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# Lanthanide-catalyzed cyclocarbonylation and cyclothiocarbonylation: a facile synthesis of benzannulated 1,3-diheteroatom five- and six-membered heterocycles

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$La[N(SiMe_3)_2]_3$ proves to be an efficient catalyst system for the cyclocarbonylation of 1,2-disubstituted benzenes with isocyanates. In this approach, aryl/alkyl isocyanates react with *o*-phenylenediamine, *o*-aminophenol, *o*-aminothiophenol, catechols and anilines *ortho*-substituted by $CH_2NH_2$ and $CONH_2$ to form, respectively, the corresponding benzimidazolones, benzoxazolones, benzothiazolones, benzodioxolones, 3,4-dihydroquinazolin-2(1*H*)-one, and quinazolinediones. These results represent the first example of lanthanide-catalyzed carbonylation. This methodology is also applicable for the preparation of various benzannulated 1,3-diheteroatom cyclic thioketones starting from aryl/alkyl isothiocyanates or $CS_2$ in good to excellent yields. Based on the results of experiments performed using an *o*-aminobenzamido dianion lanthanide complex, a general mechanism, involving the tandem reaction of two lanthanide-ligand bonds with one heterocumulene molecule, is proposed as well.

**lanthanide catalyst, 1,2-disubstituted benzene, isocyanate, isothiocyanates, cyclocarbonylation, cyclothiocarbonylation**

## 1 Introduction

Transition-metal-catalyzed carbonylative coupling reactions have become a powerful tool in organic synthesis [1–3]. Tremendous advances have been made in the development of new catalysts, reactions, and targets. However, rare-earth metal-catalyzed carbonylation remains a significant intellectual challenge, mainly because of the orbital energy mismatch between the hard rare-earth metal and the soft and poor carbon monoxide ligand, the difficulties in stabilizing the acyl complex intermediate, and the absence of conventional oxidative-addition/reductive-elimination processes on the rare earth metal center, which are usually involved in transition metal-catalyzed carbonylation processes [4].

Benzofused 1,3-diheteroatom cyclic ketones such as benzimidazolones [5], benzoxazolones [6], benzothiazolones [7], benzodioxolones [8], 3,4-dihydroquinazolin-2(1*H*)-one [9], and quinazolinediones [10], or their hydroxyl-substituted tautomers, are important structural motifs in both pharmaceutical and agrochemical products. For example, both the analgesic Paraflex [6a)] and the insecticide and acaricide phosalone [6b)] possess a benzoxazolone scaffold, whereas benazolin and chlobenthiazone are widely used in agriculture as herbicides and fungicides, respectively [7]. They are also valuable intermediates in organic synthesis [11, 12]. Furthermore, these types of heterocycles exhibit a variety of coordination modes with a wide range of metal ions due to the flexibility of their binding modes [13]. Therefore, numerous efforts in recent years have focused on the development of improved methods for the synthesis of these types of heterocyclic ketones [14–18]. Among a variety of preparation methods, the direct cyclocarbonylation of the corresponding *o*-phenylenediamines, *o*-aminophenols,

Dedicated to Professor Qian Changtao on the occasion of his 80th birthday.
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*o*-aminothiophenols, catechols or analogous *ortho*-disubstituted compounds is apparently one of the most simple and versatile methods. Traditionally, most synthetically viable applications of such reactions have to use phosgene as a carbonyl source [19]. To avoid the use of toxic phosgene, several alternative carbonyl sources such as urea [20], dimethyl carbonate [21], $ClCO_2Et$ [22], 1,10-carbonyldimidazole [23], disuccinimido carbonate [24], and $CO_2$ [25] have been reported. For example, benzimidazolones and benzoxazolones have been obtained using urea [20] or dimethyl carbonate [21] for the carbonylation of *o*-phenylenediamines and *o*-aminophenols, respectively. Using carbon monoxide as a carbonyl source is another alternative green method for traditionally stoichiometric reactions using toxic phosgene [26, 27]. Although significant advances have been made in developing new carbonyl sources, the reaction conditions are often harsh, e.g., employing strong acid or expensive catalyst, or requiring high temperature, high pressure, or superstoichiometric amounts of additives. To the best of our knowledge, catalytic cyclocarbonylation of *ortho*-disubstituted aromatic compounds with isocyanates to obtain benzannulated 1,3-diheteroatom cyclic ketones catalyzed by rare earth metal complex have not been reported.

