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N-heterocyclic carbene-catalyzed rearrangements of vinyl sulfones†

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Abstract

N-heterocyclic carbenes catalyze the rearrangement of 1,1-bis(arylsulfonyl)ethylene to the corresponding *trans*-1,2-bis(phenylsulfonyl) under mild conditions. Tandem rearrangement/cycloadditions have been developed to capitalize on this new process and generate highly substituted isoxazolines and additional heterocyclic compounds. Preliminary mechanistic studies support a new conjugate addition/Umpolung process involving the ejection and subsequent unusual re-addition of a sulfinate ion.

Metal free catalysis has undergone a renaissance over the last decade, leading to an explosion of efficient and stereoselective strategies for chemical synthesis.¹ In the area of Lewis base-promoted reactions,² *N*-heterocyclic carbene (NHC) catalysis is a rapidly growing field that employs electron lone pair-bearing heterocycles to facilitate a wide breadth of chemical transformations.³ Carbene catalysis is highly versatile and allows access to acyl anions,⁴ homoenolates,⁵ enolates,⁶ Cannizzaro-type reductions,^{3c} and oxidations.⁷ The majority of NHC catalysis currently involves the 1,2-addition of the carbene to a carbonyl-containing species which then proceeds to produce an acyl anion or homoenolate equivalent. A different mode for these nucleophilic catalysts is a conjugate addition manifold. By capitalizing on this 1,4-type reactivity, both Fu and Ye have separately reported the development of β -Umpolung-type and Morita-Baylis-Hilman reactions catalyzed by NHCs, respectively.⁸ This conjugate addition process provides a new direction beyond 1,2-additions. In this work, the combination of an NHC with a vinyl sulfone and nitrene results in the formation of an isoxazolidine product with an unusual transposition of a sulfone group (eqn 1). This process fundamentally differs from the previous 1,4 additions because it is neither an intramolecular alkylation^{8a} nor a MBH reaction.^{8b}

Vinyl sulfones are useful intermediates in organic synthesis that can act as 2π participants in cycloadditions⁹ and as electrophiles in organometallic¹⁰ and organocatalysis.¹¹ When we began these specific studies, the use of vinyl sulfones as substrates in NHC-catalyzed transformations had not been previously reported. In our attempts to achieve homoenolate equivalent annulations with 1,1-bis(phenylsulfonyl)ethylene (**1**), we discovered that the carbene derived from triazolium **A** promoted an unanticipated rearrangement to the *trans*-1,2-bis(phenylsulfonyl)ethylene in 96% yield with a $t_{1/2}$ of ~6 h at 40 °C (**2**, eqn 2).

†Electronic supplementary information (ESI) available: Experimental procedures and spectroscopic data for all new compounds. See DOI: 10.1039/c1sc00194a

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The isomerization of 1,1-bis(phenylsulfonyl)ethylene to date involves harsh, non-catalytic reaction conditions such as autoclave with high pressure (no isolated yield) or ammonium salts at 140 °C.¹² Our survey of standard Lewis bases for this process, such as 1,4-diazabicyclo[2.2.2]octane (DABCO) and triphenylphosphine, revealed there was poor and incomplete conversion when compared to the NHC catalyst generated from azolium catalyst **A** and sodium *tert*-butoxide.¹³ *Trans*-1,2-bis(arylsulfonyl)ethylene has been used in organic synthesis,¹⁴ but its preparation typically involves the use of vinyl chloride gas.¹⁵ Alternatively, the straightforward preparation of 1,1-bis(phenylsulfonyl)ethylene involves paraformaldehyde, piperidine, and acid.^{12b}

2. Results and discussion

We viewed this unusual NHC-catalyzed generation of *trans*-1,2-bis(phenylsulfonyl)ethylene *in situ* under mild reaction conditions as an interesting opportunity to develop a two-step single flash process involving a cycloaddition step (*vide infra*). The initial test bed reaction we chose was the formation of the isomerization product in a one-pot process with a nitrene in a Huisgen [3 + 2] cyclization to form the isoxazolidine product.¹⁶ Our optimization studies for this NHC-catalyzed reaction began by treating the 1,1-bis(phenylsulfonyl)ethylene with *N*-aryl nitrene and surveying various azolium salts and reaction conditions (Table 1). Of the azolium salts, triazolium **A** was the only catalyst which led to appreciable amounts of desired cycloadduct **4**. Notably, the cycloaddition yielded a single diastereomer (as observed by ¹H NMR spectroscopy).¹⁷ The reduction of catalyst loading from 20 to 10 mol% of **A** resulted in significant depression of yield for the two-step process (rearrangement/cycloaddition). Further experimentation revealed dichloromethane as the best solvent and sodium *tert*-butoxide was the optimal base, presumably since its minimal nucleophilicity did not compete with the NHC for addition to the vinyl sulfone.¹⁸

