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## Selectivity-switchable construction of benzo-fused polycyclic compounds through a gold-catalyzed reaction of enyne-lactone

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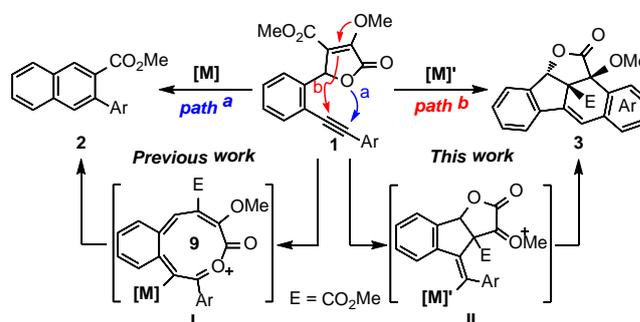
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A gold-catalyzed selectivity-switchable reaction of enyne-lactone is reported. Different products, including naphthalenes and benzo-fused polycyclic compounds, can be selectively obtained from the same starting material. The choice of gold complex is the key for the chemoselectivity of this system.

Chemoselectivity remains a long-standing challenge in the development of organic synthetic methodology and total synthesis, and constant efforts have been made by researchers to address this issue.<sup>1</sup> Currently, different strategies have been established to realize high chemoselectivity, for instance, by modulating the substrate structure<sup>2</sup> or changing the reaction conditions,<sup>3</sup> including variation of catalysts,<sup>4,5</sup> ligands,<sup>6,7</sup> solvents<sup>7</sup> and so on. Controlling the reaction chemoselectivity could result in selective formation of two or more different products from the same starting material. As part of our continuous efforts to develop highly efficient tandem reactions based on alkyne chemistry,<sup>8</sup> we are interested in how to achieve effective control of chemoselectivity as well.

Recently, we reported a gold-catalyzed ring-expansion of enyne-lactone **1** to selectively synthesize naphthalene derivatives **2** (Scheme 1, path a).<sup>9</sup> During the reaction condition screening, polycyclic product **3** was also detected as a minor side product, which aroused our great interest due to its unique structure. Obviously, the generation of product **3** should come from a tandem of 5-*exo-dig* cyclization and intramolecular Friedel-Crafts reaction (Scheme 1, path b).<sup>10-11</sup> Due to the greater steric hindrance caused by the ester group of path b, how to selectively produce the desired product **3**



**Scheme 1** Gold-catalyzed reaction of enyne-lactone

would be a challenge. In this work, we would like to report the chemoselective construction of polycyclic compounds **3** from enyne-lactone **1** by tuning the reaction conditions.

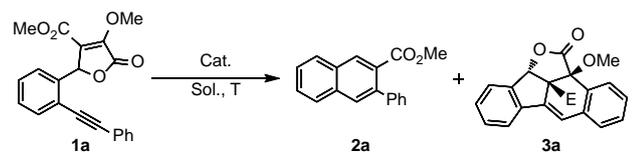
In our previous work,<sup>9</sup> under the optimized reaction conditions (Table 1, entry 1), the naphthyl ester product **2a** could be obtained in 74% yield with Ph<sub>3</sub>PAuCl/AgSbF<sub>6</sub> as catalyst, accompanied by trace amount of product **3a**. When AgBF<sub>4</sub> was applied as the halogen scavenger instead of AgSbF<sub>6</sub>, the desired product **3a** could be detected in 6% yield (Table 1, entry 2). In addition to Ph<sub>3</sub>PAu<sup>+</sup>, different nitrogen heterocyclic carbene (NHC) ligated gold complexes (NHC-AuCl) were utilized as catalysts as well. The results showed that both IMeAu<sup>+</sup> and SIMeAu<sup>+</sup> complexes were ineffective for this catalytic reaction (Table 1, entries 3 and 4). To our delight, the yield of **3a** could be improved to 42% in the presence of IPrAuCl/AgBF<sub>4</sub>, accompanied by **2a** in 58% yield (Table 1, entry 5). Changing the gold complex IPrAuCl to SIPrAuCl, the yield of **3a** could be further improved to 50% (Table 1, entry 6). The variations of silver salts could not further increase the reaction yield (Table 1, entries 7-9). Gratifyingly, the yield could be enhanced to 70% when the reaction temperature was raised to 100 °C (Table 1, entry 10). In this case, the naphthalene **2a** was suppressed to only 13% yield. Lower temperature decreased both the reaction conversion and the selectivity (Table 1, entry 11). AgBF<sub>4</sub> alone gave the products **2a**

