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# Efficient iron-catalyzed direct acylation of amines with carboxylic acids and esters under oxygenated conditions†

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Amides are ubiquitous in natural and synthetic compounds, and amidation is by far the most prevalent reaction in medicinal chemistry. In addition, atom-economical procedures for the direct amidation of esters or acids with amines are in high demand. Encouraged by the abundance and low toxicity of iron compounds, we envisaged that a new iron-catalyzed protocol for the acylation of amines with both esters and carboxylic acids could be designed if the iron catalyst was combined with dioxygen. Several experiments were carried out in order to define the iron source and to evaluate the effect of molecular oxygen, additives and different reaction media. A number of substrates were then reacted under optimized conditions, and experimental studies (kinetic, radical trapping and electron paramagnetic resonance experiments) were conducted to shed light on the reaction mechanism. As a result, a new use for dioxygen as an inducer of the direct amidation between amines and carboxylic acids or esters has been found. Thus, an earth-abundant first-row metal catalyst ( $\text{Fe}(\text{acac})_3$ ) at low loading combined with pivalic acid and molecular oxygen at atmospheric pressure triggers the reaction in a biodegradable greener solvent such as diethyl carbonate. More than 65 high-yielding examples prove the generality of the procedure, which also resulted to be scalable. In addition, insight into the mechanism behind this reaction taking place under oxygenated conditions is provided as well as an explanation for the results obtained in the absence of dioxygen.

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## Introduction

There is a growing interest in the development of new iron-catalyzed reactions, stimulated by the scarcity of precious metals and the abundance and comparatively much lower toxicity of iron compounds.<sup>1</sup> This interest, reflected in the 12-fold increase of the number of publications with the term “iron-catalyzed” in the title in the past 20 years,<sup>2</sup> has led to the discovery of a number of procedures based on iron catalysts that rival and even exceed the performance of other metal-catalyzed protocols.<sup>3</sup> However, there is much room for improvement and many unexplored applications for iron catalysts are yet to be discovered.<sup>4</sup>

Due to the need for activating agents, coupling reagents and additives to perform amidation reactions, which are the

most prevalent reactions in medicinal chemistry,<sup>5</sup> amide formation with high atom economy has been regarded as a key goal.<sup>6</sup>

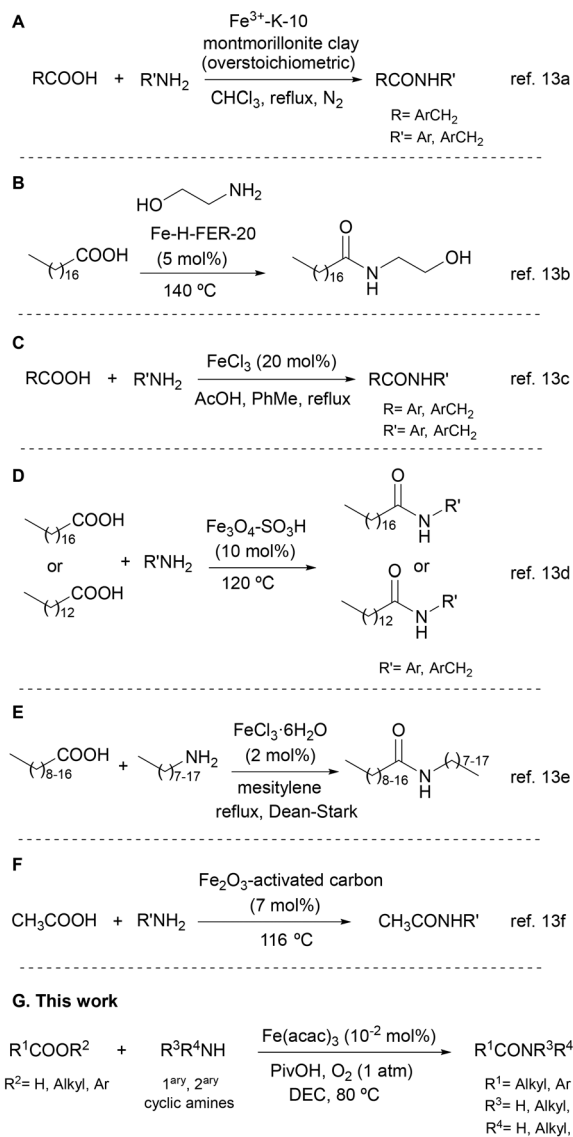
In this respect, unlike other amidation reactions that require some of the aforementioned activating agents in stoichiometric amounts (*e.g.* carbodiimides,<sup>7</sup> benzotriazoles,<sup>8</sup> carbon tetrachloride<sup>9</sup>  $\alpha,\alpha$ -dichlorodiphenylmethane<sup>10</sup> or *tert*-butyl isocyanide and *S*-phenyl benzenethiosulfonate<sup>11</sup>), direct acylation of amines with esters or carboxylic acids has been scarcely explored using iron catalysts.<sup>12,13</sup> Indeed, most of the reports on this atom-economical process (Scheme 1) show a scope limited to primary amines and/or aliphatic acid derivatives,<sup>12b,13</sup> and no general method for the iron-catalyzed direct acylation of amines using both carboxylic acids and esters as acylating agents has been reported to date.

As part of our ongoing research on iron catalysts,<sup>14</sup> we became interested in the iron-catalyzed acylation of amines with esters and unactivated acids. From the initial experiments we noticed a curious difference between reactions under inert conditions (Ar) and those conducted open to the atmosphere. Interestingly, in spite of the plethora of iron-catalyzed oxidative reactions found in the literature (oxidation of alcohols and methylene compounds to carbonyl

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**Scheme 1** Iron-catalyzed direct amidation between carboxylic acids and amines.

compounds and carboxylic acids,<sup>15</sup> oxidative cross-dehydrogenative coupling,<sup>16</sup> oxidative alkenylation of benzylic C–H bonds with diazo compounds,<sup>17</sup> oxidative homocoupling of alkenyllithiums,<sup>18</sup> alkene *syn*-dihydroxylation<sup>19</sup> or 1,2-alkylarylation of styrenes with  $\alpha$ -carbonyl alkyl bromides and indoles,<sup>20</sup> *inter alia*), no oxidant has ever been employed in this field of iron-catalyzed direct amidation, let alone molecular oxygen, which is abundant, inexpensive and completely harmless to the environment.

Several reports have shown the beneficial effect of molecular oxygen in reactions not directly related to classical oxidation processes, like the molecular oxygen-induced activation of certain bonds,<sup>21</sup> of molybdenum-based Lewis acids<sup>22</sup> and of gold catalysts.<sup>23</sup>

In addition, activation by dioxygen has resulted to be essential for certain challenging reactions such as skeletal rearrangements<sup>24</sup> photoisomerization between the *cis* and

the *trans* states of azobenzenes<sup>25</sup> and other oxygen-driven photoisomerization reactions of alkenes and polyenes,<sup>26</sup> redox-neutral nucleophilic aromatic substitutions leading to seven-membered ring formation,<sup>27</sup> conversion of pincer metal complexes into metallabenzene,<sup>28</sup> and iron-catalyzed dearomatization of 2-naphthols.<sup>29</sup>

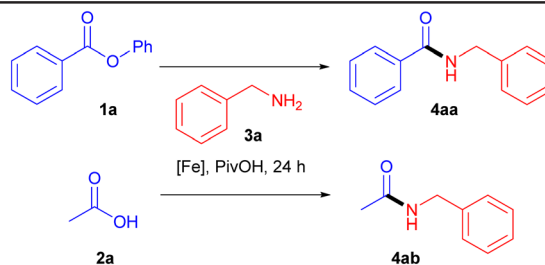
Accordingly, we decided to investigate the influence of dioxygen on iron-catalyzed amidation. In this paper we present (i) a highly efficient and general procedure for the direct acylation of amines applicable to both carboxylic acids and esters and (ii) a mechanistic insight into the role of the iron catalyst system and the aerobic reaction conditions.

## Results and discussion

Phenyl benzoate (**1a**) and acetic acid (**2a**) were chosen as model substrates to react with benzylamine (**3a**). A variety of iron sources were tested as catalysts in different solvents in a preliminary screening of reaction conditions,<sup>30</sup> and the catalyst loading was limited to 10<sup>−2</sup> mol% in order to maximize efficiency. Most of these initial assays were carried out with acid **2a** as the acylating agent, and only some promising reaction conditions were tested on benzoate **1a**. From these preliminary results FeCl<sub>3</sub>, FeBr<sub>2</sub> and Fe(acac)<sub>3</sub> were chosen as catalysts for further optimization as well as pivalic acid as an additive (Table 1).

