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Lewis acid-catalyzed nucleophilic ring-opening/intramolecular Conia-ene reactions of methylenecyclopropane 1,1-diesters with propargyl alcohols

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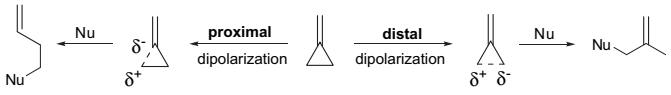
ABSTRACT

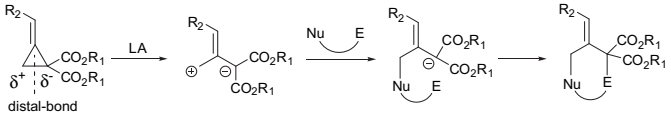
We presented a Lewis acid-catalyzed nucleophilic ring opening of methylenecyclopropane (MCP) 1,1-diesters with propargyl alcohols. Unlike the proximal-bond cleavage mode observed in cases of unactivated MCPs, the intrinsic characteristic of MCP 1,1-diesters gave a regiospecific distal-bond cleavage under attack of propargyl alcohols as nucleophiles. By combining a subsequent intramolecular Conia-ene reaction, 3,5-dimethylenetetrahydropyrans could be obtained in either a stepwise or a one-pot strategy.

1. Introduction

Methylenecyclopropanes (MCPs), a kind of highly strained molecule, have been paid much attention due to their ready availability[1] and good reactivity.[2] Recently, Lewis acid (LA)-catalyzed nucleophilic ring-opening reactions of MCPs have been extensively investigated. Typically, such nucleophilic ring-opening reactions were carried out via either proximal[3] or distal[4] mode (Scheme 1). Most of the LA-promoted nucleophilic ring-opening processes were reported on unactivated MCPs, which were triggered by an initial generation of a carbocation at one of the two sp^2 carbons. For example, Shi and Xu found that the unactivated MCPs reacted with alcoholic nucleophiles catalyzed by LAs to give the ring-opening products through a proximal mode.[3a] For activated MCPs, usually activated by an electron-withdrawing group (EWG) on sp^3 carbon of the three-membered ring, only a few researches on LA-catalyzed nucleophilic ring-opening were reported. Lautens et al. reported a MgI_2-mediated distal [3+2] cycloaddition of MCPs activated by a single EWG. This cycloaddition was proposed to be initiated by a nucleophilic ring opening with an iodide anion.[4c] MCP 1,1-diesters have been recently developed in our lab for a novel [3+3] cycloaddition[5a] and a tandem ring-opening/intramolecular Friedel–Crafts reaction[5b] under the catalysis of $Yb(OTf)_3$ or $Sc(OTf)_3$. The introduction of the two geminal EWGs on the sp^3 carbon of the three-membered ring made the MCP a stable precursor of an active 1,3-dipole and undergo the nucleophilic ring-opening reaction with a regiospecifically distal-bond cleavage mode under mild conditions.[6] We hope to explore new LA-catalyzed nucleophilic ring-opening reactions of MCP 1,1-diesters and to develop a new strategy for the construction of cyclic skeletons by combining with a subsequent cyclization of carbanion with an electrophile (Scheme 2). We now report an LA-catalyzed distally nucleophilic ring opening of MCP 1,1-diesters with propargyl alcohols, and a combination of the reaction with subsequent intramolecular Conia-ene cyclization[7,8] via either a stepwise or a one-pot way (Scheme 3).



Scheme 1. Two types of LA-catalyzed nucleophilic ring-opening modes.



Scheme 2. Combination of LA-catalyzed nucleophilic ring-opening and subsequent ring-closing of MCP 1,1-diesters.

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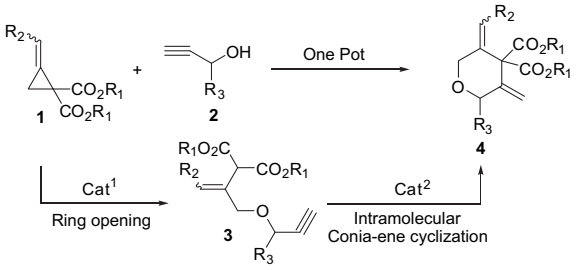


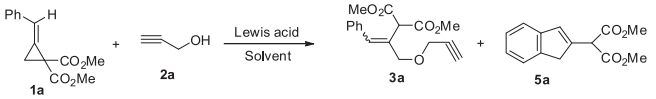
Scheme 3. Ring-opening/intramolecular Conia-ene reactions of MCP 1,1-diesters **1** with propargyl alcohols **2**.

2. Results and discussion

Initial experiments for optimal conditions were carried out with MCP 1,1-diester **1a** (1.0 equiv) and propargyl alcohol **2a** (5.0 equiv), and the results are summarized in Table 1. The reaction in 1,2-dichloroethane (DCE) proceeded smoothly at 60 °C under catalysis of $Yb(OTf)_3$ to afford **3a** in 65% yield (Table 1, entry 2). The main by-product observed in this reaction was the Friedel–Crafts alkylation product **5a** previously reported by us.[5b] When the amount of **2a** was decreased to 2.5 equiv, the yield decreased from 65% to 52% (Table 1, entry 3). When the amount of **2a** was increased to 10.0 equiv, the yield was slightly improved from 65% to 73% (Table 1, entry 4). The yield could be improved to 77% when 20.0 equiv of **2a** was used (Table 1, entry 6). Several other LAs have also been tested (Table 1, entries 8–12) and it was found that $Eu(OTf)_3$ (Table 1, entry 12) also promoted the reaction effectively. We chose the optimized conditions as in entry 4, Table 1 for further investigation.

