Dalton Transactions

Accepted Manuscript

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ROYAL SOCIETY OF CHEMISTRY

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ROYAL SOCIETY OF CHEMISTRY View Article Online
DOI: 10.1039/C8DT04630A

Journal Name

ARTICLE

Guanylation/Cyclisation of Amino Acid Esters using Imidazolin-2-iminato Titanium Initiator

Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

www.rsc.org/

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We report the catalytic guanylation/cyclisation of amino acid esters with carbodiimides and isocyanates to furnish corresponding quinazolinone and urea derivatives under mild conditions using two titanium(IV) complexes $[(Im^RN)_2Ti(NMe_2)_2]$ (R = tBu, **2a**; R = Mes, **2b**), which were synthesised by reacting tetrakis(dimethylamido)titanium(IV) $[Ti(NMe_2)_4]$ with imidazolin-2-imine (Im^RNH; R = tert-butyl (tBu) (**1a**), mesityl (Mes) (**1b**)] in a 1:2 molar ratio in toluene. Further, the reaction of titanium complex **2a** with 2,6-diisopropylphenylamine ($DippNH_2$) resulted in the corresponding mixed ligand titanium complex $[\kappa^1\text{-}(Im^{tBu}N)_2Ti(NMe_2)(HNDipp)]$ (**3a**). In contrast, the reaction of complex **2a** with 2,6-dimethyl phenol afforded the mono-imidazolin-2-iminato Ti^{IV} phenolate complex $[\kappa^1\text{-}(Im^{tBu}N)Ti(O\text{-}1,6\text{-}Me_2C_6H_3)_3]$ (**4a**). The solid-state structures of complexes **2b**, **3a,** and **4a**, established by single crystal X-ray diffraction analyses, confirmed a very short bond between titanium and imidazolin-2-iminato nitrogen in each case. Titanium complexes **2a** and **2b** exhibited relatively high conversion, superior selectivity and broad functional group tolerance in both guanylation and cyclisation rections under mild conditions. We propose the most plasubile mechanism for guanylation/cyclisation of amino acid esters to carbodiimides and isocyanates on the basis of a number of controlled reactions.

Introduction

Quinazolinones, an important class of six-membered nitrogen-containing heterocyclic compounds, have been widely used in anticancer, antimalarial, anti-inflammatory and anti-tuberculosis medication due to their diverse biological properties.[1] Additionally, quinazolinones are versatile and have been used as ligands for benzodiazepine and AMPA receptors in the central nervous system or as DNA binders.[2] Quinazolinones and their derivatives have also found considerable utility in the synthesis of natural products.[3] On the other hand, urea derivatives of amino acid esters are also used as ligands in coordination chemistry, and synthons for challenging organic transformations.[4] Due to this, over the past decade or so, the development of efficient synthetic methods for producing quinazolinones and their derivatives has garnered attention from researchers.[5–6] However, until now, the efficient and economical synthesis of quinazolinones was a challenging task and not adequately explored. In 2015, Xi et al. reported the synthesis of quinazolinones through CuI-catalysed intra-molecular N-arylations of halo benzoic acid and guanidine but the relatively narrow substrate scope and the large requirement of additives rendered it unfavourable.[7] In 2016, Odel et al. introduced a convenient and efficient approach for the synthesis of 2-amino quinazolinones via domino carbonylation/cyclisation of readily available ortho-iodo anilines with cyanamide, but the toxicity of CO gas limited this method from being used for sustainable production.[8] Pd and Mo–mediated synthesis of quinazolin-4(3H)-ones through cyclocarbonylation using microwave irradiation, as reported by Roberts et al., also falls in the same category.[9] On the other hand, Co, Cu, and Pd–metal catalysed aminolysis of isatoic anhydride followed by reaction with isocyanide,[10] isothiocyanate[11] or cyanamide[12] is a popular method for the synthesis of miscellaneous derivatives of quinazolinones. However, in all cases, toxic reagents are usually required, and long and tedious procedures leading to unsatisfactory overall yields, are both disadvantages of the above-mentioned pathways. Hence, a novel catalytic pathway starting from earth-abundant, environment-friendly and non-toxic metals as well as substrates need to be developed to construct quinazolinones.[13]

Recently Xi and Zhang introduced Zn-catalysed guanylation/amidation of amino acid esters with carbodiimides to produce various quinazolines.[14] In addition, Bei Zhao and his research group developed a rare-earth metal amide as a catalyst for the guanylation/cyclisation of amino acid esters followed by carbodiimides.[15] However, it is well known that not only are rare-

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Electronic Supplementary Information (ESI) available: Text giving experimental details for the catalytic reactions, ^1H, $^{13}C\{^1H\}$ and spectra of quinazolinones **5a - 5t,** and urea **6a – 6l** and Ti complexes **2a, 2b, 3a, 4a.** in Supporting Information. For crystallographic details in CIF see DOI: 10.1039/b000000x/.

earth metals less abundant and expensive, their compounds are also difficult to handle.[16–19] With this in mind, we wanted to develop a rich catalytic chemistry using relatively inexpensive and earth-abundant group-4 metals in the guanylation/cyclisation of amino acid followed by carbodiimides to synthesise differently substituted quinazolinone skeletons.[20] Among the group-4 metals, titanium has been given considerable attention in the last few years due to its special and versatile coordination geometry,[21–28] followed by its novel chemical reactivity in numerous stoichiometric and catalytic reactions such as hydroaminations, hydroalkoxylations, hydrosilylations, polymerisations, alkyne oligomerisations and various small-molecule activations.[21–28] However, the insertion of heterocumulenes into N–H bonds of amino acid esters followed by cyclisation to produce quinazolinones has not been explored up to now in titanium metal chemistry. Hence, employing titanium as a catalyst in the guanylation/cyclisation of amino acid esters with carbodiimides would be a rational next step.