After trying different solvents for the amidation of **2a**, we found that diethyl carbonate (DEC) provided slightly better yields if combined with Fe(acac)<sub>3</sub> (entry 7 *vs.* 1–6). To our surprise, the yield rose significantly from 15% to 83% when the reaction mixture in the latter solvent was heated in an open vessel (entry 7 *vs.* 8). Furthermore, a slight increase was observed when the reaction was carried out in an oxygen atmosphere (entry 9). Remarkably worse results were obtained from other iron(III) catalysts under the latter oxygenated conditions (entry 11). Interestingly, Fe(acac)<sub>2</sub> showed a similar catalytic profile (entry 10). On the basis of the wider availability and lower cost of Fe(acac)<sub>3</sub>, we chose this iron(III) source to continue the optimization of reaction conditions. An excellent yield (entry 12) was obtained when benzoate **1a** was subjected to the reaction conditions displayed in entry 9, but attempts to further reduce the catalyst loading were unsuccessful.<sup>30</sup> In contrast to **2a**, a moderate yield was obtained for the reaction from **1a** under argon (entry 13). No change was observed when the reaction temperature was decreased to 80 °C in the case of **1a** but the yield dropped to 39% from **2a** (entries 14 and 16). With regard to the stoichiometry of the reaction, optimal results were obtained with 1.5 equiv. of **3a**, although the yield was improved to almost quantitative values when 2 equiv. of the amine were reacted with **2a** (entry 18). After adjusting the optimal amount of the additive for each substrate (entries 18–19), blank experiments proved the need for pivalic acid, especially for **2a** (entries 21–22) and of the iron catalyst (entries 23–24).



Table 1 Optimization of reaction conditions for the aminolysis of ester **1a** and carboxylic acid **2a**

Entry	1a/2a	Conditions <sup>a</sup>	Product <sup>b</sup> (%)
1	2a	FeCl <sub>3</sub> , PhMe, Ar, 100 °C	4ab (8)
2	2a	FeBr <sub>2</sub> , dioxane, Ar, 100 °C	4ab (11)
3	2a	Fe(acac) <sub>3</sub> , DMF, Ar, 100 °C	4ab (7)
4	2a	FeCl <sub>3</sub> , DMSO, Ar, 100 °C	4ab (10)
5	2a	Fe(acac) <sub>3</sub> , EtOH, Ar, 100 °C	4ab (7)
6	2a	Fe(acac) <sub>3</sub> , DMA, Ar, 100 °C	4ab (9)
7	2a	Fe(acac) <sub>3</sub> , DEC, Ar, 100 °C	4ab (15)
8	2a	Fe(acac) <sub>3</sub> , DEC, air, 100 °C	4ab (83)
9	2a	Fe(acac) <sub>3</sub> , DEC, O <sub>2</sub> , 100 °C	4ab (91)
10	2a	Fe(acac) <sub>2</sub> , DEC, O <sub>2</sub> , 100 °C	4ab (89)
11	2a	FeCl <sub>3</sub> , DEC, O <sub>2</sub> , 100 °C	4ab (59)
12	1a	Fe(acac) <sub>3</sub> , DEC, O <sub>2</sub> , 100 °C	4aa (90)
13	1a	Fe(acac) <sub>3</sub> , DEC, Ar, 100 °C	4aa (50)
14	1a	Fe(acac) <sub>3</sub> , DEC, O <sub>2</sub> , 80 °C	4aa (90)
15	1a	Fe(acac) <sub>3</sub> , DEC, O <sub>2</sub> , 60 °C	4aa (84)
16 <sup>c</sup>	1a	Fe(acac) <sub>3</sub> , DEC, O <sub>2</sub> , 80 °C	4aa (36)
17	2a	Fe(acac) <sub>3</sub> , DEC, O <sub>2</sub> , 80 °C	4ab (39)
18 <sup>d</sup>	2a	Fe(acac) <sub>3</sub> , DEC, O <sub>2</sub> , 100 °C	4ab (98)
19 <sup>e</sup>	1a	Fe(acac) <sub>3</sub> , DEC, O <sub>2</sub> , 80 °C	4aa (92)
20 <sup>d,e</sup>	2a	Fe(acac) <sub>3</sub> , DEC, O <sub>2</sub> , 100 °C	4ab (57)
21 <sup>f</sup>	1a	Fe(acac) <sub>3</sub> , DEC, O <sub>2</sub> , 80 °C	4aa (52)
22 <sup>d,f</sup>	2a	Fe(acac) <sub>3</sub> , DEC, O <sub>2</sub> , 100 °C	4ab (12)
23	1a	DEC, O <sub>2</sub> , 80 °C	4aa (15)
24 <sup>d</sup>	2a	DEC, O <sub>2</sub> , 100 °C	4ab (9)

<sup>a</sup> Reaction conditions: **1a** or **2a** (0.54 mmol), amine **3a** (1.5 equiv.), PivOH (1 equiv.), [Fe] (0.01 mol%), solvent (1 mL mmol<sup>-1</sup> **1a/2a**), Ar, air or O<sub>2</sub> (1 atm), *T*, 24 h. See ref. 34 and the ESI† for potential safety hazards associated with the combination of DEC and O<sub>2</sub>. <sup>b</sup> Isolated yield.

<sup>c</sup> Amine **3a** (1.0 equiv.). <sup>d</sup> Amine **3a** (2.0 equiv.). <sup>e</sup> 0.5 equiv. of PivOH were added. <sup>f</sup> No PivOH was added.

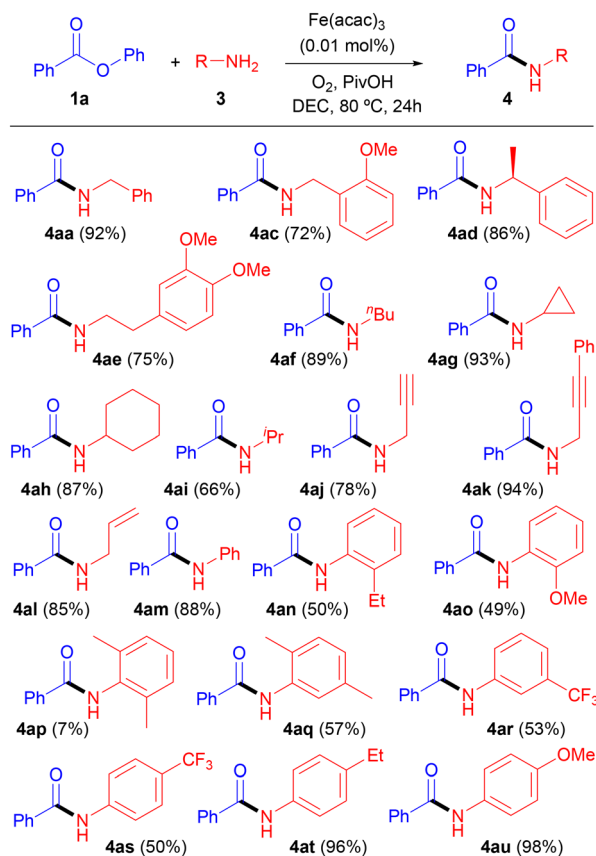
The scope of the reaction was initially explored by reacting benzoate **1a** with a number of primary amines **3**. As shown in Table 2, the corresponding secondary benzamides **4aa–4au** were isolated with moderate to good yields regardless of the structure of the amine (alkylamine, arylamine, propargylamine or allylamine) employed. However, a substantial decrease in the yield of *N*-arylamides **4an**, **4ao** and **4aq** was observed in comparison with their structural analogs **4am**, **4at** and **4au**, probably due to the steric hindrance associated to *O*-substituted 2-ethylaniline, 2-methoxyaniline and 2,5-dimethylaniline. This steric drawback became a serious limitation with *O,O'*-disubstituted anilines, and the reaction with 2,6-dimethylaniline provided only 7% of the corresponding amide **4ap**. With regard to *N*-benzylamides **4aa**, **4ac** and **4ad**, in addition to the good yield obtained, it should be pointed out that the amidation reaction of **4ad** took place with complete retention of configuration.

