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$Y(OTf)_3$-Catalyzed Cascade Propargylic Substitution/Aza-Meyer–Schuster Rearrangement: Stereoselective Synthesis of α,β-Unsaturated Hydrazones and Their Conversion into Pyrazoles

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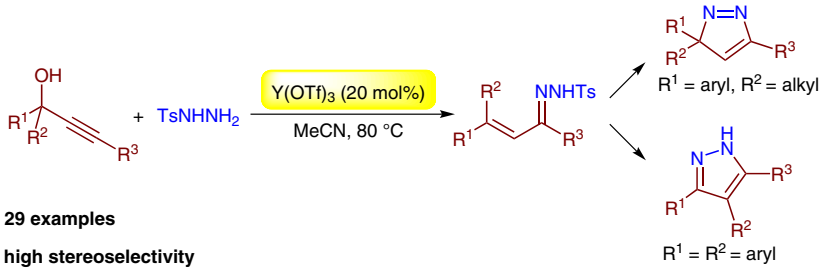

- **29 examples**
- **high stereoselectivity**
- **through a cascade propargylic substitution/*aza*-Meyer–Schuster rearrangement**

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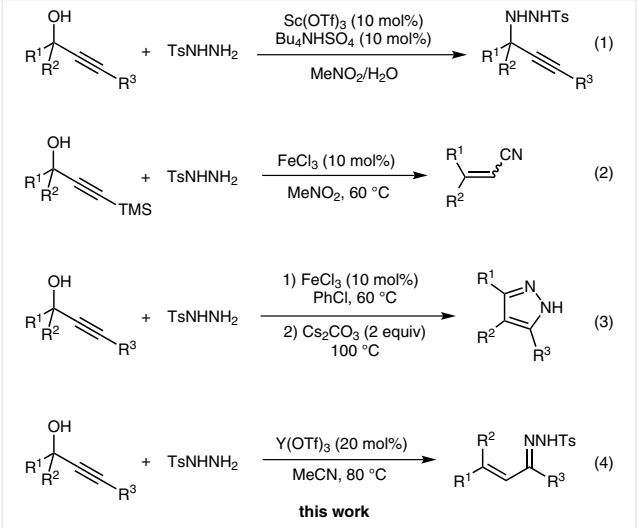
Abstract A straightforward and concise method for the highly stereoselective synthesis of α,β-unsaturated hydrazones by the $Y(OTf)_3$-catalyzed cascade propargylic substitution/aza-Meyer–Schuster rearrangement reaction of tertiary propargylic alcohols and *p*-toluenesulfonyl hydrazide under an air atmosphere is developed. A series of α,β-unsaturated hydrazones have been synthesized from simple and readily available starting materials in good yields. Furthermore, the obtained α,β-unsaturated hydrazones are converted into pyrazoles in the presence of LiO*t*-Bu.

Keywords propargylic alcohols, aza-Meyer–Schuster rearrangement, $Y(OTf)_3$, α,β-unsaturated hydrazones, pyrazoles

Currently, considerable interest has been focused on the transition-metal-catalyzed cascade reactions of propargylic alcohols, since these novel reactions can directly construct diverse complicated organic molecules from readily available starting materials under very mild conditions.[1] Among these, the Lewis acid catalyzed carbon–carbon and carbon–heteroatom bond formations of propargylic alcohols with various nucleophiles have been extensively investigated over the last few decades.[2] However, compared to the wide applications of amine nucleophiles in the C–N bond formation reactions of propargylic alcohols, particularly tertiary propargylic alcohols, the use of hydrazines as nucleophiles is barely documented.[3] In 2012, Yoshimatsu and co-workers reported the first convenient method for the preparation of propargyl hydrazides from tertiary propargylic alcohols through scandium-catalyzed hydrazination in $MeNO_2$–H_2O (Scheme 1, eq 1).[4] Almost at the same time, Zhan and co-workers reported a novel $FeCl_3$-catalyzed domino regioselective propargylic substitution/aza-Meyer–Schuster rearrangement reaction for the synthesis of acrylonitriles from trimethylsilyl-substituted tertiary propargylic alcohols and *p*-toluenesulfonyl hydrazide (Scheme 1, eq 2).[5] More recently, the same group has also developed a one-pot synthesis of pyrazoles from tertiary propargylic alcohols and *p*-toluenesulfonyl hydrazide through a two-step cascade sequence (Scheme 1, eq 3).[6] During our recent studies on propargylic chemistry,[7] we have found that tertiary propargylic alcohols with *p*-toluenesulfonyl hydrazide can be efficiently converted into α,β-unsaturated hydrazones using $Y(OTf)_3$ [yttrium(III) tifluoromethanesulfonate] as the catalyst through a cascade propargylic substitution/aza-Meyer–Schuster rearrangement reaction (Scheme 1, eq 4). Moreover, the obtained α,β-unsaturated hydrazones can be further transformed into pyrazoles in the presence of LiO*t*-Bu. Herein we report the results of this study.