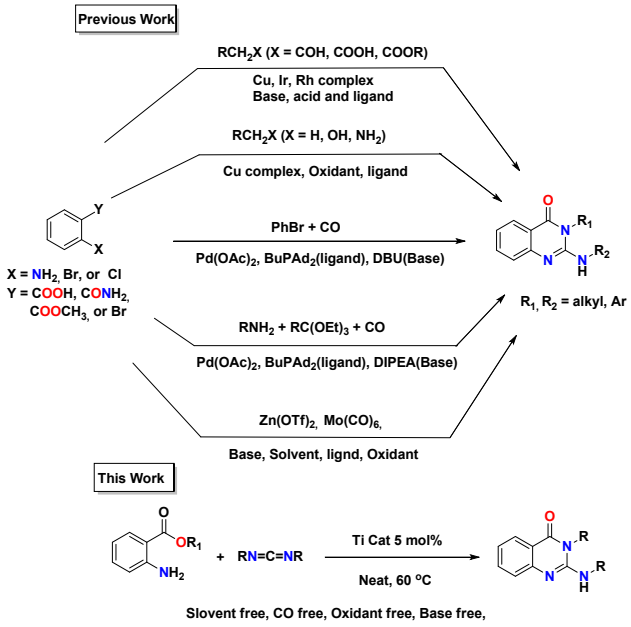
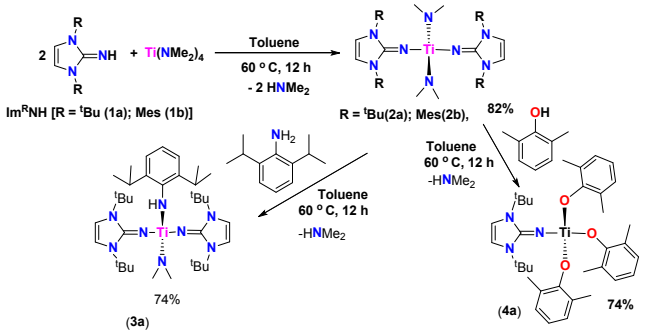


Figure 1. Reported catalysts for guanylation/cyclisation of amino acid esters with carbodiimides.

We have recently reported the use of the imidazolin-2-iminato titanium complex [($Im^{Dipp}N$)$Ti(NMe_2)_3$] (ImN = imidazolin-2-iminato, Dipp = 2,6-$^{i}Pr_2C_6H_3$) in the catalytic hydroamination of various amines to heterocumulenes.[28] We have also reported Ti^{IV} amido complex–supported phosphinamido chalcogenide ligands as pre-catalysts for the chemoselective hydroboration and cyanosilylation of carbonyl compounds followed by the addition of an E–H (E = N, O, S, P, C) bond to heterocumulenes under ambient conditions.[30–32] In a continuation of our ongoing project, we wanted to extend the applicability of Ti^{IV} complexes as catalysts for guanylation/cyclisation of amino acid esters with carbodiimides and isocyanates. We report here the synthesis of bis-imidazolin-2-iminato titanium (IV) complexes [κ^1-(Im^RN)$_2Ti(NMe_2)_2$] (R = tBu, **2a**; R = Mes, **2b**) and their catalytic application in hydroamination/cyclisation of amino acid esters with carbodiimides and isocyanates to afford corresponding quinazolinone and urea derivatives under mild conditions having a broad substrate scope.

Results and discussion

Synthesis of titanium(IV) complexes: The bis-imidazolin-2-iminato titanium(IV) complexes [κ^1-(Im^RN)$_2Ti(NMe_2)_2$] (R = tBu, **2a**; R = Mes, **2b**) were prepared by the treatment of tetrakis(dimethyl-amido)titanium(IV) [$Ti(NMe_2)_4$] with protic ligand imidazolin-2-imine [Im^RNH; R = tert-butyl (tBu) (**1a**), mesityl (Mes) (**1b**)] in a 1:2 molar ratio in toluene in high yield (Scheme 1). Further reaction of titanium complex **2a** with 2,6-diisopropylamine ($DippNH_2$) at 60°C gave the corresponding mixed ligand titanium complex [κ^1-($Im^{tBu}N$)$_2Ti(NMe_2)$(HNDipp)] (**3a**). In contrast, the reaction of complex **2a** with 2,6-diphenyl phenol under similar reaction conditions afforded the mono-imidazolin-2-iminato Ti^{IV} phenolate complex [κ^1-($Im^{tBu}N$)$Ti(O\text{-}1,6\text{-}Me_2C_6H_3)_3$] (**4a**) (Scheme 1).



Scheme 1. Synthesis of Ti^{IV} complexes **2a**, **2b**, **3a** and **4a**.

All the new titanium complexes **2a, 2b, 3a,** and **4a** showed good solubility in common organic solvents such as THF, pentane, and toluene and were characterised using standard spectroscopic and analytical techniques. The solid-state structures of complexes **2b, 3a** and **4a** were established by single-crystal X-ray diffraction analysis. The ^{1}H NMR spectra of all the Ti^{IV} complexes **2a, 2b, 3a,** and **4a** are consistent with their composition.

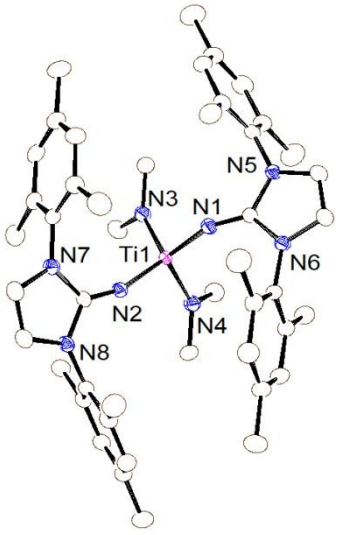


Figure 2. Molecular solid-state structure of **2b**. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°) are: Ti1–N1 1.847(2), Ti1–N2 1.858(2), Ti1–N4 1.927(2), Ti1–N3 1.930(2), N1–Ti1–N2 113.94(11), N1–Ti1–N4 114.02(11), N2–Ti1–N4 104.56(10), N1–Ti1–N3 106.40(10), N2–Ti1–N3 115.12(11), N4–Ti1–N3 102.42(11), C1–N1–Ti1 157.6(2), C2–N2–Ti1 161.9(2), C44–N3–Ti1 128.8(2), C43–N3–Ti1 120.6(2), C45–N4–Ti1 123.4(2), C46–N4–Ti1 125.84(19).

