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# Iron-Based Deep Eutectic Solvents: Versatile and Powerful Tools in Sustainable Organic Synthesis

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*Abstract*: Deep Eutectic Solvents (*DESs*) based on abundant and non-toxic first-row metals have emerged as versatile and sustainable alternatives to conventional solvents/promoters in a variety of synthetic organic protocols under greener and milder reaction conditions. In particular, Fe(III)-based *Lewis Acidic DESs* (*LADESs*) have recently shown great potential as dual solvent/promoter systems enabling efficient transformations under air and recyclable conditions without requiring toxic volatile organic compound (*VOC)* solvents at any stage in the protocol (synthesis, isolation or purification). Specifically, in this short review, we summarize our recent progress in the application of $FeCl_3$-based *DESs* as sustainable and efficient promoters/solvents in organic synthesis by presenting two representative examples: *i*) the hydration and hydration/oxidation of terminal or internal alkynes to yield methyl ketones or 1,2-diketones, respectively; and *ii*) the Friedel-Crafts benzylation reaction. The performance, recyclability, mechanistic features and green metrics for these processes are discussed, highlighting the promise of this approach for sustainable synthesis.

**Keywords**: Iron · Lewis-*ADES*s · Organic synthesis · Sustainability

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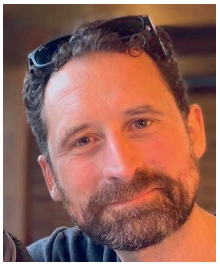

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## 1. Introduction

The use of Lewis acids as promoters or catalysts in organic synthesis remains one of the most powerful strategies for C-C and C-heteroatom bond formation.[1] However, traditional Lewis acids such as $AlCl_3$, $BF_3$, $TiCl_4$, $ZnCl_2$ or $SnCl_4$ (among others) suffer from important drawbacks, including: *i*) stoichiometric consumption; *ii*) lack of selectivity; *iii*) strong reaction conditions and protecting atmosphere; and *iv*) generation of waste streams that prevent their recycling.[2] Thus, in the context of *Greener Synthetic Organic Chemistry*,[3] there is a strong drive to develop new systems that: *i*) minimize waste; *ii*) employ abundant and low-toxicity metals; *iii*) work under mild and air/moisture compatible reactions conditions; and ideally *iv*) integrate solvent and catalytic/promoting roles in a single medium.

In general, Deep Eutectic Solvents (*DESs*) are defined as mixtures of Hydrogen Bond Donors (*HBDs*) and Acceptors (*HBAs*) that form liquids at room temperature and have attracted growing attention as innocent and sustainable reaction media during the last two decades in a variety of synthetic organic transformations, including: *i*) biocatalysis; *ii*) polar organometallic chemistry; *iii*) transition metal catalysis; and *iv*) organocatalysis.[4] Among the broad family of *DESs*, *Lewis Acidic DESs* (*LADESs*), which are prepared from metal halides and simple and sustainable *HBDs* [like ureas or naturally occurring polyalcohols (*i.e.* glycerol)] stand out for their unique dual behavior, as they act simultaneously as solvents and as Lewis acid catalysts/promoters.[5] In recent years, $FeCl_3$-based *DESs* have been recognized as particularly attractive because iron is earth-abundant, inexpensive and environmentally benign compared to noble metals.[6] Moreover, their intrinsic Lewis acidity enables them to promote a wide range of synthetic organic transformations under operationally simple and sustainable conditions, like, for example: *i*) the synthesis of amides[7] or furans[8]; *ii*) the oxidation of alcohols into carbonyl compounds;[7,9] *iii*) the Meyer-Schuster rearrangement of propargylic alcohols;[10] or *iv*) the Ritter reaction.[11]

Thus, in this mini-review, we summarize our last contributions on the application of $FeCl_3$-based *DESs* as promoters/solvents towards organic synthesis, focusing on two transformations recently explored: *i*) the hydration and hydration/oxidation of terminal or internal alkynes to yield, respectively, methyl ketones or 1,2-diketones;[12] and *ii*) the Friedel-Crafts benzylation reaction.[13] These studies showcase how Fe-*DESs* can: *i*) unlock reactivity under air; *ii*) avoid volatile organic solvents (both during the synthetic protocol and the concomitant isolation/purification steps); and *iii*) allow recycling and scale-up, thus in line with the *12 Principles of Green Chemistry*.[14] Moreover and to further validate the sustainable credentials of our transformations, key *Green Metrics* (such as the calculated *E*-factors[15]) are also discussed.

