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Cascade One-Pot Synthesis of Indanone-Fused Cyclopentanes from the Reaction of Donor-Acceptor Cyclopropanes and Enynals via a Sequential Hydrolysis/Knoevenagel Condensation/[3+2] Cycloaddition

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Abstract: A cascade reaction of donor-acceptor cyclopropanes with enynals to construct indanone-fused cyclopentanes *via* a sequential hydrolysis/Knoevenagel condensation/[3+2] cycloaddition was reported. The desired indanone-fused cyclopentanes were obtained in good yields. This method featured with mild reaction conditions and broad substrate scope, which rendered it very appealing to chemists for the synthesis of complex molecules containing indanone-fused cyclopentanes moiety. Moreover, the products could be further converted into compounds with different functional groups through the well-known transformations.

Keywords: Cascade reaction; Cycloaddition; Donor-acceptor cyclopropane; Enynal; Cyclopentane;

All-carbon polycyclic skeleton is an important structural motif in a range of natural products and pharmaceuticals. Among different types of all-carbon polycyclic skeletons, tricyclic [6,5,5]-fused system is a unique framework, and it is the core of many important natural products, such as pallidol[1], theacitrinin C[2] (Figure 1), dihydromaltophilin[3], and paralianone C[4]. Therefore, efficient synthesis methods for all-carbon tricyclic [6,5,5]-fused system should be of great importance.[5]

Cascade reaction is a powerful synthetic strategy in organic synthesis since it can introduce molecular complexity through a simple chemical operation.[6] In the past several years, our group has made a great effort in developing efficient cascade reactions based on enynals/enynones.[7,8] For example, we have recently developed an efficient one-pot synthesis of indanone-fused cyclobutenes[8a] and indanone-fused 2-methylene tetrahydrofurans[8b] from the reactions of electron-deficient enynals with alkynes and propynols. An *in situ* generated electron-deficient and high reactive indenone was regarded as key intermediate for these reactions.[8a-b]

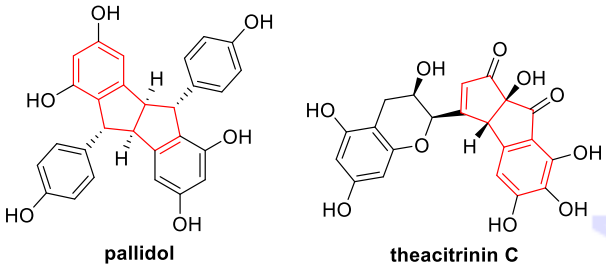
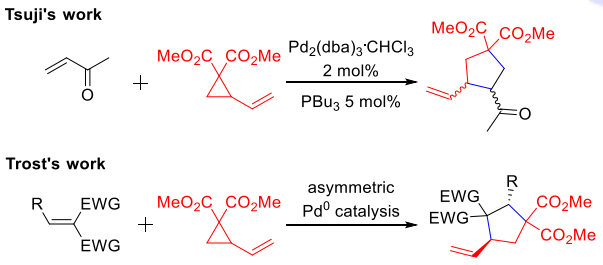


Figure 1. Representative Natural Products with All-Carbon Tricyclic [6,5,5]-Fused Skeletons.

On the other hand, donor-acceptor cyclopropanes are well-known as 1,3-dipoles in cycloaddition reactions.[9-11] For example, Tsuji reported the addition reaction of vinylcyclopropane and methyl vinyl ketone to yield the cyclopentane products as a mixture of diastereomers.[11a] Trost and co-workers have developed a palladium-catalyzed diastereo- and enantioselective formal [3+2] cycloaddition reaction between substituted vinylcyclopropanes and electron-deficient olefins in the form of azlactone- and Meldrum's acid alkylidenes to give highly substituted cyclopentane products[11b] (Scheme 1).



Scheme 1. Palladium-catalyzed Annulation of Vinylcyclopropanes with Electron-deficient Olefins.

