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$Yb(OTf)_3$- or Au^I-Catalyzed Domino Intramolecular Hydroamination and Ring-Opening of Sulfonamide-Substituted 1,1-Vinylidenecyclopropanediesters

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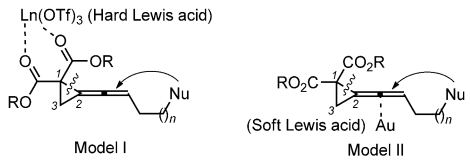
Vinylidenecyclopropanes (VDCPs),[1] which contain an allene moiety and a connected cyclopropane ring, are one of the most remarkable organic compounds in the chemistry of highly strained small rings. It is known that these highly strained cyclopropanes are thermally stable and yet reactive substances, which can easily undergo numerous intramolecular rearrangements or intermolecular reactions upon heating and photoirradiation or catalyzed by a variety of Lewis or Brønsted acids.[2–4] Our group has extensively explored the chemistry of VDCPs for several years and we have reported Lewis acid catalyzed intramolecular rearrangements to afford naphthalene, fluorine, and indene derivatives according to the substituents on the allene and cyclopropane moiety.[5] These reactions are initiated by the activation of the allene moiety through coordination with various Lewis acids. Up to now, it is known that the release of highly strained energy, associated with the ring-opening of a cyclopropane moiety in an organic molecule, can trigger multiple transformations and the selectivity depends on the electronic properties and substitution pattern of the substituents on the cyclopropane ring as well as the adjacent functional groups.[6] A typical example is the geminal installation of two electron-withdrawing groups (EWGs) at the cyclopropane ring that can further activate the cyclopropane's C–C bond between this installed carbon and the other substituted carbon through polarization, leading to a variety of highly regioselective ring-opening reactions.[7,8]

Lewis acids are an important class of catalysts in organic chemistry and have found numerous synthetic applications, because of their high catalytic activity.[9] In 1991, Kobayashi et al. discovered that $Yb(OTf)_3$ could efficiently catalyze the Mukaiyama aldol reaction in THF/H_2O.[10] Since then, the use of lanthanide triflates $Ln(OTf)_3$ in organic synthesis has been widely explored owing to their efficacy as Lewis acid catalysts and to their low environmental impact.[11] Consequently, $Ln(OTf)_3$ catalysts, in which the strongly electron-withdrawing property of the trifluoromethanesulfonate anion enhances their Lewis acidic character,[12] mainly act as hard Lewis acids through coordination with polar functional groups containing nitrogen and oxygen atoms, such as carbonyl groups and imines, but are relatively inactive towards H_2O.[13] On the other hand, homogeneous catalysis mediated by gold(I) complexes has received considerable attention in recent years,[14] and the core of these reactions relies on the interaction between gold catalysts and π-bonds of alkenes, alkynes, and allenes. The most common reaction pattern is the addition of nucleophiles to unsaturated C–C bonds, initially activated by the gold(I) complex acting as a powerful soft catalyst, to efficiently construct new carbon–carbon or carbon–heteroatom bonds.[15–19]

Inspired by the fact that hard and soft Lewis acids can selectively activate different functional groups, we designed and synthesized a novel type of sulfonamide-substituted 1,1-vinylidenecyclopropanediester (**2**) from phthalimide-substituted VDCP-diesters **1** (see Supporting Information for details). These sulfonamide-substituted VDCP-diesters contain two geminally installed EWGs at the cyclopropane ring[20] and tether an additional nucleophilic sulfonamide group, anticipating that the intramolecular nucleophilic attack can trigger a domino transformation—an intramolecular hydroamination along with a highly regioselective C1–C2 bond cleavage (proximal bond cleavage) of the cyclopropane ring in the presence of either a hard ($Ln(OTf)_3$; Scheme 1, Model I) or a soft Lewis acid (Au^I complex; Scheme 1, Model II). We found that the domino transformation of sulfonamide-substituted VDCP-diesters took place to produce two kinds of five-membered N,O-heterocycles in moderate to excellent yields in the presence of the $Yb(OTf)_3$ and a Au^I complex.



