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Lewis acid-mediated transformations of 5-acyl-*N*-fluoroalkyl-1,2,3-triazoles to cyclopentenones, indenones, or oxazoles†

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We present a transition metal-free approach to 2-*N*-substituted indenones, cyclopentenones, and 4-carbonyl oxazoles, based on the reaction of 5-acylated *N*-fluoroalkyl substituted 1,2,3-triazoles (prepared by a three-component click reaction of copper acetylides, fluoroalkyl azides, and acyl chlorides) with Lewis acids aluminium trichloride or boron trifluoride etherate, proceeding *via* the generation and cyclization of vinyl cations.

Introduction

Multi-substituted cyclopentenones, indenones and 4-carbonyl oxazoles constitute important classes of biologically active compounds known as anti-inflammatory/anticancer agents or enzyme inhibitors (Fig. 1).^{1–6} Synthetic strategies for obtaining their *N*-alkenyl derivatives (2-*N*-substituted cyclopentenones and indenones) or fully substituted oxazoles are limited because of the low availability of the starting materials and the necessity to use transition metal complexes or harsh reaction conditions. There is no general synthetic approach leading to these structures and each type of product requires a specific methodology. Despite the availability of numerous synthetic methods for the preparation of mono- or di-substituted oxazoles,⁷ access to tri-substituted 4-carbonyl oxazoles is not well explored and relies mainly on the intramolecular Cu-catalyzed cyclization of (thio)enamides⁸ or bromo(thio)enones,⁹ or on a protocol starting from 2-azido enones¹⁰ or alkenyl ketones.¹¹

2-*N*-substituted indenones can be accessed from ynamides,¹² 2-alkynylbenzoyl cyanides,¹³ or 2-hydroxy-substituted internal alkynes.¹⁴ 2-Amino indenones were also prepared *via* Au-catalyzed intermolecular oxidation of 2-carbonyl-1-ethynyl benzenes¹⁵ or by co-catalyzed annulation of thioamides with ynamides.¹⁶ Approaches leading to 2-amino-substituted cyclopentenones are limited to methods starting from previously modified cyclopentenone or cyclopentane rings.^{17–19}

Other procedures, starting from ynamides,²⁰ α -aminoenals²¹ or vinyl ketenes,²² are highly substrate-specific and do not allow for the further modification of the amino position in cyclopentenones.

We recently reported Brønsted and Lewis acid-mediated reactions of *N*-fluoroalkylated 1,2,3-triazoles,^{23–25} as an efficient approach to the generation of vinyl cation intermediates which then reacted with various nucleophiles providing *N*-alkenyl compounds such as β -enamido triflates,²⁶ β -fluoro enamides²⁷ and β -halo alkenyl imidoyl halides,²⁸ or undergo cyclization reactions to form multisubstituted cyclopentenones (Scheme 1).²⁹

Herein, we propose a new synthetic methodology to 2-*N*-substituted cyclopentenones, indenones and 4-carbonyl oxazoles from 5-acyl-*N*-fluoroalkyl-1,2,3-triazoles by a treatment with a Lewis acid (AlCl₃ or BF₃·OEt₂), proceeding *via* vinyl cations and their cyclization onto alkenes or arenes (Scheme 2). This type of cyclization is very rare.³⁰

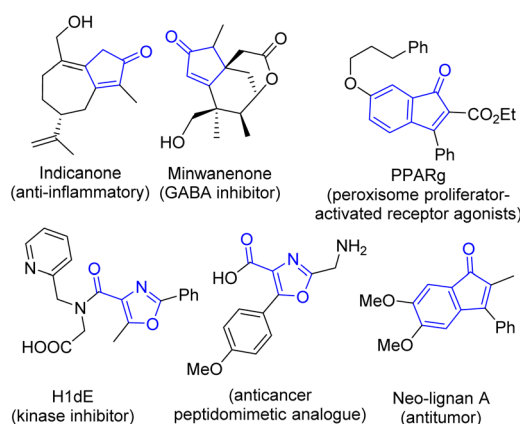


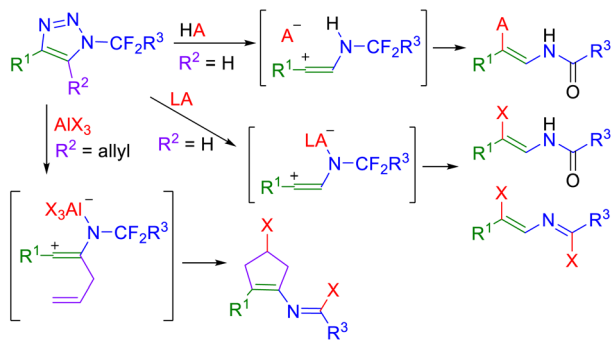
Fig. 1 Selected examples of bioactive 4-carbonyl oxazoles, cyclopentenones and indenones.

