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Diverse Reactions of 1,4-Dilithio-1,3-dienes with Nitriles: Facile Access to Tricyclic Δ^1-Bipyrrolines, Multiply Substituted Pyridines, Siloles, and (*Z*,*Z*)-Dienylsilanes by Tuning of Substituents on the Butadienyl Skeleton

Nan Yu,[a] Congyang Wang,[a] Fei Zhao,[a] Lantao Liu,[b] Wen-Xiong Zhang,[a] and Zhenfeng Xi*[a, c]

Abstract: Addition cyclization of 1,2,3,4-tetrasubstituted 1,4-dilithio-1,3-dienes (Type I) with four equivalents of various aromatic nitriles in the presence of hexamethylphosphoramide (HMPA) gives exclusively fully substituted pyridines in moderate to good yields. Similarly, trisubstituted pyridines can be prepared by the reaction of 2,3-dialkyl- or diaryl-substituted 1,4-dilithio-1,3-dienes (Type II) with nitriles. However, five- or six-membered-ring fused 2,3-disubstituted 1,4-dilithio-1,3-dienes (Type III) reacted with various aromatic and aliphatic nitriles without α-hydrogen atoms to afford tricyclic Δ^1-bipyrrolines in high yields. The reaction of six-membered-ring fused 2,3-disubstituted 1,4-dilithio-1,3-diene (Type III) with 2-cyanopyridine afforded the corresponding pyridine, and no tricyclic Δ^1-bipyrroline was observed. Seven-membered-ring fused dilithiodienes reacted with PhCN or trimethylacetonitrile to afford the corresponding pyridines in good yield. When 1,2,3,4-tetrasubstituted dilithio reagents (Type I) were treated with Me_3SiCN, a tandem silylation/intramolecular substitution process readily occurred to yield siloles, whereas the reaction of 2,3-disubstituted dilithio reagents (Types II and III) with Me_3SiCN gave rise to (*Z*,*Z*)-dienylsilanes with high stereoselectivity. These results revealed that the formation of tricyclic Δ^1-bipyrrolines, pyridines, siloles, and (*Z*,*Z*)-dienylsilanes are strongly dependent on the substitution patterns of the dilithio butadienes and the nitrile employed.

Keywords: cyclization · nitrogen heterocycles · polycycles · silanes · synthetic methods

Introduction

Organolithium compounds have a prominent role as reactive organometallic reagents throughout organic and inorganic synthesis.[1] The addition reaction of organolithium compounds to nitriles to give *N*-lithio ketimines is among the fundamental processes of organometallic chemistry. Generally, the intermolecular trapping of *N*-lithio ketimines with organic halides or protons yields imines and ketones.[2] *N*-Lithio ketimines can also be trapped with carbon monoxide to afford N-containing cyclic compounds.[3] Correspondingly, the trapping of *N*-lithio ketimines with intramolecular organic halides provides a useful route to construct N-containing heterocycles such as pyridines.[4,5] However, trapping *N*-lithio ketimines with intramolecular C=C bonds has seldom been explored.[6,7]

The development of synthetically useful methods for the preparation of N-containing heterocycles such as substituted pyridines and Δ^1-pyrrolines has continuously been an attractive research topic in synthetic chemistry, because Δ^1-pyrro-

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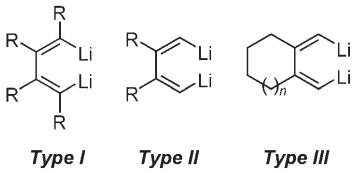
line derivatives in particular can serve as building blocks for many biologically relevant compounds[8] and as important synthetic intermediates in organic synthesis.[9] Among the many synthetic methods for various substituted pyridines and Δ^1-pyrrolines,[10,11] the addition of organolithium compounds to nitriles provides an alternatively efficient method. There is only one report on the synthesis of Δ^1-bipyrroline by the reaction of the 2,3-dimethylenebutadiene dianion with benzonitrile.[12] As far as we are aware, the synthesis of tricyclic Δ^1-bipyrrolines has not been reported.