This fact was confirmed by comparison of the optical rotation of (*S*)-(-)- $\alpha$ -methylbenzylamine and (*S*)-*N*-(1-phenylethyl)benzamide (**4ad**) with literature data.<sup>31a-c</sup>

Next, different cyclic and linear secondary amines were reacted with ester **1a** to provide tertiary benzamides **4av–4bd** (Table 3). No clear trend was observed for the results from cyclic amines (amides **4av–4ba**), but it is noteworthy that the reaction tolerated the presence of halogen substituents (**4bc**) and that steric hindrance might be the reason for the moderate yield from dibenzylamine (**4bd**).

Table 4 shows the results from the reaction of benzylamine **3a** with readily available<sup>30</sup> esters **1b–1r**. The results from the preparation of acetamide **4ab** indicate that although phenyl esters (*R*<sup>2</sup> = Ph) provided better yields, the procedure is also amenable to methyl, ethyl and trimethylsilyl esters. A similar trend was observed for phenylacetamide **4be**. Other arylacetamides **4bf**, **4bg** and **4bh** were easily prepared from the corresponding methyl and phenyl esters. Good yields were also obtained from phenylbenzoates **1k–1n**, and the presence of sterically hindering or reactive groups (*o*-methyl and *o*-hydroxy for **1m** and **1k**, respectively) did not affect the reaction yield. Ethyl 2-cyanoacetate (**1o**), butyl formate (**1p**) and phenyl pivaloylacetate (**1q**) were successfully reacted with benzylamine (**3a**) under optimized conditions,



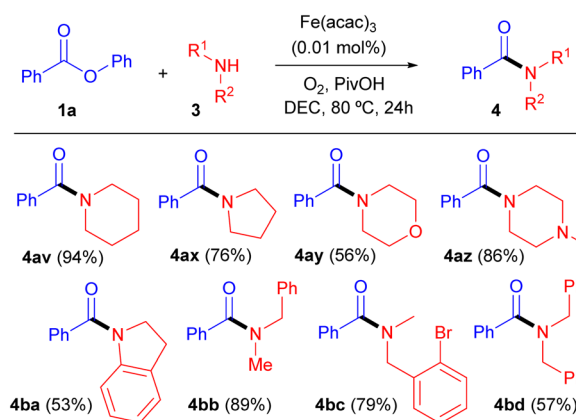
**Table 2** Synthesis of secondary amides from **1a** and primary amines<sup>a,b</sup>

<sup>a</sup> Reaction conditions: benzoate **1a** (0.54 mmol), amine **3** (0.81 mmol), PivOH (0.27 mmol), Fe(acac)<sub>3</sub> (0.01 mol%), DEC (1 mL mmol<sup>-1</sup> of **1a**), O<sub>2</sub> (1 atm), 80 °C, 24 h. <sup>b</sup> Isolated yields.

and a good yield for prolinamide **4bp** was obtained from phenyl *N*-tosylprolinate (**1r**).

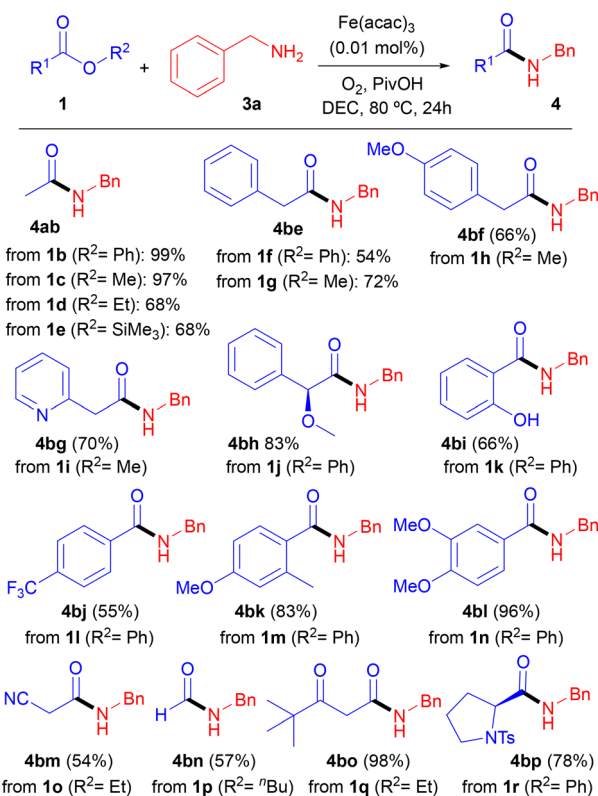
Interestingly, the reaction between commercially available ethyl 4-bromobutanoate (**1s**) and benzylamine (**3a**) provided selectively 1-benzylpyrrolidin-2-one (**4bq**) as a result of a one-pot amidation/nucleophilic substitution process (Scheme 2). Although the conversion was relatively low (unreacted starting materials were obtained along with cyclized product **4bq**), it should be pointed out that no substitution by-product (e.g. ethyl 4-(benzylamino)butanoate) was detected in the reaction crude.

Regarding the use of optically active compounds and following our previous observation on the preparation of (*S*)-*N*-(1-phenylethyl)benzamide (**4ad**, Table 2), the reaction between phenyl (*S*)-2-methoxy-2-phenylacetate (**1j**) and (*S*)-1-phenylethan-1-amine (**3c**) took place with complete stereoselectivity, as target (*S*)-2-methoxy-2-phenyl-*N*-((*S*)-1-phenylethyl)acetamide (**4br**) was obtained with excellent yield as a single diastereoisomer and enantiomer (Scheme 3). A complete retention of configuration was also observed for the reaction, leading to **4bh** (Table 4).<sup>31d-g</sup> X-ray diffractometry of both **4bh** and **4br** confirmed<sup>32</sup> the displayed stereochemistry, which is shown in Fig. 1.

**Table 3** Preparation of tertiary amides by the aminolysis of **1a** with secondary amines<sup>a,b</sup>

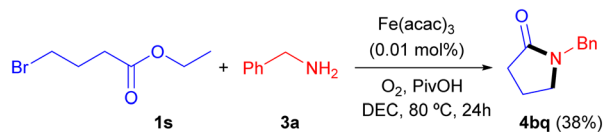
<sup>a</sup> Reaction conditions: benzoate **1a** (0.54 mmol), amine **3** (0.81 mmol), PivOH (0.27 mmol), Fe(acac)<sub>3</sub> (0.01 mol%), DEC (1 mL mmol<sup>-1</sup> **1a**), O<sub>2</sub> (1 atm), 80 °C, 24 h. <sup>b</sup> Isolated yields.

Finally, the model reaction was conveniently scaled up. Thus, 2 grams of starting benzoate **1a** were reacted with benzylamine (**3a**) to provide benzyl benzamide (**4aa**) with

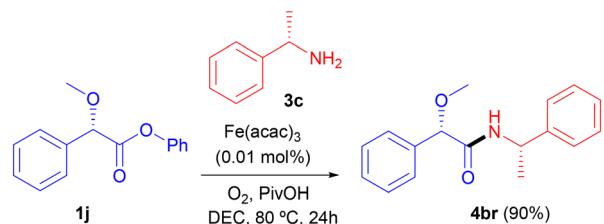
**Table 4** Aminolysis of esters **1** with benzylamine **3a**<sup>a,b</sup>

<sup>a</sup> Reaction conditions: ester **1** (0.54 mmol), amine **3a** (0.81 mmol), PivOH (0.27 mmol), Fe(acac)<sub>3</sub> (0.01 mol%), DEC (1 mL mmol<sup>-1</sup> **1**), O<sub>2</sub> (1 atm), 80 °C, 24 h. <sup>b</sup> Isolated yields.



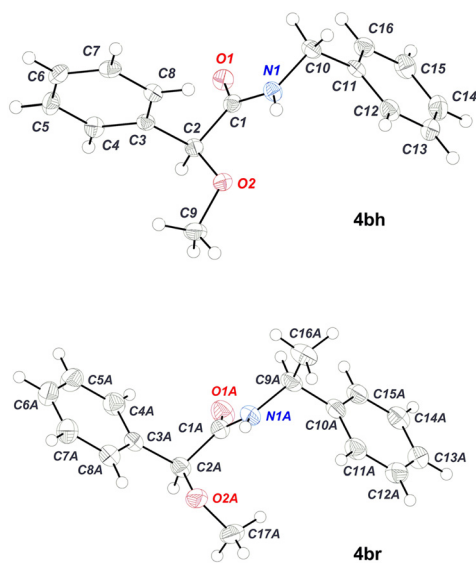


Scheme 2 One-pot amidation/nucleophilic substitution.

