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COMMUNICATION

Iron Catalyzed β -C(sp^2)-H Alkylation of EnamidesSylvain Bertho,^a Radhouan Maazaoui,^a Damla Torun,^a Ismaël Dondasse,^a Raoudha Abderrahim,^b Cyril Nicolas^{a*} and Isabelle Gillaizeau^{a*}Received 00th January 20xx,
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An attractive atom-economic way was developed for the β -C(sp^2)-H (fluoro)alkylation of a range of acyclic and cyclic non-aromatic enamides using either FeCl_2 as a catalyst or a stoichiometric amount of low-cost iron powder. This reaction is regioselective and exhibits broad substrate scope and good functional group tolerance.

Introduction

Enamides are highly valuable structural motifs that are gaining increasing interest, due to their diverse possible transformations, and also because they are found in many natural products and pharmaceutical drugs (Figure 1).^{1–10} As a result, over the past decades, various synthetic methods have been considered on enamide substrates.¹¹

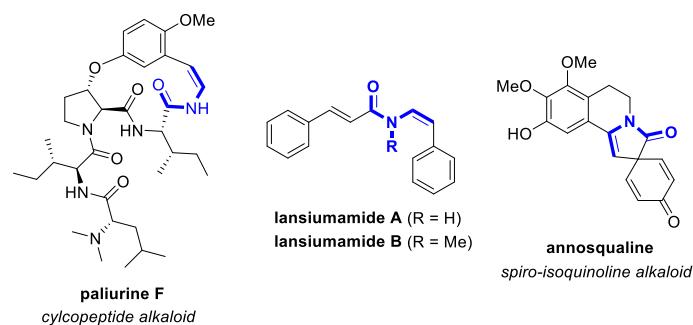
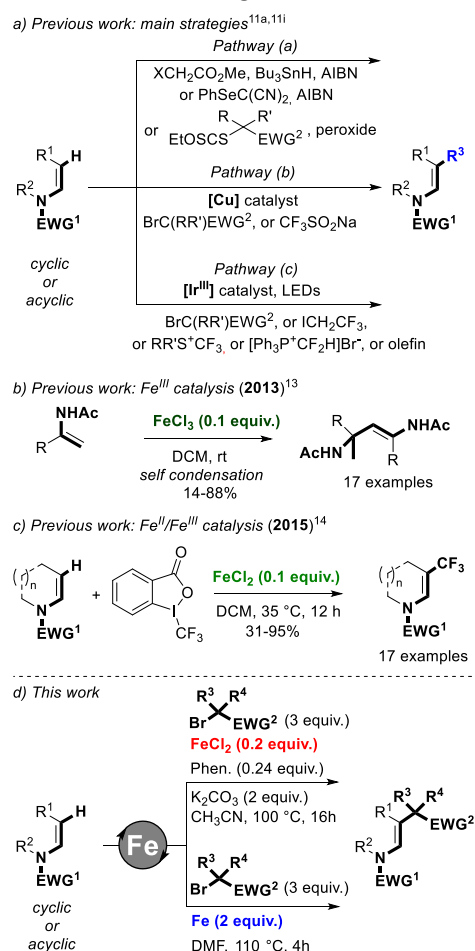


Figure 1. Selected biologically active molecules containing enamide functionalities.

In recent years, a special focus has been placed on the development of their direct β -C(sp^2)-H functionalization, including arylation, olefination, alkylation, carbonylation, sulfonylation and phosphorylation reactions among a few other useful transformations.^{11b,11e–11i} Remarkably, alkylation and/or fluoroalkylation reactions, which represent a greater challenge

as they involve a β -C(sp^2)-C(sp^3) bond formation, have also been at the forefront of investigations.^{11b,11f,11i}



Scheme 1. Strategies for direct intermolecular (fluoro)alkylation of enamides.

Significant advances have been achieved in this area, mostly through the addition of alkyl radicals, which are mainly generated by direct radical initiation or a single electron-transfer (SET) process using copper catalysts or iridium(III) salts

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† Footnotes relating to the title and/or authors should appear here.

