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Gold-Catalyzed Michael-Type Reactions and [4 + 2]-Annulations between Propiolates and 1,2-Benzisoxazoles with Ester-Directed Chemoselectivity

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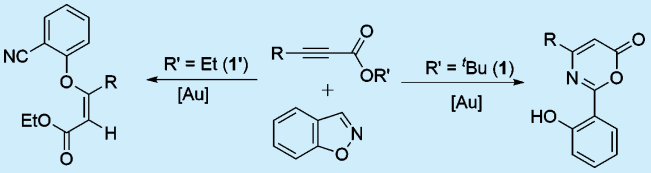
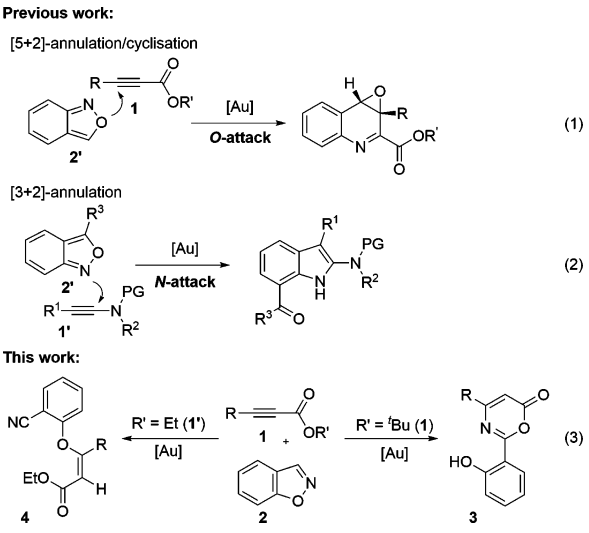
Supporting Information

ABSTRACT: This work reports gold-catalyzed reactions between 1,2-benzisoxazoles and propiolate derivatives with ester-controlled chemoselectivity. For ethyl propiolates **1′**, their gold-catalyzed reactions afforded Michael-type products **4**, whereas *tert*-butyl propiolates **1** preferably underwent [4 + 2]-annulations, further yielding 6*H*-1,3-oxazin-6-one derivatives **3**.



1,2-Benzisoxazoles (**2**)[1] and anthranils (**2′**)[2] are structurally related nitroxy containing heterocycles that are the structural cores of bioactive or naturally occurring molecules. With Au(I) and Pt(II) catalysts, these two nitroxy heterocycles can serve as nucleophiles to attack π-alkynes at the nitrogen or oxygen atoms, enabling further access to molecules of useful complexity.[3−5] Nevertheless, the reported examples focus intensively on anthranils **2′**[3,4] whereas there are few examples on 1,2-benzisoxazoles **2**.[5] We have recently reported gold-catalyzed [5 + 2]-annulations of anthranils **2′** with propiolate derivatives **1** via an *O*-attack route, which yielded quinoline oxides efficiently (eq 1).[4a] The reaction chemoselectivity was surprisingly varied



with ynamide **1′** that underwent an *N*-attack path to implement [3 + 2]-annulations with anthranils **2′** (eq 2).[4b] We sought to achieve new annulations between alkynes and 1,2- benzisoxazoles **2**. Here, we report two feasible reaction paths in the gold-catalyzed reactions of 1,2-benzisoxazoles **2** on propiolate derivatives **1** and **1′**,[6] but the chemoselectivity was controlled by the esters of propiolates **1** and **1′**. For ethyl propiolates **1′**, their gold-catalyzed reactions with 1,2-benzisoxazoles **2** afforded Michael-type products **4**, whereas *tert*-butyl propiolates **1** preferably underwent [4 + 2]-annulations with 1,2-benzisoxazoles **2**, further yielding 6*H*-1,3-oxazin-6-one derivatives **3** (eq 3). A plausible mechanism to rationalize the two reaction routes is presented herein.

