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Synthesis of 2,3-dihydroquinazolinimines and 1,3-diiminoisoindolines catalyzed by rare earth metal alkyl complexes through tandem addition/cyclization of nitriles with amines†

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Mononuclear rare earth metal alkyl complexes with an anilido-imino ligand were synthesized and characterized, and their catalytic ability for the formation of dihydroquinazolines and isoindolines from nitriles and amines was investigated. Reactions of rare earth-metal trialkyl complexes $\text{RE}(\text{CH}_2\text{SiMe}_3)_3(\text{THF})_2$ with proligand HL ($\text{L} = (\text{o}-(\text{NHDipp})\text{C}_6\text{H}_4\text{CH}=\text{N}(\text{CH}_2)_2\text{NC}_4\text{H}_8, \text{Dipp} = 2,6\text{-}^i\text{Pr}_2\text{C}_6\text{H}_3)$) in toluene afforded tridentate anilido-imino rare earth metal dialkyl complexes $\text{LRE}(\text{CH}_2\text{SiMe}_3)_2$ ($\text{RE} = \text{Gd}$ (**1a**), Y (**1b**), Yb (**1c**), Lu (**1d**)) in good yields. Further studies showed that these rare earth metal catalysts could achieve tandem addition/cyclization between *ortho* imine-functionalized benzonitriles and aromatic amines to afford 2,3-dihydroquinazolinimines for the first time. In addition, the catalysts are well applied to the reaction of substituted phthalonitriles with primary aromatic and aliphatic amines, producing various 1,3-diiminoisoindolines in moderate to excellent yields. During the process of the mechanism study, two anilido yttrium complexes $\text{LY}(\text{NHPh})_2(\text{THF})$ (**7b**) and $\text{LY}(\text{NHDipp})_2$ (**8b**) were isolated by the reaction of **1b** with aniline and 2,6-diisopropylaniline, respectively, as well as their catalytic performance.

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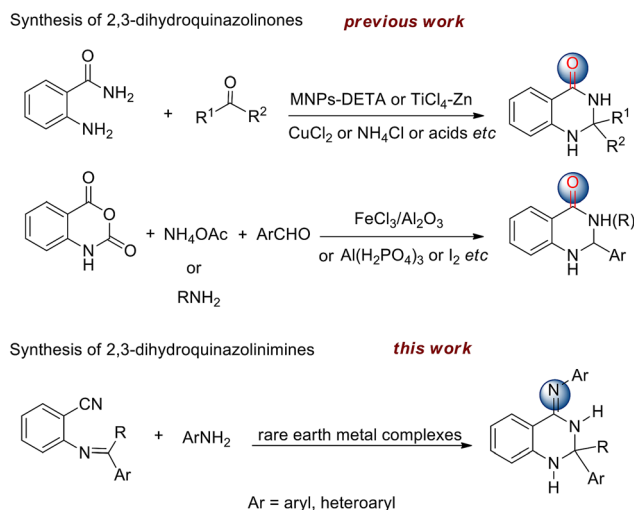
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Introduction

As one of the largest groups of organic compounds, heterocycles containing nitrogen have a considerable place in natural products, pharmaceuticals, and agrochemicals.^{1–3} Therefore, the development of convenient and straightforward synthetic approaches toward the construction of heterocycles is of great importance in organic chemistry. Recent research showed that quinazoline derivatives exhibited remarkable activity as antibacterial,⁴ antiviral,⁵ antitumor,⁶ and calcium channel antagonists.⁷ In contrast, the dihydroquinazoline scaffold features a saturated sp^3 hybridized carbon at the 2 or 4 sites of the heterocyclic ring. In recent years, several synthetic protocols for the preparation of 2,3-dihydroquinazolinones have been reported. Among them, the most frequently used synthetic approaches are based on the reaction of 2-aminobenzamide with aldehydes or ketones. As a result, a variety of catalysts were employed to accomplish this transformation involving

MNPs-DETA nanoparticles,⁸ CuCl_2 ,⁹ $\text{TiCl}_4\text{-Zn}$,¹⁰ ammonium chloride,¹¹ acids^{12,13} and ionic liquids (Scheme 1).¹⁴ In addition, a more convenient strategy for the preparation of these compounds is a one-pot, three-component reaction of isatoic anhydride, aldehydes and ammonium acetate or primary amines in the presence of homo- or heterogeneous

**Scheme 1** Synthesis of 2,3-dihydroquinazoline derivatives.

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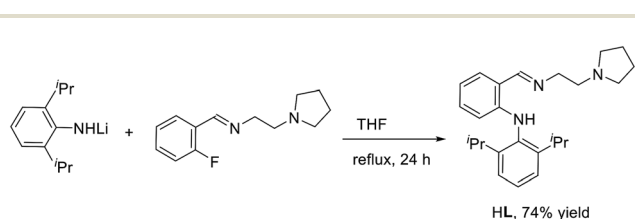
catalysts such as FeCl_3 /neutral Al_2O_3 , $[\text{Al}(\text{H}_2\text{PO}_4)_3]$, and nanoparticles.^{15–21} However, in terms of 4-arylimino-functionalized dihydroquinazolines, namely 2,3-dihydroquinazolinimines, no report has described the synthesis and characterization to date (Scheme 1).

Isoindolines, being regarded as the hydrogenated analogues of isoindoles, are almost unknown in natural compounds but have important biological activities such as the commonly used nuevamine and lennoxamine alkaloids.^{22–24} In addition, bis(arylimino)isoindolines are regarded as an interesting class of pincer ligands due to their unique structural features and diverse coordination chemistry.²⁵ A large number of complexes with varieties of transition metals derived from these ligands are known for their role as catalysts in organic transformations^{26–28} and as components of photoactive materials.^{29,30} With respect to the synthesis of bis(arylimino)isoindolines, the main methods of the direct reaction of 1,3-diiminoisoindoline with primary amines and the reaction of phthalonitrile with primary amines are involved. The condensation of 1,3-diiminoisoindoline with bulky amines or cyclic amines will lead to lower yields of products and often afford monosubstituted adducts. From 1997, several groups such as Siegl,³¹ Ziegler³² and Tang³³ successively reported the reaction of phthalonitrile with aromatic amines or 2-pyridylamines to produce 1,3-diiminoisoindolines by using different catalysts. However, those catalysts suffer from one or more disadvantages such as lower yields, limited substrates, and difficult operation. Therefore, more efficient catalysts are expected. It is well known that rare earth metal complexes could be utilized to promote C–N bond formation through inter- and intramolecular hydroamination of various C–C unsaturated compounds such as alkenes, alkynes and allenes.^{34–38} Herein, we describe the first example of rare earth metal dialkyl complex-catalyzed tandem addition/cycloamination between *ortho*-imino-benzonitriles or substituted phthalonitriles and amines to provide a wide variety of 2,3-dihydroquinazolinimines and 1,3-diiminoisoindolines through the construction of two C–N bonds.

