Iron-catalyzed homogeneous hydrogenation with precise temperature-governed chemoselectivity.

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Abstract: The chemoselective hydrogenation of unsaturated compounds has been a powerful tool for both synthetic chemistry and chemical industry. The achievement of chemoselectivity among different functionalities with a single catalyst has been a challenge for transition metal-catalyzed hydrogenation. In this paper, iron tetraphosphine complexes show high catalytic efficiency for a variety of polar unsaturated substrates such as aldehydes, ketones, enones, nitroarenes and *N*-heteroaromatics. Without an N-H group on the catalyst, the chemoselectivity was controlled precisely by the reaction temperature. The catalytic efficiency, chemoselectivity and robustness of this Fe/P_4N_2 catalyst found its merit in the preparation of several important drug intermediates. A diamagnetic *trans*-iron dihydride complex, formed under the reaction conditions, was supposed to be an *on-cycle* catalytically active species.

Keywords: iron; tetraphosphine ligand; homogeneous hydrogenation; chemoselectivity; polar unsaturated compounds.

Transition metal-catalyzed hydrogenation of unsaturated compounds has been a fundamental process in chemical industries. Compared to heterogeneous catalytic hydrogenation, homogeneous processes have enjoyed such potential advantages as milder reaction conditions and better selectivities.[1,2] Recent decades have witnessed the prosperity of transition metal catalysis in homogeneous hydrogenation and noble metal (e.g., ruthenium, rhodium, iridium) complexes have been among the most successful catalysts.[3] However, facing the challenges in high cost and limited availability of noble metals, chemists have showed increasing interest in the discovery of alternatives since the new millennium. Iron, with low cost, vast reserves and mature refining technology, is an ideal alternative to noble metals.[4] Practitioners in organometallic chemistry have spared no efforts in the development of iron catalysts in homogeneous hydrogenation.[5-7] Although some breakthroughs have been made in the hydrogenation of unsaturated compounds such as ketones, esters, nitriles and other carboxylic acid derivatives, challenges have still lied in iron catalysis.

The pursuit of high catalytic efficiency has always been a chief goal. Metal-ligand cooperation (MLC) has been widely adopted in the design of transition metal catalysts.[8] The NH effect, which can reduce the energy barrier in the hydride transfer step in the hydrogenation of polar double bonds (Figure 1), has been a commonly used strategy in ligand design.[9,10] Guided by this concept, tridentate and tetradentate ligand complexes have been prepared and applied in homogeneous hydrogenation of polar double bonds.

Iron PNP pincer complexes have been successfully applied in homogeneous hydrogenation. In previous reports by Milstein[11], Kirchner[12-14], Beller[15-17] et al., MLC has been a core strategy.[18,19] Challenging substrates such as carboxylic acid derivatives could be reduced with molecular hydrogen under a mild condition (100 ~ 140 °C). Either NH or acidic CH_2 moiety was believed to be responsible for the high catalytic efficiency.[20] The lowered energy barrier in the hydride transfer step, in return, somewhat has obstructed chemoselectivity among aldehydes, ketone, conjugated olefins. Moreover, the vacant coordination site *cis* to the hydride ligand creates the potential involvement of C=C bond hydrogenation via inner-sphere mechanism.[21,22]

Diamagnetic iron complexes with a tetradentate ligand merged in the recent decade have been an alternative to iron pincer complexes in the hydrogenation of polar substrates.[23,24] The NH effect was also an important consideration in the design of catalyst. In comparison, some tetradentate ligand such as PP_3 type could form facial iron complexes that have two coordination sites *cis* to each other. Although such complexes could be used in hydrogenation of polar double bonds[15,17], the reduction of nonpolar substrates has still been possible[25]. Based on our previous success in cobalt(I) catalysis, tetraphosphine ligand without MLC is believed to show desired chemoselectivity among different polar substrates.[26] Guided by this rationale, we envisioned that an iron(II) tetradentate ligand complex with a meridional geometry would be suitable for chemoselective hydrogenation of polar double bonds (Figure 1b).