## 2. Hydration and Hydration/Oxidation of Alkynes in $FeCl_3$-Based *DESs*

The hydration of alkynes is a cornerstone transformation in synthetic chemistry, providing direct access to carbonyl compounds from readily available starting materials.[16] Traditionally, this reaction has been catalyzed by mercury(II) salts, a process well-known for its toxicity and environmental concerns.[17] Later developments replaced Hg(II) with noble transition metals such as Au, Pt, Ru or Pd, achieving high activity and selectivity.[18,19] However, these methodologies usually suffer from significant drawbacks, including: *i*) the need for strong acidic additives and/or co-solvents (typically MeOH); *ii*) protecting atmospheres; *iii*) *VOC*s during isolation/purification steps; and *iv*) expensive/toxic catalysts,[20] that hinder their large-scale implementation (see upper part of Fig. 1). Iron salts have emerged as more sustainable alternatives due to their abundance, low cost, and reduced toxicity.[6] However, in most cases, the Fe-catalyzed alkyne hydration still required harsh conditions, such as elevated temperatures or additional acidic co-catalysts, which limited their practical utility.[21–29]

### 2.1 *Hydration of Terminal Alkynes in $3FeCl_3{\cdot}6H_2O$/Glycerol DES*

We have recently demonstrated that the combination of $FeCl_3{\cdot}6H_2O$ and glycerol (*Gly*) in a 3:1 molar ratio produces a stable *Lewis-Acidic Deep Eutectic Solvent* (*LADES*) capable of efficiently promoting the hydration of terminal alkynes.[12] This medium represents a significant advancement from conventional protocols, as it allows the reaction to proceed: *i*) under air; *ii*) at relatively mild temperatures (45–80 °C); and *iii*) without any acidic co-catalysts or *VOC* co-solvents. Depending on the substrate, reaction times ranged from 30 minutes to 24 hours, consistently delivering the corresponding methyl ketones in high efficiency and selectivity (see lower part of Fig. 1).

From an organic synthetic point of view, it is important to mention that the substrate scope is broad as a variety of aryl-substituted terminal alkynes, decorated with electron-donating or electron-withdrawing substituents, were converted into the desired methyl ketones in yields ranging from 80% to 98%. A particularly attractive feature of this system is that, in many cases, ketone products crash down directly from the *DES* medium. This spontaneous precipitation enabled a straightforward isolation procedure by simple filtration and washing with water, thereby completely avoiding the use of volatile organic solvents or labor-intensive chromatographic purifications at any stage of the synthesis or isolation/purification protocols.

In terms of sustainability, the $3FeCl_3{\cdot}6H_2O$/*Gly DES* can be recycled and reused for at least eight consecutive runs without a detectable decrease in catalytic activity. The process also exhibits highly competitive green metrics, achieving an *E*-factor of 10. Remarkably, this value is in the same order of magnitude as that reported for large-scale petrochemical processes,[15] which are often considered industrial benchmarks for efficiency. Thus, this comparison highlights not only the academic interest of this methodology but also its genuine potential for scalability and industrial application. Overall, this Fe-based *DES* offers a combination of the following advantages rarely observed in alkyne hydration chemistry: *i*) operation under air; *ii*) absence of toxic and expensive noble metals; *iii*) elimination of *VOC* solvents and acidic additives; *iv*) simplified product isolation; and *v*) recyclability. These features align with the *12 Principles of Green Chemistry*, being a robust and sustainable alternative for the synthesis of methyl ketones.