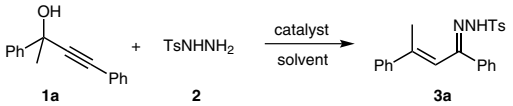


Scheme 1 The reactions of tertiary propargylic alcohols with *p*-toluenesulfonyl hydrazide

At the outset of this investigation, a series of tertiary propargylic alcohols **1a**–**u** were prepared by KO*t*-Bu-promoted alkynylation of arylacetylenes with ketones under solvent-free conditions recently developed by our group.[7b] Next, we employed the propargylic alcohol **1a** and *p*-toluenesulfonyl hydrazide (**2**) as the substrates to test this reaction. Treatment of compound **1a** with **2** in the presence of 10 mol% of $Ce(OTf)_3$ in $MeNO_2$ at 60 °C for 7.5 hours resulted in the formation of α,β-unsaturated hydrazone **3a** in 34% isolated yield, as the only stereoisomer (Table 1, entry 1). Encouraged by this result, we proceeded to optimize the reaction by first screening the rare-earth-metal catalyst (Table 1, entries 1–5). We were delighted to find that $Y(OTf)_3$ could promote the reaction (Table 1, entry 2). Other rare earth metal salts, such as $Yb(OTf)_3$, $La(OTf)_3$, and $Sc(OTf)_3$, also worked for this reaction, albeit with lower yields (Table 1, entries 3–5). For the catalyst of $Yb(OTf)_3$, much more byproducts were generated which made the product purification more difficult. So we used $Y(OTf)_3$ for the further optimizations. Next, a series of common organic solvents were examined (Table 1, entries 6–10); MeCN was found to be the most suitable solvent for this transformation (Table 1, entry 10), whereas a low yield of **3a** was obtained when dioxane or DCE was used as the solvent (Table 1, entries 6 and 7). However, the strong polar solvents, such as DMF and DMSO, were found not effective in this reaction (Table 1, entries 8 and 9). Furthermore, the reaction temperature and catalyst loading were examined, and it was found that a 20 mol% of catalyst with 80 °C of reaction temperature led to the highest yield of **3a** in the shortest reaction time (Table 1, entry 13). Finally, it is noted that the reaction proceeded with high stereoselectivity. The structure of α,β-unsaturated hydrazone **3a** was confirmed by X-ray crystallographic analysis.[8]

With the optimized reaction conditions in hand, the scope and generality of this transformation was investigated by using a variety of tertiary propargylic alcohols. As illustrated in Schene 2, the reaction proceeds smoothly over a wide range of substrates to afford the corresponding α,β-unsaturated hydrazones in moderate to excellent yields.[9] Among the Ar groups of tertiary propargylic alcohols **1**, substituents possessing an electron-rich aromatic ring gave the desired product **3** in higher yields than those with an electron-poor ring (Scheme 2, 3a–h). However, when an aliphatic alkyne derived (1-hexyne) propargylic alcohol was used, no desired product was detected. Next, substituent effects at the propargylic position were investigated (Scheme 2, 3i–t). In the examples of asymmetric propargylic alcohols (R^1 = Ar, R^2 = Alk), the α,β-unsaturated hydrazones were obtained in good yields (Scheme 2, 3i–o). Besides, we were pleased to discover that an aliphatic ketone derived propargylic alcohol **1p** is also compatible with this transformation and with satisfactory yield (Scheme 2, 3p).