The chemoselectivity has been a far less focused factor in comparison with efficiency. In our perspective, an "ideal" catalyst should meet the requests from *reaction scope*, *chemoselectivity* and *catalytic efficiency*. But these three factors are typically in a paradox since satisfying any two of them normally leads to the failure in the remaining aspect. We herein reported homogeneous hydrogenation of a series of polar unsaturated compounds (aldehydes, ketones, conjugated C=C bonds, nitroarenes and *N*-heteroarenes) with iron/tetraphosphine complexes. In this catalytic system, the reaction temperature dictates the reactivity which is featured with "downward

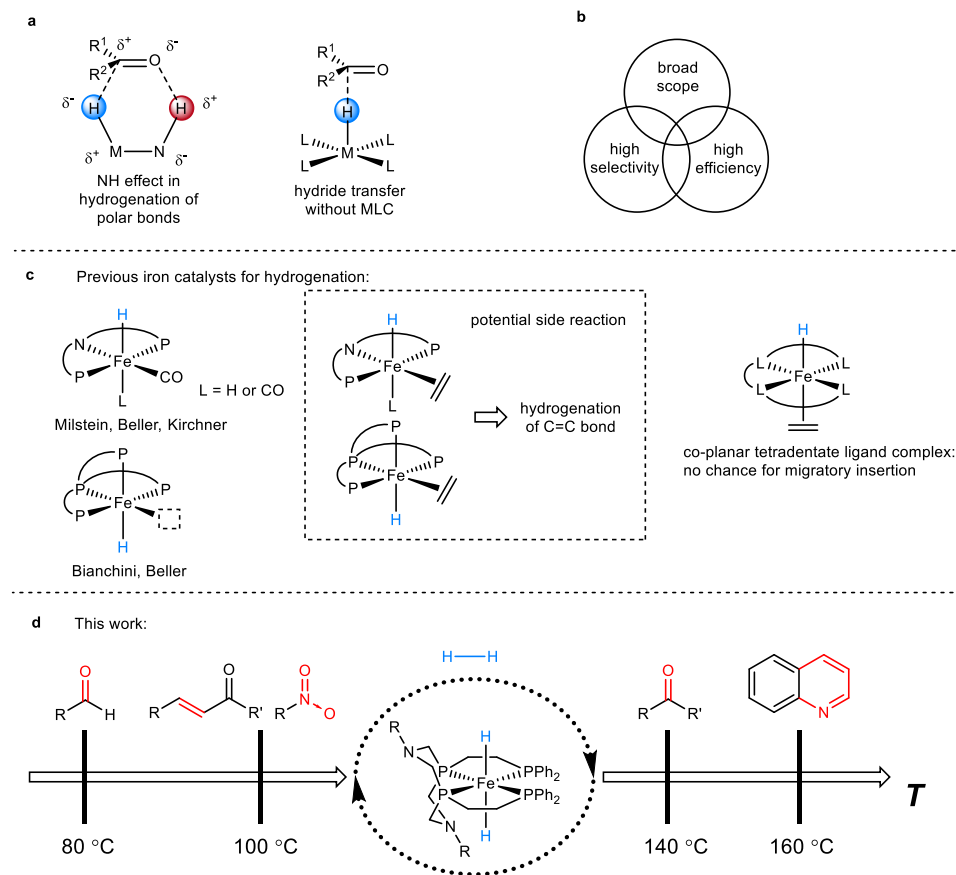compatibility". Remarkable chemoselectivities and efficiencies were observed such Fe/P$_4$N$_2$ complexes.

Fig. 1 Iron-catalyzed homogeneous hydrogenation of polar bonds. a, The hydride transfer step with or without the NH effect as MLC. **b,** Three aspects for a successful catalyst for homogeneous hydrogenation. **c,** Previous iron catalysts with a multidentate ligand with potential involvement of hydrogenation of C=C bonds. **d,** *trans*-Iron dihydride complexes with a co-planar tetraphosphine ligand and its application in hydrogenation of various unsaturated compounds.