### 2.2 *Hydration/Oxidation of Internal Alkynes in $3FeCl_3{\cdot}6H_2O$/Glycerol DES*

In contrast to terminal alkynes, the reactivity of internal alkynes in $3FeCl_3{\cdot}6H_2O$/*Gly DES* follows a distinct pathway. When subjected to the eutectic medium under air (110 °C, 4.5–24 h),

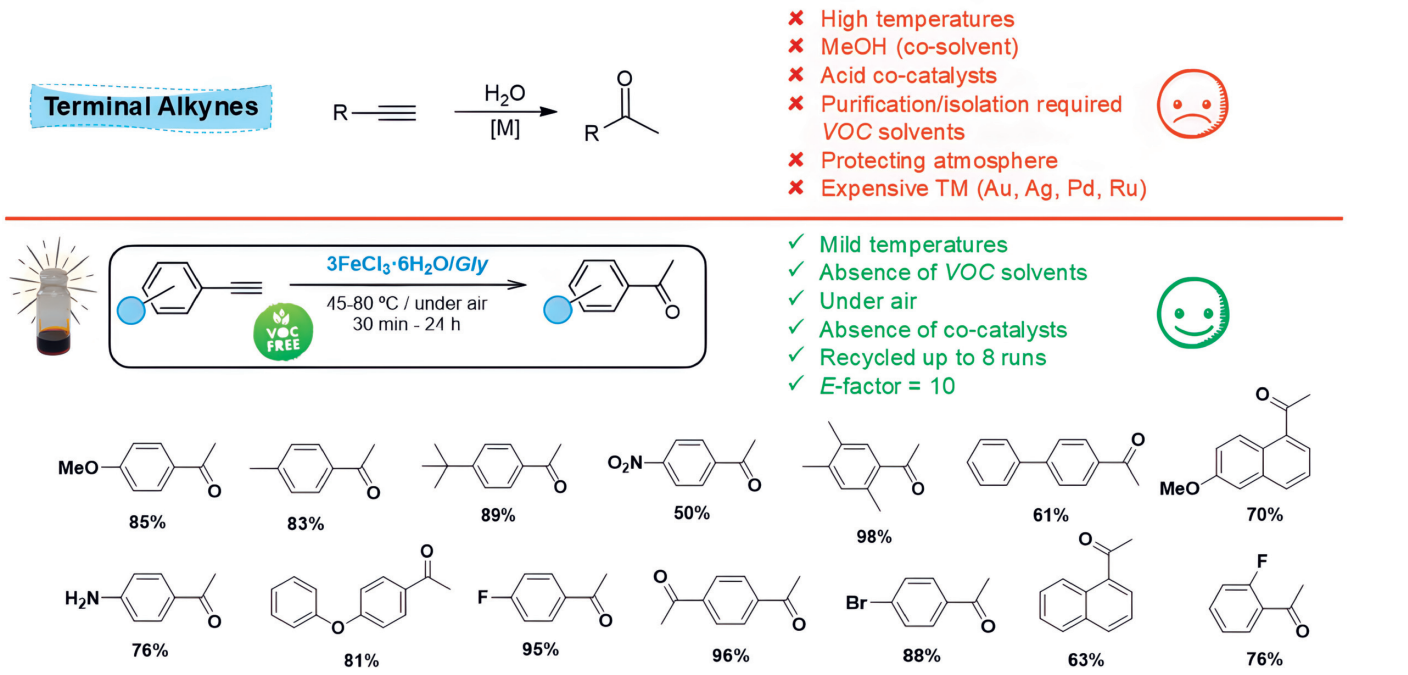


Fig. 1. Comparison between traditional transition-metal (TM)-catalyzed hydration of terminal alkynes (upper part) and the $3FeCl_3{\cdot}6H_2O$/*Gly DES* system which operates under mild, *VOC*-free, air-tolerant and recyclable conditions (lower part).

these substrates undergo a tandem hydration/oxidation sequence that selectively affords 1,2-diketones in yields of up to 94% (see upper part of Fig. 2). Importantly, the protocol remains operationally simple, requiring no additional oxidants beyond atmospheric $O_2$ and allowing the *DES* to be recycled up to three times with minimal loss of activity. Mechanistic investigations (see lower part of Fig. 2) revealed that this transformation proceeds through a formal hydrochlorination/hydration protocol. The first detectable intermediates are vinyl chlorides, which evolve into the corresponding ketones. These ketones then undergo α-chlorination, affording α-chloroketones that are subsequently oxidized under aerobic conditions to deliver the final 1,2-diketones.

