg, 0.0126 mmol) and potassium formate (273 mg, 3.25 mmol) for 24 h at 80 °C, the corresponding amine **4z** was obtained as a colorless oil (89 mg, 61 %) after purification by flash column chromatography on silica (eluent: CH₂Cl₂/MeOH [90:10]). ¹H NMR (500 MHz, CDCl₃) δ: 7.93 (2H, d, *J* = 7.9 Hz), 7.53 (1H, t, *J* = 7.6 Hz), 7.44 (2H, t, *J* = 7.6 Hz), 4.46 (1H, t, *J* = 5.1 Hz), 3.34 (6H, s), 2.95 (2H, t, *J* = 7.3 Hz), 2.49 (2H, d, *J* = 5.1 Hz), 2.39 (2H, t, *J* = 7.2 Hz), 2.27 (3H, s), 1.74 (2H, quint, *J* = 7.5 Hz), 1.51 (2H, quint, *J* = 7.5 Hz), 1.37 (2H, quint, *J* = 7.7 Hz) ppm. ¹³C NMR (125 MHz, CDCl₃) δ: 200.3, 136.9, 132.8, 128.5, 127.9, 102.7, 58.8, 58.3, 53.2, 43.2, 38.4, 27.1, 26.9, 24.1 ppm.

4.54. 6-((2-hydroxyethyl)(methylamino)-1-phenylhexan-1-one (**4aa**)²⁵

Following the general procedure B, starting from ketoaldehyde **1z** (95 mg, 0.5 mmol), *N*-methyl ethanolamine (61 μL, 1 mmol), **Fe** (5 mg, 0.01 mmol), Me₃NO (1 mg, 0.0126 mmol) and potassium formate (273 mg, 3.25 mmol) for 24 h at 80 °C, the corresponding amine **2aa** was obtained as a white powder (74 mg, 59 %) after purification by flash column chromatography on silica (eluent: CH₂Cl₂/MeOH [90:10] to [70:30]). ¹H NMR (500 MHz, CDCl₃) δ: 7.93 (2H, d, *J* = 7.8 Hz), 7.54 (1H, t, *J* = 7.2 Hz), 7.43 (2H, t, *J* = 7.2 Hz), 3.73 (2H, t, *J* = 4.2 Hz), 2.97 (2H, t, *J* = 7.0 Hz), 2.78 (2H, t, *J* = 5.0 Hz), 2.68 (2H, t, *J* = 7.6 Hz), 2.47 (3H, s), 1.75 (2H, quint, *J* = 7.2 Hz), 1.66 (2H, quint, *J* = 6.7 Hz), 1.41 (2H, quint, *J* = 7.0 Hz) ppm. ¹³C NMR (125 MHz, CDCl₃) δ: 199.1, 135.9, 132.0, 127.6, 127.0, 58.1, 56.5, 56.4, 40.4, 37.2, 25.6, 24.7, 22.7 ppm.

4.55. 6-(benzyl(methylamino)-1-phenylhexan-1-one (**4ab**)²⁵

Following the general procedure B, starting from ketoaldehyde **1z** (95 mg, 0.5 mmol), *N*-benzylmethylamine (80 μL, 1 mmol), **Fe** (5 mg, 0.01 mmol), Me₃NO (1 mg, 0.0126 mmol) and potassium formate (273 mg, 3.25 mmol) for 24 h at 80 °C, the corresponding amine **2ab** was obtained as a light yellow (115 mg, 78 %) after purification by flash column chromatography on silica (eluent: CH₂Cl₂/MeOH [90:10]). ¹H NMR (500 MHz, CDCl₃) δ: 7.90 (2H, d, *J* = 7.9 Hz), 7.49 (1H, t, *J* = 7.2 Hz), 7.40 (2H, t, *J* = 7.9 Hz), 7.29-7.23 (4H, m), 7.21-7.16 (1H, m), 3.46 (2H, s), 2.91 (2H, t, *J* = 7.3 Hz), 2.36 (2H, t, *J* = 7.3 Hz), 2.16 (3H, s), 1.70 (2H, quint, *J* = 7.6 Hz), 1.54 (2H, quint, *J* = 7.3 Hz), 1.36 (2H, quint, *J* = 7.6 Hz) ppm. ¹³C NMR (125 MHz, CDCl₃) δ: 200.3, 138.6, 137.0, 129.1, 128.5, 128.2 (2C), 127.9, 126.9, 62.2, 57.1, 42.0, 38.4, 27.1, 24.1 ppm.

4.56. (R)-5-(2-((2-hydroxyethyl)(methylamino)ethyl)-6-methylhept-6-en-2-one (**4ac**)²⁵

Following the general procedure B, starting from ketoaldehyde **1aa** (84 mg, 0.5 mmol), *N*-methyl ethanolamine (61 μL, 1 mmol), **Fe** (5 mg, 0.01 mmol), Me₃NO (1 mg, 0.0126 mmol) and

potassium formate (273 mg, 3.25 mmol) for 24 h at 80 °C, the corresponding amine **2ac** was obtained as a colorless oil (40 mg, 35 %) after purification by flash column chromatography on silica (eluent: CH₂Cl₂/MeOH [90:10] to [70:30]). ¹H NMR (500 MHz, CDCl₃) δ: 4.80 (1H, s), 4.70 (1H, s), 3.70 (2H, t, *J* = 5.0 Hz), 2.67-2.64 (3H, m), 2.55-2.52 (2H, m), 2.42 (3H, s), 2.36 (2H, t, *J* = 7.0 Hz), 2.11 (3H, s), 2.10-2.06 (1H, m), 1.72-1.62 (3H, m), 1.59 (3H, s), 1.57-1.51 (1H, m) ppm. ¹³C NMR (125 MHz, CDCl₃) δ: 208.9, 145.6, 113.5, 59.4, 57.8, 55.9, 44.6, 41.6, 41.2, 30.1, 29.6, 26.7, 17.5 ppm.