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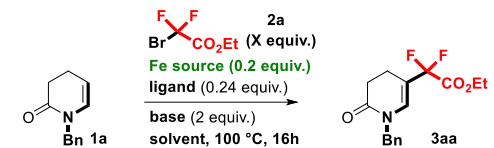
under photoredox-catalysis (Scheme 1a).^{11b} From an environmental and economical point of view, iron catalysis holds the promise of being able to cover a wide swath of organic synthesis.¹² Iron catalysts are not only expected to operate through reductive and oxidative regimes, but they are also able to embrace “early” transition metal characters. Of note, in 2013, Guan and co-workers developed a FeCl₃-catalyzed self-condensation of enamides, offering an original strategy for the synthesis of nitrogen-containing quaternary carbon centers through Lewis acid catalysis (Scheme 1b).¹³ In 2015, our group reported the first example of the iron(II)-catalyzed direct C–H trifluoromethylation of enamides using Togni’s reagent *via* a radical process (Scheme 1c).¹⁴ Fluorine is indeed an increasingly commonly found component in bioactive compounds that span all therapeutic categories. Fluorine-containing derivatives are amongst some of the top-selling and best-performing “small molecule” pharmaceutical products.^{15,16} However, to the best of our knowledge, there are no reports so far on the use of iron catalysis with the perspective of developing an efficient, straightforward and mild application with broad reagent scope in order to functionalize enamides through a direct intermolecular β -C(sp²)-H (fluoro)alkylation. Thus, there is still great room for improvement. We report herein our efforts to overcome this challenge.

Results and Discussion

In our endeavors to explore the reactivity of iron catalysis in the alkylation reaction of enamides, we started our study with the six-membered cyclic enamide **1a** and the ethyl 2-bromo-2,2-difluoro-acetate **2a** (2 equiv) which were selected as model substrates (Table 1). Based on the conditions previously developed by our team for the copper-catalyzed olefinic C–H difluoroacetylation,¹⁷ and iron-catalyzed trifluoromethylation of electron-rich olefins,¹⁴ the optimization of the reaction conditions was started by using iron(II) dichloride (0.2 equiv.) as the catalyst, 1,10-phenanthroline (0.24 equiv.) as the ligand, and K₂CO₃ (2 equiv.) as the base. The reaction proceeded at 100 °C in acetonitrile for 16 h under an argon atmosphere. The desired C3 alkylated enamide **3aa** was obtained as the unique derivative, with complete regioselectivity in 42% yield (entry 1). To improve the yield of **3aa**, screening of the catalyst loading (entries 2–3) and of the reaction time (entry 4) was thereafter carried out with success with yields up to 91%. The efficiency of the amount of α -bromo reagent (entry 5), base (entries 6–8), and solvent types (entries 10–14), as well as iron (entries 15–21) and ligand source (entries 23–24) were also evaluated, but no improvement whatsoever of the reaction outcome was observed. Importantly, when no base (entry 9) or no catalyst (entry 22) was used, the alkylation was not promoted, and no product was noted. Iron complexes of η -nitrile ligands such as acetonitrile are well known systems capable of mediating various useful synthetic transformations.¹⁸ Of note, when the alkylation reaction was performed in acetonitrile, in the absence of 1,10-phenanthroline, the enamide product was provided, albeit with lower efficiency (31% vs. 86%; entry 25 vs. entry 5). Interestingly, when iron(II) or iron(III) salts were

employed, the reaction was also amenable to compound **3aa** (entry 21).