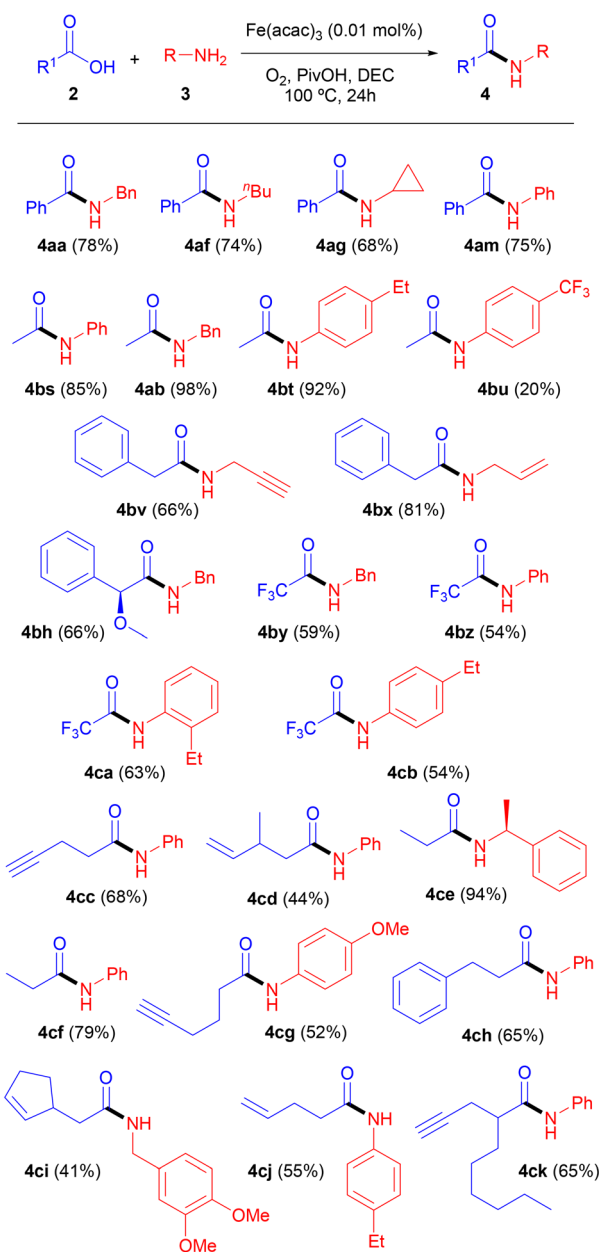


Scheme 3 Stereoselective amidation.

95% yield. Furthermore, the fact that this scalable reaction is carried out in diethyl carbonate (DEC) makes the process more sustainable. Indeed, diethyl carbonate is an environment-friendly and biodegradable solvent with mild toxicity presently used in pharmaceutical formulations, in green liquid-liquid extractions, as a component of electrolytes in lithium batteries and as a fuel additive.<sup>33</sup> However, even considering the atmospheric pressure employed and the low volatility of this solvent (b.p.: 126 °C, vapor pressure at 80 °C: 0.2 bar), its flammability in an oxygen-rich atmosphere should not be ignored,<sup>34</sup> and therefore a hazard warning note is included in the experimental procedures.<sup>30</sup> In spite of that, the use of pure dioxygen as an oxidant and organic carbonates as solvents in reactions even at high oxygen pressures has been reported without any safety issues.<sup>33b,35</sup>

Fig. 1 ORTEP diagrams of chiral amides **4bh** and **4br** with thermal ellipsoids given at 50% probability level.

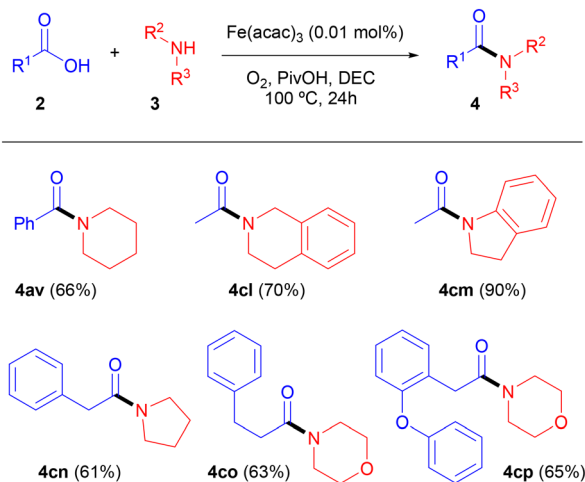
The reaction conditions optimized for the aminolysis of acetic acid (**2a**) with benzylamine (**3a**) were then applied to a variety of carboxylic acids **2** and amines **3** (Table 5). The structural diversity of both acid and amine reagents should be pointed out, and most of the 23 secondary amides prepared in this way were obtained with good yields, although slightly inferior results were achieved from unsaturated acids (amides **4cd**, **4cg**, **4ci** and **4cj**). The presence of a bulky *o*-ethyl group in 2-ethylaniline or the use of branched carboxylic acids such as 2-(prop-2-yn-1-yl)

Table 5 Acylation of primary amines with a variety of acids<sup>a,b</sup>

<sup>a</sup> Reaction conditions: acid **2** (0.54 mmol), amine **3** (1.08 mmol), PivOH (0.54 mmol), Fe(acac)<sub>3</sub> (0.01 mol%), DEC (1 mL mmol<sup>-1</sup> **2**), O<sub>2</sub> (1 atm), 100 °C, 24 h. <sup>b</sup> Isolated yields.





**Table 6** Synthesis of tertiary amides by acylation of secondary amines with carboxylic acids<sup>a,b</sup>

<sup>a</sup> Reaction conditions: acid **2** (0.54 mmol), amine **3** (1.08 mmol), PivOH (0.54 mmol), Fe(acac)<sub>3</sub> (0.01 mol%), DEC (1 mL mmol<sup>-1</sup> **2**), O<sub>2</sub> (1 atm), 100 °C, 24 h. <sup>b</sup> Isolated yields.

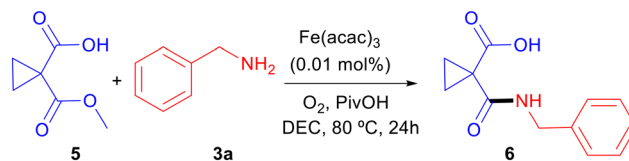
octanoic acid did not have a deleterious effect on the reaction outcome (amides **4ca** and **4ck**, respectively). In addition, as with the aminolysis of esters **1**, the acylation of amines **3** with acids **2** occurred with complete retention of configuration, and both amides **4bh** and **4ce** were isolated as single enantiomers.<sup>31,32</sup>

To conclude the scope studies of this amidation reaction, piperidine, pyrrolidine, morpholine, indoline and tetrahydroisoquinoline were reacted with a handful of structurally dissimilar carboxylic acids **2**, thus providing the tertiary amides **4** shown in Table 6. Good yields were obtained in all cases, irrespective of the structure of the amidation partner.

On another note, it should be mentioned that in addition to the morpholinamide derived from 2-(2-phenoxyphenyl) acetic acid (**4cp**), several *N*-benzylamides derived from acids **2** (**4ci** and **4ck**, Table 5) and from esters **1** (**4bh**, **4br**, **4bo**, and **4bp**, Table 4 and Scheme 3) have been synthesized for the first time in this work.

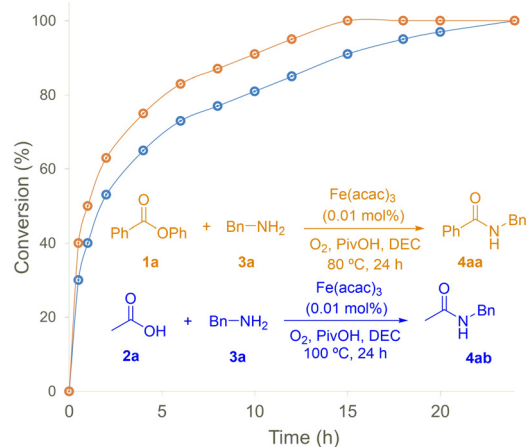
Since the presented protocol can use esters and acids as acylating agents for amines, we decided to compare the results in those cases where the same amide had been prepared. No difference could be found for acetamide **4ab** (99% vs. 98%), but for secondary benzamides **4aa**, **4af**, **4ag** and **4am** and tertiary benzamide **4av** significantly higher yields were obtained from esters **1** than from acids **2** (92%, 89%, 93%, 88% and 94% vs. 78%, 74%, 68%, 75% and 66%, respectively). However, the convenience of both atom-economical processes and the release of water as a by-product in the case of acid precursors cannot be ignored.