Results

The development of iron/tetraphosphine-catalyzed hydrogenation. We selected tetraphosphine ligand C$_2$-P$_4$N$_2$-Bn (**L1**) in the initial assessment of reactivity in iron catalyzed hydrogenation. In order to exploit the chemoselectivity of such system, conjugate carbonyl compound *trans*-cinnamaldehyde was chosen as the targeting substrate. After a screening of iron precursors (with 0.1 mol% catalyst loading at 80 °C and 30 bar H$_2$, isopropanol as the solvent and potassium carbonate as additive), we found that both Fe(II) and Fe(III) showed reactivity towards such unsaturated substrate. However, the reduction of C=C bond was inevitable for several commonly used inorganic iron salts (Table 1, entry 1 ~ 6). Gratefully, we observed a full conversion with no C=C reduction when using iron(II) acetylacetonate (entry 7). When altering the substituent on the pendant amine of the ligand from benzyl to phenyl (**L2**, C$_2$-P$_4$N$_2$-Ph, entry 8), similar reactivity but no side reaction was observed. Elongating the covalent linker between phosphorus atoms of the

ligand (**L3**, C_3-P_4N_2-Ph, entry 9) resulted in eroded conversion and noticeable over-reduction. The application of two equivalent of bisphosphine ligands failed to catalyze this reaction efficiently (entry 10, 11), which suggested the importance of the covalent linker in tetraphosphine ligands. To our surprise, a bonus for the application of such organic iron salt $Fe(acac)_2$ was that this reaction requires no need of external base (entry 12). Although the reaction without base proceeded a bit sluggish compared to that with K_2CO_3, we still chose such conditions for application since an additive-free reaction usually give a large reaction scope.

Table 1. Hydrogenation of *trans*-cinnamaldehyde with various iron precursors and ligands.

entry	[Fe]	Ligand	Conversion	Yield of **2aa**	Yield of **3aa**
1	$Fe(OAc)_2$	**L1**	95%	93%	2%
2	$Fe(ClO_4)_2 \cdot 6H_2O$	**L1**	67%	50%	17%
3	$Fe(BF_4)_2 \cdot 6H_2O$	**L1**	70%	68%	2%
4	$FeCl_2$	**L1**	67%	60%	7%
5	$FeBr_2$	**L1**	92%	90%	2%
6	FeF_3	**L1**	88%	81%	7%
7	$Fe(acac)_2$	**L1**	99%	99%	N.D.
8	$Fe(acac)_2$	**L2**	98%	98%	N.D.
9	$Fe(acac)_2$	**L3**	90%	83%	7%
10	$Fe(acac)_2$	**L4** [a]	< 5%	< 5%	N.A.
11	$Fe(acac)_2$	**dppe** [a]	17%	10%	7%
12 [b]	$Fe(acac)_2$	**L1**	87%	87%	N.D.

Reaction conditions: 0.2 mmol **1aa** in 1.0 mL isopropanol, 0.1 mol% iron precursor, 0.11 mol% ligand, 80 °C, 30 bar hydrogen, 24 hours; conversion and yield were determined by ^{1}H NMR of the crude reaction mixture using 1,2-dichloroethane as the internal standard. [a] 2.2 eq. ligand (relative to iron precursor) was applied; [b] run in the absence of K_2CO_3. N.D., not detected; N.A., not applied.

Reaction scope under different temperature. We the optimized conditions in hand, we first examined the performance of Fe/C_2-P_4N_2-Bn catalyst in hydrogenation of carbonyl groups. Aldehydes could be reduced with molecular hydrogen in this catalytic system at 80 °C (Fig. 2). A variety of α,β-unsaturated aldehydes were hydrogenated to allylic alcohols with remarkably high chemo-discrimination: not only the 1,2-reduction was more favored than the 1,4-addition, the hydrogenation of unfunctionalized C=C bond was not observed. A series of derivatives of

