

Iron(III) Chloride/Phenylsilane-Mediated Cascade Reaction of Allyl Alcohols with Maleimides: Synthesis of Poly-Substituted γ -Butyrolactones

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Abstract: A iron-catalyzed free radical cascade reaction of allyl alcohols with N-substituted maleimides for accessing poly-substituted γ -butyrolactones has been developed. In this protocol, various allyl alcohols can open N-substituted maleimide rings to form allyl ester intermediates, and the allyl ester intermediates can be converted into an allyl ester alkyl radicals and undergo intramolecular free radical addition cyclization to form a polysubstituted γ -butyrolactones. In this protocol, spiro γ -butyrolactone compounds can be also synthesized. Meanwhile, the strategy could be applied to further construct a fully substituted tetrahydrofuran. The reaction is not sensitive to oxygen or moisture and has been performed on gram-scale.

Keywords: Ferric chloride; poly-substituted γ -butyrolactones; free radical; fully substituted tetrahydrofuran; free radical cascade reaction

tone by free radical addition reaction of α -halocarboxylate with olefin.^[4] Despite these methods, it is still an important challenge to find a more convenient and efficient method for synthesizing fully substituted γ -butyrolactones from simple starting materials.

How to construct C–C bonds quickly and easily has always been the direction of organic chemists. In recent years, the transition-metal-catalyzed radical olefin hydrofunctionalization has been shown as an effective and distinct approach for C–C and C–X bonds formation.^[5] Currently, iron has been widely used as a catalyst in organic chemistry for quite a few reasons. Iron is the most abundant metal element after aluminum in earth's crust. Iron catalysts are particularly attractive because of their low cost, environmental friendliness and low toxicity.^[6] Therefore, the use of ferric chloride as the most abundant iron catalyst in organic chemistry has been reviewed by Martin.^[7] At present, iron-catalyzed non-activated olefin reduction cross-coupling reaction has shown its extraordinary significance in organic synthesis as a powerful

γ -Lactone skeletons are crucial structures in organic chemistry, which can be found in various spices, natural products and drug molecules (Figure 1).^[1]

Therefore, scientists have established a few methods for synthesizing γ -lactones.^[2] Meanwhile, the synthesis of γ -butyrolactones by N-substituted maleimide has also been reported.^[3] Additionally, there are only several reports on the synthesis of fully substituted γ -butyrolactones, such as Metzger and Liu succeeded in accessing fully substituted γ -butyrolac-

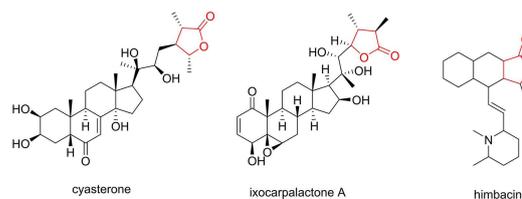


Figure 1. Biological compounds containing fully substituted γ -butyrolactone skeleton.

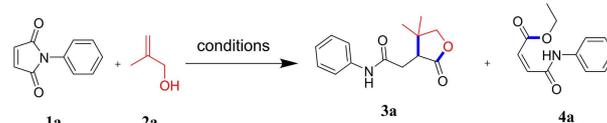
means of constructing C–C bond, C–N bond, C–X (X=F, Cl, S) bond. For example, Boger reported the hydrofluorination of non-activated olefins and the synthesis of vincristine analogs.^[8] Baran developed the free radical reduction cross-coupling of non-activated olefins using various electron-deficient olefins as acceptors, which can easily and quickly prepare various natural products that are difficult to synthesize, and he described the reaction mechanism in detail.^[9] The Cui team continued to study the functionalization of non-activated olefins.^[10] Our group reported the reduction cross-coupling reaction using chromone as the acceptor olefin.^[11] Although these studies have exhibited various olefinic acceptors, there is currently no reductive coupling reaction in which maleimide is involved as an olefin acceptor.

At present, it has been reported that N-substituted maleimide can form an ester with an alcohol ring-opening under the catalysis of Lewis acid.^[12] We suspected that the N-substituted maleimide could be opened with allyl alcohol under Lewis acid catalysis, and the formed allyl ester could undergo an intramolecular free radical addition reaction to obtain a γ -

butyrolactone. Herein, we report a less expensive Fe (III)-catalyzed radical cascade reaction to construct poly-substituted γ -butyrolactones via ring-opening/radical addition.