With the optimized reaction conditions, we examined the scope of the reaction with regard to the nitrene component (Table 2). A chloride substituent in the 4 position of the *N*-aryl ring delivered the products in good yields, presumably due to the increased electrophilicity of the nitrene being complimentary to the cyclization step (entries 1–7). Increasing the temperature to 40 °C and adding 4 Å molecular sieves generally improved conversion and yields. Reactions with *N*-aryl nitrenes with non-electron withdrawing groups provided moderate yields and an *N*-alkyl nitrene provided 86% of the desired cycloadduct (entry 13). Similar to the initial optimization reaction in Scheme 1, the isoxazolidine products were observed as a single diastereomer (¹H NMR, 500 MHz). Substituted aryl sulfones are also compatible with the system (entries 14–16), but currently both sulfones are required. With these NHC conditions, mixed sulfone/carbonyl group compounds are not substrates and neither are β-substituted bis-sulfones.

Since *N*-alkyl nitrenes are productive substrates, this tandem 1,1-1,2 rearrangement/cycloaddition with a D-ribose-based chiral auxiliary is highly selective and provides the optically active isoxazoline in 65% yield as a single diastereomer (Scheme 3, eqn 3).¹⁹ Importantly, this streamlined process is not limited to nitrenes²⁰ as the dipole coupling partner. For example, azomethine imines (such as **22**) and dienes (including furan) undergo efficient reactions in [3 + 2] and [4 + 2] cycloaddition²¹ reactions (respectively, eqn 4 and 5).

We performed the studies outlined below to a) determine if the NHC was involved in the Huisgen cycloaddition,²² and b) provide insight into the mechanism of the sulfone rearrangement process. Our initial control experiments showed the triazolium salt and base were not needed for the cycloaddition with *trans*-1,2-bis(phenylsulfonyl)ethylene, thereby supporting an uncatalyzed thermal [3 + 2] process.²³

To further probe the proposed NHC-catalyzed isomerization mechanism, a cross-over experiment with 1,1-bis(tosyl)ethylene (**24**) and 1,1-bis(phenylsulfonyl)ethylene (**1**) was performed (Scheme 4, eqn 6). The two different 1,1-sulfones were placed in the same reaction mixture and subjected to the NHC reaction conditions from Table 2. Based on the high resolution mass spectrometry (EI), the cross-over product (**25**) was present in the reaction mixture in a 1 : 1 : 1 ratio with the *trans*-1,2-bis(phenylsulfonyl)ethylene (**2**) and *trans*-1,2-bis(tosyl)ethylene (**26**).²⁴ Additionally, we have exposed a 1 : 1 mixture of **2** and **26** to the NHC conditions and observed compound **25**, thereby supporting that the NHC-addition/sulfinate ejection/addition pathway is operative with 1,2-bis(arylsulfonyl)ethylenes and underscoring the complexity and dynamic aspects of this process.

In addition to the cross over experiments, the reaction with a ¹³C-labeled isomer of bis-vinyl sulfone **1** provided evidence for the isomerization of the sulfonyl groups occurring *prior* to cyclization (Scheme 4, eqn 8). Based on the proposed reaction pathway in Scheme 5, there should be a mixture of ¹³C-labeled products (**27** and **28**) if the isomerization occurs prior to Huisgen cycloaddition with the nitron. Alternatively, if there is only ¹³C-labeled vinyl sulfone isomer present at the cycloaddition step, then this label would be in a single position in the product. A cycloadduct with a singularly labeled position would necessitate a difficult migration of a sulfone moiety after formation of an initial isoxazoline product. The use of **1*** provided a mixture of isotope-labeled isoxazolidine products as observed by NMR spectroscopy.²³

Based on the data above, our proposed pathway of the NHC-induced sulfone rearrangement involves the carbene addition to the beta position of 1,1-bis(phenylsulfonyl)ethylene (Scheme 5). The nucleophilic addition of the NHC to the vinyl sulfone drives the process. After protonation of the intermediate anion (**I**), base can remove a β-proton of **II** due to the stabilization of the anion by the triazolium catalyst, thus promoting the ejection of a sulfinate moiety from **III**.²⁵ The sulfinate group then undergoes intermolecular addition at the beta position of **IV** to produce another nucleophilic anion (**V**).²⁶ This sulfinate rebound promotes the regeneration of the NHC catalyst through elimination and the formation of the *trans*-1,2-bis(phenylsulfonyl) ethylene. The mixed arylsulfone product (**25**) from the cross over experiment in eqn 6 supports this unusual ejection/rebound of a sulfinate group.