A number of experiments were then carried out to shed light on the reaction mechanism. We had observed that aminolysis of esters **1** and acids **2** took place with similar kinetics although acids required a higher temperature to

**Scheme 4** Selective amidation of 1-(methoxycarbonyl)cyclopropane-1-carboxylic acid (**5**).

react. A meaningful example of this subtle difference was the selective monoamidation of 1,1-cyclopropanedicarboxylic acid monomethyl ester (**5**) when treated with one equivalent of amine **3a** under optimized reaction conditions (Scheme 4). Besides, as predicted, the conversion rate vs. time curves for **1a** → **4aa** and **2a** → **4ab** are very similar, both of hyperbolic shape, which probably accounts for homogeneous catalysis.<sup>36</sup> Although the reaction temperature is 20 °C higher in the case of **2a**, the reaction from **1a** shows slightly faster kinetics (Fig. 2).

UPLC-ESI-QTOF analysis of the crude (reaction time: 12 h) of the reaction between ester **1a** and amine **3a** revealed the presence of acetylacetone, *N*-benzyl-1-phenylmethanimine, phenylmethanimine, ethyl benzylcarbamate, phenol and 2,2-dimethylpropaneperoxoic acid (perpivalic acid). A small amount of both imines, along with ethyl benzylcarbamate and phenol, was also detected by GC-MS of the reaction crude. As shown in Table 1, an excess of the amine is required for both ester and acid substrates, as the use of equimolecular amounts of the amine results in moderate to low yields. Therefore we propose that the excess amine is one of the main driving forces of the reaction and that ethyl benzylcarbamate, easily formed by reaction between DEC and **3a**, acts as a reservoir for **3a**, as the acidic medium derived from pivalic acid releases **3a** by ethanolysis of the carbamate. In fact, the reaction between ester **1a** and ethyl benzylcarbamate (1.5 equiv.) under optimized reaction conditions provided target amide **4aa** with good yield (83%).

**Fig. 2** Aminolysis of phenyl benzoate (**1a**) and of acetic acid (**2a**) with benzylamine (**3a**) as a function of time.

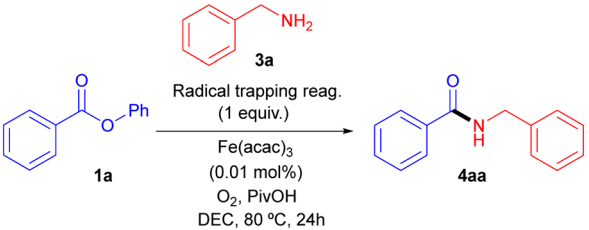
Instead of benzylamine (**3a**), commercially available *N*-benzyl-1-phenylmethanimine (*N*-benzylidenebenzylamine) was reacted with ester **1a** under optimized conditions in order to check if this imine could be a reaction intermediate. However, only 12% of **4aa** was obtained.

Additionally, in order to define the role of dioxygen in this reaction, other oxidants such as 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) and potassium peroxymonosulfate (Oxone®) were assayed under anaerobic conditions (Ar) in the the above reaction between ester **1a** and amine **3a**. Only target **4aa** was isolated in the case of potassium peroxymonosulfate, but with a poor 9% yield.

In another experiment carried out in the absence of the acylating agent **1** or **2**, the aforementioned acetylacetone, *N*-benzyl-1-phenylmethanimine, phenylmethanimine and ethyl benzylcarbamate were detected by UPLC-ESI-QTOF. Furthermore, after performing the same experiment, water was added, the mixture was extracted with dichloromethane and the resulting aqueous solution was acidified with H<sub>2</sub>SO<sub>4</sub>. Potassium permanganate titration provided evidence for the presence of Fe<sup>2+</sup> ions in the latter solution and revealed that almost half of the initial amount of Fe(acac)<sub>3</sub> had been reduced to Fe(II) species.

A significant number of iron-catalyzed reactions mediated by molecular oxygen are based on radical pathways.<sup>15c,37</sup> Therefore, the participation of radical species was investigated by adding several radical scavengers and trapping agents to the reaction between ester **1a** and amine **3a**. As shown in Table 7, little or no inhibition was observed even when this radical interception was attempted using stoichiometric amounts of the aforementioned trapping reagents. Sodium azide, a typical quenching agent for singlet oxygen, had no effect on the reaction outcome either.

Table 7 Summary of poisoning experiments



Entry	Radical trapping reagent <sup>a</sup>	<b>4aa</b> <sup>b</sup> (%)
1	TEMPO	92
2	Galvinoxyl	66
3	BHT	93
4	DPPH	94
5	PBN	95
6	NaN <sub>3</sub>	93

<sup>a</sup> Reaction conditions: ester **1a** (0.54 mmol), amine **3** (0.81 mmol), radical trapping reagent (0.54 mmol), PivOH (0.27 mmol), Fe(acac)<sub>3</sub> (0.01 mol%), DEC (1 mL mmol<sup>-1</sup> **1a**), O<sub>2</sub> (1 atm), 80 °C, 24 h.

<sup>b</sup> Isolated yields. TEMPO: 2,2,6,6-tetramethylpiperidine 1-oxyl; BHT: butylated hydroxytoluene; DPPH: 2,2-diphenyl-1-picrylhydrazyl; PBN: *N*-tert-butyl- $\alpha$ -phenylnitron.

However, electron paramagnetic resonance (EPR) analysis of the reaction at  $t = 1$  h showed two overlapping signals corresponding to two relatively stable radicals (Fig. 3a).

On the basis of the observed splitting pattern and  $g$ -factors, these stable radicals are *O*-centered radicals. After addition of PBN to the reaction mixture at  $t = 1$  h, the EPR signals of the generated spin-adducts confirmed this hypothesis (Fig. 3b). Accordingly, it seemed that radical species (probably *O*-centered radicals) were formed during the progress of the reaction but they did not intervene as intermediates and did not affect the reaction outcome.

Pivalic acid has emerged as a crucial proton shuttle in various metal-catalyzed reactions. Its unique properties, demonstrated through its effectiveness in sub- and overstoichiometric amounts and even as a solvent, have been extensively studied. Replacing pivalic acid with other carboxylic acids, such as benzoic or acetic acid, often leads to significant changes in the results of the reaction, underscoring its distinct role in facilitating proton transfer.<sup>38</sup> As mentioned before, in our case a small excess of the amine was required to obtain reasonable yields. However, the presence of pivalic acid as an additive (0.5–1.0 equiv.) had a positive impact on the reaction outcome. We therefore proposed that pivalic acid would act as a ligand facilitating the interaction of the iron center with dioxygen.