We commenced our investigations by examining the cascade reaction between N-phenylmaleimide (**1a**) and 2-methylallyl alcohol (**2a**) under various reaction conditions (Table 1). Initially we carried out the reaction using Baran's conditions^[9] at 75 °C. Gratifyingly, a γ -butyrolactone product **3a** was observed and isolated in 68% yield (entry 1). When we carried out the reaction using copper sulfate as a catalyst, the ethyl esterified product **4a** (entry 2) was obtained only in a moderate yield. This phenomenon indicated that copper sulfate was a good catalyst for the esterification, but was not a good catalyst for radical addition cyclization. Cobalt and nickel catalysts had a small amount of product formed (entries 3–4). When iron tribromide was used as a catalyst, both γ -butyrolactone and ring-opening products were formed (entry 5). In particular, Boger's catalyst^[8] iron oxalate did not give γ -butyrolactone (entry 6). To our surprise, when the reaction was conducted in FeCl₃ as a catalyst, we were

Table 1. Optimization of the Reaction Conditions.^[a,b]



entry	catalyst	reductant	solvent	T (°C)	Yield (%)	
					3a	4a
1	Fe(acac) ₃	PhSiH ₃	EtOH	75	68	0
2	CuSO ₄ ·5H ₂ O	PhSiH ₃	EtOH	75	0	30
3	Co(acac) ₂	PhSiH ₃	EtOH	75	trace	trace
4	Ni(acac) ₂	PhSiH ₃	EtOH	75	16.2	trace
5	FeBr ₃	PhSiH ₃	EtOH	75	26	36
6	Fe(ox) ₃ ·6H ₂ O	PhSiH ₃	EtOH	75	trace	trace
7	FeCl ₃	PhSiH ₃	EtOH	75	82	trace
8	FeCl ₃	HSiCl ₃	EtOH	75	0	0
9	FeCl ₃	Et ₃ SiH	EtOH	75	0	–
10	FeCl ₃	(EtO) ₃ SiH	EtOH	75	51	20
11	FeCl ₃	NaBH ₄	EtOH	75	0	–
12	FeCl ₃	NaCNBH ₃	EtOH	75	20	14
13	FeCl ₃	PhSiH ₃	cyclohexane	75	0	0
14	FeCl ₃	PhSiH ₃	MeOH	75	41	trace
15	FeCl ₃	PhSiH ₃	THF	75	trace	0
16	FeCl ₃	PhSiH ₃	2a	75	51	0
17 ^b	FeCl ₃	PhSiH ₃	EtOH	75	22	0
18	FeCl ₃	PhSiH ₃	EtOH	60	59	0
19	FeCl ₃	PhSiH ₃	EtOH	100 (seal)	68	0
20 ^[c]	FeCl ₃	PhSiH ₃	EtOH	75	32	tance

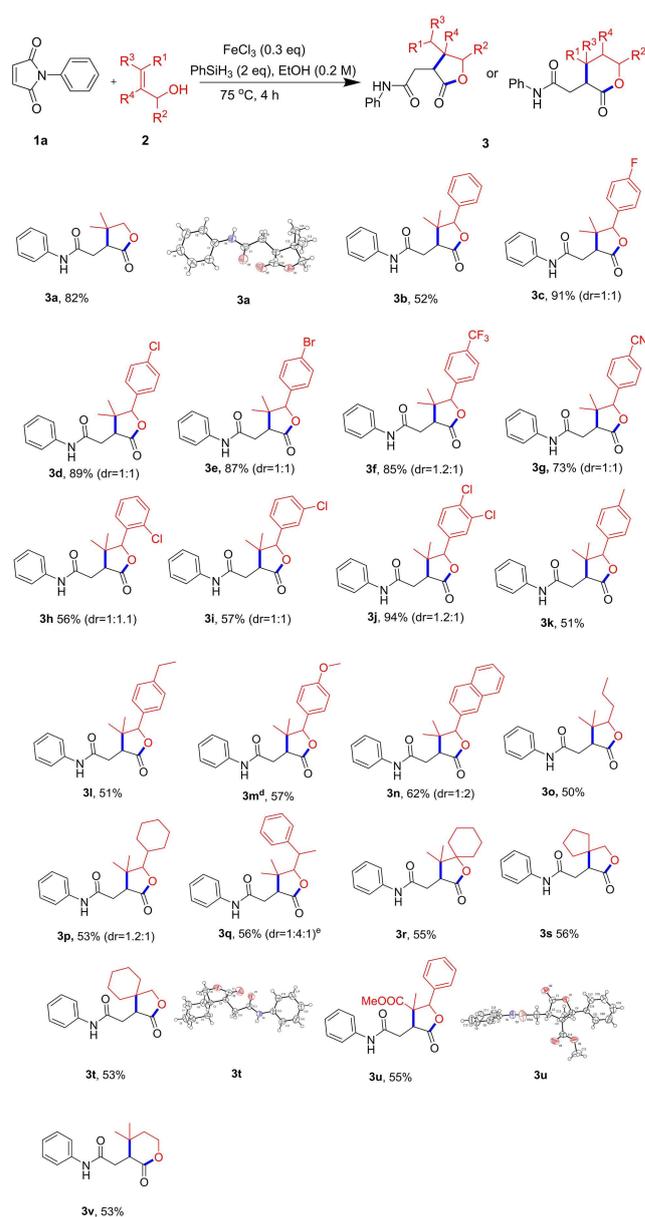
^[a] Reaction conditions: **1a** (0.2 mmol), **2a** (0.6 mmol), catalyst (30 mol%), reductant (2 equiv.), solvent (1 mL), 4 h; yield refers to isolated product.