Table 1 shows an optimization of [4 + 2]-annulation product **3** using various gold and other catalysts. Our initial tests between *tert*-butyl propiolate **1** and 1,2-benzisoxazole **2** (1.2 equiv) were run with LAuCl/$AgNTf_2$ catalysts in hot dichloroethane (DCE, 80 °C) (L = PPh_3, $P(OPh)_3$, and $P(t\text{-}Bu)_2(o\text{-biphenyl})$, leading to an 82−95% recovery of starting **1a** (entries 1−3); herein, target **3a** was found in a small proportion (10%) in one instance. The use of IPrAuCl/$AgNTf_2$ greatly increased the yield of **3a** up to 77% (entry 4). A change of silver salts as in entries 5−6 (AgX, X = OTf and SbF_6) gave compound **3a** in small yields (7−58%, entries 5−6); the poor reactivity of OTf^- might be attributed to its good binding with inactive **2a** (entry 7). IPrAuCl/$AgNTf_2$ in varied solvents gave **3a** in yields, as follows: 48% in toluene, 35% in MeCN, and 15% in 1,4-dioxane (entries 8−10) The structural elucidation of **3a** was confirmed with X-ray diffraction (CCDC-1862119).

We assessed the scope of these [4 + 2]-annulations using various *tert*-butyl propiolates **1b−1k** and 1,2-benzisoxazoles **2b−2i**; the results are summarized in Scheme 1. Various 4-phenyl-substituted propiolates **1b−1e** (R^1 = Cl, Br, CF_3, and Me) were also applicable to deliver 6*H*-1,3-oxazin-6-one derivatives **3b−3e** in satisfactory yields (74−84%). To our delight, alkyl-substituted propiolates (**1f−1i**; R = isopropyl, *n*-butyl, cyclopropyl, and cyclohexyl) were also suitable for these

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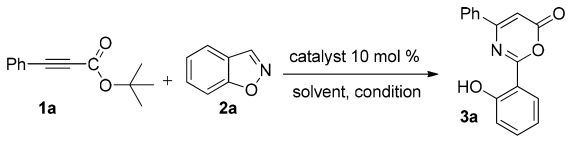
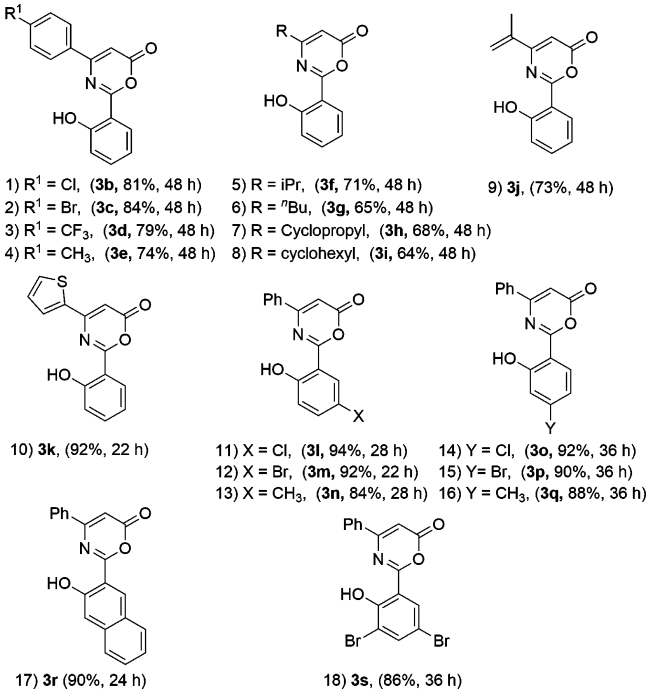
Table 1. [4 + 2]-Annulations with Various Catalysts[a]



					yield (%)[b]	
entry	catalyst	solvent	temp (°C)	time (h)	1a	3a
1	$Ph_3PAuCl/AgNTf_2$	DCE	80	60	88	0
2	$(PhO)_3PAuCl/AgNTf_2$	DCE	80	60	82	10
3	$LAuCl/AgNTf_2$	DCE	80	60	95	0
4	$IPrAuCl/AgNTf_2$	DCE	80	48	0	77
5	IPrAuCl/AgOTf	DCE	80	48	78	7
6	$IPrAuCl/AgSbF_6$	DCE	80	60	30	58
7	$AgNTf_2$	DCE	80	48	97	0
8	$IPrAuCl/AgNTf_2$	toulene	100	60	35	48
9	$IPrAuCl/AgNTf_2$	MeCN	80	60	50	35
10	$IPrAuCl/AgNTf_2$	1,4-dioxane	100	60	76	15