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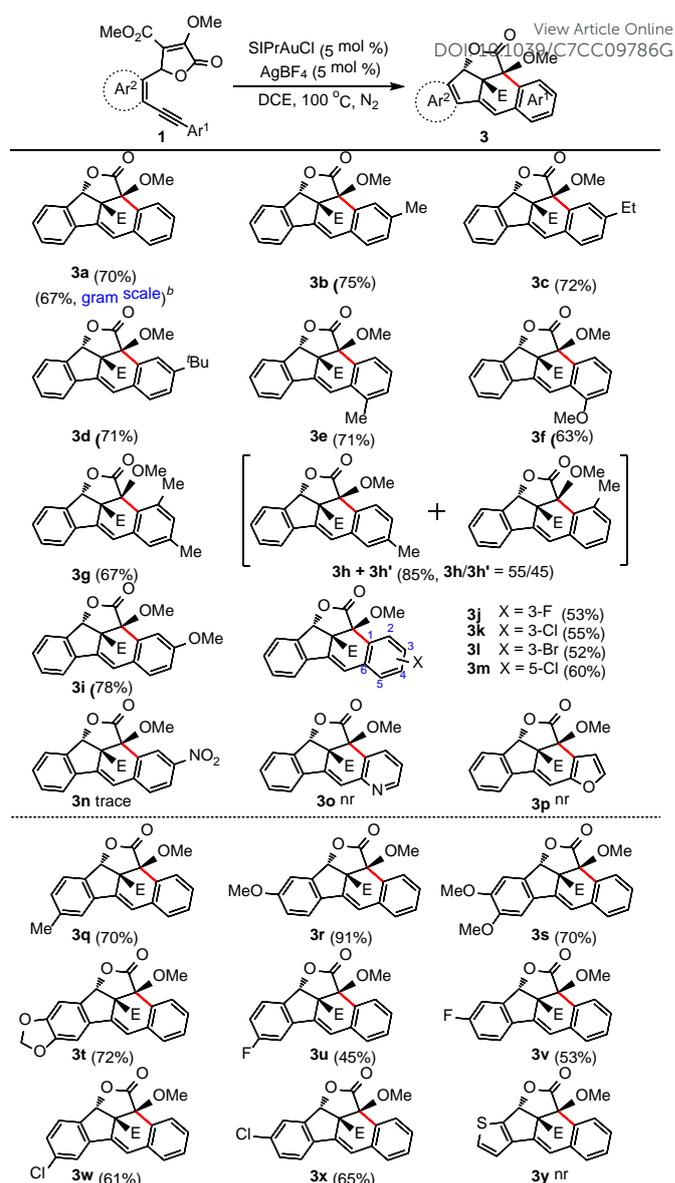
**Table 1** Optimization of the reaction conditions<sup>a</sup>


Entry	Cat.	Add.	T (°C)	Yield <sup>b</sup> (%)	
				2a	3a
1	Ph <sub>3</sub> PAuCl	AgSbF <sub>6</sub>	80	74	Trace
2	Ph <sub>3</sub> PAuCl	AgBF <sub>4</sub>	80	40	6
3	IMesAuCl	AgBF <sub>4</sub>	80	Trace	Trace
4	SIMesAuCl	AgBF <sub>4</sub>	80	Trace	Trace
5	IPrAuCl	AgBF <sub>4</sub>	80	58	42
6	SIPrAuCl	AgBF <sub>4</sub>	80	22	50
7	SIPrAuCl	AgSbF <sub>6</sub>	80	26	39
8	SIPrAuCl	AgNTf <sub>2</sub>	80	Trace	Trace
9	SIPrAuCl	AgOTf	80	41	31
10	<b>SIPrAuCl</b>	<b>AgBF<sub>4</sub></b>	<b>100</b>	<b>13</b>	<b>70<sup>c</sup></b>
11	SIPrAuCl	AgBF <sub>4</sub>	60	41	18
12		AgBF <sub>4</sub>	100	7	12
13			100	NR	NR

<sup>a</sup> Unless otherwise noted, the reaction was performed with **1a** (0.2 mmol) in DCE (2 mL), 12 h, under N<sub>2</sub>, E = CO<sub>2</sub>Me. <sup>b</sup> The yield was determined by <sup>1</sup>H NMR using 1-methyl-4-nitrobenzene as an internal standard. <sup>c</sup> Isolated yield.

and **3a** in only 7% and 12% yield, respectively (Table 1, entry 12). Furthermore, the reaction did not occur at all without the catalyst and additive (Table 1, entry 13). Several other Lewis acids were also tested, showing unsatisfactory performances (see the Electronic supplementary information for more details).

