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Fe-Catalyzed C−H Alkenylation of Dialkyl Anilines with Disulfonylethenes

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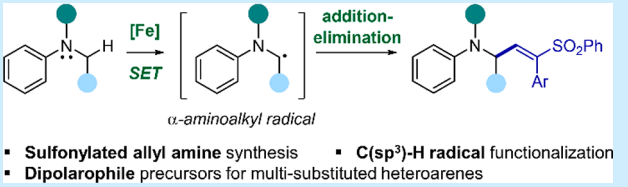
ABSTRACT: The oxidative alkenylation reaction of α-aminoalkyl C(sp^3)−H bonds has been investigated with (*E*)-1,2-bis(sulfonyl)-ethenes. The catalytic process of iron-polypyridyl complexes drives the single-electron oxidation of dialkyl anilines, resulting in the formation of α-aminoalkyl radical species. Subsequent cascades of radical addition and elimination reactions ensue, ultimately leading to the generation of sulfonylated allylic amine products. The utility of these products extends further, enabling the synthesis of multisubstituted heterocycles like pyrroles, pyrazines, and triazoles.



Allylic amines hold significant importance in the realm of organic chemistry due to their pivotal role in advancing synthetic methodology. They are widely recognized for their presence as functional groups in natural products, their versatility as intermediates in medicinal chemistry, and their utility as starting materials for the synthesis of α- and β-amino acids, alkaloids, and carbohydrate derivatives.[1] Notably, sulfonylated allyl amines have emerged as a novel category of small molecule electrophilic inactivators of cysteine proteases, a type of proteolytic enzyme with implications in diseases like cardiovascular, inflammatory, and cancer.[2] These inhibitors form stable thioether adducts through the electrophilic capture of Cys nucleophiles via 1,4-conjugate addition, irreversibly deactivating the enzyme.

The synthesis of sulfonylated allylic amines employs a diverse array of disconnection strategies, as outlined in Scheme 1. To begin, intermolecular Pd(II)-catalyzed 1,2-carboamination of electron-deficient dienes with ureas enables the synthesis of functionalized indolines (Scheme 1, II-a).[3] In a complementary approach, the allylic amines are obtained through the insertion reaction of chromium aminocarbenes into the β-CH bond of the electron-deficient alkenes (II-b).[4] Employing Horner−Emmons−Wadsworth methodologies, olefination of aldehydes smoothly yields the desired molecules (II-c).[5] Expanding the repertoire, radical hydrosulfonylation of alkynes with sulfonyl chlorides, under photoredox catalysis, delivers vinyl sulfones with moderate *Z*-selectivity (II-d).[6] Notably, among these synthetic methods, recent research highlights an intriguing avenue: the α-amino C(sp^3)−H bond functionalization reaction with SOMOphiles through radical addition−elimination (II-e).

To directly access the α-C(sp^3)−H activation of amides, one approach involves generating α-amidoalkyl radical intermediates by abstracting hydrogen from amides, facilitated by $M_2S_2O_8$ (M = K or NH_4) under elevated temperatures.[7] Alternatively, a distinct line of investigation centers on homolytic activation reactions of the α-amido C(sp^3)−H bond, utilizing photosensitizers such as aryl ketones.[8] Further diversification is evident in the exploration of single electron oxidation of α-amido carboxylic acids via Ir or anthracene photoredox catalysis.[9] This innovative strategy presents a platform for the formation of the reactive α-amidoalkyl radical, which effectively engages with electron-deficient radical acceptors, including sulfonyl substituents as proficient leaving groups, ultimately facilitating α-C(sp^3)−H alkenylation through addition−elimination reactions.

Building upon our previous investigation into iron-catalyzed α-amino C(sp^3)−H bond functionalization of dialkyl anilines via amine radical cation intermediates,[10] we have applied this strategy to the construction of sulfonylated allylic amines, employing diverse sulfonyl alkene acceptors. Notably, our exploration of vinyl sulfone derivatives as radical acceptors has unveiled the substantial influence of various alkene substituents on the outcome of the addition−cyclization versus addition−elimination reactions.[11] For instance, treatments involving 1,2-bis(sulfonyl)ethene and vinyl sulfone with a nitrile group primarily yield cycloadducts, whereas reactions with 1,2-bis(sulfonyl)ethene bearing phenyl substituents predominantly yield alkenylation products. This observation underscores the critical role of meticulous design in achieving α-amino C(sp^3)−H bond functionalization to α-aminoalkyl radicals, given the inherent versatile reactivity and the potential for competing oxidative pathways, particularly concerning aryl amines.