With the optimal reaction conditions established, the scope of these ring-opening reactions was then studied. As revealed in Table 2, various MCPs **1** were suitable for such transformation (Table 2, entries 1–10). Reactions of aryl-substituted MCPs containing either an electron-withdrawing group or an electron-donating group on the benzene ring proceeded successfully (Table 2, entries 2–6). The reaction of benzyl-substituted MCP 1,1-diester **1i** with propargyl alcohol **2a** afforded **3i** in 21% yield together with a Friedel–Crafts by-product **5i** (24% yield, Table 2, entry 9). The reaction of heptyl-substituted MCP 1,1-diester **1j** with propargyl alcohol **2a** also proceeded successfully (Table 2, entry 10). Under the similar conditions, reactions of **1a** with

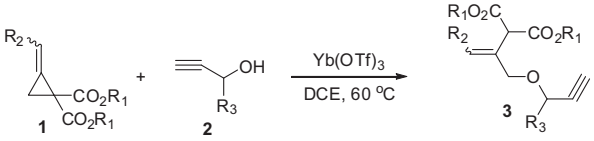
Table 1
Optimization of conditions for the ring-opening reaction of MCP 1,1-diester **1a** with propargyl alcohol **2a**[a]



Entry	Ratio	Lewis acid	Temp (°C)	Time (h)	Yield[b] (%)	
	1a/**2a**				**3a**	**5a**
1	1:5	$Yb(OTf)_3$	rt	24	Nr[c]	
2	1:5	$Yb(OTf)_3$	60	18.5	65	17
3	1:2.5	$Yb(OTf)_3$	60	22	52	38
4	1:10	$Yb(OTf)_3$	60	26.5	73	15
5[d]	1:10	$Yb(OTf)_3$	60	22	75	14
6	1:20	$Yb(OTf)_3$	60	43	77	8
7[d]	1:5	$Yb(OTf)_3$	80	4.5	54	44
8[d]	1:10	$Zn(OTf)_2$	80	7	Nr[c]	
9[d,e]	1:10	$In(OTf)_3$	60	17	—	Trace
10[d]	1:10	$Bi(OTf)_3$	60	8	—	Trace
11[d]	1:10	$InCl_3$	60	5	Trace	—
12	1:5	$Eu(OTf)_3$	60	88	54	22

[a] Reaction conditions: 0.5 mmol scale of **1a**, 20 mol % of LA, 5.0 mL of DCE, Ar.
[b] Isolated yields by silica gel chromatography.
[c] No reaction occurred.
[d] LA (50 mol %) was used.
[e] Compound **1a** was consumed.

Table 2
Ring-opening reactions of MCPs **1** with propargyl alcohols **2**[a]



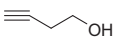
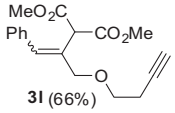
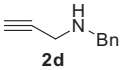
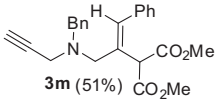
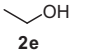
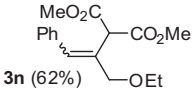
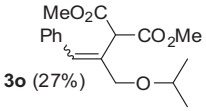
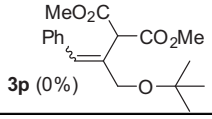
Entry	Substrate **1**	R_1	R_2	*E*/*Z* ratio of **1**[b]	Substrate **2**	R_3	Time (h)	Product **3**	Yield[c,d] (%)	*E*/*Z* ratio of **3**[b]
1	**1a**	Me	C_6H_5	100:0	**2a**	H	26.5	**3a**	73	87:13
2	**1b**	Me	4-FC_6H_4	100:0	**2a**	H	75	**3b**	43	76:24
3	**1c**	Me	4-ClC_6H_4	100:0	**2a**	H	64	**3c**	70	88:12
4[e]	**1d**	Me	3-ClC_6H_4	100:0	**2a**	H	16	**3d**	60	83:17
5	**1e**	Me	4-BrC_6H_4	100:0	**2a**	H	41.5	**3e**	65	>20:1
6	**1f**	Me	2-BrC_6H_4	65:35	**2a**	H	22	**3f**	52	90:10
7	**1g**	Me	4-$MeOC_6H_4$	100:0	**2a**	H	15	**3g**	61	92:8
8	**1h**	Et	C_6H_5	100:0	**2a**	H	44	**3h**	56	86:14
9	**1i**	Me	Bn	67:33	**2a**	H	15.5	**3i**	21	88:12
10	**1j**	Me	*n*-C_7H_{15}	70:30	**2a**	H	23	**3j**	52	30:70
11	**1a**	Me	C_6H_5	100:0	**2b**	Me	46.5	**3k**	67	84:16
12	**1a**	Me	C_6H_5	100:0	 **2c**		41.5	 **3l** (66%)		81:19
13[e]	**1a**	Me	C_6H_5	100:0	 **2d**		20	 **3m** (51%)		>20:1
14	**1a**	Me	C_6H_5	100:0	 **2e**		11	 **3n** (62%)		75:25

Table 2 (*continued*)

Entry	Substrate **1**	R_1	R_2	*E*/*Z* ratio of **1**[b]	Substrate **2**	R_3	Time (h)	Product **3**	Yield[c,d] (%)	*E*/*Z* ratio of **3**[b]
15	**1a**	Me	C_6H_5	100:0	 **2f**		15.5	 **3o** (27%)		76:24
16	**1a**	Me	C_6H_5	100:0	 **2g**		8.5	 **3p** (0%)		—

[a] Reaction conditions: 0.5 mmol scale of **1**, 10.0 equiv of **2**, 20 mol % of $Yb(OTf)_3$, 5.0 mL of DCE, 60 °C, Ar.
[b] Determined by ^1H NMR after purification.
[c] Isolated yields by silica gel chromatography.
[d] The total yield is given for a mixture of the two diastereomers.
[e] Reaction was carried out at 80 °C.

nucleophiles 3-butyn-2-ol **2b**, 3-butyn-1-ol **2c**, and *N*-benzyl propargyl amine **2d** were also carried out successfully and the ring-opening products **3k**–**m** were obtained in moderate yields (Table 2, entries 11–13). In addition, several other aliphatic alcohols were also investigated. Ethanol worked well and gave ring-opening product **3n** in 62% yield (Table 2, entry 14), *iso*-propanol gave **3o** in 27% yield (Table 2, entry 15). However, probably due to the steric hindrance, no ring-opening product was obtained for *tert*-butanol (Table 2, entry 16).