Table 1. Optimization studies of the iron(II)-catalyzed β -C(sp²)-H alkylation of enamide **1a**^a



Entry	Fe source	BrCF ₂ CO ₂ Et (equiv.)	Base	Solvent	Yields (%) ^b
1 ^c	FeCl ₂	2	K ₂ CO ₃	CH ₃ CN	42
2 ^d	FeCl ₂	2	K ₂ CO ₃	CH ₃ CN	79
3 ^e	FeCl ₂	2	K ₂ CO ₃	CH ₃ CN	65
4 ^f	FeCl ₂	2	K ₂ CO ₃	CH ₃ CN	91
5	FeCl₂	3	K₂CO₃	CH₃CN	86(82^g)
6	FeCl ₂	3	Na ₂ CO ₃	CH ₃ CN	80
7	FeCl ₂	3	Cs ₂ CO ₃	CH ₃ CN	41
8	FeCl ₂	3	Et ₃ N	CH ₃ CN	9
9	FeCl ₂	3	–	CH ₃ CN	0
10	FeCl ₂	3	K ₂ CO ₃	CH ₂ Cl ₂	63
11	FeCl ₂	3	K ₂ CO ₃	DCE ^h	10
12	FeCl ₂	3	K ₂ CO ₃	Toluene	31
13	FeCl ₂	3	K ₂ CO ₃	DMSO	N.D. ⁱ
14	FeCl ₂	3	K ₂ CO ₃	Dioxane	47
15	FeBr ₂	3	K ₂ CO ₃	CH ₃ CN	57
16	Fe(OTf) ₂	3	K ₂ CO ₃	CH ₃ CN	67
17	FeCl ₂ ·4H ₂ O	3	K ₂ CO ₃	CH ₃ CN	52
18	Ferrocene	3	K ₂ CO ₃	CH ₃ CN	19
19	Fe(OAc) ₂	3	K ₂ CO ₃	CH ₃ CN	35
20	Fe(acac) ₂	3	K ₂ CO ₃	CH ₃ CN	3
21	FeCl ₃	3	K ₂ CO ₃	CH ₃ CN	60
22	–	3	K ₂ CO ₃	CH ₃ CN	0
23 ^j	FeCl ₂	3	K ₂ CO ₃	CH ₂ Cl ₂	21
24 ^k	FeCl ₂	3	K ₂ CO ₃	CH ₂ Cl ₂	12
25 ^l	FeCl ₂	3	K ₂ CO ₃	CH ₃ CN	31
26 ^m	FeCl ₂	3	K ₂ CO ₃	CH ₃ CN	18
27 ⁿ	FeCl ₂	3	K ₂ CO ₃	CH ₃ CN	18
28 ^o	FeCl ₂	3	K ₂ CO ₃	CH ₃ CN	54

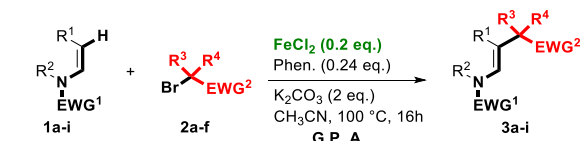
^a Reaction conditions: **1a** (0.5 mmol, 1.0 equiv.), **2a** (2–3 equiv.), 1,10-phenanthroline (0.12 mmol, 0.24 equiv.), dry base (1.0 mmol, 2.0 equiv.), solvent (3.0 mL), 100 °C, 16 h, under Ar. ^b Yields determined by ¹⁹F NMR analysis of the crude mixture using α,α,α -trifluorotoluene as an internal standard. ^c 0.1 equiv. of FeCl₂ was used. ^d 0.2 equiv. of FeCl₂ was used. ^e 0.3 equiv. of FeCl₂ was used. ^f Reaction time of 42h. ^g Isolated yield. ^h DCE = 1,2-dichloroethane was used. ⁱ N.D. = not determined. ^j 1,2-Bis(diphenylphosphino)ethane, instead of 1,10-phenanthroline was used as ligand. ^k *N,N,N',N'*-tetramethylethylenediamine (TMEDA), instead of 1,10-phenanthroline was used as ligand. ^l No ligand. ^m Reaction mixture heated at 80 °C. ⁿ The reaction mixture was heated at 150 °C for 1h under μ W irradiation. ^o Reaction performed in open air.