We have recently found that addition cyclization of 1-lithio-1,3-dienes with aromatic nitriles affords multiply substituted pyridines, pyrroles, and linear butadienyl imines, depending on the substituents on the butadienyl skeleton.[7] Herein we report reactions of various substituted dilithio reagents such as 1,2,3,4-tetrasubstituted 1,4-dilithio-1,3-dienes, 2,3-disubstituted 1,4-dilithio-1,3-dienes, and cyclic 2,3-disubstituted 1,4-dilithio-1,3-dienes (Scheme 1, Types I–III) with



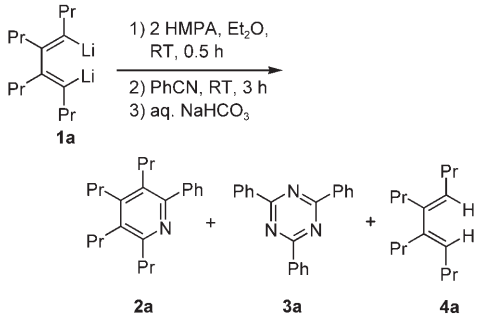
Scheme 1. Variously substituted 1,4-dilithio-1,3-dienes.

nitriles to yield a series of substituted tricyclic Δ^1-bipyrrolines, pyridines, siloles, and dienylsilanes that can not be readily obtained by other means. In these processes, the substitution patterns on the butadienyl skeleton play a vital role in determining the structure of the products. Furthermore, cleavage of the Si–C bond in the SiCN moiety was observed,[13] which is in contrast to the normal reaction pattern, in which nitriles are attacked at the C≡N bond by organolithium reagents. A portion of this work on the synthesis of pyridines was communicated previously.[7a]

Results and Discussion

Formation of pyridines: Unlike the reaction of 1-lithio-1,3-dienes with nitriles,[7a,b] an excess of nitrile is necessary to ensure high-yield formation of pyridines from 1,4-lithio-1,3-dienes because of self-cyclotrimerization of nitriles leading to the formation of triazines as by-products.[14] To optimize the reaction conditions, the reactions of 1,2,3,4-tetrapropyl-1,4-dilithio-1,3-diene (**1a**), generated in situ by lithiation of the corresponding 1,4-diiodo-1,3-diene,[15] with different amounts of benzonitrile (PhCN) in the presence of hexamethylphosphoramide (HMPA) were conducted (Table 1). When one equivalent of PhCN was employed, pyridine **2a** was isolated in only 16% yield along with triazine **3a** in 49% yield. Simultaneously, diene **4a** was recovered in 51% yield, derived from hydrolysis of **1a**. At least three equivalents of PhCN are required for complete consumption of **1a**.

Table 1. Reactions of 1,2,3,4-tetrapropyl-1,4-dilithio-1,3-diene with different amount of nitrile.



Nitrile [equiv]	Yield of **2a** [%][a]	Yield of **3a** [%][b]	Yield of **4a** [%][a]
1	16	49	51
2	35	55	30
3	50	57	0
4	62	60	0

[a] Yield of isolated product. [b] Yield of isolated product calculated based on nitrile.

However, **2a** was isolated in 62% yield of in the presence of four equivalents of PhCN.

Four equivalents of nitrile were then chosen as the standard amount for the present reaction. Representative results are summarized in Tables 2 and 3. As shown in Table 2, a wide range of aromatic nitriles react with 1,2,3,4-tetrasubstituted 1,4-dilithio-1,3-dienes (Type I) to afford fully substituted pyridines in moderate to good yields (Table 2). The aromatic C–Br bond could survive under the present conditions (Table 2, entry 4), although it is vulnerable to organolithium reagents. The reaction of PhCN with a tetrasubstituted dilithium compound having a fused six-membered ring gave exclusively tetrahydroisoquinoline **2j** in a high yield (Table 2, entry 9).