For all of the MCPs 1,1-diesters except **1j**, the ring-opening products **3** were formed with good stereoselectivities (*E*/*Z*=75:25 to >20:1). The different stereoselectivity in **3j** (*E*/*Z*=30:70) was probably caused by the steric effect of the long aliphatic chain. NOESY experiment confirmed *E*-**3a** as a major isomer (Fig. 1). By comparing the change of the configuration of carbon–carbon double bond in the MCPs and the ring-opening products, we can see that no matter the *E*/*Z* ratios of MCPs are higher (e.g., Table 2, entry 1: *E*/*Z*=100:0) or lower (e.g., Table 2, entry 6: *E*/*Z*=65:35), the *E*/*Z* ratios of the ring-opening products are in the same level (for **3a**: *E*/*Z*=87:13; for **3f**: *E*/*Z*=90:10). This strongly supported that a polarized TMM (trimethylenemethane) intermediate was involved in the nucleophilic ring-opening process and thus an S_N1 mechanism might be implied (Scheme 4), which is different from that proposed in the case of cyclopropane 1,1-diester.[7]

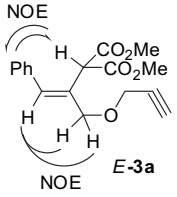
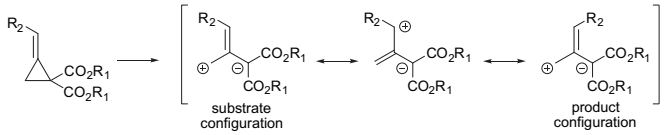


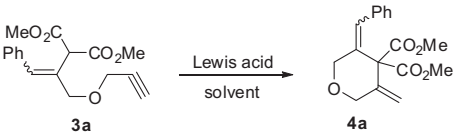
Fig. 1. NOESY analysis of the ring-opening product *E*-**3a**.



Scheme 4. A proposed polarized TMM S_N1 mechanism.

Following the successfully established nucleophilic ring-opening process, an intramolecular Conia-ene cyclization was then considered to be carried out on the nucleophilic ring-opening product **3a**. Under the catalysis of 0.5 equiv of $InCl_3$, the reaction proceeded smoothly to afford 3,5-dimethylenetetrahydropyran **4a** in 47% yield (Table 3, entry 1). When 0.1 equiv of Et_3N was added, the yield was improved to 57% (Table 3, entry 3). Further investigation indicated that other LAs, such as Ph_3PAuCl, AuOTf, and $Ni(ClO_4)_2\cdot 6H_2O$ were

Table 3
Optimization of conditions for the ring-closing reaction of nucleophilic ring-opening product **3a**[a]



3a **4a**

Entry	Lewis acid (equiv)	Solvent	Temp (°C)	Time (h)	Yield[b] (%)
1	$InCl_3$ (0.50)	DCE	60	21.5	47
2	$InCl_3$ (0.30)	DCE	60	12.5	16
3[c]	$InCl_3$ (0.50)	DCE	65	15	57
4	Ph_3PAuCl (0.10)	DCE	80	7	Nr[d]
5[c,e]	AuOTf (0.10)	DCE	10	16	—
6[c]	$Ni(ClO_4)_2\cdot 6H_2O$ (0.50)	DCE	80	15	Nr[d]
7[c]	$InCl_3$ (0.50)	THF	66	10	Nr[d]
8[c,f]	$InCl_3$ (0.50)	Toluene	65	38	16

[a] Reaction conditions: 0.25 mmol scale of **3a**, 7.0 mL of solvent, Ar.
[b] Isolated yields by silica gel chromatography.
[c] Et_3N (0.10 equiv) was added.
[d] No reaction occurred.
[e] Compound **3a** was slowly decomposed.
[f] Compound **3a** (20%) was recovered.

ineffective (Table 3, entries 4–6). In addition, several solvents were tested and it was found that DCE is the best one for this transformation. The structure of *E*-**4a** was established by ^1H and ^{13}C NMR spectroscopy as well as single-crystal X-ray diffraction (Fig. 2).[9]

With the optimized reaction conditions in hand (Table 3, entry 3), we next extended the ring-closing reactions to several other nucleophilic ring-opening products **3** (Table 4). Substrates with chlorine or

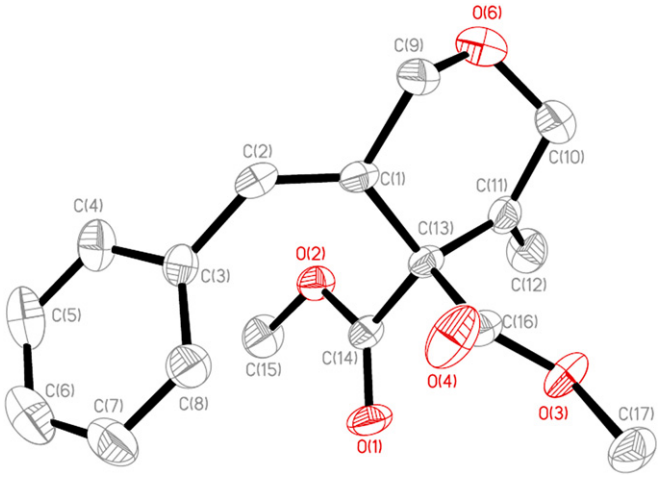
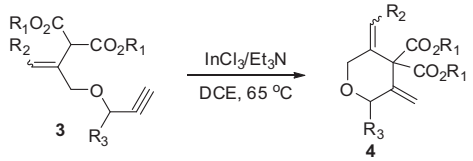


Fig. 2. X-ray crystal structure of *E*-**4a**.

