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$CoCl_2$•$6H_2O$-PROMOTED PINNER-DIMROTH TANDEM REACTION: FACILE SYNTHESIS OF 3-SUBSTITUTED ISOINDOLINONES

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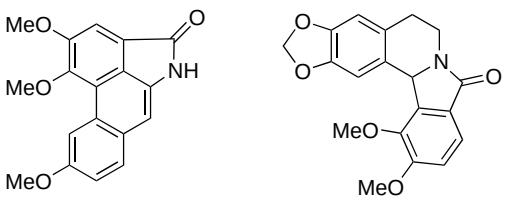
Abstract – A convenient one-pot synthesis of 3-substituted isoindolinones were reported in good yield *via* Pinner-Dimroth tandem reaction of 1,3-dicarbonyl compounds and 2-cyanobenzaldehyde in the catalysis of $CoCl_2$•$6H_2O$. This method has advantages of time efficiency and mild reaction conditions.

Isoindolinone is one of the most important nitrogen heterocycles, being widespread among many naturally occurring substances (Figure 1, aristololactam B,[1a] nuevamine[1b]) and present as a key structural unit in a large number of families of therapeutic activities[2-8] such as antioxidant,[2] anxiolytic,[3] antibacterial,[4] anticancer,[5] platelet aggregation inhibitory,[6] antipsychotic[7] and reduced the dependence of nicotine[8] agents. Therefore, much attention has been devoted to the synthesis of 3-substituted isoindolinones. The classical methods include the condensation of 2-cyanobenzaldehyde with nitroalkanes,[9] organolithiums,[10] alkenes,[11] alcohols,[12] amines.[13] Palladium-catalyzed reaction of 2-iodo-*N*-substituted benzamides was proved a highly efficient synthesis of the isoindolinone scaffold.[14] But there is still a clear need for versatile methods that give access to 3-substituted isoindolinone systems under environmentally benign conditions, a cheap catalytic system, and easily available starting.



aristololactam B nuevamine

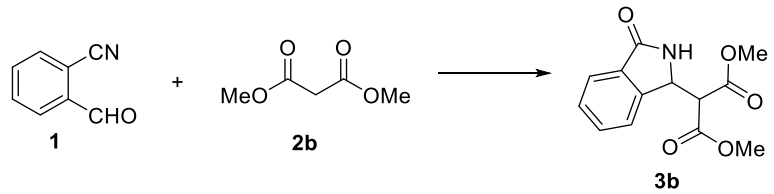
Figure 1. Representative isoindolinone natural products

During the development of synthetic methodologies, many advantages in terms of sustainability and green chemistry are offered by one-pot domino or tandem processes. Those methods provide synthetic

target products and avoid multistep protocols and tedious purification of intermediates. This kind of strategy has been used for the construction of 3-substituted isoindolinones. For example, Ramström *et al*.[9] successfully assessed a base-promoted tandem reaction to access 3-substituted isoindolinones *via* Henry reaction, heterocyclization and rearrangement. And in a little while, Massa *et al*.[15] described an efficient method for synthesizing 3-substituted isoindolinones through tandem aldol/cyclization reactions in the presence of potassium carbonate. Mola *et al*.[16] discovered that the electrochemical methodology for synthesizing 3-substitued isoindolinones. Afterwards Massa *et al*.[17] first reported a asymmetric synthesis of 3-substituted isoindolinones by organocatalyst.

In the light of the above considerations and our previous investigations on the Pinner-Dimroth tandem methodologies for the synthesis of dihydroquinazolinones,[18] we envisaged $CoCl_2$•$6H_2O$-promoted tandem reaction of 2-cyanobenzaldehyde with 1,3-dicarbonyl compounds to provide a convenient synthesis of 3-substitued isoindolinone derivatives.

