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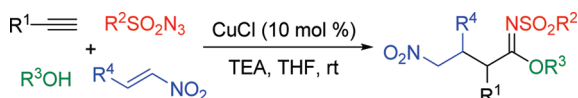
# A Facile Route to $\gamma$ -Nitro Imidates via Four-Component Reaction of Alkynes with Sulfonyl Azides, Alcohols, and Nitroolefins

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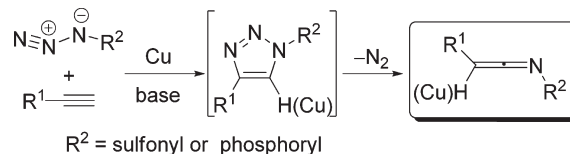
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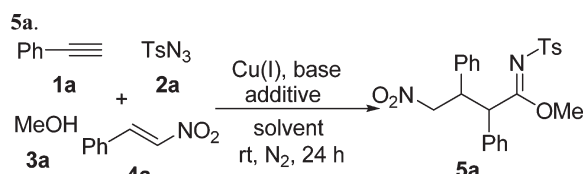
$\gamma$ -Nitro imidates were synthesized via a copper-catalyzed four-component cascade reaction of sulfonyl azides, alkynes, alcohols, and nitroolefins. This one-step procedure is general and efficient, and the reaction condition is mild.

In recent years, various multicomponent reactions (MCRs) have been developed not only for their facileness and efficiency, but also for their economy and ecology in organic synthesis.<sup>1</sup> Ketenimine as a useful intermediate has attracted much attention in this area due to its easy formation, its relative reactivity, its tolerance of procedure, and its diversity of products.<sup>2</sup> The most attractive and sustainable method generating ketenimine could be attributed to the copper-catalyzed azide–alkyne cycloaddition (CuAAC), which was

## SCHEME 1. Copper-Catalyzed Azide–Alkyne Cycloaddition



## SCHEME 2. Four-Component Reaction Leading to $\gamma$ -Nitro Imidate 5a



reported by Fokin and Meldal in 2002 (Scheme 1).<sup>3</sup> This method is suitable for MCRs. Chang,<sup>4</sup> our group,<sup>5</sup> and others<sup>6</sup> developed a number of three-component reactions by trapping ketenimines generated in situ from sulfonyl azides and terminal alkynes via this CuAAC process.

Michael addition of activated methylenes to nitroolefins is an efficient synthetic tool for the construction of nitrogen-containing ketoesters.<sup>7</sup> Transformation of the corresponding adducts could yield a variety of useful synthetic intermediates, such as  $\gamma$ -amino acids or  $\gamma$ -lactams, which are widely used for the synthesis of biologically and pharmaceutically relevant molecules, for instance, in treatment of epilepsy,<sup>8</sup> HIV,<sup>9</sup> neurodegenerative diseases, and depression.<sup>10</sup>

The success of our previous MCRs involving ketenimines provided the impetus for us to synthesize  $\gamma$ -nitro imidates via Michael addition of ketenimine-generating activated methylenes to nitroolefins. By this consideration, we designed a four-component reaction to obtain  $\gamma$ -nitro imidate (**5a**) from phenylacetylene (**1a**), *p*-toluenesulfonyl azide (**2a**), methanol (**3a**), and (*E*)-(2-nitrovinyl)benzene (**4a**) in a single step

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**TABLE 1.** Condition Optimization for the Four-Component Reaction in Scheme 2<sup>a</sup>