During the course of our investigations into the stoichiometric reaction of $[Cp_2Yb(SC_6H_4NH_2\text{-}2)]_2\cdot 2THF$ with PhNCO, benzothiazole-2-oxide complex $Cp_2Yb(\mu\text{-}\eta^1,\eta^3\text{-}OSNC_7H_4)]_2$ was unexpectedly obtained [28]. This result offers an alternative route to the construction of benzothiazolone skeleton. As a part of a continuing effort in our laboratory to develop new methods for the expeditious synthesis of biologically relevant heterocyclic compounds [29], we were interested in incorporating the tandem intermolecular addition/cyclization/amine elimination reaction in some catalytic context. Herein, we report our results on a one-step synthesis of benzofused 1,3-diheteroatom cyclic ketones through organolanthanide-catalyzed cyclocarbonylations of bifunctional substrates with isocyanates. This methodology is also quite general in preparing benzannulated 1,3-diheteroatom cyclic thioketones. They represent the first examples of lanthanide-catalyzed cyclocarbonylation and cyclothiocarbonylation, respectively.

## 2 Experimental

### 2.1 Materials and methods

All reactions were carried out under nitrogen atmosphere using the standard Schlenk techniques. The solvent was refluxed and distilled over sodium/benzophenone ketyl under nitrogen immediately prior to use. The functionalized amines, pyrocatechols, isocyanates, isothiocyanates used in this study were purchased from Sigma Aldrich (USA) with further purification. All of the solid reagents were treated in a vacuum oven at 40 °C overnight before use, and stored in the glove box. All of the liquid reagents were refluxed overnight with calcium hydride and distilled under a nitrogen atmosphere and stored in the glove box with the 5 Å molecular sieve. $Ln[N(SiMe_3)_2]_3$ was synthesized according to the literature [30]. Flash-column chromatography was carried out using 300–400 mesh silica gel with ethyl acetate/petroleum ether or acetone/petroleum ether as eluent. NMR spectra were recorded in $CDCl_3$ or DMSO-$d_6$ on a Bruker Avance 400 (Bruker, Germany) operating at 400 MHz with TMS as internal standard. X-ray diffraction data for **3aa** and **3ga′** (CCDC 993823, 993824) were collected on a SMART APEX CCD diffractometer (Bruker, Germany) with graphite-monochromated Mo-Kα radiation ($\phi$-$\omega$-scan technique, $\lambda$ = 0.71073 Å). The intensity data were integrated by means of the SAINT program. SADABS was used to perform area-detector scaling and absorption corrections. The structures were solved by direct methods and were refined against $F^2$ using all reflections with the aid of the SHELXTL package. All non-hydrogen atoms were found via Fourier syntheses and refined anisotropically. The H atoms were included in calculated positions with isotropic thermal parameters related to those of the supporting carbon atoms but were not included in the refinement. All calculations were performed using the Bruker Smart program. The characterizations, $^1$H NMR and $^{13}$C NMR spectra of the intermolecular and products are shown in the Supporting Information online.

### 2.2 General procedure for cyclization of functionalized amines and isocyanates catalyzed by $La[N(SiMe_3)_2]_3$

A mixed solution of functionalized amines (1 mmol), isocyanates (1.2 mmol) and catalyst (0.02 mmol, 2 mol%) in 5 mL toluene was stirred at 80 °C for 24 h. Next, 10 mL water was added to the solution to quench the reaction. The mixture was extracted with $CHCl_3$ (3 × 10 mL). Then the combined organic layer was washed successively with brine and water, and dried over anhydrous $Na_2SO_4$. Evaporation of the solvent followed by purification on silica gel (eluted with $CH_2Cl_2/CH_3OH$, *v*/*v* = 20:1) provided the pure product **3**.

### 2.3 General procedure for cyclization of functionalized amines and isothiocyanates catalyzed by $La[N(SiMe_3)_2]_3$

Under nitrogen, a solution of functionalized amines (1 mmol), isothiocyanates (1.2 mmol), and catalyst (0.02 mmol, 2 mol%) in 5 mL toluene was stirred at 80 °C (oil-bath temperature) under $N_2$ atmosphere for 24 h. The reaction was quenched by 10 mL water, after which the crude product was purified on silica gel using 1:1 PE/EA as eluent.