Table 4
Ring-closing reactions of several nucleophilic ring-opening products **3** in the presence of $InCl_3/Et_3N$[a]



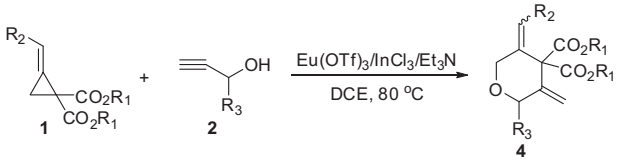
Entry	Substrate **3**	R_1	R_2	R_3	Time (h)	Product **4**	Yield[b,c] (%)	*E*/*Z* ratio of **4**[d]
1	**3a**	Me	C_6H_5	H	15	**4a**	57	86:14
2	**3b**	Me	4-FC_6H_4	H	9	**4b**	—	—
3	**3c**	Me	4-ClC_6H_4	H	25.5	**4c**	39	88:12
4	**3d**	Me	3-ClC_6H_4	H	23	**4d**	38	87:13
5	**3e**	Me	4-BrC_6H_4	H	16.5	**4e**	<10	—
6	**3f**	Me	2-BrC_6H_4	H	42.5	**4f**	55	88:12
7	**3g**	Me	4-$MeOC_6H_4$	H	15.5	**4g**	—	—
8	**3h**	Et	C_6H_5	H	42	**4h**	17	72:28
9[e]	**3j**	Me	*n*-C_7H_{15}	H	16	**4j**	—	—
10	**3k**	Me	C_6H_5	Me	24	**4k**	10	78:22

[a] Reaction conditions: 0.20–0.30 mmol scale of **3**, 50 mol % of $InCl_3$, 10 mol % of Et_3N, 7.0 mL of DCE, 65 °C, Ar.
[b] Isolated yields by silica gel chromatography.
[c] The total yield is given for a mixture of two diastereomers.
[d] Determined by ^1H NMR after purification.
[e] Compound **3j** was consumed.

bromine on the phenyl group could also give the corresponding products **3c**, **3d**, and **3f** (Table 4, entries 3, 4, and 6), however we cannot explain the negative results on **3e** (Table 4, entry 5) and fluorophenyl-substituted substrate **3b** (Table 4, entry 2). The reactions of more sterically hindered substrates **3h** and **3k** resulted in decreased yields (Table 4, entries 1, 8, and 10). For substrate **3g** with methoxyl on the phenyl group or heptyl-substituted substrate **3j**, the reactions did not work (Table 4, entries 7 and 9).

Finally, we started to carry out the combination of nucleophilic ring-opening reaction and intramolecular Conia-ene cyclization in a one-pot process. It was found in the previous investigation that a single LA was not enough effective for the one-pot operation, challenge for this was a proper combination of selected catalysts, especially the LAs. After many attempts devoted to the optimization of conditions in the one-pot process of substrates **1a** and **2a**, Eu $(OTf)_3/InCl_3/Et_3N$ system was proved to be the most suitable one, although the yield was not good (Table 5, entry 1). Several other examples were also employed and the results are summarized in Table 5. It should be noted that stereoselectivity in the one-pot tandem process was higher, which is different from the stepwise process.

Table 5
Tandem ring-opening/intramolecular Conia-ene reactions of MCPs **1** with propargyl alcohols **2**[a]



Entry	Substrate **1**	R_1	R_2	Substrate **2**	R_3	Time (h)	Product **4**	Yield[b,c] (%)	*E*/*Z* ratio of **4**[d]
1	**1a**	Me	C_6H_5	**2a**	H	22	**4a**	39	>20:1
2	**1b**	Me	4-FC_6H_4	**2a**	H	11	**4b**	26	>20:1
3	**1h**	Et	C_6H_5	**2a**	H	23	**4h**	17	>20:1
4	**1a**	Me	C_6H_5	**2b**	Me	10.5	**4k**	37	>20:1
5	**1k**	Me	4-MeC_6H_4	**2a**	H	57.5	**4n**	32	92:8

[a] Reaction conditions: 0.5 mmol scale of **1**, 5.0 equiv of **2a** or **2b**, 20 mol % of $Eu(OTf)_3$, 50 mol % of $InCl_3$, 10 mol % of Et_3N, 7.0 mL of DCE, 80 °C, Ar.
[b] Isolated yields by silica gel chromatography.
[c] The total yield is given for a mixture of two diastereomers.
[d] Determined by ^1H NMR after purification.

3. Conclusions

In summary, an LA-catalyzed nucleophilic ring opening of MCP 1,1-diesters with propargyl alcohols has been achieved in a distal-bond cleavage mode. This regiospecific reaction differs considerably from the LA-promoted addition of alcohols to unactivated MCPs. An LA-catalyzed intramolecular Conia-ene reaction of the ring-opening products has also been disclosed. Finally, a highly stereoselective one-pot tandem ring-opening/intramolecular Conia-ene protocol has also been developed.

4. Experimental section

4.1. General method

All NMR spectra were recorded with a spectrometer at 400 MHz (^1H NMR) and 100 MHz (^{13}C NMR) in $CDCl_3$. The chemical shifts were reported in parts per million referenced to $CDCl_3$ (δ=7.26 ppm) for ^1H NMR and relative to the central $CDCl_3$ resonance (δ=77.0 ppm) for ^{13}C NMR spectroscopy. Column chromatography was performed on silica gel (100–200 or 200–300 mesh) using petroleum ether and EtOAc as eluents. Thin layer chromatography (TLC) was performed on Merck silica gel GF254 plates and visualized by UV light (254 nm). Melting points were uncorrected. All solvents were purified and dried using standard procedures. Methylenecyclopropane 1,1-diesters **1** were prepared according to literature methods.[5,10]

4.2. General procedure for the ring-opening reactions of MCPs 1 and propargyl alcohols 2

$Yb(OTf)_3$ (62 mg, 0.10 mmol, 20 mol %), MCPs **1** (0.50 mmol, 1.0 equiv), propargyl alcohols **2** (5.00 mmol, 10.0 equiv), and 5 mL of dry DCE were introduced into an oven-dried three-necked flask. The mixture was stirred at 60 °C in an argon atmosphere. After completion of the reaction (as monitored by TLC), the solvent was evaporated in vacuo and the residue was purified on silica gel chromatography (ethyl acetate/petroleum ether) to afford ring-opening products **3**. *E*- and *Z*-Isomers can be separated by silica gel chromatography if desired.