Furthermore, blank experiments carried out with independently prepared intermediates fully validated this mechanistic picture (see Fig. 3). Both the isolated propiophenone and its α-chloroketone analogue could be cleanly converted into the corresponding 1,2-diketone under the standard reaction conditions ($3FeCl_3{\cdot}6H_2O$/*Gly*, 110 °C, aerial $O_2$), thus demonstrating the stepwise evolution of the process and confirming the intermediacy of these species. The ability to directly access 1,2-diketones from

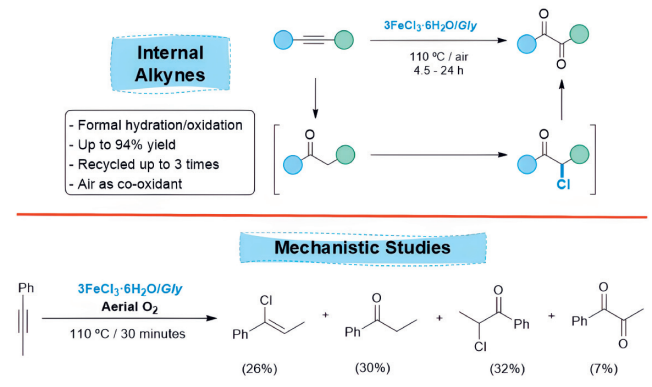


Fig. 2. Recyclable $3FeCl_3{\cdot}6H_2O$/*Gly DES* promoted aerobic hydration/oxidation of internal alkynes into 1,2-diketones under air.

internal alkynes in this way is synthetically valuable, as diketones are versatile precursors in heterocycle synthesis, ligand design, and materials science.[30]

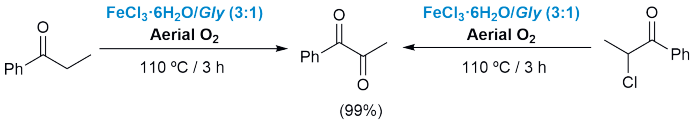


Fig. 3. Blank experiments showing the sequential aerobic conversion of propiophenone and α-chloropropiophenone into the corresponding 1,2-diketone in $3FeCl_3{\cdot}6H_2O$/*Gly* at 110 °C, confirming the stepwise chlorination-oxidation pathway.

## 3. Friedel-Crafts Benzylation in $3FeCl_3{\cdot}6H_2O$/Glycerol *DES*

Friedel-Crafts benzylations are among the most iconic Lewis acid-promoted electrophilic aromatic substitution reactions,[31] providing direct access to 1,1-diarylalkanes,[32,33] which are considered key motifs in pharmaceuticals, fragrances and advanced materials. However, classical protocols typically rely on stoichiometric amounts of $AlCl_3$ or other strong Lewis acids under strictly anhydrous conditions. Moreover, these methods are inherently wasteful as, in most of the cases, the employed Lewis acid is destroyed in a subsequent quench step, producing large quantities of by-products. Furthermore, these traditional methodologies usually require: *i*) large excesses of arene; *ii*) toxic alkyl halides as coupling partners; and *iii*) large amounts of *VOC* solvents for the isolation/purification of the desired 1,1-diarylalkanes, which strongly limits the atom economy and sustainability of the overall synthetic protocol.

Over the past decade, several *Acidic Deep Eutectic Solvents* (*ADESs*, both based on Brønsted and Lewis acidic motifs) have opened a new pathway toward greener Friedel-Crafts benzylations.[34] In this field, our group systematically explored (with 132 different 1,1-diarylalkanes) the use of the aforementioned $3FeCl_3{\cdot}6H_2O$/*Gly DES* as a highly efficient medium and

promoter for this transformation. Screening experiments revealed that either Brønsted acidic *DESs* [*e.g. ChCl/p-TSA*·$H_2O$ (ChCl = choline chloride, *p-TSA* = *p*-toluenesulfonic acid) or *ChCl/HFIP* (*HFIP* = hexafluoroisopropyl alcohol)] or different *LADESs* (based on Co, Ni, or Cu) were totally inactive under standard conditions, whereas the $3FeCl_3·6H_2O$/*Gly DES* furnished a myriad of *para*-benzylated products in up to 93% isolated yield with excellent *para*/*ortho* (*p*/*o*) selectivity under air at 120 °C (see Fig. 4).