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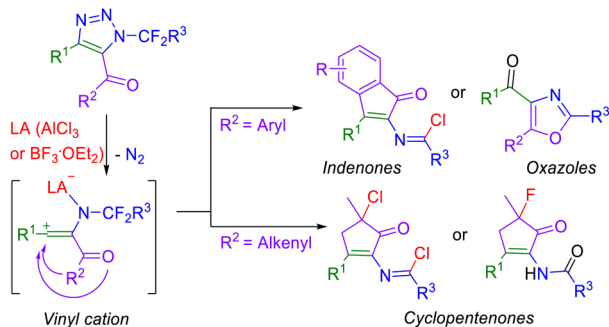
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Scheme 1 Brønsted and Lewis acid-mediated denitrogenation of *N*-fluoroalkyl-1,2,3-triazoles (HA = TfOH or FSO₃H, LA = BF₃·OEt₂ or AlX₃).



Scheme 2 Proposed Lewis acid-mediated transformation of 5-acyl-1,2,3-triazoles into new cyclic products.

Results and discussion

Synthesis of 5-acetyl- and 5-benzoyl-substituted 1,2,3-triazoles by an intercepted click reaction was briefly described in the literature.³¹ For our study it was necessary to prepare a library of 1-(per)fluoroalkyl-4-substituted-5-acyl-1,2,3-triazoles. However, application of Wu's conditions³¹ (phenylacetylene, CuI, Et₃N and benzoyl chloride or acetyl chloride) with our fluorinated azides^{23,32,33} (CF₃N₃ or C₂F₅N₃) did not afford the desired 5-acylated triazoles. Therefore, we turned to the use of (phenylethynyl)copper (**1a**), which was shown to be reactive with azido(per)fluoroalkanes in intercepted click iodination or allylation.²⁸ A three-component reaction of **1a**, azidopentafluoroethane (**2a**) and methacryloyl chloride was used for the optimization of the synthesis of triazole **3a** (Table 1). Initially, a mixture of **3a** and triazole side-product **3a-H** formed (entry 1). Increasing the amount of acyl chloride and using anhydrous conditions improved the yield of **3a** and suppressed the formation of **3a-H** (entries 2–4). To further increase the yield of **3a**, screening for an additional base was conducted (entries 5–11), identifying DIPEA as the most efficient one (entry 12). Finally, the use of 2 equiv. of acyl chloride and 3 equiv. of DIPEA provided **3a** in optimized yield (entry 14).

Having established the optimal reaction conditions for the intercepted click reaction and acylation sequence, the scope of the protocol was investigated on diverse acetylenic substrates,