## 3 Results and discussion

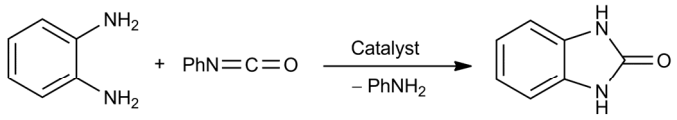
We initiated our research on the model reaction of *o*-pheny-

lenediamine (**1a**) with phenylisocyanate (**2a**) under different reaction conditions (Table 1). Treatment of a mixture of **1a** and **2a** with 2 mol% $La[N(SiMe_3)_2]_3$ in toluene at 80 °C led to the formation of **3aa** in 96% yield (Table 1, entry 1). The reaction also proceeded smoothly at temperature as high as 100 °C (Table 1, entry 2). Elevating or decreasing the reaction temperature was adverse to the reaction (entries 3 and 4). Among the various solvents tested (Table 1, entries 6–9), xylene and toluene were found to be equally effective in giving excellent yields but for convenience toluene was chosen for all other reactions. Among the rare-earth metals screened, ytterbium afforded the best result by giving 98% yield (Table 1, entry 13). Taking into account the price of $Yb[N(SiMe_3)_2]_3$, however, the reactions were carried out with $La[N(SiMe_3)_2]_3$ alone thereafter. Utilization of other rare-earth metal sources as replacements (e.g., $LaCl_3$ or $La(OTf)_3$) was ineffective (Table 1, entries 14, 15). Further investigation results indicated that no desired product could be formed in the absence of catalyst (Table 1, entry 16).

Having established an optimal protocol, we next investigated the generality and the scope of this transformation via variations of diamines **1** and isocyanates **2**. The results are summarized in Table 2. With the exception of aliphatic diamines, aromatic diamines could react well with phenyl isocyanate, giving the desired product **3** in good to excellent isolated yields (Table 2, entries 1–8). Cyclohexane-1,2-diamine failed to provide the cyclization product even with prolonged heating (Table 2, entry 9). Nevertheless, this method is applicable to 2-(aminomethyl)aniline (**1f**) and 2-aminobenzamide (**1g**) (Table 2, entries 6, 7). We were pleased to find that this methodology was also applicable to the preparation of heteroaryl benzimidazolone (Table 2, entry 5). Alkyl isocyanates gave inferior results for the preparation of 1*H*-benzimidazol-2(3*H*)-one (**3aa**) (Table 2, entries 11, 12). These results demonstrate that the nature of amines and isocyanates plays an important role in enhancing the rate and product yield of the reactions. The higher reactivity of aromatic amines, compared with aliphatic amines, is consistent with relative acidity of these substrates. Because aliphatic amine is not acidic enough to deprotonate under the conditions involved, cyclization with isocyanates is prevented. The arylisocyanates are more reactive than the alkylisocyanates, which may be attributed to the easier elimination of arylamines than alkylamine.

We were pleased to find that this methodology was also applicable to the preparation of benzoxazolones, benzothiazolones, and benzodioxolones (Table 2, entries 13–18). For example, 2-aminophenol (**1j**) and 2-amino-4-chlorophenol (**1k**) reacted with **2a** to give benzoxazol-2(3*H*)-one (**3ja**) and 5-chlorobenzoxazol-2(3*H*)-one (**3ka**) in moderate yields (entries 13, 14). 2-Aminobenzenethiols (entries 15,