The solid-state structure of all the complexes **2b**, **3a**, **4a**, established by single-crystal X-ray diffraction analysis. Details of the structural parameters are given in Table S1 in the Supporting Information. The solid-state structure of complex **2b** is shown in Figure 2, whereas Figures 3 and 4 represent the solid-state structures of complexes **3a** and **4a** respectively. In all the titanium complexes, a κ^1-coordination mode of the imidazolin-2-iminato ligand was observed. Complex **2b** crystallises in the orthorhombic space group *P*ccn with eight molecules in the unit cell. In complex **2b** the titanium ion is bonded with two imidazolin-2-iminato ligands along with two dimethyl amido groups. Complexes **3a** and **4a** crystallise in the monoclinic space group *C* 2/c and triclinic space group *P*-1 respectively. In case of **3a**, titanium ion is attached with one imidazolin-2-iminato ligand, one dimethylamido ($-NMe_2$) group and one 2,6-diisopropylphenyl anilido group. However, three 2,6-dimethyl phenoxide ligands are attached to the titanium ion in complex **4a**. Thus, in all the complexes – **2a, 3a,** and **4a** – the titanium (IV) ion is tetra-coordinated to adopt a distorted tetrahedral geometry around the metal ion.

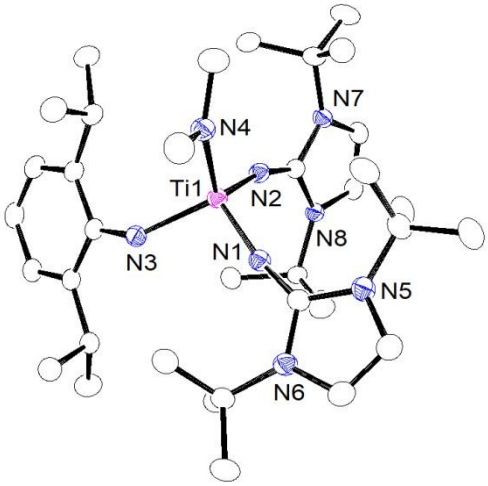


Figure 3. Molecular solid-state structure of **3a**. Selected bond lengths (Å) and angles (°) are: Ti1–N1 1.8242(18), Ti1–N2 1.8334(17), Ti1–N4 1.9355(19), Ti1–N3 2.0249(17), N1–Ti1–N2 112.04(8), N1–Ti1–N4 105.32(8), N2–Ti1–N4 113.17(8), N1–Ti1–N3 105.85(7), N2–Ti1–N3 109.75(8), N4–Ti1–N3 110.40(8), C1–N1–Ti1 170.85(16), C12–N2–Ti1 164.72(16), C23–N3–Ti1 140.02(14), C36–N4–Ti1 134.80(17), C35–N4–Ti1 115.98(16).

In all complexes, very short Ti–$N_{iminato}$ bond lengths – [1.847(2) Å and 1.858(2) Å for complex **2b**; 1.8242(18) Å and 1.8334(17) Å for complex **3a** and 1.7738(16) Å] for **4a** – are observed due to the strong 2σ, 4π-electron donation of the monoanionic imidazolin-2-iminato ligands and these values are consistent with those of the previously reported complexes [κ^1-($Im^{tBu}N$)$_2$$TiMe_2$] and [$\kappa^1$-($Im^{tBu}N$)$_2$$TiCl_2$] by Tamm et al.[33] In complexes **3a** and **4a**, the imidazolin-2-iminato moiety coordinates with the titanium ion in an essentially linear fashion [Ti1–N1–C1 = 170.85(16)° and Ti1-N2-C12 164.72(16)° for complex **3a** and Ti1–N1–C1 = 168.30(15)° for complex **4a**]. However, a slight deviation from linearity was observed in complex **2b** [Ti1–N1–C1 = 157.6(2)°, Ti1-N2-C2 161.9(2)], due perhaps to the presence of tert-butyl groups around the titanium ion. The Ti–N_{amide} distances in complex **2b** [1.927(2) and 1.930(2) Å] and complex **3a** [1.9355(19) Å] are very similar and consistent with those in previously reported titanium amido complexes[29] and slightly shorter than the Ti–$N_{anilido}$ bond measuring 2.0249(17) Å in complex **3a**. It is noteworthy that 2,6-diisopropylaniline replaced one dimethylamido group to form the titanium complex **3a** with three different ligand systems keeping the titanium imidazolin-2-iminato bond unperturbed. In contrast, complex **4a** represents the imidazolin-2-iminato titanium tris arylphenoxide complexes obtained from the cleavage of two titanium amido bonds and one titanium imidazolin-2-iminato bond of complex **2a**.

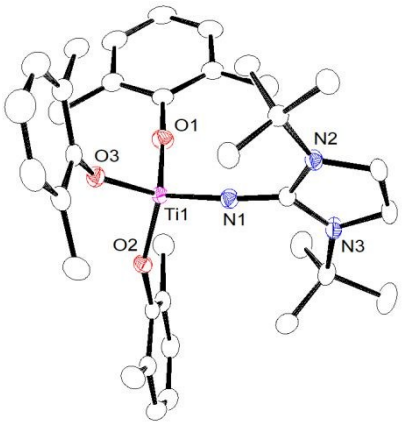


Figure 4. Molecular solid-state structure of **4a**. Selected bond lengths (Å) and angles (°) are: Ti1–N1 1.7738(16), Ti1–O1 1.8128(14), Ti1–O2 1.8465(14), Ti1–O3 1.8505(13), N1–Ti1–O1 110.35(7), N1–Ti1–O2 111.73(8), O1–Ti1–O2 108.29(7), N1–Ti1–O3 111.35(7), O1–Ti1–O3 107.26(7), O2–Ti1–O3 107.70(6), C12–O1–Ti1 175.08(14), C20–O2–Ti1 157.80(12), C28–O3–Ti1 148.25(12), C1–N1–Ti1 168.30(15).

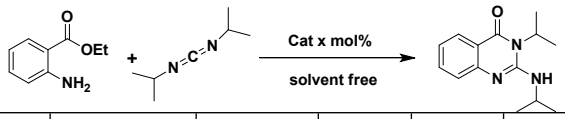
Catalysis

All the titanium complexes **2a**, **2b**, **3a,** and **4a** were first tested as pre-catalysts for the guanylation/cyclisation of amino acid esters with carbodiimides to afford the corresponding quinazolinones. Initial screening of the catalytic activity of the respective titanium complexes was performed with a catalyst loading of 5 mol% starting with ethyl 2-aminobenzoate and N,N′ diisopropylcarbodiimide (DIC) under solvent-free conditions.