2,3-Dialkyl- and diaryl-substituted 1,4-dilithio-1,3-dienes **5** (Type II) can undergo smooth addition cyclization with aromatic nitriles to yield trisubstituted pyridines **6** (Table 3). Heteroatom-containing nitriles such as 2-cyanopyridine were also employed in this reaction to yield 2,2′-bipyridines (Table 2, entry 8 and Table 3, entries 4–6). The reaction of PhCN with dilithium reagent **5d** having a seven-membered ring in the 2,3-positions gave exclusively pyridine **6g** in 56% yield. The reaction of trimethylacetonitrile with dilithium **5d** gave exclusively pyridine **6h**, although aliphatic nitriles with α-hydrogen atoms were not suitable for this reaction, probably because of rapid protonolysis of the dilithium compounds by the α-hydrogen atoms. However, when the dilithium compounds **5a**,**e** were treated with trimethylacetonitrile, corresponding pyridines **6i**,**j** were isolated in 29 and 22% yield, respectively. After careful investigation into this reaction, unexpected Δ^1-bipyrrolines **7a**,**b** were characterized (Scheme 2). However, attempts to obtain the Δ^1-bipyrrolines as the only products by reaction of these dilithium compounds (Types I and II) with trimethylacetonitrile were unsuccessful.

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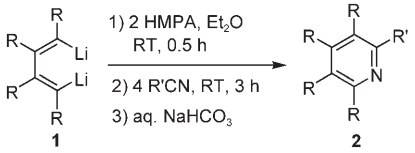
Table 2. Reaction of 1,2,3,4-tetrasubstitued 1,4-dilithio-1,3-dienes with aromatic nitriles.



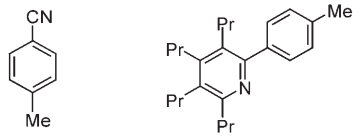
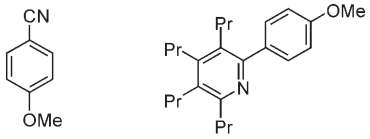
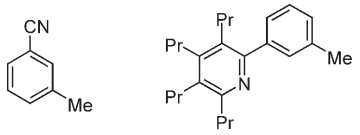
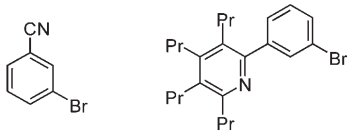
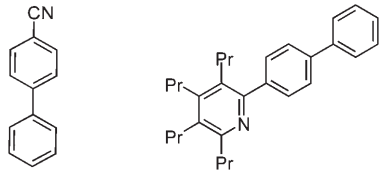
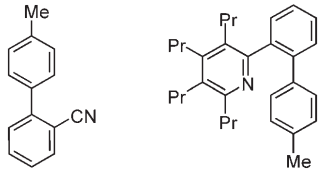
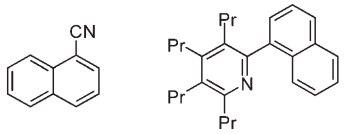
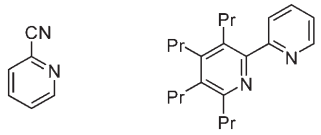
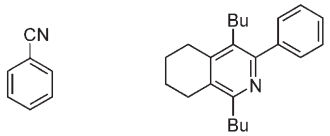
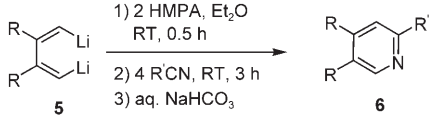
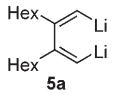
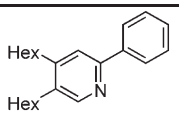
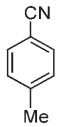
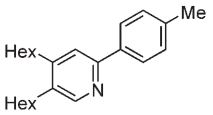
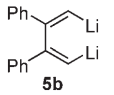
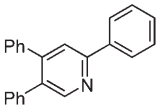
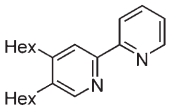
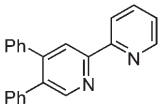
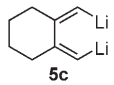
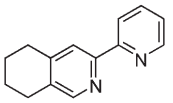
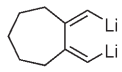
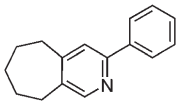
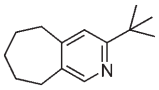
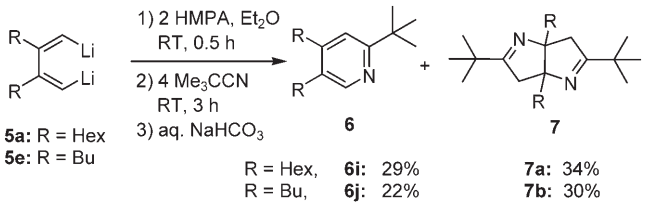
Entry	Nitrile	Pyridine **2**	Isolated product (yield [%])
1			**2b** (63)
2			**2c** (80)
3			**2d** (60)
4			**2e** (53)
5			**2f** (58)
6			**2g** (55)
7			**2h** (57)
8			**2i** (55)
9			**2j** (73)

