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Synthesis of Allenamides and Structurally Related Compounds by a Gold-Catalyzed Hydride Shift Process

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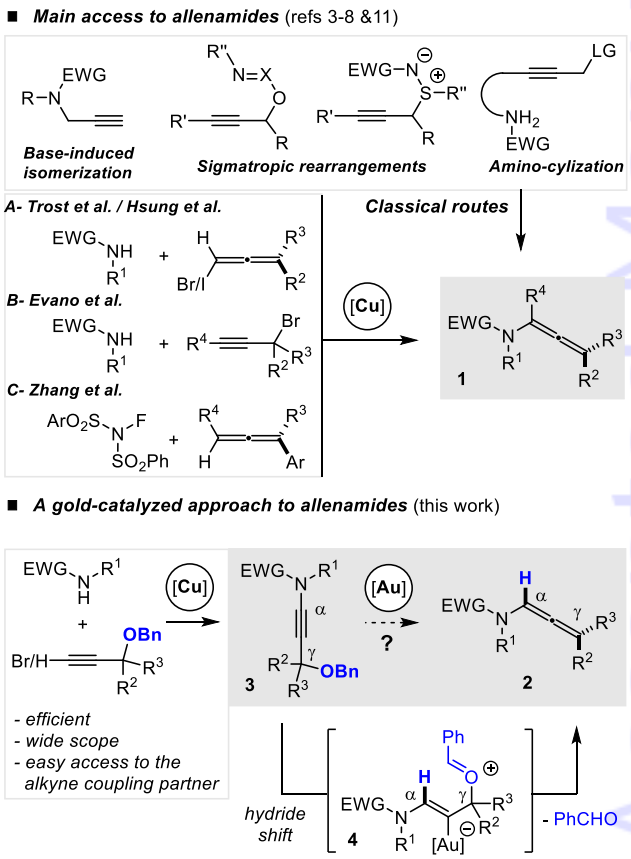
Abstract. A new procedure for the synthesis of allenamides and structurally related compounds is reported. Under gold catalysis, a series of ynamides possessing a benzyloxy group at the propargylic position were efficiently converted into the corresponding allenamides following a 1,5 hydride shift process. The scope of the reaction was shown to be extremely broad allowing the formation of γ-mono or γ-disubstituted allenes possessing various functional groups. Notably, and in contrast to previously reported methods, not only *N*-allenyl sulfonamido but also urea, phosphonamido and the rarely studied phthalimido, pyrrolo, indolo and carbazolo derivatives could be readily and efficiently accessed.

Keywords: allenamide, gold, catalysis, hydride shift

Allenamides **1**, which exhibit a higher stability than their parent allenamines, have received considerable attention from the synthetic organic community during the last ten years.[1] Due to the presence of the nitrogen atom which electronically enriches and polarizes the allenic moiety, they possess a singular reactivity as compared to simple allenes and thus can be functionalized in a highly regioselective manner. Their synthetic potential has been highlighted in a great variety of regio- and stereoselective transformations[1,2] as for examples metal-mediated hydrofunctionalizations, cyclizations, cycloadditions or aldol reactions.

In contrast with the ongoing increasing interest for the chemistry of allenamides, relatively little effort has been devoted to their synthesis. Currently available methods to access them are not only relatively limited, but they most often suffer from lack of generality, what may eventually hamper future synthetic developments. Classical routes such as base-induced isomerizations,[3] sigmatropic rearrangements[4] or amino-cyclizations[5] are either poorly efficient, exhibit a poor substrate scope or do not allow structural diversity (Scheme 1, top). The copper-catalyzed coupling of nitrogen nucleophiles with allenyl halides, developed by the Trost[6] and Hsung[7] groups (Scheme 1A), or with propargyl bromides as recently reported by Evano *et al.*[8] (Scheme 1B) represent so far, the most general methods to access allenamides.



Scheme 1. Main access to allenamides and our approach to their synthesis by gold catalysis.

While being generally efficient and complementary in terms of polysubstitution of the allene moiety,[9] these procedures are still suffering some limitations. Access to the required halogenated coupling partners is not always straightforward or even possible[10] and limited structural functionalization has been reported.