One may therefore wonder about the mechanism and oxidation state of the iron catalyst. In fact, it could suggest possible Fe^{II}/Fe^{III} catalytic cycle. Lastly, changing the heating temperature and the mode, or performing the reaction in open air (entries 26–28), led to a poorer performance in the transformation, revealing that the best conditions are those reported in entry 5.

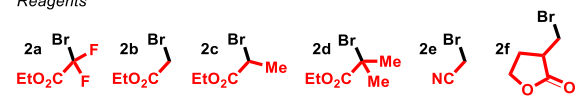
With the optimal conditions in hand (i.e., **G.P. A**), we next explored the scope of this iron-catalyzed C(sp²)-H alkylation

with a range of enamides (**1a–i**) in presence of α -bromo reagents (**2a–f**). The results are shown in Table 2.

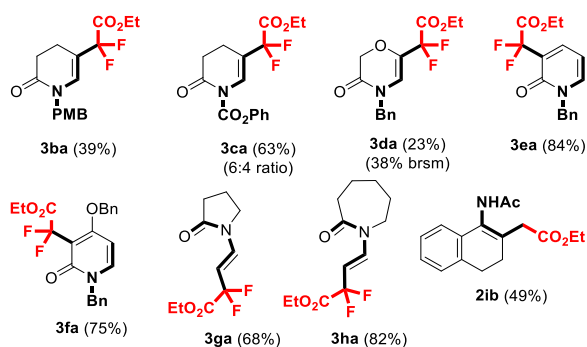
Table 2. Substrate and reagent scope for the FeCl_2 -catalyzed $\beta\text{-C}(sp^2)\text{-H}$ alkylation of enamides.^{a,b}



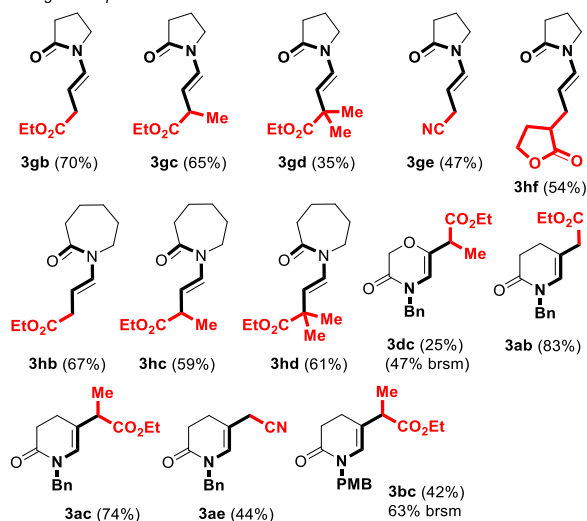
Reagents



Substrate scope



Reagent scope



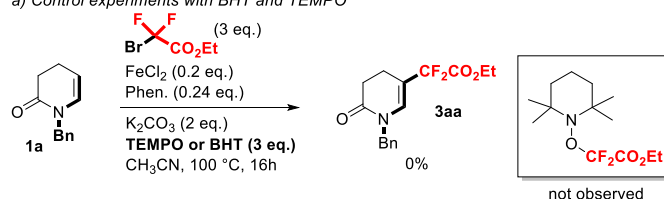
^a Reaction conditions: Enamides **1a–i** (0.5 mmol), α -bromo reagents **2a–f** (1.5 mmol), 1,10-phenanthroline (0.12 mmol), FeCl_2 (0.1 mmol), dry K_2CO_3 (1.0 mmol), CH_3CN (3.0 mL), 100 °C, 16 h, under Ar atmosphere. ^b Isolated yields. ^c brsm = based on recovered starting material.