4.57. (R)-5-(2-((2,2-dimethoxyethyl)(methylamino)ethyl)-6-methylhept-6-en-2-one (**4ad**)²⁵

Following the general procedure B, starting from ketoaldehyde **1aa** (84 mg, 0.5 mmol), *N*-methylaminoacetaldehyde dimethyl acetal (99 μL, 1 mmol), **Fe** (5 mg, 0.01 mmol), Me₃NO (1 mg, 0.0126 mmol) and potassium formate (273 mg, 3.25 mmol) for 24 h at 80 °C, the corresponding amine **4ad** was obtained as a colorless oil (71 mg, 52 %) after purification by flash column chromatography on silica (eluent: CH₂Cl₂/MeOH [98:2]). ¹H NMR (500 MHz, CDCl₃) δ: 4.76 (s, 1H), 4.67 (s, 1H), 4.47 (1H, t, *J* = 5.0 Hz), 3.35 (6H, s), 2.49 (2H, d, *J* = 5.0 Hz), 2.33 (4H, q, *J* = 7.3 Hz), 2.28 (3H, s), 2.10 (3H, s), 2.05-1.98 (1H, m), 1.70-1.61 (1H, m), 1.56 (3H, s), 1.55-1.47 (3H, m) ppm. ¹³C NMR (125 MHz, CDCl₃) δ: 208.9, 146.2, 112.7, 102.7, 58.9, 56.6, 53.3, 44.8, 43.2, 41.5, 30.4, 30.0, 26.9, 17.5 ppm.

4.58. (R)-5-(2-((S)-2-(hydroxymethyl)pyrrolidin-1-yl)ethyl)-6-methylhept-6-en-2-one (**4ae**)²⁵

Following the general procedure B, starting from ketoaldehyde **1aa** (84 mg, 0.5 mmol), L-prolinol (100 μL, 1 mmol), **Fe** (5 mg, 0.01 mmol), Me₃NO (1 mg, 0.0126 mmol) and potassium formate (273 mg, 3.25 mmol) for 24 h at 80 °C, the corresponding amine **4ae** was obtained as a colorless oil (62 mg, 49 %) after purification by flash column chromatography on silica (eluent: CH₂Cl₂/MeOH [99:1]). ¹H NMR (500 MHz, CDCl₃) δ: 4.79 (1H, s), 4.70 (1H, d, *J* = 1.6 Hz), 3.59 (1H, dd, *J* = 2.9, 10.6 Hz), 3.36 (1H, d, *J* = 10.6), 3.21-3.15 (1H, br. s), 2.68-2.63 (1H, m), 2.60-2.55 (1H, m), 2.35 (2H, t, *J* = 7.5 Hz), 2.21-2.12 (2H, m), 2.11 (3H, s), 1.89-1.81 (1H, m), 1.80-1.71 (4H, m), 1.68-1.61 (2H, m), 1.59-1.51 (6H, m) ppm. ¹³C NMR (125 MHz, CDCl₃) δ: 209.0, 146.1, 113.2, 65.1, 61.8, 54.1, 52.5, 44.8, 41.5, 32.80, 30.1, 27.5, 27.1, 23.6, 17.2 ppm.

General procedure C for the synthesis of chalcone indanone derivatives. In a 50 mL round-bottom flask was charged the indanone (1.322 g, 5 mmol, 1 equiv.), the appropriate aldehyde (5 mmol, 1 equiv.) and methanol (25 mL). Then KOH (0.140 mg, 2.5 mmol, 0.25 equiv.) was added and the reaction mixture was stirred during 2 h at room-temperature. Then the precipitate was filtered and washed with cold methanol to afford the pure product. Data of the enones are in agreement with the literature.

4.59. (E)-2-Benzylidene-2,3-dihydro-1H-inden-1-one (**5l**)⁴⁵

Following the general procedure C starting from benzaldehyde (508 μL, 5 mmol), enone **5l** was obtained as a white solid (1.46 g, 66 %). ¹H NMR (500 MHz, CDCl₃) δ: 7.92 (1H, d, *J* = 7.6 Hz), 7.69-7.68 (3H, m), 7.63-7.61 (1H, m), 7.57-7.55 (1H, m), 7.48-7.39 (4H, m), 4.06 (2H, s) ppm. ¹³C NMR (125 MHz, CDCl₃) δ: 194.4, 149.7, 138.0, 135.4, 134.7, 134.7, 134.0, 130.8 (2C), 129.7, 129.0 (2C), 127.7, 126.2, 124.5, 32.5 ppm.

4.60. (E)-2-(4-methoxybenzylidene)-2,3-dihydro-1H-inden-1-one (**5m**)⁴⁶

Following the general procedure C starting from 4-methoxybenzaldehyde (608 μL , 5 mmol), enone **5m** was obtained as a white solid (2.25 g, 90 %). ^1H NMR (500 MHz, CDCl_3) δ : 7.90 (1H, d, $J = 7.6\text{ Hz}$), 7.65-7.63 (3H, m), 7.61-7.59 (1H, m), 7.56-7.54 (1H, m), 7.43-7.41 (1H, m), 6.99-6.97 (2H, m), 4.01 (2H, s), 3.86 (3H, s) ppm. ^{13}C NMR (125 MHz, CDCl_3) δ : 194.4, 160.9, 149.5, 138.3, 134.4, 133.8, 132.6 (2C), 132.4, 128.2, 127.2, 126.1, 124.3, 114.5 (2C), 55.4, 32.5 ppm.

4.61. 2-[Benzo[1,3]dioxol-5-yl-methylene]-indan-1-one (**5n**)⁴⁶

Following the general procedure C starting from piperonal (751 mg, 5 mmol), enone **5n** was obtained as a white solid (2.40 g, 91 %). ^1H NMR (500 MHz, CDCl_3) δ : 7.90 (1H, d, $J = 7.6\text{ Hz}$), 7.62-7.55 (3H, m), 7.42 (1H, t, $J = 7.4\text{ Hz}$), 7.21-7.19 (2H, m), 6.04 (2H, s), 4.00 (2H, s) ppm. ^{13}C NMR (125 MHz, CDCl_3) δ : 194.3, 149.4, 149.1, 148.3, 138.2, 134.5, 133.9, 132.8, 129.8, 127.7, 127.0, 126.1, 124.4, 109.5, 108.9, 101.7, 32.5 ppm.

4.62. (E)-2-(4-(trifluoromethyl)benzylidene)-2,3-dihydro-1H-inden-1-one (**5o**)⁴⁵

Following the general procedure C starting from 4-(trifluoromethyl)benzaldehyde (683 μL , 5 mmol), enone **5o** was obtained as a white solid (2.60 g, 90 %). ^1H NMR (500 MHz, CDCl_3) δ : 7.92 (1H, d, $J = 7.8\text{ Hz}$), 7.78-7.77 (2H, m), 7.72-7.71 (2H, m), 7.68-7.66 (1H, br. s), 7.66-7.64 (1H, m), 7.59-7.57 (1H, m), 7.47-7.44 (1H, m), 4.07 (2H, s) ppm. ^{13}C NMR (125 MHz, CDCl_3) δ : 194.0, 149.5, 138.8, 138.8, 137.7, 136.9, 135.1, 132.0, 130.9 (q, $J = 32.7\text{ Hz}$, 1C), 130.6, 127.9, 126.3, 125.8 (q, $J = 3.8\text{ Hz}$, 1C), 124.7, 32.3 ppm. ^{19}F NMR (500 MHz, CDCl_3) δ : -62.79 ppm.