Scheme 1. A reaction proposal.

Initial examinations were carried out by using sulfonamide-substituted VDCP-diester **2a** as the substrate in the

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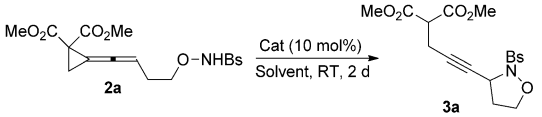
Supporting information for this article (^{13}C and ^1H NMR spectroscopic and analytic data for **1**, **2**, **3**, and **4** and X-ray crystal data of **4c**) is available on the WWW under http://dx.doi.org/10.1002/chem.201102159.

presence of two kinds of Lewis acids and the results are summarized in Table 1 and 2. We found that the use of 10 mol% of hard Lewis acids, such as $Yb(OTf)_3$, $Bi(OTf)_3$, $BF_3{\cdot}OEt_2$, $In(OTf)_3$ and $Sc(OTf)_3$, produced the corresponding five-membered N,O-heterocyclic compound **3a**, containing an alkyne moiety, in 70–92% yield in toluene at room temperature after 2 d through a domino intramolecular hydroamination and ring-opening of cyclopropane (Table 1, entries 1–5). Here, $Yb(OTf)_3$ gave the best result. $Ti(OiPr)_4$ did not catalyze this transformation and the addition of a hard Lewis acid was essential for this reaction (Table 1, entries 6 and 7). An examination of solvents with $Yb(OTf)_3$ as the catalyst revealed that toluene was the solvent of choice (Table 1, entries 1, 8 and 9). Moreover, we investigated the reaction outcome in the presence of a Brønsted acid and found that a complex product mixture was obtained when using trifluoromethanesulfonic acid (HOTf, 10 mol%; Table 1, entry 10).

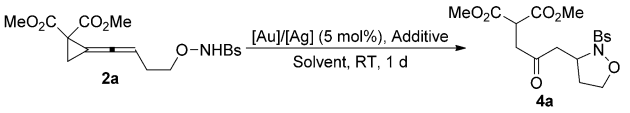
Table 1. Optimization of the reaction conditions with sulfonamide-substituted VDCP-diester **2a** in the presence of hard Lewis acids, $Ti(iPr)_4$ and HOTf.[a]



Entry	Cat [10 mol%]	Solvent	Yield of **3a** [%][b]
1	$Yb(OTf)_3$	toluene	92
2	$Bi(OTf)_3$	toluene	70
3	$BF_3{\cdot}OEt_2$	toluene	83
4	$In(OTf)_3$	toluene	79
5	$Sc(OTf)_3$	toluene	86
6	$Ti(OiPr)_4$	toluene	n.r.
7	–	toluene	n.r.
8	$Yb(OTf)_3$	THF	68
9	$Yb(OTf)_3$	CH_2Cl_2	79
10	HOTf	toluene	complex

[a] All reactions were carried out with **2a** (0.1 mmol) and the catalyst (10 mol%) in the solvent (1.0 mL) at room temperature for 2 days and monitored by TLC, if not otherwise specified. [b] Isolated yield.

Table 2. Optimization of the reaction conditions with sulfonamide-substituted VDCP-diester **2a** in the presence of Au^I complexes.[a]