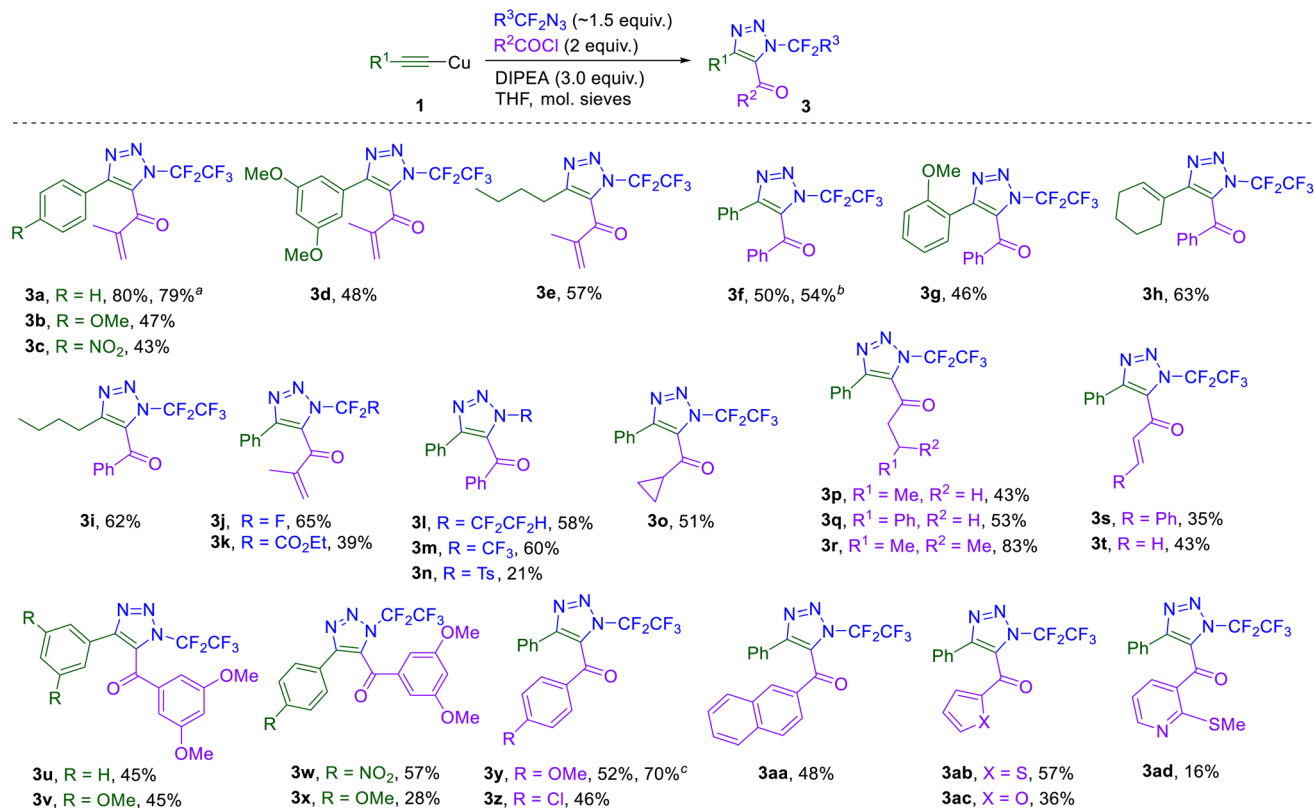
Table 1 Optimization of reaction conditions leading to triazole **3a**^a

Entry	RCOCl (equiv.)	Base (equiv.)	Ratio 3a / 3a-H ^b	Yield 3a (%) ^c
1 ^d	1	—	75 : 25	n.d.
2	1.2	—	99 : 1	51
3	2	—	100 : 0	53
4	5	—	100 : 0	33
5	1.2	Pyridine (1)	61 : 39	n.d.
6	1.2	NaOMe (2)	22 : 78	n.d.
7	1.2	Et ₃ N (2)	80 : 20	n.d.
8	1.2	NaNH ₂ (3)	38 : 62	n.d.
9	1.2	KF (1)	100 : 0	45
10	1.2	DBU (2)	0 : 100	0
11	1.2	<i>i</i> -Pr ₂ NH (2)	22 : 78	n.d.
12	1.2	DIPEA (2)	100 : 0	63
13	2	DIPEA (2)	100 : 0	75
14	2	DIPEA (3)	100 : 0	80
15	2	DIPEA (5)	100 : 0	46

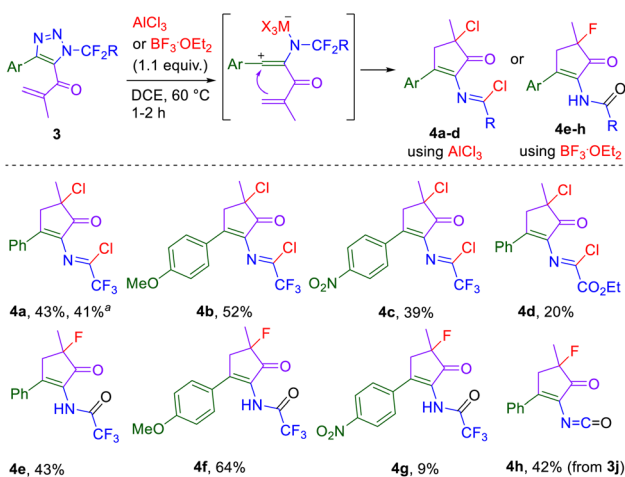
^a Reaction conditions: **1a** (1 mmol), **2a** (1.5 equiv.), THF (4 mL), 0–25 °C, then RCOCl, base, 3 Å MS (240 mg), rt, 18 h. ^b ¹⁹F NMR ratio. ^c Isolated yield. ^d Without 3 Å molecular sieves. n.d. not determined.