cinnamaldehyde underwent hydrogenation smoothly, regardless the electronic and steric properties of the substitution groups (Fig. 2, **2aa** to **2ai**). When increasing the number of conjugated π-bonds that led to closer energies barrier in 1,2-, 1,4- and 1,6-reduction (**2aj**), the chemoselectivity was still excellent. The heterocycles that might cause inhibition of the catalyst did not bring problems in this chemical transformation (**2ak** and **2al**). Isolated aldehydes were also tested to evaluate the compatibility of other functionalities. Under the same conditions, both aromatic and alkyl aldehydes were reduced smoothly, commonly seen functional groups such as ketone (**2bf**), olefin (**2bg**), ester (**2bh**), alkyne (**2bi**) and nitro groups (**2bl** and **2bm**) survived without any erosion in reactivity. sp^2-C-Br bond, which tends to undergo dehalogenation in hydrogenation with palladium on charcoal, was fully compatible in this iron-catalyzed reaction (**2ae**, **2bd** and **2bl**).
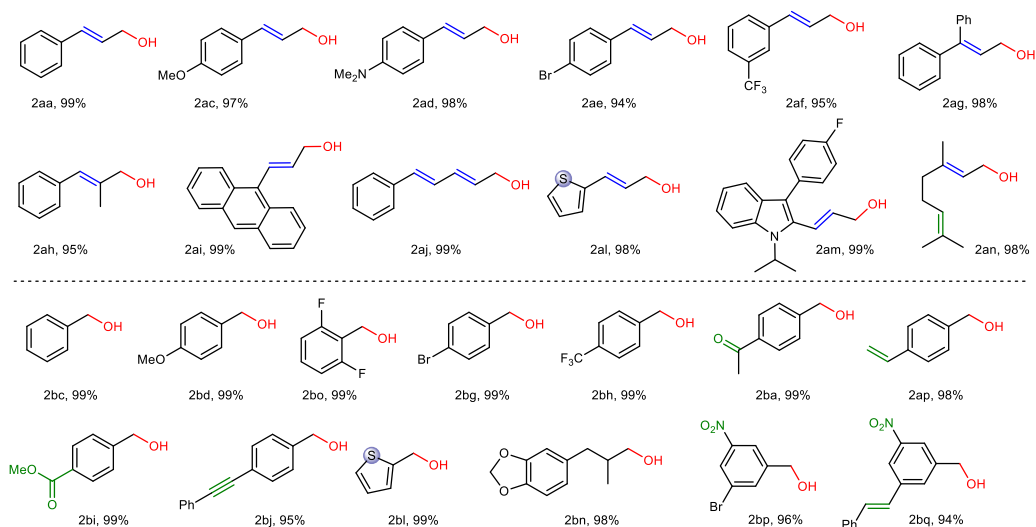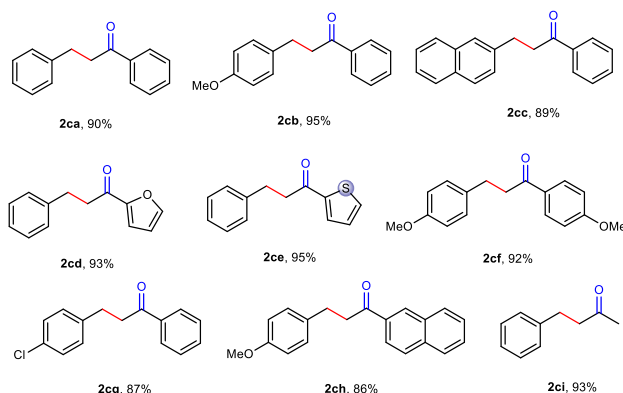
Aldehyde: 80 °C

Fig. 2 Hydrogenation of aldehydes with Fe/C$_2$-P$_4$N$_2$-Bn catalyst. Reaction conditions: 0.2 mmol substrate in 1.0 mL isopropanol, 0.1 mol% Fe(acac)$_2$, 0.11 mol% C$_2$-P$_4$N$_2$-Bn, 80 °C, 30 bar hydrogen, 24 hours. Isolated yields were recorded.

Ketones did not show any reactivity at 80 °C. This is in sharp comparison with previously reported Co/tetraphosphine system in which no preference was observed at the optimized conditions.[26] When increasing the temperature to 100 °C, to our surprise, the C=C bond of conjugated ketones was hydrogenated via 1,4-reduction (**2ca** – **2ci**). The carbonyl group was kept under the reaction conditions. After a careful screening of reaction temperature, we finally found that the reduction of ketone carbonyl needs a temperature of 140 °C. This pronounced temperature difference required in hydrogenation reaction creates a valuable opportunity for chemo-discrimination between aldehydes and ketones. A variety of ketones, matter aryl alkyl ketones, dialkyl or diaryl ketones, could be reduced by molecular hydrogen with high efficiency (**2da** to **2dj**). Carboxylic acid derivatives were not hydrogenated in this chemical transformation (**2dl** to **2dn**). When enone substrate was applied, both C=C and C=O bond were reduced at 140 °C (**2dk**).

