EurJIC
European Journal of Inorganic Chemistry

Full Papers
doi.org/10.1002/ejic.202100141

Chemistry Europe
European Chemical Societies Publishing

Conjugated Bis-Guanidines (CBGs) as β-Diketimine Analogues: Synthesis, Characterization of CBGs/Their Lithium Salts and CBG Li Catalyzed Addition of B–H and TMSCN to Carbonyls

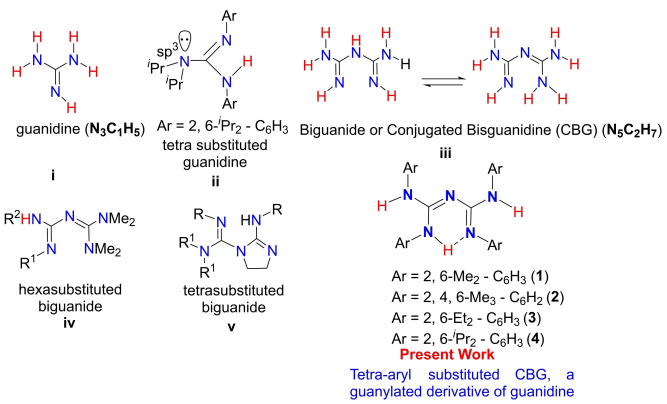
Thota Peddarao[+],[a] Ashim Baishya[+],[a] Nabin Sarkar,[a] Rudresh Acharya,[b] and Sharanappa Nembenna*[a]

Herein, we report a range of conjugated bis-guanidines (CBGs) L [L = {(ArHN)(ArHN)C=N–C=(NAr)(NHAr)}; Ar = 2, 6-Me_2 - C_6H_3, (**1**), 2, 4, 6-Me_3–C_6H_2, (**2**), 2, 6-Et_2–C_6H_3, (**3**), 2, 6-$^iPr_2$–C_6H_3, (**4**)]. These compounds can be easily accessed by the reaction between *N,N′*-diaryl carbodiimide, and aq. ammonia in acetonitrile. Deprotonation of **1** with *n*-BuLi in a 1:1 ratio in THF resulted in the formation of four coordinate lithium complex, [**1**Li·$(THF)_2$] (**5**), while at the same reaction conditions, ligands **3** and **4** gave three coordinate lithium complexes, [**3**Li·THF] (**6**) and [**4Li**·THF] (**7**), respectively. However, both compounds **1** and **4** upon deprotonation with *n*-BuLi in diethyl ether allowed [**1**Li·Et_2O] (**8**) and [**4**Li·Et_2O] (**9**), respectively, while compounds **1** and **3** in toluene afforded un-solvated lithium complexes [**1**Li] (**10**) and [**3**Li] (**11**), respectively. Significantly, a reaction between compound **4** and *n*-BuLi in a 1:1 ratio in toluene yielded sandwich lithium complex [**4**Li] (**12**). All new CBGs **1**–**4** and lithium salts of CBG, **5**, **8**, and **12** were characterized by single-crystal X-ray structural analysis. The compounds **5**–**12** were characterized by multinuclear magnetic resonance spectroscopy. Moreover, we have investigated the catalytic application of lithium salts of CBGs for the addition of B–H and TMSCN to carbonyls.

Introduction

Much effort has been devoted to ligand design in order to influence the reactivity of metal complexes by steric and electronic ligand properties.[1] In particular, monoanionic and bidentate nitrogen-based ancillary ligands such as β-diketiminates,[2] triazapentadienate,[3] dipyrromethene,[4] formazanate,[5] amidinates,[6] guanidinates,[7] amine-imine„[8] etc. have attained much importance in coordination chemistry. Moreover, bulky monoanionic *N,N′*-chelating ligands are ideal supporting frameworks for the stabilization of low valent and/or low oxidation state metallacycles.[9] The choice of a bulky supporting ligand is one of the key factors to isolate such unusual molecules. Given this, our group is currently focusing on designing new bulky *N,N′*-chelating ligands[10] and utilizing those precursors for the construction of unusual metal complexes.[11] We have earlier published a metal-free approach of numerous bulky *N,N′*-diarylcarbodiimides (CDIs).[12] These CDIs are good starting materials for the synthesis of several bulky nitrogen-donor ligands such as formamidines, zwitterionic type amidinates, or N-heterocyclic carbene-carbodiimide (NHC-CDI) adducts,[10a,b] amidines,[13] guanidines,[10c] etc.

Guanidines[14] are a particular class of organic molecules consisting of a Y-shaped N3 C functional group, in which the carbon atom is linked to one imino and two amino nitrogen atoms ($N_3C_1H_5$) (Scheme 1, **i**). Guanidines are stronger bases compared to closely related amidines.[15] Therefore, they are useful in various base-catalyzed reactions.[16] Prior motifs are found to be essential components in many biological, pharmaceutical molecules, and natural products.[17] Primarily, guanidinate anions have been known for their crucial role in the coordination chemistry of various elements of the periodic table



Scheme 1. Unsubstituted and substituted guanidines and biguanides.

[a] *Dr. T. Peddarao,[+] Dr. A. Baishya,[+] N. Sarkar, Dr. S. Nembenna*
School of Chemical Sciences
National Institute of Science Education and Research (NISER)
Homi Bhabha National Institute (HBNI)
Bhubaneswar, 752050, India
E-mail: snembenna@niser.ac.in
http://www.niser.ac.in/scs/professor/snembenna
[b] *Dr. R. Acharya*
School of Biological Sciences
National Institute of Science Education and Research (NISER)
Homi Bhabha National Institute (HBNI)
Bhubaneswar, 752050, India
[+] *Both the authors contributed equally to this work.*
Supporting information for this article is available on the WWW under https://doi.org/10.1002/ejic.202100141

(Scheme 1, **ii**).[7d,18] Further, metal complexes bearing guanidinate ligands have been used as catalysts in organic transformations and polymerization reactions.[7e,19]

As far as synthesis and mechanistic aspects of guanidines are concerned, there have been some review articles.[20] Guanidine synthesis can be achieved either by stoichiometric reactions using guanylating reagents[21] or by metal-catalyzed reactions.

On the other hand, biguanides are nitrogen-rich organic compounds in which the amidine fragment is directly connected to the guanidine unit at N2 position to form –C=N–C=N– conjugated system (Scheme 1, **iii**).[22] The first report on the synthesis of unsubstituted biguanide ($N_3C_2H_7$) was described by Rathke in 1879.[23] Since that time, the synthesis of substituted biguanides and their applications as ligands and in medicinal chemistry are well developed.[24] Notably, substituted biguanide, metformin,[25] is a novel drug for diabetes II that helps control sugar levels. In 2013, the Eckert-Maksic group reported the hexasubstituted biguanides (Scheme 1, **iv**).[26]

Moreover, there have been reports on biguanide systems formed by metal-mediated cyanamide-guanidine coupling.[27] At the time of drafting our manuscript, Kretschmer et al. reported the 3,4-ethylene bridged 1,1,2,5-tetrasubstituted biguanides (Scheme 1, **v**).[28] As far as we know, tetra aryl-substituted conjugated bis-guanidines (CBG) are not known in the literature (Scheme 1).[29]

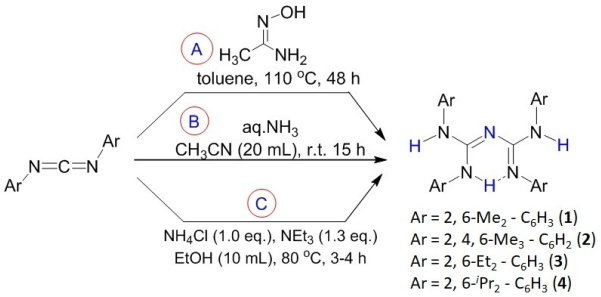
Therefore, herein, we report a synthesis of structurally characterized CBGs by the reaction of amidoxime or aqueous (aq.) ammonia with *N,N′*-diarylCDI. Further, we offer a first insight into the coordination chemistry of CBG ligands **1, 3**–**4** towards lithium cations. More importantly, CBG lithium catalyzed hydroboration and cyanosilylation of carbonyls have been studied.

Results and Discussion

The tetra aryl substituted-conjugated bis-guanidines (CBGs) were accessed conveniently by three synthetic routes.

In the first approach, the reaction between corresponding bulky *N,N′*-diarylcarbodiimide (CDI) (2.0 equiv), and acetamidoxime[30] (1.0 equiv) in toluene at refluxing temperature for two days resulted in the formation of desired products (**1**–**4**) (Scheme 2, Method A). The pure compounds were obtained by column chromatography (ethyl acetate/*n*-hexane 5:95 (v/v) as eluent). We utilized four CDIs with varying steric bulk to produce the corresponding CBG ligands. Typically, CBG is a combination of one ammonia and two CDI molecules. Therefore, we were curious to know the outcome of the reaction between CDI and aq. ammonia. Accordingly, we performed a reaction between one equiv. of CDI and four equiv. of aq. ammonia in acetonitrile at room temperature conditions.

We observed the formation of CBGs in good yields (Scheme 2, Method B). Furthermore, we developed a high yield access protocol for the preparation of CBGs. The one-pot reaction of CDI, NH_4Cl, and Et_3N at 80 °C for 3–4 h after work-up afforded CBGs in high yields (Scheme 2, Method C). All CBG



Yields of CBG Ligands **1-4**	Method A	Method B	Method C
	18-40 %	50-64 %	65-72 %

Scheme 2. Synthesis of conjugated bis-guanidines **1**–**4**.

ligands **1**–**4** were confirmed by ^1H, $^{13}C\{^1H\}$ NMR, and IR analyses. The purity of compounds **1**–**4** was further confirmed by high-resolution mass spectrometry (HRMS), high-performance liquid chromatography (HPLC), and elemental analyses. All CBGs are thermally stable and melt in the range of 163–231 °C.

A Mechanism for the Formation of CBGs (1–4)

Bulky *N,N′*-diarylcarbodiimide undergoes a nucleophilic addition reaction with an *in situ* generated ammonia molecule, which leads to the formation of the *N,N′*-diaryl substituted guanidine intermediate, which further reacts with another molecule of a CDI, resulting in the formation of a tetra-aryl substituted conjugated bis-guanidine (CBG). Fylaktakidou, Hadjipavlou-Litina, and coworkers observed the formation of 5-amino substituted 1,2,4-oxadiazoles and urea as products when amidoximes treated with CDIs.[31] The authors suggested a mechanism for the establishment of the above products in such a way that an initial formation of *O*-amidoxime-CDI adduct (upon the reaction of amidoxime with CDI), which further reacts with another molecule of CDI and undergoes cyclization leading to the formation of 5-amino substituted 1,2,4-oxadiazole and *N,N′*-disubstituted guanidine intermediate, which further reacts with water resulting in the formation of urea. Nevertheless, in our case, we presumed that the initial formation of *O*-amidoxime-CDI adduct is hindered due to the steric nature of *ortho*-disubstituted aryl CDIs. Therefore, CDI reacts with an ammonia molecule, which leads to the formation of a stable *N,N′*-diaryl substituted guanidine, which further reacts with another molecule of a CDI to afford a CBG molecule. In the first method, CBGs are isolated in moderate yields, which can be attributed to a series of reactions when the CDI and amidoxime were heated at 110 °C for 48 h.

Moreover, the proposed mechanism was verified by reacting to CDI and aq. ammonia in acetonitrile to obtain CBGs in good yields. In the conjugated bis-guanidine molecule, a relocation of the proton from amine to imine nitrogen was

noticed, thus exhibiting amine-imine tautomerism. Four possible tautomers for the CBG ligands are shown in Figure 1.

Resonance Forms and Coordination Modes of CBG

Like β-diketiminate anion, conjugation/deconjugation can be observed in complexes with CBG ligands.[32] Resonance structures of the monoanionic, dianionic, and possible coordination modes of CBGs are shown in Scheme 3.

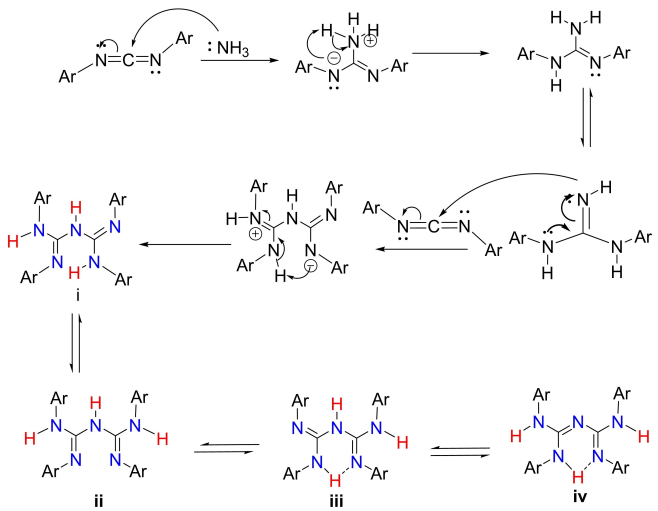
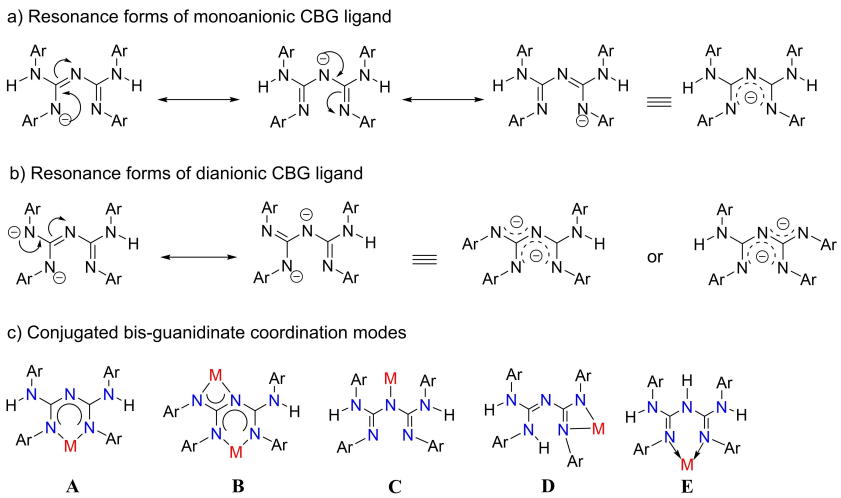


Figure 1. A possible mechanism for the formation of CBG and its tautomeric structures.