Results and discussion

Synthesis of anilido-imino rare earth metal alkyl complexes

Treatment of lithium (2,6-diisopropylphenyl)amide with pyrrolidine-ligated fluorobenzene afforded an anilido-imino tridentate proligand HL ($\text{L} = (o\text{-(NHDipp)C}_6\text{H}_4\text{CH}=\text{N}(\text{CH}_2)_2\text{NC}_4\text{H}_8$, Dipp = 2,6- $\text{iPr}_2\text{C}_6\text{H}_3$) in 74% yield (Scheme 2). Subsequently,

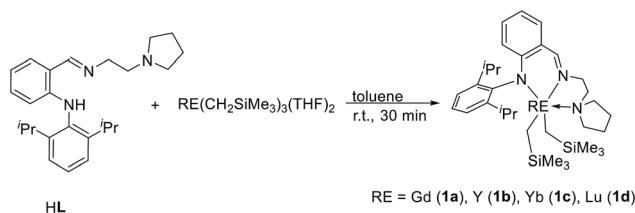


Scheme 2 Synthesis of the proligand.

the reactions of rare earth metal trialkyl complexes $\text{RE}(\text{CH}_2\text{SiMe}_3)_3(\text{THF})_2$ with an equimolar amount of HL in toluene at room temperature for 30 min afforded four distorted anilido-imino rare earth metal dialkyl complexes LRE ($\text{CH}_2\text{SiMe}_3)_2$ ($\text{RE} = \text{Gd}$ (**1a**), Y (**1b**), Yb (**1c**), Lu (**1d**)) (Scheme 3). Complexes **1a–1d** have good solubility in toluene and THF.

The ^1H NMR spectrum of **1b** clearly shows the singlet of the $\text{CH}=\text{N}$ group at 7.80 ppm, the presence of the $\text{Y}-\text{CH}_2$ species and the disappearance of the NH proton (at 10.54 ppm in HL). The diastereotopic methylene protons of the Y-alkyl groups are split into two doublets due to coupling to the ^{89}Y metal with coupling constants of $^2J_{\text{H-H}} = 11.2$ Hz and $^2J_{\text{Y-H}} = 3.2$ Hz (Fig. S4 and S6 in the ESI†). These values are consistent with the reported yttrium alkyl complexes,^{39,40} and similar results were observed in **1d** (Fig. S8 in the ESI†).

These complexes were characterized by single-crystal X-ray crystallography and elemental analysis. The representative structural diagram of **1b** is shown in Fig. 1, and those of other complexes are presented in the ESI.† Selected bond distances of **1a–1d** are listed in Table 1. X-ray analysis revealed that the anilido-imino ligand is in a κ^3 N,N,N -coordinated fashion with the metal center, and the atoms N1, N2, N3, and C26 constitute a plane forming a distorted square pyramidal with one of the alkyl groups (labeled C30) taking the apical position (Fig. 1). The bond distance of Y1-N1 2.281(3) Å is obviously shorter than that of Y1-N2 2.390(5) Å in **1b**. It is noteworthy that this difference of 0.1 Å for the Y–N bonds is greater than that of 0.02 Å in a tridentate β -diketiminato yttrium dialkyl complex (2.325(2) Å vs. 2.346(2) Å).³⁹ Additionally, the bond distance of C13-N1 1.360(5) Å is clearly longer than that of C19-N2 1.298(7) Å in **1b**, further demonstrating that the anilido/imino fragment exists in the rare earth metal alkyl complex due to phenyl ring embedding, resulting in electronic localization of the β -diketiminato unit, which is greatly different from the classical β -diketiminato analogues derived from acetylacetone with arylamines.⁴¹ Notably, the bond distance of Y1-N3 2.502(4) Å is significantly longer than that of Y1-N2 2.390(5) Å, suggesting that the steric effect has a great influence on the interaction between rare earth metal ions and adjacent atoms (Table 1). The same findings are also observed in gadolinium, ytterbium, and lutetium complexes (**1a–1d**). The RE–C bond distances ranging from 2.318(7) to 2.464(5) Å in **1a–1d** are comparable to the values observed in reported five-coordinate rare earth alkyl complexes.^{42,43}



Scheme 3 Synthesis of tridentate anilido-imino rare earth metal dialkyl complexes.

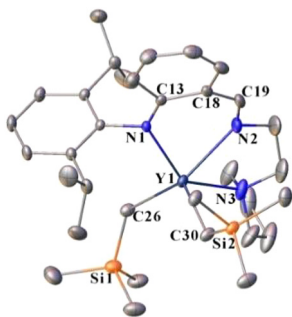


Fig. 1 Molecular structure of **1b**. All the hydrogen atoms are omitted for clarity.

Table 1 Selected bond lengths (Å) of **1a–1d**

	1a (Gd)	1b (Y)	1c (Yb)	1d (Lu)
RE1–N1	2.311(3)	2.281(3)	2.256(5)	2.245(5)
RE1–N2	2.443(5)	2.390(5)	2.331(8)	2.337(7)
RE1–N3	2.552(4)	2.502(4)	2.463(7)	2.462(6)
RE1–C26	2.464(5)	2.430(4)	2.326(7)	2.380(6)
RE1–C30	2.410(5)	2.377(4)	2.372(7)	2.318(7)
C13–N1	1.360(5)	1.360(5)	1.354(8)	1.369(7)
C19–N2	1.279(7)	1.298(7)	1.278(12)	1.283(10)
C13–C18	1.434(6)	1.431(6)	1.427(10)	1.434(8)
C18–C19	1.437(12)	1.406(7)	1.437(12)	1.421(11)