C=C bond in conjugate ketone: 100 °C
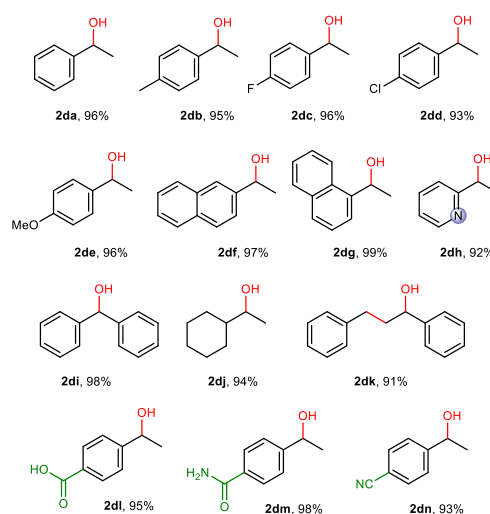
ketone: 140 °C

2ca, 90% **2cb**, 95% **2cc**, 89%
2cd, 93% **2ce**, 95% **2cf**, 92%
2cg, 87% **2ch**, 86% **2ci**, 93%

2da, 96% **2db**, 95% **2dc**, 96% **2dd**, 93%
2de, 96% **2df**, 97% **2dg**, 99% **2dh**, 92%
2di, 98% **2dj**, 94% **2dk**, 91%
2dl, 95% **2dm**, 98% **2dn**, 93%

Fig. 3 Hydrogenation of ketones with Fe/C$_2$-P$_4$N$_2$-Bn catalyst. Reaction conditions: 0.2 mmol substrate in 1.0 mL isopropanol, 0.1 mol% Fe(acac)$_2$, 0.11 mol% C$_2$-P$_4$N$_2$-Bn, 30 bar hydrogen, 24 hours. Isolated yields were recorded.

The reduction of nitroarenes to corresponding anilines has been a fundamental catalytical process in the fine and bulk chemical industries. Although the catalytic hydrogenation of nitroarenes could be realized with 3d metals heterogeneously[27], the homogeneous processes that enjoy better chemoselectivity and milder conditions have still been in demand. Beller and co-workers reported a case of iron-catalyzed selective homogenous hydrogenation of nitroarenes, but strong Brønsted acid was needed.[28] We were looking forward to the application of this Fe/P$_4$N$_2$ catalyst in the hydrogenation of nitroarenes. To our delight, nitro compounds were hydrogenated smoothly under the optimized conditions at 100°C. Functional groups that might be sensitive in heterogeneous hydrogenation such as C-X bond (**2ee**, **2ef, 2ej**, **2em**), C=C bond (**2eg**) survive in this catalytic process. In addition, other polar functionalities such as ketone (**2eh**) and carboxylic acid derivatives (**2ec**, **2ed**, **2el**, **2pm**, **2ep**, **2eq**) are also compatible under the reaction conditions. This compatibility with a broad scope of functionalities demonstrated the potential industrial application of this catalytic system. It is noteworthy that although no additive was introduced, the catalytic efficiency was still satisfactory for nitroarenes, regardless the electronic and steric properties of the substituents on the aromatic ring (TON = 1000 for most nitro substrates). As a bonus, the avoidance of base additive could effectively supress the formation of base-related by-products. (e.g., **2el**, see supplementary information for details)
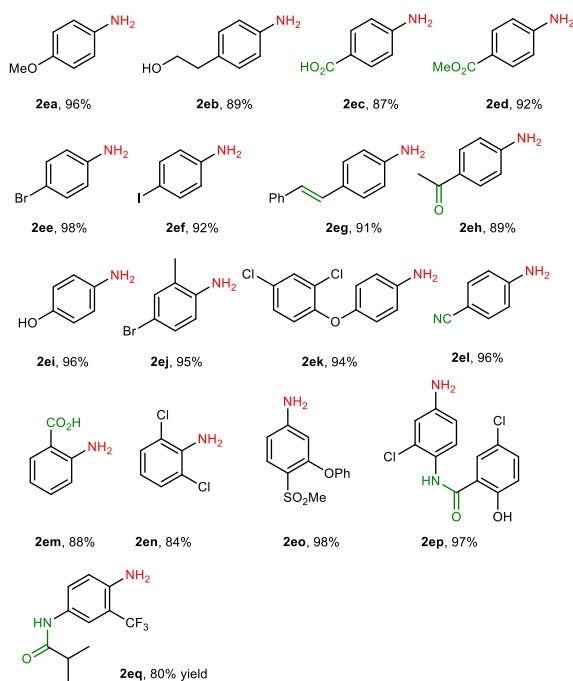
nitro group: 100 °C