entry	Cu(I)	solvent	base/equiv	additive	yield (%) <sup>b</sup> ( <i>syn</i> : <i>anti</i> ) <sup>c</sup>
1	CuI	DCM	TEA/3		39
2	CuI	MeCN	TEA/3		24
3	CuI	DCE	TEA/3		37
4	CuI	CHCl <sub>3</sub>	TEA/3		25
5	CuI	1,4-dioxane	TEA/3		61 (53:47)
6	CuI	THF	TEA/3		61 (49:51) <sup>d</sup>
7	CuCl	DCM	TEA/3		19
8	CuCl	MeCN	TEA/3		10
9	CuCl	CHCl <sub>3</sub>	TEA/3		27
10	CuCl	1,4-dioxane	TEA/3		64 (57:43)
11	CuCl	THF	TEA/3		71 (51:49)
12	CuBr	THF	TEA/3		66 (56:44)
13	CuCl	THF	Pyridine		34
14	CuCl	THF	DIPEA		58 (63:37)
15	CuCl	THF	DBU		none
16	CuCl	THF	TEA/1		59 (56:44)
17	CuCl	THF	TEA/5		59 (51:49)
18	CuCl	THF	TEA/3	MgCl <sub>2</sub> (1 equiv)	44 (56:44)
19	CuCl	THF	TEA/3	MgSO <sub>4</sub> (1 equiv)	61 (44:56)
20	CuCl	THF	TEA/3	LiCl (1 equiv)	trace

<sup>a</sup>Reaction conditions: **1a** (1.2 mmol), **2a** (1.2 mmol), **3a** (5 mmol), **4a** (1 mmol), Cu(I) (0.1 mmol), base, solvent, additive, room temperature, under N<sub>2</sub>, 24 h. <sup>b</sup>Isolated yield. <sup>c</sup>Diastereomeric ratio (*syn*/*anti*) was determined by <sup>1</sup>H NMR. <sup>d</sup>Reaction was performed for 20 h.

**TABLE 2.** Reaction of Phenyl Acetylene with TsN<sub>3</sub>, MeOH, and Various Nitroolefins<sup>a</sup>

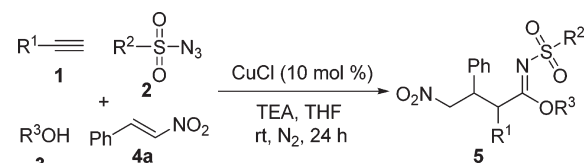
entry	Ar ( <b>4</b> )	product ( <i>syn</i> / <i>anti</i> ) <sup>b</sup>	yield (%) <sup>c</sup>	
1	Ph ( <b>4a</b> )	<b>5a</b> (51:49)	71	
2	<i>p</i> -MeOC <sub>6</sub> H <sub>4</sub> ( <b>4b</b> )	<b>5b</b>	41 for <b>5b-syn</b> <sup>d</sup> 34 for <b>5b-anti</b> <sup>d</sup>	
3	<i>m</i> -MeOC <sub>6</sub> H <sub>4</sub> ( <b>4c</b> )	<b>5c</b> (53:47)	55	
4	2-Furyl ( <b>4d</b> )	<b>5d</b> (4:96)	66	
5	<i>p</i> -Br ( <b>4e</b> )	<b>5e</b> (41:59)	45	
6	<i>p</i> -NO <sub>2</sub> C <sub>6</sub> H <sub>4</sub> ( <b>4f</b> )	<b>5f</b> (1:99)	34	

<sup>a</sup>Reaction conditions: **1a** (1.2 mmol), **2a** (1.2 mmol), **3a** (5 mmol), **4** (1 mmol), CuCl (0.1 mmol), TEA (3 mmol), THF (2 mL), N<sub>2</sub>, rt, 24 h.

<sup>b</sup>Diastereomeric ratio (*syn*:*anti*) was determined by <sup>1</sup>H NMR of isolated product. <sup>c</sup>Isolated yield. <sup>d</sup>Diastereomers were isolated and characterized respectively.

(Scheme 2). Fortunately, the reaction was performed smoothly.

To gain a greater understanding of this conversion, optimization of reaction conditions was first performed, including copper source, solvent, base, and inorganic additive (Table 1). As we can see, either THF or 1,4-dioxane is suitable for this transformation (Table 1, entries 1–6) in comparison with dichloromethane (DCM), acetonitrile (MeCN), dichloroethane (DCE), and chloroform (CHCl<sub>3</sub>). A similar situation was observed when CuCl was applied as the catalyst (Table 1, entries 7–11). As to the source of copper(I), CuCl presented a slightly higher yield (Table 1, entries 6, 11, and 12). When different bases, such as pyridine or diisopropylethylamine (DIPEA), were applied for this reaction instead of triethylamine (TEA), no obvious improvements were achieved (Table 1, entries 11, 13, and 14). Moreover, no desired product