4.63. (E)-2-(4-Dimethylaminobenzylidene)-indan-1-one (**5p**)⁴⁶

Following the general procedure C starting from 4-(dimethylamino)benzaldehyde (756 mg, 5 mmol), enone **5p** was obtained as a yellow solid (1.57 g, 60 %). ^1H NMR (500 MHz, CDCl_3) δ : 7.89 (1H, d, $J = 7.7\text{ Hz}$), 7.64 (1H, br. s), 7.60-7.53 (4H, m), 7.42-7.40 (1H, m), 6.76-6.74 (2H, m), 3.98 (2H, s), 3.04 (6H, s) ppm. ^{13}C NMR (125 MHz, CDCl_3) δ : 194.4, 151.2, 149.4, 138.8, 135.0, 133.8, 132.8 (2C), 129.9, 127.4, 126.0, 124.1, 123.3, 111.9 (2C), 40.1 (2C), 32.7 ppm.

4.64. (E)-2-(furan-2-ylmethylene)-2,3-dihydro-1H-inden-1-one (**5q**)⁴⁷

Following the general procedure C starting from furfural (414 μL , 5 mmol), enone **5q** was obtained as a yellow solid (1.3 g, 62 %). ^1H NMR (500 MHz, CDCl_3) δ : 7.88 (1H, d, $J = 7.8\text{ Hz}$), 7.63-7.59 (2H, m), 7.54 (1H, d, $J = 7.8\text{ Hz}$), 7.46-7.45 (1H, m), 7.41 (1H, t, $J = 7.5\text{ Hz}$), 6.76 (1H, d, $J = 3.3\text{ Hz}$), 6.56-6.52 (1H, m), 4.04 (2H, s) ppm. ^{13}C NMR (125 MHz, CDCl_3) δ : 194.0, 152.3, 149.8, 145.4, 138.5, 134.5, 132.6, 127.5, 126.2, 124.2, 120.1, 116.6, 112.7, 32.4 ppm.

4.65. (E)-2-(thiophen-2-ylmethylene)-2,3-dihydro-1H-inden-1-one (**5r**)⁴⁷

Following the general procedure C starting from 2-thiophenecarboxaldehyde (469 μL , 5 mmol), enone **5r** was obtained as a white solid (1.77 g, 80 %). ^1H NMR (500 MHz, CDCl_3) δ : 7.90-7.89 (2H, m), 7.63-7.56 (3H, m), 7.45-7.41 (2H, m), 7.18 (1H, dd, $J = 5.0, 3.7\text{ Hz}$), 3.93 (2H, s) ppm. ^{13}C NMR (125 MHz, CDCl_3) δ : 193.8, 149.0, 139.9, 138.5, 134.6, 133.1, 132.8, 130.55, 128.2, 127.7, 126.6, 126.2, 124.3, 32.3 ppm.

4.66. (E)-2-((1H-pyrrol-2-yl)methylene)-2,3-dihydro-1H-inden-1-one (**5s**)⁴⁸

Following the general procedure C starting from pyrrole-2-carboxaldehyde (476 mg, 5 mmol), enone **5s** was obtained as a yellow solid (1.77 g, 80 %). ^1H NMR (500 MHz, CDCl_3) δ : 9.17-8.98 (1H, br. s), 7.89 (1H, d, $J = 7.6\text{ Hz}$), 7.67 (1H, br. s), 7.62-7.59 (1H, m), 7.56-7.55 (1H, m), 7.44-7.41 (1H, m), 7.09-7.08 (1H, m), 6.76 (1H, br. s), 6.44-6.42 (1H, m), 3.90 (2H, s) ppm. ^{13}C NMR (125 MHz, CDCl_3) δ : 194.1, 148.9, 134.2, 129.4, 129.3, 127.6, 126.1, 124.1, 123.7, 122.9, 114.9, 112.0, 32.4 ppm.

4.67. 1,3-Diphenyl-1-propanone (**6a**)^{19d}

Following the general procedure A, starting from chalcone (107 mg, 0.5 mmol), **Fe** (5 mg, 0.01 mmol), Me_3NO (1 mg, 0.0126 mmol) and potassium formate (210 mg, 2.5 mmol) for 24 h at 45 $^\circ\text{C}$, the corresponding ketone **6a** was obtained as a white powder (99 mg, 94 %) after purification by flash column chromatography on silica (eluent: pentane/AcOEt [95:5]). ^1H NMR (500 MHz, CDCl_3) δ : 7.95 (2H, d, $J = 7.8\text{ Hz}$), 7.56 (1H, t, $J = 7.4\text{ Hz}$), 7.46 (2H, t, $J = 7.7\text{ Hz}$), 7.30 (2H, t, $J = 7.6\text{ Hz}$), 7.27-7.20 (5H, m), 3.31 (2H, t, $J = 7.7\text{ Hz}$), 3.08 (2H, t, $J = 7.7\text{ Hz}$) ppm. ^{13}C NMR (125 MHz, CDCl_3) δ : 199.3, 141.3, 136.9, 133.1, 128.6, 128.5, 128.4, 128.1, 126.2, 40.5, 30.2 ppm.

4.68. 1-(4-Methoxyphenyl)-3-(3,4,5-trimethoxyphenyl)-1-propanone (**6b**)^{19d}

Following the general procedure A, starting from enone (164 mg, 0.5 mmol), **Fe** (5 mg, 0.01 mmol), Me_3NO (1 mg, 0.0126 mmol) and potassium formate (210 mg, 2.5 mmol) for 24 h at 45 $^\circ\text{C}$, the corresponding ketone **6b** was obtained as a white powder (161 mg, 98 %) after purification by flash column chromatography on silica (eluent: pentane/AcOEt [95:5]). ^1H NMR (500 MHz, CDCl_3) δ : 7.93 (2H, d, $J = 8.6\text{ Hz}$), 6.92 (2H, d, $J = 8.6\text{ Hz}$), 6.45 (2H, s), 3.85 (3H, s), 3.83 (6H, s), 3.81 (3H, s), 3.23 (2H, t, $J = 7.6\text{ Hz}$), 2.99 (2H, t, $J = 7.6\text{ Hz}$) ppm. ^{13}C NMR (125 MHz, CDCl_3) δ : 197.8, 163.5, 153.2, 137.3, 136.3, 130.3, 130, 113.8, 105.3, 60.9, 56.1, 55.5, 40.3, 30.8 ppm.