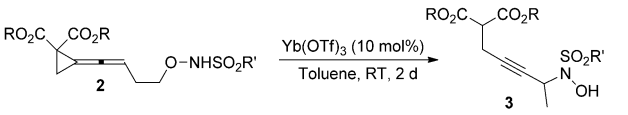
Entry	[Au]	[Ag]	Solvent	Additive (X equiv)	Yield [%][b]
1[c]	$[AuCl(PPh_3)]$	AgOTf	toluene	–	56
2	–	AgOTf	toluene	–	81[c,d]
3	$[AuCl(PPh_3)]$	AgOTf	toluene	H_2O (1.0)	76
4	$[AuCl(PPh_3)]$	AgOTf	toluene	H_2O (2.0)	69
5	$[AuCl(PPh_3)]$	$AgSbF_6$	toluene	H_2O (1.0)	62
6	$[\{Au(PPh_3)\}_3O]BF_4$	–	toluene	H_2O (1.0)	69
7	[AuClIPr]	AgOTf	toluene	H_2O (1.0)	61
8	$[AuCl\{P(CH_3)_3\}]$	AgOTf	toluene	H_2O (1.0)	68
9	$[AuCl(PPh_3)]$	AgOTf	CH_2Cl_2	H_2O (1.0)	58
10	$[AuCl(PPh_3)]$	AgOTf	CH_3NO_2	H_2O (1.0)	49
11	$[AuCl(PPh_3)]$	AgOTf	toluene	4 Å MS[e]	94[d]

[a] All reactions were carried out with **2a** (0.1 mmol), [Au] (5 mol%), [Ag] (5 mol%) and the additive in the solvent (1.0 mL) at room temperature and monitored by TLC, if not otherwise specified. [b] Isolated yield. [c] The reaction was carried out for 2 days. [d] The product was **3a**. [e] 4 Å MS (50 mg) was used.

Furthermore, using $[AuCl(PPh_3)]$ (5 mol%) and Ag(OTf) (5 mol%) as the catalyst afforded another five-membered N,O-heterocyclic compound **4a**, containing a carbonyl moiety, in 56% yield in toluene at room temperature after 2 d (Table 2, entry 1). The use of only AgOTf as the catalyst produced **3a** in 81% yield, indicating that the Au^I complex was essential for the formation of compound **4a** (Table 2, entry 2). On the basis of the structure of **4a**, we believed that ambient H_2O in the reaction system was involved in this Au^I-catalyzed reaction. The addition of 1.0 equivalent of H_2O not only accelerated the reaction, but also raised the yield of **4a** up to 76% (Table 2, entry 3). However, adding 2.0 equivalents of H_2O decreased the yield of **4a**, presumably owing to the decomposition of the active Au^I species by the excess of water (Table 2, entry 4). Changing the silver salt to $AgSbF_6$ and using $[\{Au(PPh_3)\}_3O]BF_4$, [AuClIPr], and $[AuCl\{P(CH_3)_3\}]$ as the Au catalysts did not improve the reaction outcome (Table 2, entries 5–8). A screening of solvent effects revealed that toluene was again the best solvent for this Au^I-complex-catalyzed reaction (Table 2, entries 9 and 10). When adding 4 Å MS (50 mg) to remove any excess water, the reaction afforded **3a** in 94% yield, rather than **4a**, under such anhydrous reaction conditions (Table 2, entry 11).

With these identified optimal reaction conditions in hand, the generality of the reactions was further investigated with respect to various sulfonamide-substituted VDCP-diesters **2**, and the results of these experiments are summarized in Tables 3 and 4. For substrates **2b**–**2g** (R = Me) the reactions

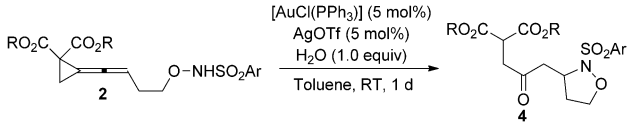
Table 3. $Yb(OTf)_3$-catalyzed domino transformation of sulfonamide-substituted VDCP-diester **2**.[a]