Five bonding modes (**A**–**E**), as illustrated in Scheme 3c,[33] are observed for the main group and first-row transition elements. **A** and **C** bonding modes have been observed for the lithium element, while **B**/**D** and **E** are observed for aluminum and zinc/cobalt elements, respectively.[34] The *N,N′*- chelating framework is distinguished as an LX-type ligand (**A** and **D**), consisting of both sigma (σ) and pi(π)-donor characteristics; **B** shows double chelation that means L_2X_2 type ligand contains two σ and two π donor properties. In contrast, **C** exhibits a monodentate X-type ligand comprising only σ property. Interestingly, the bonding mode **E** also shows *N,N′*- chelation like **A**, but it is distinguished as an L_2 type ligand, including both pi characteristics.

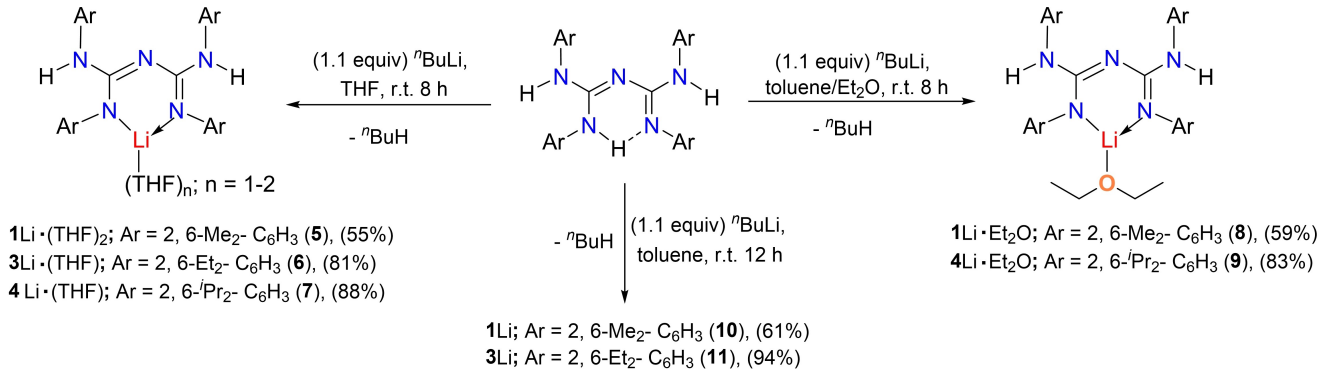
In the ^{1}H NMR spectra of CBG ligands, two sets of chemically non-equivalent N–*H* protons were observed. The N–*H* proton (N–*H*–N) resonates as a broad singlet in the deshielded region in the range of 12.82–13.02 ppm for compounds **1**–**4** in C_6D_6, which is due to intramolecular hydrogen-bonding. Another well-resolved sharp singlet is displayed in the range of 4.62–4.94 ppm, assigned to the N–*H* resonances of the side-arm Ar–N*H* groups. In the ^{13}C NMR spectra, all compounds (**1**–**4**) display a characteristic signal for the N_3C carbon atom in the range of 154.4–156.6 ppm, which is in good agreement with the described guanidines (148–160 ppm).[7e,35]

All compounds were characterized by their IR spectra, which exhibit N–H and C=N stretching frequencies in the range of 3080–3400 cm^{-1} and 1560–1655 cm^{-1}, respectively. These values are well in accord with previously reported guanidines (3317–3394 cm^{-1} for NH and 1595–1645 cm^{-1} for C=N).[7e] Furthermore, the purity of newly reported bulky conjugated bis-guanidines was confirmed by HRMS, HPLC, and elemental analyses. Besides, solid-state structures of compounds **1**–**4** were



Mode	(κ^2 - *N*, *N*)	(κ^2 - *N*, *N*)$_2$	(κ^1 - *N*)	(κ^2 - *N*, *N*)	(κ^2 - *N*, *N*)
e- donation	3	6	1	3	4
Ligand type(CBC)[33]	LX	L_2X_2	X	LX	L_2

Scheme 3. Resonance forms and coordination modes of CBG.



Scheme 4. Synthesis of compounds **5**–**11**.

affirmed by single-crystal X-ray structural analysis. The molecular structures of compounds **1** and **4** are shown in Figure 2 (for compounds **2** and **3**, see Figure S33 in the supporting information) along with selected bond parameters.

Single crystals of compounds **1**–**4** suitable for X-ray analysis were grown from ethyl acetate solution at room temperature. Compounds **1** and **4** crystallized in triclinic space group $P\bar{1}$, and orthorhombic space group *Pbca*, respectively, while compounds **2** and **3** crystallized in monoclinic space group $P2_1/n$.

The molecular structures revealed that tetra-aryl substituted CBGs, guanylated derivatives of guanidine structures incorporating five N atoms, and two C atoms with a conjugated –C=N–C=N core. In compounds **1**–**3**, one imino N atom is placed at the central position, and the other one is at the terminal site (conjugation), while in compound **4**, two imino N atoms are situated at the terminal positions (deconjugation). The compounds **1**–**3** show intramolecular resonance assisted hydrogen bond N–H···N in the solid-state, which is caused by the π delocalization that involves hydrogen.[36] However, this is not observed in compound **4**, which is ascribed to the tautomeric and steric nature of the ligand. In compound **4**, the hydrogen atom is attached to the central nitrogen atom of the biguanide. In all the cases, the other two hydrogen atoms are attached to two side-arm nitrogen atoms.

Further, we studied the coordination chemistry of CBG/biguanides[37] with lithium elements. The synthesis of lithium salts of CBG ligands (**5**–**12**) was achieved by adding *n*-BuLi to a corresponding free ligand, either in ethereal or hydrocarbon solvents. The addition of *n*-BuLi to a solution of **1**, **3**, and **4** in THF and toluene/Et_2O in a 1:1 stoichiometric ratio at room temperature, independently, continued by stirring the reaction mixture for 8 h, yielded the lithium salts of CBG ligands **5**, **6**, **7**, **8** and **9**, respectively as their solvent adducts (Scheme 4). The reaction of *n*-BuLi with **1** and **3** in toluene solution in a 1:1 stoichiometric ratio at ambient temperature for 12 h yielded the lithium salts of CBG **10** and **11** in the unsolvated form (Scheme 4). Unfortunately, we could not obtain the single crystals of compounds **10** and **11** appropriate for X-ray diffraction. However, compounds **10** and **11** were isolated in pure form as colorless crystalline solids in good yields of 61% and 94%, respectively. The compound **12** was synthesized by stirring the reaction mixture of **4** and *n*-BuLi in toluene in a 1:1 stoichiometric ratio at room temperature for 12 h. Colorless crystals for **12** were obtained from toluene in a good yield of 60% (Scheme 5).

Compounds **5**–**12** are highly air and moisture-sensitive. All compounds **5**–**12** were confirmed by multinuclear (^1H, ^{13}C, and ^7Li) magnetic resonance spectroscopy. Furthermore, compounds **5**, **8**, and **12** were confirmed by single-crystal X-ray structural analysis.

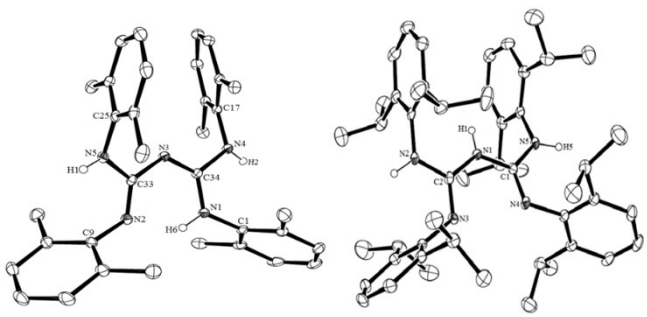
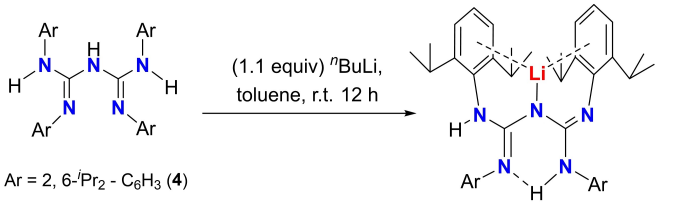


Figure 2. Solid-state structures of **1** (left) and **4** (right).Selected bond distances (Å) and bond angles (deg) for **1**: N2-C33 1.305(2), N3-C33 1.3740(19), N3-C34 1.312(2), N1-C34 1.353(2), N5-C33 1.381(2), N4-C34 1.3778(19), N1-C1 1.424(2); N2-C33-N3 124.25(14), C34-N3-C33 120.80(14), N3-C34-N1 125.31(14), N3-C33-N5 113.04(14), N3-C34-N4 117.63(14); for **4**: N3-C2 1.324(3), N1-C2 1.343(2), N1-C1 1.348(2), N4-C1 1.306(3), N2- C2 1.360(2), N5-C1 1.369(2); N3-C2-N1 123.05(18), C2- N1-C1 122.27(17), N4-C1-N1123.62(18), N1-C2-N2 116.18(18), N1- C1-N5 114.49(18).



Scheme 5. Synthesis of compound **12**.

The ^{1}H NMR spectra of compounds **5**, **8**, and **10** each revealed the complete disappearance of a broad singlet in the deshielded region at 12.91 ppm, which corresponds to the N–*H*–N resonance of the free ligand **1**. Similarly, a complete vanishing of an N–*H*–N signal of the free ligand **3** at 12.97 ppm in compounds **6** and **11** was observed. Likewise, a complete absence of N–*H*–N resonance of the free ligand **4** at 13.02 ppm was observed in compounds **7** and **9**. The ^{1}H NMR spectrum of compound **5** displays two peaks that integrate into eight protons each at 0.92 (OCH_2CH_2) ppm and 2.86 (OCH_2CH_2) ppm in C_6D_6, indicating that two THF molecules coordinated to the lithium atom, while in compounds **6** and **7**, these two resonances integrate into four protons; each was suggesting that only one THF molecule is coordinated to the lithium atom.

The ^{1}H NMR spectra of **8** and **9** show one triplet and one quartet that integrate into six protons and four protons, respectively, at 0.82 and 0.72 ppm(OCH_2CH_3) and 2.96 and 2.99 (OCH_2CH_3) ppm, which corresponds to the coordination of one diethyl ether molecule to the Li atom. However, the ^{1}H NMR spectra of **10** and **11** reveal no solvent is coordinated to the Li atom. In contrast, the ^{1}H NMR spectrum of **12** exhibits two singlets that integrate into one proton, each at 13.01 ppm and 4.95 ppm; this is due to the amine-imine tautomeric structure of the compound **12**.

The ^{7}Li NMR signals at 2.06, 5.11, 4.96, 0.79, 3.87, −0.77, 3.97, and 2.17 ppm for compounds **5**–**12**, respectively, confirm the presence of lithium atom in all the compounds.

Single crystals of compounds **5**, **8**, and **12** suitable for X-ray crystallography were obtained by crystallization from *n*-hexane/THF, toluene/diethyl ether, and toluene, respectively. The molecular structures are shown in Figure 3 (for compounds **5** and **8**) and Figure 4 (for compound **12**), along with selected bond parameters. Compounds **5** and **8** were crystallized in the triclinic space group $P\bar{1}$, and compound **12** was crystallized in the orthorhombic space group *Pbca*.

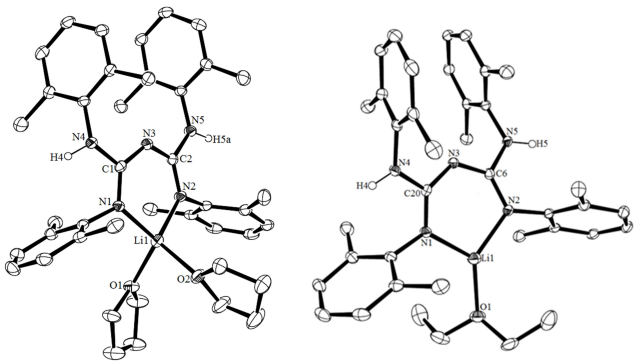


Figure 3. Solid-state structures of **5** (left) and **8** (right). Selected bond distances (Å) and bond angles (deg) for **5**: Li1-O1 2.001(6), Li1-O2 2.029(6), N1-Li1 1.963(6), N2-Li1 1.958(6), C1-N1 1.322(4), N3-C1 1.339(4), N3-C2 1.348(4), N2-C2 1.323(3), N4- C1 1.404(4), C2-N5 1.380(4); N2- Li1- N1 92.3(2), N1-Li1- O1 112.4(3), N2-Li1- O2 113.8(3), N1-Li1- O2 123.1(3), O1-Li1-O2 92.6(2), N1-C1-N3 128.6(3), C1-N3-C2 123.5(2), N2-C2-N3 127.2(3), N3-C1-N4 112.5(2), N3-C2-N5 112.4(2); for **8**: Li1-O1 1.930(4), N1-Li1 1.903(4), N2-Li1 1.902(4), C20-N1 1.326(2), C20-N3 1.340(2), C6-N3 1.341(2), C6-N2 1.321(2), C20-N4 1.381(2), C6-N5 1.381(2); N2-Li1-N1 98.15(17), N1-Li1-O1 124.6(2), N2-Li1-O1 137.2(2), N1-C20-N3 126.95(18), C20-N3- C6 124.39(16), N2-C6-N3 127.50(17), N3-C20-N4 112.88(16), N3-C6-N5 112.59(16).

