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Synthesis of Thiocarbamoyl Fluorides and Isothiocyanates Using CF_3SiMe_3 and Elemental Sulfur or $AgSCF_3$ and KBr with Amines

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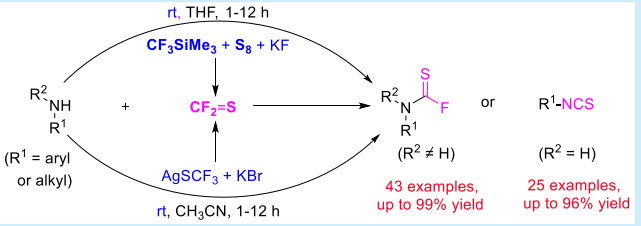
Supporting Information

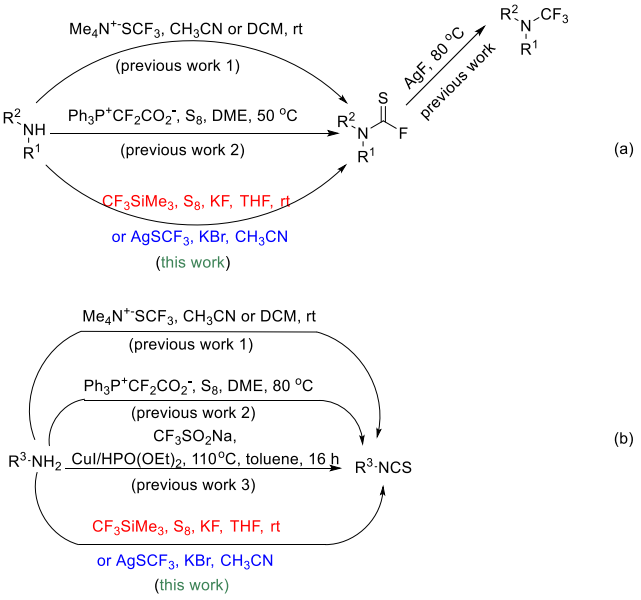
ABSTRACT: Reactions of thiocarbonyl fluoride derived from cheap, readily available, and widely used CF_3SiMe_3, elemental sulfur, and KF with secondary amines and primary amines at room temperature in THF provided a wide variety of thiocarbamoyl fluorides and isothiocyanates in moderate to excellent yields, respectively. The two reactions show broad substrate scope and good functional group tolerance. Moreover, $AgSCF_3$ reacts with secondary/primary amines under KBr at room temperature, affording quantitative thiocarbamoyl fluorides/isothiocyanates, which feature late-stage application.



Thiocarbamoyl chlorides are well-known[1] and have been used for the syntheses of biologically active compounds.[2] However, preparation of thiocarbamoyl chlorides requires the use of toxic reagents such as thiophosgene[3] or Cl_2 gas.[4] Moreover, the strong electrophilicity of thiocarbamoyl chlorides limits their late-stage applications. Their fluoride equivalents should have advantages of better functional group tolerance and higher chemoselectivity on polyfunctional molecules due to their lower electrophilicity. In addition, nitrogen, sulfur, and fluorine elements are very important in pharmaceuticals,[5] all of which are contained in the structures of thiocarbamoyl fluorides. However, thiocarbamoyl fluorides received little attention before 2017 due to the lack of safe and efficient processes to access them.[6] Developing methods for synthesizing thiocarbamoyl fluorides from readily available, safe, and cheap starting materials would enable their use as practical and available building blocks. Isothiocyanates are important building blocks which have been ubiquitously used in organic synthesis, materials science, biological, and pharmaceutical fields,[7] and many isothiocyanates themselves show significant biological activities.[8] Traditional methods for preparation of isothiocyanates involve highly toxic and/or highly electrophilic reagents such as thiophosgene,[9] CS_2,[10] phosgene,[11] thiocarbonyldiimidazole,[12] or dipyridylthionocarbonate (DPT).[13] Safety, functional group tolerance, and selectivity issues still need to be addressed.