To our satisfaction, the titanium metal compounds we used, including amido as well as phenolato derivatives of the imidazolin-2-iminato Ti(IV) complexes, gave the desired cyclic product in good-to-moderate yields, whereas the corresponding cyclic quinazolinone

product was obtained up to 86% when complex **2b** was used as the pre-catalyst at 60°C and after 12 hours of reaction time. Hence, complex **2b** was chosen as the ideal catalyst. All the results are summarised in Table 1. Additionally, we investigated the effect of solvent on the guanylation/cyclisation reaction, for which various solvents such as THF, hexane, and toluene, were screened. However, in all cases, we observed sluggish reactivity even after prolonged reaction times (Table 1, entries 7–9). Subsequent screening of temperature of the guanylation/cyclisation reaction based on the titanium complexes suggested that 60°C was optimal (Table 1, entries 6). Further, catalyst loading of 2.5% or 1% substantially lowered the reaction rate and yields of 62% and 43% respectively were observed after 24 hours of reaction (Table 1, entries 10-11).

Table 1. Screening of Ti^{IV} pre-catalysts for guanylation/cyclisation of amino acid esters with carbodiimides.

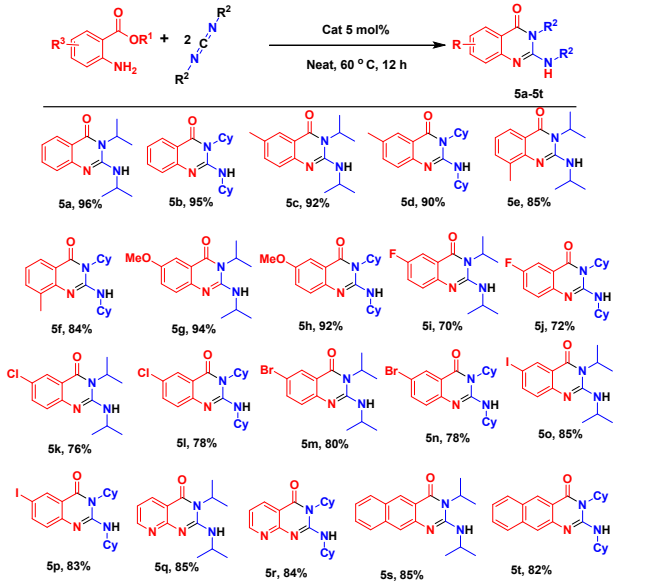


Entry	Catalyst	Solvent	t (h)	T (°)	Yield[a](%)
1	None	Neat	12	80	None
2	**2a**	Neat	12	60	78
3	**2b**	Neat	12	60	86
4	**3a**	Neat	12	60	70
5	**4a**	Neat	12	60	65
6	**2b**	Neat	24	100	85
7	**2b**	Toluene	24	80	68
8	**2b**	THF	24	60	62
9	**2b**	Hexane	24	60	58
10[b]	**2b**	Neat	12	60	62
11[c]	**2b**	Neat	12	60	43
12[d]	**2b**	Neat	12	60	92
13	$Ti(NMe_2)_4$	Neat	24	60	30

[a]Isolated yield. [b,c]Reaction was performed using 2.5 mol % (entry 10) and 1 mol% (entry 11) of catalyst **2b**. [d]molar ratio of DIC: ethyl 2-aminobenzoate to 2:1.

At first, we carried out the reaction with ethyl 2-aminobenzoate and N,N' diisopropylcarbodiimide (DIC), having a molar ratio of 1:1, which substantially lowered the product yield. From TLC detection it was clearly observed that a certain amount of reactant amino acid ester always remained unreacted even after the reaction was quenched, while DIC was fully consumed, indicating there was some side reaction occurred with DIC which prevented the other substrate amino acid ester from the complete reaction. During this reaction, alcohol is released as a side product which further reacts with one molecule of carbodiimides in the presence of catalyst **2b** to afford the corresponding isourea product. This observation is already well reported by our group using μ-imido titanium complexes as catalysts.[31] However, to overcome this difficulty, we increased the molar ratio of DIC to 2:1 with respect to the amino acid ester, which dramatically increased the yields of the product up to 92% (Table 1, entry 12). Thus, with 60°C and solvent-free condition taken as optimal, we set out to examine the scope of various substrates of amino acid esters followed by carbodiimides having molar ratio of DIC to 2:1 in the presence of 5 mol% titanium complex **2b**. The results of all catalytic guanylation/cyclisation reactions are summarised in Table 2. A linear Plot of the product concentration vs time at a different concentration of catalyst (**2b**) confirms that with the increases of catalyst ratio, the rate of the guanylation/cyclisation reaction increases linearly observed in Figure FS78, 79, 80 in SI.

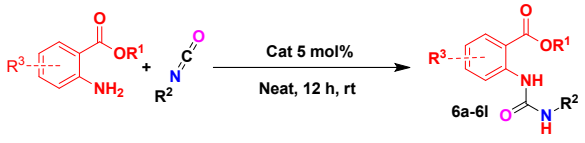
Table 2. Substrate scope for the guanylation/cyclisation of amino acid esters with carbodiimides catalysed by complex **2b**.



All reactions were performed in neat conditions using the amino acid ester (0.6060 mmol, 1 equiv.), carbodiimide (1.212 mmol, 2 equiv.), and complex **2b** (23 mg, 0.0303 mmol, 5 mol%). Yields were calculated by isolated yield.

A series of substituted esters was examined to observe the electronic effect of the substituents on the outcomes. Methyl 2-aminobenzoates, bearing the electron-donating methyl, methoxy and naphthyl groups, gave the corresponding aminoquinazolinones in excellent yield, up to 95% (Table 2, **5a–5h** and **5s–5t**). Electron-withdrawing groups such as fluoro, chloro, bromo, iodo, and pyridinyl were also converted to the corresponding aminoquinazolinones in good yield, within 12 hours of reaction time (Table 2, **5i–5r**). When we changed from DIC to a bulkier carbodiimide, such as DCC, we were also able to obtain excellent yields from various substituted amino acid esters (Table 2, **5b–5t**). Furthermore, we examined the effect of the ester group of 2-aminobenzoates, which showed that esters bearing bulky leaving groups, such as tBu, gave the corresponding products in outstanding yields (Table 2, entries **5s** and **5t**). All the products (**5a–5t**) were fully characterised with the help of NMR and mass spectrum studies (Figs FS11–FS50 in SI) and yields were calculated from isolated yields.