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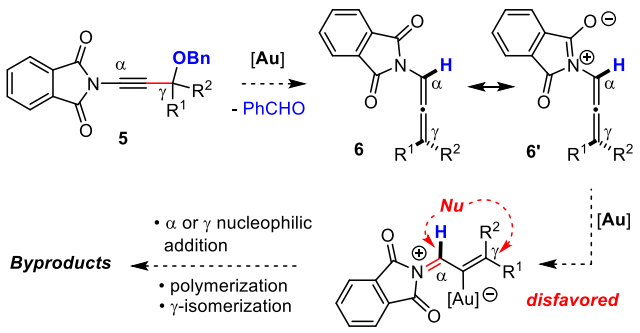
Competitive formation of 1,3-diene byproducts is also frequently encountered when allenyl halides are employed and the use of propargyl bromides is limited to the use of oxazolidinones or hydantoins coupling partners. The alternative Cu-catalyzed direct coupling of fluorosulfonimide with allenes described by Zhang *et al.*[11] (Scheme 1C) is also limited in terms of substitution both on the allene moiety and on the nitrogen atom.[12]

In this context and following our interest in the development of gold-catalyzed transformations,[13,14] we conceived a novel approach to allenamides **2** based on a gold catalyzed hydride shift[15] from an ynamide precursor **3** (Scheme 1, bottom). As previously demonstrated,[16] the benzyloxy group in **3** could serve as a potent internal "hydride donor" for the reduction of the α-position to the nitrogen atom upon activation of the alkyne moiety by an electrophilic gold complex. The intermediate oxocarbenium species **4** thus formed would then evolve into allenamide **2** after loss of benzaldehyde and concomitant regeneration of the catalyst. While this approach might appear at first sight less appealing than the direct copper-catalyzed procedures previously reported, it offers several advantages that motivated us to study its feasibility: a) ynamide substrates **3** could be readily accessed by copper catalysis with a wide variation of structure and functionalization on both the nitrogen nucleophilic partner and the alkyne, b) gold catalysis is known to be tolerant of a large number of commonly used functional groups, c) gold catalyzed experimental conditions are generally mild enough to prevent the formation of byproducts.

Phthalimido derivatives of type **5** were initially chosen as model substrates to validate our approach (Scheme 2).

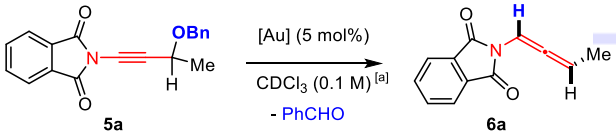


Scheme 2. Phthalimidoalkynes as model substrates.

This choice was made on the following considerations: a) **5** are easily accessible by Cu-catalyzed coupling between phthalimide and terminal alkynes under aerobic conditions,[17] b) the corresponding phthalimidoallenes **6** have been rarely studied and no general route to access them has been reported to date,[18] c) importantly, the significant contribution of resonance form **6'**[19] in the allenyl product was hypothesized to limit its activation under electrophilic catalytic conditions and therefore prevent the competitive formation of byproducts frequently observed during the formation of allenamides, d) advantageously, the phthaloyl group could be easily removed in compounds resulting from the post-functionalization of the targeted phthalimidoallenes **6**.

Our investigations started with phthalimidoalkyne **5a** and we looked for suitable catalytic conditions allowing its conversion into allene **6a**. Main results are compiled in Table 1. Substrate **5a** was initially treated with 5 mol% of $[(XPhos)Au(NCCH_3)]SbF_6$ (**7**) in dry $CDCl_3$ and the reaction was monitored by ^1H NMR spectroscopy.[20] While no reaction occurred at 20°C (entry 1), a rapid (1.5 h) and complete consumption of **5a** took place when the temperature was raised to 60°C (entry 2). We were pleased to observe that, under these conditions, the desired phthalimidoallene **6a** was produced as a highly predominant product (92% NMR yield) which could be isolated in 86% yield. Several other gold(I) complexes were screened but no improvement could be made in terms of catalytic efficiency (entries 3-6). While other biphenylphosphine gold(I) complexes such as **8** and **9** were shown to be less selective (entries 3 and 4), the NHC-gold complex **10** exhibited a poor reactivity (entry 5) and the simple $[(Ph_3P)Au(NCCH_3)]SbF_6$ complex mainly led to degradation products (entry 6).[21] Based on these results, gold complex **7** was retained to study the scope of the transformation.