Catalytic activity

The catalytic activities of **1b** were first evaluated by using 2-(benzylideneamino)benzonitrile and 2-aminopyridine as the model substrates for the preparation of 4-arylimino-substituted 2,3-dihydroquinazoline under different conditions. The representative results are shown in Table 2. The reaction of **2aa** with **3a** cannot take place in the absence of a catalyst even under heating condition; however, the rare earth metal complex **1b** exhibits high activity in the catalytic formation of (2,3-dihydroquinazolin-4(1*H*)-ylidene)pyridin-2-amine **4aaa** (CCDC 2416305†) (entries 1 and 2). Further tests showed that the yield of the catalytic product can be improved to 98% by adjusting reaction temperatures and substrate ratios (entries 3–7). It was noticed that no further conversion was observed even after prolonging the reaction time to 36 h (entry 8). The reaction proceeds well in the presence of 4 mol% **1b** with 95% good yield (entry 9). Rare earth catalysts **1a–1d** all showed high efficiencies where larger radius ions of Gd and Y performed better than those of Yb and Lu, probably due to a more favorable and open environment provided by larger metal ions (entries 10–12). The precursor $\text{Y}(\text{CH}_2\text{SiMe}_3)_3(\text{THF})_2$ of **1b** gave the catalytic product in 70% yield under the same conditions, suggesting the positive role of the *N,N,N*-tridentate anilido-imino ancillary ligand (entry 13).

To evaluate the scope of the synthesis of 2,3-dihydroquinazolinimines, various 2-imine-functionalized benzonitriles and amines were examined under the optimized conditions and the results are represented in Table 3. The results indicated that some substituents such as methyl, methoxyl and bromine

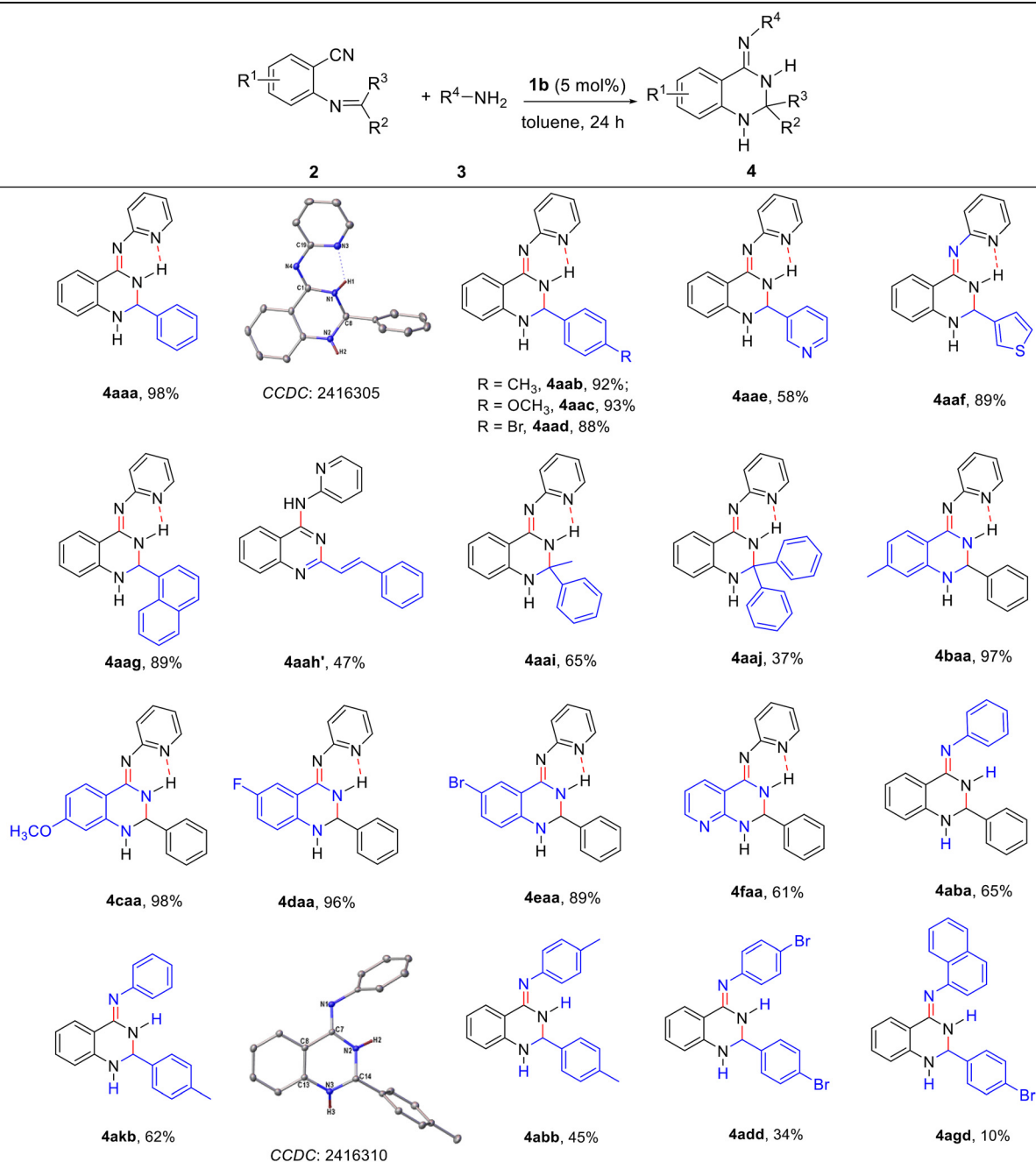
Table 2 Optimization of the reaction conditions^a

Entry	Cat. (mol%)	Temp. (°C)	Amine (equiv.)	Time (h)	Yield ^b (%)
1	—	110	1	24	NR
2	1b (5)	110	1	24	85
3	1b (5)	120	1	24	75
4	1b (5)	100	1	24	80
5	1b (5)	110	1.2	24	87
6	1b (5)	110	1.5	24	90
7	1b (5)	110	2	24	98
8	1b (5)	110	2	36	98
9	1b (4)	110	2	24	95
10	1a (5)	110	2	24	97
11	1c (5)	110	2	24	95
12	1d (5)	110	2	24	92
13	$\text{Y}[\text{C}_3]_3$ ^c (5)	110	2	24	70

^a Reaction conditions: into a Schlenk glass reactor were successively placed **2a** (1.0 mmol), **3a** and the catalyst in toluene (1.5 mL).