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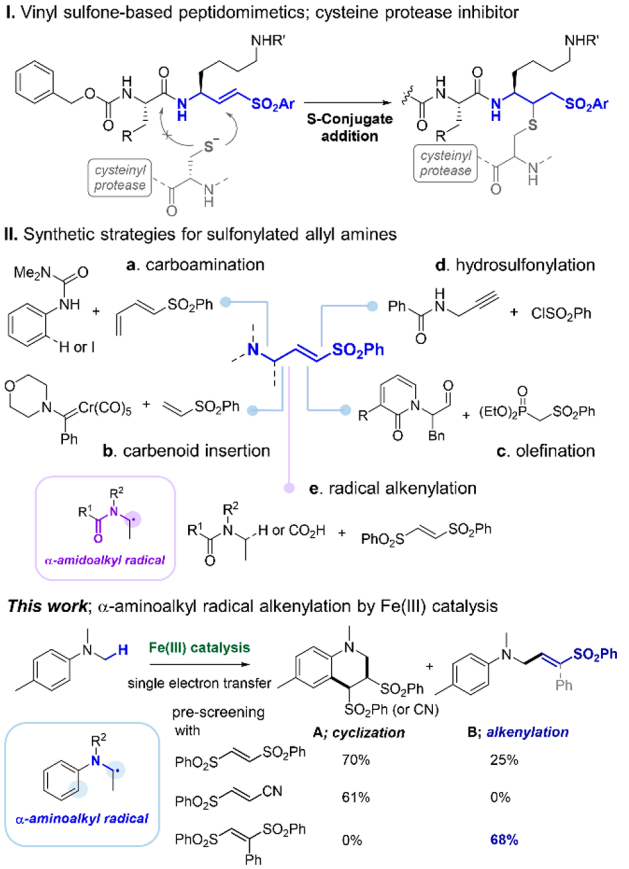
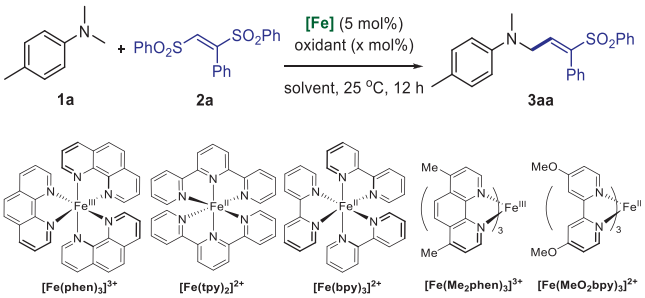
Scheme 1. Synthetic Strategies for Sulfonylated Allyl Amines



Our current research represents a pioneering achievement: the successful demonstration of the first iron-catalyzed α-amino alkenylation of dialkyl anilines employing 1,2-bis(sulfonyl)ethene derivatives. This transformation yields sulfonyl allyl amines, which not only hold promise as valuable entities themselves but also exhibit potential as efficient 1,3-dipolarophiles in subsequent cycloaddition reactions.

