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An efficient ZnO-catalyzed synthesis of novel indole-annulated thiopyrano-chromene derivatives via Domino Knoevenagel-hetero-Diels–Alder reaction

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ABSTRACT

An efficient synthesis of pentacyclic indole derivatives is achieved via domino Knoevenagel-hetero-Diels–Alder reactions of indolin-2-thiones and O-propargylated salicylaldehyde derivatives in CH_3CN in the presence of 10 mol % of ZnO as a heterogeneous catalyst. The products are formed in good to excellent yields.

The indole moiety is frequently encountered in medicinal chemistry and is considered to be a privileged scaffold.[1] Several compounds possessing an indole moiety show antitumor activity,[2] and can lead to inflammation and vessication of human skin.[3] Compounds containing a thiopyranoindole moiety are important because of their biological activity,[4] and various pentacyclic indole alkaloids such as reserpine, rauniticine, yohimbine, and aspidospermine show extensive bioactivity profiles.[5]

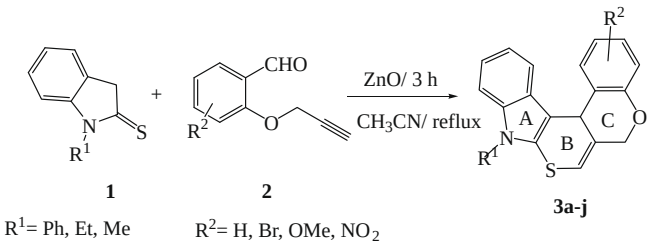
There are several examples of the synthesis of benzopyran and pyranobenzopyran moieties while those of their sulfur-containing analogs are rare.[6] A literature survey revealed that there are only a few reports on the synthesis of polycyclic pyranothiopyrans.[7]

An important objective in organic synthesis is the development of highly efficient synthetic procedures toward complex molecules. The hetero-Diels–Alder reaction represents an effective method for the synthesis of heterocyclic compounds, especially natural products.[8] In recent years, intramolecular-hetero-Diels–Alder reactions have been widely used in numerous reactions in organic synthesis, because of their economical and stereocontrolled nature.[9] These reactions allow the formation of two or more rings at once, avoiding sequential chemical transformations. However, it is a prerequisite that activating groups have to be built into dienophiles to achieve the desired reactivity.[10]

Recently, domino reactions have been used as highly efficient processes for the improvement of reaction efficiency.[11] Among these reactions, the domino Knoevenagel-hetero-Diels–Alder reaction is a very efficient process, especially in the area of heterocycles and natural products.[12]

For a long time, the use of alkynes in hetero-Diels–Alder reactions was limited because of the lower reactivity of unactivated alkynes compared to the corresponding alkenes. The use of different Lewis acids[13] provides new opportunities for various catalytic alkyne reactions. Furthermore, the surface of metal oxides exhibit both Lewis acid and Lewis base characters. This is typical of many metal oxides, especially TiO_2, Al_2O_3, and ZnO. They are excellent adsorbents for a wide variety of organic compounds, and increase the reactivity of the reactants.[14] ZnO is a very interesting metal oxide as it has surface properties which potentially favor diverse organic chemistry.[15]

Balalaie et al. recently described the domino Knoevenagel-hetero-Diels–Alder reaction (DKHDA) of several 1,3-dicarbonyl



1 **2** **3a-j**

R^1= Ph, Et, Me R^2= H, Br, OMe, NO_2

Scheme 1.

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Table 1
Effect of catalyst and solvent on the domino Knoevenagel-hetero-Diels–Alder reaction of **1a** and **2a**

Entry	Catalyst	Solvent	Temperature	Time (h)	Yield[a] (%)
1	—	PhMe	rt	48	33
2	—	CH_3CN	rt	48	35
3	—	H_2O	rt	48	0
4	—	PhMe	80 °C	5	38
5	—	CH_3CN	80 °C	5	42
6	CuI[b] (100%)	CH_3CN	Reflux	3	10
7	$ZrOCl_2$ (100%)	CH_3CN	Reflux	3	40
8	ZnO (100%)	CH_3CN	Reflux	3	90
9	ZnO (50%)	CH_3CN	Reflux	3	90
10	ZnO (10%)	CH_3CN	Reflux	3	90