Table 3. Reaction of 2,3-disubstituted 1,4-dilithio-1,3-dienes with aromatic nitriles.



Entry	Dilithium **5**	Nitrile	Pyridine **6**	Isolated product (yield [%])
1	 **5a**			**6a** (60)
2	**5a**			**6b** (59)
3	 **5b**			**6c** (57)
4	**5a**			**6d** (86)
5	**5b**			**6e** (60)
6	 **5c**			**6f** (58)
7	 **5d**			**6g** (56)
8	**5d**			**6h** (60)



Scheme 2. Reaction of 2,3-disubstituted 1,4-dilithio-1,3-dienes with trimethylacetonitrile.

To gain insights into the mechanism of pyridine formation, **1a** was allowed to react with 2-cyanopyrdine from −130 to 35 °C in Et_2O (Table 4). A mixture of pyridine **2i** and cyclopentadienyl amine **8a** was formed, even at temperature as low as −130 °C, along with **1a**. When the reaction of **1a** with 2-cyanopyrdine was carried out at −60 °C for 3 h in the presence of HMPA, **1a** was converted to **2i** and **8a**. Although the yield of **2i** increased with increasing reaction temperature, the amount of **8a** remained almost unchanged between −130 and 35 °C. On the basis of these observations, the reaction mechanisms shown in Scheme 3 are proposed.

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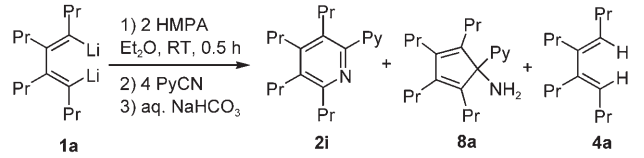
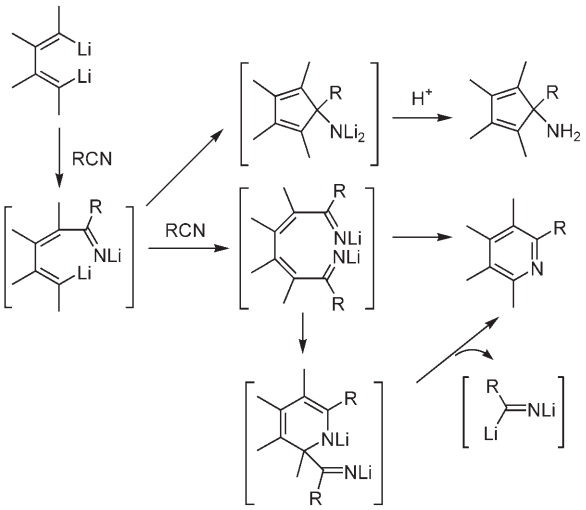
Table 4. Formation of pyridine **2i** and cyclopentadienyl amine **8a**.