Conclusions

We have discovered that triazolium-derived carbenes promote the facile rearrangement of 1,1-bis(arylsulfonyl)ethylenes to *trans*-1,2-bis(arylsulfonyl)ethylenes. We have combined this new sulfone transposition reaction with subsequent cycloadditions to provide a single flask, tandem rearrangement/cycloaddition process. The combination of the 1,1-bis(arylsulfonyl)ethylene, a nitron and an NHC provides highly substituted isoxazolines through a stereoselective [3 + 2] Huisgen cycloaddition. Mechanistic studies support an unusual carbene-promoted ejection and then re-addition of a sulfinate group. This NHC-catalyzed reaction is unusual in that the substrates are vinyl sulfones and not the standard reaction partner: α,β-unsaturated carbonyl compound, ketone, or aldehyde. Further methodology development with this promising NHC reactivity pattern and its application in chemical synthesis is under investigation.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

Acknowledgments

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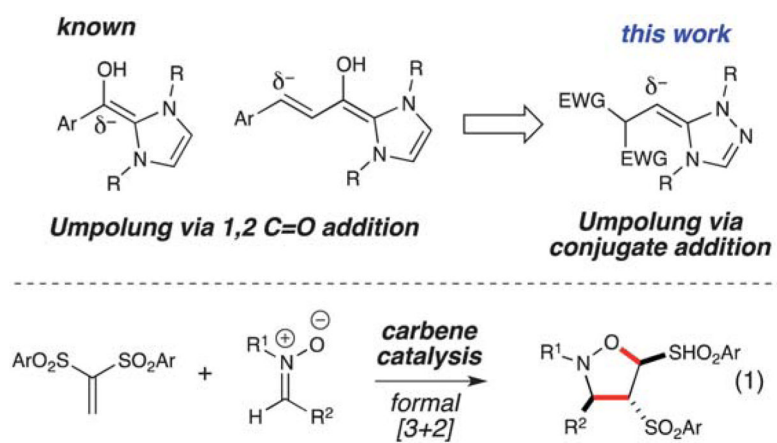
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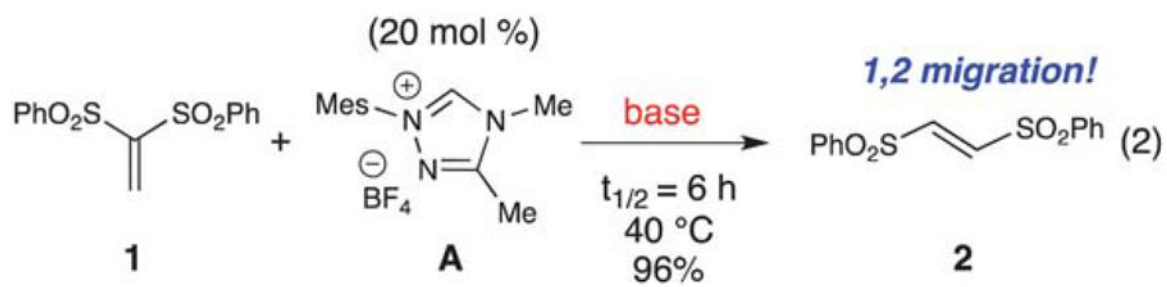
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18. Additional bases (Et₃N, DBU, *i*-Pr₂EtN, TBD, 2,6-lutidine, sodium amylate, KO *t*-Bu, K₂CO₃) were also examined and gave inferior results.
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22. A possible NHC-catalyzed Huisgen cycloaddition pathway would involve the addition of the Lewis base to *trans*-1,2-bis(phenylsulfonyl)ethylene (**2**) produced *in situ*, thereby generating a stabilized carbanion. The addition of this plausible intermediate to the nitron followed by an intramolecular S_N2 reaction would generate the free NHC catalyst and isoxazoline product.
23. The possible role of the NHC in the [3 + 2] cycloaddition was investigated through the comparison of the overall rates with a) *trans*-1,2-bis(phenylsulfonyl)ethylene and nitron **3**, b) *trans*-1,2-bis(phenylsulfonyl)ethylene with nitron **3**, azolium **A**, and sodium *tert*-butoxide, and c) *trans*-1,2-bis(phenylsulfonyl)ethylene with nitron **3** and sodium *tert*-butoxide. Based on the observed rates of these three reactions (as determined by HPLC), the NHC does not accelerate the [3 + 2] cycloaddition step relative to the thermal process.
24. See supporting information[†] for details.
25. Alexakis has reported an unusual 1,2 to 1,1 rearrangement under a proline-mediated organocatalytic addition of aldehydes to *cis*-1,2-bis(phenylsulfonyl)ethylene. This process is fundamentally different than carbene catalyzed reaction here (vs. proline catalysis) and proceeds in the opposite sense of migration relative to the results reported herein. They propose an intramolecular migration of the sulfinate ion: Quintard A, Alexakis A. *Chem-Eur J.* 2009; 15:11109–11113. [PubMed: 19777516]
26. Balenkova observed the unexpected phenylsulfonyl group migration to the beta position with their work with β -trifluoroacetylketene diphenyldithioacetal *S*, *S*-tetroxide, see: Krazovsky AL, Druzhinin SV, Nenajdenko VG, Balenkova ES. *Tetrahedron Lett.* 2004; 45:1129–1132.