**Table 1** Optimization of the reaction conditions [a)]

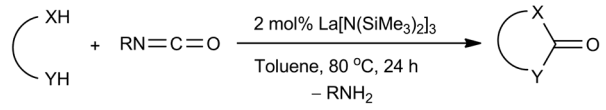



**1a** **2a** **3aa**

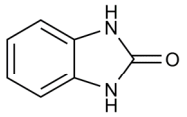
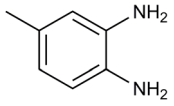
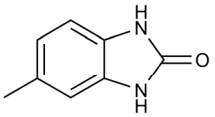
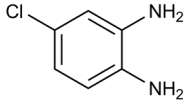
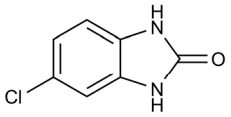
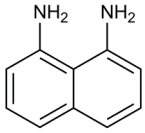
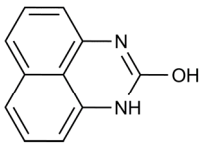
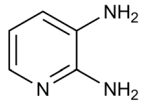
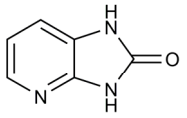
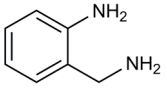
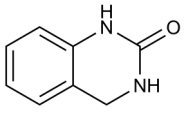
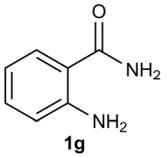
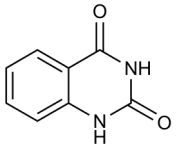
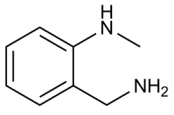
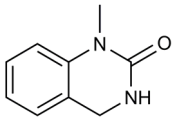
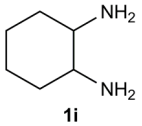
| Entry | Solvent | Catalyst | Cat. (mol%) | *T* (°C) | *t* (h) | Yield (%) [b)] |
|---|---|---|---|---|---|---|
| 1 | toluene | $La[N(SiMe_3)_2]_3$ | 2 | 80 | 24 | 96 |
| 2 | toluene | $La[N(SiMe_3)_2]_3$ | 2 | 100 | 24 | 97(96) |
| 3 | toluene | $La[N(SiMe_3)_2]_3$ | 2 | 60 | 24 | 32 |
| 4 | toluene | $La[N(SiMe_3)_2]_3$ | 2 | 120 | 24 | 81 |
| 5 | toluene | $La[N(SiMe_3)_2]_3$ | 2 | 80 | 12 | 76 |
| 6 | toluene | $La[N(SiMe_3)_2]_3$ | 2 | 80 | 48 | 95 |
| 7 | xylene | $La[N(SiMe_3)_2]_3$ | 2 | 80 | 24 | 97 |
| 8 | $C_6H_5Cl$ | $La[N(SiMe_3)_2]_3$ | 2 | 80 | 24 | 90 |
| 9 | THF | $La[N(SiMe_3)_2]_3$ | 2 | 80 | 24 | 67 |
| 10 | toluene | $La[N(SiMe_3)_2]_3$ | 1 | 80 | 24 | 69 |
| 11 | toluene | $La[N(SiMe_3)_2]_3$ | 5 | 80 | 24 | 98 |
| 12 | toluene | $Sm[N(SiMe_3)_2]_3$ | 2 | 80 | 24 | 96 |
| 13 | toluene | $Yb[N(SiMe_3)_2]_3$ | 2 | 80 | 24 | 98 |
| 14 [c)] | toluene | $LaCl_3$ | 10 | 80 | 24 | |
| 15 [c)] | toluene | $Ln(OTf)_3$ | 10 | 80 | 24 | |
| 16 [c)] | toluene | – | – | 80 | 24 | |

a) Reaction conditions: **1a** (1 mmol), **2a** (1.2 mmol), catalyst (0.02 mmol), solvent (5 mL); b) GC yield based on amine, and isolated yield in brackets; c) 1-(2-aminophenyl)-3-phenylurea was obtained in 74%–87%, with a small amount of 1,1'-(1,2-phenylene)bis(3-phenylurea).

**Table 2** $La[N(SiMe_3)_2]_3$ catalyzed cyclocarbonylation [a)]

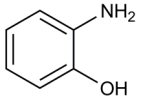
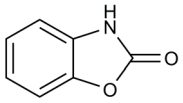
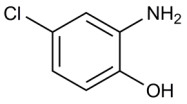
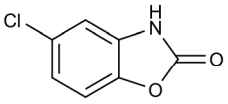
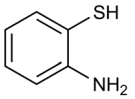
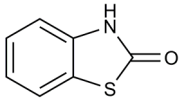
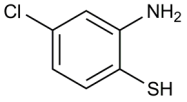
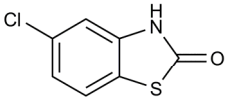
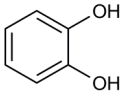
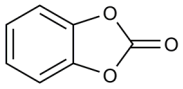
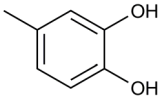
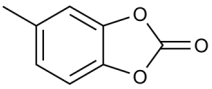



1 2 3

| Entry | 1 | 2 | 3 (Yield) [b)] |
|---|---|---|---|
| 1 | **1a** | **2a** (R = Ph) |  **3aa** (96%) |
| 2 |  **1b** | **2a** |  **3ba** (96%) |
| 3 |  **1c** | **2a** |  **3ca** (91%) |
| 4 |  **1d** | **2a** |  **3da** (86%) |
| 5 |  **1e** | **2a** |  **3ea** (96%) |
| 6 |  **1f** | **2a** |  **3fa** (90%) |
| 7 |  **1g** | **2a** |  **3ga** (79%) |
| 8 |  **1h** | **2a** |  **3ha** (85%) |
| 9 |  **1i** | **2a** | – |
| 10 | **1a** | **2b** (R = *p*-$MeC_6H_4$) | **3aa** (92%) |
| 11 | **1a** | **2c** (R = *n*-Bu) | **3aa** (34%) |
| 12 | **1a** | **2d** (R = cyclohexyl) | **3aa** (47%) |