Entry	**2**	R	R′	Yield of **3** [%][b]
1	**2b**	Me	$4\text{-}MeC_6H_4$	**3b**, 95
2	**2c**	Me	$2,4,6\text{-}(iPr)_3C_6H_2$	**3c**, 88
3	**2d**	Me	C_6H_5	**3d**, 95
4	**2e**	Me	$2\text{-}NO_2C_6H_4$	**3e**, 85
5	**2f**	Me	$4\text{-}NO_2C_6H_4$	**3f**, 88
6	**2g**	Me	$2,4\text{-}(NO_2)_2C_6H_3$	**3g**, 80
7	**2h**	Bn	$4\text{-}BrC_6H_4$	**3h**, 89
8	**2i**	Bn	$4\text{-}MeC_6H_4$	**3i**, 90
9	**2j**	Bn	C_6H_5	**3j**, 87
10	**2k**	Et	$4\text{-}MeC_6H_4$	**3k**, 92
11	**2l**	Et	$4\text{-}BrC_6H_4$	**3l**, 87
12	**2m**	Et	C_6H_5	**3m**, 90
13	**2n**	Et	$2\text{-}NO_2C_6H_4$	**3n**, 82
14	**2o**	Me	Me	**3o**, 73

[a] All reactions were carried out with **2** (0.1 mmol) and $Yb(OTf)_3$ (10 mol%) in toluene (1.0 mL) at room temperature for 2 days and monitored by TLC, if not otherwise specified. [b] Isolated yield.

Table 4. Au^I-catalyzed domino transformation of sulfonamide-substituted VDCP-diester **2**.[a]

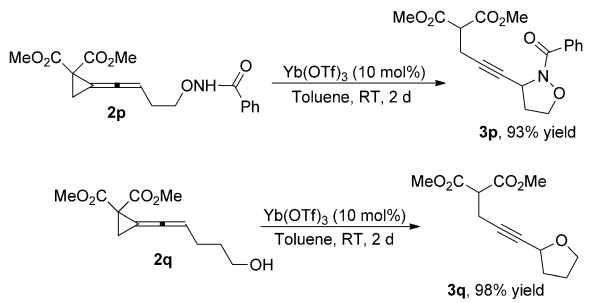


Entry	2	R	R′	Yield of 4 [%][b]
1	**2b**	Me	4-MeC_6H_4	**4b**, 69
2	**2c**	Me	2,4,6-(iPr)$_3C_6H_2$	**4c**, 72
3	**2d**	Me	C_6H_5	**4d**, 74
4	**2e**	Me	2-$NO_2C_6H_4$	**4e**, 64
5	**2f**	Me	4-$NO_2C_6H_4$	**4f**, 65
6	**2g**	Me	2,4-$(NO_2)_2C_6H_3$	**4g**, 58
7	**2h**	Bn	4-BrC_6H_4	**4h**, 71
8	**2i**	Bn	4-MeC_6H_4	**4i**, 66
9	**2j**	Bn	C_6H_5	**4j**, 63
10	**2k**	Et	4-MeC_6H_4	**4k**, 65
11	**2l**	Et	4-BrC_6H_4	**4l**, 69
12	**2m**	Et	C_6H_5	**4m**, 70
13	**2n**	Et	2-$NO_2C_6H_4$	**4n**, 55

[a] All reactions were carried out using **2** (0.1 mmol), Ph_3PAuCl (5 mol%) and AgOTf (5 mol%) in toluene (1.0 mL) with the addition of H_2O (1.0 equiv) at room temperature for 1 day and monitored by TLC, if not otherwise specified. [b] Isolated yield.

proceeded smoothly to furnish the desired products **3b–3g** in good to excellent yields, regardless of whether they have electron-rich, electron-poor, or electron-neutral aromatic rings at their sulfonamide moietiy (Table 3, entries 1–6). Changing the diester substitution to Bn and Et produced the corresponding products **3h–3n** in 82–92% yield (Table 3, entries 7–13). Substrate **2o**, with an aliphatic sulfonamide moiety (R′ = Me), afforded the desired product **3o** in 73% yield (Table 3, entry 14).

Amide-substituted VDCP-diester **2p** and VDCP-diester **2q**, bearing an hydroxyl group, were also suitable for this $Yb(OTf)_3$-catalyzed domino transformation, giving the five-membered heterocycles **3p** and **3q** in 93 and 98% yield, respectively (Scheme 2).