2ea, 96%   **2eb**, 89%   **2ec**, 87%   **2ed**, 92%

2ee, 98%   **2ef**, 92%   **2eg**, 91%   **2eh**, 89%

2ei, 96%   **2ej**, 95%   **2ek**, 94%   **2el**, 96%

2em, 88%   **2en**, 84%   **2eo**, 98%   **2ep**, 97%

2eq, 80% yield

Fig. 4 Hydrogenation of nitroarenes with Fe/C$_2$-P$_4$N$_2$-Bn catalyst. Reaction conditions: 0.2 mmol substrate in 1.0 mL isopropanol, 0.1 mol% Fe(acac)$_2$, 0.11 mol% C$_2$-P$_4$N$_2$-Bn, 100 °C, 30 bar hydrogen, 24 hours. Isolated yields were recorded.

N-Heteroaromatic compounds such as quinoline and acridine could also been hydrogenated at a higher temperature (Fig. 5). However, the reactivity of such challenging aromatic substrates is much lower than other unsaturated compounds. A reaction temperature of 160 ~ 180 °C was needed while the introduction of catalytic amount of inorganic base would drive the conversion to complete. Compared to Co/P$_4$N$_2$ catalysts that have similar structural features[26], this Fe/P$_4$N$_2$ catalyst showed lower reactivity in the catalytic hydrogenation of *N*-heteroarenes. But in return, the elevated energy barrier in this process creates a considerable chemoselectivity.
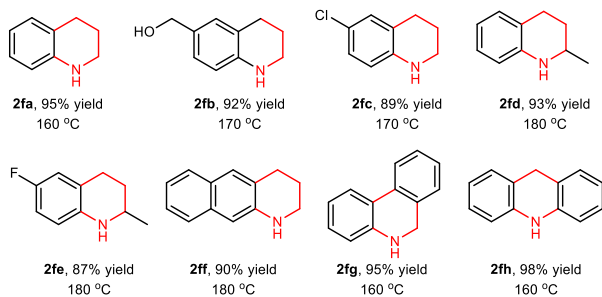
N-heteroarene: 160 - 180 °C

2fa, 95% yield   **2fb**, 92% yield   **2fc**, 89% yield   **2fd**, 93% yield
160 °C   170 °C   170 °C   180 °C

2fe, 87% yield   **2ff**, 90% yield   **2fg**, 95% yield   **2fh**, 98% yield
180 °C   180 °C   160 °C   160 °C

Fig. 5 Hydrogenation of *N*-heteroarenes with Fe/C$_2$-P$_4$N$_2$-Bn catalyst. Reaction conditions: 0.2 mmol substrate in 1.0 mL isopropanol, 2 mol% Fe(acac)$_2$, 2.2 mol% C$_2$-P$_4$N$_2$-Bn, 10 mol% KOH, 50 bar hydrogen, 48 hours. Isolated yields were recorded.