Table 1. Optimization of the catalytic conditions [a,b]



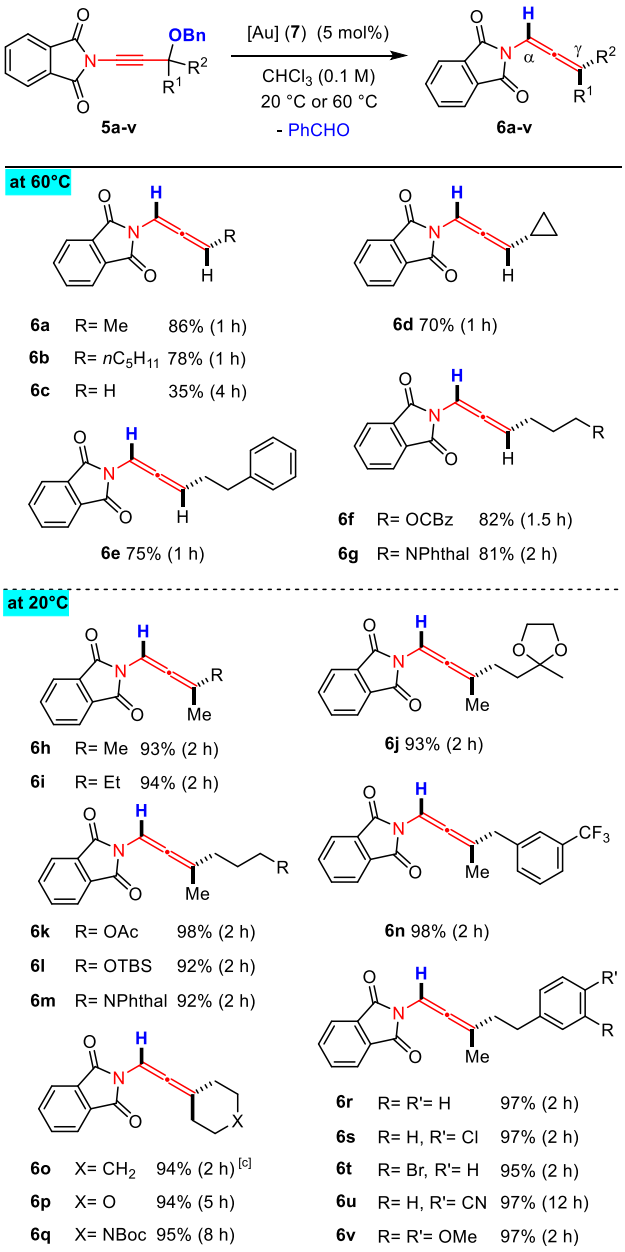
Entry	[Au] Catalyst	T [°C]	Time	Conversion [%][b]	Yield [%][b]
1	$[(XPhos)Au(NCCH_3)]SbF_6$ **7**	20	1.5h	0	0
2	$[(XPhos)Au(NCCH_3)]SbF_6$ **7**	60	1.5h	100	92 (86)[c]
3	$[(RuPhos)Au(NCCH_3)]SbF_6$ **8**	60	1.5h	100	65
4	$[(BrettPhos)Au(NCCH_3)]SbF_6$ **9**	60	1.5h	100	80
5	$[(IPr)Au(NCCH_3)]SbF_6$ **10**	60	24h	5	4
6	$[(Ph_3P)Au(NCCH_3)]SbF_6$	60	1.5h	100	<10[d]

[a] $CDCl_3$ was dried over 4Å MS prior to use. [b] Yields assessed by 1H NMR spectroscopy using 1,2-dichloroethane as an internal standard. [c] Isolated yield. Substrate concentration was 0.1 M. [d] Degradation was observed.