Table 3. Substrate scope for the hydroamination of amino acid ester with isocyanate catalysed by catalyst **2b**.



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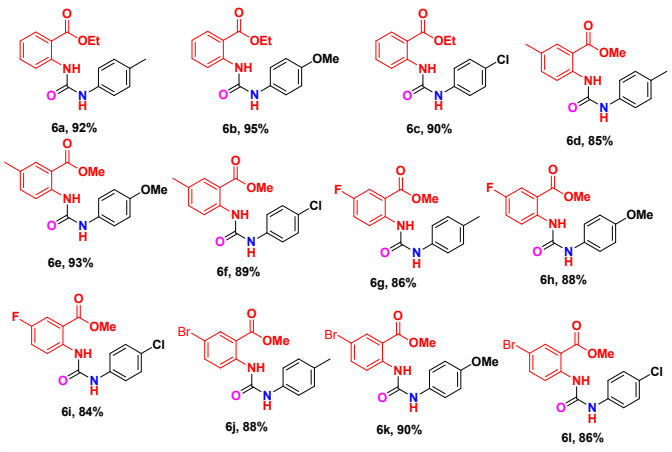


All reactions were performed in neat condition using amino acid ester (0.6060 mmol, 1equiv) isocyanate (0.6060 mmol, 1 equiv.), and catalyst **2b** (23 mg, 0.0303 mmol, 5 mol%). Yields were calculated by isolated yield.

Further, to increase the generality of the catalytic hydroamination of amino acid esters, the nature of the substrate scope was extended to isocyantes to illustrate the robust nature of catalyst **2b**. Using phenyl isocyanate and its derivatives such as 4-cholro, 4-methyl or 4-methoxy phenyl isocyanate as the heterocumulene source, the insertion of amino acid esters was studied, and the results are summarised in Table 3 (**6a–6l** in Table 3, Figs FS51–FS74 in SI). We observed that in all cases the insertion of the relevant amino acid ester proceeded rapidly at room temperature to give the corresponding urea product in quantitative yields (Table 3, **6a–6l**), but it failed to form its corresponding cyclic product. Insertion of substituted methyl 2-aminobenzoates bearing both electron-donating and electron-withdrawing groups to isocyanates proceeded rapidly at room temperature to give corresponding inserted products in excellent yields – up to 98%. The enhanced reactivity of phenyl isocyanate with various amino acid esters with respect to carbodiimides can be explained by the stronger electrophilic character of the isocyanate carbon atom.

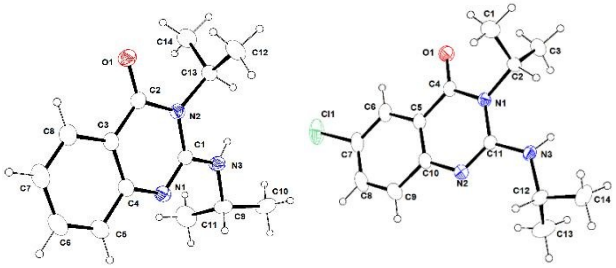
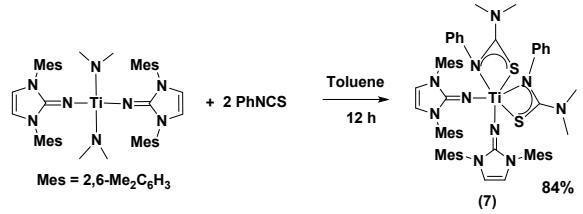


Figure 5. Molecular structures of quinazolinones **5a** (left) and **5k** (right) in the solid state.

In addition, to confirm the products of cyclisation, we isolated their crystal structures by means of single-crystal x-ray analysis. The solid-state structures of cyclisation products **5a** and **5k** obtained from DIC followed by ethyl 2-aminobenzoate and 5-chloro-methyl 2-aminobenzoate are shown in Figure 5.

Plausible mechanism

To explore the most plausible mechanism of the catalytic guanylation/cyclisation of amino acid esters to carbodiimides, we performed some controlled reactions. The stoichiometric reaction of catalyst **2b** with amine or alcohol independently showed the displacement of dimethylamido group of the titanium complexes by either anilide or alkoxide groups respectively under mild conditions, and we have presented their respective solid-state structures in Figures 2 and 3 respectively (Figs FS5–FS6 and FS7–FS8 in SI). In contrast, the same reaction of DIC, DCC or N-phenyl isocyanate with catalyst **2b** did not proceed smoothly and required harsh conditions to displace the dimethylamido group of the relevant titanium complexes, as we have previously reported.[29,31] However, we reacted Ti complex **2b** with the more reactive N-phenyl isothiocyanate in a 1:2 molar ratio to obtain a bis-insertion product [(Im^{Mes}N)$_2$Ti{κ^2-SC(NMe$_2$)NPh}$_2$] (**7**) in good yield at ambient temperature (Scheme 2) (Figs FS9–FS10 in SI). Due to the high reactivity of N-phenyl isothiocyanate, a mixture of products was always obtained when amino acid esters were reacted with N-phenyl isothiocyanate and catalysed by complex **2b**.



Scheme 2. Reaction of Ti^{IV} complex **2b** with N-phenyl-isothiocyanate to give **7**.

Ti complex **7** was characterised using spectroscopic methods (Figs FS9–FS10 in SI) and its solid-state structure was established by single-crystal x-ray analysis. As shown in Figure 6, the solid-state structure of complex **7** confirmed the attachment of two thioureate fragments to the titanium metal in κ^2-coordination mode through the sulphur and nitrogen atoms. Two four-membered metallacycles (S1–C7–N7–Ti1 and S2–C10–N9–Ti1) were formed by the chelation of two thioureate building blocks, having an average bite angle of 64.48° (S–Ti–N).