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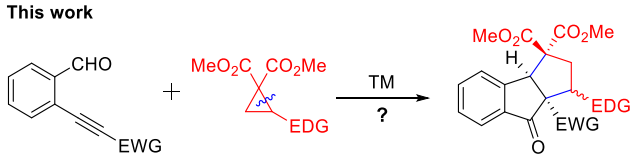
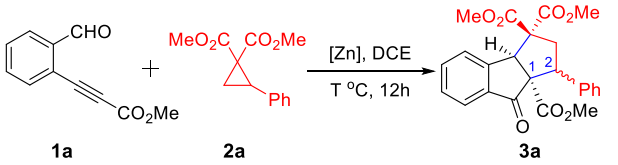
As part of our continuous efforts to develop new cascade reactions based on enynals/enynones, we envisioned that donor-acceptor cyclopropanes should be used as efficient 1,3-dipoles to trap the *in situ* generated electron-deficient indenones through [3+2] cycloaddition reaction. Such reaction would allow a facile synthesis of the all-carbon tricyclic [6,5,5]-fused skeleton of indanone-fused cyclopentane (Scheme 2).



Scheme 2. Synthesis of Indanone-Fused Cyclopentanes.

Initial efforts have been made to investigate the reaction of enynal **1a** with donor-acceptor cyclopropane **2a** under different reaction conditions. As shown in Table 1, $AgNTf_2$, AgOTf, $AgSbF_6$, $In(OTf)_3$, and $Fe(OTf)_3$, which have been proven to be good catalysts for the reaction of enynals,[8a-b] however, were not able to promote this transformation (Table 1, entries 1-5). Using 20 mol% of ZnI_2 as catalyst, the reaction could produce the desired product cyclopentane **3a** in 36% yield at 60 °C, with 12% of starting material **1a** being recovered (entry 6). Gratifyingly, when increasing the catalyst amount to 50 mol%, the product yield of **3a** was improved to 69% (entry 7). Nevertheless, the yield didn't display an obvious improvement when 100 mol% ZnI_2 was used instead (entry 8). $ZnCl_2$ and $ZnBr_2$ were also effective for this reaction, but with inferior results than ZnI_2 (entries 9-10). ZnF_2 and $Zn(OTf)_2$, however, were ineffective for the reaction (entries 11-12). Trials to improve the product yields by either reducing or raising the reaction temperature failed (entries 13-14). The product yield remained almost unchanged when 2.0 equivalents of **2a** was used, indicating that the reaction was insensitive to the substrate ratio (entry 15). The reaction did not occur when the 4Å molecular sieves were added to remove the adventitious water introduced by solvent, catalyst and substrate (entry 16). Furthermore, only trace amount of **3a** was detected when freshly dried DCE was used as the solvent (entry 17). When 0.5 equivalent of H_2O was added to the above reaction mixture, the yield of product **3a** can be improved to 72% (entry 18). Nevertheless, the yield can't be further improved by increasing the amount of water (entries 19-20). These results implied that the reaction should be a water-involved process. The mixed solvents of DCE and MeOH failed to afford the desired product (entry 21). It is noted that both isomers of **3a** have been observed for the ZnI_2-catalyzed reactions. The stereochemistry of the major isomer, in which the ester group at C1 position and the aryl group at C2 position oriented in the opposite direction, has been determined by the X-ray diffraction analysis (See **3f** in SI for detail).[12]

Table 1. Reaction Optimization between **1a** and **2a**.[a]



1a **2a** **3a**

entry	cat	T/°C	Yield[b] (%)	*d.r.*[c]
1	$AgNTf_2$ (5 mol%)	60	n.d.	-
2	AgOTf (5 mol%)	60	n.d.	-
3	$AgSbF_6$ (5 mol%)	60	n.d.	-
4	$In(OTf)_3$ (20 mol%)	60	n.d.	-
5	$Fe(OTf)_3$ (20 mol%)	60	n.d.	-
6[d]	ZnI_2 (20 mol%)	60	36	67:33
7	**ZnI_2 (50 mol%)**	**60**	**69**[e]	**80:20**
8	ZnI_2 (100 mol%)	60	72	71:29
9	$ZnCl_2$ (50 mol%)	60	32	77:23
10	$ZnBr_2$ (50 mol%)	60	43	73:27
11	ZnF_2 (50 mol%)	60	NR	-
12	$Zn(OTf)_2$ (50 mol%)	60	NR	-
13	ZnI_2 (50 mol%)	40	51	80:20
14	ZnI_2 (50 mol%)	80	56	63:37
15[f]	ZnI_2 (50 mol%)	60	67	71:29
16[g]	ZnI_2 (50 mol%)	60	NR	-
17[h]	ZnI_2 (50 mol%)	60	Trace	-
18[i]	ZnI_2 (50 mol%)	60	72	78:22
19[j]	ZnI_2 (50 mol%)	60	68	79:21
20[k]	ZnI_2 (50 mol%)	60	56	82:18
21[l]	ZnI_2 (50 mol%)	60	n.d.	-