[a]**1a** = 0.16 M, **2a** = (1.2 equiv). [b]Product yields are reported after purification from a silica gel column. L = P(*t*-Bu)$_2$(*o*-biphenyl), IPr = 1,3-bis(diisopropylphenyl)imidazole-2-ylidene). DCE = 1,2-dichloroethane.

Scheme 1. Scope of [4 + 2]-Annulations[a,b]

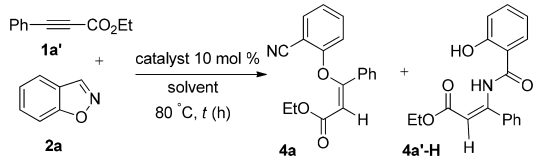


[a]**1a** = 0.16 M, **2a** = (1.2 equiv). [b]Product yields are reported after purification from a silica gel column. IPr = 1,3-bis(diisopropylphenyl)imidazole-2-ylidene).

annulations, rendering 6*H*-1,3-oxazin-6-ones **3f**–**3i** in 64–71% yields (entries 5–8). For alkenyl and 2-thienyl substituted propiolates **1j** and **1k**, their corresponding products **3j** and **3k** were obtained in 73% and 92% yields, respectively (entries 9–10). The substrate scope was further expanded with applicable 1,2-benzisoxazoles **2b**–**2d** substituted at the C(5)-carbon (X = Cl, Br, Me), delivering desired compounds **3l**–**3n** in 84–94% yields (entries 11–13). For 1,2-benzisoxazoles **2e**–**2g** bearing C(6)-substituents (Y = Cl, Br, and Me), their gold-catalyzed reactions furnished compounds **3o**–**3q** in 88–92% yields (entries 14–16). With naphtho[2,3-*d*]isoxazole (**2h**) and 5,7-dibromo-1,2-benzisoxazole (**2i**), these annulations proceeded well, affording compounds **3r** and **3s** in 90% and 86% yields, respectively (entries 17–18).

Table 2 shows distinct gold-catalyzed reactions of ethyl propiolate **1a′** with 1,2-benzisoxazole **2a**. $IPrAuCl/AgNTf_2$ and

Table 2. Effect of Ester on Chemoselectivity[a]



			yield (%)[b]		
entry	catalyst	time (h)	1a′	4a	4a′-H
1	$IPrAuCl/AgNTf_2$	30	20	60	0
2	$LAuCl/AgNTf_2$	24	0	68	14
3	LAuCl/AgOTf	30	25	45	8
4	$LAuCl/AgSbF_6$	20	0	80	8
5	$AgNTf_2$	24	96	4	0

[a]**1a′** = 0.11 M, **2a** = (1.5 equiv). [b]Product yields are reported after purification from a silica gel column. L = P(*t*-Bu)$_2$(*o*-biphenyl). IPr = 1,3-bis(diisopropylphenyl)imidazole-2-ylidene). DCE = 1,2-dichloroethane.

P(*t*-Bu)$_2$(*o*-biphenyl)AuCl/$AgNTf_2$ gave ethyl *Z*-3-phenoxyacrylate **4a** in 60% and 68% yields, respectively (entries 1–2). For P(*t*-Bu)$_2$(*o*-biphenyl)AuCl, various silver salts including AgOTf and $AgSbF_6$ greatly affected the production of desired **4a** with 45% and 80% yields respectively (entries 3–4); in these instances, we also produced ethyl *Z*-3-aminoacrylate **4a′-H** in minor proportions (8–14%). Again, $AgNTf_2$ alone was catalytically inefficient, affording product **4a** in only 4% yield (entry 5).