[a] Yield of isolated product.
[b] Decomposition of **1a** took place in the presence of CuI.

compounds with O-propargylated salicylaldehyde derivatives for the synthesis of tetracycles with a pyran ring,[16] however, to the best of our knowledge, there is no report on the domino Knoevenagel-intramolecular-hetero-Diels–Alder reaction of indolin-2-thiones with O-propargylated salicylaldehydes. In the context of our general interest in ZnO-catalyzed organic synthesis,[17] and the synthesis of heterocyclic compounds using thioamides,[18] we herein report a highly efficient strategy for the preparation of polycyclic compounds **3a–j**, which consist of an indole ring (A), a dihydrothiopyran ring (B) annulated to a dihydrochromene ring (C) (Scheme 1).

The O-propargylated salicylaldehydes **2a–d** were prepared from the corresponding substituted salicylaldehydes in good to excellent yields via Williamson ether synthesis.[19] The reaction of compound **1a** with **2a** was used as a model to optimize the reaction conditions. The experimental results are summarized in Table 1.

Table 2
Domino Knoevenagel-hetero-Diels–Alder reactions of **1a–c** with **2a–d**[a]

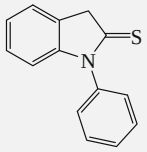
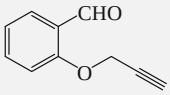
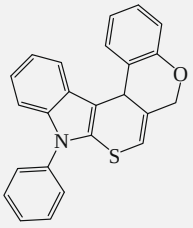
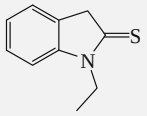
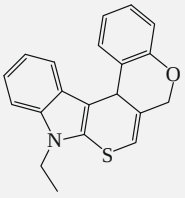
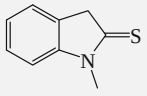
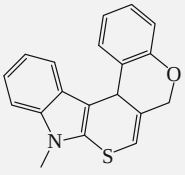
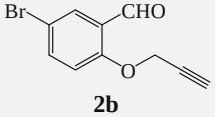
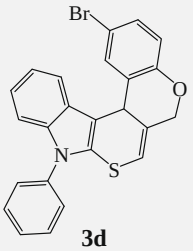
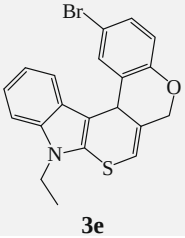
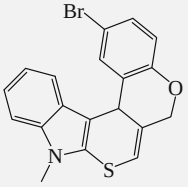
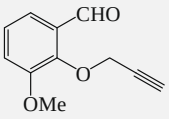
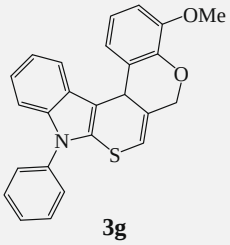
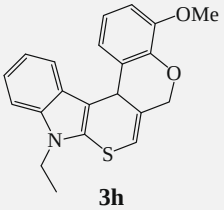
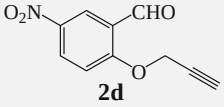
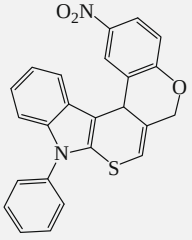
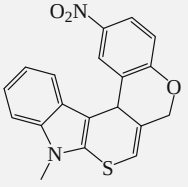
Entry	Aldehyde	Indolin-2-thione	Product	Yield[b] (%)
1	 **1a**	 **2a**	 **3a**	90
2	 **1b**	**2a**	 **3b**	85
3	 **1c**	**2a**	 **3c**	88
4	**1a**	 **2b**	 **3d**	95
5	**1b**	**2b**	 **3e**	90

Table 2 (*continued*)