Scheme 2. $Yb(OTf)_3$-catalyzed domino transformations of VDCP-diesters **2p** and **2q**.

Furthermore, these sulfonamide-substituted VDCP-diesters **2** were applied successfully in the Au^I-catalyzed domino reaction under the optimal reaction conditions to give the desired heterocyclic products **4** in moderate to good yields (Table 4). In the case of substrates **2b–2g** (R = Me), the reactions proceeded smoothly to afford products **4b–4g** in moderate yields with various electron-rich, electron-deficient, and electron-neutral aromatic rings at their sulfonamide moiety (Table 4, entries 1–6). When using substrates **2h–2n** in the Au^I-catalyzed domino reaction, similar results were obtained (Table 4, entries 7–13). All of the above results demonstrate a wide substrate scope in these domino transformations.

The structure of the heterocyclic product **4c** has been unambiguously determined by X-ray diffraction. The ORTEP drawing is shown in Figure 1 and its CIF data are available from the Cambridge Crystallographic Data Centre.[21]

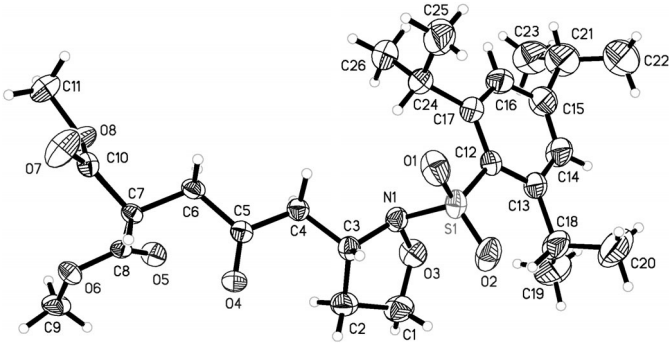
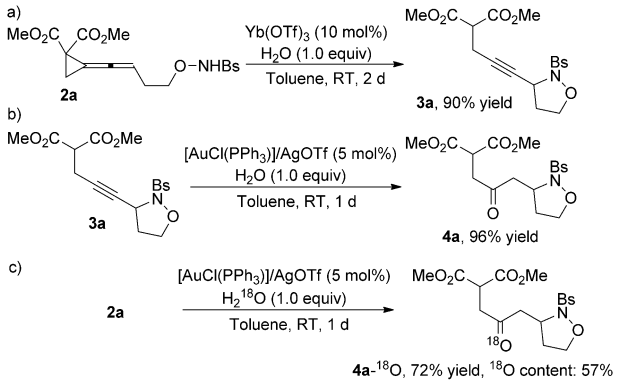


Figure 1. ORTEP drawing of **4c**.

To investigate the mechanism of these domino reactions catalyzed by different Lewis acids, we conducted three control experiments under the standard conditions. As shown in Scheme 3, with addition of 1.0 equivalent of H_2O to the Yb-

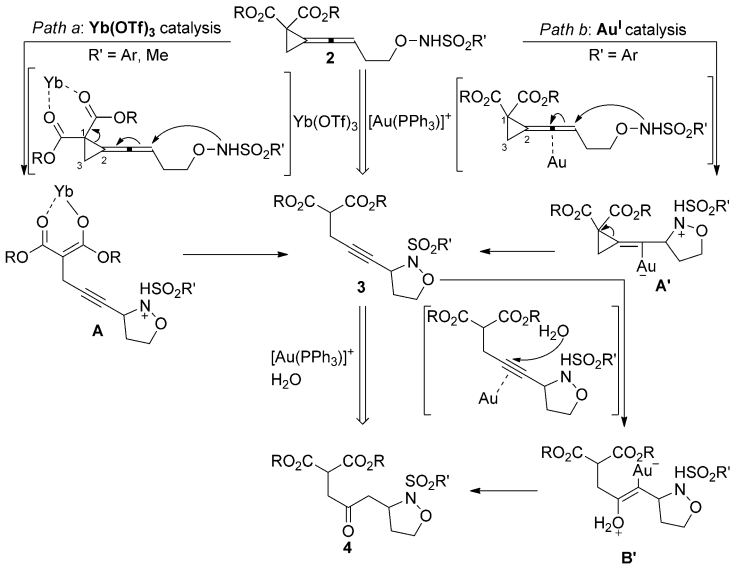


Scheme 3. Control experiments.