Scheme 2 summarizes the Michael-type reactions of ethyl propiolates **1b′**–**1k′** with 1,2-benzisoxazoles **2b**–**2i**; the former have the same substituents as those of *tert*-butyl propiolates **1b**–**1k** to assess the reaction generality. In most instances, ethyl *Z*-3-aminoacrylates **4′-H** were not isolated because of their small yields (<5%), whereas entries 5, 6, and 9 afforded **4f′-H**, **4g′-H**, and **4j′-H** in significant proportions (8–15%). Various aryl-substituted propiolates (**1b′**–**1e′**, R^1 = Cl, Br, CF_3, Me) afforded ethyl phenoxyacrylates **4b**–**4e** in satisfactory yields (71–82%) using P(*t*-Bu)$_2$(*o*-biphenyl)AuCl/$AgSbF_6$ (10 mol %, entries 1–4). The molecular structure of compound **4c** was confirmed with X-ray diffraction (CCDC-1862120). Alkyl-substituted propiolates (**1f′**–**1i′**; R = isopropyl, *n*-butyl, cyclopropyl, and cyclohexyl) were also compatible with these Michael reactions, delivering ethyl 3-phenoxyacrylates **4f**–**4i** in 67–78% yields (entries 5–8). For alkenyl and 2-thienyl substituted propiolates **1j′** and **1k′**, their resulting products **3j** and **3k** were obtained in 69% and 80% yields, respectively (entries 9–10). These Michael reactions are applicable also to various 1,2-benzisoxazoles **2b**–**2g** substituted at the C(5) and C(6) carbons (X = Cl, Br, and Me, Y = H; X = H, Y = Cl, Br, and Me), delivering **4l**–**4q** in 76–88% yields (entries 11–16). Naphtho[2,3-*d*]isoxazole (**2r**) and 5,7-dibromo-1,2-benzisoxazole (**2s**) were amenable to these reactions to generate desired **4r** and **4s** in 84% and 74% yields, respectively (entries 17–18).

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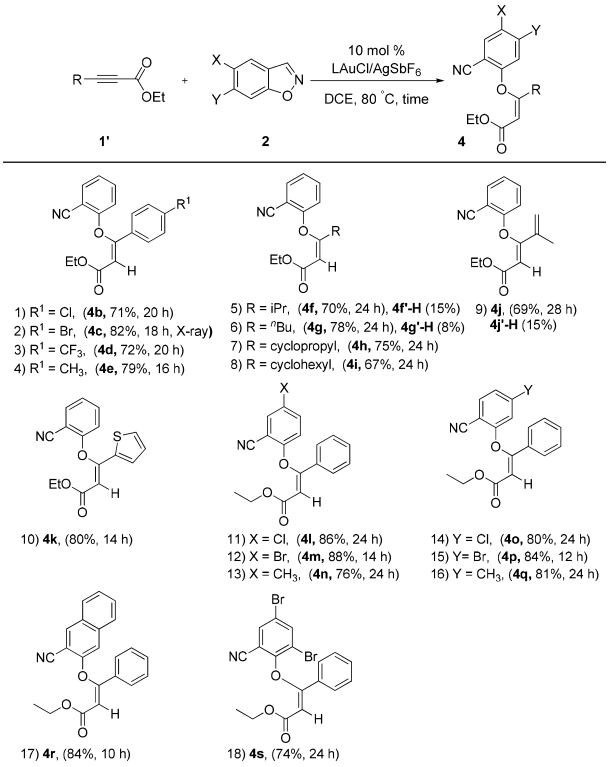
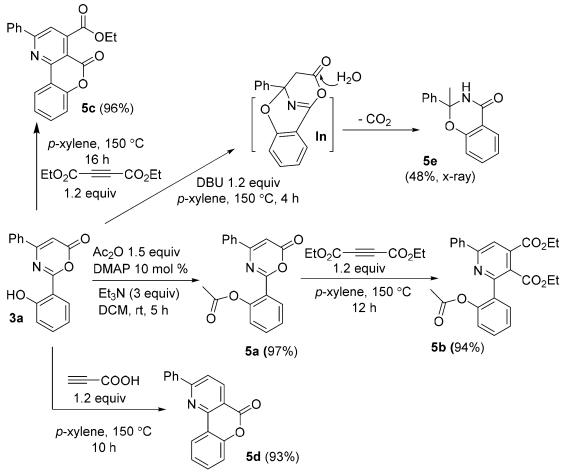
Scheme 2. Scope of Michael-Type Reactions[a,b]