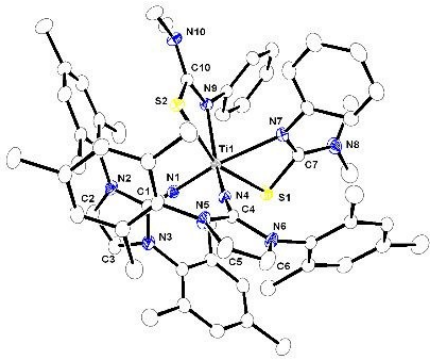


Figure 6. Molecular solid-state structure of complex **7**. Selected bond lengths (Å) and angles (°) are: Ti1–N4 1.8377(16), Ti1–N1 1.8568(16), Ti1–N9 2.2590(16), Ti1–N7 2.2980(17), Ti1–S1 2.4889(6), Ti1–S2 2.5141(6), N4–Ti1–N1 105.26(7), N4–Ti1–N9 153.01(7), N1–Ti1–N9 93.21(7), N4–Ti1–N7 93.16(6), N4–Ti1–N7 152.16(7), N9–Ti1–N7 78.01(8), N4–Ti1–S1 104.59(5), N1–Ti1–S1 90.38(5), N9–Ti1–S1 94.61(4), N7–Ti1–S1 64.48(5), N4–Ti1–S2 91.72(5), N1–Ti1–S2 103.50(5), N9–Ti1–S2 64.49(4), N7–Ti1–S8 96.48(5), S1–Ti1–S2 155.12(2), C7–S1–Ti1 82.07(7), C10–S2–Ti1 81.30(7), C1–N1–Ti1

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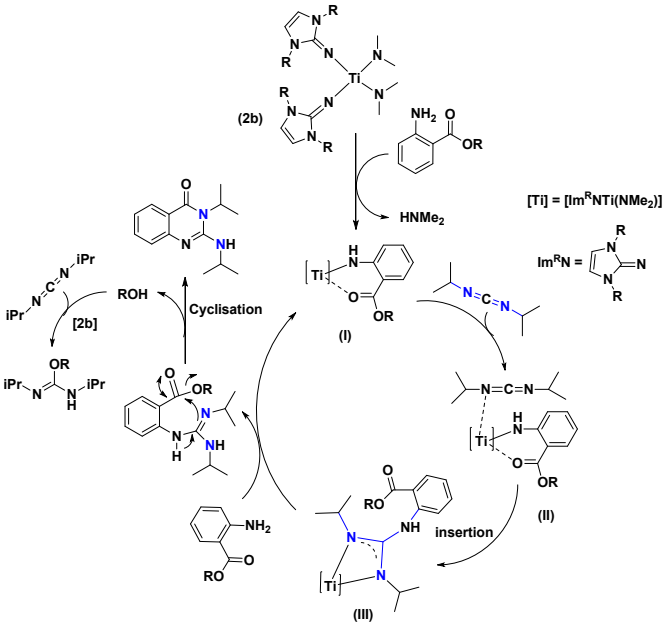
169.74(15), C4–N4–Ti1 173.18(15), C7–N7–Ti1 99.34(13), C49–N7–Ti1 136.42(13), C10–N9–Ti1 101.38(12), C55–N9–Ti1 129.56(13).



Scheme 3. Proposed catalytic cycle for guanylation/cyclisation of amino acid esters with diisopropylcarbodiimide by Ti^{IV} complex **2b**.

Based on the above observations, a plausible mechanism for the catalytic guanylation/cyclisation of amino acid esters is given in Scheme 3. The first step is the aminolysis of bis-imidazolin-2-iminato titanium(IV) amide complex (**2b**) [κ^1-$(Im^RN)_2Ti(NMe_2)_2$] with the relevant aminobenzoate, resulting in the generation of an intermediate product (**I**) with the displacement of the dimethylamine group of complex **2b**. The next step is the migratory insertion of DIC into the corresponding Ti-amide bond in rapid equilibrium, providing the intermediate product (**II**). Next, intramolecular nucleophilic amidation in product (**II**) occurs, yielding the active species (**III**) with the release of a molecule of alcohol by-product at the same time. Finally, intermediate product (**III**) follows a protonolytic cleavage, with an additional molecule of the aminobenzoate species to regenerate the active species (**I**) with the release of the target cyclisation product under the reaction condition. The by-product alcohol is captured by another molecule of DIC in the presence of catalyst **2b** to yield the corresponding isourea under the same conditions which were isolated and fully characterize by NMR spectroscopy (Figs FS75–FS76 in SI). Similar observation is also reported in literature.[29] However, in case of hydroamination of amino acid ester with isocyanate catalysed by catalyst **2b** gives only un-cyclised products (Table 3).

Experimental

General: All manipulations of air-sensitive materials were performed with the rigorous exclusion of oxygen and moisture in flame-dried Schlenk-type glassware either on a dual manifold Schlenk line, interfaced to a high vacuum (10^{-4} torr) line or in an argon-filled M. Braun glove box. Hydrocarbon solvents (toluene and *n*-pentane) were distilled under nitrogen from $LiAlH_4$ and stored in the glove box. ^1H NMR (400 j) and $^{13}C\{^1H\}$ NMR (100 MHz) spectra were recorded on a BRUKER AVANCE III-400 spectrometer. BRUKER ALPHA FT-IR was used for FT-IR measurement. Elemental analyses were performed on a BRUKER EURO EA at the Indian Institute of Technology Hyderabad. Imidazolin-2-imine [Im^RNH] (R = *t*Bu, **1a**; R = Mes, **2b**] were prepared according to published procedure.[34] The starting materials 2,6-disopropylaniline, 2,6-dimethylalcohol, and phenylisocynate, phenylisothiocynate were purchased from Sigma Aldrich and used without further purification. The NMR solvent C_6D_6 were purchased from Sigma Aldrich.

Preparation of [$(Im^RN)_2Ti(NMe_2)_2$] (R = ^{t}Bu, 2a; Mes, 2b): In a dry 25 mL Schlenk flask, compound [Im^RNH; R = ^{t}Bu; (200 mg, 1.024 mmol) and 5 mL of toluene were placed together. To this solution a mixture of tertrakis(dimethylamino)titanium (114 mg, 0.512 mmol) was added and the resulting reaction mixture was stirred at 60°C for 12 hours. The solvent was evaporated under vacuum, and a red-coloured residue was obtained.