T [°C]	t [h]	Yield of **2i** [%][a]	Yield of **8a** [%][a]	Yield of **4a** [%][a]
−130	1	39	19	25
−130	3	40	21	20
−78	1	50	23	14
−78	3	61	20	9
−60	1	67	16	5
−60	3	66	23	0
−30	1	70	17	0
0	1	71	20	0
20	1	73	18	0
35	1	72	21	0

[a] Determined by GC.



Scheme 3. Proposed mechanisms for the formation of pyridines.

Addition of one lithium alkenyl bond to the nitrile gives the *N*-lithio ketimine, which undergoes 5-*exo* cyclization to afford the cyclopentadienyl amine via hydrolysis of the dilithium cyclopentadienyl amide. The intermediate *N*-lithio ketimine reacts further with another equivalent of nitrile to give dilithio bis-ketimine. Then 6-*endo* cyclization followed by elimination of C,N-dilithioaldehyde imine yields a pyridine derivative.

Formation of tricyclic Δ^1-bipyrrolines: The reaction of Type II dilithium reagents with trimethylacetonitrile yielded a mixture of pyridines and unexpected Δ^1-bipyrrolines (Scheme 2). However, cyclic dilithio reagent **5c** (Type III) reacted with trimethylacetonitrile to afford exclusively tricyclic Δ^1-bipyrroline **9a** in 90% yield (Table 5, entry 1). Similarly, **9b**,**c** were easily prepared by reaction of **5c** with 2-ethyl-2-methylbutanenitrile and 1-adamantanecarbonitrile, respectively (Table 5, entries 2 and 3). Aliphatic nitriles with α-hydrogen atoms such as butyronitrile and acrylonitrile were not suitable for the present reaction, presumably due to rapid proton abstraction by the dilithium compounds.[12] The reaction of trimethylacetonitrile with dilithium compound **5f** having a five-membered ring in the 2,3-positions gave tricyclic Δ^1-bipyrroline **9d** in 64% yield (Table 5, entry 4). Besides aliphatic nitriles without α-hydrogen atoms, a wide range of aromatic nitriles was suitable for the formation of tricyclic Δ^1-bipyrrolines. The reaction was not affected by electron-withdrawing or -donating substituents or their positions on the phenyl ring of an aromatic nitrile (Table 5, entries 5–13). The aromatic C–Br bond could survive under the present reaction conditions. Traces of pyridine derivatives were observed in some cases by gas chromatographic monitoring when aromatic nitriles were used. The reactions in entries 1–4 of Table 5 involving aliphatic nitriles without α-hydrogen atoms gave similar yields of products with or without HMPA. In the other cases listed in Table 5, good to high yields of products could be obtained in the presence of HMPA, but without HMPA messy mixtures of products were obtained. In contrast to the synthesis of pyridines (Tables 2 and 3), 2.4 rather than 4 equivalents of organonitrile were used, because self-cyclotrimerization of nitriles did not occur. No triazine derivatives were observed.

2-Cyanopyridine was not suitable for the formation of a tricyclic Δ^1-bipyrroline. Conversely, the reaction of 2-cyanopyridine with dilithio reagent **5c** gave exclusively pyridine **6f** (Table 3, entry 6). Although the reaction of five- and six-membered-ring fused dilithio reagents with nitriles gave tricyclic Δ^1-bipyrrolines (Table 5), seven-membered-ring fused dilithium compound **5d** reacted with PhCN or trimethylacetonitrile to afford the corresponding pyridines in good yield (Table 3, entries 7 and 8). All results for the formation of tricyclic Δ^1-bipyrrolines show that both the substituents in the 1,4-positions and the size of the fused ring in 1,4-dilithio-1,3-diene play an important role in determining the structure of the products.