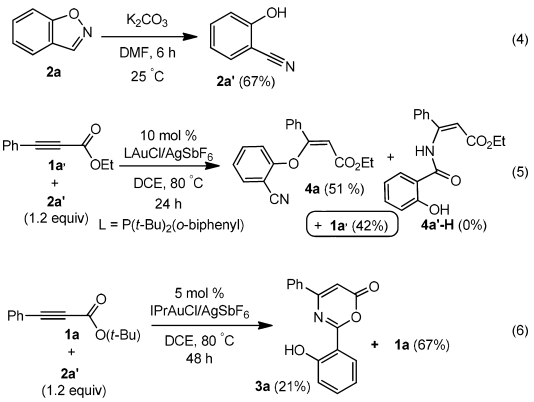
[a]**1a′** = 0.11 M, **2a** = (1.5 equiv). [b]Product yields are reported after purification using a silica gel column. L = P(*t*-Bu)$_2$(*o*-biphenyl).

A 6*H*-1,3-oxazin-6-one derivative such as **3a** was versatile to react with electron-deficient alkynes in a [4 + 2]-cycloaddition, accompanied by a loss of CO_2 (see Scheme 3).[7] Species **3a** was initially acylated to form compound **5a** which reacted with diethyl but-2-ynedioate to yield 2-phenylpyridine derivative **5b**. This method was applicable to the synthesis of related derivative **5c** with no prior acylation procedure. A direct reaction between species **3a** and propiolic acid afforded compound **5d** in 93% yield. Finally, treatment of species **3a** with DBU (1.2 equiv) induced an intramolecular Michael reaction to form intermediate **In** that was subsequently hydrolyzed with water to affect a decarboxylation reaction, to give compound **5e** in 48% yield. The molecular structure of compound **5e** was confirmed with X-ray diffraction (CCDC-1862121). With ethyl propiolate **1a′**, its resulting 3-phenoxyacylate **4a** and 3-aminoacrylate **4a′-H** might indicate that 2-hydroxy benzonitrile **2a′** was generated as a common intermediate for the two catalytic reactions.

Scheme 3. Functionalizations with 6*H*-1,3-Oxazin-6-one Derivatives



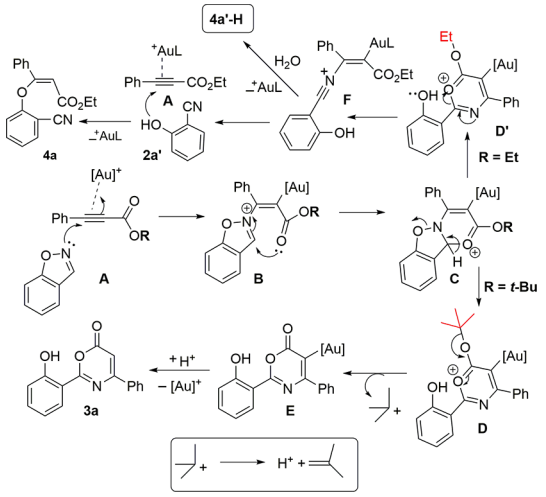
We note that only a strong base enables the transformation of 1,2-benzisoxazole **2a** into 2-hydroxybenzonitrile **2a′**;[8] this preparation was achieved with K_2CO_3 (eq 4). Nevertheless,