[a] The reaction of **1a** (0.20 mmol, 0.1M) and **2a** (0.24 mmol), was carried out under N_2 for 12h.
[b] The yield was determined by ^1H NMR spectroscopy.
[c] *d.r.* was determined by ^1H NMR spectroscopy.
[d] 12% of **1a** was recovered.
[e] Yield of isolated products.
[f] 2.0 eq. of **2a** was used.
[g] 4 Å M.S.(100 mg) was added.
[h] Freshly dried DCE was used as the solvent.
[i] 0.5 eq. of H_2O was added into the reaction system of entry 17.
[j] 1.0 eq. H_2O was added.
[k] 2.0 eq. H_2O was added.
[l] DCE/MeOH (1:1) was used as the mixture solvent.

With the optimal reaction conditions in hand (Table 1, entry 7), the substrate scope was then investigated. As shown in Table 2, the cyclopropanes bearing different aromatic substituents can be utilized as effective substrates, affording the desired products **3a-k** in 48-70% yields. The sterically-bulky aryl groups had little effects on the product yields (**3g-k**). Product **3c** was not detected when dimethyl 2-(4-methoxyphenyl)cyclopropane-1,1-dicarboxylate **2c** was used as the substrate, perhaps the catalyst was poisoned by the coordination with the methoxy group on **2c**. In most cases, the electron-withdrawing group at C1 position and the electron-donating group at C2 position of the major isomers are oriented in the

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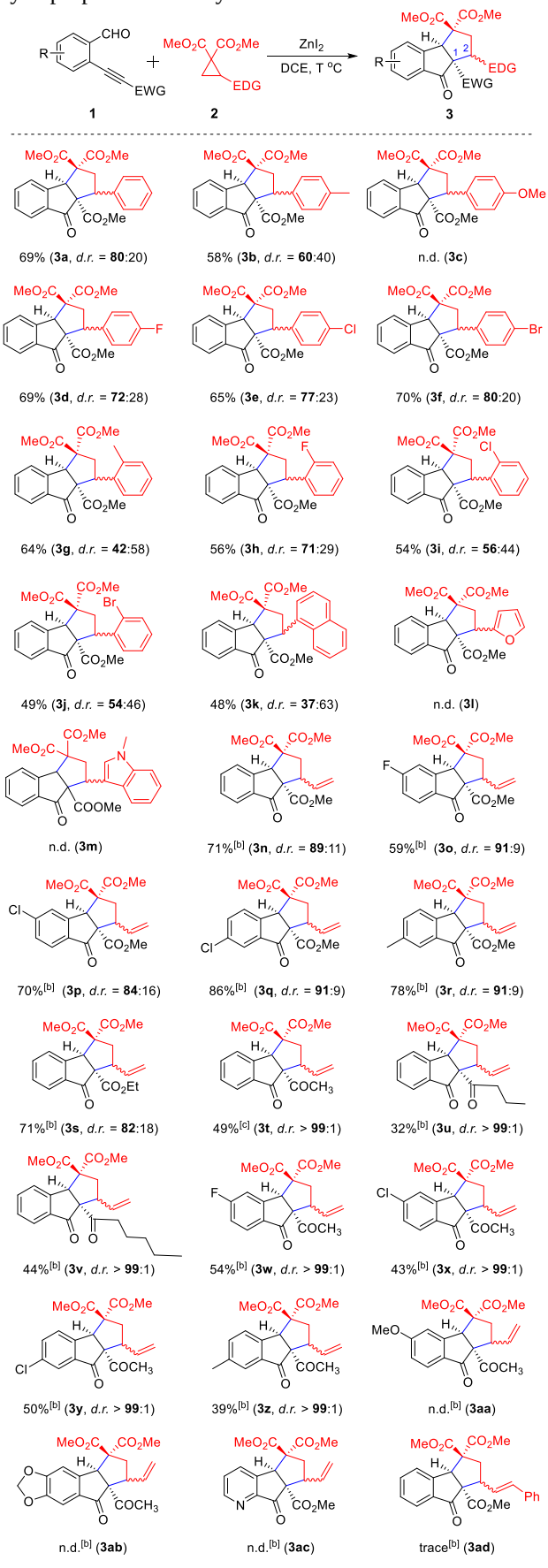
Table 2. Substrate Scope of Donor-Acceptor Cyclopropanes with Enynals.[a]