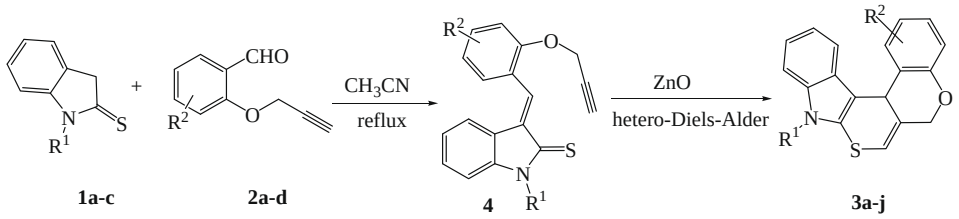
Entry	Aldehyde	Indolin-2-thione	Product	Yield[b] (%)
6	**1c**	**2b**	 **3f**	88
7	**1a**	 **2c**	 **3g**	85
8	**1b**	**2c**	 **3h**	85
9	**1a**	 **2d**	 **3i**	95
10	**1c**	**2d**	 **3j**	95

[a] All reactions were carried out at reflux in CH_3CN with ZnO (10 mol %) for 3 h.
[b] Isolated yield.

When the reaction was carried out at room temperature using **1a** (0.5 mmol, 1 equiv) and **2a** (0.5 mmol, 1 equiv) in toluene or CH_3CN, the reaction rate was slow and the product was obtained in only 33% or 35% yield after 48 h, (entries 1 and 2). Running the reaction in water did not provide the desired product (entry 3). When the reaction was carried out under refluxing conditions using **1a** (0.5 mmol, 1 equiv), **2a** (0.5 mmol, 1 equiv) and ZnO (100 mol %) in CH_3CN the reaction time was reduced to 3 h affording **3a** in 90% yield (entry 8). Decreasing the ratio of ZnO to 10 mol % afforded the same result, but with 5 mol % of ZnO, the reaction took longer. Hence, the conditions used in entry 10 are optimal. Using the optimized conditions, we studied the domino Knoevenagel-hetero-Diels–Alder reactions of compounds **1a–c** and **2a–d** to give products **3a–j** in high yields (85–95%) (Table 2).

The structures of the products were established from their NMR spectroscopic data (^{1}H NMR, ^{13}C NMR, DEPT) and elemental analyses.[20] The characteristic signals for **3a–j** in the ^{1}H NMR spectra were an AB quartet for the $-OCH_2$ group between 4.60 and 5.05 ppm, a singlet for the aliphatic CH group at 5.17–5.46 ppm, and another singlet for the SCH= group at 6.00–6.34 ppm. The diastereotopic nature of the two protons of the OCH_2 group is due to the helical shape of rings A–C in products **3a–j**.[16] The corresponding signals of the $-OCH_2$ and aliphatic CH groups in the ^{13}C NMR spectra appeared at 73.0–73.8 ppm and 36.0–36.5 ppm, respectively.

A plausible mechanism for the reaction is shown in Scheme 2. The initial step is a Knoevenagel condensation between indolin-2-thiones **1a–c** and aldehydes **2a–d** in which the aldehyde function may be activated by ZnO to facilitate the condensation. Next, the triple bond is activated with ZnO through formation of a π-complex and provides the necessary conditions for the subsequent intramolecular-hetero-Diels–Alder reaction.



Scheme 2. A plausible mechanism for the formation of compounds **3a–j**.

In summary, we have described a ZnO-catalyzed domino Knoevenagel-intramolecular-hetero-Diels–Alder reaction, which provides an efficient route for the formation of polycyclic indole derivatives in a single step. The major advantage of this reaction is the ease of the work-up during which the products can be isolated without chromatography. This method also offers other advantages such as clean reactions, low loading of catalyst, high yields of products, short reaction times, and the use of ZnO as a non-toxic, non-corrosive, commercially available, and inexpensive heterogeneous catalyst, which make it a useful and attractive strategy for the synthesis of pentacyclic indole derivatives. Further studies to extend the scope and synthetic utility of indolin-2-thiones and indolin-2-ones in domino Knoevenagel-intramolecular-hetero-Diels–Alder reactions are in progress in our laboratory.

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Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tetlet.2009.09.106.