^[b] FeCl₃ (10 mol%) was used.

^[c] Argon atmosphere reaction.

pleased to find that the yield of **3a** could be dramatically improved to 82% (entry 7). What's more, when other reductants like HSiCl_3 , Et_3SiH , $(\text{EtO})_3\text{SiH}$ were used, only $(\text{EtO})_3\text{SiH}$ was able to obtain the target product in a moderate yield (entries 8–10). When NaBH_4 and NaCNBH_3 were used as a reducing agent, NaCNBH_3 could obtain γ -butyrolactone in a lower yield (entries 11–12). The survey of solvents showed that cyclohexane did not give the target product (entry 13), while THF and MeOH were inferior to give the product in lower yield (entries 14–15). To our surprise, when the reaction was conducted in **2a** as a solvent, the γ -butyrolactone product could also be formed, albeit in moderate yield (entry 16). We also tried to decrease the amount of FeCl_3 to 10 mol% and found the yield was lower (entry 17). In addition, changing the temperature to 60°C and 100°C (seal) also resulted in a lower yield (entries 18–19). The argon atmosphere yield is only 32% under standard conditions (entry 20).

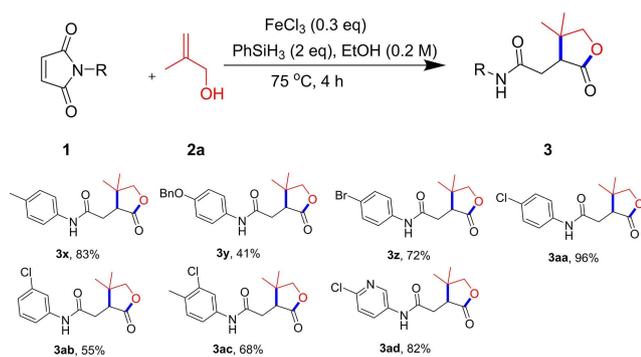
With the optimized reaction conditions in hand, we next set out to explore the universality of this method (Scheme 1). Therefore, a series of allyl alcohols with significant structural diversity, including chain and cyclic allyl alcohols, were subjected to this process. In addition, the single-crystal structure of **3a**, **3t**, **3u** further confirmed that the product of the cascade reaction was γ -butyrolactone.^[13] When we carried out the reaction with 1-phenyl-2-methyl-allyl alcohol, we obtained 4-phenyl substituted γ -butyrolactone in moderate yield (**3b**). Interestingly, the phenyl para-electron-withdrawinggroup substituted 2-methyl-1-substituted allyl alcohols, such as fluoro, chloro, bromo, trifluoromethyl and cyano, were also amenable to this protocol to generate the corresponding γ -butyrolactones in good to excellent yield (**3c–3g**). When the phenyl ortho and meta substituted 2-methyl-1-substituted allyl alcohols were used, the γ -butyrolactone products could also be formed, in moderate yield (**3h–3i**). The 2-methyl-1-disubstituted phenyl allyl alcohol could engage in this process to afford the product in excellent yield (**3j**, 94%). Moreover, phenyl para-electron-donating -group substituted 2-methyl-1-substituted allyl alcohols were also applicable in this process to furnish the product in moderate yield (**3k–3m**). It is possible that the electron withdrawing group enhances the electron withdrawing power of the ester group in the allyl ester intermediate to the acceptor olefin, and the acceptor olefin is more polarized to make the alkyl radical easier to attack the acceptor olefin. The 2-methyl-1-(naphthalen-2-yl)prop-2-en-1-ol were well amenable to this protocol to furnish the product in moderate yield (**3n**). When the 2-methyl-1-alkyl-substituted allyl alcohols were used, the γ -butyrolactone products could also be formed, albeit in moderate yield (**3o–3r**). In addition, cyclic allyl alcohols, such as cyclopent-1-en-1-ylmethanol and cyclohex-1-en-1-



