# Organic Letters

# Zinc(II)-Catalyzed [2+2+1] Annulation of Internal Alkenes, Diazooxindoles, and Isocyanates to Access Spirooxindoles

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the construction of multisubstituted spirooxindoles. This multicomponent transformation involves in situ generation of a sulfurcontaining spirocyclic intermediate from the [4+1] annulation of diazooxindole to sulfonyl isocyanate, which subsequently reacts as a toluene, 80 °C, No

1,3-dipole with the internal alkene, that is,  $\alpha$ -oxo ketene dithioacetal, to furnish a formal [2+2+1] annulation in a one-pot manner. This synthetic protocol features a low-toxicity main group metal catalyst, readily available reagents, and  $\leq$ 96% yields, offering an efficient route to multisubstituted spirooxindole derivatives.

ulticomponent reactions (MCRs) in which three or more Compounds react in a highly selective manner to construct complex molecules have attracted much attention in organic synthesis.<sup>1</sup> Atom economy, cost-effectiveness, and rapid assembly of complicated molecules from relatively simple building blocks are features of MCR processes. As one of the most versatile building blocks, diazo compounds have been employed in many multicomponent transformations, including carbene migratory insertion,<sup>2</sup> trapping of protic onium ylides with electrophiles,<sup>3</sup> and radical-mediated cascade reactions.<sup>4</sup> For instance, Wang et al. reported a Rh(II)-catalyzed relay carbene insertion and allylic alkylation process that afforded  $\alpha$ quaternary  $\alpha$ -amino acid derivatives.<sup>5a</sup> Gong and co-workers documented the synthesis of  $\beta$ -amino- $\alpha$ -hydroxyl acid derivatives via Rh(II)-initiated generation of oxonium ylide intermediates,<sup>5b</sup> and the Hu group achieved a three-component aminomethylation by trapping of zwitterionic intermediates derived from  $\alpha$ -diazo ketones with alcohols.<sup>6</sup> Recently, Doyle et al. reported cascade multicomponent Minisci reactions by generation of free radicals from diazo compounds.<sup>4</sup> These processes have expanded the application of diazo compounds for the construction of challenging molecules.7

Spirocycle scaffolds are important organic motifs,<sup>8</sup> and spirooxindole-dihydropyrrole frameworks are found in biologically active spirooxindole alkaloids (Figure 1).9 Thus, synthetic methodologies with diazo compounds through



Figure 1. Examples of biologically active spirooxindoles.

MCRs to rapidly assemble diverse spirooxindoles are highly desirable. Diazooxindoles have proven to be straightforward building blocks for establishing carbo- and heterocyclic frameworks with remarkable efficiency.<sup>8b,10</sup> For the synthesis of five-membered spirooxindole compounds, efforts have usually been devoted to [4+1] annulation processes,<sup>11</sup> and multicomponent reactions have been employed in recent years.<sup>7,12</sup> Wang et al. reported an acid-initiated [2+2+1] reaction by applying two 1,4-oxazepine molecules to react with diazooxindoles.<sup>13</sup> Recently, the Fan group realized a [3+1+1] annulation of N-phenoxyacetamide with two diazooxindole molecules.<sup>14</sup> In this regard, three different substrates could also be applied for the same purpose. Tan and co-workers conducted organocatalytic MCRs of diazooxindoles, nitrosoarenes, and nitroalkenes, in which the active intermediates were generated from diazooxindoles and nitroso compounds to be subsequently trapped by activated alkenes (Scheme 1a).<sup>15</sup> However, these methods are usually limited by the substrate scopes and low catalytic efficiencies.

During the continuous investigation of annulations of alkylthio-functionalized internal alkenes, we found that they could be employed for the construction of five-membered heterocycles.<sup>16</sup> Inspired by those reports on diazooxindoles and our previous relevant work on [4+1] annulations of these internal alkenes to access spirooxindoles, <sup>16b,17</sup> we envisioned a Lewis acid-catalyzed three-component [2+2+1] annulation of

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# Scheme 1. MCRs of Diazooxindoles for Spiro Compounds



 $\alpha$ -oxo ketene dithioacetals, diazooxindoles, and isocyanates for the construction of spirooxindole derivatives (Scheme 1b).