fluorinated azides, and acid chlorides (Scheme 3). 5-Methacryloyl triazoles (**3b–e**) with strongly electron-poor or electron-rich aryl rings in position 4 were prepared in moderate yields. To demonstrate the scalability of reaction, triazole **3a** was prepared on 1.76 g (10.7 mmol) scale in high yield. 5-Benzoyl-substituted triazoles (**3f–i**) were also prepared in good yields. Varying the azide reagent revealed that highly fluorinated azidoalkanes afforded better product yields than tosyl azide or ethyl azidodifluoroacetate. Modification of triazoles in position 4 with aryl, alkyl and alkenyl groups and modification in position 5 with aryl, heteroaryl, alkyl, cycloalkyl and alkenyl groups afforded products mostly in satisfactory yields. Scale-up of **3f** and **3y** to 4–5 mmol was also successful.

Next, AlCl₃ was chosen as a suitably strong and easily available Lewis acid to investigate the denitrogenative transformation of 5-acyloyl substituted triazoles. Cyclization of the formed vinyl cation intermediate onto the alkene moiety and chloride capture of the resulting carbocation led to the formation of cyclopentenone imidoyl chlorides (**4a–d**) in moderate yields (Scheme 4). The cation-stabilizing *p*-methoxyphenyl group in position 4 of triazole **3** improved the product yields. This observation, together with the necessity of triazole denitrogenation in the initial step of the reaction, speaks against an alternative reaction mechanism involving Nazarov cyclization, typically starting from a divinyl ketone. BF₃·OEt₂ was used for the preparation of fluorinated cyclopentenone amides **4e–g** from triazoles **3** (Scheme 4). In the case of *N*-CF₃ triazole **3j**, the final product is not a cyclopentenone amide but cyclopentenone isocyanate **4h** due to the facile HF elimination of the NHC(O)F intermediate.



Scheme 3 Substrate scope of the intercepted click reaction leading to 5-acyl triazoles **3**. Reaction conditions: **1** (1.0 mmol), **2** (1.5 mmol), DIPEA (3.0 mmol), acyl halide (2.0 mmol), THF (4 mL), 3 Å MS (240 mg), rt, 18 h. ^a10.7 mmol scale. ^b4.16 mmol scale. ^c5.0 mmol scale.



Scheme 4 AlCl₃-mediated denitrogenation/cyclization of triazoles **3** leading to cyclopentenone imidoyl chlorides **4a–d** and BF₃·OEt₂-mediated denitrogenation/cyclization of triazoles **3** leading to cyclopentenone amides **4e–g** and cyclopentenone isocyanate **4h**. Reaction conditions: **3** (1.0 mmol), AlCl₃ or BF₃·OEt₂ (1.1 mmol), DCE (0.1M), 60 °C, 1–2 h. ^a2.2 mmol scale.

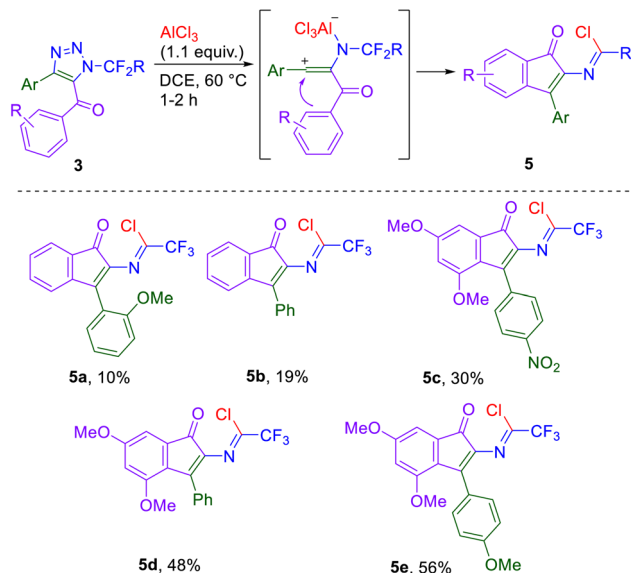
Triazole **3r** was a special case, as the vinyl cation intermediate induced a 1,5-hydride shift to form a tertiary carbocation and an α,β -unsaturated ketone. Cyclization and proton elimination afforded cyclopentenone **4i** (Scheme S1 in the ESI[†]).

