Supporting Information

BF₃·OEt₂-mediated cyclization of β , γ -unsaturated oximes and hydrazones with *N*-(arylthio/arylseleno)succinimides: An efficient approach to isoxazoles or dihydropyrazoles

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1. General Considerations

All ¹H NMR and ¹³C NMR spectra were recorded on a 400 MHz (or 600 MHz) Bruker FT-NMR spectrometers 400 MHz (or 600 MHz) and 100 MHz (or 150 MHz), respectively). All chemical shifts are given as δ value (ppm) with reference to tetramethylsilane (TMS) as an internal standard. The peak patterns are indicated as follows: s, singlet; d, doublet; t, triplet; m, multiplet; q, quartet. The coupling constants, *J*, are reported in Hertz (Hz). High resolution mass spectroscopy data of the products were collected on an Agilent Technologies 6540 UHD Accurate-Mass Q-TOF LC/MS (ESI) and a Thermo Fisher Scientific LTQ FTICR-MS instrument. Melting points were determined in open capillary tube using WRS-1B digital melting point apparatus.

The β, γ -unsaturated oximes starting materials, such and as *N*-(arylthio/arylseleno)succinimides, are prepared according to the reported methods, respectively (Y. He, L. Li, Y. Yang, Y. Wang, J. Luo, X. Liu and Y. Liang, Chem. Commun., 2013, 49, 5687; Z. Song, Y. Wu, T. Xin, C. Jin, X. Wen, H. Sun and Q.-L. Xu, Chem. Commun., 2016, 52, 6079; H. Zhang, S. Lin and E. N. Jacobsen, J. Am. Chem. Soc. 2014, 136, 16485). All the solvents were dried and freshly distilled prior to use. Products were purified by flash chromatography on silica gels, eluting with petroleum ether/ethyl acetate (5:1-9:1).

2. Mechanistic studies

(1) Intermediate- detection using HRMS



A 10 mL reaction tube was charged with (*E*)-1-phenylbut-3-en-1-one oxime (**1a**, 32.2 mg, 0.2 mmol), *N*-(*p*-tolylthio)succinimide (**2a**, 44.2 mg, 0.2 mmol), and DCE (1.0 mL), then BF₃·OEt₂ (1.0 equiv) was added to the resulted mixture. The reaction tube was placed at room temperature and stirred for 1 h. Then the mixture in reaction tube

was detected by HRMS, showing that a cationic species PhS^+ ([M]⁺ = 123.0262) was observed. After that, the remains was concentrated under reduced pressure to yield the crude product, which was purified by flash chromatography (silica gel, petroleum ether/ethyl acetate = 9:1 to 20:1), affording the desired product **3a** as a white solid (14.8 mg, ~26 % yield).



(2) Radical-trapping experiment



A 10 mL reaction tube was charged with (*E*)-1-phenylbut-3-en-1-one oxime (1a, 32.2 mg, 0.2 mmol), *N*-(*p*-tolylthio)succinimide (2a, 44.2 mg, 0.2 mmol), and DCE (1.0 mL), BF₃·OEt₂ (1.0 equiv), TEMPO (62.5 mg, 0.4 mmol) then was added to the resulted mixture. The reaction tube was placed at room temperature and stirred for 4 h. Then, the mixture in reaction tube was detected by TLC. After the reaction was completed, and concentrated under reduced pressure to yield the crude product, which was purified by flash chromatography (silica gel, petroleum ether/ethyl acetate = 9:1 to 20:1), affording the desired product **3a** as a white solid (25.6 mg, 45 % yield).





$\begin{array}{c} 7.587\\ 7.566\\ 7.333\\ 7.333\\ 7.124\\ 7.104\\ 7.104\\ 7.104\\ 7.104\\ 7.104\\ 7.104\\ 7.124\\ 7.124\\ 7.124\\ 7.124\\ 2.377\\ -2.325\\$

YJY-11





7.595 7.352 7.352 7.352 7.352 6.895 6.895 6.895 6.895 6.895 6.895 7.342 6.895 6.895 7.342 6.895 7.342 6.895 7.342 6.895 7.342 6.895 7.342 6.895 7.342 6.895 7.342 6.895 7.342 6.895 7.342 6.895 7.342 6.895 7.342 7.342 6.895 7.342 7.3447 7.3447 7.3447 7.3447 7.3447 7.3447 7.3447 7.3447 7.3447 7.3447 7.3447 7.3447



YJY-13







YJY-8







YJY-10



14



ују-5



$\begin{array}{c} & 7,509 \\ & 7,314 \\ & 7,314 \\ & 7,314 \\ & 7,118 \\ & 7,118 \\ & 7,314 \\ & 3,387 \\ & 3,387 \\ & 7,324 \\ & 2,326 \\ & 7,324 \\ & 2,326 \\ & 7,2324 \\ & 2,326 \\ & 7,2324 \\ & -2,334 \\ & -1,599 \end{array}$



ују-З

-1.627

YJY-14



7.373 7.364 7.364 7.364 7.167 7.167 7.167 7.167 7.167 7.167 7.167 7.167 7.169 7.167 7.385 7.3385 7.3385 7.3385 7.2915 7.2028 7.2029 7.2028 7.2029 7.2



YJY-7

7,7.284 7,7.008 7,7.008 7,7.008 7,7.009 7,7.0007 7,7.009 7,7.009 7,7.009 7,7.009 7,7.009 7,7.009 7,7.009 7,7.009 7,7.009 7,7.009 7,7.009 7,7.009 7,7.009 7,7.009 7,7.009 7,7.0007 7,7.00007 7,7.00000



YJY-6









7,5665 7,7416 7,7416 7,7416 7,289 7,297 7,299 7,297 7,299 7,200 7,







7,564 7,564 7,563 7,563 7,553 7,553 7,553 7,553 7,553 7,553 7,553 7,553 7,553 7,553 7,553 7,553 7,553 7,553 7,558 7,375



7.577 7.551 7.1226 7.422 7.278 7.279 7.279 7.279 7.279 7.279 7.279 7.279 7.279 7.279 7.279 7.279 7.279 7.279 7.279 7.279 7.279 7.229



7,556 7,7495 7,7495 7,384 7,384 7,3378 7,3378 7,3378 7,3358 7,3358 7,3358 7,3358 7,3358 1,570 1,570 1,570













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-1.646











-2.472