Scheme 1. Substrate scope of allyl alcohol.^{a,b,c}

ylmethanol, could engage in this process to afford the spiro γ -butyrolactone products in moderate to good yields (**3s–3t**). The methyl 2-(hydroxy(phenyl)methyl) acrylate was also applicable in this process to furnish the product in moderate yield (**3u**, 55%). Furthermore, the 3-methylbut-2-en-1-ol was used, and the δ -valerolactone product could also be formed, albeit in moderate yield (**3v**, 53%).

We next focused our attention to the scope of maleimides (Scheme 2). Gratifyingly, various maleimides were well applicable in this free radical reduction cascade reaction process. For example, the

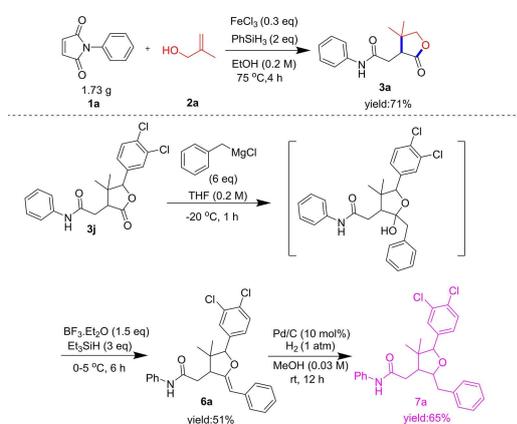


^{a)}Reaction conditions: **1a** (0.3 mmol), **2a** (0.9 mmol), FeCl_3 (0.3 eq), PhSiH_3 (2 eq), EtOH (0.2 M), 75°C , 4 h. ^{b)}Isolated yields.

Scheme 2. Substrate scope of allyl maleimide.^{a,b}

N-4-substituted phenyl maleimides, regardless of the electron-donating or electron-withdrawing substitution, could proceed smoothly in this process to deliver corresponding γ -butyrolactones in moderate to good yields (**3x–3aa**), with the valuable functional group such as methyl, benzyloxy, chloro and bromo. When the N-3-chlorophenyl maleimide was used, the γ -butyrolactone product could also be formed, albeit in moderate yield (**3ab**, 55%). Interestingly, the N-disubstituted phenyl and heterocyclic substituted maleimide, like pyridine, were also amenable to this protocol to generate the corresponding γ -butyrolactones in moderate to good yield (**3ac–3ad**).

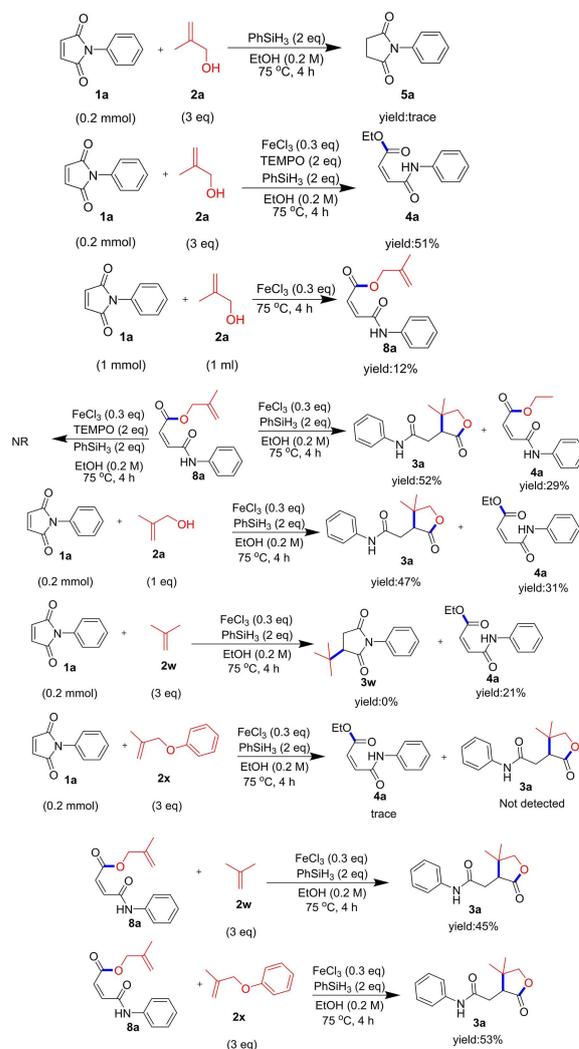
In order to reveal the potential application of this protocol, an amplification scale reaction was implemented. A 1.73 g scale reaction was carried out for allyl alcohol **2a** and N-phenylmaleimide **1a**, and the γ -butyrolactone product **3a** was isolated in 71% yield (Scheme 3). Fully substituted tetrahydrofuran is a very important structural model widely found in various natural products.^[14] At present, there are only several reports about the synthesis of some special fully



