

# Direct Copper-Free Domino Conjugate Addition-Cycloallylation using Organozinc Reagents

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**Abstract:** *The Direct Approach:* Enones possessing appendant allylic carbonates react directly with diorganozinc reagents in the presence of zinc diiodide [ZnI<sub>2</sub>] to provide 5- and 6-membered ring products of tandem or domino conjugate addition-cycloallylation in good to excellent yield. In a related copper-

free transformation, allylic carbonates are found to engage in direct allylic substitution with diorganozinc reagents.

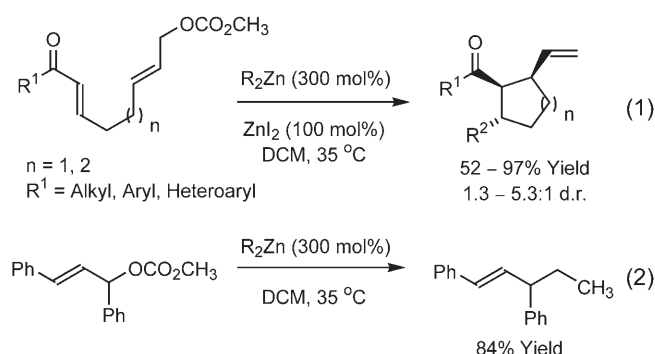
**Keywords:** allylic substitution; catalysis; C–C bond formation; domino reactions; organozinc reagents

## Introduction

The development of “tandem,” “cascade” or “domino” C–C bond forming processes remains at the forefront of research, as such transformations promote large increases in molecular complexity.<sup>[1,2]</sup> As part of a broad program in catalytic reaction development, we have examined conjugate addition-electrophilic trapping<sup>[3]</sup> as a modular means of devising catalytic processes wherein sequential construction of two C–C bonds is accompanied by ring formation. Through variation of the nucleophilic initiator and terminal electrophile, a diverse family of conjugate addition-cyclization reactions has been devised.<sup>[4–7]</sup> These include highly diastereoselective Co-catalyzed conjugate reduction-aldol and Michael cyclizations mediated by silane,<sup>[4]</sup> Rh-catalyzed conjugate reduction-aldol cyclizations mediated by hydrogen,<sup>[5]</sup> diastereo- and enantioselective Rh-catalyzed conjugate addition-aldol cyclizations employing arylboronic acids,<sup>[6]</sup> as well as Cu-catalyzed conjugate addition of diorganozinc reagents with subsequent aldol, Blaise–Thorpe–Ziegler, Dieckmann and Michael cyclizations.<sup>[7]</sup> Beyond the transformations developed in our lab, several elegant examples of tandem or “domino” processes predicated on metal-catalyzed conjugate addition-electrophilic trapping have been reported by others.<sup>[8,12–16]</sup>

Recently, the development of catalytic methods for the direct<sup>[9]</sup> and indirect<sup>[10]</sup> asymmetric allylation of ketones has received considerable attention. In con-

nection with our interest in catalytic conjugate addition-electrophilic trapping,<sup>[3–6]</sup> the direct allylation of ketone enolates that arise upon enone conjugate addition was examined. It is known that zinc enolates produced in the course of copper-catalyzed conjugate addition<sup>[11]</sup> may be trapped by aldehydes,<sup>[12]</sup> tethered halides and tosylates,<sup>[13]</sup> oxocarbenium ions (by way of acetal decomposition),<sup>[14]</sup> and allylic carboxylates.<sup>[12a,15,16]</sup> All of these transformations involve capture of stoichiometrically preformed zinc enolates and, in the latter case, allylation is achieved by exposing the preformed zinc enolate to an allylic acetate in the presence of a palladium catalyst. However, related conjugate addition-cyclizations onto tethered enones, ketones, esters and nitriles establish that enolate preformation is not a precondition for such anionic cascades.<sup>[6]</sup> Indeed, here we disclose that conjugate addition-intramolecular allylation requires neither a copper nor palladium catalyst.<sup>[17]</sup> Both primary and secondary organozinc reagents react directly with mono-enone mono-allylic carbonates to afford 5- and 6-membered ring products of domino conjugate addition-allylation [Eq. (1)]. Additionally, we find that allylic carbonates engage in direct substitution with diorganozinc reagents under copper-free conditions [Eq. (2)].<sup>[18]</sup>