With the results of all these studies in hand, we proposed the mechanism depicted in Scheme 5 to explain the

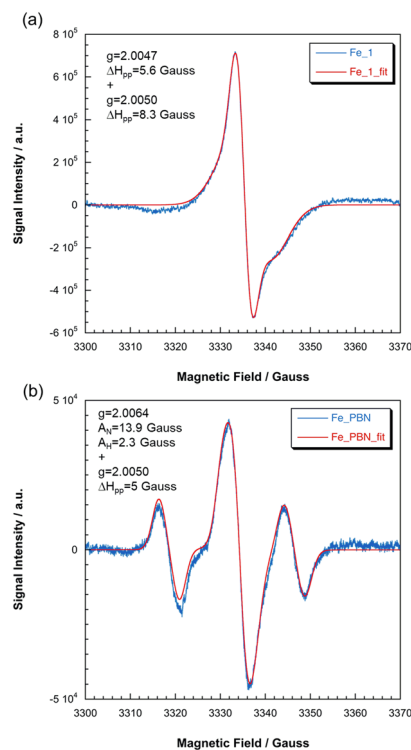
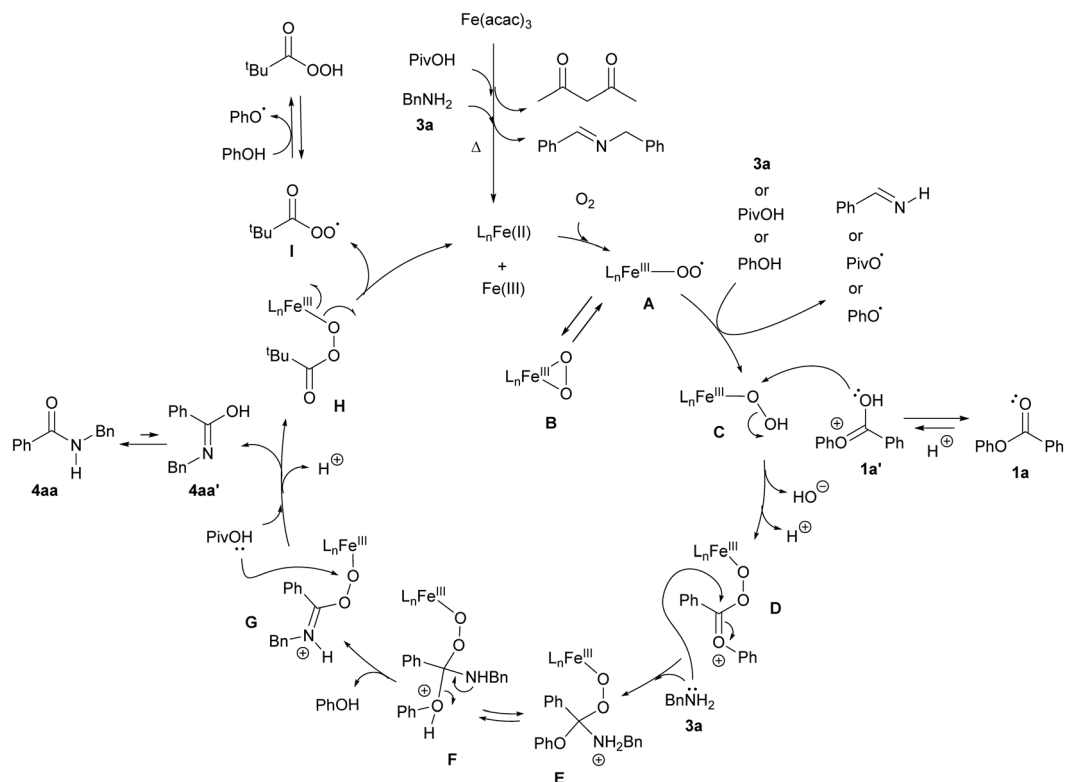


Fig. 3 Experimental (blue line) and least squares fit (red line) EPR spectra of the reaction (**1a** + **3a** → **4aa**) at  $t = 1$  h before (a) and after (b) addition of *N*-tert-butyl- $\alpha$ -phenylnitron (PBN).





**Scheme 5** A mechanistic proposal for the iron-catalyzed aminolysis of phenyl benzoate **1a** in the presence of dioxygen.

formation of **4aa** by aminolysis of **1a** with **3a** under oxygenated conditions. After protonation of the acetylacetonate ligands of Fe(acac)<sub>3</sub> by pivalic acid, the resulting Fe(III) ions would partially oxidize benzylamine in the presence of oxygen, as described by Castro<sup>39</sup> and Xu.<sup>40</sup> This process would release catalytic amounts of Fe(II) species, which are essential for the next step. Additionally, as a result of the interaction between Fe(acac)<sub>3</sub> and pivalic acid, the so-formed trinuclear pivalate complex–pivalic acid adduct [Fe<sub>3</sub>-O(OPiv)<sub>6</sub>(PivOH)<sub>3</sub>] contains a high-spin Fe(II) core and shows a temperature-dependent mixed-valence state.<sup>41</sup> These Fe(II) species would readily interact with dioxygen to generate ferric superoxo species **A** and/or iron(III) peroxy intermediate **B**, which in the presence of hydrogen atom donors (*e.g.* starting amine **3a**, pivalic acid or later released phenol) would transform into iron(III)-hydroperoxy intermediate **C**.<sup>42</sup> Nucleophilic attack at this intermediate **C** by **1a** or protonated **1a'** would form iron(III) acylperoxy complex **D**, which would undergo addition by amine **3a** to the electrophilic carbonyl center. After prototropic tautomerism **E–F**, condensation would release phenol and generate key intermediate **G**. A nucleophilic attack by pivalic acid, akin to that experienced by iron(III)-hydroperoxy species **C**, would liberate *N*-benzylacetimidic acid **4aa'**, in equilibrium with target amide **4aa**. As a result, iron(III)-pivaloylperoxy complex **H** would form. The thermodynamically favourable homolytic cleavage of the Fe(III)–O bond of high-spin Fe(III)-alkylperoxy complexes to generate Fe(II) complexes and alkylperoxy

radicals has been discussed by Solomon and Que.<sup>43</sup> This process would take place at complex **H** so that Fe(II) species that would reinstate the catalytic cycle would be released, along with unstable acyl peroxy radical **I**.

Reaction of the latter with previously liberated phenol would generate persistent phenoxy radical,<sup>44</sup> one of the aforementioned radical species detected by EPR. Considering the radical scavenging ability of pivalic acid,<sup>45</sup> formation of pivaloxyl radical cannot be discarded. A similar mechanism would account for the formation of **4ab**.<sup>46</sup> At this point, and although all the mechanistic steps are based on experimental results or literature reports, it should be pointed out that our proposal is purely tentative. Indeed, our assumptions that the aminolysis step takes place on intrinsically unstable peroxide species (**E–G**) and about the subsequent homolysis of the Fe–O bond at complex **H** are somewhat questionable. However, the kinetic, radical trapping, detection by UPLC-ESI-QTOF analysis, electron paramagnetic resonance and additional experiments conducted along with the literature precedents on related processes offer tentative support for our proposal.

## Conclusions

To sum up, a highly efficient procedure for the iron-catalyzed direct acylation of amines with carboxylic esters and acids has been developed. This scalable and atom-economical process requires the use of molecular oxygen as an inducer of the reaction along with pivalic acid as an additive. The





generality of the procedure, applicable to a wide range of primary and secondary amines, is demonstrated by more than 65 examples presented in this paper. In addition, the reaction is carried out in a greener solvent, diethyl carbonate. A main mechanism based on a Fe(II)/Fe(III) cycle and the interaction of the former ion with dioxygen has been proposed to explain the role of the components in the reaction. On the basis of the experimental studies carried out, a subsidiary mechanism responsible for the results in the absence of oxygen is also suggested.

## Author contributions

MTH, GU and RS contributed to searching and collating of the relevant literature and the proof-reading of the document. MO and GU carried out the investigation, experiments, and analysis. MTH and RS conceptualized and supervised the study and wrote the body of the article. All authors have read and agreed to the published version of the manuscript.

## Conflicts of interest

There are no conflicts to declare.