To our delight, most of the reactions proceeded smoothly to afford the corresponding β -alkylated enamides **3** in moderate to good yields. A good functional group tolerance was observed except for the substrates **1b** and **1d** which are more electron-rich than the other enamides because of the presence of the *N*-PMB protective group (**1b**) or of the oxygen atom in the morpholine moiety **3d**. Interestingly, in the difluoro series, the deactivated *N*- CO_2Ph -protected piperidinone adduct **3ca** was isolated in moderate yield as a 6:4 ratio of rotamers. Of note, a C-5 selective alkylation of 2-pyridone **1e** and **1f** was observed

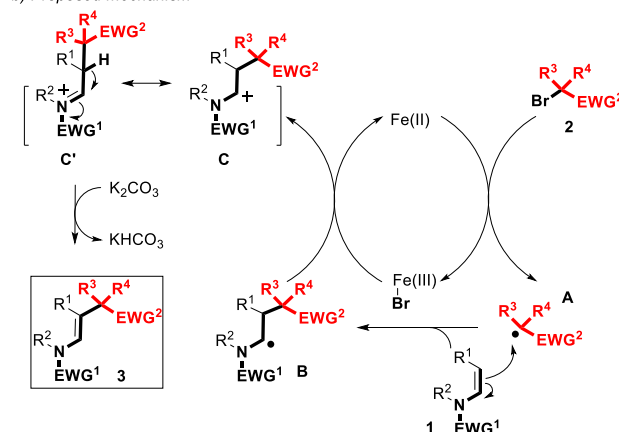
with good yields, and no trace of the other regioisomers was detected. Reaction with *N*-acyl enamide **1i** was also possible and a decent 49% isolated yield of **2ib** was achieved. In addition, the acyclic enamides **1g–h** were well tolerated and a clean regio- and excellent diastereoselectivity was observed (e.g., **3g–h**). Their *E* configuration was confirmed by nOe and $^1\text{H-NMR}$ experiments (see SI).

With a view to enhancing molecular diversity, the reagent scope was exemplified onto *exo*-enamides **1g–h** and a few other derivatives in the piperidinone and morpholinone series. Remarkably, similar results were obtained for all derivatives, leading to the corresponding alkylated adducts in moderate to good yields (59–83%), apart from compounds **3ae**, **3bc** and **3dc** which were respectively obtained in non-optimized 44%, 42% (63% brsm) and 25% (47% brsm) isolated yields.

a) Control experiments with BHT and TEMPO



b) Proposed mechanism

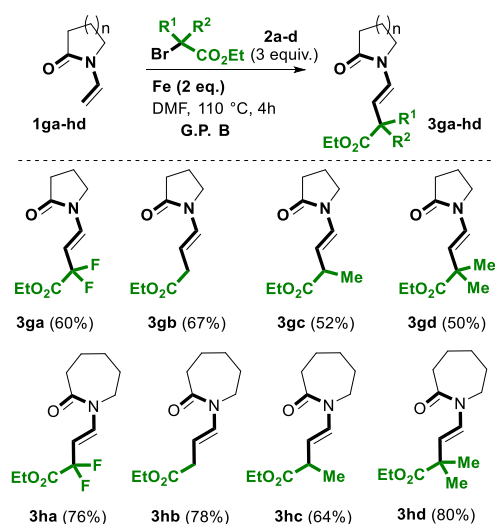


Scheme 2. Mechanistic studies on FeCl_2 -catalyzed alkylation of enamides **1**.

To have a better understanding of the Fe(II) -catalyzed $\beta\text{-C}(sp^2)\text{-H}$ alkylation of enamides **1**, some mechanistic experiments were carried out. As depicted in scheme 2 (a), when the reaction of **1a** and **2a** was conducted under the above optimal conditions in the presence of 3 equiv. of TEMPO (2,2,6,6-tetramethyl-1-piperidinyloxy) free radical, the reaction was suppressed and the desired product **3a** was obtained only in trace quantity. A complete inhibition was also observed in presence of BHT (2,6-di-*tert*-butyl-4-methylphenol). These results indicate that the reaction might proceed through a radical pathway. Based on these experimental results and previous reports,^{14,19} a plausible reaction mechanism is proposed (Scheme 2 (b)). Initially, a single electron transfer reaction initiated by Fe^{II} and the α -bromo reagent delivers the free radical **A** stabilized by the carbonyl or cyano group. Subsequently, radical **A** undergoes regioselective addition at the C-3 olefinic carbon of the nucleophilic enamide derivative **1** to give the radical intermediate **B**. After a single-electron oxidation of **B** by a high

valent iron complex, Fe^{II} is regenerated leading to the formation of a carbocation species **C** and its corresponding resonance structure **C'**. Finally, a base mediated deprotonation furnishes the desired alkylated product derivative **3** with a total *trans*-diastereoselectivity ($R^1 \neq O$).