^b Isolated yields were based on *o*-(benzylideneamino)benzonitrile. ^c $\text{Y}[\text{C}_3]_3$ refers to the catalyst of $\text{Y}(\text{CH}_2\text{SiMe}_3)_3(\text{THF})_2$.

on the phenyl ring of the imines can smoothly react with 2-aminopyridine, affording the corresponding products **4aab–4aad** in good yields (88–93%). In addition, pyridine and thiophene-functionalized imino nitriles could be used in this reaction, producing 2,3-dihydroquinazolinimine derivatives **4aae** and **4aaf**, respectively. Notably, (*Z*)-*N*-(2-(naphthalen-1-yl)-2,3-dihydroquinazolin-4(1*H*)-ylidene)pyridin-2-amine **4aag** was obtained in 89% yield regardless of the use of the bulky naphthyl group. It is remarkable to find that an aromatic compound of the quinazoline **4aah'** was generated from the reaction of 2-aminopyridine with a conjugated α,β -unsaturated imine. Subsequently, the reactions of ketimino-functionalized nitriles with the primary amine **2aa** were tested, affording 2,2-bis(substituted) dihydroquinazolinimine products **4aai** and **4aaj** in moderate yields. Further studies showed that not only electron-donating (Me and OMe) but also electron-withdrawing (F and Br) substituents on the phenyl ring of benzonitrile were tolerated with a limited effect on the reaction yields. Even *o*-(benzylideneamino) nicotinonitrile can work with **2aa** to deliver product **4faa** in 61% isolated yield. The scope of this methodology for the preparation of 2,3-dihydroquinazolinimines was demonstrated by the synthesis of **4aba**, **4akb** (CCDC 2416310†) and **4abb** in moderate yields by the reactions of 2-imine-functionalized benzonitriles with aniline or *p*-toluidine. Two electron-withdrawing bromine atoms or a sterically-bulky naphthalenyl group were used in this reaction, resulting in lower yields of the products of 2-aryl-4-arylimino-2,3-dihydroquinazolines **4add** and **4agd**. Generally, the rare earth metal alkyl catalyst provides direct and flexible access to

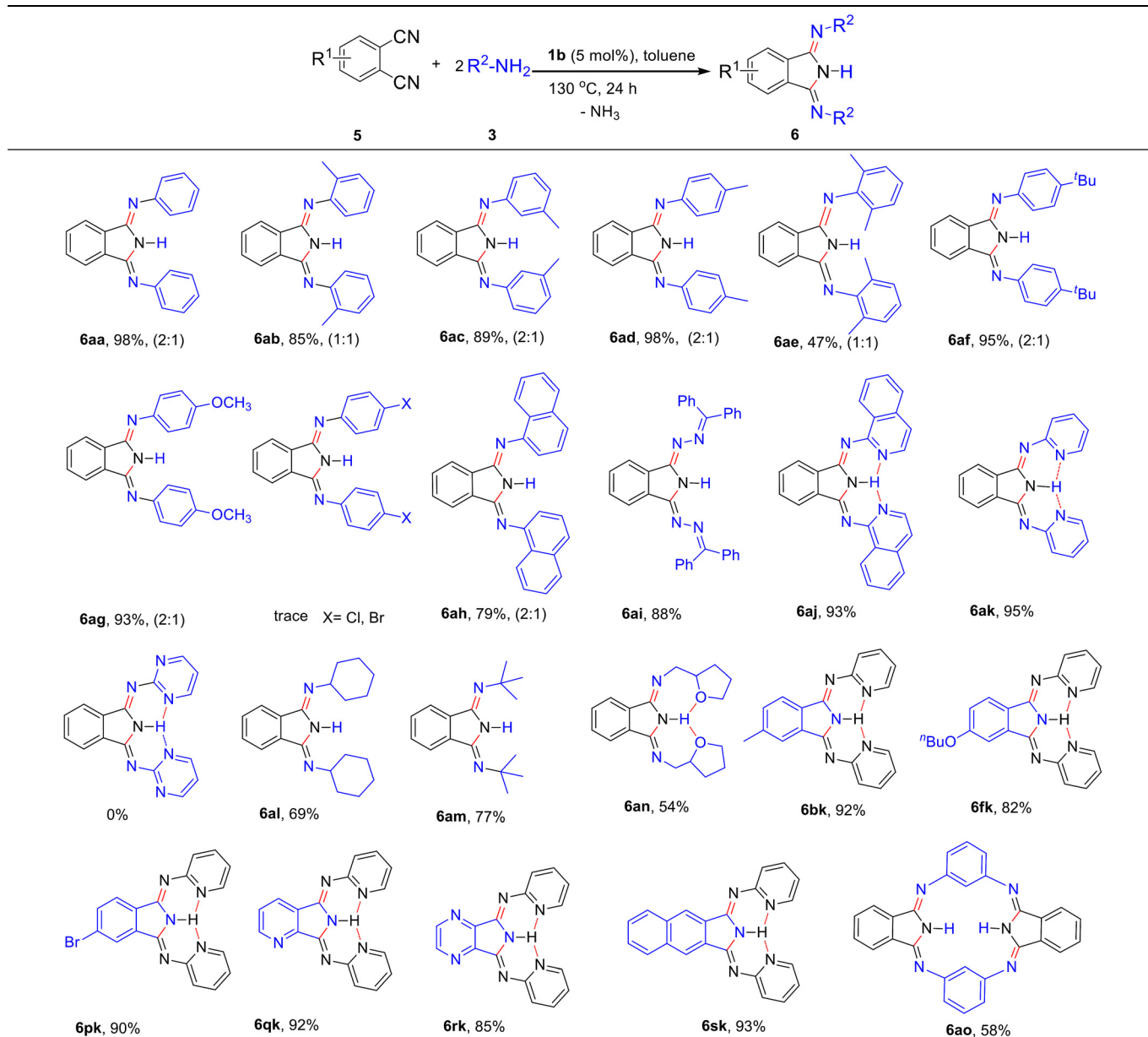
Table 3 Scope of 2-iminobenzonitriles and amines^a

^a Reaction conditions: into a Schlenk glass reactor were successively placed **2** (1.0 mmol), **3** (2.0 mmol) and **1b** in toluene (1.5 mL), 110 °C.

diverse 2,3-dihydroquinazolinimines substituted at the C2, N4-positions.