Table 1. Catalyst screening for the synthesis of compound **3b**[a]



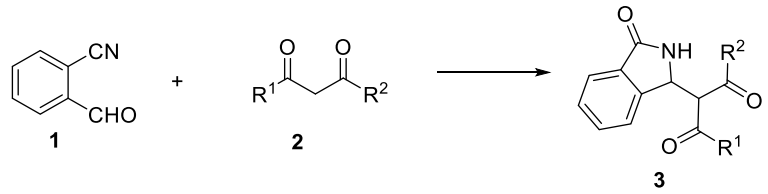
Entry	Solvent	Catalyst (Eq)	Time (h)	Temperature (°C)	Yield[b] (%)
1	MeCN	--	24	25	0
2	MeCN	$FeCl_3$ (0.4)	24	25	21
3	MeCN	$AlCl_3$ (0.4)	24	25	13
4	MeCN	$CuCl_2$ (0.4)	24	25	0
5	MeCN	$BiCl_3$ (0.4)	24	25	0
6	MeCN	$TiCl_4$ (0.4)	8	25	90
7	MeCN	$CoCl_2$•$6H_2O$ (0.4)	8	25	92
8	EtOH	$CoCl_2$•$6H_2O$ (0.4)	8	25	56
9	PhMe	$CoCl_2$•$6H_2O$ (0.4)	8	25	13
10	MeCN	$CoCl_2$•$6H_2O$ (0.2)	12	25	76
11	MeCN	$CoCl_2$•$6H_2O$ (0.6)	8	25	93
12	MeCN	$CoCl_2$•$6H_2O$ (0.8)	8	25	93
13	MeCN	$CoCl_2$•$6H_2O$ (0.4)	8	50	93
14	MeCN	$CoCl_2$•$6H_2O$ (0.4)	8	80	93

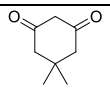
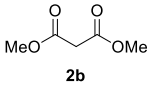
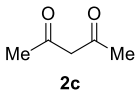
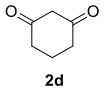
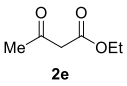
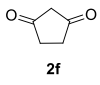
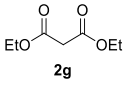
[a] Reactions conditions: **1** (1 mmol), **2b** (1.2 mmol) and catalyst in solvent (10 mL). [b] Isolated yields.

Initially, 2-cyanobenzaldehyde (**1**) and dimethyl malonate (**2b**) were chosen as model substrates to find the appropriate reaction conditions. As outlined in Table 1, no target product was observed by performing the process without catalyst or in the presence of $CuCl_2$ and $BiCl_3$ (Table 1, entries 1, 4, 5). $FeCl_3$ and $AlCl_3$ could promote this reaction easily under mild conditions (Table 1, entries 2, 3). However, the yield

was lower and the reaction time was longer than $CoCl_2•6H_2O$ (Table 1, entry 7). The catalytic properties of $TiCl_4$ was similar to $CoCl_2•6H_2O$ (Table 1, entry 6). Taking into account the extremely water-sensitive of $TiCl_4$, we selected $CoCl_2•6H_2O$ as the appropriate catalyst. The solvent can affect the stability and catalytic behaviors of the catalyst. Gratifyingly, we found the yield was higher using acetonitrile as solvent than using other solvent (Table 1, entries 8, 9). The amount of catalyst also had effect on the reaction, and the 0.4 equivalent amount of $CoCl_2•6H_2O$ was the appropriate choice (Table 1, entries 10-12). The temperature had no influence on the yield of reaction. So the room temperature was selected (Table 1, entries 13, 14).

Table 2. Synthesis of 3-substituted isoindolinones from **1** and **2**[a]



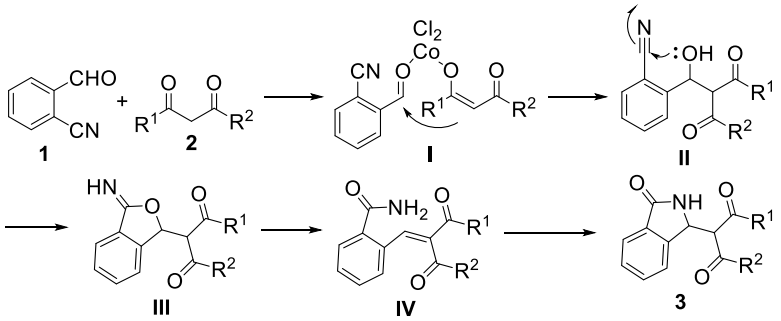
Entry	Adduct **2**	Product **3**	Yield[b] (%)
1	 **2a**	**3a**	78
2	 **2b**	**3b**	96
3	 **2c**	**3c**	67
4	 **2d**	**3d**	81
5	 **2e**	**3e**	71
6	 **2f**	**3f**	80
7	 **2g**	**3g**	92
8[c]	 **2h**	**3h**	53

[a] Reactions conditions: **1** (1 mmol), **2** (1.2 mmol) and $CoCl_2•6H_2O$ in MeCN (10 mL). [b] Isolated yields. [c] The catalyst was $TiCl_4$.