(*To be continued on the next column*)

(*Continued*)

| Entry | 1 | 2 | 3 (Yield) [b)] |
|---|---|---|---|
| 13 |  **1j** | **2a** |  **3ja** (76%) |
| 14 |  **1k** | **2a** |  **3ka** (69%) |
| 15 |  **1l** | **2a** |  **3la** (84%) |
| 16 |  **1m** | **2a** |  **3ma** (74%) |
| 17 |  **1n** | **2a** |  **3na** (74%) |
| 18 |  **1o** | **2a** |  **3oa** (65%) |

a) Reaction conditions: **1** (1 mmol), **2** (1.2 mmol), catalyst (0.02 mmol), solvent (5 mL), 80 °C, 24 h; b) isolated yield based on functionalized amine.

16) and pyrocatechols (entries 17, 18) reacted accordingly and afforded benzothiazol-2(3*H*)-ones and benzodioxol-2-ones, respectively. It was noted that chloro and methyl substituents on the benzoate moiety of **1m** and **1o** were efficient in this transformation. Apparently, the method is applicable for the preparation of both 5- and 6-membered *N*,*O*,*S*-heterocyclic ketones. All compounds **3** were isolated and characterized; the spectroscopic data were consistent with assigned structures reported in the literature. The structure of compound **3aa** was further confirmed by X-ray diffraction analysis (Figure 1).

In order to better understand the mechanism of the cyclocarbonylation process, we performed a few more experiments. Firstly, attempts to separate the intermediates were made. Our initial attempts with the stoichiometric reaction of $La[N(SiMe_3)_2]_3$ with 2-aminobenzamide (**1g**) failed to obtain the satisfied structural information of the metal-containing intermediates. Simply switching the catalyst $La[N(SiMe_3)_2]_3$ into $Cp_3La$ gave a mixture of **3ga** and **3ga′** (Scheme 1). The structure of **3ga′** was confirmed by X-ray diffraction analysis (Figure 2). Two parallel reactions (**3ga′** in toluene vs **3ga′** with 10 mol% of $La[N(SiMe_3)_2]_3$ in toluene) were carried out at 80 °C. Results showed that no

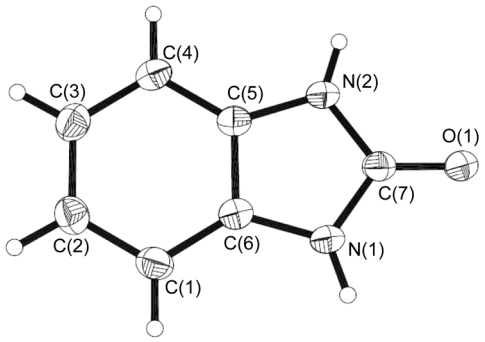



**Figure 1** Thermal ellipsoid (30%) plot of complex **3aa**. Selected bond lengths (Å) and angles (°): N(1)–C(7) 1.356(3), N(1)–C(6) 1.387(2), N(2)–C(7) 1.361(2), N(2)–C(5) 1.386(3), O(1)–C(7) 1.240(2), C(7)–N(1)–C(6) 110.2(2), C(7)–N(2)–C(5) 110.0(2), O(1)–C(7)–N(1) 126.8(2), O(1)–C(7)–N(2) 126.5(2), N(1)–C(7)–N(2) 106.7(2).

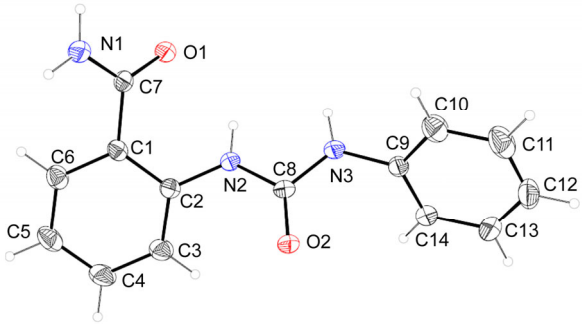
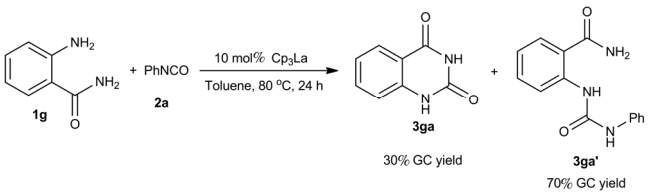