## Results and Discussion

Our studies began with an examination of mono-ene mono-allylic carbonate **1a**. Exposure of **1a** to Et<sub>2</sub>Zn (300 mol%) in the presence of Cu(OTf)<sub>2</sub> (2.5 mol%) and (EtO)<sub>3</sub>P (5 mol%) at –78 °C in dichloromethane solvent (0.1 M) results in conjugate addition without cyclization onto the tethered allylic carbonate. However, when the reaction was allowed to warm to ambient temperature, a 71% isolated yield (5.2:1 *dr*) of the conjugate addition-cycloallylation product **1b** was obtained (Table 1, entry 1). At this point, control experiments were performed and a significant background reaction was revealed: cycloallylation product **1b** is formed in 14% isolated yield (3.4:1 *dr*) when the reaction is conducted at ambient temperature in the *absence* of the copper catalyst (Table 1, entry 2). In the interest of optimizing this copper-free process, the effect of various additives was examined. Eventually it was found that reactions conducted in the presence of ZnI<sub>2</sub> proceed with great-

**Table 1.** Conjugate addition-cycloallylation of **1a** using Et<sub>2</sub>Zn.<sup>[a]</sup>

Reaction scheme: **1a** (Ph-CH=CH-CH<sub>2</sub>-CH<sub>2</sub>-OCO<sub>2</sub>CH<sub>3</sub>) reacts with Et<sub>2</sub>Zn (300 mol%) and a catalyst or additive in DCM at T °C to form **1b** (Ph-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH=CH<sub>2</sub>).

| Entry | Catalyst/Additive                          | T [°C]    | [DCM] | Yield <b>1b</b> ( <b>1a</b> ) | <i>dr</i> |
|-------|--------------------------------------------|-----------|-------|-------------------------------|-----------|
| 1     | Cu(OTf) <sub>2</sub> , P(OEt) <sub>3</sub> | –78 to 25 | 0.1 M | 71%                           | 5.2:1     |
| 2     | —                                          | 25        | 0.1 M | 14%                           | 3.4:1     |
| 3     | ZnI <sub>2</sub> (25 mol%)                 | 25        | 0.1 M | 41%                           | 3.4:1     |
| 4     | ZnI <sub>2</sub> (100 mol%)                | 25        | 0.1 M | 54%                           | 3.5:1     |
| 5     | ZnI <sub>2</sub> (100 mol%)                | 25        | 0.2 M | 50%                           | 4.0:1     |
| 6     | Bu <sub>4</sub> NI (100 mol%)              | 25        | 0.1 M | 5%                            | 1.6:1     |
| 7     | Zn(OTf) <sub>2</sub> (100 mol%)            | 25        | 0.1 M | 41% (28%)                     | 2.4:1     |
| 8     | —                                          | 35        | 0.1 M | 58%                           | 5.2:1     |
| 9     | ZnI <sub>2</sub> (100 mol%)                | 35        | 0.1 M | 72%                           | 5.2:1     |
| 10    | ZnI <sub>2</sub> (100 mol%)                | 50        | 0.1 M | 59%                           | 3.9:1     |

<sup>[a]</sup> See experimental section for detailed experimental procedures.

er efficiency.<sup>[19]</sup> Indeed, the yield of **1b** is increased from 14% to 54% when the reaction is conducted using one equivalent of ZnI<sub>2</sub> (Table 1, entry 4). Other sources of iodide ion, such as Bu<sub>4</sub>NI, suppress the reaction (Table 1, entry 6). In contrast, the addition of zinc(II) ion, for example Zn(OTf)<sub>2</sub>, appears to be generally beneficial, and ZnI<sub>2</sub> is the best promoter among those screened (Table 1, entry 7). A slight increase in temperature to 35 °C was also found to facilitate conjugate addition-cycloallylation. The isolated yield of **1b** is 58% and 72% for reactions conducted in the absence and presence of ZnI<sub>2</sub>, respectively, at 35 °C (Table 1, entries 8 and 9). The latter reaction conditions represent our standard protocol for conjugate addition-cycloallylation (Table 1, entry 9).