Development of synthetically useful methods for N-containing heterocycles, especially those with new central skeletons, has continuously been an attractive research topic in synthetic chemistry, since they have diverse applications in many areas. This work provides a very convenient and high-yield method for the synthesis of unprecedented tricyclic Δ^1-pyrroline derivatives. Interesting applications of this new type of Δ^1-pyrroline derivatives can be expected.

An X-ray analysis of **9e** revealed that two Δ^1-pyrroline rings and one cyclohexyl ring share one C–C single bond (Figure 1).

A proposed mechanism for the formation of tricyclic Δ^1-bipyrrolines is shown in Scheme 4. Intermolecular nucleophilic addition of **5c** to nitriles initially affords dilithio bis-ketimines **10**. The subsequent double 5-*exo* lithiation/cyclization of **10** proceeds in an intramolecular manner to give tricyclic Δ^1-bipyrroline **9** via protonolysis of 1-azaallylic dianion **11**.[16] Deuterated tricyclic Δ^1-bipyrroline **9aD** was isolated in 85% yield with slightly less than two deuterium

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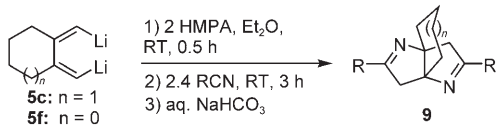
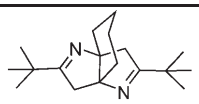
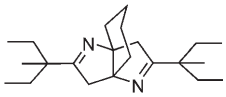
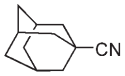
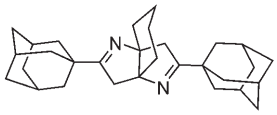
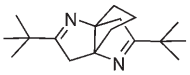
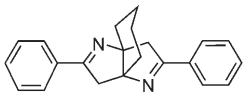
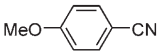
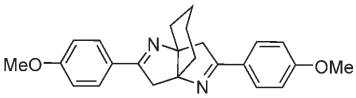
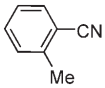
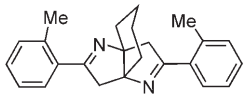
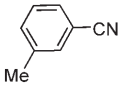
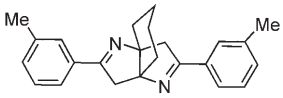
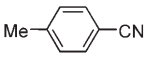
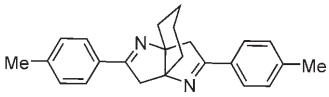
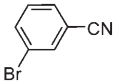
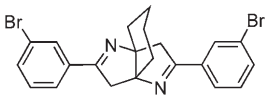
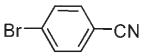
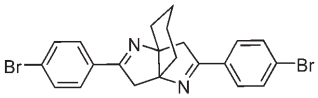
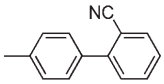
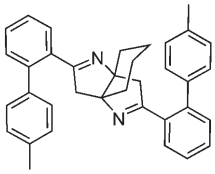
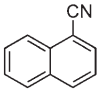
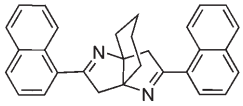
Table 5. Reaction of 2,3-disubstituted cyclic 1,4-dilithio-1,3-dienes with nitriles.



Entry	Nitrile	Pyrroline **9**	Isolated product (yield [%])
1			**9a** (90)[a]
2			**9b** (81)[a]
3			**9c** (95)[a]
4			**9d** (64)[a]
5			**9e** (54)
6			**9f** (53)
7			**9g** (57)
8			**9h** (52)
9			**9i** (60)
10			**9j** (70)
11			**9k** (55)
12			**9l** (56)
13			**9m** (55)

[a] Without HMPA.

atoms in the methylene positions (*endo*:*exo* = 2: 3) when the *t*Bu-substituted 1-azaallylic dianion was quenched with DCl/D_2O (20 wt%). Attempts to isolate intermediate **10** or dianion **11** failed.