**TABLE 3.** Substrate Scope of Alkynes **1** and Sulfonyl Azides **2**<sup>a</sup>

entry	R <sup>1</sup>	R <sup>2</sup>	R <sup>3</sup>	product ( <i>syn</i> / <i>anti</i> ) <sup>b</sup>	yield (%) <sup>c</sup>
1	Ph ( <b>1a</b> )	4-MeC <sub>6</sub> H <sub>4</sub> ( <b>2a</b> )	Me ( <b>3a</b> )	<b>5a</b> (51:49)	71
2	4-MeC <sub>6</sub> H <sub>4</sub> ( <b>1b</b> )	<b>2a</b>	<b>3a</b>	<b>5g</b> (82:18)	66
3	4-MeOC <sub>6</sub> H <sub>4</sub> ( <b>1c</b> )	<b>2a</b>	<b>3a</b>	<b>5h</b> (68:32)	35
4	<b>1a</b>	Ph ( <b>2b</b> )	<b>3a</b>	<b>5i</b> (67:33)	67
5	<b>1a</b>	Mesityl ( <b>2c</b> )	<b>3a</b>	<b>5j</b> (57:43)	49
6	<b>1a</b>	4-ClC <sub>6</sub> H <sub>4</sub> ( <b>2d</b> )	<b>3a</b>	<b>5k</b> (39:61)	59
7	<b>1a</b>	4-NO <sub>2</sub> C <sub>6</sub> H <sub>4</sub> ( <b>2e</b> )	<b>3a</b>	<b>5l</b> (17:83)	35
8	<b>1a</b>		<b>3a</b>	<b>5m</b> (52:48)	73
9	<b>1a</b>	<b>2a</b>	All ( <b>3b</b> )	<b>5n</b> (82:18)	61
10	<b>1a</b>	<b>2a</b>	Bn ( <b>3c</b> )	<b>5o</b> (74:26)	57
11	<b>1a</b>	<b>2a</b>	<i>i</i> -Pr ( <b>3d</b> )	<b>5p</b> (75:25)	46
12	<b>1a</b>	<b>2a</b>	Et ( <b>3e</b> )	<b>5q</b> (60:40)	69
13	<b>1a</b>	<b>2a</b>	<i>n</i> -Pr ( <b>3f</b> )	<b>5r</b> (65:35)	68
14	2-Py ( <b>1d</b> )	<b>2a</b>	<b>3a</b>	<b>5s</b> (2:98)	68
15	<b>1d</b>	<b>2a</b>	<b>3b</b>	<b>5t</b> (1:99)	33
16	<b>1d</b>	<b>2b</b>	<b>3a</b>	<b>5u</b> (1:99)	50
17	<b>1a</b>	Me ( <b>2g</b> )	<b>3a</b>	<b>5v</b> (99:1)	41
18	<b>1b</b>	<b>2g</b>	<b>3a</b>	<b>5w</b> (84:16)	39
19 <sup>d</sup>	<b>1a</b>	<b>2g</b>	<b>3a</b>	<b>5x</b> (57:43)	35
20	<b>1d</b>	<b>2g</b>	<b>3a</b>	<b>5y</b> (66:34)	43

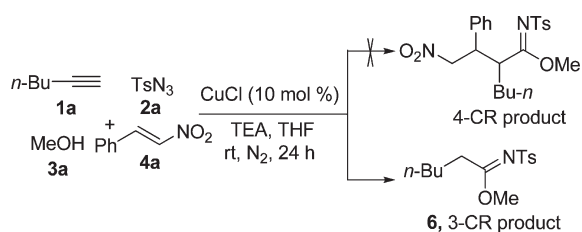
<sup>a</sup>Reaction conditions: **1** (1.2 mmol), **2** (1.2 mmol), **3** (5 mmol), **4a** (1 mmol), CuCl (0.1 mmol), TEA (3 mmol), THF (2 mL), N<sub>2</sub>, rt, 24 h.