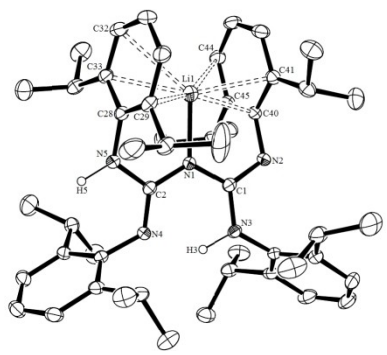


Figure 4. The solid-state structure of **12**. Selected bond distances (Å) and bond angles (deg): N1-Li1 1.979(5), N4-C2 1.318(3), N1-C21.364(3), N1-C1 1.380(3), N3-C1 1.345 (3), N5-C2 1.367(3), N2-C11.333(3); C2-N1-Li1 120.8(2), C1-N1-Li1 117.47(19), N4-C2-N1 124.5(2), C2-N1-C1 121.76(19), N3-C1-N1 121.5(2), N1-C2-N5 115.1(2), N2-C1-N1 119.05(19).

The molecular structure of compound **5** discloses that the lithium center adopts a distorted four-coordinate tetrahedral geometry bonded to one monoanionic *N,N′*-chelated CBG ligand, and oxygen atoms of the neutral THF occupy the other two sites molecules. The solid-state structure of compound **8** shows a three-coordinate metal center with a distorted trigonal planar geometry, in which lithium metal ion is bound to the CBG ligand in an *N,N′*- chelating manner, and another position is resided by the oxygen atom of the diethyl ether molecule. It is important to note that upon deprotonation of a tetra-substituted guanidine using a base, we can expect an N2CLi four-membered metallacycle. In contrast, we observed a six-membered metallacycle in compounds **5** and **8** (C_2N_3Li ring). Thus, these are analogues of lithium complexes of the β-diketiminate anion.

The Li–O and Li–N bond lengths for the compounds **5** are Li1-O1 2.001(6) Å, Li1-O2 2.029(6) Å, N1-Li1 1.963(6) Å and N2-Li1 1.958(6) Å, which are close to the reported Li–O and Li–N bond lengths of tetra-coordinated lithium complex $[\{(2,6\text{-}^{i}Pr_2C_6H_3)N(CH_3)C\}_2CH]Li(THF)_2$ Li1-O1 1.994(3) Å, Li1-O2 1.947(3) Å, and N1-Li1 1.955(2) Å.[38] The bite angle in compound **5** N2-Li1-N1 92.3(2) (°) is acute when compared to the bite angle of $[\{(2,6\text{-}^{i}Pr_2C_6H_3)N(CH_3)C\}_2CH]Li(THF)_2$ N(1)# –Li(1) –N(1) 95.84(14) (°). The Li–O and Li–N bond lengths for the compounds **8** are Li1-O1 1.930(4) Å, N1-Li1 1.903(4) Å and N2-Li1 1.902(4) Å, which are comparable with the bond distances of tri-coordinated lithium complex $[\{(2,6\text{-}^{i}Pr_2C_6H_3)N(CH_3)C\}_2CH]Li(Et_2O)$,[39] Li1-O1 1.911(4) Å, N1-Li1 1.917(4) Å, N2-Li1 1.912(4) Å. The geometry at lithium has been well described as distorted trigonal planar in **8**, N–Li–O bond angles for **6** are N1-Li1-O1 124.6(2) (°), N2-Li1-O1 137.2(2) (°), which have shown the deviation from the idealized value 120°. The N2-Li1-N1 bite angle in compound **8** is 98.15(17) (°). All these values are lying in the range of reported values for the tri coordinated lithium complex $[\{(2,6\text{-}^{i}Pr_2C_6H_3)N(CH_3)C\}_2CH]Li(Et_2O)$.[39]

Surprisingly, an unusual coordination mode was observed in the solid-state structure of **12** (Figure 4), in which the tautomer of CBG acts as a monoanionic ligand that binds the lithium metal through the central N1 atom. Besides, there are

approximately η^6-metal···π -arene interactions for the amide. Li1···Cπ interactions are in the range of 2.312-3.010 Å;[40] all these data are summarized in the supporting information Table S1. The centroid (Ct) is estimated for any six-membered ring in which any of the Li···C bond distances are lower the sum of the van der Waals radii (Σvdw, Li, C = 3.51 Å), considered using values from the literature.[41] Moreover, Li1···Cπ bond distance range is in agreement with other sandwich lithium complexes, *i.e.*, lithocene anion [$(Cp_2Li^-)(Ph_4P^+)$] (average C–Li bond distance 2.318(4) Å) and [$(Cp_2Li)^-(NHC^{dipp}H^+)$; 2.217(9)-2.442(8) Å].[42] Note that there have been some crystal structures of Li^+ sandwiched between π–electron systems in the literature.[43] The N1–Li1 bond distance in compound **12** is 1.979(5) Å and is shorter than those in the lithium guanidinate (unsubstituted), LiN_3H_4 (2.113(3) Å)[44] or [{Li(Mes)N}$_2$SiMe$_2$]$_2$ (2.007(8) and 2.015(8) Å).[45] The N1–Li1 bond distance in compound **12** is longer than those of Li-cation stabilized amide ligands, [Li{(N(^{tBu}Ar$^{\#}$)(SiMe$_3$)}(Et$_2$O)$_2$] (N–Li 1.944(2) Å) and [Li{N(^{tBu}Ar$^{\#}$)(SiPh$_3$)}(Et$_2$O)], (N–Li 1.908(3) Å, (Ar$^{\#}$= bulky aromatic substituent).[40a]

Catalysis: CBG Lithium Catalyzed Hydroboration and Cyanosilylation of Aldehydes and Ketones

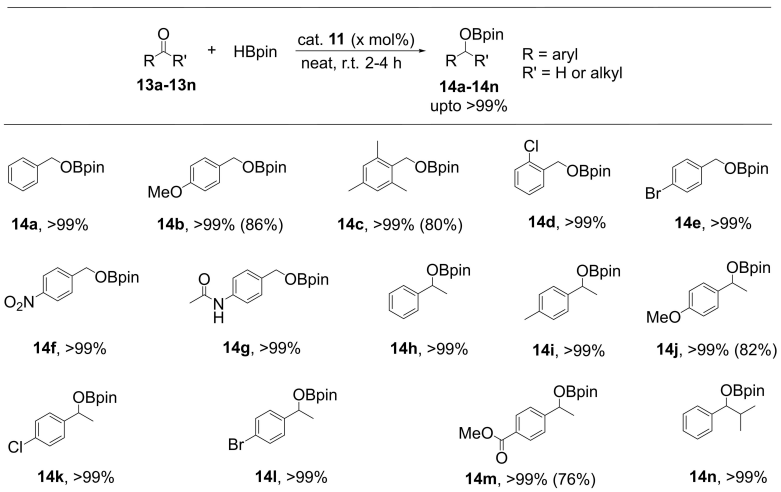
More recently, we published cheaper and sustainable aluminum/zinc catalyzed hydroboration of unsaturated organic substrates.[34a,46] There are not many reports on lithium catalyzed hydroboration[47] and cyanosilylation[48] of aldehydes and ketones. Thus herein, we report CBG lithium catalyzed hydroboration and cyanosilylation of carbonyls. We chose benzaldehyde as a model substrate to optimize the reaction conditions for the hydroboration of aldehydes, and the reaction's progress was verified by ^{1}H NMR analysis (see the Supporting Information Table S4). The reaction of a 1 : 1 molar ratio of benzaldehyde and HBpin catalyzed by CBGLi (**11**) was performed at room temperature under neat conditions.

A complete conversion of benzaldehyde into its corresponding boronate ester was observed using 3 mol% of catalyst loading for 6 h. There was no decrease in the conversion to further reduced timings 4 h and 2 h at similar reaction conditions.

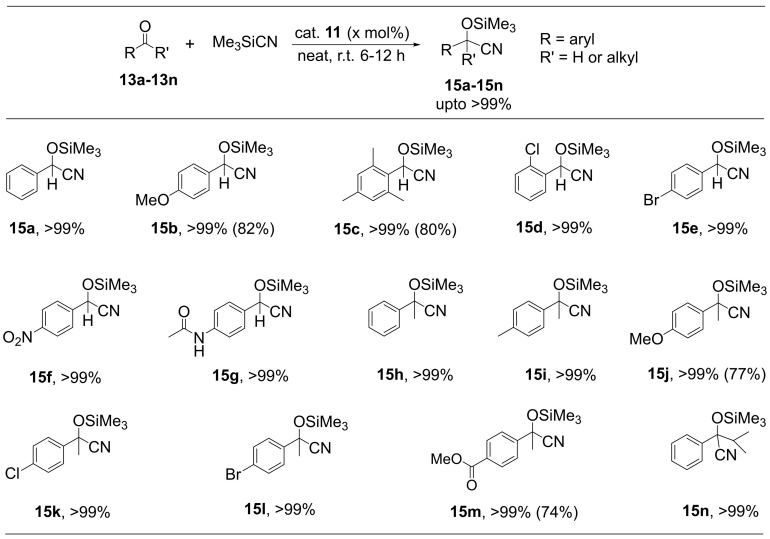
A decrease in catalyst loadings to 2 mol% and 1 mol% yielded the product near quantitative at 2 h. Moreover, solvated-CBGLi salt (**6**) exhibits similar catalytic activity as that of CBG Li.

Predictably, a slight excess amount of catalyst (2 mol%) and longer time (4 h) are required for the complete conversion of acetophenone into corresponding boronate ester. Thus, 1 mol% and 2 h for aldehydes and 2 mol% and 4 h for ketones are optimized conditions. Further, 4-methoxy benzaldehyde, mesitaldehyde, 2-chlorobenzadehyde, 4-bromobenzaldehyde, 4-nitrobenzaldehyde, and 4-acetamidobenzaldehye were explored. As shown in Scheme 6, all seven aldehydes attained near full conversion within 2 h with 1 mol% catalyst loading. Next, 4-methyl acetophenone, 4-methoxyacetophenone, 4-chloroacetophenone, 4-bromoacetophenone, methyl4-acetylbenzoate, isobutyrophenone were investigated. As illustrated in Scheme 6, all these ketones achieved complete conversion within 4 h with 2 mol% catalyst loading.

Examine whether trimethylsilyl cyanide Me_3SiCN addition to aldehydes and ketones could be broadened to the catalysts **6** and **11**; we explored the cyanosilylation reaction with the same aldehydes and ketones (Scheme 7). The reaction of benzaldehyde with trimethyl cyanide with 1 mol% catalyst **6** gave near quantitative conversion to the cyanosilylated product within 6 h at ambient temperature under neat conditions. Catalyst **11** also exhibits similar catalytic activity at the same reaction conditions (see the Supporting Information Tables S6). Unsurprisingly, an excess amount of catalyst loading (3 mol%) and longer reaction

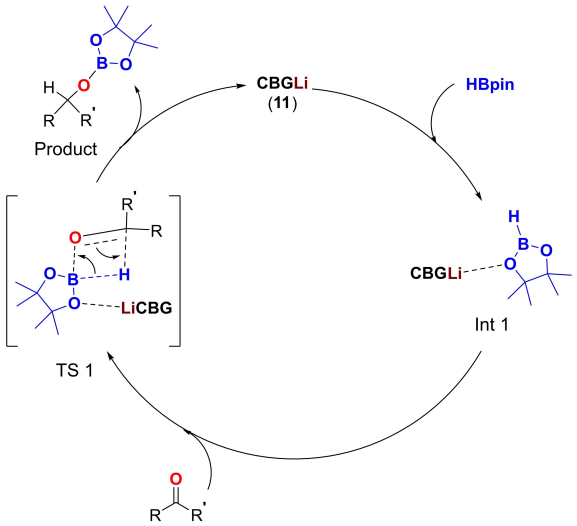


Scheme 6. Hydroboration of aldehydes and ketones catalyzed by CBG Li complex (**11**). Reaction conditions: aldehydes or ketones (0.3–1.0 mmol, 1.0 equiv.), pinacolborane (0.3–1.0 mmol, 1.0 equiv.), catalyst **11** x = 1 mol% for aldehydes and x = 2 mol% for ketones, time 2 h for aldehydes and 4 h for ketones at rt under N_2. Yields were analyzed by ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) integration of newly formed proton (RC*H*$_2$OBpin/RC*H*R'OBpin) resonance peak of the reaction mixture. Isolated yields were given in parenthesis.



Scheme 7. Cyanosilyation of aldehydes and ketones catalyzed by CBG Li complex (**11**). Reaction conditions: aldehydes or ketones (0.3–1.0 mmol, 1.0 equiv.), trimethylsilyl cyanide (0.3–1.0 mmol, 1.0 equiv.), catalyst **11**x = 1 mol% for aldehydes and x = 3 mol% for ketones, time 6 h for aldehydes and 12 h for ketones at rt under N_2. Yields were analyzed by ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) integration of newly formed proton (RCH*C*NOTMS / RR'*C*NOTMS) resonance peak of the reaction mixture. Isolated yields were given in parenthesis.

time (12 h) are required for the complete cyanosilylation of ketones (see the Supporting Information Tables S7). The reaction of acetophenone and Me_3SiCN with 3 mol% catalyst **6** or **11** gave near quantitative conversion to the cyanosilylated product within 12 h. A series of aldehydes and ketones react with trimethylsilyl cyanide at standard reaction conditions in the presence of CBG lithium catalyst **11** gave cyanohydrin trimethylsilyl ethers in nearly quantitative yields. It is important to note that lithium catalyzed hydroboration and cyanosilylation reactions; a tolerance of halide, nitro, amide, and ester functionalities was noticed. There have been reports on catalyst-free and solvent-free hydroboration of aldehydes and ketones and cyanosilylation of aldehydes in the literature. Note that such reactions were performed by using an excess amount of hydride source and harsh reaction conditions.[49]



Scheme 8. A probable mechanism for hydroboration of carbonyl compounds.