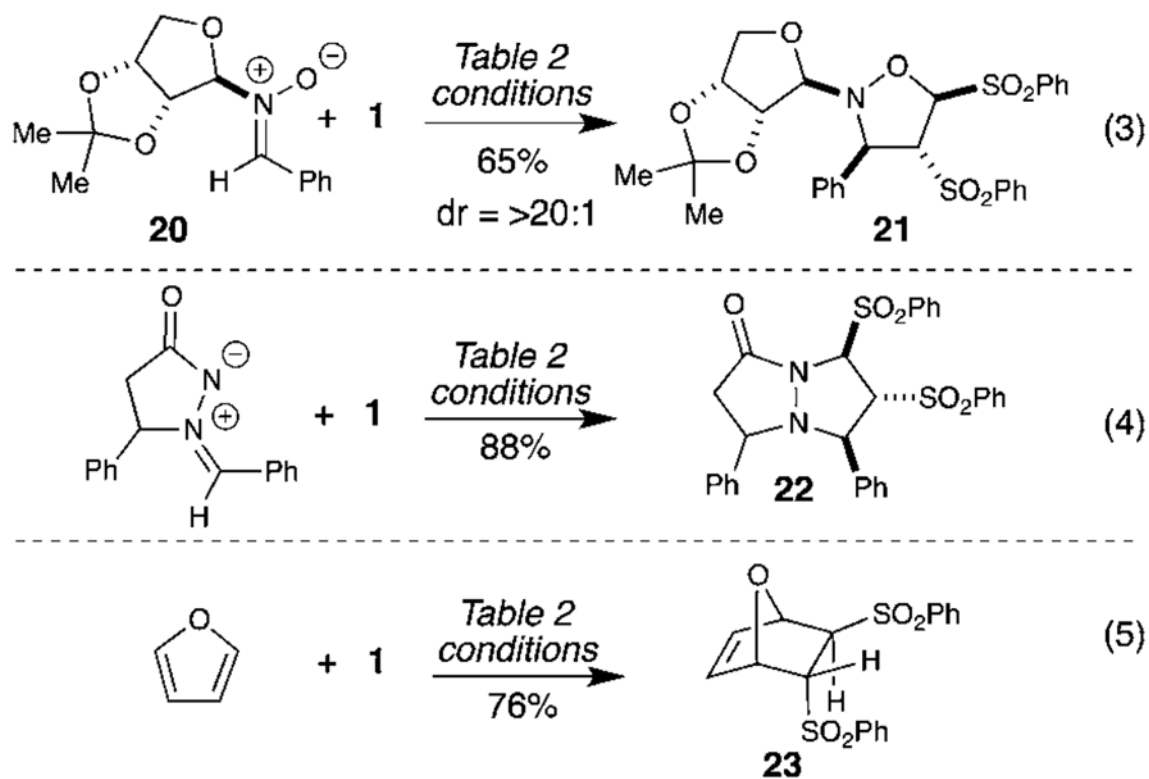
[†]Electronic supplementary information (ESI) available: Experimental procedures and spectroscopic data for all new compounds. See DOI: 10.1039/c1sc00194a