With these pleased results in hand, we felt encouraged to explore the substrate scope for this processes, so a series of *β*-dicarbonyl compounds were studied and the results were presented in Table 2. As shown in

Table 2, different *β*-dicarbonyl compounds had a certain effect on this reaction because they contained various ring tension and steric hindrance. The reaction of 2-cyanobenzaldehyde and malonic acid diesters provided the highest yield (Table 2, entries 2, 7). Cyclic *β*-diketones tested gave the target products in good yields (Table 2, entries 1, 4, 6). And the reaction of linear *β*-dicarbonyl compounds gave the corresponding products in fair to good yields (Table 2, entries 3, 5). It should be noted that acetophenone can't reacted with 2-cyanobenzaldehyde under the same conditions. However, the target compound was obtained in the presence of $TiCl_4$ (Table 2, entry 8). The result showed that Lewis acid was superior to base.[19]

The possible reaction mechanism for the 3-substitued isoindolinones **3** from the 2-cyanobenzaldehyde **1** is illustrated in Scheme 1. Carbonyl compounds **2** transform into enol **I** under the presence of $CoCl_2$•$6H_2O$ Then enol **I** reacts with **1** to provide the key intermediate **II**. The latter carries out intramolecular nucleophilic addition to form the cyclization product **III**, which ring-opened to the intermediate **IV**. And the final product **3** was obtained through the cyclization of **IV**. (Dimroth rearrangement[20]).



Scheme 1. Possible mechanism for the reaction catalyzed by $CoCl_2$•$6H_2O$

All products were characterized by IR, ^{1}H NMR, ^{13}C NMR and ESI spectra. And the structure **3b** was undoubtedly confirmed by X-ray crystallographic analysis (Figure 2).[21]

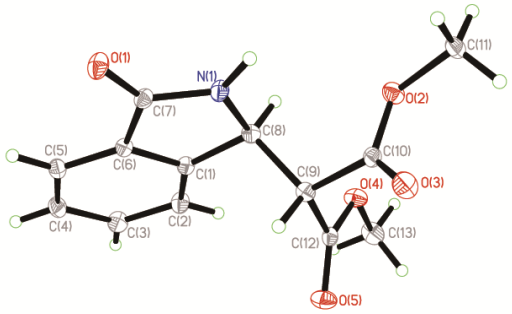


Figure 2. Molecular structure of compound **3b**

EXPERIMENTAL

Melting points were measured on XT4 microscope melting point apparatus (uncorrected). Infrared (IR) spectra were performed on Perkin Elmer FT-IR spectrophotometer with KBr pellets. ^{1}H and ^{13}C NMR spectra were performed on Bruker 400 MHz spectrometer with TMS as internal standard. Mass spectra were performed on ZAB-HS mass spectrometer using ESI ionization. Elemental analyses were performed on Elementar Vario EL. All reagents and solvents were commercially available and used without further purification.

General procedure for the synthesis of 3a-h: 2-Cyanobenzaldehyde (**1**, 1.0 mmol) was added to a mixture of 1,3-dicarbonyl compound (**2**, 1.2 mmol) and $CoCl_2$•$6H_2O$ (0.4 mmol) in MeCN (5.0 mL). At the end of the reaction (TLC monitoring), the mixture was diluted was water and extracted with EtOAc (3×10 mL). The combined organic layers were dried with Na_2SO_4 and evaporated under reduced pressure. The residue was purified by column chromatography on silica gel (200-300 mesh silica gels) to afford pure **3**.