Scheme 3. Scale-up reaction and synthetic application.

substituted tetrahydrofuran.^[15] However the rapid and simple synthesis of fully substituted tetrahydrofuran still faces challenges. Therefore, the derivatization of the fully substituted γ -butyrolactone demonstrated the comprehensive utility of the method (Scheme 3). Initially, we used benzyl magnesium chloride to carry out the addition reaction with **3j**, and simultaneously carried out dehydration reaction to obtain intermediate **6a**.^[16] We found the carbon-carbon double bond could be successively reduced by H_2 ,^[17] and the fully substituted tetrahydrofuran products **7a** could be afforded in moderate yield.

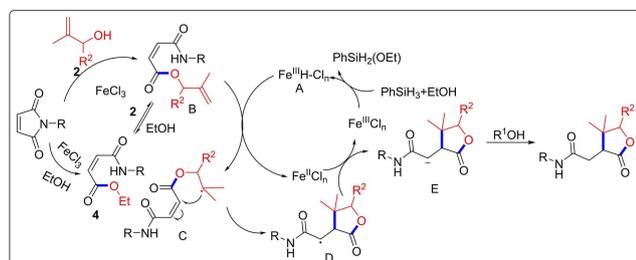
To gain insight into the reaction mechanism, some control experiments were carried out (Scheme 4). Omission of FeCl_3 resulted in obtaining trace carbon-carbon double bond-reduced product (**5a**) and recovery of the starting material, demonstrating that the Fe(III) catalyst was necessary for the free radical reduction cascade reaction. Interestingly, when the reaction was performed using **2a** as the solvent in the absence of



Scheme 4. Control experiments.

PhSiH₃, intermediate **8a** was obtained in 12% yield. When a radical scavenger such as TEMPO was added, the γ -butyrolactone product was not observed and ring-opened product (**4a**) was observed, when intermediate **8a** is added to the TEMPO reaction under standard conditions, no γ -butyrolactone is formed, indicating that the transformation proceeded via a radical process. Moreover, intermediate **8a** could form γ -butyrolactone under standard conditions in moderate yield, while 29% of the ethyl ester product **4a** was formed. This result was consistent with the reaction of one equivalent of allyl alcohol, demonstrating that intermediate **8a** was not stable. There was a transesterification equilibrium in the reaction. Unfortunately, when 2-methylpropene (**2w**) was reacted with N-phenylmaleimide under standard conditions, no free radical addition product (**3w**) was obtained, and the ring-opening product (**4a**) was obtained in only 21% yield. Regrettably, we did not obtain the γ -butyrolactone product when ((2-methylallyl)oxy)benzene (**2x**) and N-phenylmaleimide reacted under standard conditions. It is indicated that N-phenylmaleimide needed to be opened before free radical addition. In addition, when the intermediate **8a** reacted with **2w** or **2x** under standard conditions and no coupling product was produced, the γ -butyrolactone product was obtained only in a moderate yield, indicating that the intramolecular cyclization reaction was advantageous.

Based on these results and others previously reported in the literature,^{[9][10]} a plausible mechanism was proposed in Scheme 5. Initially, the Fe(III)-



Scheme 5. Proposed mechanism.

catalyst was converted to Fe hydride species A in the presence of phenylsilane and ethanol. Meanwhile, N-substituted maleimide and alcohol were ring-opened under Lewis acid catalysis to form intermediate **4** and B.^[12] Intermediate **4** had a transesterification equilibrium reaction with intermediate B, but with the consumption of intermediate B, intermediate **4** was continuously converted to intermediate B. The following step involved the transfer of a hydrogen atom from the transient Fe hydride (A) to the donor olefin B, giving the intermediate alkyl radical C, which could be able to carry out intramolecular free radical addition to

form radical adduct D. Then the single-electron transfer between FeIIICl_n and D delivers E, which was protonated to lactone.