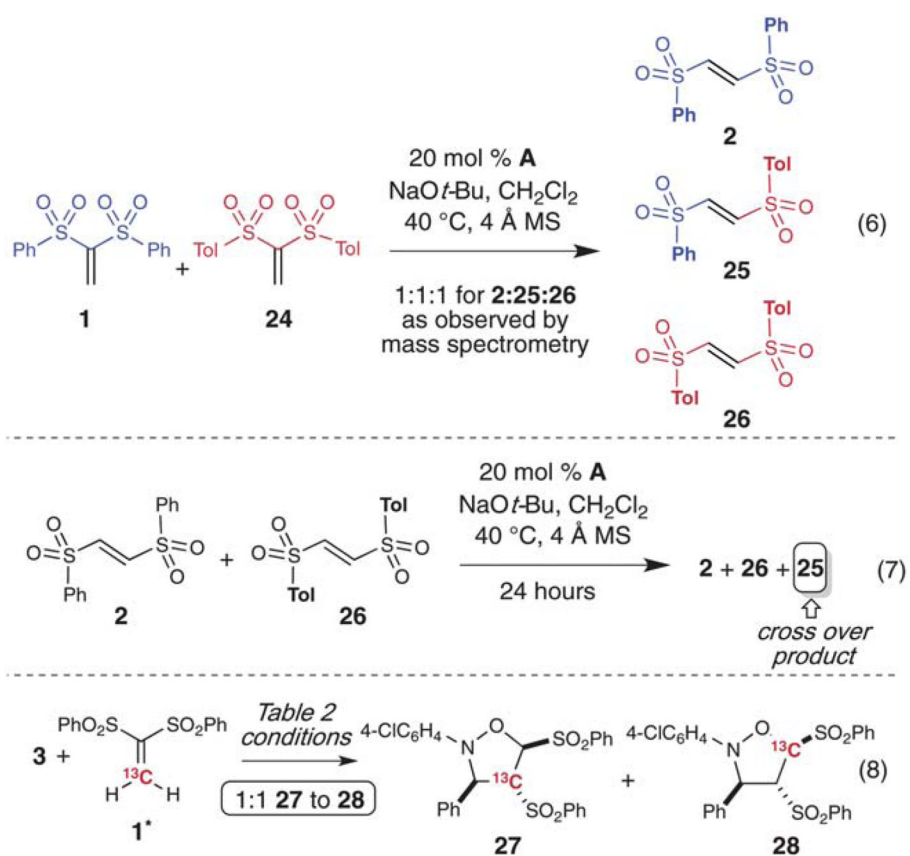
Scheme 1.
Known NHC methodology and this work.



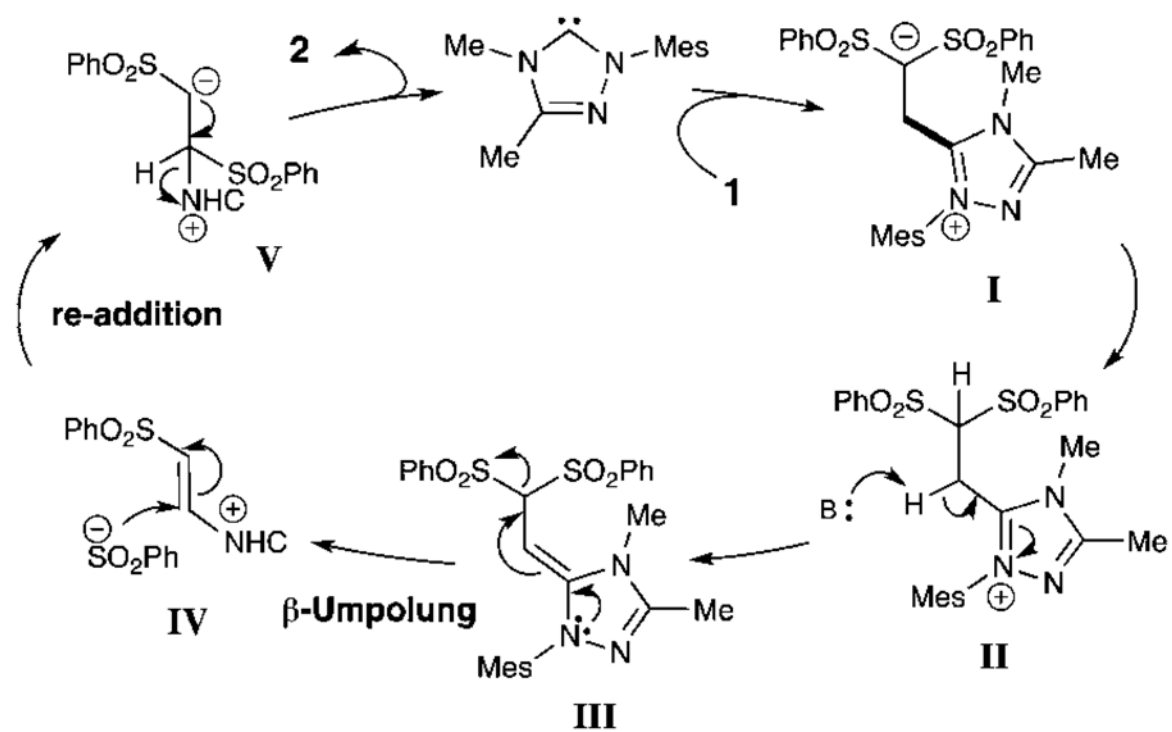
Scheme 2.
Isomerization of 1,1-bis(phenylsulfonyl)ethylene.