Thus, our system tolerates a broad substrate scope in both partners of the Friedel-Crafts benzylation, being compatible with different:

*i*) *Nucleophiles*: mono-, di- and tri-substituted arenes (including *o*-, *m*-, *p*-xylene, mesitylene, anisole and heteroarenes) delivered the benzylated products in moderate-to-excellent yields (30–99%) with consistent *para*-regioselectivity. Arenes with electron-donating groups (EDGs) showed higher reactivity, whereas deactivated arenes bearing strong electron withdrawing groups (EWGs) ($NO_2$, $CF_3$) required longer reaction times (up to 67 h) or showed low conversion (see Fig. 5)

*ii*) *Electrophiles*: benzyl alcohols, acetates, ethers and even benzyl chlorides were competent substrates. Secondary benzyl alcohols proved particularly effective, affording the desired 1,1-diarylalkanes in >90% yields, often superior to the analogous styrenes and with significantly shorter reaction times. The system also tolerated challenging electrophiles such as fluorostyrenes, allowing the synthesis of fluorinated diarylalkanes (see Fig. 5) that are typically inaccessible under $FeCl_3$-catalyzed conditions.

Moreover, the process could be scaled up without loss of efficiency. On a 10 mmol scale, the synthesis of 1-phenyl-1-xylyl ethane (PXE, an important industrial chemical) was achieved in 77% isolated yield demonstrating excellent reproducibility and robustness (see Fig. 6). Notably, the reaction mixture undergoes spontaneous phase separation after completion, forming a recyclable Fe-*DES* bottom layer and an upper organic phase containing the product. This allows simple decantation and recovery of the *DES*, avoiding column chromatography or *VOC* extraction (see Fig. 6). Finally, a key strength of our methodology lies in its recyclability and green metrics. The $3FeCl_3·6H_2O$/*Gly DES* could be recycled at least 20 consecutive times with negligible activity loss, maintaining high yields and regioselectivity. The calculated *E*-factor for the model reaction was as low as 0.23, representing the best value reported to date, to the best of our knowledge. This fact, together with the avoidance of corrosive stoichiometric reagents, inert atmosphere, and *VOC* solvents, clearly positions our method as a paradigm of a *Green Chemistry-aligned C-C* bond-forming protocol.

## 3. Conclusions

This mini-review tries to highlight the power of the iron-based *LADESs* $3FeCl_3·6H_2O$/*Gly* as a truly powerful and versatile synthetic organic tool capable of promoting both the activation of C≡C triple bonds (through hydration and tandem hydration/oxidation sequences to access methyl ketones and 1,2-diketones) and highly efficient C-C bond-forming reactions such as Friedel-Crafts benzylations, working in all cases under operationally simple, aerobic-tolerant and *VOC*-free conditions. Thus, the described examples illustrate how the Fe-*LADESs* deliver high selectivity, broad substrate scope and excellent functional group tolerance, even when applied to challenging or deactivated substrates. The dual function of these eutectic mixtures as both solvent and Lewis acid promoter allows reactions to be performed under air, without stoichiometric corrosive additives, and with simplified downstream processing. Product isolation often benefits from spontaneous phase separation or precipitation, eliminating the need for chromatography and significantly reducing solvent consumption and waste generation.

From a sustainability standpoint, it is important to mention that the recyclability of the Fe-*LADESs* (up to 8 cycles for alkyne hydration and 20 cycles for Friedel-Crafts benzylations), combined with their exceptionally low *E*-factors (as low as 0.23) demonstrates their excellent green metrics. Their robustness and reproducibility, together with the successful scale-up of key transformations (*e.g.* PXE synthesis on a 10 mmol scale), further emphasizes their potential for industrial implementation.

Overall, Fe-based *LADESs* represent a genuinely green and scalable platform for modern organic synthesis, offering a pathway toward cleaner, safer, and more circular chemical manufacturing. Their ability to integrate efficiency, functional group tolerance and waste minimization places them in direct alignment with several of the *12 Principles of Green Chemistry* and emphasizes their relevance as next-generation tools for sustainable synthetic methodology development.