Table 1 Optimization of Reaction Conditions[a]



1a **2** **3a**

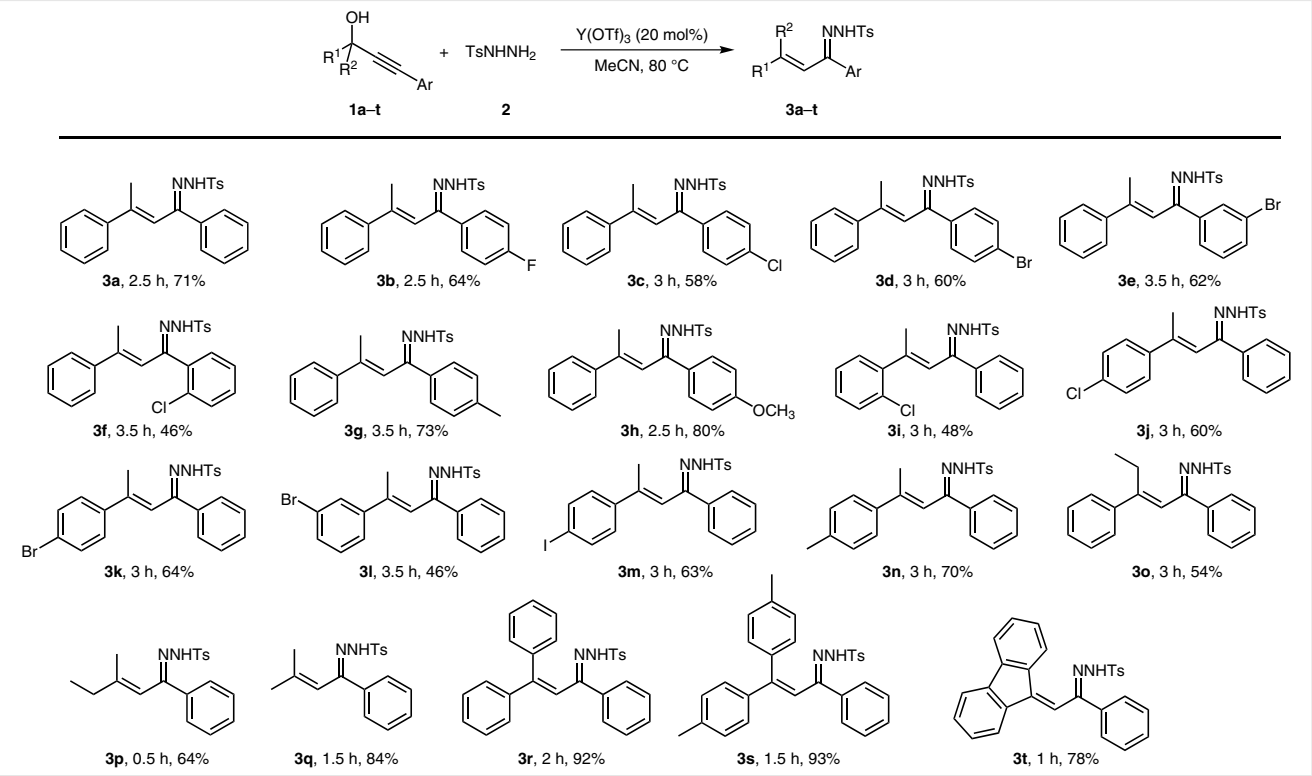
Entry	Cat. (mol%)	Solvent	Temp (°C)	Time (h)	yield (%)[b]
1	$Ce(OTf)_3$ (10)	$MeNO_2$	60	7.5	34
2	$Y(OTf)_3$ (10)	$MeNO_2$	60	7.5	51
3	$Yb(OTf)_3$ (10)	$MeNO_2$	60	6	48
4	$La(OTf)_3$ (10)	$MeNO_2$	60	7.5	38
5	$Sc(OTf)_3$ (10)	$MeNO_2$	60	7.5	27
6	$Y(OTf)_3$ (10)	dioxane	60	10	27
7	$Y(OTf)_3$ (10)	DCE	60	7.5	41
8	$Y(OTf)_3$ (10)	DMF	60	7.5	trace
9	$Y(OTf)_3$ (10)	DMSO	60	7.5	trace
10	$Y(OTf)_3$ (10)	MeCN	60	7.5	60
11	$Y(OTf)_3$ (10)	MeCN	80	6	65
12[c]	$Y(OTf)_3$ (10)	MeCN	100	6	62
13	$Y(OTf)_3$ (20)	MeCN	80	2.5	71

[a] All the reactions were carried out with **1a** (0.3 mmol) and **2** (0.6 mmol) in 2.0 mL of solvent.
[b] Yield of isolated product after chromatography.
[c] The reaction was carried out in a sealed tube.