<sup>b</sup>Diastereomeric ratio (*syn*/*anti*) was determined by <sup>1</sup>H NMR of isolated product. <sup>c</sup>Isolated yield. <sup>d</sup>Nitroalkene **4b** was used instead of **4a**.

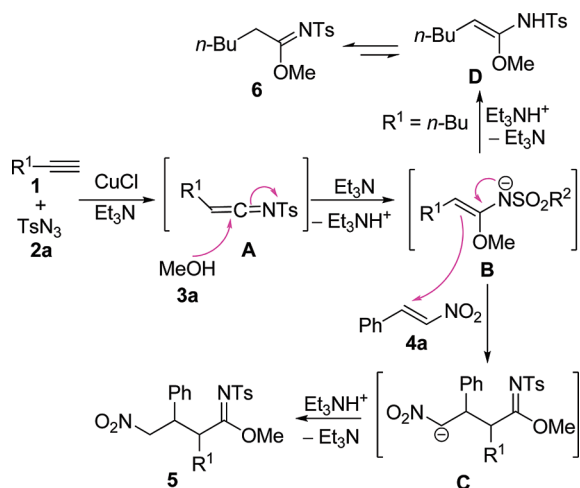
was detected when 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) was used as a base. The ratio of reactants to base has slightly affected the isolation yield (Table 1, entries 11, 16, and 17) as well as the addition of inorganic magnesium salts (Table 1, entries 18 and 19). Lithium chloride severely suppressed the reaction, with only a trace of desired product being detected by thin layer chromatography.

Having optimized the reaction conditions in hand, the versatility of this transformation was first assessed by altering nitroolefins **4** (Table 2). Isolated yield was tuned by the property of the substituted groups on compound **4**. When the electron density of the benzene ring of **4** was enriched by the substituted group (Table 2, entries 2–4), isolated yields were comparable to those of the phenyl case

## SCHEME 3. Formation of Three-Component Product 6



## SCHEME 4. Possible Mechanism for the Cascade Reaction



(Table 2, entry 1). In the case of furyl (Table 2, entry 4), high diastereoselectivity (*syn:anti* = 4:96) and moderate yield (66%) were obtained.

The substrate diversity of sulfonyl azides, terminal alkynes, and alcohols was further investigated (Table 3). Various aromatic alkynes (Table 3, entries 1–3), aromatic azides (Table 3, entries 4–8), and alcohols (Table 3, entries 9–13) readily participated in this 4-CRs to generate  $\gamma$ -nitro imidates in moderate yields without notable stereoselectivity (Table 3, entries 1–8 and 16–20). In the case of 2-pyridinyl acetylene (Table 3, entries 14–16), excellent diastereoselectivity was detected after analysis of isolated product by proton NMR. The anti/syn ratio of the isolated product exceeded 98:2. In case of methanesulfonyl azide (Table 3, entries 17–20), *syn* was obtained as the major product.

When aliphatic terminal alkyne **1e** was used instead of aromatic ones, compound **6** was isolated in 74% yield (Scheme 3). The nitroalkene did not participate in this cascade transformation.

Structures of products were fully characterized by <sup>1</sup>H NMR, <sup>13</sup>C NMR, MS, and HMRS. On the basis of the crystal analysis of **5v** (see the Supporting Information) and coupling constants of NMR, we assigned the ratio of *syn/anti* for all other products.

A possible mechanism for this cascade reaction is shown in Scheme 4. First, alkyne **1** reacts with sulfonyl azide **2** in the presence of CuCl and TEA to generate *N*-sulfonyl ketenimine **A**. Sequential nucleophilic addition of the alcohol leads

to the formation of anion intermediate **B**. Michael addition of **B** to nitroolefin **4** and subsequent protonation yields  $\gamma$ -nitro imidate **5**. When aliphatic alkyne **1e** is used, **B** prefers protonation rather than Michael addition due to its stronger basicity. The resulting **D** immediately tautomerizes to more stable imidate **6**.

In conclusion, we have developed a facile route to  $\gamma$ -nitro imidates via the four-component reaction of alkynes with sulfonyl azides, alcohols, and nitroolefins. This one-step procedure is general and efficient. A possible mechanism is also postulated.