[a] The typical reaction of **1** (0.20 mmol, 0.1 M), **2** (0.24 mmol) was carried out using 50 mol% ZnI_2 as the catalyst under N_2 at 60 °C for 12 h; The yield is isolated one; The *d.r.* refers to the ratio of diastereomer, and the major isomer is the one where the EWG group at C1 position and the EDG group at C2 position oriented in the opposite direction.

[b] The reaction of **1** (0.20 mmol), **2** (0.30 mmol) was carried out at 40 °C for 12h;

[c] The reaction of **1** (0.20 mmol), **2** (0.30 mmol) was carried out at RT for 24h.

opposite directions. In the case of **3k**, the ester group (C1) and naphthyl group (C2) existing in the major isomer are oriented in the same direction, which might be attributed to the greater steric hindrance of naphthyl group. It was found that the heteroaromatic cyclopropanes were not tolerated in this reaction (**3l-m**). In addition to aryl group, a vinyl group could also be utilized as an electron-donating substituent for the donor-acceptor cyclopropanes, affording the desired product **3n** in 71% yield. The substrate scope in regards to enynals bearing different groups on the alkyne or the benzene ring was further examined. As expected, a series of desired vinyl-substituted indanone-fused cyclopentanes (**3n-z**) can be obtained in 32-86% yields. It is noteworthy that the reactions with enynals bearing acyl group on the alkyne displayed excellent diastereoselectivies (**3t-z**, *d.r.* > 99:1). The enynals with ester group on the alkyne (**3n-s**, 59-86%) displayed better performances than those with acyl group (**3t-z**, 32-54%). Furthermore, the major diastereomer of **3n** was also verified by the X-ray diffraction analysis (See **3n** in SI for detail).[13] The reactions were unsuccessful for the enynals with alkyoxy groups on the benzene ring (**3aa-ab**). Besides, the enynal tethered with a heteroaryl was also ineffective for the transformation (**3ac**). The cyclopropane with an internal vinyl substituent was not a suitable substrate (**3ad**). Replacing the donor-acceptor cyclopropane with aziridine failed to give the desired product either.[14]

The vinyl group of the indanone-fused cyclopentanes **3n-z** could be further converted into different functional groups through the well-known transformations. Taking **3n** as an example (Scheme 3), the vinyl group can be coupled with iodobenzene through Heck reaction[15], affording the desired product **3ad** in 63% yield (Scheme 3, eq. 1). In addition to the cross coupling reaction, the vinyl group of **3k** could be reduced to ethyl group by Pd-C/H_2,[16] giving the desired product **4** in 72% yield (eq. 2). Moreover, the vinyl group could be selectively oxidized into an acyl group and expoxide ring under Wacker oxidation[17] condition and in the presence of *m*-CPBA as oxidant[18], respectively, producing the corresponding products **5** and **6**[19] in good yields.