4.69. 3-(4-fluorophenyl)-1-(4-methoxyphenyl)propan-1-one (**6c**)^{19d}

Following the general procedure A, starting from enone (128 mg, 0.5 mmol), **Fe** (5 mg, 0.01 mmol), Me_3NO (1 mg, 0.0126 mmol) and potassium formate (252 mg, 3 mmol) for 24 h at 45 $^\circ\text{C}$, the corresponding ketone **6c** was obtained as a white powder (109 mg, 85 %) after purification by flash column chromatography on silica (eluent: pentane/AcOEt [95:5]). ^1H NMR (500 MHz, CDCl_3) δ : 7.93 (2H, d, $J = 8.5\text{ Hz}$), 7.20 (2H, t, $J = 6.7\text{ Hz}$), 6.97 (2H, t, $J = 8.5\text{ Hz}$), 6.92 (2H, d, $J = 8.5\text{ Hz}$), 3.86 (3H, s), 3.22 (2H, t, $J = 7.6\text{ Hz}$), 3.03 (2H, t, $J = 7.5\text{ Hz}$) ppm. ^{13}C NMR (125 MHz, CDCl_3) δ : 197.6, 163.5, 162.4 (d, $J_{\text{C-F}} = 243.8\text{ Hz}$), 137.1 (d, $J_{\text{C-F}} = 3.1\text{ Hz}$), 130.3, 129.9, 129.8 (d, $J_{\text{C-F}} = 7.8\text{ Hz}$), 115.2 (d, $J_{\text{C-F}} = 21.1\text{ Hz}$), 113.8, 55.5, 40.1, 29.5 ppm. ^1H NMR (500 MHz, CDCl_3) δ : -117.4 ppm.

4.70. 1-(4-methoxyphenyl)-3-(4-nitrophenyl)propan-1-one (**6d**)⁴⁴

Following the general procedure A, starting from enone (143 mg, 0.5 mmol), **Fe** (5 mg, 0.01 mmol), Me_3NO (1 mg, 0.0126 mmol) and potassium formate (210 mg, 2.5 mmol) for 24 h at 45 $^\circ\text{C}$, the corresponding ketone **6d** was obtained as a white powder (86 mg, 60 %) after purification by flash column chromatography on silica (eluent: pentane/AcOEt [90:10]). ^1H NMR (500 MHz, CDCl_3) δ : 8.15 (2H, d, $J = 8.7\text{ Hz}$), 7.93 (2H, d, $J = 9.0\text{ Hz}$), 7.42 (2H, d, $J = 8.7\text{ Hz}$), 6.93 (2H, d, $J = 9.0\text{ Hz}$), 3.87 (3H, s), 3.30

(2H, t, $J = 7.3$ Hz), 3.17 (2H, t, $J = 7.3$ Hz) ppm. ^{13}C NMR (125 MHz, CDCl_3) δ : 196.7, 163.7, 149.4, 146.5, 130.3, 129.6, 129.4, 123.8, 113.9, 55.5, 39.1, 29.9 ppm.

4.71. 1-(4-bromophenyl)-3-phenylpropan-1-one (**6e**)

Following the general procedure A, starting from enone (144 mg, 0.5 mmol), **Fe** (5 mg, 0.01 mmol), Me_3NO (1 mg, 0.0126 mmol) and potassium formate (210 mg, 2.5 mmol) for 24 h at 45 °C, the corresponding ketone **6e** was obtained as a white powder (92 mg, 64 %) after purification by flash column chromatography on silica (eluent: pentane/AcOEt [95:5]); n_{max} (liquid film) 3025, 2924, 1681, 1603, 1581, 1494, 1452, 1394, 1359, 1329, 1289, 1202, 1179, 1101, 1071, 1054, 1028, 1008, 976, 844, 829, 778, 743, 698, 627, 557, 521 cm^{-1} . ^1H NMR (500 MHz, CDCl_3) δ : 7.71 (2H, d, $J = 8.5$ Hz), 7.48 (2H, d, $J = 8.5$ Hz), 7.20 (2H, t, $J = 7.5$ Hz), 7.15-7.09 (3H, m), 3.16 (2H, t, $J = 7.6$ Hz), 2.9 (2H, t, $J = 7.6$ Hz) ppm. ^{13}C NMR (125 MHz, CDCl_3) δ : 198.2, 141.1, 135.6, 132, 129.6, 128.6, 128.5, 128.3, 126.3, 40.5, 30.1. HRMS: MH^+ , found: 289.0230. $\text{C}_{15}\text{H}_{14}\text{OBr}$ requires 289.0228.

4.72. 1-(4-Bromophenyl)-3-(2-methoxyphenyl)-1-propanone (**6f**)^{19d}

Following the general procedure A, starting from enone (159 mg, 0.5 mmol), **Fe** (5 mg, 0.01 mmol), Me_3NO (1 mg, 0.0126 mmol) and potassium formate (210 mg, 2.5 mmol) for 24 h at 45 °C, the corresponding ketone **6f** was obtained as a white powder (123 mg, 77 %) after purification by flash column chromatography on silica (eluent: pentane/AcOEt [95:5]). ^1H NMR (500 MHz, CDCl_3) δ : 7.84 (2H, d, $J = 8.5$ Hz), 7.58 (2H, d, $J = 8.5$ Hz), 7.24-7.19 (2H, m), 6.92-6.86 (2H, m), 3.83 (3H, s), 3.23 (2H, t, $J = 7.7$ Hz), 3.04 (2H, t, $J = 7.7$ Hz) ppm. ^{13}C NMR (125 MHz, CDCl_3) δ : 198.9, 157.5, 135.7, 131.9, 130.2, 129.7, 129.3, 128.1, 127.7, 120.6, 110.3, 55.2, 38.9, 25.8 ppm.

4.73. 1,3-bis(4-bromophenyl)propan-1-one (**6g**)

Following the general procedure A, starting from enone (183 mg, 0.5 mmol), **Fe** (5 mg, 0.01 mmol), Me_3NO (1 mg, 0.0126 mmol) and potassium formate (210 mg, 2.5 mmol) for 24 h at 45 °C, the corresponding ketone **6g** was obtained as a white powder (145 mg, 79 %) after purification by flash column chromatography on silica (eluent: pentane/AcOEt [95:5]); n_{max} (liquid film) 2922, 1740, 1682, 1584, 1486, 1447, 1396, 1360, 1290, 1267, 1199, 1178, 1102, 1068, 1008, 977, 840, 807, 771, 711, 689, 565, 523 cm^{-1} . ^1H NMR (500 MHz, CDCl_3) δ : 7.79 (2H, d, $J = 8.1$ Hz), 7.59 (2H, d, $J = 8.4$ Hz), 7.40 (2H, d, $J = 8.1$ Hz), 7.11 (2H, d, $J = 7.8$ Hz), 3.23 (2H, t, $J = 7.6$ Hz), 3.01 (2H, t, $J = 7.4$ Hz) ppm. ^{13}C NMR (125 MHz, CDCl_3) δ : 197.8, 140, 135.4, 132, 131.6, 130.3, 129.6, 128.4, 120.0, 40.1, 29.3 ppm. HRMS: MH^+ , found: 366.9334. $\text{C}_{15}\text{H}_{13}\text{OBr}_2$ requires 366.9333.