Mechanism of LLi (11) Catalyzed Reduction of Carbonyl Compounds via hydroboration

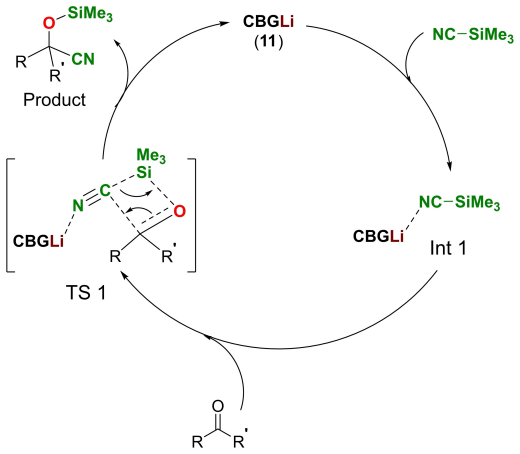
Considering the earlier provided mechanisms[48a,b] for alkali metal-catalyzed hydroboration of carbonyl compounds, herein we propose that the CBG Li catalyzed hydroboration of carbonyl compounds as depicted in Scheme 8.

Initially, the interaction of the O atom of HBpin to the Lewis acidic site of the Li atom of the catalyst has been proposed. Next, the oxygen atom of either aldehyde or ketone adds to the boron site of HBpin, with the migration of hydride from B to carbonyl carbon. Finally, the catalytic cycle closes by eliminating the boronate ester product and regeneration of the CBG lithium catalyst via four-membered transition state TS1.

Mechanism of LLi (11) Catalyzed Cyanosilyation of Carbonyl Compounds

We also proposed the mechanism for the CBG catalyzed cyanosilylation of carbonyl compounds following previous reports (Scheme 9).[48d] The catalyst CBG Li interacts with TMSCN to give an Int 1, in which the N atom of the cyanide group interacts with the Li atom of the catalyst. Next, the nucleophilic addition by the carbonyl oxygen of aldehyde or ketone to the silicon center of TMSCN in TS1.

The breaking of the Si-CN bond and CN to carbonyl carbon atom *via* C–C bond formation and oxygen adds to the Si atom $SiMe_3$ group. Finally, the catalytic cycle ends by the elimination



Scheme 9. A probable mechanism for cyanosilyation of carbonyl compounds.

cyanoether product and regeneration of the product *via* TS1. Overall, CBG Li catalysts exhibit comparable catalytic activities to main group and transition based metal catalysts.[47f,48e]

Conclusions

A series of structurally characterized N-tetra-arylated bis-guanidines or conjugated bis-guanidine(CBG)s have been reported. Also, we provided the first insight into the coordination chemistry of free CBG ligands towards lithium cations. We have reported the solvated and un-solvated lithium salts bearing the ligands **1**, **3**, and **4**. Some exciting features of these ligands have been observed while coordinating with the lithium metal. In the case of ligand **1**, solvated lithium salts were obtained when the lithiation was carried out in the ethereal solvent, either THF or Et_2O, while un-solvated lithium salt was observed in toluene. Ligand **4** showed a peculiar coordination behavior with lithium, in which the central nitrogen atom of the ligand coordinates the Li atom in a k^1-fashion. Also, there are η^6 interactions of the Li center with the Dipp substituents of N5 and N2 atoms. Thus, two bonding modes of CBG are observed for the lithium element. Notably, CBG lithium salt **11** acts as an effective catalyst for the hydroboration and cyanosilylation of carbonyl compounds. These CBG salts (**5**–**12**) can be used as ligand transfer reagents to obtain CBG metal halides. Moreover, these N-donor ligands will have broad applications in coordination, organometallic, medicinal chemistry, organic syntheses, and catalysis. Such studies are underway in our laboratory.

Experimental Section

General Methods

All air and moisture sensitive reactions were performed by using standard Schlenk line and glovebox techniques under an inert atmosphere of dinitrogen. Unless otherwise noted, all the reagents and solvents required were bought from commercial suppliers and used without further purification to prepare air-stable organic molecules. However, for the air and moisture sensitive compounds, solvents such as toluene, benzene, and *n*-hexane were collected from the MBraun solvent purification system, degassed, and stored under an atmosphere of dinitrogen before use. THF was dried over sodium wire and distilled before use. *N,N'*-diarylcarbodiimides[12a] and acetamidoxime[50] were prepared by following the literature procedures. NMR spectroscopic data were recorded on a Bruker AV 400 MHz spectrometer (^{13}C {^1H} (101 MHz; ^7Li 156 MHz). Deuterated benzene (C_6D_6), chloroform ($CDCl_3$), [D_8] toluene, and tetrahydrofuran (THF-d_8) were used for NMR measurements; chemical shift values (δ) were reported in parts per million relatives to the residual signals of their respective solvents.[51] The ^7Li NMR spectra are reported with reference to the standard ^7Li NMR of LiCl in D_2O. High-resolution mass spectra (HRMS) were recorded on a Bruker micrOTOF–Q II spectrometer. IR spectra were recorded on the Perkin-Elmer FTIR spectrometer. Melting points were recorded on digital melting point apparatus and are uncorrected. The purity of the conjugated bis-guanidines has been determined by high-pressure liquid chromatography (HPLC) using a Finepak-SIL-C18T-5 column. Analytical HPLC was performed on a JASCO-EXTREMA Technologies BS-4000 Series system equipped with an FP-4020 fluorescence detector. The compounds were dissolved in acetonitrile. The following eluent system was used: 5% *n*-hexane/95% isopropanol (v/v). HPLC retention times (HPLC t_R) were obtained at flow rates of 1 mL min^{-1} using an isocratic run. Elemental analyses were performed in a Euro Vector EA 3000 CHNS analyzer.

Synthesis of compound (1)

Method A: The reaction mixture of 1,3-bis(2, 6-dimethyl phenyl) carbodiimide (6.0 g, 24 mmol, 2.0 equiv) and acetamidoxime (0.845 g, 0.0114 mmol, 1.0 equiv) in toluene (~40 mL) was stirred under refluxing conditions for two days. The resultant reaction mixture is filtered off and washed with dichloromethane (~80 mL). Removal of volatiles in vacuo followed by purification with column chromatography on silica gel yielded the desired product (5:95 ethyl acetate /*n*-hexane as eluent). The desired compound **1** was further crystallized from ethyl acetate to obtain single crystals for X-ray diffraction. Yield: 1.42 g, 2.746 mmol, 23%.

Method B: To a solution of 1,3-bis(2, 6-dimethyl phenyl) carbodiimide (1 g, 4 mmol, 1.0 equiv) in acetonitrile (~15 mL) was added aqueous ammonia (25%) (68 μL, 16 mmol, 4.0 equiv) at room temperature and continued the stirring for 15 h. Formation of white precipitate was observed. This was filtered off, dried the solid residue, and recrystallized from dichloromethane to give compound **1** colorless solid. Yield: 0.559 g, 1.07 mmol, 54%.

Method C: To a stirred solution of 1,3-bis(2, 6-dimethylphenyl) carbodiimide (5.0 g, 19.95 mmol, 2.0 equiv) and NH_4Cl (0.435 g, 8.15 mmol, 1.0 equiv) in 8 mL ethanol in a sealed tube was added triethylamine (1.5 mL, 10.6 mmol, 1.3 equiv) slowly. The reaction mixture was heated at 80 °C for 3 h to afford a white precipitate. After completion of reaction, the crude mixture was filtered off and wash with cold (−40 °C) ethanol (5–10 ml) and recrystallized from dichloromethane at room temperature to give as a colorless solid. Yield: 3.7 g, 7.156 mmol, 72%; Mp: 210–212 °C; ^1H NMR (400 MHz, C_6D_6, 25 °C): (major isomer) $\delta = 1.89$ (s, 12H, C*H*$_3$), 2.37 (s, 12H, C*H*$_3$), 4.62 (s, 2H, N*H*), 6.68 (d, $^3J_{HH} = 8.0$ Hz, 4H, Ar*H*), 6.84 (t, $^3J_{HH} = 8.0$ Hz, 2H, Ar*H*), 6.96–6.99 (m, 2H, Ar*H*), 7.04 (d, $^3J_{HH} = 8.0$ Hz, 4H, Ar*H*), 12.91 ppm (s, 1H, N*H*N); $^{13}C\{^1H\}$ NMR (101 MHz, C_6D_6, 25 °C): $\delta =$ 18.25 (Ar-*C*H$_3$), 18.29 (Ar-*C*H$_3$), 124.8 (Ar-*C*), 125.4 (Ar-*C*), 127.1 (Ar-*C*), 128.4 (Ar-*C*), 133.8 (Ar-*C*), 135.7 (Ar-*C*), 136.6 (Ar-*C*), 140.8 (Ar-*C*), 154.3 ppm (N$_3$*C*); IR (KBr pellet, cm^{-1}) 3380s, 3019 m, 2920 m, 1618 s, 1586 m, 1567 s, 1499 m, 1468 m, 1399 s, 1356 s, 1295 m,

1251 m, 1225 s, 890s, 768 s; HRMS (ESI-TOF-Q) *m/z*: $[M+H]^+$ calcd. for $C_{34}H_{40}N_5$ 518.3278, found: 518.3294; HPLC: P_{HPLC} (major isomer) 98.0%, t_R 2.11 and (minor isomer) 2.05%, t_R 2.78; Anal. Calcd. for $C_{34}H_{39}N_5$ (517.71): C, 78.88; H, 7.59; N,13.53. Found: C, 79.09; H, 8.11; N, 13.80.

Synthesis of compound (2)

Method A: The reaction mixture of 1,3-bis(2, 4, 6–trimethylphenyl) carbodiimide (6 g, 21.58 mmol, 2.0 equiv) and acetamidoxime (0.759 g, 10.26 mmol, 1.0 equiv) in toluene (~40 mL) was stirred under refluxing conditions for two days. The resultant reaction mixture is filtered off and washed with dichloromethane (~80 mL). Removal of volatiles in vacuo followed by purification with column chromatography on silica gel yielded the desired product (5:95 ethyl acetate /*n*-hexane as eluent). The desired compound **2** was further crystallized from ethyl acetate to obtain single crystals for X-ray diffraction. Yield: 1.36 g, 2.37 mmol, 22%.

Method B: To a solution of 1,3-bis(2, 4, 6–trimethylphenyl) carbodiimide (1 g, 3.592 mmol, 1.0 equiv) in acetonitrile (20 mL) was added aqueous ammonia (25%) (61 μL, 14.368 mmol, 4.0 equiv) at room temperature and continued the stirring for 15 h. Formation of white precipitate was observed. This was filtered off, dried the solid residue, and recrystallized from dichloromethane to give compound **2** a colorless solid. Yield: 0.526 g, 0.9175 mmol, 52%.

Method C: The synthetic procedure was similar to $[L^1(3H)]$ (**1**) by using 1,3-bis(2, 4, 6–trimethylphenyl) carbodiimide (5.0 g, 17.97 mmol, 2.0 equiv), NH_4Cl (0.435 g, 8.15 mmol, 1.0 equiv) and triethylamine (1.5 mL, 10.6 mmol, 1.3 equiv). Compound **2** (3.30 g, 5.755 mmol, 65%). Mp: 229–231 °C; ^{1}H NMR (400 MHz, C_6D_6, 25 °C): δ = 1.94 (s, 12H, C*H*$_3$), 2.21 (s, 12H, C*H*$_3$), 2.40 (s, 12H, C*H*$_3$), 4.70 (s, 2H, N*H*), 6.51 (s, 4H, Ar*H*), 6.86 (s, 4H, Ar*H*), 12.82 ppm (s, 1H, N*H*N);^{13}C{^{1}H}NMR (101 MHz, C_6D_6, 25 °C): δ = 18.2 (*o*-Ar-*C*H$_3$), 18.3 (*o*-Ar-*C*H$_3$), 20.6 (*p*-Ar-*C*H$_3$), 20.7 (*p*-Ar-*C*H$_3$), 127.5 (Ar-*C*), 127.8 (Ar-*C*), 129.1 (Ar-*C*), 133.4 (Ar-*C*), 134.0 (Ar-*C*), 134.2 (Ar-*C*), 135.5 (Ar-*C*), 138.3 (Ar-*C*), 154.6 ppm (N$_3$*C*); IR (KBr pellet, cm^{-1}) 3665 m, 3383 s, 2915 m, 2854 m, 1621 m, 1601 m, 1567 s, 1474 m, 1396 m, 1356 m, 1233 s, 1030 m, 1010 m, 874 m, 845 s, 785 m; HRMS (ESI-TOF–Q) *m/z*: $[M+H]^+$calcd. for $C_{38}H_{48}N_5$ 574.3904, found: 574.3932; HPLC: P_{HPLC} (major isomer) 98.4%, t_R 1.98 and (minor isomer) 2.47%, t_R1.59; Anal. Calcd. for $C_{38}H_{47}N_5$ (573.81): C, 79.54; H, 8.26; N,12.20. Found: C, 78.71; H, 8.82; N, 12.55.

Synthesis of compound (3)

Method A: The reaction mixture of 1,3-bis(2, 6–diethyl phenyl) carbodiimide (6.0 g, 19.57 mmol, 2.0 equiv) and acetamidoxime (0.69 g, 9.32 mmol, 1.0 equiv) in toluene (~40 mL) was stirred under refluxing conditions for two days. The resultant reaction mixture was filtered off and washed with dichloromethane (~80 mL). Removal of volatiles in vacuo followed by purification with column chromatography on silica gel yielded the desired product (5:95 ethyl acetate /n-hexane as eluent). The desired compound **3** was further crystallized from ethyl acetate to obtain single crystals for X-ray diffraction. Yield: 1.11 g, 1.76 mmol, 18%.

Method B: To a solution of 1,3-bis(2, 6-diethyl phenyl) carbodiimide (1 g, 3.263 mmol, 1.0 equiv) in acetonitrile (20 mL) was added aqueous ammonia (25%) (55.5 μL, 13.052 mmol, 4.0 equiv) at room temperature and continued the stirring for 15 h. Formation of white precipitate was observed. This was filtered off, dried the solid residue, and recrystallized from dichloromethane to give compound **3** a colorless solid. Yield: 0.65 g, 1.03 mmol, 64%.