After the successful formation of dihydroquinazolines, we want to continue to expand the variety of reactions available. The initial studies were carried out by the reaction of phthalonitrile with aniline under similar conditions, and the detailed results are presented in Table S1 in the ESI.† To our delight, 1,3-bis(benzylideneamino)isoindoline **6aa** was synthesized and isolated. The ratio of *Z,Z* to *Z,E*-isomers was about 2 : 1, as

determined by NMR spectroscopy. After screening, the reaction of phthalonitrile with aniline to furnish 1,3-bis(benzylideneamino)isoindoline was performed in the presence of 5 mol% of **1b** in toluene at 130 °C for 24 h with an excellent 98% isolated yield. Next, a variety of substituted phthalonitriles and amines were examined and the results are shown in Table 4. Under the same conditions, treatment of phthalonitrile with *ortho*-, *meta*- and *para*-substituted toluidine gave products **6ab–6ad** in 85%, 89%, and 98% yields, respectively. The results implied

Table 4 Scope of substituted phthalonitriles and amines^a

^a Reaction conditions: into a Schlenk glass reactor were successively placed **5** (1.0 mmol), **3** (4.0 mmol) and the catalyst in toluene (1.5 mL), isolated yields. The ratios in brackets refer to isomers of *Z,Z* to *Z,E*-products as determined by ¹H NMR spectroscopic analysis.

that a great steric effect of the substituents on the reactivity was observed in the reaction, which was further reflected by the substrate 2,6-dimethylaniline, affording the desired product **6ab** in 47% yield. Similarly, satisfactory yields of **6af** and **6ag** were obtained when 4-(*tert*-butyl) and 4-methoxy aniline were employed in this reaction. Unfortunately, 4-chloroaniline or 4-bromoaniline failed to afford the corresponding isoindoline derivatives. However, naphthylamine can work well with phthalonitrile affording **6ah** in 79% yield. More significantly, benzophenone hydrazine and 1-aminoisoquinoline could undergo tandem addition and cyclization, affording the

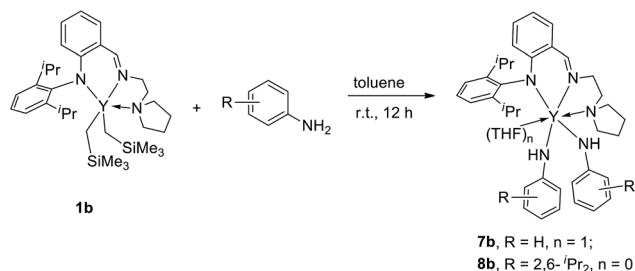
corresponding products **6ai** and **6aj** in high yields with exclusive *Z,Z*-configuration, probably due to larger steric hindrance or intramolecular hydrogen bond formation. As for the hetero-aromatic amines, 2-aminopyridine exhibited excellent activity, producing 1,3-bis(2-pyridylimino)isoindoline **6ak** in 95% isolated yield, which was widely used as a chelating ligand in organometallic chemistry.⁴⁴ In contrast to 2-aminopyridine, 2-aminopyrimidine showed an inert feature in this reaction. Catalyst **1b** is also applicable for aliphatic amines, such as cyclohexanamine, *tert*-butylamine and tetrahydrofurfurylamine, delivering 1,3-bis(aliphatic imino)-functionalized isoindolines.

dolines **6al**, **6am** and **6an** in 54%–67% yields under the optimized conditions. Further studies showed that some substituents (Me, ⁿBuO and Br) on the phenyl ring of phthalonitrile were tolerated, giving 1,3-diiminoisoindolines with little influence on the activity, and the result is completely different from the reaction of phthalonitrile with 4-bromoaniline. In addition, other types of *o*-dicarbonitriles, such as pyridine-, pyrazine- and naphthalene-2,3-dicarbonitriles, were reacted with 2-aminopyrimidine to produce the corresponding products **6qk**–**6sk** in good yields. Remarkably, treatment of phthalonitrile with an equimolar amount of *meta*-phenylenediamine produced a macrocyclic compound **6ao** in 58% yield.

Reaction of **1b** with arylamines

In order to gain more insights into the catalytic mechanism, several control experiments were carried out. The reaction of **1b** with an equimolar amount of aniline at room temperature for 12 h afforded a solvated yttrium bis(anilido) complex **LY**(NHPH)₂(THF) **7b**. During the process, the deprotonation of the NH₂ group and the release of two molecules of SiMe₄ took place (Scheme 4). When increasing the amount of aniline to 2 equiv., complex **7b** was obtained in 68% isolated yield. Similarly, treatment of **1b** with a bulky substrate 2,6-diisopropylaniline under the same conditions produced an unsolvated yttrium bis(anilido) complex **LY**(NHDipp)₂ **8b**. Next, upon treatment of **7b** with 2-(benzylideneamino)benzonitrile or phthalonitrile in a 1 : 1 molar ratio at 120 °C for 24 h, no desired rare earth metal complex was isolated except for the catalytic products detected. As for the role of the anilido complex in the catalytic reaction, ¹H NMR spectral monitoring of **7b** with **2aa** was performed in toluene-*d*₈ (Fig. S96 in the ESI†). The insertion reaction between the Y–N bond and the cyano group occurred quickly to form the yttrium complex bearing an amidinate functional group (*ab* at 5.79 ppm in Fig. S96 in the ESI†), and it disappeared completely after 24 h reaction time. At the same time, the signal of 2,3-dihydroquinazolinimine **4aba** was found in this reaction, indicating that the anilido complex could be regarded as an active intermediate in this catalytic reaction.

In the ¹H NMR (C₆D₆, 500 MHz) spectra, signals at 4.16 ppm for **7b** and 4.58 ppm for **8b** are associated with the NHAr group (Fig. S10 and S12†). The values are similar to that of 4.83 ppm in a β-diketiminato yttrium anilido complex.⁴⁵



Scheme 4 Reaction of **1b** with arylamines.

X-ray analysis showed that the geometry of the six-coordinate **7b** is different from that of the five-coordinate **1b**. These atoms (N1, N2, N3 and N5) in **7b** constitute a plane and other atoms of N4 and O1 occupy two apical positions, respectively. In contrast, the structure of **8b** is similar to that of **1b**, and two alkyl groups in **1b** were replaced by two anilido groups, forming a five-coordinate yttrium complex (Fig. 2). The bond distances of 2.238(2) Å and 2.271(3) Å of Y–N_{anilido} are obviously shorter than those of 2.335(2) and 2.435(2) Å of Y–N_{anilido-imino} in **7b**, probably due to the bulky steric hindrance of the anilido-imino ligand, and this finding was also observed in **8b**.