**Figure 2** Thermal ellipsoid (30%) plot of complex **3ga′**. Selected bond lengths (Å) and angles (°): N(1)–C(7) 1.318(3), N(2)–C(8) 1.359(3), N(2)–C(2) 1.410(3), N(3)–C(8) 1.354(3), N(3)–C(9) 1.419(3), O(1)–C(7) 1.237(3), O(2)–C(8) 1.229(3), C(8)–N(2)–C(2) 125.6(2), C(8)–N(3)–C(9) 124.7(2), O(1)–C(7)–N(1) 122.3(2), O(2)–C(8)–N(3) 122.7(2), O(2)–C(8)–N(2) 124.0(2), N(3)–C(8)–N(2) 113.3(2).

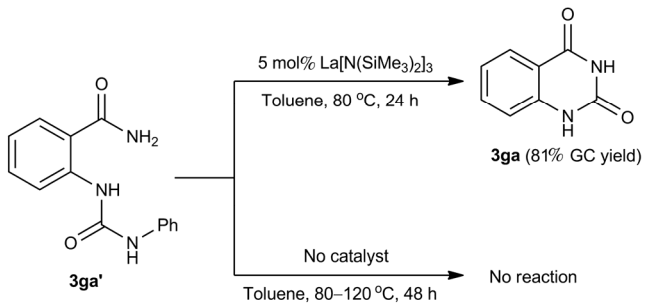
cyclization product was observed in the absence of the catalyst, even at higher temperature for a longer reaction time. However, under the aforementioned conditions, the presence of 10 mol% of La[N(SiMe$_3$)$_2$]$_3$ resulted in the formation of **3ga** in 81% GC yield (Scheme 2). This observation implies that the catalyst is essential for the cyclization step and that the preferred formation of *N*-benzoylbenzamide can be ruled out.

On the basis of these results, a reaction pathway for the cyclocarbonylation of **2a** with **1g** is proposed in Scheme 3. The deprotonation of bifunctional substrate **1** leads to the formation of a lanthanium-amido species (**A**). An intermolecular insertion of isocyanate into the higher reactive Ln–N bond affords **B**. A sequential intramolecular attack of another Ln–N onto the resulting carbonyl moiety leads to the occurrence of the cyclization. Elimination of PhNH$_2$ generates the quinazolyldiolate ring. Acid-base reaction of **D** with **1g** regenerates **A** to complete the catalytic cycle and releases quinazolinedione. Obviously, the formation of a more-stable aromatic quinazolyldiolate skeleton might contribute to the occurrence of the cyclization/amine-elimination reaction of the amido intermediate (**B**). If an *o*-phenylenediamine, *o*-aminophenol, *o*-aminothiophenol, or catechol is used as the starting material, a similar reaction pathway results in the production of benzimidazolones, benzoxazolones, benzothiazolones, and benzodioxolones, respectively.

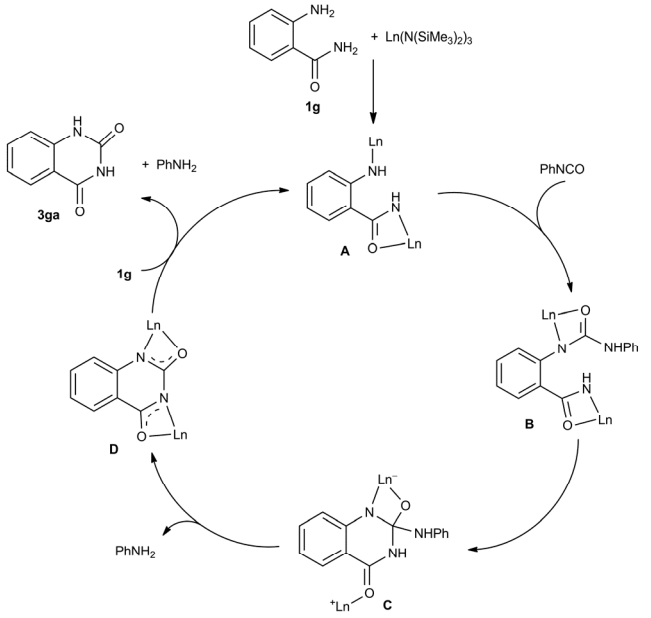
There has also been considerable interest in developing methods to obtain the benzannulated 1,3-diheteroatom cyclic thioketones because of their unique and interesting properties [31]. For example, benzimidazole-2-thione (or mercaptobenzimidazole) derivatives have important roles in medicinal chemistry because of their utility as antiulcerous