Scheme 3.
Compatibility with other cycloaddition reactions.



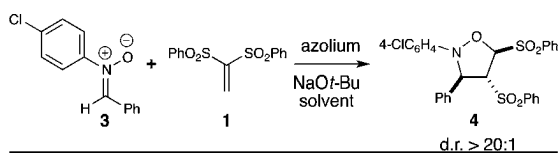
Scheme 4.
Mechanistic studies.



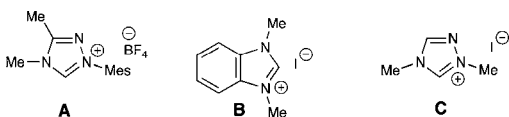
Scheme 5.
Proposed reaction pathway.

Table 1

Optimization of reaction conditions



Entry	Conditions ^a	Yield [%] ^b
1	20 mol% B, 40 °C, CH ₂ Cl ₂	Trace
2	20 mol% C, 40 °C, CH ₂ Cl ₂	4
3	20 mol% A, 40 °C, CH ₂ Cl ₂	94
4	10 mol% A, 40 °C, CH ₂ Cl ₂	37
5	20 mol% A, 40 °C, CH ₃ CN	0
6	20 mol% A, 40 °C, THF	50



^a General conditions: vinyl sulfone (1 equiv), nitronium (3 equiv), NaOt-Bu (20 mol%), solvent (0.10 M), 4 Å MS.

^b Yield of isolated products.

Table 2

Substrate scope^{a,b}

Entry	R	Ar	Ar ¹	d.r.	Yield [%]
1	4-ClPh	Ph	Ph	>20 : 1	94 (4)
2	4-ClPh	4-BrPh	Ph	>20 : 1	87 (5)
3	4-ClPh	4-MePh	Ph	>20 : 1	61 (6)
4	4-ClPh	4-ClPh	Ph	>20 : 1	76 (7)
5	4-ClPh	2-Naphth	Ph	>20 : 1	74 (8)
6	4-ClPh	2-ClPh	Ph	>20 : 1	75 (9)
7	4-ClPh	4-MeOPh	Ph	>20 : 1	71 (10) ^c
8	Ph	2-ClPh	Ph	>20 : 1	81 (11) ^c
9	Ph	4-MeOPh	Ph	>20 : 1	63 (12) ^c
10	Ph	4-MePh	Ph	>20 : 1	70 (13) ^c
11	Ph	2-Naphth	Ph	>20 : 1	77 (14) ^c
12	4-MePh	4-ClPh	Ph	>20 : 1	75 (15) ^c
13	PhCH ₂	Ph	Ph	>20 : 1	86 (16) ^c
14	4-ClPh	Ph	4-MePh	>20 : 1	72 (17) ^d
15	4-ClPh	Ph	4-BrPh	>20 : 1	60 (18) ^d
16	Ph	Ph	4-MePh	>20 : 1	77 (19) ^d

^a General conditions: vinyl sulfone (1 equiv), nitron (1.05 equiv), azolium salt **A** (20 mol%), NaOt-Bu (20 mol%), CH₂Cl₂ (0.10 M).

^b Yield of isolated products.

^c Vinyl sulfone (2 equiv), nitron (1 equiv).

^d 1,2-dichloroethane (0.10 M), 40 °C, no 4 Å MS.