$(OTf)_3$-catalyzed domino reaction of **2a**, **3a** was obtained in 90% yield as the sole product without the formation of **4a** (Scheme 3a). Under the Au^I-catalyzed standard reaction conditions, **3a** was transformed to heterocyclic product **4a** in 96% yield (Scheme 3b). Therefore, we can conclude that the formation of products is dependent on the Lewis acid

employed and that the heterocyclic product **3** can be transformed to heterocyclic product **4** through Au^I-catalyzed hydration of the alkyne moiety of compound **3**. On the basis of ^1H NMR spectroscopic tracing experiments under the Au^I-catalyzed standard reaction conditions, we confirmed that, as the reaction is proceeding, **2l** is initially transformed to the corresponding alkynyl product **3l** within 2 h, indicating that the reaction rate for the formation of **3l** is very fast (see Supporting Information for details). After 24 h, the alkyne-moiety-containing compound **3l** was completely transformed to the corresponding carbonyl-group-containing product **4l** through Au^I-catalyzed hydration of the alkyne moiety of compound **3l**. When $H_2{}^{18}O$ was added to the reaction system, product **4a**-^{18}O with 57% ^{18}O content was formed in 72% yield, further indicating that external H_2O is involved in this reaction (Scheme 3c).

On the basis of the above experiments, plausible reaction mechanisms for the formation of **3** and **4** catalyzed by $Yb(OTf)_3$ and the Au^I complex are proposed in Scheme 4 to rationalize the reaction outcomes. $Yb(OTf)_3$ acts as the hard Lewis acid to initiate the domino reaction through coordination with the two carbonyl oxygen atoms of **2** (Scheme 4, path a) and the Au^I complex acts the soft Lewis acid to initiate the domino reaction through coordination with the allene moiety (Scheme 4, path b). In path a, the common intramolecular hydroamination along with the ring-opening of cyclopropane[8,22] takes place to give intermediate **A**, which gives the corresponding heterocyclic product **3** through proton transfer. In path b, the common intramolecular hydroamination takes place to give intermediate **A′**, which affords the corresponding heterocyclic product **3** through a ring-opening of cyclopropane, elimination of the Au^I complex, and a proton transfer sequence. Herein, the C–C triple bond can be further activated by the regenerated Au^I to exclusively afford the final carbonyl-group-containing product **4** through alkyne hydration via the olefinic gold species **B'**, presumably owing to a steric effect (Scheme 4, path b).[23]



Scheme 4. A plausible reaction mechanism.

In conclusion, we have established two efficient Lewis acid catalyzed reaction systems to construct five-membered N,O-heterocyclic products containing an alkyne moiety or a carbonyl group from sulfonamide-substituted VDCP-diesters under mild conditions through a domino intramolecular hydroamination and ring-opening of cyclopropane. The employed Lewis acids, $Yb(OTf)_3$ and a Au^I complex, played a significant role to effect the reaction outcomes. Further efforts regarding the scope and mechanistic details are in progress.

Experimental Section

General remarks: ^1H and ^{13}C NMR spectra were recorded at 400 (or 300) and 100 (or 75) MHz, respectively. Mass and HRMS spectra were recorded by ESI (or MALDI) method. Organic solvents used were dried by standard methods, when necessary. Satisfactory CHN microanalyses were obtained with an analyzer. Commercially obtained reagents were used without further purification. All reactions were monitored by TLC with silica gel coated plates. Flash column chromatography was carried out using silica gel at increased pressure.