To explore the scope of this process, mono-ene mono-allylic carbonates **1a–7a** were exposed to the diorganozinc reagent (300 mol%) in the presence of ZnI<sub>2</sub> (100 mol%) at 35 °C in DCM (0.1 M). For each substrate, reactions with Et<sub>2</sub>Zn and *i*-Pr<sub>2</sub>Zn were examined. As demonstrated by the cyclizations of substrates **1a** and **2a**, both 5- and 6-membered ring formation is possible (Table 2, entries 1 and 2). Heteroaromatic enones **3a** and **4a**, which incorporate 2-furyl and 3-indolyl residues, participate in the cyclization (Table 2, entries 3 and 4), as do aliphatic enones **5a** and **6a** (Table 2, entries 5 and 6). Interestingly, the α,β-unsaturated ester **7a** does not cyclize upon exposure to Et<sub>2</sub>Zn. Rather, the product of allylic substitution **7b**, in which the enone moiety remains intact, was obtained in 35% yield. However, use of *i*-Pr<sub>2</sub>Zn, which is more reactive with respect to conjugate addition, provides the cyclized product **7c** in good yield (Table 2, entry 7). Diastereoselectivities range from 1.3–5.2:1. The relative stereochemistry of the five- and six-membered ring products **1b,c–7b,c** was determined as follows. Hydrogenation of the five-membered ring product **1b** generates a mixture of two diastereomers. The non-symmetric diastereomer **1d** appears as the major isomer and the symmetric diastereomer **1e** appears as the minor isomer. The stereochemical assignment of the remaining five-membered ring products is made in analogy to the stereochemical assignment of **1b**. The stereochemical assignment of the six-membered ring products is based upon evaluation of the coupling constants in the <sup>1</sup>H NMR. For example, in the <sup>1</sup>H NMR spectrum of compound **2b**, proton H<sub>a</sub> appears as a triplet at δ = 3.05 ppm with a coupling constant *J*<sub>a,b</sub> = *J*<sub>a,c</sub> = 10.8 Hz. These data suggest a *trans*-diaxial relationship between the methine hydrogens H<sub>a</sub>, H<sub>b</sub>, and H<sub>c</sub> (Scheme 1, *top*). A plausible model enabling prediction of relative stereochemistry involves addition of the *Z*-enolate to the tethered allylic carbonate, which resides in an extended conformation (Scheme 1, *bottom*).

The divergent outcome observed in the reaction of enoate **7a** with Et<sub>2</sub>Zn *versus* *i*-Pr<sub>2</sub>Zn merited further

**Table 2.** Conjugate addition-cycloallylation **1a–7a** employing Et<sub>2</sub>Zn and *i*-Pr<sub>2</sub>Zn.<sup>[a]</sup>

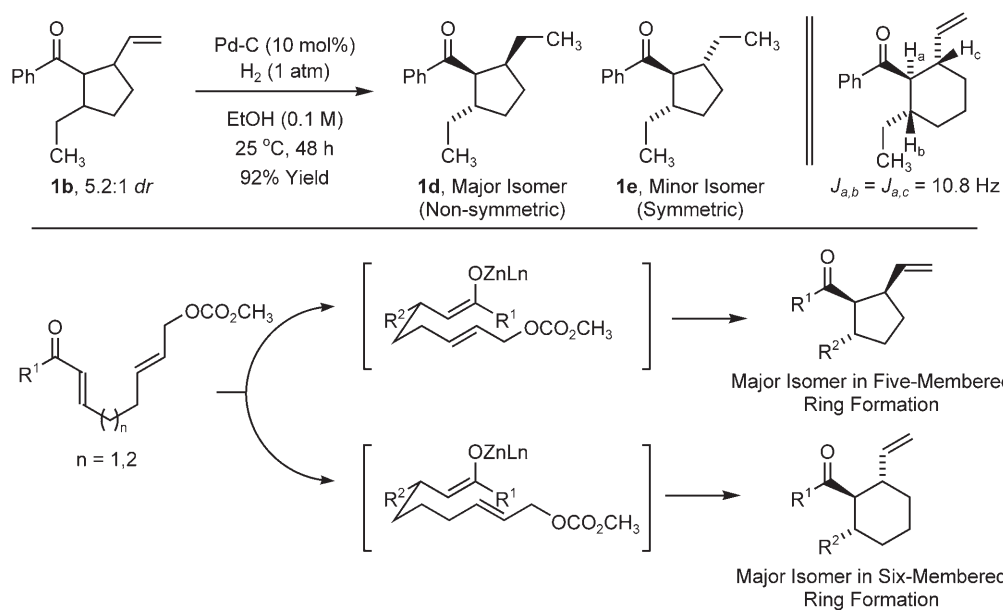
| Entry | Substrate | R <sub>2</sub> Zn            | Product | Yield (dr)  |
|-------|-----------|------------------------------|---------|-------------|
| 1     |           | Et <sub>2</sub> Zn           |         | 72% (5.2:1) |
|       |           | <i>i</i> -Pr <sub>2</sub> Zn |         | 97% (3.8:1) |
| 2     |           | Et <sub>2</sub> Zn           |         | 60% (2.5:1) |
|       |           | <i>i</i> -Pr <sub>2</sub> Zn |         | 78% (1.4:1) |
| 3     |           | Et <sub>2</sub> Zn           |         | 71% (3.1:1) |
|       |           | <i>i</i> -Pr <sub>2</sub> Zn |         | 80% (2.6:1) |
| 4     |           | Et <sub>2</sub> Zn           |         | 52% (2.6:1) |
|       |           | <i>i</i> -Pr <sub>2</sub> Zn |         | 54% (2.9:1) |
| 5     |           | Et <sub>2</sub> Zn           |         | 66% (4:1)   |
|       |           | <i>i</i> -Pr <sub>2</sub> Zn |         | 75% (4:1)   |
| 6     |           | Et <sub>2</sub> Zn           |         | 61% (1.3:1) |
|       |           | <i>i</i> -Pr <sub>2</sub> Zn |         | 87% (1.5:1) |
| 7     |           | Et <sub>2</sub> Zn           |         | 35%         |
|       |           | <i>i</i> -Pr <sub>2</sub> Zn |         | 77% (2.6:1) |