Formation of siloles and (*Z*,*Z*)-dienylsilanes: The reaction of 1,2,3,4-tetrapropyl-1,4-dilithio-1,3-diene **1a** (Type I) with Me_3SiCN yielded silole **12a** instead of the pyridine via cleavage of the Si–C bond of Me_3SiCN. Similarly, the reaction of cyclic tetrasubstituted dilithio reagent **1b** with Me_3SiCN afforded silole **12b**. We recently reported that lithiation of 1-bromo-4-trisubstituted silyl-1,3-butadiene derivatives with *t*BuLi gave substituted siloles in high yields.[17] We also described the facile synthesis of lithio siloles from silyl 1,4-dilithio-1,3-butadiene derivatives.[18] By using Me_3SiCN, both silylation and intramolecular nucleophilic substitution can be achieved in a one-pot procedure to prepare siloles (Scheme 5). This reaction is an alternative convenient method for the preparation of multiply substituted siloles from 1,4-dilithio-1,3-dienes.

When 2,3-disubstituted 1,4-dilithio-1,3-dienes **5** were treated with Me_3SiCN, an interesting double silylation reaction took place to afford (*Z*,*Z*)-dienylsilanes **13** with perfect stereoselectivity (Scheme 6).[15g] To the best of our knowledge, synthesis of (*Z*,*Z*)-dienylsilanes has remained unexplored, although (*E*,*E*)-dienylsilanes were prepared previously by cyclization of silyl-capped terminal diynes mediated by low-valent organometallic compounds of Group 4 metals.[15,19]

Conclusion

In summary, we have demonstrated diverse reactions of 1,4-dilithio-1,3-dienes with nitriles. Pyridines, tricyclic Δ^1-bipyrrolines, siloles, and (*Z*,*Z*)-dienylsilanes can be readily pre-

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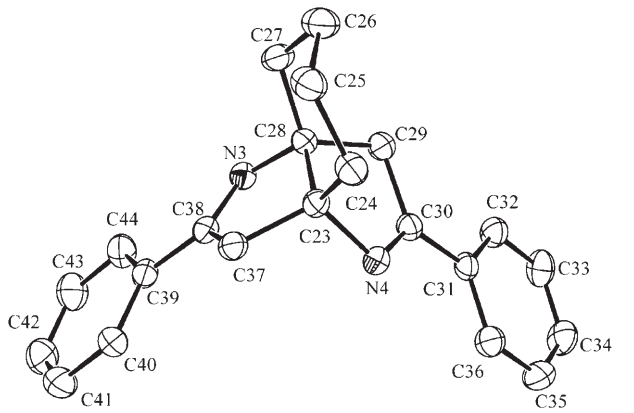
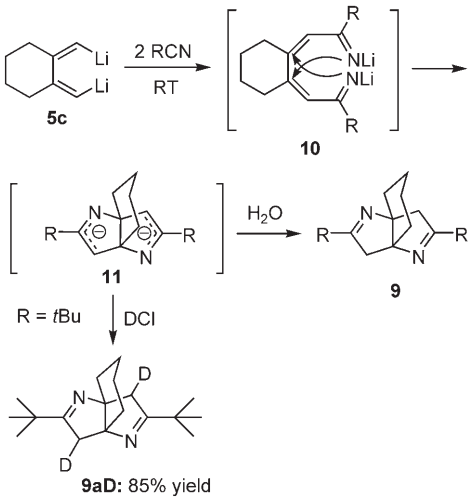
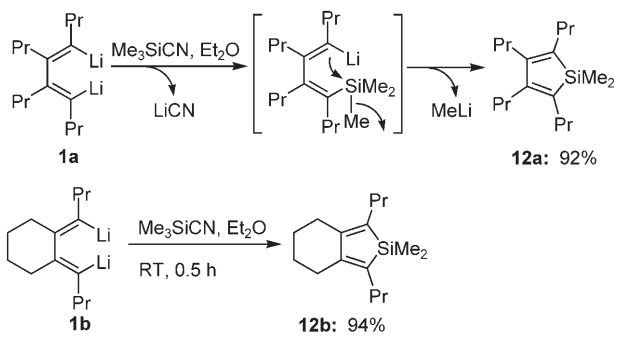