In summary, an iron-catalyzed free radical reduction cascade reaction of allyl alcohols with N-substituted maleimides has been reported for the preparation of polysubstituted γ -butyrolactones. This protocol is not only featured with mild conditions and broad scope, but also reveals a free radical cascade reaction of N-substituted maleimides, which would offer a new insight for synthesis of γ -butyrolactones and spiro γ -butyrolactones. Meanwhile, the fully substituted γ -butyrolactone can be further derivatized as a fully substituted tetrahydrofuran. In the future, we will examine the biological activities of this series of compounds to explore the application value of these compounds.

Experimental Section

General Procedure for Polysubstituted γ -Butyrolactone (**3a–3x**, **3aa–3ad**)

Add FeCl₃ (14.6 mg, 0.09 mmol) to the reaction tube and dissolve immediately with ethanol (1.5 ml). Afterwards, allyl alcohol **2** (0.9 mmol), and PhSiH₃ (64.9 mg, 0.6 mmol) were added via syringe. The solution was heated to 75 °C. Afterwards, N-substituted maleimide **1** (0.3 mmol) added to the solution. The solution was kept at 75 °C for 4 h. Then the solution was diluted with H₂O. Ethyl acetate extracted and transferred to a round bottom flask. Silica gel was added to the flask and volatiles were evaporated under vacuum. The purification was performed by column chromatography on silica gel using ethyl acetate/petroleum ether (v/v, 1:3) as eluent to give polysubstituted γ -butyrolactone **3**.

General Procedure for Fully Substituted Tetrahydrofuran (**7a**)

2-(5-(3,4-dichlorophenyl)-4,4-dimethyl-2-oxotetrahydrofuran-3-yl)-N-phenylacetamide **3j** (118 mg, 0.3 mmol) was added to the reaction tube which was dried under an argon atmosphere and dissolved in dry THF (1.5 ml). Benzyl magnesium chloride (1 M, 1.8 ml) was added dropwise at –20 °C and kept for one hour. Then the solution was diluted with 1 N HCl. Ethyl acetate extracted and transferred to a round bottom flask. The volatiles were evaporated to dryness and dissolved in dichloromethane (1 ml) to be transferred to a reaction tube. Et₃SiH (105 mg, 0.9 mmol), BF₃·Et₂O (64 mg, 0.45 mmol) were added in sequence, and kept at 0–5 °C for 6 hours. Then the solution was diluted with H₂O. Ethyl acetate extracted and transferred to a round bottom flask. Silica gel was added to the flask and volatiles were evaporated under vacuum. The purification was performed by column chromatography on silica gel using ethyl acetate/petroleum ether (v/v, 1:7) as eluent to give **6a** (2-(2-benzylidene-5-(3,4-dichlorophenyl)-4,4-dimethyltetrahydrofuran-3-yl)-N-phenylacetamide) as a white solid (71 mg, 51% yield).

To a solution of **6a** (70 mg, 0.15 mmol) in MeOH (5 ml) under an inert atmosphere, was added 10 percent Pd/C (16 mg). H₂ was bubbled through the resulting suspension for 30 min. The reaction mixture was then stirred under 1 atmosphere of H₂ for 12 h. Pd/C was filtered off and silica gel was added to the flask and volatiles were evaporated under vacuum. The purification was performed by column chromatography on silica gel using ethyl acetate/petroleum ether (v/v, 1:15) as eluent to give **7a** (2-(2-benzyl-5-(3,4-dichlorophenyl)-4,4-dimethyltetrahydrofuran-3-yl)-N-phenylacetamide) as a white solid (46 mg, 65% yield).

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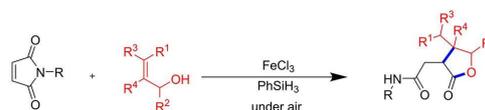
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Iron(III) Chloride/Phenylsilane-Mediated Cascade Reaction of Allyl Alcohols with Maleimides: Synthesis of Poly-Substituted γ -Butyrolactones

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- Cheap, environmentally friendly iron as a catalyst
- Poly-substituted butyrolactones and spiro lactones
- 29 examples in 41-96% yield
- Mild conditions and broad substrate scope

R¹, R³=alkyl, H; R²=alkyl, aryl, H; R⁴=alkyl, ester, H; R=aryl, heterocycle