Interestingly, it was found that the symmetric tertiary propargylic alcohols ($R^1 = R^2$), derived from an aliphatic ketone or an aromatic ketone, were also effective and gave excellent product yields (Scheme 2, 3q–t). Moreover, it is noteworthy that the steric effect of *ortho* substituent was obviously observed in the formation of **3f** and **3i**.

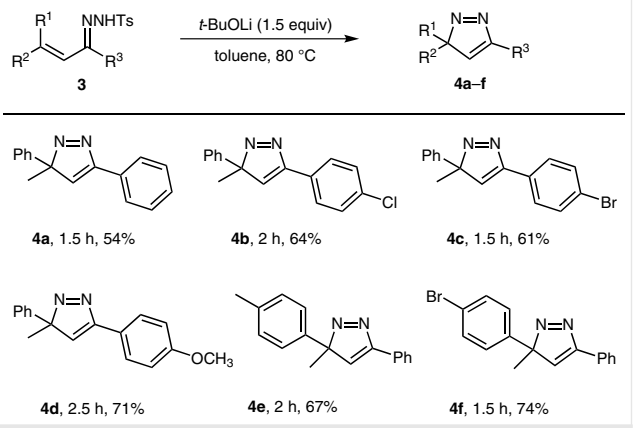
The corresponding α,β-unsaturated hydrazones are attractive and can be further converted into organic synthesis.[10] First, we were delighted to find that a novel trisubstituted 3*H*-pyrazole **4a** was obtained in moderate yield when treatment of α,β-unsaturated hydrazone **3a** with LiO*t*-Bu in toluene at 80 °C for 1.5 hours. Considering the importance of pyrazoles in organic chemistry,[11] we then proceeded to investigate this pyrazole formation reaction using various α,β-unsaturated hydrazones which were synthesized above (Scheme 3).[12] It was noted that a wide range of α,β-unsaturated hydrazone substrates can be employed in this transformation to afford the corresponding 3*H*-pyrazole in moderate to good yields (Scheme 3, 4a–f).

More interestingly, when α,β-unsaturated hydrazones **3r** and **3s** were employed in this pyrazole formation reaction, we found that the novel 1*H*-pyrazoles **5a** and **5b** rather than 3*H*-pyrazoles were obtained in 73% and 56% isolated yields, respectively (Scheme 4). We attributed the result of 1*H*-pyrazole formation to a [1,5]-sigmatropic shift as well as aromatization sequence (Scheme 4). These results are consistent with Zhan's report.[6]



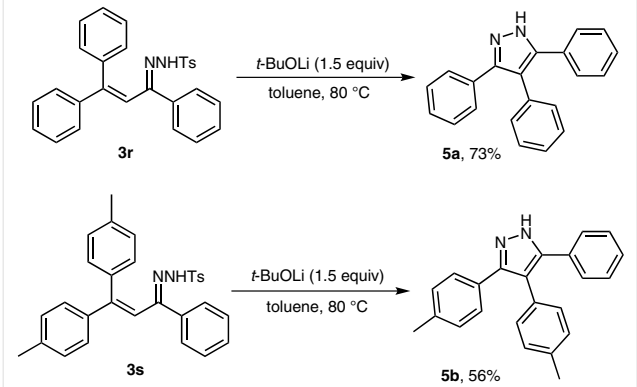
Scheme 2 $Y(OTf)_3$-catalyzed reaction of various tertiary propargylic alcohols with *p*-toluenesulfonyl hydrazide. All the reactions were carried out with propargylic alcohols **1a**–**t** (0.3 mmol), *p*-toluenesulfonyl hydrazide (**2**, 0.6 mmol), $Y(OTf)_3$ (0.06 mmol) in 2.0 mL of MeCN. Isolated yields are reported.