<sup>[a]</sup> See experimental section for detailed experimental procedures.

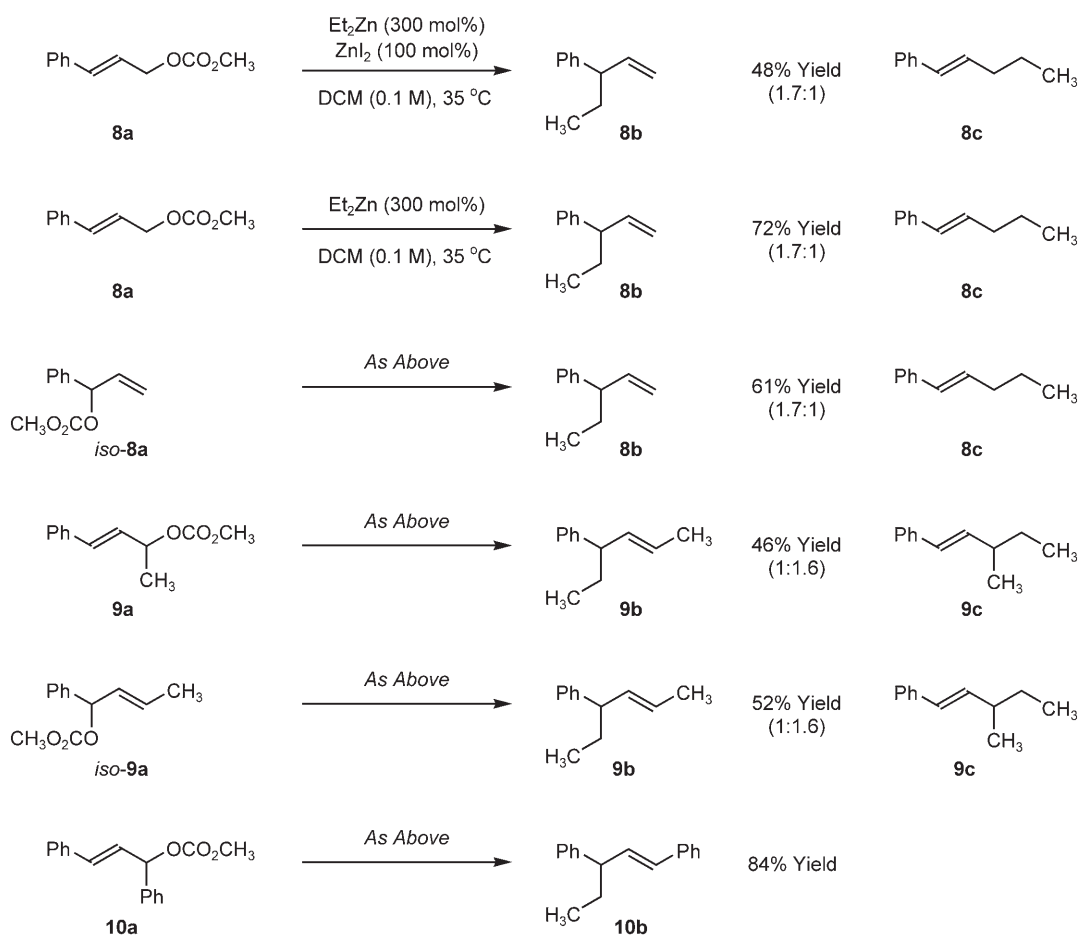
investigation in view of the fact that direct substitution reactions of allylic acetates or allylic carbonates with diorganozinc reagents or zinc enolates, to our knowledge, has not been described.<sup>[18]</sup> Surprisingly, direct substitution of methyl carbonate **8a** occurs spontaneously upon exposure to Et<sub>2</sub>Zn (300 mol%) in the presence of ZnI<sub>2</sub> (100 mol%) to deliver the products of allylic substitution **8b** and **8c** in 48% yield as a 1.7:1 mixture of regioisomers, respectively. The yield of **8b** and **8c** is increased to 72% if ZnI<sub>2</sub> is omitted from the reaction. In order to evaluate the nature of the reactive intermediate, the regioisomeric carbonate *iso*-**8a** was exposed to Et<sub>2</sub>Zn under identical conditions in the absence of ZnI<sub>2</sub>. The products of allylic substitution **8b** and **8c** were produced in 61% yield as a 1.7:1 mixture of regioisomers. Similarly, **9a** and *iso*-**9a** were exposed to Et<sub>2</sub>Zn under identical conditions to produce allylic substitution products **9b** and **9c**. In each case, a 1:1.6 ratio was observed. These data suggest intervention of a common reactive intermediate, such as a zinc- $\pi$ -allyl, or possibly an equimolar distribution of  $\sigma$ -allyl haptomers which rapidly equilibrate through the intermediacy the  $\pi$ -allyl haptomer. As demonstrated by the reaction of allylic carbonate **10a**, this method is preparatively useful in the case of systems possessing identical allylic termini. Corresponding reactions of allylic acetates gave diminished yields of substitution product (Scheme 2).<sup>[20]</sup>