Finally, this chemistry can be advantageously extended to low-cost and high-abundant iron powder. Noteworthy, we noticed a good conversion of the acyclic enamides of type **1g** and **1h** when treated with difluoroacetate **2a** and a stoichiometric equivalent of iron-powder in DMF at 110 °C. Interesting results using iron powder were recently described by Iwasaki, Nishihara and co-workers on a practical synthesis of γ -lactones from alkenes and α -halocarboxylic acids and their derivatives.²⁰ As depicted in Scheme 3, iron powder showed the catalytic activity needed to drive the β -C(*sp*²)-H alkylation of enamides **1g–1h** in the presence of α -haloesters **2a–d** (e.g., **G.P. B**). To our delight the reaction proceeded smoothly without using ligands, bases or additives to afford the related adducts in good yields, with again a total control of the regio- and stereoselectivity in favor of the *E*-diastereomers. However, surprisingly, this alkylative coupling was not amenable to cyclic *endo*-enamides.



^a Reaction conditions: Enamides **1ga–hd** (0.5 mmol), α -bromo reagents **2a–d** (1.5 mmol), iron powder (58 mg, 1.0 mmol), DMF (3.0 mL), 110 °C, 4 h, under Ar atmosphere. ^b Isolated yields.

Scheme 3. Substrate scope for the iron-powder-catalyzed β -C(*sp*²)-H alkylation of enamides **1ga–hd**.^{a,b}

Conclusions

In summary, we have developed a mild and novel method for the β -C(*sp*²)-H (fluoro)alkylation of cyclic and acyclic enamides using either a catalytic or a stoichiometric amount of iron species and various α -bromo activated reagents. Mechanistic studies reveal that the reaction might proceed through a radical process. Interestingly, the β -C(*sp*²)-H alkylation of enamides was also originally achieved using a stoichiometric amount of low-cost and high-abundant iron powder without using additional ligands, bases, or additives. Further applications based on this chemistry are in progress in our laboratory.