In 2017, several safe reagents were reported to prepare trifluoromethylated amines and/or isothiocyanates from secondary amines and/or primary amines.[14] These reagents include bench-stable solid reagent $(Me_4N)SCF_3$ (Scheme 1a,,b, previous work 1),[14a,b] $Ph_3P^+CF_2CO^{2-}$ (PDFA) and elemental sulfur (Scheme 1a,b, previous work 2),[14c] and Langlois reagent (F_3CSO_2Na) (Scheme 1b, previous work 3).[14d] Thiocarbamoyl fluorides are formed as intermediates in

Scheme 1. Methods for Thiocarbamoyl Fluorides/Isothiocyanates through Safe Reagents



the above-reported one-pot, two-step process for trifluoromethylation of amines (Scheme 1a,b, previous work 1, 2).[14a−c] However, some problems and challenges still exist. $(Me_4N)SCF_3$ was prepared from CF_3SiMe_3, elemental sulfur, and hydrophilic Me_4NF.[15] Although $(Me_4N)SCF_3$ is stable, the preparation of $(Me_4N)SCF_3$ requires very careful and inert conditions, and preparation without a glovebox often fails due

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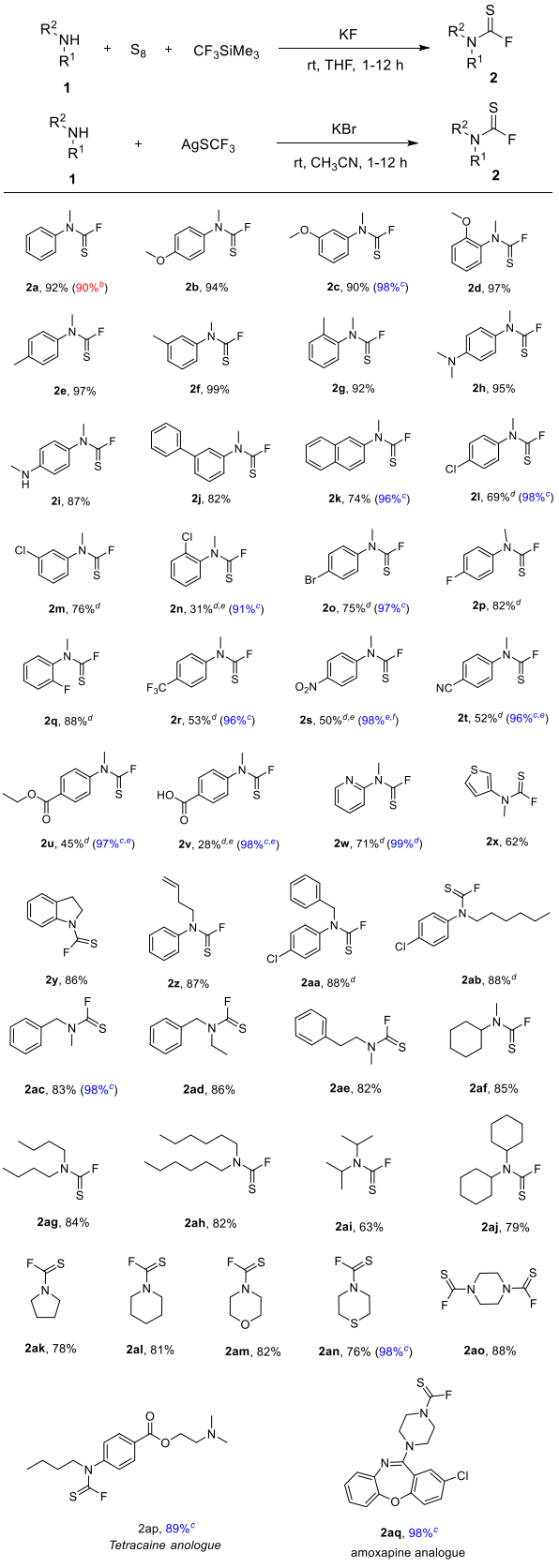
to the extremely hygroscopic nature of Me_4NF. $Ph_3P^+CF_2CO^{2-}$ (PDFA) reagent is relatively expensive to buy, especially on a mole basis. Several groups have reported the preparation of PDFA from hygroscopic potassium bromodifluoroacetate.[16] In addition, although F_3CSO_2Na is cheap, reaction with it to achieve isothiocyanates requires high temperature (110 °C) and long reaction times (16 h), and the reaction suffers from a relatively narrow substrate scope and low functional group tolerance (e.g., pyridinyl and terminal alkynyl groups are not tolerated).[14d] The use of readily available and cheap reagents to prepare thiocarbamoyl fluorides and/or isothiocyanates with broad substrate scope and good functional tolerance under mild conditions is in high demand. Ruppert−Prakash reagent (CF_3SiMe_3) is a stable, readily available, easy to handle, relatively cheap, and widely used reagent.[17] CF_3SiMe_3, S_8, and a base have been used for trifluoromethylthiolation.[18] To the best of our knowledge, although transformations involving in situ generated thiocarbonyl fluoride ($S{=}CF_2$) have made rapid progress in recent years,[14c,d,19] the use of CF_3SiMe_3, elemental sulfur, and KF to generate thiocarbonyl fluoride ($S{=}CF_2$) in situ for useful transformations has never been reported. Herein, we reported that reactions of thiocarbonyl fluoride derived from readily available and cheap CF_3SiMe_3 and elemental sulfur and KF with secondary amines/primary amines with THF as solvent at room temperature provided a wide variety of thiocarbamoyl fluorides/isothiocyanates in moderate to excellent yields. In addition, $AgSCF_3$ reacts with secondary/primary amines in the presence of KBr in CH_3CN at room temperature, providing thiocarbamoyl fluorides/isothiocyanates in almost quantitative yields, which feature late-stage application (Scheme 1a,b, this work).