## Conclusions

In summary, through the use of enone-electrophile templates, one may systematically evaluate the reactivity of various transition metal enolates, thereby discovering new patterns of reactivity and, ultimately, new C–C coupling processes. In the present study, we find that diorganozinc reagents engage enones in direct conjugate addition reactions.<sup>[17]</sup> More surprisingly, the resulting zinc enolates engage appendant allylic carbonates in S<sub>N</sub>2' type substitution reactions in the absence of a copper or palladium catalyst.<sup>[12a,15,16]</sup> Finally, in a related copper-free transformation, allylic carbonates are found to participate in direct allylic substitution reactions with the diorganozinc reagent, Et<sub>2</sub>Zn.<sup>[18]</sup> The new patterns of reactivity uncovered by this study set the stage for the development of corresponding stereoselective variants of the transformations reported herein.<sup>[17d]</sup>



**Scheme 1.** Top: Stereochemical assignment of compounds **1b** and **2b**. Bottom: Proposed stereochemical model.



**Scheme 2.** Direct substitution of allylic carbonates **8a**, *iso-8a*, **9a**, *iso-9a*, and **10a** by diethylzinc.

## Experimental Section

See Supporting Information for spectroscopic data.

### Carbonic Acid Methyl 8-Oxo-8[1-(toluene-4-sulfonyl)-1*H*-indol-3-yl]-octa-2,6-dienyl Ester (4a)

To a solution of carbonic acid 8-(1*H*-indol-3-yl)-8-oxo-octa-2,6-dienyl methyl ester<sup>[16b]</sup> (240 mg, 0.76 mmol, 100 mol%) at 0 °C in dichloromethane (4.0 mL) were added tosyl chloride (220 mg, 1.15 mmol, 150 mol%), triethylamine (0.16 mL, 1.15 mmol, 150 mol%) and a catalytic amount of DMAP (9 mg, 0.07 mmol, 10 mol%). The reaction mixture was stirred at ambient temperature for 2 h and quenched with aqueous ammonium chloride solution and extracted with dichloromethane (2 × 20 mL). The organic layer was washed with brine solution (20 mL), dried (Na<sub>2</sub>SO<sub>4</sub>), filtered and the resulting liquor was concentrated under vacuum. Purification of the oily residue by flash column chromatography (SiO<sub>2</sub>: 20% ethyl acetate:hexanes, *R*<sub>f</sub>=0.25) provides the title compound as a yellow solid, mixture of *E*:*Z* (8:1) isomers; yield: 330 mg (0.70 mmol, 92%).