To further validate whether this reaction can be practically useful, two gram-scale experiments have been carried out for propargylic alcohols **1a** and **1r** under standard reaction conditions. The reaction proceeded smoothly, providing the corresponding α,β-unsaturated hydrazone products **3a** and **3r** in 56% and 81% yields, respectively.

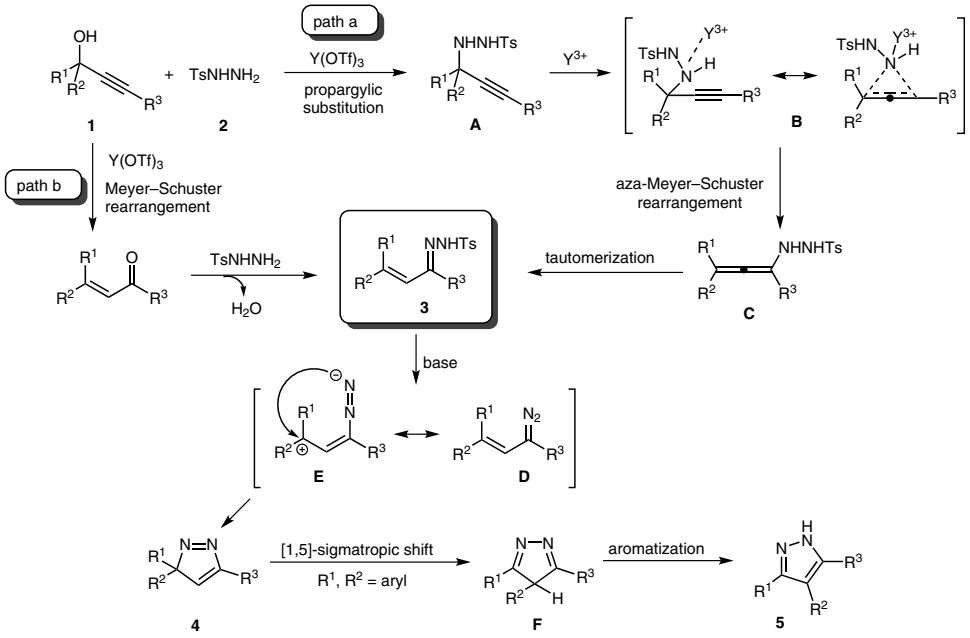


Scheme 3 Synthesis of 3*H*-pyrazoles from the corresponding α,β-unsaturated hydrazones. All the reactions were carried out with α,β-unsaturated hydrazones **3** (0.3 mmol), LiO*t*-Bu (0.45 mmol) in 2.0 mL of toluene at 80 °C. Isolated yields are reported.

On the basis of the above results and related literature,[4–6] two plausible reaction pathways to account for the formation of α,β-unsaturated hydrazones and pyrazoles from tertiary propargylic alcohols with *p*-toluenesulfonyl hydrazide is outlined in Scheme 5. In path a, the $Y(OTf)_3$-catalyzed direct substitution of a propargylic alcohol with a *p*-toluenesulfonyl hydrazide occurred to afford propargyl hydrazide intermediate **A**. Next, the intermediate **A** undergoes a [1,3]-shift of the NHNHTs group through the aza-Meyer–Schuster rearrangement, which leads to allene intermediate **B**. Final-



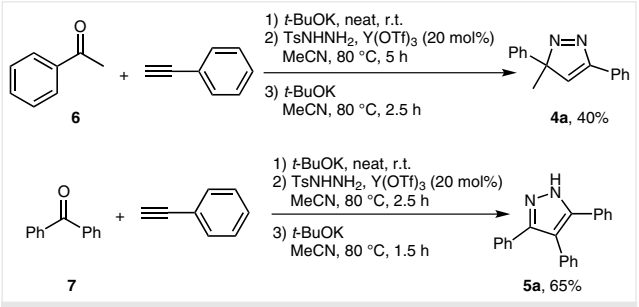
Scheme 4 Synthesis of 1*H*-pyrazoles from α,β-unsaturated hydrazones