First, optimization of the iron-catalyzed alkenylation reaction conditions was performed with 4,*N*,*N*-trimethylaniline **1a** and 1,2-bis(phenylsulfonyl)ethene **2a** as the model substrates (Table 1). Initial reactions with $Fe(phen)_3(PF_6)_3$, $Fe(phen)_3(PF_6)_2$, and other polypyridyl Fe(II) catalysts were carried out in DMSO at 70 °C under aerobic conditions.[12] The alkenylated product **3aa** was obtained in promising yields (33−54%, entries 1−7), suggesting that the Fe complex acted as a single electron oxidant and selectively oxidized the trimethylaniline to a nucleophilic α-aminoalkyl radical species. While the $Fe(phen)_n^{2+/3+}$ catalytic cycle was efficiently maintained by O_2 as the terminal oxidant in our previous report on the [4 + 2] cycloaddition reaction of aniline **1a**,[10] it was necessary to use an additional oxidant. More than an equimolar amount of peroxy oxidants was then examined under the milder conditions in CH_3CN at 25 °C. The use of benzoyl peroxide, peroxy benzoic acid, and hydrogen peroxide was detrimental to the reaction efficiency, with cumene hydroperoxide (CHP, $C_6H_5C(CH_3)_2OOH$) emerging as the optimal oxidant to afford the product **3aa** in 73% yield (entries 8−11). Performing the reaction with 5 equiv of aniline in CH_3CN and DMSO solvent increased the efficiency of the entire reaction in each 90% and 89% yield, similarly (entries 12−13).

Table 1. Optimization of the Reaction Conditions[a]



entry	Fe complex	oxidant (*x*)	solvent	yield (%)[b]
1[c]	$Fe(phen)_3(PF_6)_3$	–	DMSO	43
2[c]	$Fe(phen)_3(PF_6)_2$	–	DMSO	54
3[c]	$Fe(Me_2phen)_3(PF_6)_2$	–	DMSO	43
4[c]	$Fe(Me_4phen)_3(PF_6)_2$	–	DMSO	33
5[c]	$Fe(Ph_2phen)_3(PF_6)_2$	–	DMSO	39
6[c]	$Fe(bpy)_3(PF_6)_2$	–	DMSO	35
7[c]	$Fe(MeO_2bpy)_3(PF_6)_2$	–	DMSO	46
8	$Fe(phen)_3(PF_6)_2$	BPO (150)	CH_3CN	42
9	$Fe(phen)_3(PF_6)_2$	mCPBA (150)	CH_3CN	20
10	$Fe(phen)_3(PF_6)_2$	H_2O_2 (150)	CH_3CN	10
11	$Fe(phen)_3(PF_6)_2$	CHP (150)	CH_3CN	73
12[d]	$Fe(phen)_3(PF_6)_2$	CHP (150)	CH_3CN	90
13[d]	$Fe(phen)_3(PF_6)_2$	CHP (150)	DMSO	89
14[d]	$Fe(phen)_3(PF_6)_2$	CHP (50)	DMSO	88
15[d]	**$Fe(phen)_3(PF_6)_2$**	**CHP (30)**	**DMSO**	**95**
16[d]	–	CHP (30)	DMSO	–
17[c]	–	CHP (30)	DMSO	80

[a]Reaction conditions: **1a** (0.2 mmol), **2a** (0.1 mmol), solvent (0.1 M), 25 °C, under Ar for 12 h. [b]Isolated yield. [c]Reaction at 70 °C under air. [d]Reaction with 0.5 mmol of **1a**. phen = 1,10-phenanthroline, Me_2phen = 4,7-dimethyl-1,10-phenanthroline, Me_4phen = 3,4,7,8-tetramethyl-1,10-phenanthroline, Ph_2phen = 4,7-diphenyl-1,10-phenanthroline, $(MeO)_2$bpy = 4,4′-dimethoxy-2,2′-bipyridine, BPO = benzoyl peroxide, CHP = cumene hydroperoxide.

The amount of CHP was gradually decreased to check the feasibility of radical chain reaction; 30 mol % of CHP exhibits a prominent effect to give the product in 95% yield (entries 14−15). Control experiments verified the importance of the Fe catalyst for initial oxidation, and experiments conducted in the absence of the Fe catalyst failed to generate any product (entry 16). CHP under thermal conditions (70 °C) is cleaved to the reactive oxyl radicals, and the alkenylation reaction operated without Fe catalyst resulted in an 80% yield (entry 17).