We began our optimization studies with the reaction of 0.15 mmol of *N*-methylaniline **1a**, 6.0 equiv of S_8, 5.0 equiv of CF_3SiMe_3, and 3.0 equiv of KF in DMF at room temperature. Under these conditions, the desired methyl(phenyl)-carbamothioic fluoride **2a** was obtained in 50% yield. After the bases, solvent, and equivalents of the starting materials were screened (details in the Supporting Information (SI)), it was found that the solvent THF plays a key role in the formation of **2a** in high yield. The identified optimized conditions were 1 mmol of *N*-methylaniline **1a**, 4.0 equiv of S_8, 5.0 equiv of CF_3SiMe_3, and 3.0 equiv of KF in THF at room temperature under N_2, affording **2a** in 92% yield (Scheme 2). In addition, $ClCF_2CO_2Na$[19f] and S_8 were also used in the reaction with **1a** in THF or DMF at rt or 80 °C. The best yield of **2a** was only 39% (SI).

With the optimized conditions in hand, we investigated the substrate scope of the reaction of CF_3SiMe_3, elemental sulfur, KF, and secondary amines (Scheme 2). *N*-Aryl-*N*-alkylamines were first investigated. Aryl groups containing *ortho*-, *meta*-, and *para*-electron-donating or electron-neutral substituents afforded the desired thiocarbamoyl fluorides products **2a**−**i** in excellent yields in 1 h. In particular, tertiary amine was tolerated (**2h**). N^1,N^4-Dimethylbenzene-1,4-diamine reacted selectively at one secondary amine, and the other was preserved (**2i**). *N*-Methyl-[1,1′-biphenyl]-4-amine (**1j**) and *N*-methylnaphthalen-2-amine (**1k**) also gave the desired **2j** and **2k** in good yields, respectively. When aryls bore electron-withdrawing substituents, the corresponding *N*-aryl-*N*-alkyl-amines were found to require 8.0 equiv of CF_3SiMe_3 (details in the SI) at otherwise identical conditions to furnish various corresponding thiocarbamoyl fluorides in moderate to good

Scheme 2. Substrate Scope for the Reaction of CF_3SiMe_3, Elemental Sulfur, and KF with Secondary Amines as Well as the Reaction of $AgSCF_3$ and KBr with Secondary Amines[a,g]



[a]Conditions 1: 1.0 mmol of **1**, 5.0 mmol of CF_3SiMe_3, 4.0 mmol of elemental sulfur, and 3.0 mmol of KF in 20 mL of THF at room

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Scheme 2. continued

temperature reacted for 1 h under N_2. [b]10 mmol scale. [c]Conditions 2: 0.2 mmol of **1**, 0.3 mmol of $AgSCF_3$, and 0.3 mmol of KBr in 4 mL of CH_3CN at room temperature reacted for 1 h. [d]8.0 mmol of CF_3SiMe_3. [e]12 h. [f]1 mmol scale. [g]Isolated yield (the yields in parentheses with blue color and the yield of **2ao**, **2ap** were obtained under conditions 2; other yields were obtained under conditions 1).