Subjecting 5-benzoyl triazoles **3** to a reaction with AlCl₃ led to the cyclization on the aryl ring of the benzoyl moiety, forming indenone imidoyl chlorides **5** (Scheme 5). Again, the presence of vinyl cation-stabilizing groups in position 4 of the starting triazole and electron-rich groups on the aryl ring of the substituted benzoyl moiety in position 5 of the triazole both increased product yields. Using 5-benzoyl triazoles instead of dimethoxybenzoyl triazoles afforded only low to moderate indenone yields.

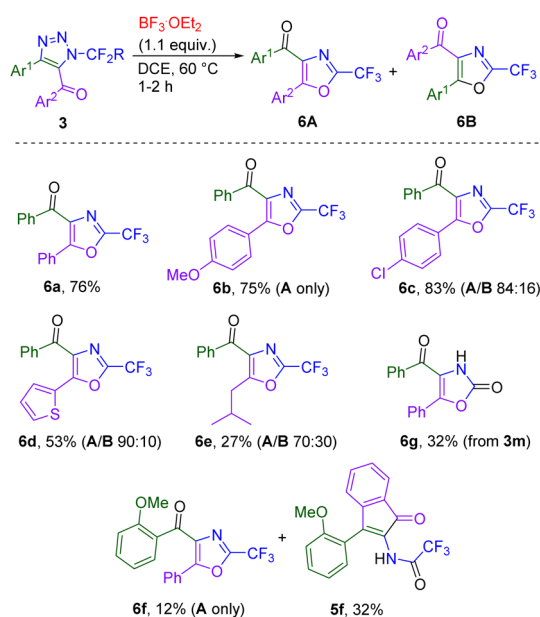
The formation of 4-acyl oxazoles **6a–g** was observed upon boron trifluoride-mediated transformation of 5-benzoyl triazoles (Scheme 6). Two isomers of products **6** can be formed: electron-rich or -neutral aryl groups in position 5 of the starting triazole cyclized selectively to form isomer **A** and triazoles with deactivated aryl groups in position 5 gave a mixture of isomers **A** and **B** with good to high selectivity for isomer **A**. Heating the mixture of isomers in a microwave did not lead to their interconversion, ruling out the possibility of Cornforth rearrangement in 2-trifluoromethyloxazoles. Oxazole **6f** was accompanied by indenone **5f** side-product. Oxazolone **6g** was prepared selectively from **3m**, as 2-fluorooxazoles are hydrolytically unstable.

To rationalize the formation of products **6A** and **6B**, we considered the following reaction mechanism (Scheme 7). As demonstrated in our earlier report,²⁷ the coordination of BF₃ to nitrogen atoms of the triazole ring (particularly the coordination to N1) led to opening of the triazole ring and the



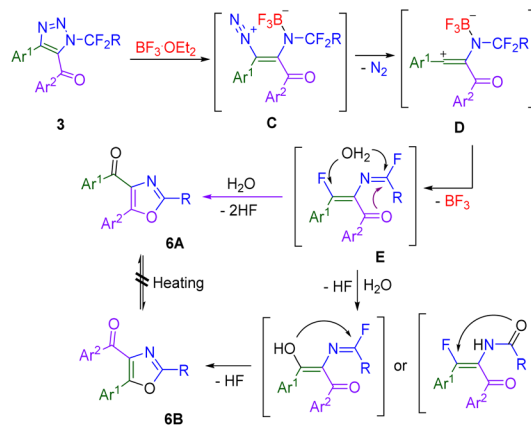


Scheme 5 AlCl_3 -mediated denitrogenation/cyclization of triazoles **3** leading to indenone imidoyl chlorides **5**. Reaction conditions: **3** (1.0 mmol), AlCl_3 (1.1 mmol), DCE (0.1M), 60 °C, 1–2 h.