treatment of ethyl propiolate **1a′** with 2-hydroxbenzonitrile **2a′** gave only 3-phenoxyacylate **4a** whereas 3-aminoacrylate **4a′-H** was completely absent, which is inconsistent with our observation in Table 2 (entries 2−4). Furthermore, we observed that the reaction between *tert*-butyl propiolate **1a** and 2-hydroxybenzonitrile **2a′** with 5 mol % IPrAuCl/$AgNTf_2$ in hot DCE (80 °C, 48 h) afforded 6*H*-1,3-oxazin-6-one derivative **3a** in only 21% yield (eq 6), featuring an efficient route.

Scheme 4 depicts a mechanism involving an initial *N*-attack of 1,2-benzisoxazole at gold-π-alkyne **A** to yield intermediate **B**;

Scheme 4. Effects of Esters on Chemoselectivity



this *N*-attack arises from the potent nucleophilicity of the nitrogen atom. A subsequent cyclization of species **B** via an ester attack at the iminium moiety forms six-membered heterocyclic intermediate **C**. We envisage that the C−H proton of species **C** is acidic because dissociation of this proton enables an aromatization to form gold-containing 6-alkoxy-1,3-oxazin-1-ium species **D** or **D′**. For species **D**, a loss of the *tert*-butyl cation generates stable gold-containing 6*H*-1,3-oxazin-6-one derivative

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E, and, ultimately, the observed product **3a**. In the case of intermediate **D′** the ethyl group is chemically stable to undergo ring cleavage, further yielding a nitrium intermediate **F**. This process rationalizes a side product such as 3-aminoacrylate **4a′-H** after hydration of this nitrilium species. A further dissociation of this nitrilium is expected to form gold-π-alkyne species **A** and 2-hydroxybenzonitrile **2a′**, which react with each other to afford observed 3-phenoxyacrylate **4a**.

In summary, this work reports two distinct reactions between 1,2-benzisoxazoles and propiolate derivatives. For ethyl propiolates **1′**, their gold-catalyzed reactions afford 3-phenoxyacrylates **4** whereas *tert*-butyl propiolates **1** preferably undergo [4 + 2]-nitrile annulations, further yielding 6*H*-1,3-oxazin-6-one derivatives **3**. Resulting [4 + 2]-annulation products **3** are further elaborated into useful 2-phenylpyridine derivatives upon treatment with electron-deficient alkynes. We postulate a plausible mechanism in which the two propiolates have the same initial steps to form gold-containing 6-alkoxy1,3-oxazin-1-ium intermediates, which undergo distinct chemoselectivity as effected by the alkoxy groups.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.8b02663.

Experimental procedures, characterization data, and copies of ^{1}H and ^{13}C NMR spectra (PDF)

Accession Codes

CCDC 1862119−1862121 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

The authors declare no competing financial interest.