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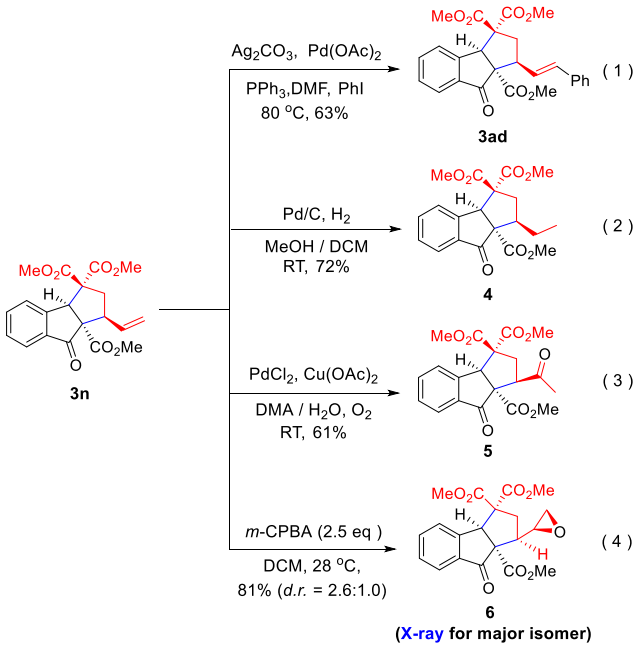
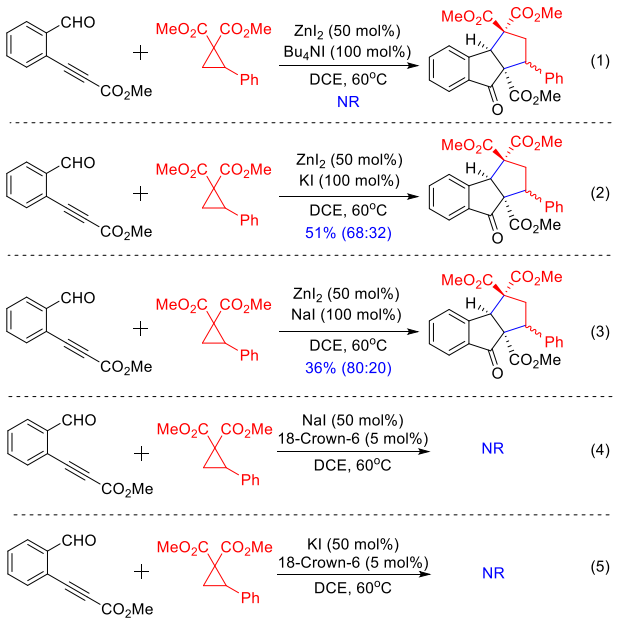


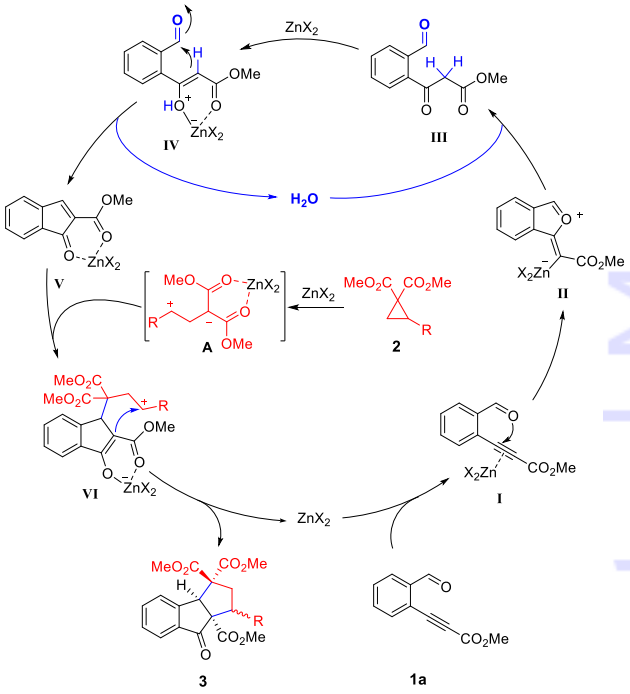
Scheme 3. Synthetic Transformations of **3k**.

To understand the role of the iodide, several control experiments were conducted (Scheme 4). Firstly, the reaction was completely depressed when 1.0 equivalent of Bu_4NI was used as an additive under the standard condition (Scheme 4, eq.1), indicating that the free iodide (I^-) ion might poison the catalyst through the coordination with the metal center. Secondly, the addition of 1.0 equivalent of KI or NaI to the reaction has a negative effect on the catalytic performance, the yields have been cut down to 51% and 36%, respectively (eqs. 2-3). Thirdly, instead of ZnI_2, the combination of KI or NaI with 18-crown-6 can't promote the reaction at all (eqs. 4-5).