Initially, the reaction of an internal alkene, that is,  $\alpha$ -oxo ketene dithioacetal (1a), and diazo compound 3-diazooxindole (2a) with tosyl isocyanate (3a) was conducted to screen the reaction conditions (Table 1). In the presence of a noble metal

#### Table 1. Optimization of the Reaction Conditions<sup>a</sup>



<sup>a</sup>Conditions: 1a (0.2 mmol), 2a (0.6 mmol), 3a (0.6 mmol), catalyst (10 mol %), solvent (2.0 mL), 12 h, N<sub>2</sub>. <sup>b</sup>Determined by <sup>1</sup>H NMR analysis by using 1,3,5-trimethoxybenzene as the internal standard. <sup>c</sup>2a (0.4 mmol). <sup>d</sup>3a (0.4 mmol). <sup>e</sup>1a (0.3 mmol), 2a (0.9 mmol), and 3a (0.9 mmol). <sup>f</sup>Isolated yield in parentheses.

salt catalyst such as Rh(OAc)<sub>2</sub>, RhCl<sub>3</sub>, Pd(PPh<sub>3</sub>)<sub>4</sub>, PdCl<sub>2</sub>, or  $Pd(OAc)_{2}$ , diazo compound 2a was completely decomposed without generation of any desired product (see the Supporting Information for details). By means of a Lewis acid catalyst (10 mol %) of a transition metal, that is, FeCl<sub>2</sub>, FeCl<sub>3</sub>, CoCl<sub>2</sub>, NiCl<sub>2</sub>, or CuCl<sub>2</sub>, the 1:3:3 molar ratio reaction of internal alkene 1a, diazo compound 2a, and isocyanate 3a at 80 °C in toluene led to 21-63% yields of spirooxindole 4a (see the Supporting Information). To our delight, further screening of Lewis acids led to discovery of the most efficient catalyst, that is, low-toxicity Lewis acid ZnCl<sub>2</sub>, for the studied reaction, and 4a was thus formed in 94% yield (Table 1, entry 1). Zinc(II) salts such as  $ZnF_2$ ,  $ZnBr_2$ , and  $Zn(OTf)_2$  exhibited only poor to moderate catalytic activity (Table 1, entries 2-4, respectively). The suitable coordination strength and weaker steric hindrance of ZnCl<sub>2</sub> may benefit this annulation process. Other solvents such as 1,2-dichloroethane (DCE), 1,4-dioxane, and MeCN were also

tested, giving less efficient results (Table 1, entries 5–7, respectively). Variation of the temperature did not improve the reaction (Table 1, entries 8 and 9). Decreasing the loading of **2a** or **3a** diminished the product yield to 66-75% (Table 1, entry 10 or 11, respectively). Under the optimal conditions, a 92% isolated yield was achieved for **4a** (Table 1, entry 12). The molecular structure of **4a** was further confirmed by X-ray single-crystal structural determination (see Scheme 2 and the

# Scheme 2. Scopes of Internal Alkenes $\alpha$ -Oxo Ketene Dithioacetals (1)<sup>*a*</sup>

![](_page_1_Figure_13.jpeg)

<sup>a</sup>Conditions: 1 (0.3 mmol), 2a (0.9 mmol), 3a (0.9 mmol),  $ZnCl_2$  (0.03 mmol), toluene (3 mL), 80 °C, 12 h, N<sub>2</sub>. Isolated yields. <sup>b</sup>1a (3 mmol), 2a (9 mmol), 3a (9 mmol),  $ZnCl_2$  (0.3 mmol), toluene (20 mL), 16 h.

Supporting Information for details). It is noteworthy that chiral ligands such as (R)-MONOPHOS, (R)-(+)-1-(2-diphenylphosphino-1-naphthyl)isoquinoline, bis[(S)-4-benzyl-4,5-dihydrooxazol-2-yl]methane, and (S)-(+)-DTBM-SEGPHOS were also examined to regulate the optical activity of the product, but no enantioselectivity was observed (see the Supporting Information).