*4.2.1. Dimethyl 2-(1-phenyl-3-(prop-2-ynyloxy)prop-1-en-2-yl)-malonate (**3a**).* Yellow oil; *E*/*Z*=87:13; the *E*-isomer: ^1H NMR ($CDCl_3$, 400 MHz): δ 7.40–7.33 (m, 2H), 7.30 (d, *J*=7.2 Hz, 1H), 7.23 (d, *J*=7.2 Hz, 1H), 6.98 (s, 1H), 4.70 (s, 1H), 4.39 (s, 2H), 4.16 (d, *J*=2.4 Hz, 2H), 3.73 (s, 6H), 2.45 (t, *J*=2.4 Hz, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 168.4, 135.6, 134.4, 129.8, 128.5, 127.7, 79.6, 74.5, 71.4, 57.3, 52.7, 51.6; HRMS (ESI) calcd for $C_{17}H_{18}O_5Na$ $(M+Na)^+$: 325.1046; found: 325.1052.

*4.2.2. Dimethyl 2-(1-(4-fluorophenyl)-3-(prop-2-ynyloxy)prop-1-en-2-yl)malonate (**3b**).* Slightly yellow oil; *E*/*Z*=76:24; the *E*-isomer: ^1H NMR ($CDCl_3$, 400 MHz): δ 7.25–7.19 (m, 2H), 7.05 (t, *J*=8.4 Hz, 2H), 6.92 (s, 1H), 4.63 (s, 1H), 4.37 (s, 2H), 4.16 (s, 2H), 3.73 (s, 6H), 2.45 (s, 1H); the *Z*-isomer: ^1H NMR ($CDCl_3$, 400 MHz): δ 7.32–7.28 (m, 2H), 7.03 (t, *J*=8.4 Hz, 2H), 6.72 (s, 1H), 4.39 (s, 1H), 4.29 (s, 2H), 4.09 (s, 2H), 3.78 (s, 6H), 2.39 (s, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 169.2, 168.6, 168.3, 163.5, 161.1, 134.1, 133.4, 131.6, 130.8, 130.8, 130.4, 130.4, 130.3, 130.0, 79.5, 79.2, 74.7, 74.6, 71.4, 66.9, 57.8, 57.3, 56.3, 52.8, 51.5,

31.2, 29.7; HRMS (ESI) calcd for $C_{17}H_{17}FO_5Na$ $(M+Na)^+$: 343.0952; found: 343.0952.

*4.2.3. Dimethyl 2-(1-(4-chlorophenyl)-3-(prop-2-ynyloxy)prop-1-en-2-yl)malonate (**3c**).* Yellow oil; *E*/*Z*=88:12; the *E*-isomer: ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.32 (d, *J*=8.4 Hz, 2H), 7.18 (d, *J*=8.0 Hz, 2H), 6.90 (s, 1H), 4.61 (s, 1H), 4.36 (s, 2H), 4.16 (s, 1H), 4.15 (s, 1H), 3.71 (s, 6H), 2.45 (s, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 168.1, 134.0, 133.7, 133.0, 130.6, 130.4, 129.9, 128.7, 79.5, 74.7, 71.2, 57.4, 52.8, 51.5; HRMS (ESI) calcd for $C_{17}H_{17}ClO_5Na$ $(M+Na)^+$: 359.0657; found: 359.0654.

*4.2.4. Dimethyl 2-(1-(3-chlorophenyl)-3-(prop-2-ynyloxy)prop-1-en-2-yl)malonate (**3d**).* Slightly yellow oil; *E*/*Z*=83:17; the *E*-isomer: ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.31–7.20 (m, 3H), 7.13 (d, *J*=6.8 Hz, 1H), 6.90 (s, 1H), 4.61 (s, 1H), 4.37 (s, 2H), 4.17 (s, 1H), 4.16 (s, 1H), 3.73 (s, 6H), 2.45 (t, *J*=2.0 Hz, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 168.1, 137.4, 134.4, 132.7, 131.2, 129.8, 128.7, 127.8, 126.7, 79.4, 74.7, 71.1, 57.4, 52.8, 51.5; HRMS (ESI) calcd for $C_{17}H_{17}ClO_5Na$ $(M+Na)^+$: 359.0657; found: 359.0652.

*4.2.5. (E)-Dimethyl 2-(1-(4-bromophenyl)-3-(prop-2-ynyloxy)prop-1-en-2-yl)malonate (**3e**).* Yellow oil; the sole *E*-isomer: ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.48 (d, *J*=8.4 Hz, 2H), 7.12 (d, *J*=8.0 Hz, 2H), 6.89 (s, 1H), 4.60 (s, 1H), 4.36 (s, 2H), 4.16 (s, 1H), 4.15 (s, 1H), 3.72 (s, 6H), 2.45 (s, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 168.1, 134.5, 133.0, 131.7, 130.7, 130.2, 121.8, 79.4, 74.7, 71.2, 57.4, 52.8, 51.5; HRMS (ESI) calcd for $C_{17}H_{17}BrO_5Na$ $(M+Na)^+$: 403.0152; found: 403.0153.