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## Notes and references

- (a) C. Bolm, J. Legros, J. Le Paih and L. Zani, *Chem. Rev.*, 2014, **104**, 6217–6254; (b) H. Du, F. Deng, R. R. Kommalapati and A. S. Amarasekara, *Renewable Sustainable Energy Rev.*, 2020, **134**, 110292; (c) P. DaBell and S. P. Thomas, *Synthesis*, 2020, **52**, 949–963; (d) Y. Hong, L. Jarrige, K. Harms and E. Meggers, *J. Am. Chem. Soc.*, 2019, **141**, 4569–4572.
- Data derived from Clarivate Web of Science, © Copyright Clarivate, 2023. All rights reserved, <https://www.webofscience.com/wos/woscc/basic-search>, (accessed August 2023).
- (a) M. M. Beromi, C. R. Kennedy, J. M. Younker, A. Carpenter, S. J. Mattler, J. A. Throckmorton and P. J. Chirik, *Nat. Chem.*, 2021, **13**, 156–162; (b) L. Yang, D. Cheng, H. Xu, X. Zeng, X. Wan, J. Shui, Z. Xiang and D. Cao, *Proc. Natl. Acad. Sci. U. S. A.*, 2018, **115**, 6626–6631; (c) R. Shang, L. Ilies and E. Nakamura, *Chem. Rev.*, 2017, **117**, 9086–9139.
- (a) A. Fürstner, *ACS Cent. Sci.*, 2016, **2**(11), 778–789; (b) F. Moccia, L. Rigamonti, A. Messori, V. Zanotti and R. Mazzoni, *Molecules*, 2021, **26**, 2728; (c) H. Fujisaki, T. Ishizuka, H. Kotani, Y. Shiota, K. Yoshizawa and T. Kojima, *Nature*, 2023, **616**, 476–481; (d) J. Zhu, P. Wang, X. Zhang, G. Zhang, R. Li, W. Li, T. P. Senftle, W. Liu, J. Wang, Y. Wang, A. Zhang, Q. Fu, C. Song and X. Guo, *Sci. Adv.*, 2022, **8**, eabm3629; (e) C. Empel, S. Jana and R. M. Koenigs, in *Iron Catalysis: Design and Applications*, ed. J. M. Palomo, World Scientific, Singapore, 2021, ch. 7, pp. 203–252.
- (a) D. G. Brown and J. Boström, *J. Med. Chem.*, 2016, **59**, 4443–4458; (b) J. Magano, *Org. Process Res. Dev.*, 2022, **26**, 1562–1689.
- (a) J. S. Carey, D. Laffan, C. Thomson and M. T. Williams, *Org. Biomol. Chem.*, 2006, **4**, 2337–2347; (b) R. Marcia de Figueiredo, J. S. Suppo and J. M. Campagn, *Chem. Rev.*, 2016, **116**, 12029–12122; (c) A. Taussat, R. Marcia de Figueiredo and J. M. Campagne, *Catalysts*, 2023, **13**, 366.
- (a) P. Xiao, Z. Zhang, J. Ge, Y. Deng, X. Chen, J.-R. Zhang, Z. Deng, Y. Kambe, D. V. Talapin and Y. Wang, *Nat. Commun.*, 2023, **14**, 49; (b) Z.-C. Liu, Z.-Q. Wang, X. Zhang and L. Yin, *Nat. Commun.*, 2023, **14**, 2187.
- (a) F. Rey-Tarrio, R. Rodriguez, E. Quinoa and F. Freire, *Nat. Commun.*, 2023, **14**, 1742; (b) B. C. Sanders, S. Pokhrel, A. D. Labbe, I. I. Mathews, C. J. Cooper, R. B. Davidson, G. Phillips, K. L. Weiss, Q. Zhang, H. O'Neill, M. Kaur, J. G. Schmidt, W. Reichard, S. Surendranathan, J. Parvathareddy, L. Phillips, C. Rainville, D. E. Sterner, D. Kumaran, B. Andi, G. Babnigg, N. W. Moriarty, P. D. Adams, A. Joachimiak, B. L. Hurst, S. Kumar, T. R. Butt, C. B. Jonsson, L. Ferrins, S. Wakatsuki, S. Galanie, M. S. Head and J. M. Parks, *Nat. Commun.*, 2023, **14**, 1733.
- C. Chu and R. Liu, *Appl. Catal., B*, 2011, **101**, 343–347.
- C.-H. Lee, S.-M. Lee, B.-H. Min, D.-S. Kim and C.-H. Jun, *Org. Lett.*, 2018, **20**, 2468–2471.
- Y.-P. Zhu, S. Sergeev, P. Franck, R. V. A. Orru and B. U. W. Maes, *Org. Lett.*, 2016, **18**, 4602–4605.
- (a) B. D. Mkhonazi, M. Shandu, R. Tshinavhe, S. B. Simelane and P. T. Moshapo, *Molecules*, 2020, **25**, 1040; (b) S.-S. Weng, C.-S. Ke, F.-K. Chen, Y.-F. Lyu and G.-Y. Lin, *Tetrahedron*, 2011, **67**, 1640–1648.
- (a) K. V. N. S. Srinivas and B. Das, *J. Org. Chem.*, 2003, **68**, 1165–1167; (b) P. Mäki-Arvela, J. Zhu, N. Kumar, K. Eränen, A. Aho, J. Linden, J. Salonen, M. Peurla, A. Mazur, V. Matveev and D. Y. Murzin, *Appl. Catal., A*, 2017, **542**, 350–358; (c) H. Basavaprabhu, K. Muniyappa, N. R. Panguluri, P. Veladi and V. V. Sureshbabu, *New J. Chem.*, 2015, **39**, 7746–7749; (d) J. Kothandapani, A. Ganesan and S. S. Ganesan, *Synthesis*, 2017, **49**, 685–692; (e) Y. Terada, N. Ieda, K. Komura and Y. Sugi, *Synthesis*, 2008, 2318–2320; (f) B. Sreedhar, V. Bhaskar, Ch. Sridhar, T. Srinivas, L. Kótai and K. Szentmihályi, *J. Mol. Catal. A: Chem.*, 2003, **191**, 141–147.
- J. Diaz de Sarralde, E. Astobieta, A. Sevilla, Y. Rincón, M. T. Herrero, G. Urgoitia and R. SanMartin, *Environ. Chem. Lett.*, 2022, **20**, 3421–3427.
- (a) B. Stanje, P. Traar, J. A. Schachner, F. Belaj and N. C. Mösche-Zanetti, *Dalton Trans.*, 2018, **47**, 6412–6420; (b) L. Xu, Y. Chen, Z. Shen, Y. Wang and M. Li, *Tetrahedron Lett.*, 2018, **59**, 4349–4354; (c) P. Hu, M. Tan, L. Cheng, H. Zhao, R. Feng, W.-J. Gu and W. Han, *Nat. Chem.*, 2019, **10**, 2425–2434; (d) H. Yu, Q. Zhao, Z. Wei, Z. Wu, Q. Li, S. Han and Y. Wei, *Chem. Commun.*, 2019, **55**, 7840–7843.