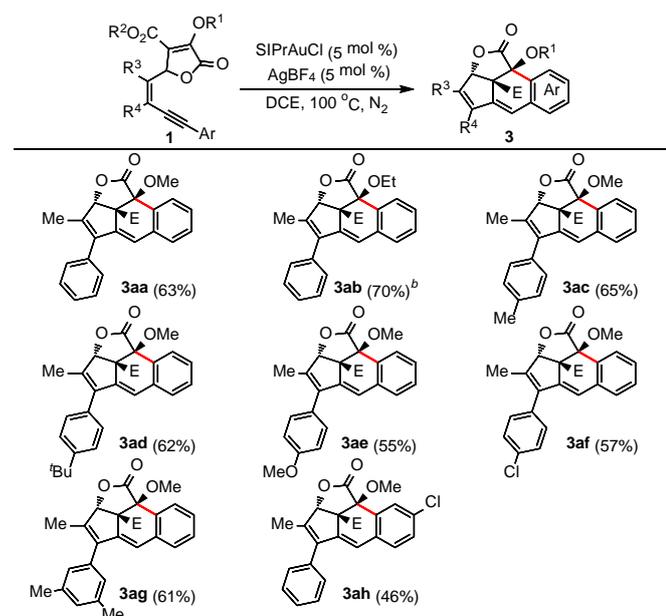
With the optimized reaction conditions (Table 1, entry 10) in hand, the substrate scope was then examined. As shown in Scheme 2, this catalytic system could be successfully extended to a variety of aryl enyne-lactones **1**. Various derivatives of **1** tethered with aryl groups on the distal alkyne could serve as effective substrates, producing the desired products **3b-m** in 52–78% yields. The reaction results revealed that the substrates with an electron-rich aryl group (**3b-i**) functioned better than those with electron-poor aryl group (**3j-m**). Furthermore, the reaction did not take place when a nitro group was introduced to the Ar<sup>1</sup> group (**3n**). These results were well consistent with the proposed Friedel-Crafts reaction mechanism. The structure of products **3a** and **3l** were verified by X-ray crystallography analysis (see the ESI<sup>†</sup>). It is noted that no reaction occurred with enyne-lactone containing a 2-pyridyl terminal group under the standard conditions (see **3o**), which could probably be attributed to the strong coordination of pyridine to the cationic Au center, thus inhibiting the catalyst turnover. The enyne-lactones **1** tethered with furan group on the distal alkyne was ineffective for this transformation either (see **3p**). For the enyne-lactone with a meta-substituted Ar<sup>1</sup> group, a mixture of isomers could be obtained (see **3h** and **3h'**). Furthermore, the substrates bearing different fused arylene rings (Ar<sup>2</sup>) were also tested. The substrates with electron-donating arylene (**3q-t**, 70–91%) proceeded much



**Scheme 2** Reaction scope for the formation of **3**. <sup>a</sup> Reaction conditions: **1** (0.2 mmol), SIPrAuCl (5 mol%) and AgBF<sub>4</sub> (5 mol%) in DCE (2 mL) at 100 °C under N<sub>2</sub> for 12 h, isolated yield, E = CO<sub>2</sub>Me. <sup>b</sup> **1a** (3.03 mmol, 1.05 g), SIPrAuCl (7.5 mol %) and AgBF<sub>4</sub> (7.5 mol %).

better than those with electron-withdrawing arylene (**3u-x**, 45–65%). The thienyl-tethered enyne-lactone, which was effective in our previous Ph<sub>3</sub>PAu<sup>+</sup>-catalyzed system,<sup>9</sup> was not compatible with this catalytic system (**3y**), probably due to the stronger coordination of sulphur atom in thienyl moiety to the softer gold center of the SIPrAu<sup>+</sup> catalyst, which then entirely retarded the reaction. What's more, the reaction proceeded smoothly on a gram scale, leading to the corresponding product **3a** in good yield (67%).

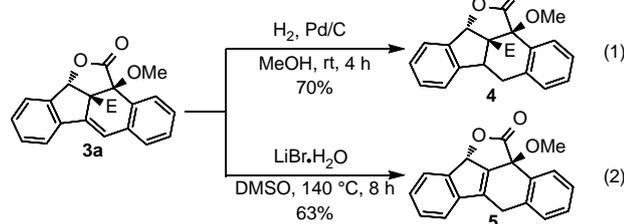
In order to further explore the substrate scope, the enyne-lactones with a simple C=C double bond rather than the fused arylene ring were also subjected to the reaction under the



**Scheme 3** Reaction scope for the formation of **3**. <sup>a</sup> The reaction was conducted in DCE at 100 °C for 12 h using 5 mol % SIPrAuCl and 5 mol % AgBF<sub>4</sub> under N<sub>2</sub>, enyne-lactones **1** (0.2 mmol), DCE (2 mL), isolated yield, E = CO<sub>2</sub>Me. <sup>b</sup> E = CO<sub>2</sub>Et.