*4.2.6. Dimethyl 2-(1-(2-bromophenyl)-3-(prop-2-ynyloxy)prop-1-en-2-yl)malonate (**3f**).* Yellow oil; *E*/*Z*=90:10; the *E*-isomer: ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.59 (d, *J*=8.0 Hz, 1H), 7.32–7.27 (m, 2H), 7.20–7.12 (m, 1H), 6.87 (s, 1H), 4.45 (s, 1H), 4.42 (s, 2H), 4.21 (s, 1H), 4.20 (s, 1H), 3.69 (s, 6H), 2.45 (s, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 168.0, 136.1, 133.8, 132.6, 130.9, 130.3, 129.4, 127.4, 124.0, 79.6, 74.6, 70.9, 57.0, 52.7, 51.7; HRMS (ESI) calcd for $C_{17}H_{17}BrO_5Na$ $(M+Na)^+$: 403.0152; found: 403.0152.

*4.2.7. Dimethyl 2-(1-(4-methoxyphenyl)-3-(prop-2-ynyloxy)prop-1-en-2-yl)malonate (**3g**).* Slightly yellow oil; *E*/*Z*=92:8; the *E*-isomer: ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.18 (d, *J*=8.0 Hz, 2H), 6.89 (s, 2H), 6.87 (s, 1H), 4.71 (s, 1H), 4.36 (s, 2H), 4.14 (s, 2H), 3.80 (s, 3H), 3.72 (s, 6H), 2.44 (s, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 168.5, 159.1, 134.4, 129.9, 128.5, 127.9, 114.0, 79.6, 74.5, 71.7, 57.1, 55.2, 52.7, 51.5; HRMS (ESI) calcd for $C_{18}H_{20}O_6Na$ $(M+Na)^+$: 355.1152; found: 355.1155.

*4.2.8. Diethyl 2-(1-phenyl-3-(prop-2-ynyloxy)prop-1-en-2-yl)malonate (**3h**).* Slightly yellow oil; *E*/*Z*=86:14; the *E*-isomer: ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.37–7.31 (m, 2H), 7.28–7.21 (m, 3H), 6.96 (s, 1H), 4.64 (s, 1H), 4.39 (s, 2H), 4.21–4.13 (m, 6H), 2.44 (s, 1H), 1.25 (t, *J*=7.2 Hz, 6H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 166.9, 134.8, 132.9, 128.9, 127.6, 127.4, 126.6, 78.6, 73.5, 70.2, 60.7, 56.1, 51.1, 12.9; HRMS (ESI) calcd for $C_{19}H_{22}O_5Na$ $(M+Na)^+$: 353.1359; found: 353.1364.

*4.2.9. Dimethyl 2-(4-phenyl-1-(prop-2-ynyloxy)but-2-en-2-yl)malonate (**3i**).* Yellow oil; *E*/*Z*=88:12; the *E*-isomer: ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.38–7.25 (m, 2H), 7.22–7.13 (m, 3H), 6.06–5.96 (m, 1H), 4.73 (s, 1H), 4.20 (s, 2H), 4.08 (s, 2H), 3.74 (s, 6H), 3.45 (d, *J*=7.2 Hz, 2H), 2.39 (s, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 168.4, 139.1, 135.1, 134.7, 128.6, 128.5, 128.4, 126.3, 79.6, 74.4, 72.4, 56.8, 52.7, 51.2, 34.3; HRMS (ESI) calcd for $C_{18}H_{20}O_5Na$ $(M+Na)^+$: 339.1203; found: 339.1210.

*4.2.10. Dimethyl 2-(1-(prop-2-ynyloxy)dec-2-en-2-yl)malonate (**3j**).* Slightly yellow oil; *E*/*Z*=30:70: ^{1}H NMR ($CDCl_3$, 400 MHz): δ 5.82 (t, *J*=7.2 Hz, 0.30H), 5.68 (t, *J*=7.2 Hz, 0.70H), 4.22 (s, 1H), 4.19 (s, 1H), 4.16 (s, 1H), 4.06 (s, 1H), 4.05 (s, 1H), 3.73 (s, 6H), 2.40 (t, *J*=2.4 Hz, 1H), 2.17 (dd, *J*=14.4, 7.2 Hz, 1.36H), 2.06 (dd, *J*=14.4, 7.2 Hz, 0.64H), 1.42–1.35 (m, 2H), 1.35–1.18 (m, 8H), 0.87 (t, *J*=7.2 Hz, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 168.9, 168.5, 137.1, 136.9, 127.8, 127.4, 79.7, 74.4, 74.3, 72.4, 65.8, 56.8, 56.6, 55.9, 52.6, 52.6, 51.0, 31.8, 29.3, 29.2, 29.1, 29.1, 29.0, 28.1, 27.9, 22.6, 14.1; HRMS (ESI) calcd for $C_{18}H_{28}O_5Na$ $(M+Na)^+$: 347.1829; found: 347.1832.

*4.2.11. Dimethyl 2-(3-(but-3-yn-2-yloxy)-1-phenylprop-1-en-2-yl)-malonate (**3k**).* Yellow oil; *E*/*Z*=84:16; the *E*-isomer: ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.37–7.33 (m, 2H), 7.31–7.24 (m, 3H), 6.98 (s, 1H), 4.70 (s, 1H), 4.55 (d, *J*=12.4 Hz, 1H), 4.32 (d, *J*=12.4 Hz, 1H), 4.25 (dd, *J*=6.8, 2.0 Hz, 1H), 3.72 (s, 6H), 2.45 (d, *J*=2.0 Hz, 1H), 1.45 (d, *J*=6.8 Hz, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 168.5, 168.3, 135.7, 133.9, 130.1, 128.6, 128.5, 127.6, 83.5, 73.2, 70.5, 64.5, 52.7, 52.6, 51.6, 21.9; HRMS (ESI) calcd for $C_{18}H_{20}O_5Na$ $(M+Na)^+$: 339.1203; found: 339.1207.