Based on the control experiments, a plausible reaction mechanism was proposed by using the synthesis of 2,3-dihydroquinazolinimines as an example (Scheme 5). The deprotona-

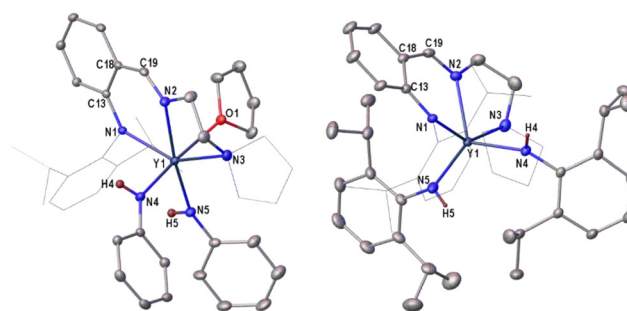
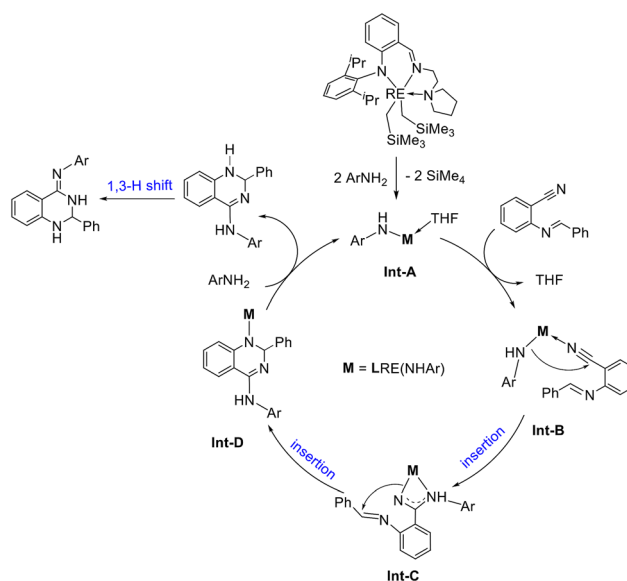


Fig. 2 Molecular structures of **7b** (left) and **8b** (right). All the hydrogen atoms are omitted for clarity except for H4 and H5. Selected bond lengths (Å) and angles (deg.). **7b**: Y1–N1 2.335(2), Y1–N2 2.435(2), Y1–N3 2.599(3), Y1–N4 2.238(2), Y1–N5 2.271(3), Y1–O1 2.4655(19), C13–N1 1.373(3), C19–N2 1.283(4), C13–C18 1.441(3), C18–C19 1.426(4), N4–Y1–O1 169.55(8). **8b**: Y1–N1 2.311(3), Y1–N2 2.367(3), Y1–N3 2.569(3), Y1–N4 2.210(3), Y1–N5 2.218(4), C13–N1 1.360(5), C19–N2 1.294(5), C13–C18 1.425(5), C18–C19 1.417(6), N5–Y1–N4 125.53(14).



Scheme 5 A proposed mechanism for the synthesis of 2,3-dihydroquinazolinimines.

tion of arylamines with the anilido-imino rare earth metal dialkyl complexes produced **Int-A** by the release of SiMe_4 (as **7b** and **8b**). Then the coordination of *ortho* imine-functionalized benzonitriles with the metal center generated **Int-B**, which underwent the first insertion of RE–N to the C=N unit to produce **Int-C**. Subsequently, the second insertion led to the formation of a six-membered heterocyclic intermediate **Int-D**. Treatment of **Int-D** with an amine resulted in the release of dihydroquinazolines following a 1,3-H shift to form the catalytic product 2,3-dihydroquinazolinimines and, meanwhile, regenerated the amido species **Int-A** to fulfill a catalytic cycle. The formation of 1,3-diiminoisoindolines is given in the ESI† as it is similar to the reaction described in Scheme 5.

Conclusions

In summary, novel *N,N,N*-tridentate anilido-imino rare earth metal dialkyl complexes were synthesized and characterized. Further investigation showed that these dialkyl complexes provided a convenient and atom-economical approach for the construction of 5- and 6-membered heterocyclic architectures including quinazolines and isoindolines *via* tandem addition and cyclization. 4-Arylimino-2,3-dihydroquinazoline derivatives were readily achieved by the reaction of 2-imine-functionalized benzonitriles with (hetero)aromatic primary amines for the first time. Moreover, a series of 1,3-diiminoisoindolines were synthesized in moderate to excellent yields from the reaction of *o*-dicarbonitriles with aromatic or aliphatic amines. The rare earth metal catalysts featured some advantages such as step economy, high activity and good tolerance to functional groups. During the process of determining the catalytic reaction mechanism, two yttrium anilido complexes were isolated and fully characterized.

Experimental

General remarks

All experiments were performed under an argon atmosphere using standard Schlenk techniques or in a glovebox. Solvents (toluene, hexane, and THF) were dried by refluxing over sodium/benzophenone ketyl and distilled before use. Amines and nitriles were purchased from commercial vendors and distilled before use. Pyrrolidine-ligated fluorobenzene⁴⁶ and 2-arylimino-benzonitriles were prepared according to the literature.⁴⁷ Elemental analysis data were obtained on a PerkinElmer Model 2400 Series II elemental analyzer. The ^1H NMR and ^{13}C { ^1H } NMR spectra were recorded on a Bruker Model spectrometer. Chemical shifts (δ) were reported in ppm. *J* values were reported in Hz. HRMS was obtained on a Thermo Scientific LTQ Orbitrap XL mass spectrometer.