## Experimental Section

**General Procedure for Preparation of  $\gamma$ -Nitro-*N*-sulfonylimidates.** To a mixture of CuCl (10 mg, 0.1 mmol), nitroalkene **4** (1 mmol), alkyne **1** (1.2 mmol), and azide **2** (1.2 mmol) in THF (1 mL) were added TEA (0.304 g, 3 mmol) and alcohol **3** (5 mmol) in solvent THF (1 mL) under N<sub>2</sub> atmosphere. The mixture was then stirred at room temperature for 24 h and then evaporated under vacuum. The residue was subjected to silica gel column chromatography with petroleum ether (Pet)/ethyl acetate (EA) as eluent. The products were recrystallized from EA/hexane or EA/Pet.

Data for methyl 4-nitro-2,3-diphenyl-*N*-tosylbutanimidate (**5a**, *syn:anti* = 51:49): white crystal (71%); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.83 (d, *J* = 8.4 Hz, 1.01H), 7.68 (d, *J* = 7.6 Hz, 0.97H), 7.55 (d, *J* = 7.6 Hz, 0.97H), 7.45–7.37 (m, 2.40H), 7.36–7.26 (m, 3.58H), 7.19–7.09 (m, 5.10H), 5.51 (d, *J* = 12.0 Hz, 0.49H), 7.27 (d, *J* = 11.6 Hz, 0.51H), 4.93 (dd, *J* = 12.4, 10.2 Hz, 0.51H), 4.68 (dd, *J* = 12.4, 5.0 Hz, 0.51H), 4.56–4.50 (m, 0.49H), 4.36–4.27 (m, 1.50H), 3.81 (s, 1.54H), 3.50 (s, 1.47H), 2.43 (s, 1.53H), 2.37 (s, 1.46H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  173.0, 171.0, 143.7, 143.2, 138.6, 138.5, 136.7, 136.4, 134.4, 134.3, 129.5, 129.4, 129.2, 129.1, 128.925, 128.892, 128.7, 128.5, 128.3, 128.2, 128.0, 127.934, 127.851, 126.7, 126.5, 79.0, 78.8, 56.1, 55.5, 53.0, 51.1, 47.3, 47.2, 21.5, 21.4; IR (KBr)  $\nu$  3033, 1618, 1554, 1439, 1289, 1156, 1093, 685, 603 cm<sup>-1</sup>; MS (ESI) *m/z* 475.2 ([M + Na]<sup>+</sup>); HRMS (ESI) *m/z* calcd for C<sub>24</sub>H<sub>24</sub>N<sub>2</sub>O<sub>5</sub>SNa [M + Na]<sup>+</sup> 475.1298, found 475.1283.

Data for methyl *N*-methylsulfonyl-4-nitro-2,3-diphenylbutanimidate (**5v-syn**): white crystal (41%); mp 179–181 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.33–7.30 (m, 2H), 7.18–7.12 (m, 5H), 7.11–7.08 (m, 3H), 5.08 (d, *J* = 11.6 Hz, 1H), 4.88 (dd, *J* = 12.8, 9.6 Hz, 1H), 4.66 (dd, *J* = 12.8, 4.4 Hz, 1H), 4.32–4.26 (m, 1H), 3.88 (s, 3H), 3.13 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  173.5, 136.3, 134.1, 129.3, 128.7, 128.5, 128.0, 127.9, 79.0, 56.0, 53.3, 47.2, 43.1; IR (KBr)  $\nu$  2954, 1621, 1555, 1440, 1383, 1291, 1136, 1020, 969, 818, 780, 703, 587 cm<sup>-1</sup>; MS (ESI) *m/z* 399.3 ([M + Na]<sup>+</sup>); HRMS (ESI) *m/z* calcd for C<sub>18</sub>H<sub>20</sub>N<sub>2</sub>O<sub>5</sub>SNa [M + Na]<sup>+</sup> 399.0985, found 399.0967.

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**Supporting Information Available:** Detailed experimental procedures, characterization data, copies of <sup>1</sup>H and <sup>13</sup>C NMR spectra for all products, and crystallographic information files for compounds **5v**. This material is available free of charge via the Internet at <http://pubs.acs.org>.