Next, we performed the α-amino alkenylation of a wide range of anilines **1** and disulfonylethenes **2** (Scheme 2). The substituent on the benzene of the arylsulfone could be varied with halogen, methyl, and methoxy groups,[13] and the alkenylation took place smoothly to afford the products **3ab**−**3ag** in yields of 60−87%. The structures of **3ab** and **3ac** were evaluated by X-ray analysis, confirming the (*E*)-configured isomers. Employing the halogenated phenyl substituents on disulfonylethenes (**2h**−**2j**) provided the alkenylated products **3ah**−**3aj** in good yields; moreover, the CF_3 functional group in **2l** was well tolerated under the reaction conditions. Various *N*,*N*-dimethylanilines incorporating 4-F, 4-Br, 3-Br, 4-*t*Bu, and 4-OMe delivered a range of alkenylated products in good to high yield. Substrates other than dimethylanilines were more challenging. In the reaction of **1i** and **1j** having two different *N*-alkyl groups, aminomethyl

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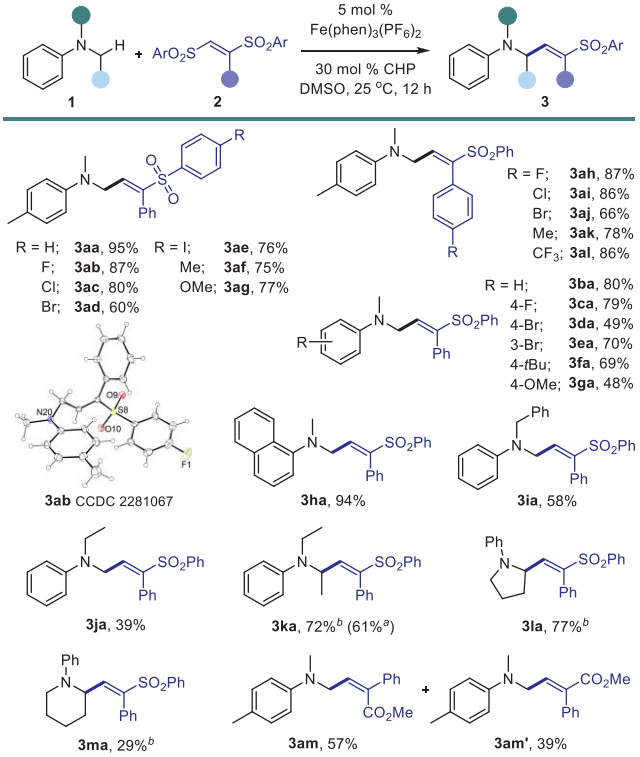
Scheme 2. Reaction Scope in α-Amino Alkenylation[a]

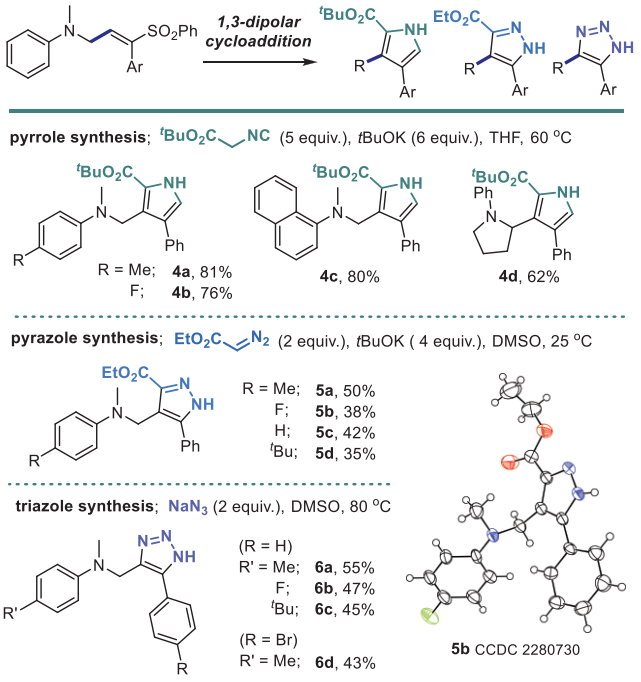


[a]Reaction conditions: **1** (0.5 mmol), **2** (0.1 mmol), $Fe(phen)_3(PF_6)_2$ (5 mol %), CHP (30 mol %), DMSO (0.1 M), 25 °C, 12 h, under Ar. [b]CH_3CN solvent.

radicals were exclusively generated and alkenylation took place on the *N*-methyl carbon. While the secondary radical was more stable than the primary one, we hypothesized that the reaction tended to proceed to the primary position due to fast deprotonation rates after single electron oxidation of amines. The reaction of *N*-methyl-lacking anilines generated the corresponding products **3ka**−**3ma** in moderate to good yield under CH_3CN conditions. When 2-phenyl-3-(phenylsulfonyl)-acrylate **2m** was used, a roughly 1.5:1 mixture of diastereoisomers (**3ma** and **3ma′**) was formed, suggesting that the sulfonyl radical is eliminated after the formation of the α-carbonyl radical intermediate.