Next, the scopes of  $\alpha$ -oxo internal alkenes (1) were explored (Scheme 2). Gram-scale synthesis of 4a was achieved in 73% isolated yield. Obvious electronic and steric effects of the substituents on the aroyl moiety of  $\alpha$ -oxo ketene dithioacetals (1) were observed. 4-Electron-donating groups such as methyl, ethyl, and methoxy facilitated the reaction to form 4b-4d, respectively (92-96%), while 4-electron-withdrawing groups trifluoromethyl, chloro, and iodo had various impacts on the reaction, leading to target products 4e-4g, respectively, in 79-90% yields. Methyl and bromo groups at position 3 showed a mixed steric/electronic impact on the formation of 4h (85%) and 4i (79%); 2-methoxyl exhibited an obvious steric effect, and 2-fluoro compromised its steric/electronic effect to generate 4j (77%) and 4k (83%). Bulky 1-naphthyl-based  $\alpha$ -oxo ketene dithioacetal reacted to afford product 4l (77%), showing an obvious steric effect compared to the 2-naphthyl-based  $\alpha$ -oxo

ketene dithioacetal substrate to form product **4m** (84%). 2-Furanoyl- and 2-thienoyl-supported ketene dithioacetals also efficiently underwent the reaction to give **4n** (81%) and **4o** (90%), respectively. The alkylthio group in  $\alpha$ -oxo ketene dithioacetals (**1**) could be altered from methyl to ethyl and benzyl, resulting in products **4p** (89%) and **4q** (73%), respectively. Five-membered cyclic  $\alpha$ -benzoyl ketene dithioacetal **1r** did not react with **2a** and **3a** to produce the desired product **4r**, which suggests that the departure of the alkylthio group in internal alkene **1** is crucial for the completion of the annulation process. Somehow,  $\alpha$ -acetyl ketene dithioacetals **1s** reacted less efficiently to afford target product **4s** in 69% yield.

Then, the synthetic generality regarding the scopes of 3diazooxindoles (2) and isocyanates (3) was investigated (Scheme 3). The substituents on the nitrogen atom of the

![](_page_2_Figure_5.jpeg)

<sup>*a*</sup>Conditions: 1 (0.3 mmol), 2 (0.9 mmol), 3 (0.9 mmol),  $ZnCl_2$  (0.03 mmol), toluene (3 mL), 80 °C, 12 h, N<sub>2</sub>. Isolated yields.

indolyl ring could be altered from methyl to isopropyl, allyl, propargyl, and benzyl, resulting in target products 5a-5d, respectively, in 80-92% yields. Notably, N-unprotected and N-Boc (tert-butoxycarbonyl)-protected 3-diazooxindoles could not undergo the same type of reaction under the stated conditions, suggesting that the appropriate electron-donating capability of the N-heterocycle in 3-diazooxindoles (2) is required to render the desired annulation process.<sup>1</sup> А remarkable steric effect was observed from the 4-methyl group on the benzo ring of 3-diazooxindole, which completely inhibited the desired multicomponent reaction. However, no obvious steric effect was observed from electron-donating groups such as methyl and methoxyl and electron-withdrawing groups fluoro, chloro, and iodo at position 5, and the reaction gave 5f-5j in 72-94% yields. 6-Fluoro, 7-fluoro, and 7-chloro groups were also tolerant to render the corresponding functionalized diazooxindoles to efficiently undergo the reaction

to afford products 5k-5m, respectively (77-89%). By means of the synthetic protocol presented here, multisubstituted annulation products 5n-5r were synthesized in 77-84% yields by varying the electron-donating and -withdrawing groups in the  $\alpha$ -aroyl moieties of 1 in the case of using a 5-substituted 3diazooxindole substrate. Other diazo compounds such as diphenyldiazo-methane, ethyl phenyldiazoacetate, and diethyl diazomalonate were also tested in their reaction with 1a and 3a, but no desired spirooxindoles were detected, suggesting that the five-membered indolone substructure in the diazo compounds facilitates the studied multicomponent reaction. Isocyanates such as phenylsulfonyl isocyanate and 4-fluorobenzenesulfonyl isocyanate were also examined, effectively giving products 5s-5u (88-95%). It should be noted that benzyl, phenyl, and benzoyl isocyanates as well as benzenesulfonyl isothiocyanate could not undergo the same annulation with all of the substrates of types 1 and 2 under the stated conditions, suggesting that the strong electron-withdrawing property of the tosyl group in isocyanates is required and the suitable coordination mode of the isocyanate moiety is crucial for switching on the annulation process. The protocol generality was further investigated by using 3-diazoindolin-2-imines under the standard conditions, but the steric/electronic effect of the imine group hindered the annulation process without forming target product 5v.