### General Procedure for Tandem Conjugate Addition–Cycloallylation Reaction with Diorganozinc Reagents; Preparation of (2-Ethyl-5-vinylcyclopentyl)phenylmethanone (1b)

To a suspension of the substrate **1a**<sup>[21]</sup> (50 mg, 0.18 mmol, 100 mol%) and zinc iodide (58 mg, 0.18 mmol, 100 mol%) in dichloromethane at 0 °C in a 15-mL sealed tube under argon atmosphere was added a 1.0 M diethylzinc solution in hexanes (0.54 mL, 0.54 mmol, 300 mol%) over a period of 5 min. Once the addition was complete, the reaction vessel was flushed with argon, sealed tightly and the reaction mixture was stirred at 35 °C for 10.5 h. The reaction mixture was cooled to room temperature, quenched with four drops of water and stirred for 30–40 min. The reaction mixture was filtered through a pad of celite and the resulting liquor was concentrated under vacuum. Purification of the oily residue by flash column chromatography (SiO<sub>2</sub>: 3% diethyl ether:hexanes, *R*<sub>f</sub>=0.30) provides the title compound as a colorless oil, 5.2:1 mixture of diastereomers; yield: 30 mg (0.13 mmol, 72%).

### (2-Isopropyl-5-vinylcyclopentyl)phenylmethanone (1c)

In accordance with the general procedure, substrate **1a** (50 mg, 0.18 mmol, 100 mol%) was exposed to diisopropylzinc (0.54 mL, 0.54 mmol, 300 mol%) and zinc iodide (58 mg, 0.18 mmol, 100 mol%). Purification by flash column chromatography (SiO<sub>2</sub>: 2% diethyl ether:hexanes, *R*<sub>f</sub>=0.3) provides the title compound as a colorless oil, 3.8:1 mixture of diastereomers; yield: (43 mg, 0.18 mmol, 97%).

### (2-Ethyl-6-vinyl-cyclohexyl)phenylmethanone (2b)

In accordance with the general procedure, substrate **2a** (100 mg, 0.36 mmol, 100 mol%) was exposed to diethylzinc (1.04 mL, 1.10 mmol, 300 mol%) and zinc iodide (110 mg, 0.36 mmol, 100 mol%). Purification by flash column chro-

matography (SiO<sub>2</sub>: 2% diethyl ether:hexanes, *R*<sub>f</sub>=0.24) provides the title compound as a colorless oil, 2.5:1 mixture of diastereomers; yield: 50 mg (0.21 mmol, 60%).

### (2-Isopropyl-6-vinylcyclohexyl)phenylmethanone (2c)

In accordance with the general procedure, substrate **2a** (50 mg, 0.17 mmol, 100 mol%) was exposed to diisopropylzinc (0.52 mL, 0.52 mmol, 300 mol%) and zinc iodide (55 mg, 0.17 mmol, 100 mol%). Purification by flash column chromatography (SiO<sub>2</sub>: 2% diethyl ether:hexanes, *R*<sub>f</sub>=0.26) provides the title compound as a colorless oil, 1.4:1 mixture of diastereomers; yield: 33 mg (0.13 mmol; 78%).

### (2-Ethyl-5-vinylcyclopentyl)furan-2-ylmethanone (3b)

In accordance with the general procedure, substrate **3a** (66 mg, 0.27 mmol, 100 mol%) was exposed to diethylzinc (0.80 mL, 0.80 mmol, 300 mol%) and zinc iodide (85 mg, 0.27 mmol, 100 mol%). Purification by flash column chromatography (SiO<sub>2</sub>: 5% ethyl acetate:hexanes, *R*<sub>f</sub>=0.30) provides the title compound as a yellow oil, 3.1:1 mixture of diastereomers; yield: 41 mg (0.19 mmol, 71%).

### (2-Isopropyl-5-vinylcyclopentyl)furan-2-ylmethanone (3c)

In accordance with the general procedure, substrate **3a** (76 mg, 0.31 mmol, 100 mol%) was exposed to diisopropylzinc (0.92 mL, 0.92 mmol, 300 mol%) and zinc iodide (98 mg, 0.31 mmol, 100 mol%). Purification by flash column chromatography (SiO<sub>2</sub>: 5% ethyl acetate:hexanes, *R*<sub>f</sub>=0.30) provides the title compound as a yellow oil, 2.6:1 mixture of diastereomers; yield: 59 mg (0.29 mmol, 80%).

### (2-Ethyl-5-vinylcyclopentyl)-[1-(toluene-4-sulfonyl)-1-*H*-indol-3-yl]methanone (4b)

In accordance with the general procedure, substrate **4a** (50 mg, 0.11 mmol, 100 mol%) was exposed to diethylzinc (0.32 mL, 0.32 mmol, 300 mol%) and zinc iodide (34 mg, 0.11 mmol, 100 mol%). Purification by flash column chromatography (SiO<sub>2</sub>: 5% ethyl acetate:hexanes, *R*<sub>f</sub>=0.23) provides the title compound as a yellow oil, 2.6:1 mixture of diastereomers; yield: 23 mg (0.05 mmol, 51%).