Scheme 5 Proposed mechanism of the reaction

ly, the intermediate **B** then isomerizes to give the corresponding α,β-unsaturated hydrazone **3**. The product **3** can be easily converted into the diazo compound **C** in the presence of a base.[10a,d] Next, the 1,5-dipole isomer of the diazo compound **C** undergoes an intramolecular 6π-electrocyclic ring closure; which affords the corresponding 3*H*-pyrazole product **4**. On the other hand, when R^1 and R^2 are aryl groups, the [1,5]-sigmatropic shift occurs and produces the 4*H*-pyrazoles intermediate **E**, which subsequently experience a rapid isomerization to afford the trisubstituted 1*H*-pyrazoles **5**. However, since the Meyer–Schuster rearrangement of the propargylic alcohol can be catalyzed by Lewis acid,[13] a prior Meyer–Schuster rearrangement followed by nucleophilic attack of the *p*-toluenesulfonyl hydrazide cannot be strictly ruled out. In such case, an α,β-unsaturated ketone intermediate is generated, which is attacked by the *p*-toluenesulfonyl hydrazide and accompanied with the elimination of water to afford the corresponding α,β-unsaturated hydrazone **3** (path b).

Finally, a one-pot transformation of three-step reactions from ketones with phenylacetylene to pyrazoles directly was explored. Thus, ketones **6** and **7** were reacted with phenylacetylene in the presence of KO*t*-Bu under solvent-free conditions at room temperature. After completion of the alkynylation, *p*-toluenesulfonyl hydrazide, $Y(OTf)_3$, and MeCN were added, respectively, to the reaction mixture. The resulting mixture was heated at 80 °C for several hours. After completion of this hydrazone formation reaction, KO*t*-Bu was added to the reaction mixture again and continued to heat at 80 °C for 1.5 hours. After workup, the pyrazoles **4a** and **5a** were isolated in 40% and 65% overall yields, respectively (Scheme 6).



Scheme 6 One-pot reactions from ketones

In summary, we have developed a simple and efficient $Y(OTf)_3$-catalyzed cascade propargylic substitution/aza-Meyer–Schuster rearrangement reaction of tertiary propargylic alcohols and *p*-toluenesulfonyl hydrazide for the synthesis of α,β-unsaturated hydrazone derivatives. Moreover, the obtained α,β-unsaturated hydrazones have been converted into pyrazoles in the presence of LiO*t*-Bu.

Acknowledgement

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Supporting Information

Supporting information for this article is available online at http://dx.doi.org/10.1055/s-0034-1381057.

References and Notes

(1) For selected reviews, see: (a) Ding, C.; Hou, X. *Chem. Rev.* **2011**, *111*, 1914. (b) Hao, L.; Zhan, Z. *Curr. Org. Chem.* **2011**, *15*, 1625. (c) Ljungdahl, N.; Kann, N. *Angew. Chem. Int. Ed.* **2009**, *48*, 642. (d) Detz, R. J.; Hiemstra, H.; van Maarseveen, J. H. *Eur. J. Org. Chem.* **2009**, 6263.

(2) For selected reviews and examples, see: (a) Bauer, E. B. *Synthesis* **2012**, *44*, 1131. (b) Guillena, G.; Ramon, D. J.; Yus, M. *Chem. Rev.* **2010**, *110*, 1611. (c) Bandini, M.; Tragni, M. *Org. Biomol. Chem.* **2009**, *7*, 1501. (d) Kabalka, G. W.; Yao, M. *Curr. Org. Synth.* **2008**, *5*, 28. (e) Wang, X.; Li, S.; Pan, Y.; Wang, H.; Liang, H.; Chen, Z.; Qin, X. *Org. Lett.* **2014**, *16*, 580. (f) Fang, Z.; Liu, J.; Liu, Q.; Bi, X. *Angew. Chem. Int. Ed.* **2014**, *53*, 7209. (g) Zhu, Y.; Yin, G.; Hong, D.; Lu, P.; Wang, Y. *Org. Lett.* **2011**, *13*, 1024. (h) Yin, G.; Zhu, Y.; Zhang, L.; Lu, P.; Wang, Y. *Org. Lett.* **2011**, *13*, 940. (i) Yan, W.; Wang, Q.; Chen, Y.; Petersen, J. L.; Shi, X. *Org. Lett.* **2010**, *12*, 3308. (j) Chatterjee, P. N.; Roy, S. *J. Org. Chem.* **2010**, *75*, 4413. (k) Debleds, O.; Gayon, E.; Ostaszuk, E.; Vrancken, E.; Campagne, J. M. *Chem. Eur. J.* **2010**, *16*, 12207. (l) Yoshimatsu, M.; Watanabe, H.; Koketsu, E. *Org. Lett.* **2010**, *12*, 4192. (m) Fang, C.; Pang, Y.; Forsyth, C. J. *Org. Lett.* **2010**, *12*, 4528. (n) Sanz, R.; Martínez, A.; Miguel, D.; Älvarez-Gutiérrez, J. M. *Org. Lett.* **2007**, *9*, 727. (o) Zhan, Z.; Yang, W.; Yang, R.; Yu, J.; Li, J.; Liu, H. *Chem. Commun.* **2006**, 3352.