2a. Yield: 0.150 g, 75%. ^1H NMR (400 MHz, C_6D_6, 25 ºC): δ_H 5.98 (s, 2H, NCH), 3.58 (s, 6H, $N(CH_3)_3$), 1.64 (s, 18H, $C(CH_3)_3$), $^{13}C\{^1H\}$ NMR (100 MHz, C_6D_6): δ_H 140.7 (NCN), 106.5 (NCH=CHN), 54.9 ($C(CH_3)_3$), 47.2 ($N(CH_3)_2$), 28.4 ($C(CH_3)_3$), 28.1 ($C(CH_3)_3$) ppm. Elemental Analysis: $C_{26}H_{52}N_8Ti$ (524.61): Calcd. C 59.53, H 9.99, N 21.36. Found C 59.37, H 9.68, N 23.09.

2b. The method of preparation of this complex was similar to that used to prepare **2a**, but with the use of [$Im^{Mes}NH$ (200 mg, 0.63 mmol) and tetrakis(dimethylamino)titanium (70 mg, 0.32 mmol).

Yield: 0.170 g, 85%. ^1H NMR (400 MHz, C_6D_6, 25 ºC): δ_H 6.81 (s, 4H, Ar), 5.73 (s, 2H, NC*H*), 2.63 (s, 6H, $N(CH_3)_3$), 2.29 (s, 12H, o-attached CH_3), 2.22 (s, 6H, p-attached CH_3) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, C_6D_6): δ_C 146.9 (ipso-phenyl), 138.6 (NCN), 136.8 (o-phenyl), 134.4 (p-phenyl), 128.7 (m-phenyl), 111.7 (N*C*=N*C*), 46.7 (NCH_3), 21.0 (p-attach CH_3), 18.6 (o-attached CH_3) ppm. Elemental Analysis: $C_{46}H_{60}N_8Ti$ (772.89): Calcd. C 71.48, H 7.82, N 14.50. Found C 71.22, H 7.53, N 14.37.

Preparation of [κ^1-$(Im^{tBu}N)_2Ti(NMe_2)(HNDipp)$] (3a): In a dry 25 mL Schlenk flask, compound **2a** (200 mg, 0.39 mmol) and 5 mL of toluene were added. To this solution 2,6-diisopropyl aniline (67 mg, 0.39 mmol) was added and the resulting reaction mixture was stirred at 60°C for 12 hours. The solvent was evaporated under vacuum, the red-coloured residue was dissolved in 3 mL of *n*-pentane and was

crystallised at –35°C. Yellow-coloured crystals were obtained after three days.

3a: Yield: 0.135 g, 68%. ^{1}H NMR (400 MHz, C_6D_6): δ_H 7.28 - 7.26 (d, 1H, Ar), 7.07 - 7.05 (m, 2H, Ar), 6.91 (t, 1H, $^3J_{HH}$ = 7.36 Hz, Ar), 5.92 (s, 2H, NC*H*), 3.52 (s, 6H N(CH_3)$_2$), 3.20 (s, 1H, N*H*), 2.65 (sept, 2H, $^3J_{HH}$ = 6.84 Hz, C*H*(CH$_3$)$_2$), 1.61 (s, 18H, C(CH_3)$_3$), 1.14 (d, 12H, $^3J_{HH}$ = 6.84 Hz, CH(*CH*$_3$)$_2$) ppm. ^{13}C{^{1}H} NMR (100 MHz, C_6D_6): δ_C 152.1 (*ipso*-Ar), 141.7 (*ipso*-Ar), 140.5 (N*C*N), 134.5 (*o*-phenyl), 132.1 (*o*-phenyl), 123.1 (*m*-phenyl), 118.6 (*m*-phenyl), 115.9 (*m*-phenyl), 106.9 (N*C*H=*C*HN), 55.4 (C(CH$_3$)$_3$) 47.2 (N(*C*H$_3$)$_2$), 28.8 (C(*C*H$_3$)$_3$), 28.0 (C(*C*H$_3$)$_3$) 24.6 (*C*H(CH$_3$)$_2$), 22.4 (*C*H(CH$_3$)$_2$), ppm. Elemental Analysis: $C_{48}H_{83}N_9Ti$ (**3a**. DippNH$_2$ 834.10): Calcd. C 69.12, H 10.03, N 15.11. Found C 68.83, H 9.86, N 15.01.

Preparation of [κ^1-(Im^{tBu}N)Ti(O-2,6-Me$_2$C$_6$H$_3$)$_3$] (4a).

In a flame-dried 25 mL Schlenk flask, compound **2a** (200 mg, 0.38 mmol) and 5 mL of toluene were taken. To this solution, 2,6-dimethylphenol (139.6 mg, 1.15 mmol) was added along with 5 mL of toluene. The resulting reaction mixture was stirred at 60°C for 12 hours. The solvent was evaporated under vacuum and a red-coloured solid was obtained. The title compound was re-crystallised from toluene at –35°C. Yellow-coloured crystals were obtained after three days.

Yield: 0.145 g, 72%. ^{1}H NMR (400 MHz, C_6D_6): δ_H 7.14 (m, 4H, Ar), 7.11 - 7.06 (m, 6H, Ar), 7.04 - 6.90 (m, 3H, Ar), 6.76 (s, 6H, Ar), 5.67 (s, 2H, NC*H*), 2.56 (s, 12H, N(CH$_3$)$_3$), 3.22 (s, 12H, N(CH_3)$_2$), 2.23 (s, 12H, p- phenyl CH$_3$), 2.10 (s, 12H, o-phenyl CH$_3$), ppm. ^{13}C{^{1}H} NMR (100 MHz, C_6D_6): 162.4 (N=*C*H), 149.5 (*ipso*-C$_6$H$_3$), 142.5 (N*C*N), 140.0 (2-pyr), 139.6 (3-pyr), 136.9 (*o*-C$_6$H$_3$), 126.0 (*p*-C$_6$H$_3$), 123.2 (*m*-C$_6$H$_3$), 118.1 (4-pyr), 113.6 (5-pyr), 107.2 (N*C*H=*C*HN), 56.1 (*C*(CH$_3$)$_3$), 50.2 (N(*C*H$_3$)$_2$), 28.3 (*C*(CH$_3$)$_3$), 26.1 (CH(*C*H$_3$)$_2$), 22.8 (CH(*C*H$_3$)$_2$) ppm. Elemental Analysis: $C_{35}H_{47}N_3O_3Ti$ (605.63): Calcd. C 69.41, H 7.82, N 6.94. Found C 69.19, H 7.59, N 6.84.