4.74. 1-(2-Furanyl)-3-phenyl-2-propanone (**6h**)^{19d}

Following the general procedure A, starting from enone (99 mg, 0.5 mmol), **Fe** (5 mg, 0.01 mmol), Me_3NO (1 mg, 0.0126 mmol) and potassium formate (210 mg, 2.5 mmol) for 24 h at 45 °C, the corresponding ketone **6h** was obtained as a white powder (80 mg, 80 %) after purification by flash column chromatography on silica (eluent: pentane/AcOEt [95:5]). ^1H NMR (500 MHz, CDCl_3) δ : 7.57 (1H, dd, $J = 0.8$ Hz), 7.31-7.16 (6H, m), 6.52 (1H, dd, $J = 1.7$ Hz), 3.16 (2H, t, $J = 7.7$ Hz), 3.05 (2H, t, $J = 7.7$ Hz) ppm. ^{13}C NMR (125 MHz, CDCl_3) δ : 188.5, 152.7, 146.3, 141, 128.5, 128.4, 126.2, 117.1, 112.2, 40.2, 30.0 ppm.

4.75. 3-Phenyl-1-(2-thienyl)-2-propanone (**6i**)^{19d}

Following the general procedure A, starting from enone (107 mg, 0.5 mmol), **Fe** (5 mg, 0.01 mmol), Me_3NO (1 mg, 0.0126 mmol) and potassium formate (210 mg, 2.5 mmol) for 24 h at 45 °C, the corresponding ketone **6i** was obtained as a white powder (84 mg, 78 %) after purification by flash column chromatography on silica (eluent: pentane/AcOEt [95:5]). ^1H NMR (500 MHz, CDCl_3) δ : 7.69 (1H, d, $J = 3.8$ Hz), 7.62 (1H, d, $J = 4.9$ Hz), 7.32-7.19 (5H, m), 7.11 (1H, t, $J = 3.8$ Hz), 3.24 (2H, t, $J = 7.8$ Hz), 3.08 (2H, t, $J = 7.8$ Hz) ppm. ^{13}C NMR (125 MHz, CDCl_3) δ : 192.2, 144.2, 141, 133.6, 131.8, 128.6 (2C), 128.5 (2C), 128.1, 126.3, 41.2, 30.4 ppm.

4.76. 3-Phenyl-1-(1H-pyrrol-2-yl)-2-propanone (**6j**)^{19d}

Following the general procedure A, starting from enone (99 mg, 0.5 mmol), **F** (5 mg, 0.01 mmol), Me_3NO (1 mg, 0.0126 mmol) and potassium formate (210 mg, 2.5 mmol) for 24 h at 45 °C, the corresponding ketone **6j** was obtained as a white powder (98 mg, 98 %) after purification by flash column chromatography on silica (eluent: pentane/AcOEt [95:5]). ^1H NMR (500 MHz, CDCl_3) δ : 9.37 (1H, s, (NH)), 7.23 (2H, t, $J = 7.4$ Hz), 7.18-7.11 (4H, m), 6.95 (1H, td, $J = 1.6, 1.3$ Hz), 6.83-6.81 (1H, m), 6.20-6.19 (1H, m), 3.05-3.02 (2H, m), 2.99-2.95 (2H, m) ppm. ^{13}C NMR (125 MHz, CDCl_3) δ : 189.6, 141.3, 131.8, 128.5, 128.4, 126.2, 124.4, 116, 110.7, 39.6, 30.8 ppm.

4.77. 2-Methyl-1,5-diphenyl-1-pentanone (**6k**)^{19d}

Following the general procedure A, starting from enone (126 mg, 0.5 mmol), **Fe** (5 mg, 0.01 mmol), Me_3NO (1 mg, 0.0126 mmol) and potassium formate (210 mg, 2.5 mmol) for 24 h at 45 °C, the corresponding ketone **6k** was obtained as a colorless oil (56 mg, 44 %) after purification by flash column chromatography on silica (eluent: pentane/Et₂O [95:5]). ^1H NMR (500 MHz, CDCl_3) δ : 7.93 (2H, d, $J = 7.5$ Hz), 7.55 (1H, t, $J = 7.3$ Hz), 7.46 (2H, t, $J = 7.7$ Hz), 7.27-7.24 (2H, m), 7.18-7.14 (3H, m), 3.48 (1H, sext., $J = 6.8$ Hz), 2.61 (2H, ABX₂, $J_{AB} = 12.7$ Hz, $J_{AX} = 6.0$ Hz, $J_{BX} = 6.0$ Hz), 1.92-1.84 (1H, m), 1.65 (2H, qt, $J = 7.8$ Hz), 1.54-1.48 (1H, m), 1.20 (3H, d, $J = 6.8$ Hz) ppm. ^{13}C NMR (125 MHz, CDCl_3) δ : 204.4, 142.2, 136.7, 132.9, 128.7, 128.4, 128.3, 128.2, 126.8, 40.5, 36.0, 33.3, 29.2, 17.4 ppm.