(3) For selected examples using second propargylic alcohols and hydrazines as the substrates, see: (a) Xu, S.; Hao, L.; Wang, T.; Ding, Z.; Zhan, Z. *Org. Biomol. Chem.* **2013**, *11*, 294. (b) Reddy, C. R.; Vijaykumar, J.; Grée, R. *Synthesis* **2013**, *45*, 830.

(4) Yoshimatsu, M.; Ohta, K.; Takahashi, N. *Chem. Eur. J.* **2012**, *18*, 15602.

(5) Hao, L.; Wu, F.; Ding, Z.; Xu, S.; Ma, Y.; Chen, L.; Zhan, Z. *Chem. Eur. J.* **2012**, *18*, 6453.

(6) Hao, L.; Hong, J.; Zhu, J.; Zhan, Z. *Chem. Eur. J.* **2013**, *19*, 5715.

(7) (a) Chen, S.; Wang, J. *J. Org. Chem.* **2007**, *72*, 4993. (b) Chen, S.; Yuan, F.; Zhao, H.; Li, B. *Res. Chem. Intermed.* **2013**, *39*, 2391.

(8) For the crystal structure of **3a**, please see the Supporting Information.

(9) **General Procedure for the Y(OTf)$_3$-Catalyzed Reaction of Tertiary Propargylic Alcohols with *p*-Toluenesulfonyl Hydrazide**
To a solution of propargylic alcohols (0.3 mmol) and *p*-toluenesulfonyl hydrazide (0.6 mmol) in MeCN (2.0 mL) was added Y(OTf)$_3$ (0.06 mmol) under an air atmosphere. The resulting mixture was heated at 80 °C for the indicated time. After completion of the reaction, the mixture was cooled to r.t. The solvent was removed in a vacuum, and the resulting residue was purified on a silica gel column (PE–EtOAc) to provide the desired α,β-unsaturated hydrazone products **3**.
Representative Spectroscopic Data
Compound **3b**: white solid; mp 128–130 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.86 (s, 3 H), 2.43 (s, 3 H), 6.19 (s, 1 H), 7.00–7.07 (m, 2 H), 7.33 (d, *J* = 8.0 Hz, 2 H), 7.39–7.44 (m, 3 H), 7.53–7.55 (m, 2 H), 7.63–7.68 (m, 2 H), 7.84 (s, 1 H), 7.89 (d, *J* = 8.5 Hz, 2 H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 18.2, 21.6, 115.5, 125.9, 128.0, 128.8, 128.8, 129.1, 129.7, 131.9, 135.6, 139.5, 144.2, 146.6, 150.9, 162.9, 164.8. ESI-HRMS: *m/z* calcd for $C_{23}H_{22}FN_2O_2S$ [M + H]$^+$: 409.1381; found: 409.1379.
Compound **3q**: white solid; mp 114–117 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.29 (s, 6 H), 2.43 (s, 3 H), 3.65 (s, 1 H), 6.07 (s, 1 H), 7.30 (d, *J* = 7.0 Hz, 5 H), 7.36–7.39 (m, 2 H), 7.83(d, *J* = 8.0 Hz, 2 H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 21.6, 27.0, 83.3, 91.6, 122.4, 128.3, 128.3, 128.4, 129.4, 131.7, 135.3, 143.8. Anal. Calcd for $C_{18}H_{20}N_2O_2S$: C, 65.83; H, 6.14; N, 8.53. Found: C, 65.81; H, 6.20; N, 8.41.