Synthetic applications. Encouraged by the broad reaction scope, we carried out a series of experiments to exploit the application in synthetic chemistry. First, this catalytic reaction could be scaled up, and the TONs could reach a level of 100000 for simple aldehyde and 50000 for enal. This catalyst functioned well after a period of 72 hours, which indicates a satisfactory robustness. (Fig. 6a) Second, the hydrogenation of a mixture of simple ketone and enal was carried out at 80 °C (Fig. 6b). To our delight, the conjugate aldehyde converted to corresponding allylic alcohol with 99% yield while no ketone reduction product was observed, which demonstrated an outstanding chemo-discrimination between aldehyde and ketone. The catalytic reduction of C=O double bond with molecular hydrogen could be utilized for sophisticated molecules such as pregnenolone (Fig. 6c). In addition, the hydrogenation of nitro compounds to corresponding anilines was proved to be practical in the preparation of intermediates for many important bioactive molecules as linezolid, clofazimine, tizanidine and vismodegib (Fig. 6d). These successes gained our confident for the application this Fe/P_4N_2 catalyst in the fine chemical and pharmaceutical industries.
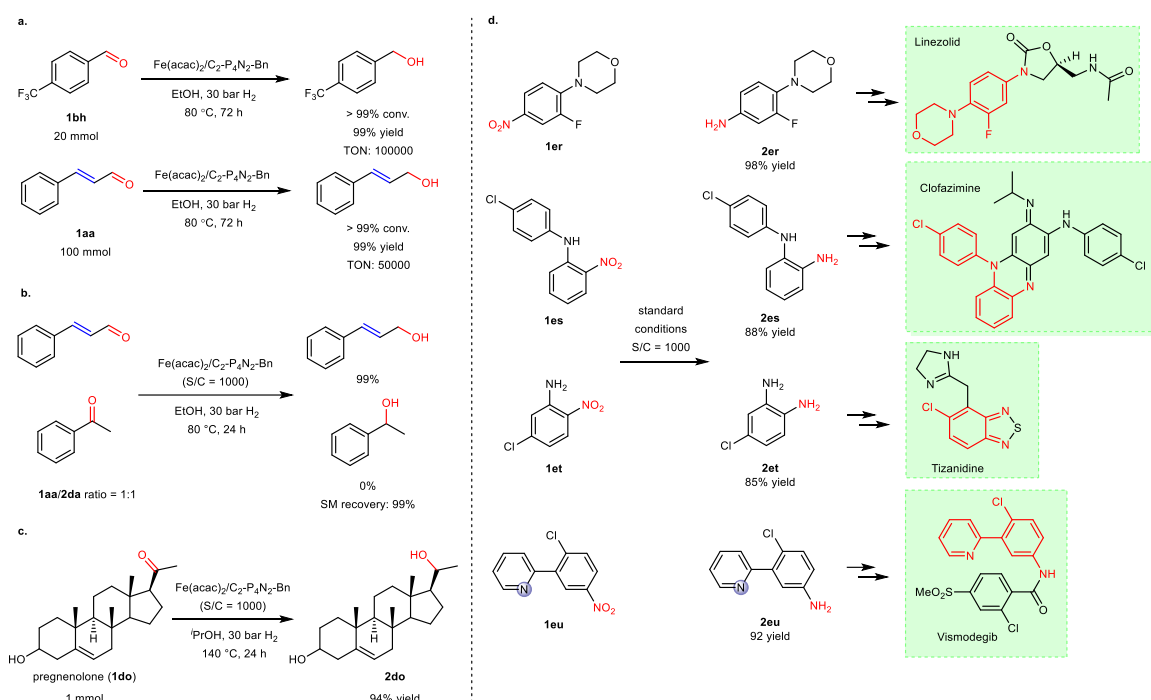

Fig. 6 Chemoselectivity and application in synthetic chemistry. a. Large-scale reactions for the demonstration of high catalytically efficiency. **b**. Reaction of a mixture of conjugate aldehyde and simple ketone for the test of chemoselectivity. **c**. Hydrogenation of pregnenolone. **d**. Hydrogenation of nitroarenes in the preparation of aniline compounds.

Identification of catalytically active iron species. Our curiosity was drawn to the mechanism in this catalytic reaction. We commence the investigation of the catalytically active species. The complexation of tetraphosphine ligand C2-P_4N_2-Ph with iron(II) precursor $FeBr_2$ at room temperature resulted in a quantitative yield of *trans*-Fe(P_4N_2)Br_2 (Fig. 6, **Fe-1**). **Fe-1** is a diamagnetic iron complex with two doublet peaks in ^{31}P NMR spectrum (δ 87.4 and 72.6, $^{P-P}J =$ 87.5 Hz). Reduction of this bromide complex with lithium aluminum hydride gave a *trans*-dihydride complex **Fe-2** (Fig. 6, equation 2). The ^1H NMR spectroscopy of this diamagnetic