4.78. 2-benzyl-2,3-dihydro-1H-inden-1-one (**6l**)

Following the general procedure A, starting from enone **5l** (110 mg, 0.5 mmol), **Fe** (5 mg, 0.01 mmol), Me_3NO (1 mg, 0.0126 mmol) and potassium formate (210 mg, 2.5 mmol) for 24 h at 45 °C, the corresponding ketone **6l** was obtained as a colorless oil (99 mg, 89 %) after purification by flash column chromatography on silica (eluent: pentane/AcOEt [90:10]); n_{max} (liquid film) 3027, 2920, 2852, 1705, 1603, 1496, 1464, 1453, 1432, 1327, 1289, 1274, 1207, 1181, 1150, 1092, 1092, 1030, 1001, 953, 897, 879, 822, 777, 741, 699, 628, 608, 587, 545 cm^{-1} . ^1H NMR (500 MHz, CDCl_3) δ : 7.79 (1H, d, $J = 7.5$ Hz), 7.57 (1H, td, $J = 7.5, 1.1$ Hz), 7.40 (1H, dt, $J = 7.6, 0.8$ Hz), 7.37 (1H, td, $J = 7.8, 0.7$ Hz), 7.32-7.29 (2H, m), 7.26-7.21 (3H, m), 3.41 (1H, ABX, $J_{AB} = 14.0$ Hz, $J_{AX} = 4.3$ Hz), 3.17 (1H, ABX, $J_{AB} = 17.2$ Hz, $J_{AX} = 7.9$ Hz), 3.01 (1H, ddt, $J = 10.4, 7.9, 4.0$ Hz), 2.86 (1H, ABX, $J_{AB} = 17.1$ Hz, $J_{AX} = 4.0$ Hz), 2.67 (1H, ABX, $J_{AB} = 13.9$ Hz, $J_{AX} = 10.4$ Hz) ppm. ^{13}C NMR (125 MHz, CDCl_3) δ : 207.9, 153.7, 139.7, 136.6, 134.9, 128.9, 128.6, 127.5, 126.6, 126.4, 124.1, 49.0, 37.0, 32.2 ppm. HRMS: MH^+ , found: 223.1123. $\text{C}_{16}\text{H}_{15}\text{O}$ requires 223.1123.

4.79. 2-(4-methoxybenzyl)-2,3-dihydro-1H-inden-1-one (**6m**)

Following the general procedure A, starting from enone **5m** (126 mg, 0.5 mmol), **Fe** (5 mg, 0.01 mmol), Me_3NO (1 mg, 0.0126

mmol) and potassium formate (210 mg, 2.5 mmol) for 24 h at 45 °C, the corresponding ketone **6m** was obtained as a colorless oil (123 mg, 97 %) after purification by flash column chromatography on silica (eluent: pentane/AcOEt [90:10]); n_{max} (liquid film) 3030, 2931, 2835, 1705, 1609, 1585, 1511, 1463, 1433, 1324, 1294, 1272, 1244, 1207, 1177, 1151, 1108, 1092, 1032, 1002, 811, 796, 758, 729, 679, 621, 602, 589, 572, 564 cm^{-1} . ^1H NMR (500 MHz, CDCl_3) δ : 7.77 (1H, d, $J = 7.4$ Hz), 7.57 (1H, td, $J = 7.0, 0.9$ Hz), 7.40 (1H, d, $J = 7.7$ Hz), 7.36 (1H, t, $J = 7.4$ Hz), 7.16 (2H, d, $J = 8.4$ Hz), 6.83 (2H, d, $J = 8.7$ Hz), 3.79 (3H, s), 3.31 (1H, ABX, $J_{AB} = 14.1$ Hz, $J_{AX} = 4.3$ Hz), 3.16 (1H, ABX, $J_{AB} = 17.2$ Hz, $J_{AX} = 7.8$ Hz), 2.97 (1H, ABX, $J_{AB} = 8$ Hz, $J_{AX} = 4$ Hz), 2.85 (1H, ABX, $J_{AB} = 17.2$ Hz, $J_{AX} = 3.9$ Hz), 2.65 (1H, ABX, $J_{AB} = 14$ Hz, $J_{AX} = 10.2$ Hz) ppm. ^{13}C NMR (125 MHz, CDCl_3) δ : 208.1, 158.2, 153.7, 136.6, 134.8, 131.6, 129.9, 127.4, 126.6, 124.2, 113.9, 55.3, 49.2, 36.1, 32.1 ppm. HRMS: MH^+ , found: 253.1232. $\text{C}_{17}\text{H}_{17}\text{O}_2$ requires 253.1229.

4.80. 2-(benzo[d][1,3]dioxol-5-ylmethyl)-2,3-dihydro-1H-inden-1-one (**6n**)

Following the general procedure A, starting from enone **5n** (132 mg, 0.5 mmol), **Fe** (5 mg, 0.01 mmol), Me_3NO (1 mg, 0.0126 mmol) and potassium formate (210 mg, 2.5 mmol) for 24 h at 45 °C, the corresponding ketone **6n** was obtained as a white powder (111 mg, 83 %) after purification by flash column chromatography on silica (eluent: Pentane/AcOEt [90:10]); n_{max} (liquid film) 3073, 2904, 2783, 1702, 1608, 1587, 1502, 1489, 1465, 1441, 1364, 1330, 1296, 1281, 1247, 1232, 1208, 1188, 1153, 1118, 1098, 1035, 1003, 959, 928, 898, 879, 843, 807, 789, 765, 748, 721, 685, 641, 602, 585, 573, 549, 521 cm^{-1} . ^1H NMR (500 MHz, CDCl_3) δ : 7.77 (1H, d, $J = 7.7$ Hz), 7.57 (1H, td, $J = 7.4, 0.9$ Hz), 7.41 (1H, d, $J = 7.7$ Hz), 7.37 (1H, t, $J = 7.4$ Hz), 6.74 (1H, d, $J = 1.6$ Hz), 6.73 (1H, s), 6.68 (1H, dd, $J = 6.5, 1.4$ Hz), 5.93 (2H, s), 3.29 (1H, ABX, $J_{AB} = 14.1, 4.4$ Hz), 3.17 (1H, ABX, $J_{AB} = 17.1$ Hz, $J_{AX} = 7.8$ Hz), 2.94 (1H, ABX, $J_{AB} = 7.7$ Hz, $J_{AX} = 4.0$ Hz), 2.86 (1H, ABX, $J_{AB} = 17.1, J_{AX} = 4.1$ Hz), 2.62 (1H, ABX, $J_{AB} = 14.1$ Hz, $J_{AX} = 10.2$ Hz) ppm. ^{13}C NMR (125 MHz, CDCl_3) δ : 207.8, 153.7, 147.7, 146.1, 136.6, 134.9, 133.4, 127.5, 126.6, 124.1, 121.9, 109.3, 108.3, 100.9, 49.1, 36.7, 32.1 ppm. HRMS: MH^+ , found: 267.1022. $\text{C}_{17}\text{H}_{15}\text{O}_3$ requires 267.1021.