As seen in Table 2, the transformation was shown to be widely applicable. A series of phthalimidoalkynes **5a-b** and **5d-v** were efficiently (70-88%) and generally rapidly (≈ 1-2 h) converted into the corresponding phthalimidoallenes **6a-b and 6d-v**. Both γ-mono- and γ-disubstituted allenes could be produced. It is worth noting that while substrates monosubstituted at the propargylic position had to be reacted at 60°C, the temperature could be lowered to

20°C in the case of disubstituted substrates (**5h-v**). This can probably be related to the involvement of a Thorpe-Ingold effect which would be more pronounced in the case of disubstituted substrates: the 1,5-H shift step would be facilitated and the overall efficiency of the reaction consequently increased (yields > 90% for **6h-v**).[22]

Table 2. Scope of the reaction with *N*-alkynyl phthalimide substrates [a,b]

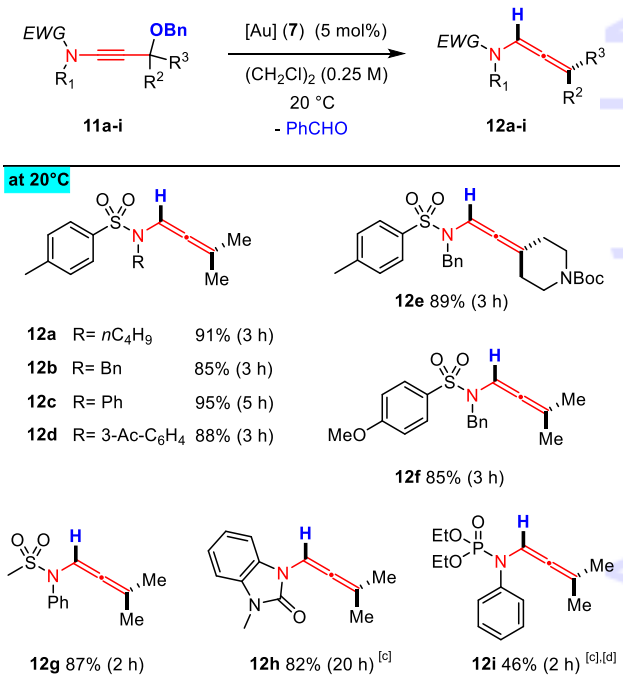


[a] Reaction scale: 0.5 mmol. Chloroform was dried over 4Å MS prior to use. [b] Isolated yields. [c] Reaction run in dry 1,2-dichloroethane.

Conversely, a limit in reactivity was found with unsubstituted substrate **5c** which delivered the unsubstituted phthalimido allene **6c** in low yield (35%) after a prolonged reaction time (4 h).[23] It is also important to note that the transformation exhibits an impressive functional group tolerance, which was not reached with the previously reported procedures. Indeed, the reaction was compatible with the presence of an aromatic (**6e**, **6n**, **6n-v**), an ester (**6k**), a silyl ether (**6l**), an imide (**6m**), a carbonate (**6f**), a carbamate (**6q**), an ether (**6k**) or a cyano group (**6k**) and with halogen atoms (**6s-t** and **6n**). While most of the phthalimidoallenes synthesized could be isolated using regular silica gel chromatography, some of them (**6b,d,o**) proved to be sensitive to both acidic and basic conditions. The use of deactivated neutral alumina was found appropriate for their efficient isolation by chromatography.[24]

We then turned our attention on the possibility to employ the same catalytic conditions to produce allenamides possessing different electron withdrawing groups on the nitrogen atom. As shown in Table 3, the process could be extended to the synthesis of a series of other allenes **12a-i** possessing either a sulfonamide (**12a-g**), a urea (**12h**) or a phosphonamide group (**12i**).[25] The reaction proceeded with the same efficiency (82-95%) with the exception of **11i** which was converted into **12i** in a more moderate 46% yield. It should be noted that the reactions were performed at 20°C in 1,2-dichloroethane as significant amounts of 1,3-dienes byproducts arising from a subsequent γ-isomerization were formed when chloroform was used as the solvent.[26]

Table 3. Scope of the reaction with sulfonamide, phosphonamide and urea derivatives [a,b]