(10) For reviews, see: (a) Xiao, Q.; Zhang, Y.; Wang, J. *Acc. Chem. Res.* **2013**, *46*, 236. (b) Attanasi, O. A.; Bianchi, L.; D'Auria, M.; Mantellini, F.; Racioppi, R. *Curr. Org. Synth.* **2013**, *10*, 631. (c) Shao, Z.; Zhang, H. *Chem. Soc. Rev.* **2012**, *41*, 560. (d) Barluenga, J.; Valdés, C. *Angew. Chem. Int. Ed.* **2011**, *50*, 7486. (e) Lazny, R.; Nodzewska, A. *Chem. Rev.* **2010**, *110*, 1386. (f) Fulton, J. R.; Aggarwal, V. K.; de Vicente, J. *Eur. J. Org. Chem.* **2005**, 1479.

(11) For recent reviews and examples about the synthesis of pyrazoles, see: (a) Gulevich, A. V.; Dudnik, A. S.; Chernyak, N.; Gevorgyan, V. *Chem. Rev.* **2013**, *113*, 3084. (b) Fustero, S.; Sánchez-Roselló, M.; Barrio, P.; Simón-Fuentes, A. *Chem. Rev.* **2011**, *111*, 6984. (c) Dadiboyena, S.; Nefzi, A. *Eur. J. Med. Chem.* **2011**, *46*, 5258. (d) Wen, J.; Tang, H.; Xiong, K.; Ding, Z.; Zhan, Z. *Org. Lett.* **2014**, *16*, 5940. (e) Tang, X.; Huang, L.; Yang, J.; Xu, Y.; Wu, W.; Jiang, H. *Chem. Commun.* **2014**, *50*, 14793. (f) Matcha, K.; Antonchick, A. P. *Angew. Chem. Int. Ed.* **2014**, *53*, 11960. (g) Schneider, Y.; Prévost, J.; Gobin, M.; Legault, C. Y. *Org. Lett.* **2014**, *16*, 596. (h) Li, X.; He, L.; Chen, H.; Wu, W.; Jiang, H. *J. Org. Chem.* **2013**, *78*, 3636. (i) Zhu, Y.; Lu, W.; Sun, H.; Zhan, Z. *Org. Lett.* **2013**, *15*, 4146.

(12) **General Procedure for the Synthesis of Pyrazoles from the Corresponding α,β-Unsaturated Hydrazones**
To a solution of α,β-unsaturated hydrazones (0.3 mmol) in toluene (2.0 mL) was added LiO*t*-Bu (0.45 mmol) under an air atmosphere. The resulting mixture was heated at 80 °C for the indicated time. After completion of the reaction, the solvent was removed in a vacuum. The resulting residue was purified on a silica gel column (EtOAc–PE) to provide the desired pyrazole products **4** and **5**.
Representative Spectroscopic Data Compound **4a**: yellow solid; mp 68–71 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.83 (s, 3 H), 7.28–7.36 (m, 4 H), 7.39–7.44 (m, 3 H), 7.48 (t, *J* = 7.5 Hz, 2 H), 8.12–8.05 (m, 2 H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 22.2, 100.3, 126.5, 127.3, 128.1, 128.8, 128.9, 129.3, 130.7, 136.34, 136.6, 154.9. ESI-HRMS: *m/z* calcd for $C_{16}H_{15}N_2$ [M + H]$^+$: 235.1230; found: 235.1230.
Compound **4f**: yellow solid; mp 84–87 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.80 (s, 3 H), 7.29 (d, *J* = 8.5 Hz, 2 H), 7.41–7.51 (m, 5 H), 8.07 (d, *J* = 8.0 Hz, 2 H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 22.2, 99.7, 122.1, 127.3, 128.2, 129.0, 129.5, 130.4, 131.9, 135.4, 135.8, 155.3. Anal. Calcd for $C_{16}H_{13}BrN_2$: C, 61.36; H, 4.18; N, 8.94. Found: C, 61.29; H, 4.31; N, 8.95.

(13) For reviews on Meyer–Schuster rearrangement, see: (a) Cadierno, V.; Crochet, P.; García-Garrido, S. E.; Gimeno, J. *Dalton Trans.* **2010**, *39*, 4015. (b) Engle, D. A.; Dudley, G. B. *Org. Biomol. Chem.* **2009**, *7*, 4149. (c) Swaminathan, S.; Narayanan, K. V. *Chem. Rev.* **1971**, *71*, 429.