Preparation of [(Im^{Mes}N)$_2$Ti{κ^2-SC(NMe$_2$)NPh}$_2$] (7):

In a flame-dried 25 mL Schlenk flask, compound **2b** (200 mg, 0.259 mmol) and 5 mL of toluene were taken. To this solution, N-phenyl isothiocynate (68.9 mg, 0.534 mmol) was added along with 5 mL of toluene. The resulting reaction mixture was stirred at room temperature for 12 hours. The solvent was evaporated under vacuum and a red-coloured solid was obtained. The title compound was re-crystallised from toluene at –35°C. Yellow-coloured crystals were obtained after three days.

Yield: 0.160 g, 80%. ^{1}H NMR (400 MHz, C_6D_6): δ 7.07-7.00 (m, 2H, Ar), 6.89-6.87 (m, 4H, Ar), 6.77 - 6.73 (m, 2H, Ar), 5.93 (s, 2H, NC*H*), 1.98 (s, 18H, C(CH$_3$)$_3$), 1.38 (s, 18H, C*H*$_3$), ppm. ^{13}C{^{1}H} NMR (100 MHz, C_6D_6): 163.1 (N=*C*H), 145.2 (*ipso*-C$_6$H$_3$), 140.5 (N*C*N), 128.7 (*o*-C$_6$H$_3$), 120.2 (*p*-C$_6$H$_3$), 107.6 (N*C*H=*C*HN), 56.7 (*C*(CH$_3$)$_3$), 29.9 (C(CH$_3$)$_3$), 17.7 (*C*H$_3$), 17.1 (*C*H$_3$) ppm. Elemental Analysis: $C_{60}H_{70}N_{10}S_2Ti$ (1043.25): Calcd. C 69.08, H 6.76, N 13.43. Found C 67.79, H 6.53, N 13.29.

X-ray crystallographic analyses: Single crystals of complexes **2b, 3a, 4a** and **7** were grown from a concentrated solution of toluene or toluene/n-pentane (3:1) in an argon-filled atmosphere at -35 °C. However, single crystals of **5a** and **5k** were obtained from a solution of ethanol at room temperature. A crystal of suitable dimensions of complexes **2b, 3a, 4a** and **7** was mounted on a CryoLoop (Hampton Research Corp.) with a layer of light mineral oil and placed in a nitrogen stream at 150(2) K. The crystals of **5a** and **7k** were measured at 298 K. All measurements were made on a Rigaku Supernova X-calibur Eos CCD detector with graphite monochromatic Cu-Kα (1.54184 Å) (**2b, 4a, 7, 5a** and **5k)** or Mo-Kα (0.71073 Å) (**3a**) radiation. Crystal data and structure refinement parameters of complexes **2b, 3a, 4a, 7, 5a** and **5k** are summarized in Table TS1. The structures were solved by direct methods (SIR2004)[35] and refined on F^2 by full-matrix least-squares methods, using SHELXL-97.[36] Non-hydrogen atoms were anisotropically refined. H-atoms were included in the refinement on calculated positions riding on their carrier atoms. The function minimized was [$\sum w(Fo^2 - Fc^2)^2$] (w = 1 / [σ^2 (Fo^2) + (aP)^2 + bP]), where P = (Max(Fo^2,0) + 2Fc^2) / 3 with σ^2(Fo^2) from counting statistics. The function $R1$ and $wR2$ were ($\Sigma||Fo| - |Fc||$) / $\Sigma|Fo|$ and [$\Sigma w(Fo^2 - Fc^2)^2$ / $\Sigma(wFo^4)$]$^{1/2}$, respectively. The ORTEP-3 program was used to draw the molecules of **2b, 3a, 4a, 7, 5a** and **5k**. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC 1880612 (**5a**), 1880613 (**5k**), 1880614 (**4a**), 1880615 (**3a**), 1880616 (**2a**), and 1880617 (**7**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: + (44)1223-336-033; email: deposit@ccdc.cam.ac.uk).

General procedure for catalytic titanium-mediated guanylation/cyclisation of amino acid esters in presence of heterocumulene:

In a 25 mL dry Schlenk flask inside a glovebox, a solution of respective amino acid esters (0.606 mmol) was added drop-wise into the mixture of the relevant heterocumulene (1.212 mmol) and catalyst **2b** (23 mg, 0.0303 mmol). The yellow-coloured reaction mixture was kept under room temperature or heated to 40–60°C, depending on the nature of nucleophiles. The progress of the reactions was monitored by TLC. Subsequently, the reaction mixture was quenched by adding 20 mL of ethylacetate solvent, after which the basic workup was made by adding 5 mL of saturated sodium bicarbonate solution to reaction mixture. The product was collected in organic layers and finally purified by column chromatography in (5:100) hexane/ethylacetate eluent solvent. The products were identified by according to ^{1}H, ^{13}C, and DEPT NMR spectroscopy (where necessary), as well as MS analysis.

Conclusion

In conclusion, the synthesis of two bis(imidazolin-2-iminato) titanium(IV) complexes [(Im^{R}N)$_2$Ti(NMe$_2$)$_2$] (R = tBu, **2a**; R = Mes, **2b**) is reported, along with further reactions with 2,6-diisopropylphenylamine and 2,6-dimethylphenol to give titanium complexes **3a** and **4a**. Ti^{IV} complexes **2a** and **2b** acted

as efficient pre-catalysts for catalytic guanylation/cyclisation of amino acid esters to carbodiimides and isocyanates, resulting in corresponding quinazolinone and urea derivatives under mild conditions. The Ti^{IV} catalyst **2b** exhibited a large substrate scope with relatively high conversion, superior selectivity and broad functional group tolerance in both carbodiimide and isocyanate reactions.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

This work was financially supported by the Science and Engineering Research Board (SERB), Department of Science and Technology (DST), India, under project no. (EMR/2016/005150). We thank Dr. Hari Pada Nayek, Indian Institute of Technology (IITISM) Dhanbad for his help in crystallography. We also thank to reviewers for their valuable comments to improve the manuscript.

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