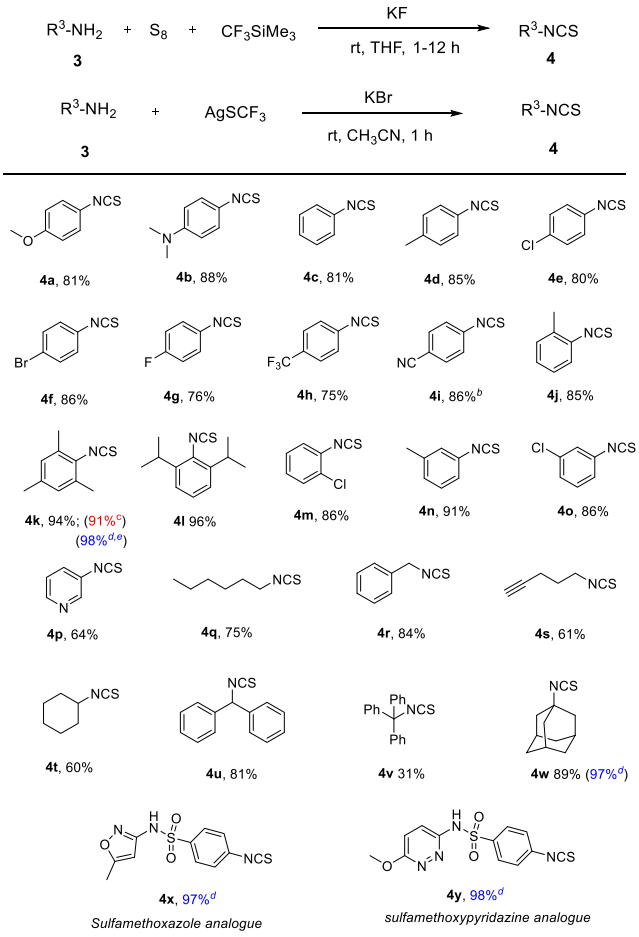
yields (**2l**–**v**). Fluoro, chloro, bromo, trifluoromethyl, nitro, cyano, and ester functional groups were all tolerated. Compound **1v** containing carboxylic acid functionality also gave the desired **2v**, albeit in low yield. In addition, heterocycles such as pyridine (**2w**) and thiophene (**2x**) were also compatible. Indoline (**1y**) performed well. The alkenyl group was also tolerated (**2z**). *N*-Benzyl-4-chloroaniline (**1aa**) and *N*-hexyl-4-chloroaniline (**1ab**) gave higher yields than *N*-methyl-4-chloroaniline (**1l**).

Next, *N*,*N*-dialkylamines were investigated and consistently gave the corresponding thiocarbonyl fluoride products in good yields under the optimized conditions (**2ac**–**ao**) in addition to **2ai**. Compound **2ai** is volatile, leading to a decreased isolated yield. In particular, a series of heterocycles including pyrrolidine (**1ak**), piperidine (**1al**), morpholine (**1am**), and thiomorpholine (**1an**) were smoothly converted to the corresponding thiocarbamoyl fluoride products **2ak**–**an**, which could be used in the biological and medicinal fields. Piperazine (**1ao**) reacted at both of the secondary amine positions, resulting in **2ao** in 88% yield. On a 10 mmol scale of **1a**, the reaction also proceeds readily to afford **2a** (1.52 g, 9.0 mmol) in 90% yield.