Method C: The synthetic procedure was similar to $[L^1(3H)]$ (**1**) by using 1,3-bis(2, 6–diethylphenyl) carbodiimide (5.0 g, 16.32 mmol, 2.0 equiv), NH_4Cl (0.435 g, 8.15 mmol, 1.0 equiv) and triethylamine (1.5 mL, 10.6 mmol, 1.3 equiv). Compound **3** (3.7 g, 5.878 mmol, 71%). Mp: 163–167 °C; ^{1}H NMR (400 MHz, C6D6, 25 °C): δ = 1.02 (t, $^3J_{HH}$ = 8.0 Hz, 12H, CH_2CH_3), 1.28 (t, $^3J_{HH}$ = 8.0 Hz, 12H, CH_2CH_3), 2.20–2.27 (m, 4H, CH_2CH_3), 2.30–2.35 (m, 4H, CH_2CH_3), 2.62–2.73 (m, 4H, CH_2CH_3), 3.01–3.12 (m, 4H, CH_2CH_3), 4.86 (s, 2H, N*H*), 6.77–6.79 (d, $^3J_{HH}$ = 8.0 Hz, 4H, Ar*H*), 6.98–7.01 (m, 2H, Ar*H*), 7.09–7.13 (m, 6H, Ar*H*), 12.97 ppm (s, 1H, N*H*N);^{13}C NMR (101 MHz, C6D6, 25 °C): δ = 14.3 (Ar-CH_2CH_3), 14.7 (Ar-CH_2CH_3), 24.8 (Ar-CH_2CH_3), 24.9 (Ar-CH_2CH_3), 125.2 (Ar-*C*), 125.4 (Ar-*C*), 126.1 (Ar-*C*), 126.6 (Ar-*C*), 135.2 (Ar-*C*), 139.4 (Ar-*C*), 139.6 (Ar-*C*), 141.7 (Ar-*C*), 155.0 ppm (N$_3$*C*); IR (KBr pellet, cm^{-1}) 3378s, 3048m, 3066m, 2962s, 2933s, 2349 s, 2340s, 2361s, 1609m, 1568m, 1514m, 1507m, 1457m, 1423m, 1291s, 1265s, 1222s, 897s, 868s, 789s, 717s; HRMS (ESI-TOF-Q) *m/z*: $[M+H]^+$ calcd. for $C_{42}H_{56}N_5$ 630.4530, found: 630.4519; HPLC: P_{HPLC} 100%, t_R2.29; Anal. Calcd. for $C_{42}H_{55}N_5$ (629.92): C, 80.08; H, 8.80; N,11.12. Found: C, 78.96; H, 9.48; N, 11.42.

Synthesis of compound (4)

Method A: The reaction mixture of 1,3-bis(2, 6-diisopropylphenyl) carbodiimide (6.0 g, 16.55 mmol, 2.0 equiv) and acetamidoxime (0.583 g, 7.88 mmol, 1.0 equiv) in toluene (~40 mL) was stirred under refluxing conditions for two days. The resultant reaction mixture is filtered off and washed with dichloromethane (~80 mL). Removal of volatiles in vacuo followed by purification with column chromatography on silica gel yielded the desired product (5:95 ethyl acetate /*n*-hexane as eluent). The desired compound **4** was further crystallized from ethyl acetate to obtain single crystals for X-ray diffraction. Yield: 2.456 g, 3.311 mmol, 40%.

Method B: To a solution of 1,3-bis(2,6-diisopropylphenyl) carbodiimide (1.0 g, 2.759 mmol, 1.0 equiv) in acetonitrile (~15 mL) was added aqueous ammonia (25%) (46.75 μL, 11.03 mmol, 4.0 equiv) at room temperature and continued the stirring for 15 h. Formation of white precipitate was observed. This was filtered off, dried the solid residue, and recrystallized from dichloromethane to give **4** a colorless solid. Yield: 0.511 g, 0.6989 mmol, 50%.

Method C: The synthetic procedure was similar to $[L^1(3H)]$ (**1**) by using 1,3-bis(2,6-diisopropylphenyl) carbodiimide (5.0 g, 13.8 mmol, 2.0 equiv), NH_4Cl (0.435 g, 8.15 mmol, 1.0 equiv) and triethylamine (1.5 mL, 10.6 mmol, 1.3 equiv). Compound **4** (3.5 g, 4.716 mmol, 68%). Mp: 212–214 °C; ^{1}H NMR (400 MHz, C_6D_6, 25 °C): δ = 0.94 - 0.95 (d, $^3J_{HH}$ = 4.0 Hz, 12H, CH(C*H*$_3$)$_2$), 0.99–1.00 (d, $^3J_{HH}$ = 4.0 Hz, 12H, CH(C*H*$_3$)$_2$), 1.24–1.26 (d, $^3J_{HH}$ = 8.0 Hz, 12H, CH(C*H*$_3$)$_2$), 1.31-1.33 (d, $^3J_{HH}$ = 8.0 Hz, 12H, CH(C*H*$_3$)$_2$), 3.06–3.13 (sept, $^3J_{HH=}$8.0 Hz, 4H, C*H*-(CH$_3$)$_2$), 3.59–3.66 (sept, $^3J_{HH=}$8.0 Hz, 4H, C*H*(CH$_3$)$_2$), 4.94 (s, 2H, N*H*), 6.89–7.14 (m, 12H, Ar*H*), 13.02 ppm (s, 1H, N*H*N); ^{13}C{^{1}H}NMR (101 MHz, C_6D_6, 25 °C): δ = 21.7 (Ar-CH(*C*H$_3$)$_2$), 23.2 (Ar-CH(*C*H$_3$)$_2$), 23.6 (Ar-CH(*C*H$_3$)$_2$), 25.3 (Ar-CH(*C*H$_3$)$_2$), 28.1 (Ar-*C*H(CH$_3$)$_2$), 28.4 (Ar-*C*H(CH$_3$)$_2$), 122.6 (Ar-*C*), 123.4 (Ar-*C*), 126.0 (Ar-*C*), 127.3 (Ar-*C*), 133.6 (Ar-*C*), 137.9 (Ar-*C*), 143.9 (Ar-*C*), 146.9 (Ar-*C*), 156.5 ppm (N$_3$*C*); IR (KBr pellet, cm^{-1}) 3399s, 2958s, 2867m, 1607m, 1586m, 1566m, 1460m, 1395m, 1358 m, 1326m, 1256s, 792m, 757m; HRMS (ESI-TOF-Q) *m/z*: $[M+H]^+$ calcd. for $C_{50}H_{72}N_5$ 742.5782, found: 742.5772; HPLC: P_{HPLC} 100%, t_R2.23; Anal. Calcd. for $C_{50}H_{71}N_5$ (742.13): C, 80.92; H, 9.64; N, 9.44. Found: C, 80.75; H, 9.77; N, 10.39.

Synthesis of compound (5). To a solution of compound **1** (0.25 g, 0.482 mmol, 1.0 equiv) in THF (~10 mL) was added ^{n}BuLi (1.6 M in *n*-hexane, 0.31 mL, 0.507 mmol, 1.1 equiv) at 0 °C. The reaction mixture was allowed to warm to room temperature and continued the stirring for 8 h. The volatiles were removed under reduced pressure. The obtained solid residue was dried under high vacuum

and crystallized from *n*-hexane and THF mixture to provide **5** as a colorless crystal. Yield: 0.177 g, 0.265 mmol, 55%. Mp: 177–186 °C; ^{1}H NMR (400 MHz, C_6D_6, 25 °C): δ = 0.92 (br, s, 8H, OCH_2CH_2), 2.06 (s, 12H, CH_3), 2.46 (s, 12H, CH_3), 2.86 (br, s, 8H, OCH_2CH_2), 4.63 (s, 2H, N*H*), 6.73 (d, $^3J_{HH}$ = 8.0 Hz, 5H, Ar*H*), 6.86–6.89 (m, 3H, Ar*H*), 6.93–6.96 (m, 2H, Ar*H*), 7.13 ppm (s, 2H, Ar*H*); ^{13}C{^{1}H} NMR (101 MHz, C_6D_6, 25 °C): δ = 18.8 (Ar-CH_3), 19.1 (Ar-CH_3), 25.0 (OCH_2CH_2), 67.7 (OCH_2CH_2), 122.6 (Ar-*C*), 125.0 (Ar-*C*), 127.5 (Ar-*C*), 128.6 (Ar-*C*), 132.6 (Ar-*C*), 136.1 (Ar-*C*), 139.2 (Ar-*C*), 149.1 (Ar-*C*), 155.1 ppm (N_3C); ^{7}Li NMR (155.5 MHz, C_6D_6, 25 °C): δ = 2.06 ppm (s).

Synthesis of compound (6). The compoundwas synthesized by employing a similar procedure to that used for the synthesis of **5**but by using compound **3** (0.25 g, 0.396 mmol, 1.0 equiv) ^{n}BuLi (2.0 M in cyclohexane, 0.22 mL, 0.436 mmol, 1.1 equiv). Yield: 0.228 g, 0.322 mmol; 81%. Mp: 170–178 °C; ^{1}H NMR (400 MHz, C_6D_6, 25 °C): δ = 0.95 (br, s, 4H, OCH_2CH_2), 1.11 (t, $^3J_{HH}$ = 8.0 Hz, 12H, CH_2CH_3), 1.30 (t, $^3J_{HH}$ = 8.0 Hz, 12H, CH_2CH_3), 2.33–2.40 (m, 4H, CH_2CH_3), 2.55–2.62 (m, 4H, CH_2CH_3), 2.75–2.84 (m, 4H, CH_2CH_3), 2.93 (br, s, 4H, OCH_2CH_2), 3.04–3.13 (m, 4H, CH_2CH_3), 4.74 (s, 2H, N*H*), 6.76–6.79 (m, 4H, Ar*H*), 6.97–7.01 (m, 2H, Ar*H*), 7.06–7.11 (m, 2H, Ar*H*), 7.15–7.19 ppm(m, 4H, Ar*H*); ^{13}C{^{1}H} NMR (101 MHz, C_6D_6, 25 °C): δ = 14.5 (Ar-CH_2CH_3), 14.7 (Ar-CH_2CH_3), 24.3 (Ar-CH_2CH_3), 24.6 (Ar-CH_2CH_3),), 25.2 (OCH_2CH_2), 67.5 (OCH_2CH_2), 122.8 (Ar-*C*), 125.1 (Ar-*C*), 125.3 (Ar-*C*), 126.1 (Ar-*C*), 126.6 (Ar-*C*), 137.5 (Ar-*C*), 137.9 (Ar-*C*), 141.5 (Ar-*C*), 141.7 (Ar-*C*), 147.4 (Ar-*C*), 155.3 ppm(N_3C); ^{7}Li NMR (155.5 MHz, C_6D_6, 25 °C): δ = 5.11 ppm (s).

Synthesis of compound (7). The compound was synthesized by employing a similar procedure to that used for the synthesis of **5** but by using compound **4** (0.25 g, 0.336 mmol, 1.0 equiv),^{n}BuLi (2.0 M in cyclohexane, 0.19 mL, 0.370 mmol, 1.1 equiv). Yield: 0.246 g, 0.299 mmol, 88%; Mp: 182–188 °C; ^{1}H NMR (400 MHz, C_6D_6, 25 °C): δ = 0.93 (br, s, 4H, OCH_2CH_2), 0.96– 1.05 (m, 12H, $CH(CH_3)_2$), 1.24–1.25 (d, $^3J_{HH}$ = 4.0 Hz, 24H, $CH(CH_3)_2$), 1.43–1.45 (d, $^3J_{HH}$ = 8.0 Hz, 12H, $CH(CH_3)_2$), 2.80 (br, s, 4H, OCH_2CH_2), 3.30–3.36 (m, 4H, $CH(CH_3)_2$), 3.73–3.76 (m, 4H, $CH(CH_3)_2$), 5.13 (s, 2H, N*H*), 6.92–6.94 (d, $^3J_{HH}$ = 8.0 Hz, 4H, Ar*H*), 7.01–7.05 (m, 2H, Ar*H*), 7.11–7.17 (m, 2H, Ar*H*), 7.23–7.25 ppm(d, $^3J_{HH}$ = 8.0 Hz, 4H, Ar*H*);^{13}C NMR (101 MHz, C_6D_6, 25 °C): δ = 23.1 (Ar-$CH(CH_3)_2$), 24.5 (Ar-$CH(CH_3)_2$), 24.5 (Ar-$CH(CH_3)_2$), 25.8 (OCH_2CH_2), 27.9 (Ar- $CH(CH_3)_2$), 28.2 (Ar-$CH(CH_3)_2$), 67.4 (OCH_2CH_2), 122.1 (Ar-*C*), 123.3 (Ar-*C*), 125.6 (Ar-*C*), 135.7 (Ar-*C*), 142.6 (Ar-*C*), 145.2 (Ar-*C*), 145.7 (Ar-*C*), 155.8 ppm(N_3C);^{7}Li NMR (155.5 MHz, C_6D_6, 25 °C): δ = 4.96 ppm (s).