General procedure for the preparation of sulfonamide-substituted VDCP-diesters 2: Hydrazine hydrate (85% , 0.2 mL) was added to a solution of phthalimide-substituted VDCP-diester **1** (2.0 mmol) in THF (20 mL). The reaction mixture was stirred at room temperature for 30 min and during this time white solids appeared. The mixture was filtered to remove the precipitates and the filter cake was washed with Et_2O. The filtrate was concentrated to afford the crude alkoxylamine-substituted VDCP-diester, which was applied to the next transformation without further purification. Et_3N (2.5 mmol) and subsequently the corresponding sulfonyl chloride (2.0 mmol) were added to a chilled solution of alkoxylamine-substituted VDCP-diester (2.0 mmol) in dry CH_2Cl_2 (20 mL). The reaction mixture was then stirred at room temperature. After the substrate was consumed, the solvent was removed under reduced pressure and the residue was purified by silica gel flash column chromatography to give the desired sulfonamide-substituted VDCP-diester **2**.

General procedure for the $Yb(OTf)_3$-catalyzed domino intramolecular hydroamination and ring-opening of sulfonamide-substituted 1,1-vinylidenecyclopropanediesters: Under an argon atmosphere, sulfonamide-substituted VDCP-diester **2** (0.1 mmol) and $Yb(OTf)_3$ (10 mol%) were added to a Schlenk tube, and then toluene (1.0 mL) was added. The mixture was stirred at room temperature (20°C) for 2 d. After the substrate was consumed, the solvent was removed under reduced pressure and the residue was purified by silica gel flash column chromatography to afford the desired product **3**.

General procedure for the Au-catalyzed domino intramolecular hydroamination and ring-opening of sulfonamide-substituted 1,1-vinylidenecyclopropanediesters: Under an argon atmosphere, sulfonamide-substituted VDCP-diester **2** (0.1 mmol) and $[AuCl(PPh_3)]$ (5 mol%) were added to a Schlenk tube, and then toluene (1.0 mL) was added. The mixture was stirred at room temperature (20°C) for 5 min and AgOTf (5 mol%) was added to the reaction system, followed by the addition of H_2O (0.1 mmol, 1.0 equiv). After the substrate was consumed, the solvent was removed under reduced pressure and the residue was purified by silica gel flash column chromatography to afford the desired product **4**.

Sulfonamide-substituted VDCP-diester 2a: A light yellow oil. ^1H NMR ($CDCl_3$, 400 MHz,): $\delta = 2.32$ (dd, $J = 8.0$ Hz, 4.8 Hz, 1H; CH_2), 2.35–2.42 (m, 1H), 2.46–2.56 (m, 2H), 3.74 (s, 3H; OCH_3), 3.75 (s, 3H; OCH_3),

4.03–4.15 (m, 2H; OCH_2), 5.60–5.66 (m, 1H; CH=), 7.67 (d, $J=8.4$ Hz, 2H; Ar), 7.80 (d, $J=8.4$ Hz, 2H; Ar), 8.01 ppm (s, 1H, NH); ^{13}C NMR ($CDCl_3$, 100 MHz,): $\delta=19.7$, 27.4, 34.8, 52.9, 53.1, 75.2, 84.5, 96.3, 128.7, 130.0, 132.1, 135.8, 167.3, 168.5, 189.4 ppm; IR (CH_2Cl_2): $\tilde{\nu}=$ 3359, 3206, 2956, 1732, 1575, 1437, 1170, 1108, 757, 703 cm^{-1}; MS (ESI): *m/z*: 482.6 $[M+Na]^+$; HRMS (ESI): *m/z* calcd for $C_{17}H_{18}BrNO_7S$: 481.9880 $[M+Na]^+$; found: 481.9881.

Acknowledgements

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Keywords: domino reactions · hydroamination · Lewis acids · N,O-heterocycles · ring-opening

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