**Scheme 1** $Cp_3La$ catalyzed cyclocarbonylation.



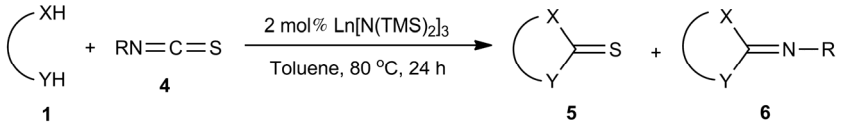

**Scheme 2** Cyclocarbonylation of **3ga′** under different conditions.



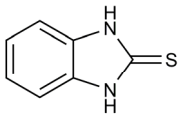
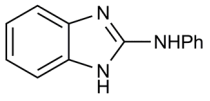
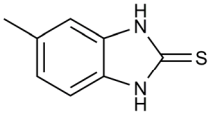
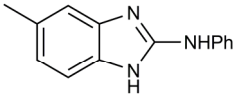
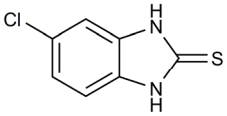
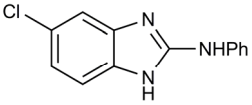
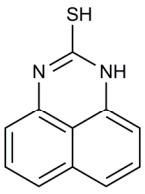
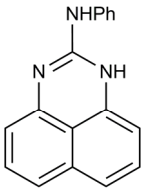
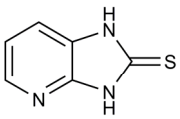
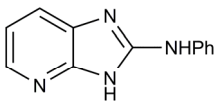
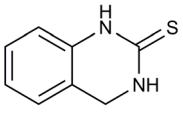
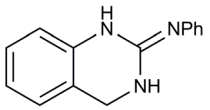

**Scheme 3** Possible mechanism of cyclization between diamines and isocyanates.

[32a)], antiseptic [32b)], analgesic [32c)], and antibacterial [32d)] agents. Moreover, mercaptobenzimidazoles have had important industrial applications as anticorrosive agents [33a)], friction attenuators [33b)], and heavy-metal adsorbents [33c)]. Although many methods have been developed for their synthesis, to our knowledge a synthetic pathway that starts from anilines *ortho*-substituted by $NH_2$, OH, and SH groups and isothiocyanates and utilizes a metal catalyst has never been reported. Encouraged by the above results, we made an extension of this reaction to synthesis of benzoheterocycle-thiones. Results are summarized in Table 3. It was found that aromatic diamines **1a–h** were suitable reactants. In addition, desirable products **5aa–ha** were generated in moderate to good yields, although small amounts of cyclic guanidines **6** were occasionally observed. Alkyl isocyanates were also successful in this transformation and provided the corresponding products in moderate yields (Table 3, entries 10, 11). The reaction of **1j** and **1k** with phenylisothiocyanate **4a** proceeded smoothly as well, giving a mixture of **5** and **6** (Table 3, entries 12, 13). Significantly, $La[N(SiMe_3)_2]_3$ could also catalyze the cyclic reaction between 2-aminobenzenethiols (Table 3, entries 14, 15) or pyrocatechols (Table 3, entries 16, 17) and isothiocyanates. It was noted that **5aa** can also be obtained in 89% yield by the cyclic reaction between **1a** and $CS_2$ in the presence of 2 mol% $La[N(SiMe_3)_2]_3$ (Table 3, entry 18).