3-(2-Hydroxy-4,4-dimethyl-6-oxocyclohex-1-en-1-yl)isoindolin-1-one (3a): White solid; mp 234-237 °C; R_f = 0.33 (EtOAc : HCOOH = 60 : 1); ^{1}H NMR (400 MHz, DMSO-d_6) (δ, ppm): 8.31 (s,1H), 8.13 (s, 1H), 7.59-7.57 (d, J = 7.6 Hz, 1H), 7.48-7.44 (t, J = 8.4 Hz, 1H), 7.39-7.35 (t, J =7.2 Hz, 1H), 7.18-7.16 (d, J = 7.6 Hz, 1H), 5.75 (s, 1H), 2.22 (s, 4H), 1.00 (s, 6H); ^{13}C NMR (100 MHz, DMSO-d_6) (δ, ppm): 170.0, 163.0, 148.5, 133.3, 131.0, 131.0, 126.8, 122.2, 121.7, 109.6, 56.1, 50.0, 50.0, 31.7, 27.8, 27.8; IR (KBr, v, cm^{-1}): 3210, 2966, 2902, 2569, 1724, 1663, 1563, 1384, 1285, 1032, 679; ESI-MS (*m/z*) = 294 ($[M+Na]^+$); Anal. Calcd for $C_{16}H_{17}NO_3$: C, 70.83; H, 6.32; N, 5.16%. Found: C, 71.01; H, 6.22; N, 5.09%.

Dimethyl 2-(3-oxoisoindolin-1-yl)malonate (3b):[22] White solid; mp 154-156 °C; R_f = 0.29 (EtOAc : petroleum ether = 1 : 1); ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm): 7.88-7.86 (d, J = 8 Hz, 1H), 7.59-7.50 (m, 2H), 7.34-7.32 (d, J = 7.2 Hz, 1H), 6.81 (s, 1H), 5.20-5.18 (d, J = 8 Hz, 1H), 3.87 (s, 3H), 3.70 (s, 3H), 3.63-3.61 (d, J = 8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm): 170.0, 167.7, 167.2, 143.7, 132.2, 132.1, 129.2, 124.2, 123.0, 56.1, 54.9, 53.2, 53.1; IR (KBr, v, cm^{-1}): 3183, 3083, 1744, 1701, 1435, 1267, 1144, 965, 769, 751; ESI-MS (*m/z*) = 286 ($[M+Na]^+$).

3-(3-Oxoisoindolin-1-yl)pentane-2,4-dione (3c):[22] White solid; mp 152-153 °C; R_f = 0.33 (EtOAc : petroleum ether = 1 : 1); ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm): 7.87-7.86 (d, J = 7.2 Hz, 1H), 7.56-7.51 (m, 2H), 7.31-7.29 (d, J = 8 Hz, 1H), 6.85 (s, 1H), 5.26-5.24 (d, J = 6.8 Hz, 1H), 4.04-4.02 (d, J = 6.8 Hz, 1H), 2.33 (s, 3H), 2.08 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm): 202.3, 201.1, 170.1, 144.3, 132.4, 132.1, 129.2, 124.5, 122.9, 71.3, 55.0, 31.6, 30.8; IR (KBr, v, cm^{-1}): 3188, 3079, 2914, 2871, 1718, 1416, 1359, 1318, 1275, 1148, 747, 686; ESI-MS (*m/z*) = 230 ($[M-H]^-$).

3-(2-Hydroxy-6-oxocyclohex-1-en-1-yl)isoindolin-1-one (3d):[22] White solid; mp 271-274 °C. R_f = 0.25

(EtOAc : HCOOH = 60 : 1); ^{1}H NMR (400 MHz, DMSO-d_6) (δ, ppm): 10.87 (s, 1H), 8.25 (s, 1H), 7.58-7.56 (d, J = 8 Hz, 1H), 7.47-7.44 (t, J = 7.2 Hz, 1H), 7.38-7.35 (t, J = 7.2 Hz, 1H), 7.20-7.18 (d, J = 7.6 Hz, 1H), 5.75 (s, 1H), 2.32 (s, 2H), 1.86-1.84 (d, J = 6 Hz, 2H); ^{13}C NMR (100 MHz, DMSO-d_6) (δ, ppm): 194, 170.0, 145.5, 133.1, 130.9, 128.8, 122.2, 121.9, 111.0, 50.0, 30.3, 20.2; IR (KBr, v, cm^{-1}): 3287, 2932, 1646, 1630, 1387, 1302, 996, 684; ESI-MS (m/z) = 242 ([M-H]$^-$).