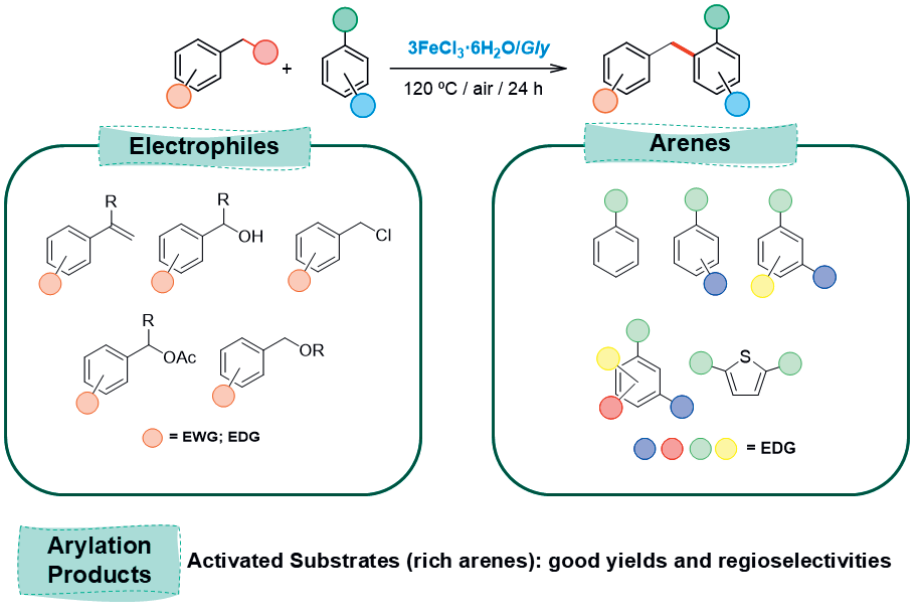


Fig. 4. Versatile $3FeCl_3·6H_2O$/*Gly DES* promoted Friedel-Crafts benzylations with a wide scope of electrophile/activated arenes and excellent yields/regioselectivity, which operate under air-tolerant conditions.