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■ REFERENCES

(1) See selected examples: (a) Liu, W.; Lau, F.; Liu, K.; Wood, H. B.; Zhou, G.; Chen, Y.; Li, Y.; Akiyama, T. E.; Castriota, G.; Einstein, M.; Wang, C.; McCann, M. E.; Doebber, T. W.; Wu, M.; Chang, C. H.; McNamara, L.; McKeever, B.; Mosley, R. T.; Berger, J. P.; Meinke, P. T. *J. Med. Chem.* **2011**, *54*, 8541−8554. (b) Basarab, G. S.; Brassil, P.; Doig, P.; Galullo, V.; Haimes, H. B.; Kern, G.; Kutschke, A.; McNulty, J.; Schuck, V. J. A.; Stone, G.; Gowravaram, M. *J. Med. Chem.* **2014**, *57*, 9078−9095. (c) Basarab, G. S.; Doig, P.; Galullo, V.; Kern, G.; Kimzey, A.; Kutschke, A.; Newman, J. P.; Morningstar, M.; Mueller, J.; Otterson, L.; Vishwanathan, K.; Zhou, F.; Gowravaram, M. *J. Med. Chem.* **2015**, *58*, 6264−6282. (d) Naidu, K. M.; Srinivasarao, S.; Agnieszka, N.; Ewa, A.-K.; Kumar, M. M. K.; Sekhar, K. V. G. S. *Bioorg. Med. Chem. Lett.* **2016**, *26*, 2245−2250. (e) Velaparthi, S.; Brunsteiner, M.; Uddin, R.; Wan, B.; Franzblau, S. C.; Petukhov, P. A. *J. Med. Chem.* **2008**, *51*, 1999−2002. (f) Chen, Y.; Wang, S.; Xu, X.; Liu, X.; Yu, M.; Zhao, S.; Liu, L.; Qiu, Y.; Zhang, T.; Liu, B.-F.; Zhang, G. *J. Med. Chem.* **2013**, *56*, 4671−4690. (g) Jain, M.; Kwon, C.-H. *J. Med. Chem.* **2003**, *46*, 5428−5436. (h) Villalobos, A.; Blake, J. F.; Biggers, C. K.; Butler, T. W.; Chapin, D. S.; Chen, Y. L.; Ives, J. L.; Jones, S. B.; Liston, D. R.; Nagel, A. A.; Nason, D. M.; Nielsen, J. A.; Shalaby, I. A.; White, W. F. *J. Med. Chem.* **1994**, *37*, 2721−2734. (i) Plattner, J. J.; Fung, A. K. L.; Parks, J. A.; Pariza, R. J.; Crowley, S. R.; Pernet, A. G.; Bunnell, P. R.; Dodge, P. W. *J. Med. Chem.* **1984**, *27*, 1016−1026.

(2) (a) Suto, M. J.; Stier, M. A.; Winters, R. T.; Turner, W. R.; Pinter, C. D.; Elliott, W. E.; Leopold, J. S. S. *J. Med. Chem.* **1991**, *34*, 3290−3294. (b) Chaker, A.; Najahi, E.; Chatriant, O.; Valentin, A.; Te'ne', N.; Treilhou, M.; Chabchoub, F.; Nepveu, F. *Arabian J. Chem.* **2017**, *10*, S2464−S2470.

(3) See selected reviews: (a) Li, L.; Tan, T. D.; Zhang, Y. Q.; Liu, X.; Ye, L. W. *Org. Biomol. Chem.* **2017**, *15*, 8483. (b) Huple, D. B.; Ghorpade, S.; Liu, R.-S. *Adv. Synth. Catal.* **2016**, *358*, 1348−1367.

(4) (a) Sahani, R. L.; Liu, R.-S. *Angew. Chem., Int. Ed.* **2017**, *56*, 12736−12740. (b) Jin, H.; Huang, L.; Xie, J.; Rudolph, M.; Rominger, F.; Hashmi, A. S. K. *Angew. Chem., Int. Ed.* **2016**, *55*, 794−797. (c) Jin, H.; Tian, B.; Song, X.; Xie, J.; Rudolph, M.; Rominger, F.; Hashmi, A. S. K. *Angew. Chem., Int. Ed.* **2016**, *55*, 12688−12692. (d) Mokar, B. D.; Jadhav, P. D.; Pandit, Y. B.; Liu, R.-S. *Chem. Sci.* **2018**, *9*, 4488−4492. (e) Hu, F.; Szostak, M. *Adv. Synth. Catal.* **2015**, *357*, 2583−2614.

(5) (a) Noguchi, T.; Nishii, Y.; Miura, M. *Chem. Lett.* **2017**, *46*, 1512−1514. (b) Han, Y.-P.; Li, X.-S.; Sun, Z.; Zhu, X.-Y.; Li, M.; Song, X.-R.; Liang, Y.-M. *Adv. Synth. Catal.* **2017**, *359*, 2735−2740.