Synthesis of compound (8). To a solution of compound **1** (0.25 g, 0.482 mmol, 1.0 equiv) in diethyl ether (10 mL) was added ^{n}BuLi (1.6 M in *n*-hexane, 0.31 mL, 0.507 mmol, 1.1 equiv) at 0 °C. The reaction mixture was allowed to warm to room temperature and continued the stirring for 8 h. The solvent was removed under reduced pressure. Finally, the solid was dried under high vacuum and the compound was recrystallized from toluene/diethylether to give **8**as a colorless crystal. Yield: 0.170 g, 0.285 mmol, 59%; Mp: 177–186 °C; ^{1}H NMR (400 MHz, C_6D_6, 25 °C): δ = 0.82 (t, $^3J_{HH}$ = 8.0 Hz, 6H, OCH_2CH_3), 2.01 (s, 12H, CH_3), 2.36 (s, 12H, CH_3), 2.96 (q, $^3J_{HH}$ = 8.0 Hz, 4H, OCH_2CH_3), 4.55 (s, 2H, N*H*), 6.70 (d, $^3J_{HH}$ = 8.0 Hz, 5H, Ar*H*), 6.83–6.86 (m, 2H, Ar*H*), 6.96 (t, $^3J_{HH}$ = 8.0 Hz, 2H, Ar*H*), 7.04 (d, $^3J_{HH}$ = 8.0 Hz, 1H, Ar*H*), 7.13 ppm(s, 2H, Ar*H*); ^{13}C{^{1}H} NMR (101 MHz, C_6D_6, 25 °C) δ = 14.8 (OCH_2CH_3), 18.8 (Ar-CH_3), 19.1 (Ar-CH_3), 65.9 (OCH_2CH_3), 122.7 (Ar-*C*), 125.1 (Ar-*C*), 127.5 (Ar-*C*), 128.6 (Ar-*C*), 132.6 (Ar-*C*), 136.0 (Ar-*C*), 139.0 (Ar-*C*), 148.9 (Ar-*C*), 154.9 ppm(N_3C); ^{7}Li NMR (155.5 MHz, C_6D_6, 25 °C): δ = 0.79 ppm (s).

Synthesis of compound (9). The compound was synthesized by employing a similar procedure to that used for the synthesis of **8** but by using compound **4** (0.25 g, 0.336 mmol, 1.0 equiv),^{n}BuLi (2.0 M in cyclohexane, 0.19 mL, 0.370 mmol, 1.1 equiv). Yield: 0.230 g, 0.279 mmol, 83%; Mp: 180–186 °C;^{1}H NMR (400 MHz, C_6D_6, 25 °C): δ = 0.72 (t, $^3J_{HH}$ = 8.0 Hz, 6H, OCH_2CH_3), 1.11–1.12 (d, $^3J_{HH}$ = 4.0 Hz, 12H, $CH(CH_3)_2$), 1.16–1.17 (d, $^3J_{HH}$ = 4.0 Hz, 12H, $CH(CH_3)_2$), 1.48–1.50 (d, $^3J_{HH}$ = 8.0 Hz, 12H, $CH(CH_3)_2$), 1.56–1.58 (d, $^3J_{HH}$ = 8.0 Hz, 12H, $CH(CH_3)_2$), 2.99 (q, $^3J_{HH}$ = 8.0 Hz, 4H, OCH_2CH_3), 3.23–3.30 (m, 4H, $CH(CH_3)_2$), 3.75–3.83 (m, 4H, $CH(CH_3)_2$), 5.11 (s, 2H, N*H*), 7.05–7.11 (m, 4H, Ar*H*), 7.20–7.26 (m, 2H, Ar*H*), 7.31–7.34 (m, 2H, Ar*H*), 7.36–7.40 ppm(m, 4H, Ar*H*);^{13}C NMR (101 MHz, C_6D_6, 25 °C): δ = 14.3 (OCH_2CH_3), 22.3 (Ar-$CH(CH_3)_2$), 22.7 (Ar-$CH(CH_3)_2$), 24.4 (Ar-$CH(CH_3)_2$), 27.2 (Ar-$CH(CH_3)_2$), 27.5 (Ar-$CH(CH_3)_2$), 64.6 (OCH_2CH_3), 121.7 (Ar-*C*), 122.5 (Ar-*C*), 125.0 (Ar-*C*), 137.0 (Ar-*C*), 142.9 (Ar-*C*), 146.0 (Ar-*C*), 155.6 ppm(N_3C);^{7}Li NMR (155.5 MHz, C_6D_6, 25 °C): δ = 3.87 ppm (s).

Synthesis of compound (10).To a solution of compound **1** (0.2 g, 0.386 mmol, 1.0 equiv) in toluene (~10 mL) was added ^{n}BuLi (1.6 M in *n*-hexane, 0.253 mL, 0.406 mmol, 1.1 equiv) at room temperature, which results immediate formation of colorless precipitate and continued the stirring for 12 h. The volatiles were removed under reduced pressure. The obtained residue was dried under high vacuum to give **10** as a colorless solid. Yield: 0.123 g, 0.235 mmol, 61%; Mp: 180–187 °C; ^{1}H NMR (400 MHz, THF-d_8, 25 °C): δ = 1.92 (s, 12H, CH_3), 2.38 (s, 12H, CH_3), 4.79 (s, 2H, N*H*), 6.50 (d, $^3J_{HH}$ = 8.0 Hz, 4H, Ar*H*), 6.59–6.62 (m, 3H, Ar*H*), 6.70–6.73 (m, 3H, Ar*H*), 6.96 ppm(d, $^3J_{HH}$ = 8.0 Hz, 4H, Ar*H*); ^{13}C {^{1}H}NMR (101 MHz, THF-d_8, 25 °C): δ = 19.0 (Ar-CH_3), 19.1 (Ar-CH_3), 121.8 (Ar-*C*), 124.6 (Ar-*C*), 127.5 (Ar-*C*), 128.4 (Ar-*C*), 132.9 (Ar-*C*), 136.1 (Ar-*C*), 140.2 (Ar-*C*), 150.5 (Ar-*C*), 155.0 ppm(N_3C); ^{7}Li NMR (155.5 MHz, THF-d_8, 25 °C): δ =-0.77 ppm (s).

Synthesis of compound (11).The compoundwas synthesized by employing a similar procedure to that used for the synthesis of **10** but by using compound **3** (1.0 g, 1.59 mmol, 1.0 equiv) in toluene (~20 mL),^{n}BuLi (2.0 M in cyclohexane, 0.88 mL, 1.74 mmol, 1.1 equiv). Yield: 0.95 g, 1.49 mmol, 94%; Mp: 180–186 °C;^{1}H NMR (400 MHz, C_6D_6, 25 °C) δ = 1.03 (t, $^3J_{HH}$ = 8.0 Hz, 12H, CH_2CH_3), 1.31 (t, $^3J_{HH}$ = 8.0 Hz, 12H, CH_2CH_3), 2.26–2.35 (m, 4H, CH_2CH_3), 2.45–2.55 (m, 4H, CH_2CH_3), 2.67–2.85 (m, 2H, CH_2CH_3),4.62 (s, 2H, N*H*), 6.69–6.71 (d, $^3J_{HH}$ = 8.0 Hz, 4H, Ar*H*), 6.92 (t, $^3J_{HH}$ = 8.0 Hz, 2H, Ar*H*), 7.14–7.12 (d, $^3J_{HH}$ = 8.0 Hz, 2H, Ar*H*), 7.24–7.22 ppm(d, $^3J_{HH}$ = 8.0 Hz, 2H, Ar*H*); ^{13}C NMR (101 MHz, C_6D_6, 25 °C): δ = 13.6 (Ar-CH_2CH_3), 14.3 (Ar-CH_2CH_3), 23.7 (Ar-CH_2CH_3), 25.0 (Ar-CH_2CH_3), 122.9 (Ar*C*), 124.9 (Ar*C*), 125.2(Ar*C*), 125.4 (Ar*C*), 126.1 (Ar*C*), 126.6 (Ar*C*), 137.1 (Ar*C*), 137.4 (Ar*C*), 139.6 (Ar*C*), 141.1 (Ar*C*), 141.7 (Ar*C*), 147.2 (Ar*C*), 154.9 ppm (N_3C); ^{7}Li NMR (155.5 MHz, C_6D_6, 25 °C): δ = 3.97 ppm (s).

Synthesis of compound (12). To a solution of compound **4** (0.20 g, 0.27 mmol, 1.0 equiv) in toluene (~10 mL) was added ^{n}BuLi (1.6 M in *n*-hexane, 0.185 mL, 0.296 mmol, 1.1 equiv) at room temperature and continued the stirring for 12 h. The volatiles were removed under reduced pressure. The obtained solid residue was dried and recrystallized from toluene to give **12** as a colorless crystal. Yield: 0.121 g, 0.16 mmol, 60%; Mp: 206–214 °C; ^{1}H NMR (400 MHz, C_6D_6, 25 °C) δ = 0.95–0.96 (d, $^3J_{HH}$ = 4.0 Hz, 12H, $CH(CH_3)_2$), 1.07–1.09 (d, $^3J_{HH}$ = 8.0 Hz, 9H, $CH(CH_3)_2$), 1.20–1.22 (d, $^3J_{HH}$ = 8.0 Hz, 6H, $CH(CH_3)_2$), 1.25–1.26 (d, $^3J_{HH}$ = 4.0 Hz, 9H, $CH(CH_3)_2$), 1.31–1.32 (d, $^3J_{HH}$ = 4.0 Hz, 12H, $CH(CH_3)_2$), 3.08–3.13 (m, 3H, $CH(CH_3)_2$), 3.17–3.22 (m, 1H, $CH(CH_3)_2$), 3.62–3.67 (m, 4H, $CH(CH_3)_2$), 4.95 (s, 1H, N*H*), 6.92–6.95 (m, 4H, Ar*H*), 7.02–7.08 (m, 4H, Ar*H*), 7.17–7.22 (m, 4H, Ar*H*), 13.01 ppm (s, 1H, N*H*N); ^{13}C{^{1}H} NMR (101 MHz, C_6D_6, 25 °C) δ = 22.1($CH(CH_3)_2$), 23.6 ($CH(CH_3)_2$), 24.0 ($CH(CH_3)_2$), 25.7 ($CH(CH_3)_2$), 28.5 ($CH(CH_3)_2$), 28.5 ($CH(CH_3)_2$), 28.8 ($CH(CH_3)_2$), 28.9 ($CH(CH_3)_2$), 123.0 (Ar-*C*), 123.8 (Ar-*C*), 126.3 (Ar-*C*), 127.7 (Ar-*C*), 128.3 (Ar-*C*), 134.0 (Ar-*C*), 138.3 (Ar-*C*), 144.3 (Ar-*C*), 147.3 (Ar-*C*), 156.9 ppm (N_3C); ^{7}Li NMR (155.5 MHz, D_8-Toluene, 25 °C): δ = 2.17 ppm (s).

Note: Reproducible microanalysis CHN data on compounds **5**–**12** could not be obtained owing to their solvated ad air/moisture sensitive nature.

General Procedure for the Catalytic Hydroboration of Aldehydes and Ketones

Aldehyde or ketone (0.3–1.0 mmol.), pinacolborane (0.3–1.0 mmol), and catalyst **11** (1 mol% or 2 mol%) were placed in a screw cap vial inside the glove box. The reaction mixture was stirred at r.t. for 2 h or 4 h. The progress of the reaction was monitored by ^{1}H (in dry $CDCl_3$) NMR spectroscopy. The ^{1}H NMR spectrum confirms the complete disappearance of the starting material and the presence of a new C*H*$_2$ or C*H* peak of boronate esters. After completion of the reaction, 3–4 mL of dry hexane was added to the crude catalytic reaction mixture and passed through a syringe filter which further dried properly in a high vacuum under N_2 atmosphere for isolating the pure aryloxyboronate esters (**14b**–**14c**; **14j** and **14m**) with 76–86% yield.

General Procedure for the Catalytic Cyanosilyation of Aldehydes and Ketones

Aldehyde or ketone (0.3–1.0 mmol), trimethylsilyl cyanide (0.3–1.0 mmol), and catalyst **11** (1 mol% or 3 mol%) were placed in a screw cap vial inside the glove box. The reaction mixture was stirred at r.t. for 6 h or 12 h. The progress of the reaction was monitored by ^{1}H (in dry $CDCl_3$) NMR spectroscopy. The ^{1}H NMR spectrum confirms the complete disappearance of the starting material and the presence of a new C*H* or shifting of C*H*$_3$ peakof cyanosilyated ethers. The crude organic product was extracted from the catalytic reaction mixture with DCM (3×10 mL) and wash thoroughly with dry hexane (3 x 5 mL). The organic compound was dried over $MgSO_4$, and all remain volatiles were completely removed using a rotary evaporator and dried adequately for 3–4 h in a high vacuum. The final addition product (**15b**–**15c; 15j** and **15m**) was characterized by ^{1}H and ^{13}C{^{1}H} NMR spectroscopy.

Supporting Information

(see footnote on the first page of this article): Crystallographic information files (CIF). ^{1}H, ^{13}C{^{1}H}, and ^{7}Li (**5**–**12**) NMR of spectra for **1**–**12**, **4a**–**4c**, borate esters (**14a**–**14n**), and cyanoethers (**15a**–**15n**); Molecular structures of compounds **2**–**3** and **4a**–**4c**, along with a list of selected bond lengths and angles; Optimization Tables for catalysis; Table S4-S7. Experimental procedures (PDF) Deposition Numbers 1546802 (for **1**), 1546803 (for **2**), 1546804 (for **3**), 1546805 (for **4**), 1546806 (for **4a**), 1546807 (for **4b**), 1546808 (for **4c**), 1546809 (for **5**), 1546810 (for **8**), and 1546811 (for **12**) contain the supplementary crystallographic data for this paper. These data are provided free of charge by the joint Cambridge Crystallographic Data Centre and Fachinformationszentrum Karlsruhe Access Structures service www.ccdc.cam.ac.uk/structures.

Acknowledgments

The authors thank the National Institute of Science Education and Research (NISER), HBNI, Bhubaneswar Department of Atomic Energy, and the Government of India for supporting this work. We thank Dr. S. Peruncheralathan, Dr. B. L. Bhargava, and Ms. Blessy M. Suresh for their help. T. P and A. B. acknowledge the University Grant Commission (UGC) Government of India for their fellowships.

Conflict of Interest

The authors declare no conflict of interest.