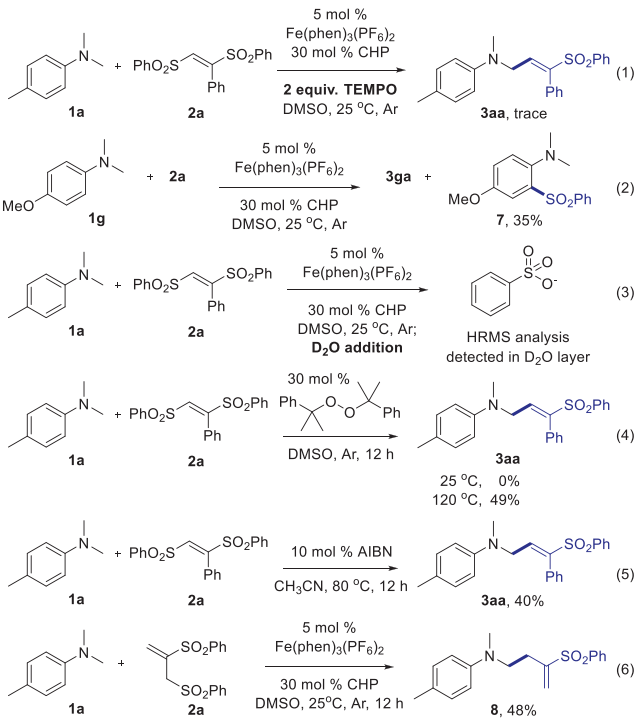
Vinyl sulfones are key structures in several bioactive molecules possessing anticancer and antitrypanosomal activity.[14] Due to their vinylogous acceptor reactivity, they readily participate in conjugate additions and cycloadditions.[15] We investigated the synthetic usefulness of the vinyl sulfonyl compounds in 1,3-dipolar cycloaddition for the synthesis of *N*-heterocycles such as pyrrole, pyrazole, and triazole (Scheme 3). 2,3,4-Multisubstituted pyrroles **4a**−**4d** were synthesized under the basic condition reaction with *tert*-butyl isocyanoacetate in 62−81% yields.[16] The reaction of vinyl sulfones and ethyl diazoacetate afforded the corresponding pyrazole heterocycles **5a**−**5d** in moderate yield. Additionally, several vinyl sulfones were transformed to 4-alkyl-5-aryl-1,2,3-triazoles (**6a**−**6d**) under the reaction with sodium azide.[17] This family of compounds is popularized as click chemistry, and several members are reported to have interesting pharmacological properties such as muscarinic anticonvulsant anti-HIV and β-lactamase inhibitory activities.

Scheme 3. Synthetic Application to 1,3-Dipolar Cycloaddition



Mechanistic investigations progressed to prove the iron-catalyzed oxidative alkenylation reaction mechanism (Scheme 4). A radical trapping reagent, TEMPO, markedly suppressed the reaction, suggesting that α-aminoalkyl radicals are significant and responsible for the reactivity in this Fe(III) catalysis (eq 1). As a detection of radical aromatic substitution byproduct in eq 2, 4-methoxy-*N*,*N*-dimethyl-2-(phenylsulfonyl)aniline (**7**) was isolated under standard