Recently, we reported that $AgSCF_3$ reacts with propargylamines in the presence of KBr in CH_3CN to give access to allenyl thiocyanates via propargyl isothiocyanate intermediates that undergo a [3,3]-sigmatropic rearrangement.[19e] However, the reaction of secondary amines with thiocarbonyl fluoride derived from $AgSCF_3$ have never been reported. We found that electron-donating (**1c**,**k**) or electro-withdrawing (**1l**,**n**,**o**,**r**–**v**) substituted *N*-aryl-*N*-alkylamines, *N*-(pyridin-2-yl)-*N*-methylamine (**1w**), or *N*,*N*-dialkylamines (**1ac**, **1an**) react with $AgSCF_3$ under KBr in CH_3CN at room temperature, consistently affording the corresponding thiocarbamoyl fluorides (**2c**,**k**,**l**,**n**,**o**,**r**–**w**, **2ac**, **2an**) in quantitative yields. Moreover, this methodology could be employed in late-stage pharmaceutical modification. The tetracaine analogue **2ap** and amoxapine analogue **2aq** were obtained in excellent yields through this transformation, leaving the other sensitive nucleophilic moieties (such as tertiary amine, imine) completely untouched (Scheme 2).

The success of the reaction of secondary amines with CF_3SiMe_3, S_8, and KF prompted us to investigate the reaction of thiocarbonyl fluoride from CF_3SiMe_3, S_8, and KF with primary amines for preparation of isothiocyanates. The reaction was carried out with primary amines instead of secondary amines under otherwise identical optimized conditions (shown in Scheme 3). To our delight, various arylamines bearing *para*- (**3a**–**i**), *meta*- (**3n**, **3o**), or *ortho*- (**3j**–**m**) electron-donating, electrom-neutral, or electron-withdrawing substitutions all afforded the desired isothiocyanates (**4a**–**o**) in good to excellent yields. Tertiary amine, ether, chloro, bromo, fluoro, trifluoromethyl, and cyano groups are all tolerated. *Ortho* hindrance has very little influence on the transformation. For instance, 2,4,6-trimethylaniline (**3k**) and

Scheme 3. Substrate Scope for the Reaction of CF_3SiMe_3, Elemental Sulfur, and KF with Primary Amines as Well as the Reaction of $AgSCF_3$ and KBr with Primary Amines[a,f]



[a]Conditions 1: 1.0 mmol of **3**, 5.0 mmol of CF_3SiMe_3, 4.0 mmol of elemental sulfur, and 3.0 mmol of KF in 20 mL of THF at room temperature reacted for 1 h under N_2. [b]12 h. [c]10 mmol scale. [d]Conditions 2: 0.2 mmol of **3**, 0.3 mmol of $AgSCF_3$, and 0.3 mmol of KBr in 4 mL of CH_3CN at room temperature reacted for 1 h. [e]1.0 mmol. [f]Isolated yield (the yields in parentheses with blue color and the yields of **4x** and **4y** were obtained under conditions 2; other yields were obtained under conditions 1).

2,6-diisopropylaniline (**3l**) afforded the corresponding isothiocyanate products **4k** and **4l** in 94% and 96% yields, respectively. On a gram scale, product **4k** (1.61 g, 9.1 mmol) was obtained in 91% yield. The pyridine heterocycle was tolerated (**4p**). Then various alkyl amines were investigated, affording the corresponding isothiocyanate products **4q**–**w** in moderate to good yields. In particular, the alkynyl functionality was also tolerated (**4s**). It has been reported that terminal alkynes react with S_8, CF_3SiMe_3, and KF in DMF under air to give alkynyl trifluoromethylsulfide products.[18a] Here, the chemoselectivity of **3s** was changed, leading to the desired isothiocyanate product **4s** with the alkyne preserved. Compound **4v** is unstable on silica gel column chromatography, leading to a decreased isolated yield. However, the stable **4w** was obtained in 89% yield. This result is higher than the yield of 78% from the reported method of $Ph_3P^+CF_2CO^{2-}$ (PDFA), elemental sulfur, and amantadine at 80 °C.