### (2-Isopropyl-5-vinylcyclopentyl)-[1-(toluene-4-sulfonyl)-1-*H*-indol-3-yl]methanone (4c)

In accordance with the general procedure, substrate **4a** (67 mg, 0.14 mmol, 100 mol%) was exposed to diisopropylzinc (0.43 mL, 0.43 mmol, 300 mol%) and zinc iodide (46 mg, 0.14 mmol, 100 mol%). Purification by flash column chromatography (SiO<sub>2</sub>: 5% ethyl acetate:hexanes, *R*<sub>f</sub>=0.26) provides the title compound as a yellow oil, 2.9:1 mixture of diastereomers; yield: 32 mg (0.07 mmol, 54%).

### (2-Ethyl-5-vinylcyclopentyl)ethanone (5b)

In accordance with the general procedure, substrate **5a** (80 mg, 0.38 mmol, 100 mol%) was exposed to diethylzinc (1.1 mL, 1.13 mmol, 300 mol%) and zinc iodide (120 mg, 0.38 mmol, 100 mol%). Purification by flash column chro-

matography (SiO<sub>2</sub>: 5% diethyl ether:hexanes,  $R_f$ =0.30) provides the title compound as a colorless oil, 4:1 mixture of diastereomers; yield: 41 mg (0.24 mmol, 66%).

### (2-Isopropyl-5-vinylcyclopentyl)ethanone (5c)

In accordance with the general procedure, substrate **5a** (52 mg, 0.24 mmol, 100 mol%) was exposed to diisopropylzinc (0.73 mL, 0.73 mmol, 300 mol%) and zinc iodide (78 mg, 0.24 mmol, 100 mol%). Purification by flash column chromatography (SiO<sub>2</sub>: 3% diethyl ether:hexanes,  $R_f$ =0.30) provides the title compound as a yellow oil, 4.0:1 mixture of diastereomers; yield: 34 mg (0.18 mmol, 75%).

### Cyclopropyl-(2-ethyl-5-vinylcyclopentyl)methanone (6b)

In accordance with the general procedure, substrate **6a** (100 mg, 0.42 mmol, 100 mol%) was exposed to diisopropylzinc (1.26 mL, 1.26 mmol, 300 mol%) and zinc iodide (134 mg, 0.42 mmol, 100 mol%). Purification by flash column chromatography (SiO<sub>2</sub>: 5% diethyl ether: pentane,  $R_f$ =0.25) provides the title compound as a colorless oil, 1.3:1 mixture of diastereomers; yield: 52 mg (0.27 mmol, 61%).

### Cyclopropyl-(2-isopropyl-5-vinylcyclopentyl)methanone (6c)

In accordance with the general procedure, substrate **6a** (50 mg, 0.21 mmol, 100 mol%) was exposed to diisopropylzinc (0.63 mL, 0.63 mmol, 300 mol%) and zinc iodide (67 mg, 0.21 mmol, 100 mol%). Purification by flash column chromatography (SiO<sub>2</sub>: 5% diethyl ether: pentane,  $R_f$ =0.30) provides the title compound as a colorless oil, 1.5:1 mixture of diastereomers; yield: 40 mg (0.19 mmol, 87%).

### Deca-2,6-dienoic Acid Ethyl Ester (7b)

In accordance with the general procedure, substrate **7a** (48 mg, 0.19 mmol, 100 mol%) was exposed to diethylzinc (0.52 mL, 0.19 mmol, 300 mol%) and zinc iodide (62 mg, 0.19 mmol, 100 mol%). Purification by flash column chromatography (SiO<sub>2</sub>: 5% diethyl ether: pentane,  $R_f$ =0.28) provides the title compound as a pale yellow oil; yield: 22 mg (0.11 mmol, 35%).

### 2-Isopropyl-5-vinylcyclopentanecarboxylic Acid Ethyl Ester (7c)

In accordance with the general procedure, substrate **7a** (100 mg, 0.41 mmol, 100 mol%) was exposed to diisopropylzinc (1.27 mL, 1.27 mmol, 300 mol%) and zinc iodide (130 mg, 0.41 mmol, 100 mol%). Purification by flash column chromatography (SiO<sub>2</sub>: 5% ethylacetate:hexanes,  $R_f$ =0.24) provides the title compound as a colorless oil, 2.6:1 mixture of diastereomers; yield: 71 mg (0.33 mmol, 77%).