4.81. 2-(4-(trifluoromethyl)benzyl)-2,3-dihydro-1H-inden-1-one (**6o**)

Following the general procedure A, starting from enone **5o** (144 mg, 0.5 mmol), **Fe** (5 mg, 0.01 mmol), Me_3NO (1 mg, 0.0126 mmol) and potassium formate (210 mg, 2.5 mmol) for 24 h at 45 °C, the corresponding ketone **6o** was obtained as a white powder (114 mg, 79 %) after purification by flash column chromatography on silica (eluent: pentane/AcOEt [90:10]); n_{max} (liquid film) 2918, 2852, 1696, 1607, 1584, 1466, 1444, 1427, 1325, 1296, 1207, 1196, 1185, 1163, 1150, 1110, 1066, 1017, 1005, 953, 911, 876, 811, 788, 758, 744, 729, 717, 688, 642, 628, 611, 594 cm^{-1} . ^1H NMR (500 MHz, CDCl_3) δ : 7.79 (1H, d, $J = 10$ Hz), 7.59 (1H, td, $J = 7.5, 1.0$ Hz), 7.56 (2H, d, $J = 8.1$ Hz), 7.41 (1H, td, $J = 7.9, 0.8$ Hz), 7.36 (3H, d, $J = 10$ Hz), 3.43 (1H, ABX, $J_{AB} = 14.1$ Hz, $J_{AX} = 4.3$ Hz), 3.20 (1H, ABX, $J_{AB} = 17.2$ Hz, $J_{AX} = 7.9$ Hz), 3.01 (1H, ABX, $J_{AB} = 7.9$ Hz, $J_{AX} = 4.0$ Hz), 2.83 (1H, ABX, $J_{AB} = 17.2$ Hz, $J_{AX} = 4.2$ Hz), 2.77 (1H, ABX, $J_{AB} = 14.1$ Hz, $J_{AX} = 10.1$ Hz) ppm. ^{13}C NMR (125 MHz, CDCl_3) δ : 207.2, 153.3, 143.8, 136.4, 135, 129.3, 127.6, 126.6, 126.5 (1C, q, $J_{C-F} = 3.7$ Hz), 123.2, 48.6, 36.7, 32.1 ppm. ^{19}F NMR (500 MHz, CDCl_3) δ : -62.37 ppm. HRMS: MH^+ , found: 291.1005. $\text{C}_{17}\text{H}_{14}\text{OF}_3$ requires 291.0997.

4.82. 2-(4-(dimethylamino)benzyl)-2,3-dihydro-1H-inden-1-one (**6p**)

Following the general procedure A, starting from enone **5p** (131 mg, 0.5 mmol), **Fe** (5 mg, 0.01 mmol), Me_3NO (1 mg, 0.0126 mmol) and potassium formate (210 mg, 2.5 mmol) for 24 h at 45 °C, the corresponding ketone **6p** was obtained as a yellow oil (44 mg, 33 %) after purification by flash column chromatography on silica (eluent: pentane/AcOEt [90:10]); n_{max} (liquid film) 2916, 2849, 2800, 1705, 1676, 1610, 1519, 1463, 1444, 1433, 1340, 1293, 1273, 1207, 1164, 1151, 1115, 1093, 1060, 1042, 1001, 980, 946, 897, 824, 804, 786, 754, 727, 673, 625, 601, 555, 513 cm^{-1} . ^1H NMR (500 MHz, CDCl_3) δ : 7.77 (1H, d, $J = 7.7$ Hz), 7.56 (1H, td, $J = 7.4, 0.9$ Hz), 7.40 (1H, d, $J = 7.7$ Hz), 7.36 (1H, t, $J = 7.4$ Hz), 7.12 (2H, d, $J = 8.5$ Hz), 6.70 (2H, d, $J = 8.2$ Hz), 3.30 (1H, ABX, $J_{AB} = 14.0$ Hz, $J_{AX} = 4.3$ Hz), 3.16 (1H, ABX, $J_{AB} = 17.2$ Hz, $J_{AX} = 7.7$ Hz), 2.96-2.90 (1H, m), 2.92 (6H, s), 2.88 (1H, ABX, $J_{AB} = 17.2$ Hz, $J_{AX} = 3.9$ Hz), 2.59 (1H, ABX, $J_{AB} = 14.0$ Hz, $J_{AX} = 10.4$ Hz) ppm. ^{13}C NMR (125 MHz, CDCl_3) δ : 208.3, 153.9, 136.7, 134.7, 129.6, 127.4, 126.6, 124.0, 112.9, 49.3, 40.8, 36.1, 32.2 ppm. HRMS: MH^+ , found: 266.1543. $\text{C}_{18}\text{H}_{20}\text{NO}$ requires 266.1545.

4.83. 2-(furan-2-ylmethyl)-2,3-dihydro-1H-inden-1-one (**6q**)

Following the general procedure A, starting from enone **5q** (105 mg, 0.5 mmol), **Fe** (5 mg, 0.01 mmol), Me_3NO (1 mg, 0.0126 mmol) and potassium formate (210 mg, 2.5 mmol) for 24 h at 45 °C, the corresponding ketone **6q** was obtained as a yellow oil (80 mg, 71 %) after purification by flash column chromatography on silica (eluent: pentane/AcOEt [90:10]); n_{max} (liquid film) 2918, 2848, 1706, 1607, 1506, 1464, 1431, 1382, 1328, 1293, 1277, 1207, 1181, 1148, 1093, 1075, 1042, 1010, 953, 929, 884, 798, 757, 724, 670, 651, 599, 584, 552 cm^{-1} . ^1H NMR (500 MHz, CDCl_3) δ : 7.78 (1H, d, $J = 8.11$ Hz), 7.58 (1H, td, $J = 7.5, 1.1$ Hz), 7.43 (1H, dt, $J = 7.6, 0.8$ Hz), 7.37 (1H, td, $J = 7.0, 0.8$ Hz), 7.29 (1H, q, $J = 0.8$ Hz), 6.27 (1H, q, $J = 1.9$ Hz), 6.06 (1H, q, $J = 0.9$ Hz), 3.32 (1H, ABX, $J_{AB} = 14.7$ Hz, $J_{AX} = 4.5$ Hz), 3.31 (1H, ABX, $J_{AB} = 17.3$ Hz, $J_{AX} = 7.8$ Hz), 3.05-2.99 (1H, m), 2.93 (1H, ABX, $J_{AB} = 15.2$ Hz, $J_{BX} = 9.7$ Hz), 2.8 (1H, ABX, $J_{AB} = 15.4$ Hz, $J_{BX} = 9.7$ Hz). ^{13}C NMR (125 MHz, CDCl_3) δ : 207.3, 153.7, 153.6, 141.5, 136.4, 134.9, 127.5, 126.6, 124.1, 110.2, 106.4, 46.5, 32.5, 29.4 ppm. HRMS: MH^+ , found: 213.0911. $\text{C}_{14}\text{H}_{13}\text{O}_2$ requires 213.0910.