Crystal structure determination

Single crystals for X-ray diffraction were sealed in a thin-walled capillary. Diffraction was carried out on a Bruker SMART CCD

area detector diffractometer using graphite-monochromated Mo-K α radiation ($\lambda = 0.71073 \text{ \AA}$). An empirical absorption correction was applied using the SADABS program.⁴⁸ All structures were solved by direct methods, completed by subsequent difference Fourier syntheses, and refined anisotropically for all non-hydrogen atoms by full-matrix least-squares calculations on F^2 using the SHELXTL program package. The program SQUEEZE in PLATON was used to remove the disordered solvents.⁴⁹

Synthesis of proligand HL

18.0 mL of *n*-BuLi in hexane (1.6 M, 28.8 mmol) was added to a solution of 2,6-diisopropylaniline (4.5 mL, 24 mmol) in THF (40 mL) at -78°C , and the mixture was warmed to room temperature for 8 h. Then *N*-(2-fluorobenzylidene)-2-(pyrrolidin-1-yl)ethanamine (4.4 g, 20 mmol) was added and the mixture was refluxed for 24 h. After filtration, the solvent was evaporated under reduced pressure. Colorless crystals were obtained by recrystallization from methanol (5.6 g, 74% yield). M.P.: $134\text{--}136^\circ\text{C}$. ^1H NMR (400 MHz, CDCl_3): δ 10.54 (s, NH, 1H), 8.49 (s, CH=N, 1H), 7.34–7.24 (m, ArH, 4H), 7.10–7.05 (m, ArH, 1H), 6.66 (t, *J* = 7.6 Hz, ArH, 1H), 6.21 (d, *J* = 8.0 Hz, ArH, 1H), 3.80 (t, *J* = 6.8 Hz, NCH₂, 2H), 3.12 (sept, *J* = 6.8 Hz, CH, 2H), 2.79 (t, *J* = 7.2 Hz, NCH₂, 2H), 2.60–2.57 (m, NCH₂, 4H), 1.80–1.76 (m, CH₂, 4H), 1.16 (d, *J* = 6.8 Hz, CH₃, 6H), 1.14 (d, *J* = 7.2 Hz, CH₃, 6H). ^{13}C { ^1H } NMR (100 MHz, CDCl_3 , ppm): δ 164.8 (C=N), 149.4, 147.5, 135.1, 133.4, 130.9, 127.1, 123.6, 116.6, 114.9, 111.6 (ArC), 61.1 (NCH₂), 57.4 (NCH₂), 54.7 (NCH₂), 28.4, 24.9, 23.4, 22.8. HRMS (ESI): calcd for $\text{C}_{25}\text{H}_{35}\text{N}_3$ [$\text{M} + \text{H}$]⁺: 378.2904, found: 378.2914.

Synthesis of complex 1

Under an argon atmosphere, proligand HL (0.37 g, 1.0 mmol) and $\text{RE}(\text{CH}_2\text{SiMe}_3)_3(\text{THF})_2$ (1.0 mmol) were mixed in toluene (1.5 mL) and stirred at room temperature for 5 min. A suitable amount of hexane (1–3 mL) was added and then filtered. The crystals were obtained by standing the solution at -30°C for 6–24 h.

Complex 1a. Orange crystals. (0.46 g, 65% yield). Anal. calcd for $\text{C}_{33}\text{H}_{56}\text{N}_3\text{Si}_2\text{Gd}$: C, 55.96; H, 7.97; N, 5.93. Found: C, 55.59; H, 7.88; N, 5.79.

Complex 1b. Yellow crystals. (0.38 g, 60% yield). ^1H NMR (400 MHz, C_6D_6 , ppm): δ 7.80 (s, HC=N, 1H), 7.36–7.29 (m, ArH, 3H), 7.07 (dd, *J* = 1.2, 8.0 Hz, ArH, 1H), 6.91–6.87 (m, ArH, 1H), 6.43–6.40 (m, ArH, 1H), 6.32 (d, *J* = 8.8 Hz, ArH, 1H), 3.36 (sept, *J* = 6.8 Hz, CHMe₂, 2H), 3.25–3.19 (m, NCH₂, 2H), 2.94 (t, *J* = 6.0 Hz, NCH₂, 2H), 2.26 (t, *J* = 6.0 Hz, NCH₂, 4H), 1.60–1.52 (m, CH₂, 2H), 1.43 (d, *J* = 6.8 Hz, CH₃, 6H), 1.29–1.25 (m, CH₂, 2H), 1.15 (d, *J* = 6.8 Hz, CH₃, 6H), 0.14 (s, SiCH₃, 18H), -0.78 (dd, *J* = 3.2, 11.2 Hz, YCH₂, 2H), -0.91 (dd, *J* = 3.2, 11.2 Hz, YCH₂, 2H). ^{13}C { ^1H } NMR (100 MHz, C_6D_6 , ppm): δ 169.4 (HC=N), 156.9, 146.0, 141.2, 137.6, 134.5, 126.7, 125.4, 118.3, 118.0, 113.7 (ArC), 57.4 (NCH₂), 55.2 (NCH₂), 53.5 (NCH₂), 35.8 (d, *J*_{Y–C} = 41.0 Hz, YCH₂), 28.5, 25.8, 25.1, 22.7, 4.5 (SiMe₃). Anal. calcd for $\text{C}_{33}\text{H}_{56}\text{N}_3\text{Si}_2\text{Y}$: C, 61.94; H, 8.82; N, 6.57. Found: C, 61.70; H, 8.94; N, 6.54.

Complex 1c. Red crystals. (0.51 g, 70% yield). Anal. calcd for $C_{33}H_{56}N_3Si_2Yb$: C, 54.74; H, 7.80; N, 5.80. Found: C, 54.45; H, 7.80; N, 5.67.

Complex 1d. Yellow crystals. (0.47 g, 65% yield). 1H NMR (500 MHz, C_6D_6 , ppm): δ 7.79 (s, $HC=N$, 1H), 7.35–7.30 (m, ArH , 3H), 7.06 (dd, $J = 1.5, 8.0$ Hz, ArH , 1H), 6.91–6.88 (m, ArH , 1H), 6.42–6.37 (m, ArH , 2H), 3.42 (sept, $J = 7.0$ Hz, $CHMe_2$, 2H), 3.22–3.17 (m, NCH_2 , 2H), 2.92 (t, $J = 6.0$ Hz, NCH_2 , 2H), 2.29–2.26 (m, NCH_2 , 2H), 2.21 (t, $J = 6.0$ Hz, NCH_2 , 2H), 1.56–1.50 (m, CH_2 , 2H), 1.46 (d, $J = 7.0$ Hz, CH_3 , 6H), 1.25–1.22 (m, CH_2 , 2H), 1.16 (d, $J = 6.5$ Hz, CH_3 , 6H), 0.13 (s, $SiCH_3$, 18H), -0.93 (d, $J = 12.0$ Hz, $LuCH_2$, 2H), -1.05 (d, $J = 12.0$ Hz, $LuCH_2$, 2H). $^{13}C\{^1H\}$ NMR (125 MHz, C_6D_6 , ppm): δ 169.6 ($HC=N$), 157.8, 145.5, 144.1, 137.3, 134.5, 126.4, 125.2, 119.1, 118.2, 113.9 (ArC), 57.3 (NCH_2), 54.6 (NCH_2), 53.1 (NCH_2), 43.4, 28.4, 25.9, 25.1, 22.5, 4.7 ($SiMe_3$). Anal. calcd for $C_{33}H_{56}N_3Si_2Lu$: C, 54.60; H, 7.78; N, 5.79. Found: C, 54.68; H, 7.43; N, 5.49.