**Table 3** $La[N(SiMe_3)_2]_3$ catalyzed cyclothiocarbonylation [a)]

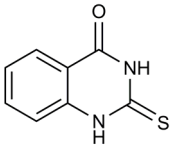
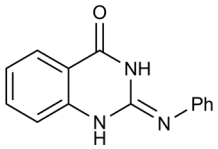
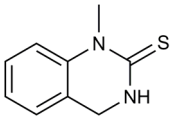
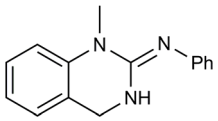
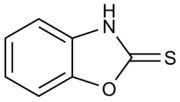
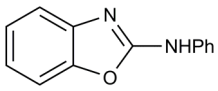
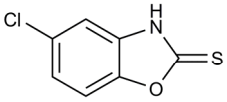
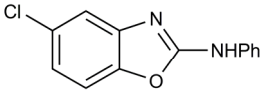
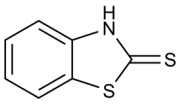
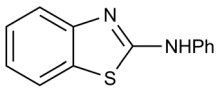
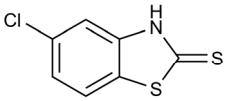
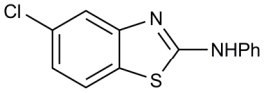
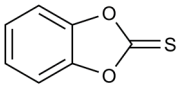
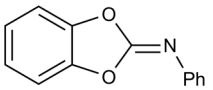
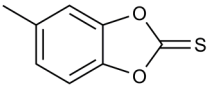
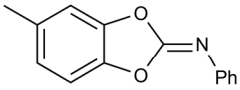



1 5 6

| Entry | 1 | 4 | 5 (Yield) [b)] | 6 (Yield) [c)] |
|---|---|---|---|---|
| 1 | **1a** | **4a** (R = Ph) |  **5aa** (86%) |  **6aa** (4%) |
| 2 | **1b** | **4a** |  **5ba** (84%) |  **6ba** (2%) |
| 3 | **1c** | **4a** |  **5ca** (69%) |  **6ca** (2%) |
| 4 | **1d** | **4a** |  **5da** (79%) |  **6da** (8%) |
| 5 | **1e** | **4a** |  **5ea** (81%) |  **6ea** (10%) |
| 6 | **1f** | **4a** |  **5fa** (80%) |  **6fa** (9%) |

(*To be continued on the next page*)

(*Continued*)

| Entry | 1 | 4 | 5 (Yield) [b] | 6 (Yield) [c] |
|---|---|---|---|---|
| 7 | **1g** | **4a** |  **5ga** (79%) |  **6ga** (4%) |
| 8 | **1h** | **4a** |  **5ha** (76%) |  **6ha** (11%) |
| 9 | **1i** | **4a** | – | – |
| 10 | **1a** | **4b** (R = $^{n}$Bu) | **5aa** (32%) | – |
| 11 | **1a** | **4c** (R = $^{t}$Bu) | **5aa** (71%) | – |
| 12 | **1j** | **4a** |  **5ja** (52%) |  **6ja** (29%) [b] |
| 13 | **1k** | **4a** |  **5ka** (46%) |  **6ka** (10%) |
| 14 | **1l** | **4a** |  **5la** (60%) |  **6la** (21%) [b] |
| 15 | **1m** | **4a** |  **5ma** (57%) |  **6ma** (9%) |
| 16 | **1n** | **4a** |  **5na** (65%) |  **6na** (4%) |
| 17 | **1o** | **4a** |  **5oa** (69%) |  **6oa** (3%) |
| 18 | **1a** | $CS_2$ | **5aa** (89%) | – |

a) Reaction conditions: **1a** (1 mmol), **4a** (1.2 mmol), catalyst (0.02 mmol), solvent (5 mL); b) isolated yield based on functionalized amines; c) GC yield.

## 4 Conclusions

We developed an efficient and practical method for one-step synthesis of a library of benzofused 1,3-diheteroatom cyclic ketones via organolanthanide-catalyzed cyclocarbonylations of bifunctional arenes with isocyanates. This method allows access to a wide range of benzofused heterocyclic ketones, such as benzimidazolones, benzoxazolones, benzothiazolones, benzodioxolones, 3,4-dihydroquinazolin-2(1*H*)-one, and quinazolinediones in reasonable yields under mild, neutral conditions without the need for gaseous carbon monoxide and additives. Based on the results of experiments performed using an *o*-aminobenzamido dianion lanthanide complex, we also propose a general mechanism involving the tandem reaction of two lanthanide-ligand bonds with one heterocumulene molecule. Such mechanistic insight

might provide an impetus for exploring the versatility and special qualities of lanthanide-catalyzed annulation reactions. This methodology is also suitable for the synthesis of various benzannulated 1,3-diheteroatom cyclic thioketones from readily available 1,2-disubstituted benzenes. Compared with other methods using similar substrates, the advantages of the present methodology include easy access to the reagents, simple operation, and high chemoselectivity, without the need for gaseous carbon monoxide and additives.

*This work was supported by the National Natural Science Foundation of China (21132002, 21272038) and the National Basic Research Program of China (2011CB825300).*

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