Keywords: Cyanosilylation · Guanidine · Hydroboration · Lithium · Main group catalysis

[1] a) R. Kretschmer, *Chem. Eur. J.* **2020**, *26*, 2099–2119; b) M. W. Drover, J. A. Love, L. L. Schafer, *Chem. Soc. Rev.* **2017**, *46*, 2913–2940; c) C. Chen, S. M. Bellows, P. L. Holland, *Dalton Trans.* **2015**, *44*, 16654–16670; d) A. L. Gavrilova, B. Bosnich, *Chem. Rev.* **2004**, *104*, 349–384; e) A. A. Kitos, N. Mavragani, M. Murugesu, J. L. Brusso, *Mater. Adv.* **2020**, *1*, 2688–2706.

[2] a) R. L. Webster, *Dalton Trans.* **2017**, *46*, 4483–4498; b) C. Camp, J. Arnold, *Dalton Trans.* **2016**, *45*, 14462–14498; c) S. P. Sarish, S. Nembenna, S. Nagendran, H. W. Roesky, *Acc. Chem. Res.* **2011**, *44*, 157–170; d) L. Bourget-Merle, M. F. Lappert, J. R. Severn, *Chem. Rev.* **2002**, *102*, 3031–3066; e) M. Stender, B. E. Eichler, N. J. Hardman, P. P. Power, J. Prust, M. Noltemeyer, H. W. Roesky, *Inorg. Chem.* **2001**, *40*, 2794–2799; f) Y. Ding, H. W. Roesky, M. Noltemeyer, H.-G. Schmidt, P. P. Power, *Organometallics* **2001**, *20*, 1190–1194.

[3] a) M. N. Kopylovich, A. J. L. Pombeiro, *Coord. Chem. Rev.* **2011**, *255* (1-2), 339–355; b) H. V. R. Dias, S. Singh, *Dalton Trans.* **2006**, (16), 1995–2000; c) H. V. R. Dias, S. Singh, T. R. Cundari, *Angew. Chem. Int. Ed.* **2005**, *44* (31), 4907–4910; *Angew. Chem.* **2005**, *117*, 4985–4988; d) H. V. R. Dias, S. Singh, *Inorg. Chem.* **2004**, *43* (23), 7396–7402; e) H. V. R. Dias, S. Singh, *Inorg. Chem.* **2004**, *43* (19), 5786–5788.

[4] a) M. J. T. Wilding, D. A. Iovan, T. A. Betley, *J. Am. Chem. Soc.* **2017**, *139*, 34, 12043–12049; b) C. Kleinlein, S.-L. Zheng, T. A. Betley, *Inorg. Chem.* **2017**, *56* (10), 5892–5901; c) C. Kleinlein, A. J. Bendelsmith, S.-L. Zheng, T. A. Betley, *Angew. Chem. Int. Ed.* **2017**, *56* (40), 12197–12201; *Angew. Chem.* **2017**, *129*, 12365–12369; d) D. A. Iovan, A. T. Wrobel, A. A. McClelland, A. B. Scharf, G. A. Edouard, T. A. Betley, *Chem. Commun.* **2017**, *53*, 10306–10309; e) C. G. Gianopoulos, N. Kumar, Y. Zhao, L. Jia, K. Kirschbaum, M. R. Mason, *Dalton Trans.* **2016**, *45* (35), 13787–13797; f) C. G. Gianopoulos, K. Kirschbaum, M. R. Mason, *Organometallics* **2014**, *33* (17), 4503–4511; g) A. Bessette, G. S. Hanan, *Chem. Soc. Rev.* **2014**, *43* (10), 3342–3405; h) E. T. Hennessy, T. A. Betley, *Science* **2013**, *340* (6132), 591–595; i) E. R. King, T. A. Betley, *Inorg. Chem.* **2009**, *48*(6), 2361–2363.

[5] a) A. Van Belois, R. R. Maar, M. S. Workentin, J. B. Gilroy, *Inorg. Chem.* **2019**, *58* (1), 834–843; b) R. Mondol, E. Otten, *Dalton Trans.* **2019**, *48* (37), 13981–13988; c) R. R. Maar, S. D. Catingan, V. N. Staroverov, J. B. Gilroy, *Angew. Chem. Int. Ed.* **2018**, *57*(31), 9870–9874; *Angew. Chem.* **2018**, *130*, 10018–10022; d) M.-C. Chang, P. Roewen, R. T. -Puente, M. Lutz, E. Otten, *Inorg. Chem.* **2015**, *54* (1), 379–388.

[6] a) A. O. Tolpygin, L. Luconi, A. S. Shavyrin, G. Tuci, A. V. Cherkasov, A. Rossin, G. K. Fukin, G. Giambastiani, A. A. Trifonov, *Eur. J. Inorg. Chem.* **2017**, (20), 2736–2744; b) A. Causero, G. Ballmann, J. Pahl, H. Zijlstra, C. Färber, S. Harder, *Organometallics* **2016**, *35* (19), 3350–3360; c) L. Álvarez-Rodríguez, J. A. Cabeza, J. M. Fernández-Colinas, P. García-Álvarez, D. Polo, *Organometallics* **2016**, *35* (15), 2516–2523; d) F. T. Edelmann, *Adv. Organomet. Chem.* (Eds. F. H. Anthony, J. F. Mark), Academic Press: **2013**; Vol. 61, pp 55–374; e) F. T. Edelmann, *Chem. Soc. Rev.* **2012**, *41* (23), 7657–7672; f) J. Obenauf, W. P. Kretschmer, T. Bauer, R. Kempe, *Eur. J. Inorg. Chem.* **2013**, (4), 537–544; g) M. L. Cole, C. Jones, P. C. Junk, M. Kloth, A. Stasch, *Chem. Eur. J.* **2005**, *11*, 4482–4491; h) P. W. Roesky, *Z. Anorg. Allg. Chem.* **2003**, *629*, (11), 1881–1894; i) A. Littke, N. Sleiman, C. Bensimon, D. S. Richeson, G. P. A. Yap, S. J. Brown, *Organometallics* **1998**, *17* (3), 446–451.

[7] a) T. Chlupaty, A. Ruzicka, *Coord. Chem. Rev.* **2016**, *314*, 103–113; b) S. T. Barry, *Coord. Chem. Rev.* **2013**, *257* (23–24), 3192–3201; c) F. T. Edelmann, *Chem. Soc. Rev.* **2009**, *38* (8), 2253–2268; d) F. T. Edelmann, *J. Organomet. Chem.* **2008**, 57, 183–352; e) M. P. Coles, *Dalton Trans.* **2006**, (8), 985–1001; f) T.-G. Ong, G. P. A. Yap, D. S. Richeson, *Organometallics* **2002**, *21* (14), 2839–2841; g) P. J. Bailey, S. Pace, *Coord. Chem. Rev.* **2001**, *214*, 91–141; h) S. Foley, G. Yap, D. Richeson, *Chem. Commun.* **2000**,

1515–1516; i) N. Thirupathi, G. P. A. Yap, D. S. Richeson, *Organometallics* **2000**, *19* (13), 2573–2579.

[8] a) V. K. Jakhar, M. K. Barman, S. Nembenna, *Org. Lett.* **2016**, *18* (18), 4710–4713; b) H. Hu, D. Chen, H. Gao, L. Zhong, Q. Wu, *Polym. Chem.* **2016**, *7* (3), 529–537; c) G. Cao, H.-Q. Yang, B.-T. Luo, F.-S. Liu, *J. Organomet. Chem.* **2013**, *745–746*, 158–165; d) H. Gao, H. Hu, F. Zhu, Q. Wu, *Chem. Commun.* **2012**, *48* (27), 3312–3314.

[9] a) C. Jones, A. Stasch, *Top. Organomet. Chem.* **2013**, *45*, 73–101; b) Y.-C. Tsai, *Coord. Chem. Rev.* **2012**, *256* (5-8), 722–758; c) S. K. Mandal, H. W. Roesky, *Acc. Chem. Res.* **2012**, *45* (2), 298–307; d) C. Jones, A. Stasch, *In The chemistry of the group 13 metals in the +1 oxidation state*, (Eds. S. Aldridge, A. J. Downs), John Wiley & Sons Ltd.: **2011**; pp 285–341; e) M. Asay, C. Jones, M. Driess, *Chem. Rev.* **2011**, *111* (2), 354–396; f) A. Stasch, C. Jones, *Dalton Trans.* **2011**, *40* (21), 5659–5672; g) C. Jones, *Coord. Chem. Rev.* **2010**, *254*, 1273–1289; h) S. Nagendran, H. W. Roesky, *Organometallics* **2008**, *27* (4), 457–492; i) M. S. Hill, P. B. Hitchcock, *Chem. Commun.* **2004**, (16), 1818–1819

[10] a) A. Baishya, L. Kumar, M. K. Barman, H. S. Biswal, S. Nembenna, *Inorg. Chem.* **2017**, *56* (16), 9535–9546; b) A. Baishya, L. Kumar, M. K. Barman, T. Peddarao, S. Nembenna, *ChemistrySelect* **2016**, *1* (3), 498–503; c) A. Baishya, T. Peddarao, M. K. Barman, S. Nembenna, *New J. Chem.* **2015**, *39* (9), 7503–7510; d) M. K. Barman, A. Baishya, S. Nembenna, *J. Organomet. Chem.* **2015**, *785*, 52–60; e) T. Peddarao, A. Baishya, S. K. Hota, S. Nembenna, *J. Chem. Sci.* **2018**, *130*, 1–7.

[11] M. K. Barman, A. Baishya, T. Peddarao, S. Nembenna, *J. Organomet. Chem.* **2014**, *772–773*, 265–270.

[12] a) T. Peddarao, A. Baishya, M. K. Barman, A. Kumar, S. Nembenna, *New J. Chem.* **2016**, *40* (9), 7627–7636; For the application of CDIs in heterocycles, see: b) Y. Wang, W.-X. Zhang, Z. Xi, *Chem. Soc. Rev.* **2020**, *49*, (16), 5810–5849; c) L. Wang, Y. Chi, W. Zhang, Z. Xi, *Chin. J. Org. Chem.* **2018**, *38*, (6), 1341–1349.

[13] R. T. Boere, V. Klassen, G. Wolmershauser, *J. Chem. Soc. Dalton Trans.* **1998**, (24), 4147–4154.

[14] T. Ishikawa, T. Kumamoto, *Synthesis* **2006**, (5), 737–752.

[15] a) K. Vazdar, R. Kunetskiy, J. Saame, K. Kaupmees, I. Leito, U. Jahn, *Angew. Chem. Int. Ed.* **2014**, *53* (5), 1435–1438; *Angew. Chem.* **2014**, *129*, 1459–1462; b) B. Kovacevic, Z. B. Maksic, *Org. Lett.* **2001**, *3* (10), 1523–1526; c) V. Raab, J. Kipke, R. M. Gschwind, J. Sundermeyer, *Chem. Eur. J.* **2002**, *8* (7), 1682–1693; d) E. D. Raczynska, J.-F. Gal, P.-C. Maria, *Chem. Rev.* **2016**, *116* (22), 13454–13511.

[16] P. Selig, A. Turockin, W. Raven, *Synlett* **2013**, *24* (19), 2535–2539.

[17] a) M. F. C. Santos, P. M. Harper, D. E. Williams, J. T. Mesquita, E. G. Pinto, T. A. da Costa-Silva, E. Hajdu, A. G. Ferreira, R. A. Santos, P. J. Murphy, R. J. Andersen, A. G. Tempone, R. G. S. Berlinck, *J. Nat. Prod.* **2015**, *78* (5), 1101–1112; b) R. G. S. Berlinck, A. E. Trindade-Silva, M. F. C. Santos, *Nat. Prod. Rep.* **2012**, *29* (12), 1382–1406; c) R. G. S. Berlinck, A. C. B. Burtoloso, M. H. Kossuga, *Nat. Prod. Rep.* **2008**, *25* (5), 919–954; d) R. G. S. Berlinck, *Nat. Prod. Rep.* **2002**,*19* (5), 617–649; e) R. G. Berlinck, *Nat. Prod. Rep.* **1996**,*13* (5), 377–409; f) G. J. Durant, *Chem. Soc. Rev.* **1985**,*14* (4), 375–398.

[18] a) J. Francos, V. Cadierno, *Dalton Trans.* **2019**, *48* (25), 9021–9036; b) R. Kumar, N. Thirupathi, *RSC Adv.* **2017**,*7* (54), 33890–33904; c) F. Kong, M. Li, X. Zhou, L. Zhang, *RSC Adv.* **2017**, *7* (47), 29752–29761; d) R. Green, A. Walker, M. Blake, P. Mountford, *Polyhedron* **2016**, *116*, 64–75; e) J. A. Baus, F. M. Mueck, R. Bertermann, R. Tacke, *Eur. J. Inorg. Chem.* **2016**, (30), 4867–4871; f) J. Francos, P. J. González-Liste, L. Menéndez-Rodríguez, P. Crochet, V. Cadierno, J. Borge, A. Antiñolo, R. Fernández-Galán, F. Carrillo-Hermosilla, *Eur. J. Inorg. Chem.* **2016**, (3), 393–402; g) A. K. Maity, A. J. Metta-Magaña, S. Fortier, *Inorg. Chem.* **2015**, *54* (20), 10030–10041; h) A. K. Maity, S. Fortier, L. Griego, A. J. Metta-Magaña, *Inorg. Chem.* **2014**, *53* (15), 8155–8164; i) C. Jones, C. Schulten, S. Nembenna, A. Stasch, *J. Chem. Crystallogr.* **2012**,*42* (8), 866–870; j) R. Fernandez-Galan, A. Antinolo, F. Carrillo-Hermosilla, I. Lopez-Solera, A. Otero, A. Serrano-Laguna, E. Villasenor, *J. Organomet. Chem.* **2012**, *711*, 35–42; k) C. Jones, L. Furness, S. Nembenna, R. P. Rose, S. Aldridge, A. Stasch, *Dalton Trans.* **2010**, *39* (37), 8788–8795; l) D. Heitmann, C. Jones, D. P. Mills, A. Stasch, *Dalton Trans.* **2010**, *39* (7), 1877–1882; m) F. T. Edelmann, *Adv. Organomet. Chem.*, (Eds. A. Hill, M. J. Fink), Academic Press: **2008**; Vol. 57, pp 183–352; n) P. J. Bailey, S. Pace, *Coord. Chem. Rev.* **2001**, *214*, 91–141; o) Y. Zhou, G. P. A. Yap, D. S. Richeson, *Organometallics* **1998**, *17* (20), 4387–4391.