4.84. 2-(thiophen-2-ylmethyl)-2,3-dihydro-1H-inden-1-one (**6r**)

Following the general procedure A, starting from enone **5r** (113 mg, 0.5 mmol), **Fe** (5 mg, 0.01 mmol), Me_3NO (1 mg, 0.0126 mmol) and potassium formate (210 mg, 2.5 mmol) for 24 h at 45 °C, the corresponding ketone **6r** was obtained as a white powder (92 mg, 81 %) after purification by flash column chromatography on silica (eluent: pentane/AcOEt [95:5]); n_{max} (liquid film) 3069, 2916, 2845, 1705, 1606, 1533, 1464, 1431, 1363, 1326, 1293, 1276, 1260, 1226, 1182, 1151, 1093, 1033, 1001, 979, 952, 895, 867, 850, 824, 800, 755, 743, 722, 693, 625, 559, 540, 514 cm^{-1} . ^1H NMR (500 MHz, CDCl_3) δ : 7.78 (1H, d, $J = 7.5$ Hz), 7.58 (1H, td, $J = 7.4, 1.0$ Hz), 7.43 (1H, dt, $J = 7.7, 0.8$ Hz), 7.37 (1H, td, $J = 7.1, 0.7$ Hz), 7.13 (1H, dd, $J = 5.1, 1.2$ Hz), 6.92 (1H, q, $J = 3.4, 1.6$ Hz), 6.86-6.85 (1H, m), 3.57-3.51 (1H, m), 3.31 (1H, ABX, $J_{AB} = 17$ Hz, $J_{AX} = 7.1$ Hz), 3.04-2.97 (2H, m), 2.94 (1H, ABX, $J_{AB} = 17$ Hz, $J_{AX} = 3.5$ Hz) ppm. ^{13}C NMR (125 MHz, CDCl_3) δ : 207.2, 153.7, 142.0, 136.5, 134.9, 127.5, 126.9, 126.6, 124.1, 123.8, 49.1, 32.4, 31.2 ppm. HRMS: MH^+ , found: 229.0690. $\text{C}_{14}\text{H}_{13}\text{OS}$ requires 229.0687.

4.85. 2-((1H-pyrrol-2-yl)methyl)-2,3-dihydro-1H-inden-1-one (6s)

Following the general procedure A, starting from enone **5s** (105 mg, 0.5 mmol), **Fe** (5 mg, 0.01 mmol), Me₃NO (1 mg, 0.0126 mmol) and potassium formate (210 mg, 2.5 mmol) for 24 h at 45 °C, the corresponding ketone **6s** was obtained as a yellow powder (98 mg, 93 %) after purification by flash column chromatography on silica (eluent: Pentane/Ethyl acetate [90:10]; n_{max} (liquid film) 3405, 3130, 2921, 2852, 1695, 1605, 1569, 1461, 1440, 1420, 1400, 1317, 1294, 1277, 1205, 1151, 1115, 1086, 1043, 1024, 1005, 954, 896, 872, 841, 809, 793, 759, 743, 672, 655, 597, 577, 564 cm⁻¹. ¹H NMR (500 MHz, CDCl₃) δ: 8.81 (1H, s (NH)), 7.76 (1H, d, *J* = 7.6 Hz), 7.58 (1H, td, *J* = 7.4, 1.1 Hz), 7.43 (1H, dt, *J* = 7.6, 0.8 Hz), 7.37 (1H, td, *J* = 7.3, 0.7 Hz), 6.67 (1H, t, *J* = 1.0 Hz), 6.08 (1H, q, *J* = 2.8 Hz), 5.96 (1H, q, *J* = 2.8 Hz), 3.37 (1H, ABX, *J*_{AB} = 16.6 Hz, *J*_{AX} = 7.8 Hz), 3.09 (2H, ABX, *J*_{AB} = 15 Hz, *J*_{AX} = 6.5 Hz, *J*_{BX} = 5.5 Hz), 3.03-2.96 (1H, m), 2.93 (1H, ABX, *J*_{AB} = 16.7 Hz, *J*_{AX} = 4.6 Hz). ¹³C NMR (125 MHz, CDCl₃) δ: 209.5, 153.8, 136.5, 135.1, 129.4, 127.5, 126.6, 124.0, 117.4, 107.8, 106.7, 48.1, 32.6, 29.7, 28.4 ppm. HRMS: MH⁺, found: 212.1077. C₁₄H₁₄NO requires 212.1075.

4.86. 5β-Pregnan-3,20-dione (6t)^{19d}

Following the general procedure A, starting from progesterone (0.5 mmol, 155 mg), **Fe** (5 mg, 0.01 mmol), Me₃NO (1 mg, 0.0126 mmol) and potassium formate (210 mg, 2.5 mmol) for 24 h at 45 °C, the corresponding ketone **6t** was obtained as a single diastereomer and as a white solid (47 mg, 30 %) after purification by flash column chromatography (CH₂Cl₂/EtOAc 1%). ¹H NMR (500 MHz, CDCl₃) δ: 2.69 (1H, t, *J* = 14.3 Hz), 2.55 (1H, t, *J* = 9.0 Hz), 2.34 (1H, td, *J* = 14.3, 5.4 Hz) 2.21-2.14 (2H, m), 2.12 (3H, s), 2.09-2.00 (3H, m), 1.93-1.79 (2H, m), 1.73-1.61 (2H, m), 1.58-1.35 (7H, m), 1.30-1.19 (4H, m), 1.02 (3H, s), 0.63 (3H, s) ppm. ¹³C NMR (125 MHz, CDCl₃) δ: 212.1, 208.5, 62.7, 55.6, 43.1, 41.3, 39.7, 38.3, 36.1, 35.9, 34.6, 34.5, 33.9, 30.5, 26.8, 25.5, 24.7, 23.4, 21.9, 21.6, 20.2, 12.4 ppm.

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Iron-catalyzed chemoselective hydride transfer reactions.

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Sébastien Coufourier,^a Daouda Ndiaye,^{a,b} Quentin Gaignard Gaillard,^a Léo Bettoni,^a Nicolas Joly,^{a,c} Mbaye Diagne Mbaye,^{a,b} Albert Poater,^c Sylvain Gaillard,^a Jean-Luc Renaud.^{a,*}

^a Normandie Univ., LCMT, ENSICAEN, UNICAEN, CNRS, 6 boulevard du Maréchal Juin, 14050 Caen, France

^b Université Assane Seck de Ziguinchor, BP 523, Ziguinchor, Sénégal

^c Departament de Química, Institut de Química Computacional i Catàlisi (IQCC), University of Girona, c/ M^a Aurèlia Capmany 69, 17003 Girona, Catalonia, Spain