*4.2.12. Dimethyl 2-(3-(but-3-ynyloxy)-1-phenylprop-1-en-2-yl)malonate (**3l**).* Yellow oil; *E*/*Z*=81:19; the *E*-isomer: ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.39–7.31 (m, 2H), 7.30–7.22 (m, 3H), 6.97 (s, 1H), 4.70 (s, 1H), 4.33 (s, 2H), 3.71 (s, 6H), 3.61 (t, *J*=6.8 Hz, 2H), 2.48 (t, *J*=6.8 Hz, 2H), 1.98 (s, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 168.4, 135.8, 133.3, 130.2, 128.6, 128.5, 127.6, 81.3, 72.5, 69.4, 68.5, 52.7, 51.5, 19.8; HRMS (ESI) calcd for $C_{18}H_{20}O_5Na$ $(M+Na)^+$: 339.1203; found: 339.1195.

*4.2.13. (E)-Dimethyl 2-(3-(benzyl(prop-2-ynyl)amino)-1-phenylprop-1-en-2-yl)malonate (**3m**).* Light golden oil; the sole *E*-isomer: ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.38–7.21 (m, 10H), 6.77 (s, 1H), 4.67 (s, 1H), 3.73 (s, 6H), 3.54 (s, 2H), 3.43 (s, 2H), 3.16 (s, 2H), 2.03 (s, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 169.0, 138.3, 136.2, 133.6, 132.3, 129.2, 129.1, 128.3, 128.1, 127.2, 127.1, 78.4, 73.2, 57.3, 55.4, 52.7, 52.6, 41.0; HRMS (ESI) calcd for $C_{24}H_{25}NO_4Na$ $(M+Na)^+$: 414.1676; found: 414.1676.

*4.2.14. Dimethyl 2-(3-ethoxy-1-phenylprop-1-en-2-yl)malonate (**3n**).* Yellow oil; *E*/*Z*=75:25; the *E*-isomer: ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.34 (dd, *J*=14.0, 6.8 Hz, 3H), 7.26 (t, *J*=6.8 Hz, 2H), 6.95 (s, 1H), 4.70 (s, 1H), 4.29 (s, 2H), 3.72 (s, 6H), 3.53 (q, *J*=7.2 Hz, 2H), 1.22 (t, *J*=7.2 Hz, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 168.5, 135.9, 133.1, 130.8, 129.0, 128.6, 128.5, 128.2, 127.5, 72.3, 66.0, 52.6, 51.5, 15.1; HRMS (ESI) calcd for $C_{16}H_{20}O_5Na$ $(M+Na)^+$: 315.1203; found: 315.1202.

*4.2.15. Dimethyl 2-(3-isopropoxy-1-phenylprop-1-en-2-yl)malonate (**3o**).* Colorless oil; *E*/*Z*=76:24; the *E*-isomer: ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.38–7.31 (m, 3H), 7.29–7.27 (m, 2H), 6.97 (s, 1H), 4.72 (s, 1H), 4.29 (s, 2H), 3.72 (s, 6H), 3.68 (q, *J*=6.0 Hz, 1H), 1.19 (d, *J*=6.0 Hz, 6H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 168.5, 132.6, 129.0, 128.6, 128.4, 128.1, 127.4, 71.7, 69.8, 52.6, 51.5, 22.0; HRMS (ESI) calcd for $C_{17}H_{22}O_5Na$ $(M+Na)^+$: 329.1359; found: 329.1358.

4.3. General procedure for the ring-closing reactions of nucleophilic ring-opening products 3

Under a positive pressure of argon, to a stirred solution of ring-opening products **3** (0.20–0.30 mmol, 1.0 equiv) in dry DCE (7 mL) were added $InCl_3$ (0.10–0.15 mmol, 50 mol %) and Et_3N (0.02–0.03 mmol, 10 mol %), followed by stirring at 65 °C. After the completion of the reaction (as monitored by TLC), the solution was concentrated under reduced pressure to afford the crude products **4**, which were purified by silica gel column chromatography using petroleum ether and EtOAc as eluents. *E*- and *Z*-Isomers can be separated by silica gel chromatography if desired.

*4.3.1. Dimethyl 3-benzylidene-5-methylene-tetrahydropyran-4,4-dicarboxylate (**4a**).* Yellow solid, mp 122–124 °C; *E*/*Z*=86:14; the

E-isomer: ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.38–7.28 (m, 4H), 7.24–7.20 (m, 1H), 6.75 (s, 1H), 5.21 (s, 1H), 4.81 (s, 1H), 4.29 (s, 2H), 4.28 (s, 2H), 3.40 (s, 6H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 168.5, 140.2, 135.9, 131.7, 129.6, 128.2, 128.0, 127.3, 114.6, 72.9, 71.6, 52.7; HRMS (ESI) calcd for $C_{17}H_{18}O_5Na$ $(M+Na)^+$: 325.1046; found: 325.1053.

*4.3.2. Dimethyl 3-(4-chlorobenzylidene)-5-methylene-tetrahydropyran-4,4-dicarboxylate (**4c**).* White solid, mp 145–147 °C; *E*/*Z*=88:12; the *E*-isomer: ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.34–7.27 (m, 4H), 6.67 (s, 1H), 5.21 (s, 1H), 4.81 (s, 1H), 4.29 (s, 2H), 4.26 (s, 2H), 3.45 (s, 6H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 168.4, 140.0, 134.4, 133.3, 132.7, 129.7, 128.3, 128.2, 114.8, 72.7, 71.6, 52.8; HRMS (ESI) calcd for $C_{17}H_{17}ClO_5Na$ $(M+Na)^+$: 359.0657; found: 359.0654.

*4.3.3. Dimethyl 3-(3-chlorobenzylidene)-5-methylene-tetrahydropyran-4,4-dicarboxylate (**4d**).* Pale yellow solid, mp 113–115 °C; *E*/*Z*=87:13; the *E*-isomer: ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.35 (s, 1H), 7.27–7.21 (m, 3H), 6.65 (s, 1H), 5.21 (s, 1H), 4.83 (s, 1H), 4.30 (s, 2H), 4.26 (s, 2H), 3.47 (s, 6H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 168.3, 140.0, 137.7, 133.8, 133.3, 129.4, 128.3, 127.9, 127.4, 126.4, 114.8, 72.5, 71.5, 52.8, 29.7; HRMS (ESI) calcd for $C_{17}H_{17}ClO_5Na$ $(M+Na)^+$: 359.0657; found: 359.0654.