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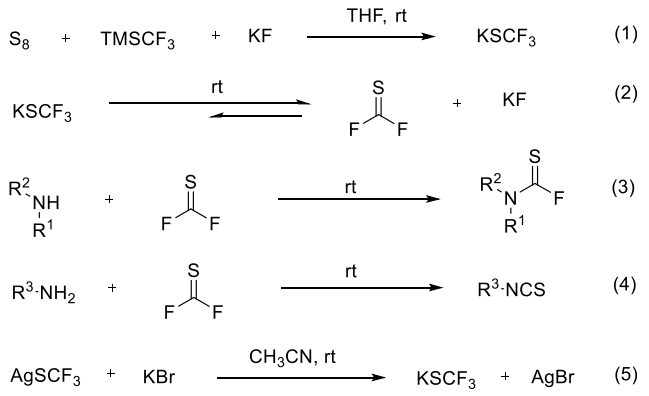
Compounds **3k** or **3w** react with $AgSCF_3$ under KBr in CH_3CN at room temperature, affording **4k** or **4w** in almost quantitative yield (Scheme 3). Sulfamethoxazole (**3x**) and sulfamethoxapyridazine (**3y**) under $AgSCF_3$ and KBr in CH_3CN were also smoothly and selectively transformed to the corresponding isothiocyanate derivatives **4x** and **4y** in quantitative yields, leaving the heterocycles oxazole in **4x** and pyridazine in **4y** untouched (Scheme 3).

To know if difluorocarbene was produced from $TMSCF_3$[20] under our conditions, the reactions of prop-1-en-2-ylbenzene with $TMSCF_3$ or with $TMSCF_3$ and KF in THF at rt were performed, but no reaction occurred (SI). ESI-HRMS analysis of the solution of CF_3SiMe_3, elemental sulfur, and KF in THF was performed, and a peak corresponding to SCF_3 anion was observed in the mass spectrum (see the SI). On the bases of this fact and the experimental observations, although we cannot totally ruling out difluorocarbene mechanism, more plausible mechanisms for these novel reactions were proposed in Scheme 4. CF_3SiMe_3 in the presence of elemental sulfur and

Scheme 4. Proposed Mechanisms



KF in THF is converted to the SCF_3 anion (might be $KSCF_3$) (Scheme 4, 1). It is well-known that there is an equilibrium between SCF_3 anion with thiocarbonyl fluoride ($S{=}CF_2$) and fluoride anion (Scheme 4, 2),[19b,21] or $KSCF_3$ is unstable and decomposes to thiocarbonyl fluoride and KF (Scheme 4, 2).[18a,21a] The secondary amine then reacts with thiocarbonyl fluoride in THF to afford the corresponding thiocarbamoyl fluorides (Scheme 4, 3). Primary amines react with the in situ generated thiocarbonyl fluoride in THF to produce the corresponding isothiocyanates (Scheme 4, 4). Alternatively, $AgSCF_3$ reacts with KBr in acetonitrile at room temperature to afford $KSCF_3$ and AgBr precipitate (Scheme 4, 5). The formation of $KSCF_3$ then follows the sequences in Scheme 4, 2−4, in acetonitrile to afford the thiocarbamoyl fluorides/isothiocyanates.

In conclusion, reactions of thiocarbonyl fluoride derived from CF_3SiMe_3, elemental sulfur, and KF with secondary amines or primary amines were developed, affording a variety of thiocarbamoyl fluorides or isothiocyanates in moderate to good yields. The two reactions highlight the use of readily available, cheap, and widely used starting materials, mild reaction conditions (rt), very broad substrate scope, good functional tolerance, and gram-scale synthesis with almost constant yields. The two reactions also represent the first examples of useful transformations involving thiocarbonyl fluoride derived from CF_3SiMe_3, elemental sulfur, and KF. Reactions of secondary/primary amines with $AgSCF_3$ and KBr in CH_3CN were also developed, affording the corresponding thiocarbamoyl fluorides/isothiocyanates at room temperature in almost quantitative yields, which are characterized by late-stage application, excellent efficiency, mild reaction conditions, as well as readily available starting materials. These novel reactions will promote thiocarbamoyl fluoride bearing N, S, F elements in a wide variety of applications. Studies on developing novel methodologies employing thiocarbamoyl fluorides as useful starting materials are underway in our laboratory.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.9b00383.

Experimental procedures and spectroscopic characterization data; ^1H and ^{13}C NMR spectra of the new compounds (PDF)

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Notes

The authors declare no competing financial interest.

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