(6) For gold-catalyzed annulations of propiolate derivatives, see selected examples: (a) Karad, S. N.; Chung, W.-K.; Liu, R.-S. *Chem. Commun.* **2015**, *51*, 13004. (b) Karad, S. N.; Chung, W.-K.; Liu, R.-S. *Chem. Sci.* **2015**, *6*, 5964. (c) Yeom, H.-S.; Koo, J.; Park, H.-S.; Wang, Y.; Liang, Y.; Yu, Z.-X.; Shin, S. *J. Am. Chem. Soc.* **2012**, *134*, 208−211. (d) Liu, F.; Wang, Y.; Ye, W.; Zhang, J. *Org. Chem. Front.* **2015**, *2*, 221. (e) Sahani, R. L.; Liu, R.-S. *Angew. Chem.* **2017**, *129*, 1046−1050. (f) Chen, M.; Sun, N.; Chen, H.; Liu, Y. *Chem. Commun.* **2016**, *52*, 6324.

(7) (a) Alajarin, M.; Vidal, A.; Andrada, P. S.; Tovar, F.; Ochoa, G. *Org. Lett.* **2000**, *2*, 965−968. (b) Alajarin, M.; Andrada, P. S.; Cossio, F. P.; Arrieta, A.; Lecea, B. *J. Org. Chem.* **2001**, *66*, 8470−8477. (c) Cainelli, G.; Giacomini, D.; Gazzano, M.; Galletti, P.; Quintavalla, A. *Tetrahedron Lett.* **2003**, *44*, 6269−6272. (d) Ge, Z.-Y.; Xu, Q.-M.; Fei, X.-D.; Tang, T.; Zhu, Y.-M.; Ji, S.-J. *J. Org. Chem.* **2013**, *78*, 4524−4529. (e) Chen, M.; Ren, Z.-H.; Wang, Y.-Y.; Guan, Z.-H. *Angew. Chem., Int. Ed.* **2013**, *52*, 14196−14199. (f) Clark, A. D.; Janowski, W. K.; Prager, R. H. *Tetrahedron* **1999**, *55*, 3637−3648.

(8) Stokker, G. *J. Org. Chem.* **1983**, *48*, 2613−2615.

(9) For gold-catalyzed cycloadditions of alkynes, see selected reviews: (a) Hashmi, A. S. K. *Chem. Rev.* **2007**, *107*, 3180−3211. (b) Patil, N. T.; Yamamoto, Y. *Chem. Rev.* **2008**, *108*, 3395−3442. (c) Abu Sohel, S.; Liu, R.-S. *Chem. Soc. Rev.* **2009**, *38*, 2269−2281. (d) Muratore, M. E.; Homs, A.; Obradors, C.; Echavarren, A. M. *Chem. - Asian J.* **2014**, *9*, 3066−3082.

(10) For gold-catalyzed [4 + 2]-annulations with alkynes, see selected examples: (a) Pagar, V. V.; Jadhav, A. M.; Liu, R.-S. *J. Am. Chem. Soc.* **2011**, *133*, 20728−20731. (b) Teng, T.-S.; Liu, R.-S. *J. Am. Chem. Soc.* **2010**, *132*, 9298−9300. (c) Dateer, R. B.; Shaibu, B. S.; Liu, R.-S. *Angew. Chem., Int. Ed.* **2012**, *51*, 113−117. (d) Giri, S. S.; Liu, R.-S. *Chem. Sci.* **2018**, *9*, 2991−2995. (e) Shu, C.; Wang, Y.-H.; Zhou, B.; Li, X.-L.; Ping, Y.-F.; Lu, X.; Ye, L.-W. *J. Am. Chem. Soc.* **2015**, *137*, 9567−9570. (f) Zhang, G.; Huang, X.; Li, G.; Zhang, L. *J. Am. Chem. Soc.* **2008**, *130*, 1814−1815. (g) Asao, N.; Nogami, T.; Lee, S.; Yamamoto, Y. *J. Am. Chem. Soc.* **2003**, *125*, 10921−10925. (h) Nieto-Oberhuber, C.; López, S.; Echavarren, A. M. *J. Am. Chem. Soc.* **2005**, *127*, 6178−6179.

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