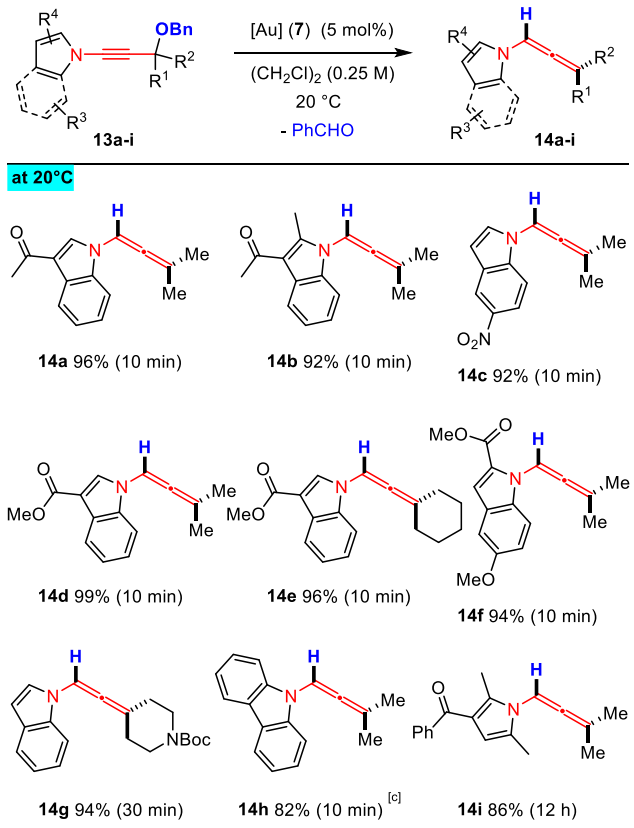


[a] Reaction scale: 0.5 mmol. 1,2-dichloroethane was dried over 4Å MS prior to use. [b] Isolated yields. [c] Substrate concentration was 0.1 M. [d] Reaction performed in acetone using 10 mol% of **7**.

With the idea to further extend the scope of the transformation, the reactivity of *N*-alkynyl indoles,

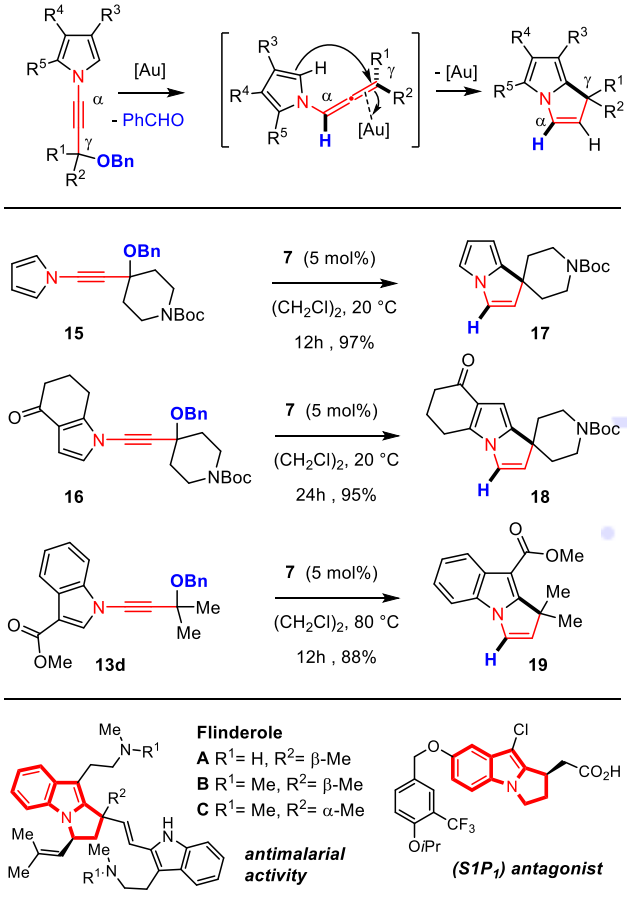
carbazoles and pyrroles was investigated. We were delighted to observe that a range of such substrates **13a-i** could be rapidly and efficiently converted (82-99%) into the corresponding allene derivatives **14a-i** under the same mild experimental conditions (5 mol% of **7** in 1,2-dichloroethane at 20°C) (Table 4).[25] It is worth mentioning that examples of such polysubstituted allenes are extremely rare in the literature probably as a lack of methods to access them in an efficient manner.[27]

Table 4. Scope of the reaction with *N*-alkynyl pyrrole, indole and carbazole substrates