### (2,5-Diethylcyclopentyl)phenylmethanone (1d)

To a solution of compound **1b** (40 mg, 0.17 mmol, 100 mol%) in ethanol (2.0 mL) in a 10-mL round-bottomed

flask, was added a catalytic amount of palladium catalyst on charcoal (18 mg, 0.017 mmol, 10 mol%) and stirred under hydrogen atmosphere at ambient temperature for 48 h. The reaction mixture was filtered through a celite pad with the aid of ethyl acetate (20 mL). The organic layer was concentrated under vacuum. Purification by flash column chromatography (SiO<sub>2</sub>: 2% ethyl acetate:hexanes,  $R_f$ =0.30) provides the title compound as a colorless oil, 5:1 mixture of diastereomers; yield: 37 mg (0.16 mmol, 92%).

### General Procedure for the Allylic Substitution of Allylic Carbonates with Diorganozinc Reagents

In a 15-mL sealable test tube charged with carbonate **8a** (100 mg, 0.52 mmol, 100 mol%) was added dichloromethane (5.2 mL). The vessel was purged with argon gas and kept under a blanket of argon gas. The reaction mixture was cooled to 0°C and a 1.0M diethylzinc solution in hexanes (1.56 mL, 1.56 mmol, 300 mol%) was added over a period of 5 min. Once the addition was complete, the vessel was immediately sealed and the reaction mixture was warmed to 35°C. The reaction mixture was allowed to stir for 16 h, at which point 5 drops of water were added to the reaction mixture. The reaction mixture was filtered through a pad of silica gel with the aid of dichloromethane and the solution was concentrated under vacuum. Purification of the residue by flash column chromatography (SiO<sub>2</sub>: neat hexanes) provides **8b** and **8c**, 1.7:1 mixture of regioisomers; yield: 54 mg (0.36 mmol, 72%).

### 3-Phenyl-1-pentene (8b) and (E)-1-Phenyl-1-pentene (8c)

In accordance with the general procedure, substrate *iso-8a* (100 mg, 0.52 mmol, 100 mol%) was exposed to diethylzinc (1.56 mL, 1.56 mmol, 300 mol%). Purification by flash column chromatography (SiO<sub>2</sub>: neat hexanes,  $R_f$ =0.50) provides **8b** and **8c** as a colorless oil, 1.7:1 mixture of regioisomers; yield: 47 mg (0.31 mmol, 61%). The NMR data obtained for **8b** are identical to those previously reported.<sup>[21]</sup> The NMR data obtained for **8c** are identical to those previously reported.<sup>[22]</sup>

### (E)-4-Phenyl-2-hexene (9b) and (E)-1-Phenyl-3-methyl-1-pentene (9c)

In accordance with the general procedure, substrate **9a** (100 mg, 0.48 mmol, 100 mol%) was exposed to diethylzinc (1.45 mL, 1.45 mmol, 300 mol%). Purification by flash column chromatography (SiO<sub>2</sub>: neat hexanes,  $R_f$ =0.60) provides **9b** and **9c** as a colorless oil, 1:1.6 mixture of regioisomers; yield: 36 mg (0.22 mmol, 46%).

In accordance with the general procedure, substrate *iso-9a* (100 mg, 0.48 mmol, 100 mol%) was exposed to diethylzinc (1.45 mL, 1.45 mmol, 300 mol%). Purification by flash column chromatography (SiO<sub>2</sub>: neat hexanes,  $R_f$ =0.60) provides **9b** and **9c** as a colorless oil, 1:1.6 mixture of two regioisomers; yield: 41 mg (0.25 mmol, 52%). The NMR data for **9b** are identical to those previously reported.<sup>[23]</sup> The NMR data obtained for **9c** are identical to those previously reported.<sup>[24]</sup>

**(E)-1,3-Diphenyl-1-pentene (10b)**

In accordance with the general procedure, substrate **10a** (100 mg, 0.37 mmol, 100 mol%) was exposed to diethylzinc (1.19 mL, 1.19 mmol, 300 mol%). Purification by flash column chromatography (SiO<sub>2</sub>; neat hexanes, *R*<sub>f</sub> = 0.60) provides **10b** as a colorless oil; yield: 70 mg (0.31 mmol, 84%). The NMR data obtained for **10b** are identical to those previously reported.<sup>[25]</sup>

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