*4.3.4. Dimethyl 3-(2-bromobenzylidene)-5-methylene-tetrahydropyran-4,4-dicarboxylate (**4f**).* Yellow solid, mp 128–131 °C; *E*/*Z*=88:12; the *E*-isomer: ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.56 (t, *J*=7.6 Hz, 2H), 7.24 (t, *J*=7.6 Hz, 1H), 7.11 (t, *J*=7.6 Hz, 1H), 6.56 (s, 1H), 5.20 (s, 1H), 4.81 (s, 1H), 4.31 (s, 2H), 4.27 (s, 2H), 3.41 (s, 6H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 168.5, 139.9, 136.1, 132.7, 132.0, 130.2, 129.1, 128.6, 127.0, 124.2, 114.7, 72.3, 71.4, 52.7; HRMS (ESI) calcd for $C_{17}H_{17}BrO_5Na$ $(M+Na)^+$: 403.0152; found: 403.0157.

*4.3.5. Diethyl 3-benzylidene-5-methylene-tetrahydropyran-4,4-dicarboxylate (**4h**).* Yellow oil; *E*/*Z*=72:28; the *E*-isomer: ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.38 (d, *J*=7.2 Hz, 2H), 7.32–7.24 (m, 3H), 6.72 (s, 1H), 5.19 (s, 1H), 4.86 (s, 1H), 4.30 (s, 2H), 4.27 (s, 2H), 3.99–3.89 (m, 2H), 3.73–3.62 (m, 2H), 1.14 (t, *J*=7.2 Hz, 6H); ^{13}C NMR ($CDCl_3$, 75 MHz): 168.1, 140.4, 136.2, 131.8, 129.4, 128.3, 127.9, 127.3, 114.5, 73.0, 71.7, 62.0, 13.8; HRMS (ESI) calcd for $C_{19}H_{22}O_5Na$ $(M+Na)^+$: 353.1359; found: 353.1358.

*4.3.6. Dimethyl 5-benzylidene-2-methyl-3-methylene-tetrahydropyran-4,4-dicarboxylate (**4k**).* Yellowish solid, mp 118–119 °C; *E*/*Z*=78:22; the *E*-isomer: ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.37–7.27 (m, 4H), 7.25–7.17 (m, 1H), 6.71 (s, 1H), 5.21 (s, 1H), 4.85 (s, 1H), 4.46 (d, *J*=14.0 Hz, 1H), 4.25 (d, *J*=14.0 Hz, 1H), 4.19 (q, *J*=6.4 Hz, 1H), 3.53 (s, 3H), 3.25 (s, 3H), 1.43 (d, *J*=6.4 Hz, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 169.0, 168.6, 144.8, 136.0, 132.4, 128.5, 128.2, 128.0, 127.2, 113.4, 74.5, 71.9, 53.0, 52.3, 19.6; HRMS (ESI) calcd for $C_{18}H_{20}O_5Na$ $(M+Na)^+$: 339.1203; found: 339.1204.

4.4. General procedure for the one-pot tandem ring-opening/intramolecular Conia-ene reactions

An oven-dried 50 mL three-necked glassware was charged with $Eu(OTf)_3$ (60 mg, 0.10 mmol, 20 mol %), $InCl_3$ (55 mg, 0.25 mmol, 50 mol %), and MCPs **1** (0.50 mmol, 1.0 equiv). Dry DCE (7 mL), propargyl alcohols **2** (2.50 mmol, 5.0 equiv), and 7 μL (0.05 mmol, 10 mol %) of Et_3N were then added sequentially under a positive pressure of argon. The reaction mixture was heated to 80 °C. After the completion of the reaction (as monitored by TLC), the mixture was evaporated in vacuo and the residue was purified by silica gel chromatography to afford products **4**.

*4.4.1. (E)-Dimethyl 3-(4-fluorobenzylidene)-5-methylene-tetrahydropyran-4,4-dicarboxylate (**4b**).* White solid, mp 138–140 °C; the sole *E*-isomer: ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.33 (dd, *J*=8.8, 6.0 Hz, 2H), 6.99 (t, *J*=8.8 Hz, 2H), 6.68 (s, 1H), 5.21 (s, 1H), 4.82 (s, 1H), 4.29 (s, 2H), 4.26 (s, 2H), 3.45 (s, 6H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 168.5, 140.1, 132.1, 130.1, 130.0, 128.5, 115.0, 114.8, 114.8, 72.7, 71.6, 52.8; HRMS (ESI) calcd for $C_{17}H_{17}FO_5Na$ $(M+Na)^+$: 343.0952; found: 343.0952.

*4.4.2. Dimethyl 3-(4-methylbenzylidene)-5-methylene-tetrahydropyran-4,4-dicarboxylate (**4n**).* Yellow solid, mp 109–111 °C; *E*/*Z*=92:8; the *E*-isomer: ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.22 (d, *J*=8.0 Hz, 2H), 7.10 (d, *J*=8.0 Hz, 2H), 6.71 (s, 1H), 5.19 (s, 1H), 4.81 (s, 1H), 4.28 (s, 2H), 4.26 (s, 2H), 3.41 (s, 6H), 2.31 (s, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 168.6, 140.3, 137.0, 133.0, 131.2, 129.7, 128.7, 128.2, 114.6, 72.9, 71.6, 52.7, 21.2; HRMS (ESI) calcd for $C_{18}H_{20}O_5Na$ $(M+Na)^+$: 339.1203; found: 339.1197.

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Supplementary data

^{1}H and ^{13}C NMR spectra and NOESY of compound **3a**. Supplementary data associated with this article can be found in the online version, at doi:10.1016/j.tet.2010.11.048. These data include MOL files and InChIKeys of the most important compounds described in this article.

References and notes

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