Experimental section

General Remarks. Unless otherwise stated, all reagents and starting materials were purchased from commercial sources and used as received. Iron ($\geq 99\%$, reduced, powder (fine)) and Iron(II) chloride (99.99% trace metal basis) were used as catalysts. Toluene (ACS reagent, $\geq 99.5\%$), Acetonitrile (ACS reagent, $\geq 99.5\%$), and *N,N*-Dimethylformamide (ACS reagent, $\geq 99.8\%$) were purified by passage through a column containing activated alumina under nitrogen pressure (Dry Solvent Station GT S100, Glass Technology, Geneva, CH). They were subsequently used as solvent in reactions under argon atmosphere. Potassium carbonate was activated at 100 °C in an oven for 24 h prior to use. NMR spectra were recorded at 298 K with a Bruker DPX 250 MHz or Bruker Avance III HD nanobay 400 and 700 MHz spectrometers equipped with BBO probes. The structures of the new compounds were assigned with the aid of 1D [¹H NMR, ¹³C NMR, Distortionless Enhancement by Polarization Transfer (DEPT)] and 2D Correlation Spectroscopy [(¹H–¹H COSY, and ¹H–¹³C Heteronuclear Single Quantum Coherence (HSQC)] experiments. When appropriate or in the event of ambiguous proton and carbon, assignments were established using ¹⁹F NMR and Heteronuclear Multiple-bond Correlation (HMBC). Unless otherwise stated, ¹³C and ¹⁹F spectra were acquired on a broad band decoupled mode. ¹H NMR (250, 400 or 700 MHz) chemical shift values are listed in parts per million (ppm), downfield from TMS as the internal standard or relative to the corresponding nondeuterated solvent. Data are reported as follows: chemical shift (ppm on the δ scale), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, o = overlapped and po = partially overlapped), coupling constant *J* (Hz), and integration. ¹³C NMR (63, 101 or 176 MHz) chemical shifts are given in ppm. Spectra were calibrated using the corresponding nondeuterated solvent. ¹⁹F NMR (235 or 376 MHz) chemical shifts are given in ppm. High-resolution mass spectra were recorded with a Bruker maXis ESI qTOF ultrahigh-resolution mass spectrometer coupled to a Dionex Ultimate 3000 RSLC system. MS data were acquired in positive mode and were processed using Data Analysis 4.4 software (Bruker). Infrared spectra were recorded neat with a Thermo Scientific Nicolet IS10 FTIR spectrometer using diamond ATR golden gate sampling and are reported in wave numbers (cm⁻¹). Analytical thin-layer chromatography (TLC) was performed with Merck Silica Gel 60 F254 pre-coated plates. Visualization of the developed chromatogram was performed under ultraviolet light (254 nm) and on staining by immersion in aqueous, acidic ceric ammonium molybdate followed by charring at ca. 150 °C. Column chromatography was performed in air on Silica Gel 60 (230–400 mesh) with petroleum ether (PE, bp 40–65 °C) and ethyl acetate as eluents, unless otherwise stated. Organic solutions were concentrated under reduced pressure with a Buchi rotary evaporator. The IUPAC name of the new compounds was generated automatically using the structure-to-name generator included in BIOVIA Draw 2020.

General Procedure for the β -C(*sp*²)-H Alkylation of Enamides **1a–i Using Catalytic FeCl₂ (**G.P. A**).** An oven-dried microwave vial under argon atmosphere was charged with the enamide substrate **1** (0.5 mmol, 1.0 eq.), FeCl₂ (13 mg, 0.1 mmol, 0.2 eq.), 1,10-phenanthroline (22 mg, 0.12 mmol, 0.24 eq.), dry K₂CO₃ (138 mg, 1.0 mmol, 2.0 eq.) and a magnetic stir bar. Anhydrous acetonitrile (3.0 mL) was added and the flask was submitted to three freeze-pump-thaw-argon cycles and placed under argon atmosphere. Next, the corresponding α -bromo reagent **2** (1.5 mmol, 3.0 eq.) was added, the reaction vessel was sealed and the reaction mixture was heated at 100 °C for 16 h. After cooling to rt (ca. 20 °C), EtOAc and H₂O were then added and

the aqueous phase was extracted with EtOAc (2 ×). The combined organic layers were washed with brine, dried over MgSO₄ and concentrated in vacuo. The crude product was purified through silica gel column chromatography to give the desired alkylated enamide product **3** in low to good yield.

General Procedure for the β-C(sp²)-H Alkylation of Enamides 1g-ahd Using Iron Powder (G.P. B). An oven-dried microwave vial under argon atmosphere was charged with the enamide substrate **1** (0.5 mmol, 1.0 equiv.), Iron powder (58 mg, 1.0 mmol, 2.0 eq.), and a magnetic stir bar. Anhydrous *N,N*-Dimethylformamide (DMF, 3.0 mL) was added and the flask was submitted to three freeze-pump-thaw-argon cycles and placed under argon atmosphere. Next, the corresponding α-bromoester **2** (1.5 mmol, 3.0 eq.) was added, the reaction vessel was sealed and the reaction mixture was heated at 110 °C for 4 h. After cooling to rt (ca. 20 °C), the reaction mixture was filtered over celite®, the cake was rinsed (EtOAc) and the solvents were evaporated under reduced pressure. DMF was removed by co-evaporating the crude mixture with heptane (3 ×) and the crude residue was purified by flash silica gel column chromatography to give the desired alkylated enamide product **3** in moderate to good yield.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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