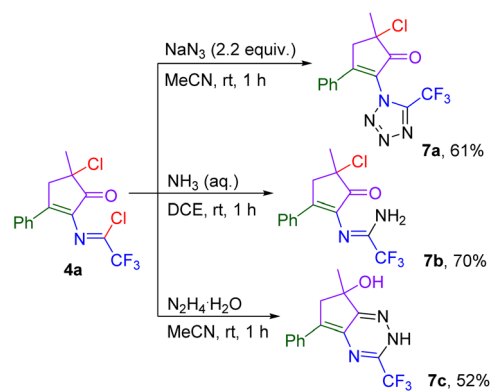


Scheme 6 $\text{BF}_3 \cdot \text{OEt}_2$ -mediated denitrogenation/cyclization of triazoles **3** leading to 4-acyl oxazoles **6**. Reaction conditions: **3** (1.0 mmol), $\text{BF}_3 \cdot \text{OEt}_2$ (1.1 mmol), DCE (0.1M), 60 °C, 1–2 h.

elimination of the nitrogen molecule from the diazonium intermediate **C**. The resulting vinyl cation **D** underwent elimination of tetrafluoroborate and fluoride transfer to form imidoyl fluoride **E**. Cyclization of the acyl oxygen led to **6A**. Alternatively, hydrolysis of the vinyl fluoride moiety of **E** created a competitive acyl moiety (oxygen nucleophile) for cyclization to **6B**. The required one molecule of water probably comes from the moisture in the solvent. Deliberate addition of a small amount of water reduced product yields,



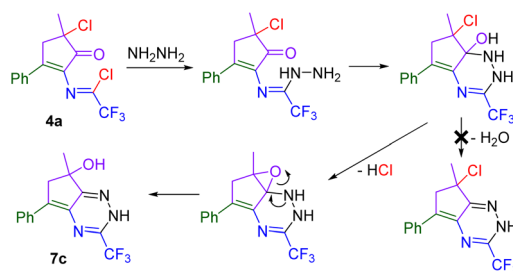
Scheme 7 Mechanism of BF_3 -mediated transformation of triazoles **3** to oxazoles **6**.



Scheme 8 Synthetic utilization of cyclopentenone **4a**.

presumably because of competitive hydrolysis of the used Lewis acid.

The synthetic utility of cyclopentenone imidoyl chlorides was demonstrated on examples of post-functionalization of **4a** (Scheme 8). Trifluoromethylated tetrazole **7a** was easily prepared from **4a** using sodium azide. The addition of an aqueous ammonia solution afforded amidine **7b**, and the addition of aqueous hydrazine led to the cyclization of the carbonyl and imidoyl chloride functional groups to give trifluoromethylated triazine **7c**. We proposed that **7c** is formed by cyclization of hydrazine nitrogen to the six-membered ring,



Scheme 9 Proposed mechanism of the formation of **7c**.



followed by the hydroxyl shift and substitution of the chlorine atom for oxygen on the cyclopentene moiety (Scheme 9).

Conclusions

In conclusion, we present the synthesis of *N*-electron-acceptor group-substituted 5-acyl-1,2,3-triazoles by an intercepted click reaction, namely a three-component cyclization of azide, copper acetylide and acyl chloride. Lewis acid-mediated triazole ring opening and nitrogen molecule elimination provided key reactive intermediates – vinyl cations, which cyclized selectively to form either cyclopentenone imidoyl chlorides, indenone imidoyl chlorides, cyclopentenone amides, or 2-trifluoromethyl oxazoles, depending on the combination of the Lewis acid used and the substitution in position 5 of the triazole ring. Post-functionalization of cyclopentenone imidoyl chloride gave access to selectively functionalized *N*-alkenyl compounds (amidines) or new nitrogen heterocycles (triazine or tetrazole). The presented methodology demonstrates a Lewis acid-mediated generation of vinyl cations from triazoles and their synthetic utilization in the formation of new C–C bonds.

Author contributions

PB supervised the project. LJ contributed to experiments and product characterization. LJ and PB jointly conceived the project, prepared the manuscript, and contributed to discussions.

Conflicts of interest

There are no conflicts to declare.

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