Scheme 4. Mechanistic Investigation



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reaction conditions for the synthesis of **3ga**.[18] Moreover, benzenesulfonate species were detected in the D_2O layer by ESI-MS analysis (found 156.9967; calculated 156.9965), which is the autoxidated byproduct of sulfonyl radical species (eq 3).[7a] These results have proven that the sulfonyl radical was generated in the elimination step after the addition of the α-aminoalkyl radical to disulfonylethene. To check the role of the cumyloxy radical species, the reaction was treated with dicumyl peroxide without Fe(III) catalyst in eq 4. At ambient temperature, which is the iron catalyst reaction temperature, the hydrogen atom transfer (HAT) reaction by homolysis of dicumyl peroxide does not seem to occur, and the desired product was obtained with a yield of 49% when heated to 120 °C. The AIBN-initiated reaction of **1a** did proceed to give alkenylated product **3aa** in a 40% yield (eq 5), which supports the HAT reaction of the sulfonyl radical species is likely to occur as a competitive pathway.[7b] The observation of product **8** with allylic sulfone **2n** also strongly proves the reaction mechanism of the sulfonyl radical elimination pathway (eq 6).

Taken together with our previous work, the iron-catalyzed alkenylation reaction mechanism was sketched (Figure 1). The

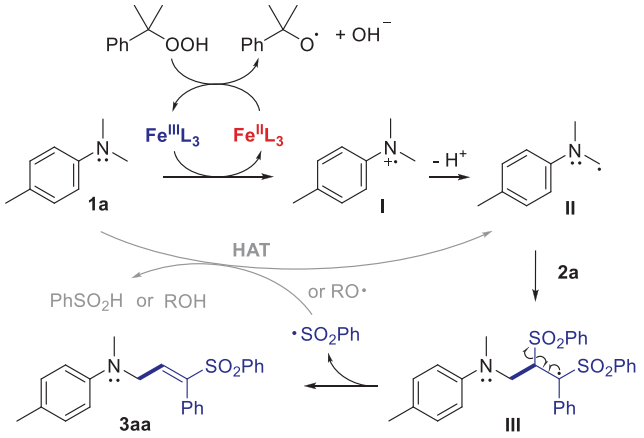

Figure 1. Proposed mechanism of Fe catalysis for radical addition/elimination reactions.

first single-electron-transfer step is proposed to proceed between the Fe(III) complex and 4,*N*,*N*-trimethylaniline (**1a**) to produce an amine radical cation and Fe(II) species. This is accountable to the potentials of the Fe(III)/Fe(II) (1.10 V vs SCE) and amine/radical cation redox pairs (0.78 V vs SCE), and the $Fe(phen)_n^{2+/3+}$ catalytic cycle was maintained by the cumene hydroperoxide oxidant. Deprotonation of the amine radical cation gives an α-aminoalkyl radical intermediate, which is added to the disulfonylethene (**2a**) to generate an α-sulfonyl radical intermediate (**III**). Finally, allyl amine product **3aa** was formed by the elimination of sulfonyl radical species. It was observed that the entire reaction proceeded very efficiently with only 5 mol % of iron catalyst and 30 mol % of CHP oxidant; the alkoxy radical generated after oxidation of Fe(II) catalyst and sulfonyl radical can promote the HAT reaction of α-C(sp^3)−H of 4,*N*,*N*-trimethylaniline (**1a**).[19]

In summary, our investigation has successfully demonstrated the iron-catalyzed alkenylation of dialkyl anilines with bis(arylsulfonyl)ethylenes. This achievement hinges on the efficient generation of α-aminoalkyl radical species and the subsequent cascade of radical addition and elimination processes, culminating in a diverse array of sulfonylated allyl amine products. The utility of these products extends further, enabling the synthesis of multisubstituted heterocycles like pyrroles, pyrazines, and triazoles through 1,3-dipolar cycloaddition with nucleophiles. Our work not only establishes the practicality of harnessing sustainable first-row transition metals under mild conditions but also underscores the potential of uncovering redox reactivity through streamlined methodologies. With this success in mind, we are optimistic about the broader applications of Fe(III)-catalyzed single-electron oxidation, envisioning its extension to a myriad of transformations and diverse reaction strategies.

■ ASSOCIATED CONTENT

Data Availability Statement

The data underlying this study are available in the published article and its Supporting Information

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.orglett.3c02812.

Experimental details; NMR spectra, crystallographic methods; and coordinates of computational output files (PDF)

Accession Codes

CCDC 2280730 and 2281067−2281068 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

The authors declare no competing financial interest.

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