Scheme 4. Control Experiments for the Role of the Iodide.

Based on the previous reports for donor-acceptor cyclopropanes[9-11] and our previous work on the enynal chemistry,[8a-b] a plausible mechanism was then proposed as shown in Scheme 5. An initial activation of alkyne **1a** through a [Zn]-π complex **I** could produce the 5-*exo-dig* intermediate **II**,[20] followed by a hydrolysis reaction, leading to the formation of the ketone ester **III** in the presence of adventitious and catalytic water. A sequential keto-enol tautomerism/Knoevenagel condensation reaction yielded the key intermediate indenone **V** and water was released for the next hydrolysis reaction. On the other hand, the 1,3-dipole **A** was generated *in situ* from the ring-opening reaction of the donor-acceptor cyclopropane **2** with the aid of zinc salt. Eventually, a [3+2] cycloaddition reaction between the indenone **V** and 1,3-dipole **A** occurred to furnish the desired product **3**.



Scheme 5. Proposed Mechanism.

In summary, we have developed an efficient one-pot approach to the synthesis of indanone-fused cyclopentanes from the reaction of electron-deficient enynals (**1**) and donor-acceptor cyclopropanes (**2**) *via* a sequential hydrolysis/Knoevenagel condensation/ [3+2] cycloaddition. The desired indanone-fused cyclopentanes were obtained in good yields. This method featured with mild reaction conditions and broad substrate scope, which is especially useful for the synthesis of complex molecules containing indanone-fused cyclopentanes moiety. Moreover, the products could be further converted into compounds with different functional groups through the well-known transformations.

Experimental Section

General Procedure for Preparation of Aryl cyclopropanes 2a-m. [21]

The cyclopropanes **2a-m** were synthesized from the corresponding aldehydes through a standard synthetic sequence of Knoevenagel/Corey-Chaykovsky reactions.

General Procedure for Preparation of Dimethyl 2-vinylcyclopropane-1,1-dicarboxylate 2n. [10d]

Dimethyl malonate (1.0 eq.) and 1, 4-dibromobut-2-ene (1.0 eq.) were added to a round bottom flask with a stir bar under an atmosphere of nitrogen. Tetrahydrofuran (0.2 M) and cesium carbonate (2.5 eq.) were added afterwards. The reaction mixture was then heated to 60 °C overnight. After cooling down to room temperature, the reaction mixture was filtered over celite and washed with diethyl ether. The organic phase was washed with saturated aqueous $NaHCO_3$, followed by water and brine. After being dried over $MgSO_4$, the solvent was removed under reduced pressure. The crude product was purified by means of silica gel chromatography to give **2n**.

General methods for synthesis of indanone-fused cyclopentanes 3.

To a solution of cyclopropane **2** in DCE was added ZnI_2 at room temperature and then the appropriate enynal **1**. The resulting reaction mixture was stirred at 40 ºC or 60 ºC overnight. After completion of the reaction, the solvent was removed under reduced pressure and the crude product was subjected to silica gel column chromatography to afford products **3**.

Acknowledgements

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Cascade One-Pot Synthesis of Indanone-Fused Cyclopentanes from the Reaction of Donor-Acceptor Cyclopropanes and Enynals via a Sequential Hydrolysis/Knoevenagel Condensation/ [3+2] Cycloaddition

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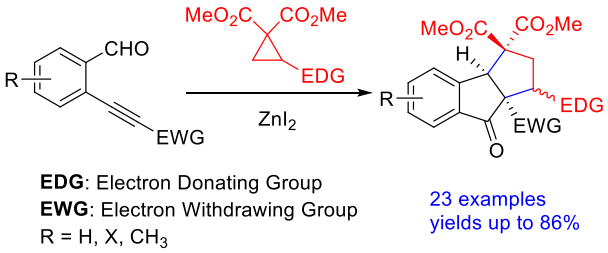

EDG: Electron Donating Group
EWG: Electron Withdrawing Group
R = H, X, CH_3

23 examples
yields up to 86%