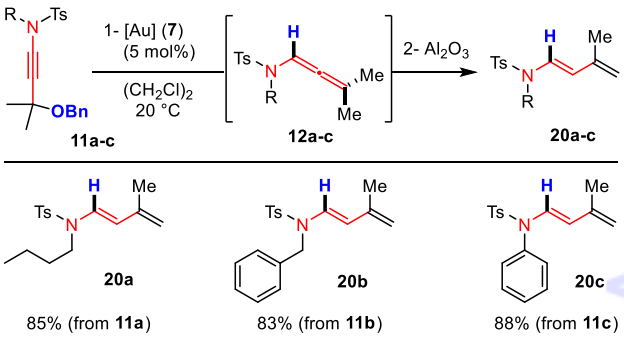
[a] Reaction scale: 0.5 mmol. 1,2-dichloroethane was dried over 4Å MS prior to use. [b] Isolated yields. [c] Substrate concentration was 0.1 M.

We also took advantage of the capacity of electrophilic gold species to activate allenes towards their nucleophilic functionalization to perform cascade reactions (Scheme 3). As examples, the intermediate allenes formed from pyrrole or indole derivatives **15**, **16** and **13d** could be converted *in situ* into the corresponding polycyclic compounds **17**, **18** and **19** by simply prolonging the reaction time. This transformation, which involves the nucleophilic addition of the nitrogen heteroaromatic motif on the γ-position of the gold-activated allene moiety, represents a rapid and efficient means to access the pyrroloindole scaffold which is found in several natural or biologically active compounds.



Scheme 3. Gold-catalyzed cascade reactions involving *N*-allenyl pyrrole or indole intermediates.

Finally, we demonstrated that γ-disubstituted allenes **12a-c**, which were produced from **11a-c** by the present gold-catalyzed process, could be cleanly converted *in situ* into 1,3-dienes **20a-c** by a subsequent treatment with Al_2O_3.



Scheme 4. One-pot, two-step synthesis of 1,3-dienes from *N*-tosylynamides.

In conclusion, we have developed a new procedure for the synthesis of allenamides and structurally related compounds. While our method is not as direct as the previously reported Cu-catalyzed processes, it possesses several clear advantages. The reaction conditions are mild enough to prevent the

overreaction or degradation of the allenamides which can then be selectively produced and isolated. The scope of the reaction is extremely broad allowing the formation of γ-mono or γ-disubstituted allenes possessing various functional groups. Notably, and in contrast to previously reported methods, not only *N*-allenyl sulfonamido but also urea, phosphonamido and the rarely studied phthalimido, pyrrolo, indolo and carabazolo derivatives can be readily and efficiently accessed. This method, which offers new opportunities for the design of polyfunctionalized allenamides, should contribute to the ongoing increasing interest in their use as building blocks in organic chemistry.

Experimental Section

Representative Procedure: To a stirred solution of ynamide **5a** (0.50 mmol) in chloroform (5 mL) was added XPhosAu(CH_3CN)SbF_6 (5 mol%) and the solution was stirred at 60°C for 1h. The reaction mixture was cooled down and directly loaded on a silica gel column chromatography. Purification with an 8:1 mixture of petroleum ether:ethyl acetate furnished allenamide **6a** in 86% yield.

Acknowledgements

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[21] Brønsted acids (HOTf) and silver salts ($AgSbF_6$) were not suitable catalysts for this reaction.

[22] At higher temperature (60°C) and under gold catalysis, allenamides are prone to γ-isomerization and polymerization what tends to lower their yields.

[23] This does not diminish the interest of the present procedure since unsubstituted phthalimidoallene **6c** can be obtained by based-mediated isomerization of the parent propargylic derivative but in low yield (24%). See: V. N. G. Lindsay, D. Fiset, P. J. Gritsch, S. Azzi, A. B. Charette, *J. Am. Chem. Soc.* **2013**, *135*, 1463.

[24] See supporting information for more details.

[25] These compounds required the use deactivated neutral alumina for their isolation by chromatography.

[26] Chloroform could be slightly acidic as compared to 1,2-dichloroethane (HCl traces), what would result in proton-induced γ-isomerization (and polymerization).

[27] See ref 6 (1 example) and E. Wenkert, E. C. Angell, V. F. Ferreira, E. L. Michelotti, S. R. Piettre, J. H. Sheu, C. S. Swindell, *J. Org. Chem* **1986**, *51*, 2343 (1 example).

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