- 16 (a) K. Qiao, D. Zhang, K. Zhang, X. Yuan, M.-W. Zheng, T.-F. Guo, Z. Fang, L. Wan and K. Guo, *Org. Chem. Front.*, 2018, **5**, 1129–1134; (b) Z.-L. Li, K.-K. Sun, P.-Y. Wu and C. Cai, *J. Org. Chem.*, 2019, **84**, 6830–6839.
- 17 J.-L. Shi, Q. Luo, W. Yu, B. Wang, Z.-J. Shi and J. Wang, *Chem. Commun.*, 2019, **55**, 4047–4050.
- 18 Z. Zhong, Z.-Y. Wang, S.-F. Ni, L. Dang, H. K. Lee, X.-S. Peng and H. N. C. Wong, *Org. Lett.*, 2019, **21**, 700–704.
- 19 M. Borrell and M. Costas, *ACS Sustainable Chem. Eng.*, 2018, **6**, 8410–8416.
- 20 X.-H. Ouyang, R.-J. Song, M. Hu, Y. Yang and J.-H. Li, *Angew. Chem., Int. Ed.*, 2016, **55**, 3187–3191.
- 21 P. Peng, Q. Lu, L. Peng, C. Liu, G. Wang and A. Lei, *Chem. Commun.*, 2016, **52**, 12338–12341.
- 22 (a) Y. Yamashita, M. M. Salter, K. Aoyama and S. Kobayashi, *Angew. Chem., Int. Ed.*, 2006, **45**, 3816–3819; (b) S. Huo, L. Meng, Y. Zeng and X. Li, *Inorg. Chem.*, 2022, **61**, 4714–4724.
- 23 (a) H. Kitahara, I. Kamiya and H. Sakurai, *Chem. Lett.*, 2009, **38**, 908–909; (b) M. Conte, H. Miyamura, S. Kobayashi and V. Chechik, *Chem. Commun.*, 2010, **46**, 145–147.
- 24 Y.-F. Wang, F.-L. Zhang and S. Chiba, *Org. Lett.*, 2013, **15**, 2842–2845.
- 25 K. Kuntze, J. Isokuortti, A. Siiskonen, N. Durandin, T. Laaksonen and A. Priimagi, *J. Phys. Chem. B*, 2021, **125**(45), 12568–12573.
- 26 O. Turque, A. Greer and O. R. Wauchope, *Org. Biomol. Chem.*, 2020, **18**, 9181–9190.
- 27 Z. Huang, X. Ji and J.-P. Lumb, *Org. Lett.*, 2021, **23**, 236–241.
- 28 K. Masada, S. Kusumoto and K. Nozaki, *Angew. Chem., Int. Ed.*, 2022, **61**, e202117096.
- 29 T. Oguma and T. Katsuki, *J. Am. Chem. Soc.*, 2012, **134**, 20017–20020.
- 30 See the ESI† for a more comprehensive survey of reaction conditions, the preparation of carboxylic acid derivatives and a mechanistic proposal for the formation of **4ba**.
- 31 (a) J. Li, M. A. Siegler, M. Lutz, A. L. Spek, R. J. M. K. Gebbink and G. van Koten, *Organometallics*, 2009, **28**, 5323–5332; (b) M. Figlus, A. C. Tarruella, A. Messer, S. L. Sollis and R. C. Hartley, *Chem. Commun.*, 2010, **46**, 4405–4407; (c) F. F. Flores, M. S. Rivadeneyra and S. Bernès, *Acta Crystallogr., Sect. E: Crystallogr. Commun.*, 2020, **76**, 1229–1233; the optical purity of the obtained chiral amides **4ad**, **4br**, **4bh** and **4ce** was confirmed by comparison of the optical rotation with literature values. See: (d) D. C. Leustra, D. T. Nguyen and J. Mecinovic, *Tetrahedron*, 2015, **71**, 5547–5553; (e) S. Porto, J. M. Seco, J. F. Espinosa, E. Quiñoá and R. Riguera, *J. Org. Chem.*, 2008, **73**, 5714–5722; (f) R. García, J. M. Seco, S. A. Vázquez, E. Quiñoá and R. Riguera, *J. Org. Chem.*, 2006, **71**, 1119–1130; (g) C. E. Rye and D. Barker, *J. Org. Chem.*, 2011, **76**, 6636–6648. See also the ESI† for further details.
- 32 Analysis of the absolute structure using likelihood methods (Hooft, Straver and Spek, 2008) was performed using PLATON (Spek, 2010). The Friedel pair coverage of the experiment is almost complete (99–100%). The results indicated that the absolute structure had been correctly assigned. The method calculated that the probability that the structure is inverted is smaller than 10<sup>−53</sup> for **4fa** and smaller than 10<sup>−16</sup> for **4fc**. The absolute structure parameter  $\gamma$  was calculated using PLATON. The resulting value was  $\gamma = -0.02(11)$ , which together with the Flack parameter value, indicates that the absolute structure has probably been determined correctly. CCDC deposition numbers for **4fa** and **4fc** are 2290369 and 2290372, respectively, and the corresponding checkCIF reports are provided as ESI.† See: (a) A. L. Spek, *J. Appl. Crystallogr.*, 2003, **36**, 7–13; (b) R. W. W. Hooft, L. H. Straver and A. L. Spek, *J. Appl. Crystallogr.*, 2008, **41**, 96–103; (c) A. L. Spek, *PLATON, A Multipurpose Crystallographic Tool*, Utrecht University, Utrecht, The Netherlands, 2010; (d) A. L. Spek, *Acta Crystallogr., Sect. D: Biol. Crystallogr.*, 2009, **65**, 148–155.
- 33 (a) K. Shukla and V. C. Srivastava, *RSC Adv.*, 2016, **6**, 32624–32645; (b) B. Schäffner, F. Schäffner, S. P. Verevkin and A. Börner, *Chem. Rev.*, 2010, **110**, 4554–4581.
- 34 (a) D. R. Stull, *Ind. Eng. Chem.*, 1947, **39**, 517–540; (b) V. Pokorný, V. Štefja, M. Fulem, C. Červinka and K. Růžička, *J. Chem. Eng. Data*, 2017, **62**, 3206–3215; (c) P. M. Osterberg, J. K. Niemeier, C. J. Welch, J. M. Hawkins, J. R. Martinelli, T. E. Johnson, T. W. Root and S. S. Stahl, *Org. Process Res. Dev.*, 2015, **19**, 1537–1543; (d) C. A. Hone, D. M. Roberge and C. O. Kappe, *ChemSusChem*, 2017, **10**, 32–41.
- 35 (a) D.-H. Liu, H.-L. He, Y.-B. Zhang and Z. Li, *ACS Sustainable Chem. Eng.*, 2020, **8**, 14322–14329; (b) C. Nunes de Melo, Y. Blanc Rodrigues and P. A. Robles-Azocar, *Inorg. Chim. Acta*, 2021, **517**, 120192; (c) J.-L. Wang, L.-N. He, C.-X. Miao and Y.-N. Li, *Green Chem.*, 2009, **11**, 1317–1320.
- 36 (a) J. A. Widegren and R. G. Finke, *J. Mol. Catal. A: Chem.*, 2003, **198**, 317–341; (b) E. Bayram, J. C. Linehan, J. L. Fulton, J. A. S. Roberts, N. K. Szymczak, T. D. Smurthwaite, S. Ozkar, M. Balasubramanian and R. G. Finke, *J. Am. Chem. Soc.*, 2011, **133**, 18889–18902.
- 37 (a) R.-M. Hu, D.-Y. Han, N. Li, J. Huang, Y. Feng and D.-Z. Xu, *Angew. Chem., Int. Ed.*, 2020, **59**, 3876–3880; (b) X. Xie, J. Cao, Y. Xiang, R. Xie, Z. Suo, Z. Ao, X. Yang and H. Huang, *Appl. Catal., B*, 2022, **309**, 121235.
- 38 (a) M. Lafrance and K. Fagnou, *J. Am. Chem. Soc.*, 2006, **128**, 16496–16497; (b) Y. Moon, D. Kwon and S. Hong, *Angew. Chem., Int. Ed.*, 2012, **51**, 11333–11336; (c) P. Wen, Y. Li, K. Zhou, C. Ma, X. Lan, C. Ma and G. Huang, *Adv. Synth. Catal.*, 2012, **354**, 2135–2140; (d) D. Kim, G. Choi, W. Kim, D. Kim, Y. K. Kang and S. H. Hong, *Chem. Sci.*, 2021, **12**, 363–373.
- 39 C. E. Castro, M. Jamin, W. Yokoyama and R. Wade, *J. Am. Chem. Soc.*, 1986, **108**, 4179–4187.
- 40 (a) E. Zhang, H. Tian, S. Xu, X. Yu and Q. Xu, *Org. Lett.*, 2013, **15**, 2704–2707; See also (b) J. P. Saucedo-Vázquez, P. M. H. Kroneck and M. E. Sosa-Torres, *Dalton Trans.*, 2015, **44**, 5510–5519.
- 41 K. Asamaki, T. Nakamoto, S. Kawata, H. Sano, M. Katada and K. Endo, *Inorg. Chim. Acta*, 1995, **236**, 155–161.
- 42 (a) Y.-M. Lee, S. Hong, Y. Morimoto, W. Shin, S. Fukuzumi and W. Nam, *J. Am. Chem. Soc.*, 2010, **132**, 10668–10670; (b) Y. Jiang, J. Telser and D. P. Goldberg, *Chem. Commun.*,



- 2009, 6828–6830; (c) F. Odden, Y. Chiba, J. Nakazawa, T. Ohta, T. Ogura and S. Hikichi, *Angew. Chem., Int. Ed.*, 2015, **54**, 7336–7339; (d) M. A. Dedushko, J. H. Pikul and J. A. Kovacs, *Inorg. Chem.*, 2021, **60**, 7250–7261.
- 43 (a) N. Lehnert, R. Y. N. Ho, L. Que Jr. and E. I. Solomon, *J. Am. Chem. Soc.*, 2001, **123**, 12802–12816; (b) J. Kim, Y. Zang, M. Costas, R. G. Harrison, E. C. Wilkinson and L. Que Jr., *J. Biol. Inorg. Chem.*, 2001, **6**, 275–284.
- 44 (a) Z. X. Chen, Y. Li and F. Huang, *Chem*, 2021, **7**, 288–332; (b) B. Dellinger, S. Lomnicki, L. Khachatryan, Z. Maskos, R. W. Hall, J. Adoukpe, C. McFerrin and H. Truong, *Proc. Combust. Inst.*, 2007, **31**, 521–528.
- 45 T. Nauser and R. E. Bühler, *J. Chem. Soc., Faraday Trans.*, 1994, **90**, 3651–3656.
- 46 For an explanation of the results obtained under argon, see the ESI†.