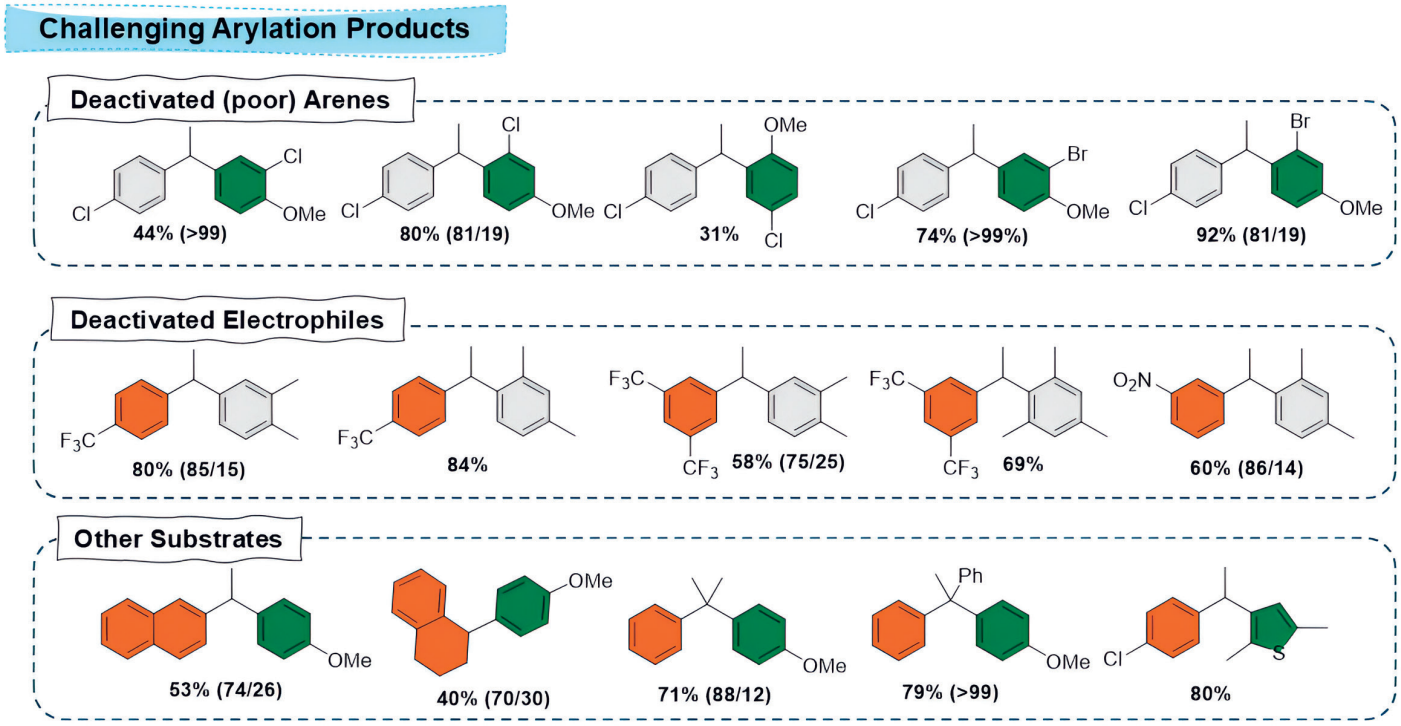


Fig. 5. $3FeCl_3{\cdot}6H_2O$/*Gly DES* promoted Friedel-Crafts benzylations with deactivated arenes, deactivated electrophiles and even with other challenging substrates.

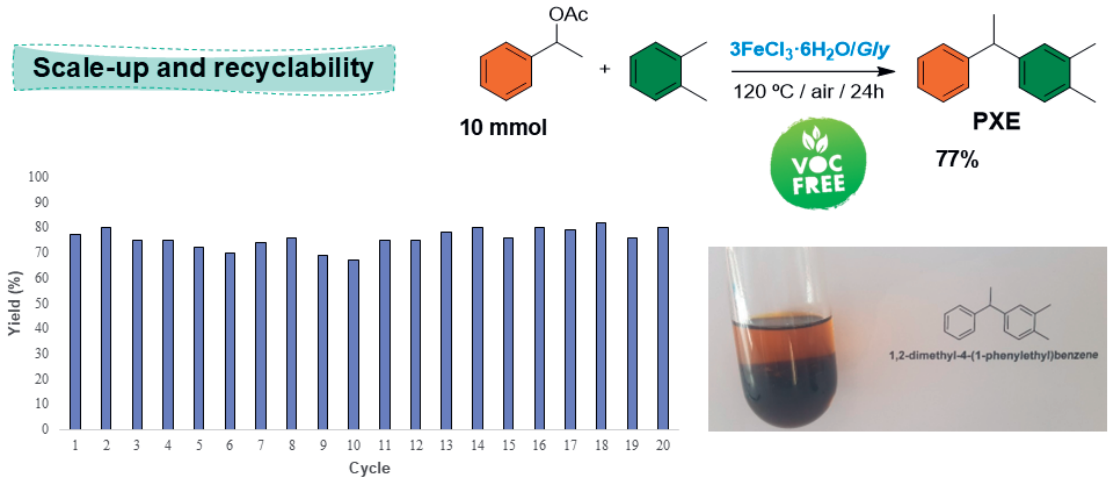


Fig. 6. *VOC*-free, robust, green, scalable (10 mmol) and recyclable (up to 20 consecutive cycles) $3FeCl_3{\cdot}6H_2O$/*Gly DES* promoted Friedel-Crafts benzylation under aerobic conditions.


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## *Author Contributions*

M. Ramos-Martín and N. Ríos-Lombardía conducted all the reactions and full characterization of the compounds and participated in the review and editing of the manuscript. S. E. García-Garrido conceptualized the project and participated in the review and editing of the manuscript. A. Presa Soto and J. García-Álvarez conceptualized and supervised the project, wrote the original draft and participated in the review and editing of the manuscript. All authors contributed to scientific discussions.

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