complex showed a quintet peak in upfield (δ -14.55, ^{P-H}J = 37.8 Hz) while the ^{31}P NMR spectroscopy showed only one fluxional signal at δ 108.8 ppm. These signals were in agreement with Bullock's report.[29] In the presence of an inorganic base, this reacted with molecular hydrogen at an elevated temperature and formed the same *trans*-dihydride species. However, without external base, this transformation could not occur at this temperature. **Fe-2** did not react with aldehyde at room temperature, but this stoichiometric reaction proceeded to complete at 80 °C (Fig. 6, equation 4) which was in agreement with the conditions for catalytic hydrogenation of aldehydes. Based on this phenomenon and literatures about Fe(II) tetraphosphine dihydride complexes[30,31], we tentatively assumed that **Fe-2** is the active species *on* the catalytic cycle. A systematic investigation to probe the catalytic cycle is currently undertaken.
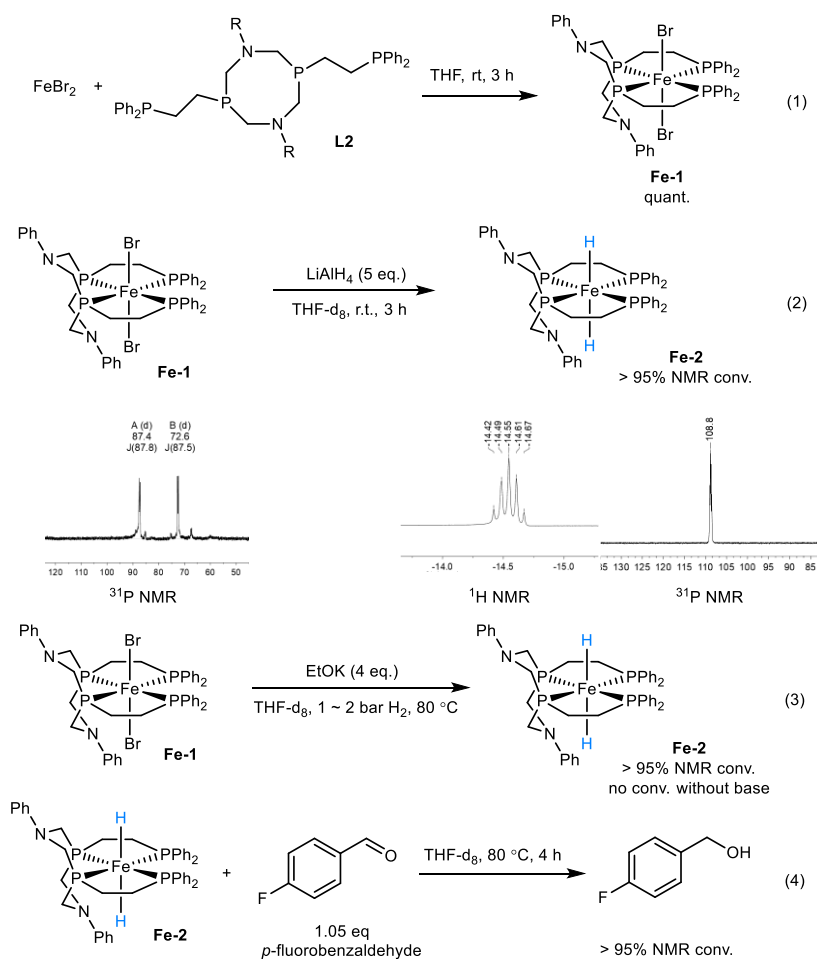

Fig. 7 Identification of catalytically active diamagnetic iron hydride species.

Conclusion

In summary, we reported the application of iron tetraphosphine complexes in homogeneous hydrogenation of polar unsaturated compounds. This type of Fe(II)/P$_4$N$_2$ complexes showed remarkable catalytic efficiency in the hydrogenation of a variety of polar unsaturated substrates such as aldehydes, ketones, enones, nitroarenes and *N*-heteroarenes. It is noteworthy that no additives were necessary for this chemical transformation, which could avoid unexpected side

reactions. Without an N-H moiety, challenging carboxylic acid derivatives could not be reduced with molecular hydrogen under a mild condition. But as a bonus, such catalysts showed precise chemoselectivity: the reaction temperature dictates the chemoselectivity among different types of functional groups. The potential application of this method in the synthesis important organic building blocks has been demonstrated. A diamagnetic *trans*-dihydride iron complex was observed under the reaction conditions, and this dihydride showed reducing ability for aldehyde substrate.

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