Synthesis of complexes 7b and 8b

Under an argon atmosphere, complex **1b** (96 mg, 0.15 mmol) and $ArNH_2$ (0.30 mmol) were mixed in tetrahydrofuran (4.0 mL) and stirred at room temperature for 5 min. A suitable amount of hexane (1–2 mL) was added and then filtered. The crystals were obtained by standing the solution at room temperature for 48 h.

Complex 7b. Yellow crystals. (73 mg, 68% yield). 1H NMR (500 MHz, C_6D_6 , ppm): δ 7.82 (s, $HC=N$, 1H), 7.28–7.22 (m, ArH , 3H), 7.13–7.10 (m, ArH , 5H), 6.88–6.85 (m, ArH , 1H), 6.57 (t, $J = 7.5$ Hz, ArH , 2H), 6.44–6.38 (m, ArH , 5H), 6.23 (d, $J = 8.5$ Hz, ArH , 1H), 4.16 (s, NH , 2H), 3.48–3.41 (m, $CHMe_2$ and OCH_2 , 6H), 3.04 (t, $J = 5.5$ Hz, NCH_2 , 2H), 2.77–2.30 (m, NCH_2 , 4H), 2.21 (t, $J = 5.5$ Hz, NCH_2 , 2H), 1.36 (s, OCH_2CH_2 , 4H), 1.28–1.26 (m, NCH_2CH_2 , 4H), 1.24 (d, $J = 6.5$ Hz, CH_3 , 6H), 1.07 (d, $J = 6.5$ Hz, CH_3 , 6H). $^{13}C\{^1H\}$ NMR (125 MHz, C_6D_6 , ppm): δ 169.8 ($HC=N$), 158.0, 157.5, 147.5, 142.0, 137.9, 134.1, 129.5, 126.6, 125.2, 119.2, 117.6, 116.3, 113.5, 113.2 (ArC), 69.5 (OCH_2), 58.5 (NCH_2), 56.9 (NCH_2), 55.6 (NCH_2), 28.6, 26.2, 25.6, 24.2, 23.0. Anal. calcd for $C_{41}H_{54}N_5OY$: C, 68.22; H, 7.54; N, 9.70. Found: C, 68.53; H, 7.48; N, 9.94.

Complex 8b. Yellow crystals. (88 mg, 72% yield). 1H NMR (500 MHz, C_6D_6 , ppm): δ 7.67 (s, $HC=N$, 1H), 7.12 (d, $J = 8.0$ Hz, ArH , 1H), 7.07 (d, $J = 8.0$ Hz, ArH , 4H), 7.01 (d, $J = 7.0$ Hz, ArH , 3H), 6.78 (t, $J = 7.5$ Hz, ArH , 2H), 6.75–6.72 (m, ArH , 1H), 6.39 (d, $J = 7.0$ Hz, ArH , 1H), 6.19 (d, $J = 9.0$ Hz, ArH , 1H), 4.58 (s, NH , 2H), 3.47 (sept, $J = 7.0$ Hz, $CHMe_2$, 2H), 3.11–3.03 (m, $CHMe_2$, 2H), 2.97–2.87 (m, $CHMe_2$ and NCH_2 , 6H), 2.36 (t, $J = 6.0$ Hz, NCH_2 , 2H), 2.10 (s, NCH_2 , 2H), 1.74–1.70 (m, NCH_2CH_2 , 2H), 1.41–1.36 (m, NCH_2CH_2 , 2H), 1.28 (d, $J = 7.0$ Hz, CH_3 , 12H), 1.17 (d, $J = 7.0$ Hz, CH_3 , 6H), 1.15 (d, $J = 6.5$ Hz, CH_3 , 12H), 1.03 (d, $J = 6.5$ Hz, CH_3 , 6H). $^{13}C\{^1H\}$ NMR (125 MHz, C_6D_6 , ppm): δ 171.2 ($HC=N$), 158.3, 151.6, 151.6, 146.9, 142.0, 137.9, 137.6, 134.2, 133.2, 129.3, 128.6, 126.8, 125.7, 125.4, 123.3, 120.4, 117.8, 115.8, 113.5 (ArC), 57.2 (NCH_2), 56.4 (NCH_2), 55.8 (NCH_2), 30.2, 28.8, 27.0, 24.8, 24.3,

24.0, 23.0, 21.4. Anal. calcd for $C_{49}H_{70}N_5Y$: C, 71.95; H, 8.63; N, 8.56. Found: C, 71.62; H, 8.61; N, 8.83.

General procedure for the synthesis of 2,3-dihydroquinolinimines

Catalyst **1b** (32 mg, 5 mol%) was dissolved in 1.5 mL of toluene. Then amines (2.0 mmol) and *ortho*-imino-functionalized benzonitriles (1.0 mmol) were added. The reaction was stirred at 110 °C for 24 h. After that, the volatiles were removed under reduced pressure, and the catalytic products were purified by silica gel column chromatography (ethyl acetate: petroleum ether = 1:1–1:30).

General procedure for the synthesis of 1,3-diiminoisoindolines

Catalyst **1b** (32 mg, 5 mol%) was dissolved in 1.5 mL of toluene. Then primary amines (4.0 mmol) and phthalonitrile (1.0 mmol) were added. The reaction was stirred at 130 °C for 24 h. After that, the volatiles were removed under reduced pressure, and the catalytic products were purified by silica gel column chromatography (ethyl acetate: petroleum ether = 1:2–1:50).

Data availability

The data used to support the findings of this study are included within the article.

Conflicts of interest

There are no conflicts to declare.

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