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20. To a stirred suspension of ZnO (10 mol %) in CH_3CN (10 ml) were added indolin-2-thione **1a–c** (0.5 mmol) and O-propargylated salicylaldehyde derivative **2a–d** (0.5 mmol). The reaction mixture was stirred at reflux for 3 h and the progress of the reaction was monitored by TLC. After completion of the reaction, the mixture was poured onto ice-cold water and stirred for 10 min, which resulted in the precipitation of the product **3a–j**. The solid precipitate was filtered, dried, washed with petroleum ether to remove any residual starting material and after drying, recrystallized from ethanol.
Selected spectroscopic data: 9-Phenyl-9,13*c*-dihydro-6*H*-chromeno[4′,3′:4,5]-thiopyrano[2,3-*b*]indole (**3a**): 90%; pale-white solid, mp 138–141 °C; δ_H (500 MHz, $CDCl_3$) 4.80 (1H, d, *J* 11.9 Hz, CH), 4.99 (1H, d, *J* 11.9 Hz, CH), 5.46 (1H, s, CH), 6.19 (1H, s, =CH), 6.82 (1H, t, *J* 7.5 Hz, H_{Ar}), 6.90 (1H, d, *J* 8.1 Hz, H_{Ar}), 7.13–7.19 (2H, m, H_{Ar}), 7.22–7.24 (2H, m, H_{Ar}), 7.30–7.32 (1H, m, H_{Ar}), 7.46–7.50 (3H, m, H_{Ar}), 7.56–7.62 (3H, m, H_{Ar}); δ_C [125 MHz, $CDCl_3$/DMSO-d_6 (10%)] 36.5 (CH), 73.1 (CH_2), 105.0 (C), 110.0 (CH), 111.3 (CH), 117.4 (CH), 118.5 (CH), 121.0 (CH), 121.1 (CH), 122.5 (CH), 126.4 (C), 127.0 (CH), 127.1 (C),

127.4 (CH), 128.3 (CH), 128.6 (CH), 128.8 (C), 129.1 (C), 129.8 (C), 130.1 (CH), 136.9 (C), 154.2 (C). Anal. Calcd for $C_{24}H_{17}NOS$: C, 78.44; H, 4.66; N, 3.81. Found: C, 77.84; H, 4.61; N, 3.77.

9-Ethyl-9,13*c*-dihydro-6*H*-chromeno[4′,3′:4,5]thiopyrano[2,3-*b*]indole (**3b**): 85%; pale-white solid, mp 118–121 °C; δ_H (500 MHz, $CDCl_3$) 1.43 (3H, t, *J* 7.2 Hz, CH_3), 4.15–4.17 (2H, m, NCH_2), 4.80 (1H, d, *J* 11.9 Hz, CH), 4.99 (1H, d, *J* 11.7 Hz, CH), 5.41 (1H, s, CH), 6.24 (1H, s, =CH), 6.78 (1H, t, *J* 7.5 Hz, H_{Ar}), 6.89 (1H, d, *J* 8.1 Hz, H_{Ar}), 7.06 (1H, d, *J* 7.6 Hz, H_{Ar}), 7.15–7.20 (2H, m, H_{Ar}), 7.27 (1H, d, *J* 8.1 Hz, H_{Ar}), 7.38 (1H, d, *J* 8.2 Hz, H_{Ar}), 7.56 (1H, d, *J* 7.8 Hz, H_{Ar}); δ_C (125 MHz, $CDCl_3$) 15.6 (CH_3), 36.5 (CH), 39.5 (NCH_2), 73.4 (CH_2), 103.3 (C), 108.9 (CH), 110.4 (CH), 117.1 (CH), 118.6 (CH), 120.2 (CH), 121.1 (CH), 121.8 (CH), 125.2 (C), 127.1 (CH), 127.7 (C), 128.2 (CH), 128.7 (C), 129.4 (C), 137.2 (C), 154.2 (C). Anal. Calcd for $C_{20}H_{17}NOS$: C, 75.20; H, 5.36; N, 4.39. Found: C, 74.53; H, 5.28; N, 4.32.