Control experiments were conducted to probe the reaction pathway (Scheme 4). Separate treatment of  $\alpha$ -oxo ketene

![](_page_2_Figure_10.jpeg)

dithioacetal 1a with diazo compound 2a or isocyanates 3a under the standard conditions led to only partial decomposition of 2a or 3a with 1a unchanged, suggesting that 1a is not involved in the reaction initiation step. Diazo compounds have been reported to undergo [4+1] annulation with sulfonyl isocyanates.<sup>18</sup> A similar [4+1] annulation process was observed to generate the corresponding spirooxindole intermediates 6 (3-4% yields) from 2 and 3 with all of the substrates consumed completely (Scheme 4a). Compounds 6 were separated and structurally characterized by NMR and HRMS analysis (see the Supporting Information for details) and thus reacted with internal alkenes 1 under the standard conditions, forming products 4a (75%) and 5t (72%), respectively (Scheme 4b). These results have suggested that intermediates 6 are initially generated via a [4+1] annulation of 2 to 3 and then act as 1,3dipoles to react with internal alkenes 1 to furnish a formal [2+2+1] annulation process.

The Hammett correlation plot was drawn by investigating the kinetics of various *para*-substituted  $\alpha$ -benzoyl ketene dithioace-tals (1) under the standard conditions (Figure 2). This plot

![](_page_3_Figure_3.jpeg)

**Figure 2.** Hammett plot for the substitution in  $\alpha$ -benzoyl of ketene dithioacetals (1).

shows a negative slope value (-0.50), which suggests that internal alkenes 1 are activated via coordination of the  $\alpha$ carbonyl group to the zinc metal atom, and the electrondonating substituents on the aroyl moieties facilitate the annulation process. To further investigate the electronic effect of such *para* substituents, competition reactions of 1d/1e with 2a and 3a were conducted (eq 1). Formation of a 1.8:1 molar

![](_page_3_Figure_6.jpeg)

ratio mixture of 4d and 4e suggests that the *para* electrondonating groups enhance the activation of compounds 1. The kinetic isotope effect (KIE) was also measured, and a  $k_{\rm H}/k_{\rm D}$ value of 0.86 was obtained (eq 2; see the Supporting Information). This inverse secondary deuterium kinetic isotope effect reveals that internal alkenyl C–H cleavage is not involved in the rate-limiting step of the overall catalytic cycle.

A mechanism is proposed in Scheme 5. Activation of isocyanate 3 may occur through coordination of the carbonyl group of isocyanate 3 to the zinc metal center,<sup>19</sup> generating species **A**. Electrophilic **A** undergoes nucleophilic attack by

Scheme 5. Proposed Mechanism

![](_page_3_Figure_10.jpeg)

diazooxindole  $2^{15}$  and subsequent intramolecular cyclization to form [4+1] annulation intermediate 6 via species **B**. Tautomerism of species 6 results in 1,3-dipole **C** *in situ*. Activation of internal alkene 1 through coordination of its carbonyl and alkylthio groups to the zinc metal center renders the further reaction of species **C** with  $1.^{16d}$  Thus, species **E** is formed by an intramolecular [3+2] cycloaddition<sup>20</sup> of species **D** with regeneration of the zinc(II) catalyst.  $\beta$ -Elimination then occurs to give target [2+2+1] product 4 with loss of one molecule of mercaptan.

In summary, a concise zinc(II)-catalyzed [2+2+1] annulation of internal alkenes, diazooxindoles, and isocyanates has been successfully developed for the construction of multisubstituted spirooxindoles. This multicomponent reaction features use of a low-toxicity main group metal zinc(II) catalyst and can be efficiently applied with simple manipulation and broad substrate scopes.

# ASSOCIATED CONTENT

#### **Data Availability Statement**

The data underlying this study are available in the published article and its Supporting Information.

#### Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.orglett.3c00715.

Experimental materials and procedures, analytical data, and NMR spectra of compounds (PDF)

#### Accession Codes

CCDC 2159423 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data\_request/cif, or by emailing data\_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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#### Notes

The authors declare no competing financial interest.

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