Ethyl 3-oxo-2-(3-oxoisoindolin-1-yl)butanoate (3e):[22] White solid; mp 210-220 °C; R_f = 0.37 (EtOAc : petroleum ether = 2 : 1); ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm): 7.85-7.83 (d, J = 8 Hz, 1H), 7.56-7.48 (m, 2H), 7.31-7.29 (d, J = 7.6 Hz, 1H), 6.75 (s, 1H), 5.24-5.23 (d, J = 7.2 Hz, 1H), 4.15-4.10 (q, J = 7.2 Hz, 2H), 3.81-3.79 (d, J = 8 Hz, 1H), 2.35 (s, 3H), 1.15-1.11 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm): 201.7, 169.9, 166.6, 144.3, 132.1, 129.0, 129.0, 128.9, 124.1, 123.0, 62.9, 62.3, 54.5, 31.2, 13.9; IR (KBr, v, cm^{-1}): 3226, 3083, 2988, 2938, 1731, 1717, 1697, 1473, 1339, 1255, 1200, 1107, 1025, 754, 702; ESI-MS (m/z) = 284 ([M+Na]$^+$).

3-(2-Hydroxy-5-oxocyclopent-1-en-1-yl)isoindolin-1-one (3f): Sepia solid; mp 202-204 °C; R_f = 0.22 (EtOAc : HCOOH = 60 : 1); ^{1}H NMR (400 MHz, DMSO-d_6) (δ, ppm): 8.27 (s, 1H), 7.58-7.56 (d, J = 7.6 Hz, 1H), 7.47-7.43 (t, J = 7.2 Hz, 1H), 7.39-7.35 (t, J = 7.2 Hz, 1H), 7.22-7.20 (d, J = 7.6 Hz, 1H), 5.32 (s, 1H), 2.26-2.19 (dt, J = 13.6 Hz, 4H); ^{13}C NMR (100 MHz, DMSO-d_6) (δ, ppm): 201.1, 199.35, 174.89, 138.19, 136.23, 132.26, 127.88, 127.83, 127.46, 103.9, 55.35, 36.14, 36.14; IR (KBr, v, cm^{-1}): 3246, 2918, 1677, 1558, 1468, 1395, 1287, 1022, 772; ESI-MS (m/z) = 252 ([M+Na]$^+$); Anal. Calcd for $C_{13}H_{11}NO_3$: C, 68.11; H, 4.84; N, 6.11%. Found: C, 68.30; H, 4.79; N, 5.99%.

Diethyl 2-(3-oxoisoindolin-1-yl)malonate (3g):[15] White solid; mp 94-96 °C; R_f = 0.32 (EtOAc : petroleum ether = 1 : 1); ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) (δ, ppm): 7.88-7.86 (d, J = 6.8 Hz, 1H), 7.59-7.50 (m, 2H), 7.39-7.37 (d, J = 7.2 Hz, 1H), 6.79 (s, 1H), 5.17-5.16 (d, J = 7.2 Hz, 1H), 4.33-4.27 (q, J =7.2 Hz, 2H), 4.15-4.09 (q, J =7.2 Hz, 2H), 3.65-3.63 (d, J = 7.6 Hz, 1H), 1.34-1.31 (t, J = 7.2 Hz, 3H), 1.14-1.11 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm): 167.5, 167.5, 166.7, 146.1, 132.2, 129.1, 129.1, 124.2, 123.1, 62.3, 62.3, 56.2, 54.9, 14.2, 13.9; IR (KBr, v, cm^{-1}): 3199, 3086, 2976, 2870, 1743, 1720, 1698, 1471, 1346, 1179, 1158, 1040, 747; ESI-MS (m/z) = 314 ([M+Na]$^+$).

3-Benzoylisoindolin-1-one (3h):[19] White solid; mp 138-140 °C; R_f = 0.22 (EtOAc : petroleum ether = 1 : 8); ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm): 7.97-7.92 (m, 4H), 7.68-7.47 (m, 6H), 6.20-6.17 (t, J = 7.2 Hz, 1H), 3.82-3.76 (d, J = 7.6 Hz, 1H), 3.43-3.37 (d, J = 7.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm): 196.3, 170.5, 156.4, 134.6, 134.2, 129.7, 129.7, 129.1, 129.1, 128.5, 128.5, 126.1, 126.0, 123.1, 77.0, 44.0; IR (KBr, v, cm^{-1}): 3064, 2912, 1769, 1681, 1596, 1447, 1291, 1080, 755; ESI-MS (m/z) = 274 ([M+Na]$^+$).

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