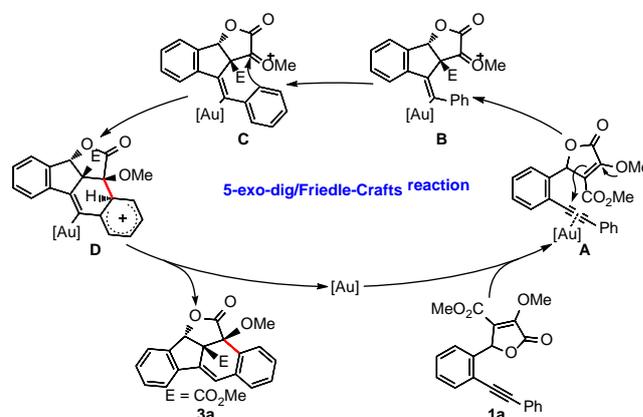
standard conditions. As summarized in Scheme 3, the catalytic process could be successfully applied to different kinds of substrates as well, obtaining the desired products **3aa–ah** in 46–70% yields. The structure and stereochemistry of the product was also confirmed by the X-ray diffraction analysis of compound **3aa** (see the ESI<sup>†</sup> for detail).

With the products **3** in hand, two further chemical transformations were carried out (Scheme 4). Taking **3a** as an example, the carbon-carbon double bond could be selectively reduced to carbon-carbon single bond under Pd/C-H<sub>2</sub> condition at room temperature, furnishing the desired product **4** in 70% yield (Scheme 4, eq. 1). Furthermore, the ester group of **3a** could be removed with LiBr·H<sub>2</sub>O in DMSO at 140 °C, and the desired product **5** was generated in 63% yield (Scheme 4, eq. 2).



**Scheme 4** Further transformations of **3a**. Reaction conditions: (1) **3a** (0.2 mmol), Pd/C (watted with ca. 55 % water) (20 MW %), H<sub>2</sub> (1 atm), MeOH (2 mL); (2) **3a** (0.2 mmol), LiBr·H<sub>2</sub>O (0.4 mmol), DMSO (2 mL). Note: E = CO<sub>2</sub>Me.

A tentative reaction mechanism for the formation of **3** under the gold-catalyzed conditions was proposed in Scheme 5. Taking substrate **1a** as an example, the triple bond of enyne-lactone was initially activated by gold salt to give the intermediate **A**, followed by 5-*exo-dig* cyclization and intramolecular Friedel-Crafts reaction to give the desired product **3a**.



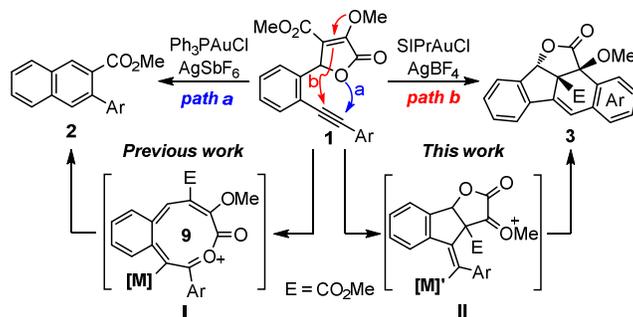
**Scheme 5** The proposed reaction mechanism.

In conclusion, we have reported an efficient gold-catalyzed reaction of enyne-lactone to selectively afford the benzo-fused polycyclic compounds. This reaction was proposed through a consecutive 5-*exo-dig* cyclization and Friedel-Crafts reaction. The choice of gold complex is the key for the selectivity of this reaction. With the combination of Ph<sub>3</sub>PAuCl/AgSbF<sub>6</sub> as the catalyst, the reaction preferred the O-attack reaction pathway (Scheme 1, path a). However, when it came to the combination of SIPrAuCl/AgBF<sub>4</sub>, the reaction selectivity was switched to C=C double bond-attack pathway (Scheme 1, path b). The chemoselectivity might be derived from the differences of electron population in the alkyne activated by gold catalysts. The SIPr ligated gold center might have more electron density owing to its strong  $\sigma$ -donor and weak  $\pi$ -acceptor properties, making the alkyne less electron-deficient, which might favour the soft vinyl ether addition. While the Ph<sub>3</sub>PAuCl could make the alkyne more electron-deficient and favourable for the hard oxygen attack. In addition, the steric hindrance differences between SIPrAuCl and Ph<sub>3</sub>PAuCl might be another contributor to affect the regioselectivity. The advantages of broad substrate scope and tunable selectivity make this system very appealing for the synthesis of different benzo-fused polycyclic compounds.

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