[19] a) X.-Y. Cui, C.-H. Tan, D. Leow, *Org. Biomol. Chem.* **2019**, *17* (19), 4689–4699; b) M. K. Barman, A. Baishya, S. Nembenna, *J. Organomet. Chem.* **2019**, *887*, 40–47; c) J. Li, J. Shi, H. Han, Z. Guo, H. Tong, X. Wei, D. Liu, M. F. Lappert, *Organometallics* **2013**, *32* (13), 3721–3727; d) F. T. Edelmann, *Chem. Soc. Rev.* **2009**, *38* (8), 2253–2268; e) H. Shen, Z. Xie, *Organometallics* **2008**, *27*, 2685–2687; f) S. Ge, A. Meetsma, B. Hessen, *Organometallics* **2008**, *27* (13), 3131–3135; g) Y. Luo, Y. Yao, H. Shen, *Macromolecules* **2002**, *35*, 8670–8671.

[20] a) W.-X. Zhang, L. Xu, Z. Xi, *Chem. Commun.* **2015**, *51* (2), 254–265; b) L. Xu, W.-X. Zhang, Z. Xi, *Organometallics* **2015**, *34* (10), 1787–1801; c) C. Alonso-Moreno, A. Antiñolo, F. Carrillo-Hermosilla, A. Otero, *Chem. Soc. Rev.* **2014**, *43* (10), 3406–3425; d) W.-X. Zhang, Z. Hou, *Org. Biomol. Chem.* **2008**, *6* (10), 1720–1730.

[21] A. R. Katritzky, B. V. Rogovoy, *Arkivoc* **2005**, (4), 49–87.

[22] E. D. Raczyńska, M. Decouzon, J.-F. Gal, P.-C. Maria, G. Gelbard, F. J. Vielfaure-Joly, *Phys. Org. Chem.* **2001**, *14* (1), 25–34.

[23] B. Rathke, *Ber. Dtsch. Chem. Ges.* **1879**, *12*, 776–784.

[24] a) D. Kathuria, A. A. Bankar, P. V. Bharatam, *J. Mol. Struct.* **2018**, *1152*,61-78; b) M. Angelo, D. Ortwine, D. Worth, L. M. Werbel, J. W. McCall, *J. Med. Chem.* **1983**, *26*, 1258–1267; c) C. J. Bailey, *Diabetic Med.* **1988**, *5*, 315–320; d) I. C. Bygbjerg, *Eur. J. Clin. Pharmacol.* **1985**, *28*, 287–290; e) P. Ray, *Chem. Rev.* **1961**, 61, 313–359.

[25] C. J. Bailey, *Diabetologia* **2017**, *60*, 1566–1576.

[26] Z. Glasovac, P. Troselj, I. Jusinski, D. Margetic, M. Eckert-Maksic, *Synlett* **2013**, *24*, 2540–2544.

[27] a) P. V. Gushchin, M. L. Kuznetsov, M. Haukka, M.-J. Wang, A. V. Gribanov, V. Y. Kukushkin, *Inorg. Chem.* **2009**, *48*, 2583–2592; b) A. G. Tskhovrebov, N. A. Bokach, M. Haukka, V. Y. Kukushkin, *Inorg. Chem.* **2009**, *48*, 8678–8688.

[28] M. Dehmel, V. Vass, L. Prock, H. Goerls, R. Kretschmer, *Inorg. Chem.* **2020**, *59*, 2733–2746.

[29] P. V. Gushchin, M. R. Tyan, N. A. Bokach, M. D. Revenco, M. Haukka, M. J. Wang, C. H. Lai, P. T. Chou, V. Y. Kukushkin, *Inorg. Chem.* **2008**, *47*, 11487–11500.

[30] a) D. S. Bolotin, N. A. Bokach, M. Y. Demakova, V. Y. Kukushkin, *Chem. Rev.* **2017**, *117*, 13039–13122; b) D. S. Bolotin, N. A. Bokach, V. Y. Kukushkin, *Coord. Chem. Rev.* **2016**, 313, 62–93.

[31] M. Ispikoudi, M. Amvrazis, C. Kontogiorgis, A. E. Koumbis, K. E. Litinas, D. Hadjipavlou-Litina, K. C. Fylaktakidou, *Eur. J. Med. Chem.* **2010**, *45*, 5635–5645.

[32] J. R. Khusnutdinova, D. Milstein, *Angew. Chem. Int. Ed.* **2015**, *54*, 12236–12273; *Angew. Chem.* **2015**, *127*, 12406–12445.

[33] M. L. H. Green, *J. Organomet. Chem.* **1995**, 500, 127–148.

[34] a) T. Peddarao, N. Sarkar, S. Nembenna, *Inorg. Chem.* **2020**, *59*, 4693–4702 Unpublished results

[35] G. Jin, C. Jones, P. C. Junk, K.-A. Lippert, R. P. Rose, A. Stasch, *New J. Chem.* **2009**,*33*, 64–75.

[36] a) G. Gilli, F. Bellucci, V. Ferretti, V. Bertolasi, *J. Am. Chem. Soc.* **1989**, *111*, 1023–1028; b) V. Bertolasi, P. Gilli, V. Ferretti, G. Gilli, *J. Am. Chem. Soc.* **1991**, *113*, 4917–4925; c) A. A. Grosch, S. C. C. van der Lubbe, C. F. Guerra, *J. Phys. Chem. A* **2018**, *122*, 1813–1820.

[37] a) E. D. Raczynska, J.-F. Gal, P.-C. Maria, F. Fontaine-Vive, *ACS Omega* **2018**, *3*, 17842–17852; b) E. D. Raczynska, J.-F. Gal, P.-C. Maria, P. Michalec, M. Zalewski, *J. Phys. Chem. A* **2017**, *121*, 8706–8718.

[38] D. T. Carey, E. K. Cope-Eatough, E. Vilaplana-Mafe, F. S. Mair, R. G. Pritchard, J. E. Warren, R. J. Woods, *Dalton Trans.* **2003**, 1083–1093.

[39] M. Stender, R. J. Wright, B. E. Eichler, J. Prust, M. M. Olmstead, H. W. Roesky, P. P. Power, *J. Chem. Soc. Dalton Trans.* **2001**, 3465–3469.

[40] a) R. J. Schwamm, C. M. Fitchett, M. P. Coles, *Chem. Asian J.* **2019**, *14*, 1204–1211; b) A. S. Mahadevi, G. N. Sastry, *Chem. Rev.* **2013**, *113*, 2100–2138; c) K. W. Hellmann, C. Galka, L. H. Gade, A. Steiner, D. S. Wright, T. Kottke, D. Stalke, *Chem. Commun.* **1998**, 549–550; d) B. Schiemenz, P. P. Power, *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 2150–2152; *Angew. Chem.* **1996**, *108*, 2288–2290; e) K. Ruhlandt-Senge, J. J. Ellison, R. J. Wehmschulte, F. Pauer, P. P. Power, *J. Am. Chem. Soc.* **1993**, *115*, 11353–11357; f) S. Kurz, E. Hey-Hawkins, *Organometallics* **1992**, *11*, 2729–2732.

[41] M. Mantina, A. C. Chamberlin, R. Valero, C. J. Cramer, D. G. Truhlar, *J. Phys. Chem. A* **2009**, *113*, 5806–5812.

[42] a) S. Harder, M. H. Prosene, *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 1744–1746; *Angew. Chem.* **1994**, *106*, 1830–1832; b) Y. Wang, Y. Xie, H. L. Threlkeld, P. Wei, H. F. Schaefer, G. H. Robinson, *Organometallics* **2019**, *38*, 4578–4584.

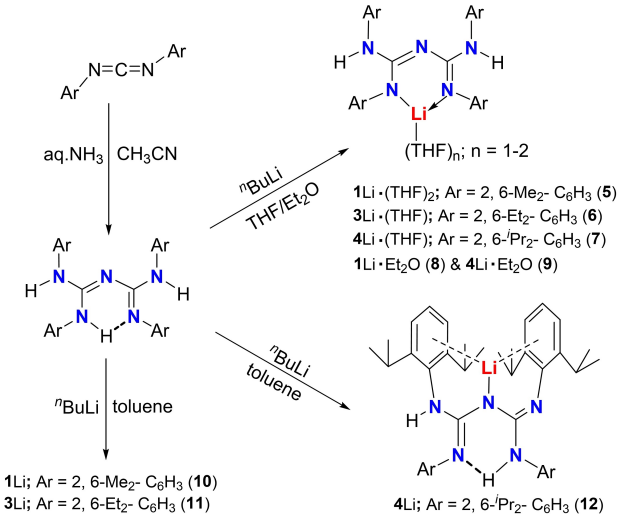
[43] a) J. Wessel, E. Lork, R. Mews, *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 2376–2378; *Angew. Chem.* **1995**, *107*, 2565–2567; b) P. Jutzi, N. Burford, *Chem. Rev.* **1999**, *99*, 969–990; c) R. Michel, R. Herbst-Irmer, D. Stalke, *Organometallics* **2011**, *30*, 4379–4386; d) A. V. Zabula, A. S. Filatov, S. N. Spisak, A. Y. Rogachev, M. A. Petrukhina, *Science* **2011**, *333*, 1008–1011.

These are not the final page numbers! ↗↗

[44] P. K. Sawinski, V. L. Deringer, R. Dronskowski, *Dalton Trans.* **2013**, *42*, 15080–15087.
[45] H. Chen, R. A. Bartlett, H. V. R. Dias, M. M. Olmstead, P. P. Power, *Inorg. Chem.* **1991**, *30*, 2487–2494.
[46] a) N. Sarkar, S. Bera, S. Nembenna, *J. Org. Chem.* **2020**, *85*, 4999–5009; b) R. K. Sahoo, M. Mahato, A. Jana, S. Nembenna, *J. Org. Chem.* **2020**, *85*, 11200–11210 c) R. K. Sahoo, N. Sarkar, S. Nembenna, *Angew. Chem. Int. Ed.* **2021**, *60*, 11991-12000; *Angew. Chem.* **2021**, *133*, 12098-12107.
[47] a) K. Kucinski, G. Hreczycho, *Green Chem.* **2019**, *21*, 1912–1915; b) J. H. Kim, A. K. Jaladi, H. T. Kim, D. K. An, *Bull. Korean Chem. Soc.* **2019**, *40*, 971–975; c) D. Mukherjee, H. Osseili, T. P. Spaniol, J. Okuda, *J. Am. Chem. Soc.* **2016**, *138*, 10790–10793; d) Z. Zhu, X. Wu, X. Xu, Z. Wu, M. Xue, Y. Yao, Q. Shen, X. Bao, *J. Org. Chem.* **2018**, *83*, 10677–10683; e) D. Willcox, J. L. Carden, A. J. Ruddy, P. D. Newman, R. L. Melen, *Dalton Trans.* **2020**, *49*, 2417–2420; f) A recent review on metal catalyzed hydroboration of carbonyls, see: K. Kucinski, G. Hreczycho, *Green Chem.* **2020**, *22*, 5210–5224.
[48] a) A. Harinath, J. Bhattacharjee, H. P. Nayek, T. K. Panda, *Dalton Trans.* **2018**, *47*, 12613–12622; b) M. K. Bisai, T. Das, K. Vanka, S. S. Sen, *Chem. Commun.* **2018**, *54*, 6843–6846; c) N. Kurono, M. Yamaguchi, K. Suzuki, T. Ohkuma, *J. Org. Chem.* **2005**, *70*, 6530–6532; d) S. Yadav, R. Dixit, K. Vanka, S. S. Sen, *Chem. Eur. J.* **2018**, *24*, 1269–1273; e) A recent review on metal catalyzed cyanosilylation of carbonyls, see: S. Pahar, G. Kundu, S. S. Sen, *ACS Omega* **2020**, *5*, 25477–25484.
[49] a) H. Stachowiak, J. Kazmierczak, K. Kucinski, G. Hreczycho, *Green Chem.* **2018**, *20*, 1738–1742; b) W. Wang, M. Luo, W. Yao, M. Ma, S. A. Pullarkat, L. Xu, P.-H. Leung, *New J. Chem.* **2019**, *43*, 10744–10749; c) W. Wang, M. Luo, W. Yao, M. Ma, S. A. Pullarkat, L. Xu, L. P.-H. Leung, *ACS Sustainable Chem. Eng.* **2019**, *7*, 1718–1722.
[50] D. Conole, T. M. Beck, M. Jay-Smith, M. D. Tingle, C. T. Eason, M. A. Brimble, D. Rennison, *Bioorg. Med. Chem.* **2014**, *22*, 2220–2235.
[51] a) G. R. Fulmer, A. J. M. Miller, N. H. Sherden, H. E. Gottlieb, A. Nudelman, B. M. Stoltz, J. E. Bercaw, K. I. Goldberg, *Organometallics* **2010**, *29*, 2176–2179; b) H. E. Gottlieb, V. Kotlyar, A. Nudelman, *J. Org. Chem.* **1997**, *62*, 7512–7515.

Manuscript received: February 16, 2021
Revised manuscript received: April 21, 2021
Accepted manuscript online: April 22, 2021

FULL PAPERS



We have developed a simple and effective procedure for preparing bulky conjugated bis-guanidines (CBG)s. Further, we have shown the coordination chemistry of ligands **1**, **3**, and **4** with the lithium element. Besides, we demonstrated that CBG Li salts act as efficient catalysts for hydroboration and cyanosilylation of carbonyl compounds. Both free-ligands and lithium salts are ideal precursors for the construction of metal complexes across the periodic table.

*Dr. T. Peddarao, Dr. A. Baishya, N. Sarkar, Dr. R. Acharya, Dr. S. Nembenna**