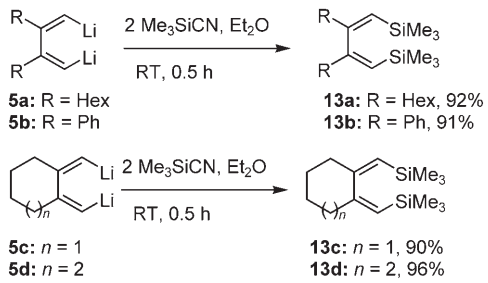
Figure 1. ORTEP drawing of one enantiomer of **9e** with 30% thermal ellipsoids. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: N3–C38 1.293(3), C37–C38 1.516(3), C23–C37 1.524(3), C23–C28 1.545(3), N3–C28 1.496(3), N4–C30 1.285(2), C29–C30 1.509(3), C28–C29 1.535(3), C23–C28 1.545(3), N4–C23 1.492(3); C28-N3-C38 108.55(19), N3-C38-C37 114.9(2), C23-N4-C30 109.14(18), N4-C30-C29 114.6(2).



Scheme 4. Proposed mechanism for the formation of the tricyclic Δ^1-bipyrrolines.



Scheme 5. Reaction of 1,2,3,4-tetrasubstituted 1,4-dilithio-1,3-dienes with Me_3SiCN.



Scheme 6. Reaction of 2,3-disubstituted 1,4-dilithio-1,3-dienes with Me_3SiCN.

pared in good yields by using appropriate combination of dilithio reagents and nitriles. 1,2,3,4-Tetrasubstituted (Type I) and 2,3-disubstituted dilithio reagents (Type II) react with aromatic nitriles to provide pyridines in good yields. When ring-fused dilithio reagents (Type III) reacted with aromatic nitriles or aliphatic nitriles without α-hydrogen atoms, tricyclic Δ^1-bipyrrolines were predominately formed. When tetrasubstituted dilithio reagents (Type I) were treated with Me_3SiCN, a tandem silylation/intramolecular substitution process readily occurred to yield siloles, while the reaction of 2,3-disubstituted dilithio reagents (Types II and III) with Me_3SiCN gave (*Z*,*Z*)-dienylsilanes with high stereoselectivity. These results reveal that the outcome of the reaction is strongly dependent on the structure of the dilithio reagents and the nature of the nitriles. Further investigations into applications of the novel tricyclic Δ^1-bipyrrolines are underway.

Experimental Section

General: All reactions were conducted under a slightly positive pressure of dry, prepurified nitrogen by using standard Schlenk line techniques where appropriate. Unless otherwise noted, all starting materials were commercially available and were used without further purification. Diethyl ether was refluxed and distilled from sodium benzophenone ketyl under a nitrogen atmosphere. All organolithium reagents were obtained from Acros Organics. All the butadienyl iodides were synthesized by the reported procedure. All yields refer to isolated products.[15]

^1H and ^{13}C NMR spectra were recorded at 300 and 75.4 MHz, respectively, in $CDCl_3$ solution containing 0.1% TMS on a JEOL JNM-AL300 NMR spectrometer.

CCDC-240170 (**9e**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Typical procedure for the preparation of pyridines 2 from 1,2,3,4-tetrasubstituted 1,4-diiodo-1,3-dienes: *t*BuLi (4.0 mmol, 1.5 M in pentane) was added to a solution of 1,2,3,4-tetrasubstituted 1,4-diiodo-1,3-diene (1.0 mmol) in diethyl ether (5 mL) at −78 °C. The reaction mixture was then stirred at −78 °C for 1 h to generate 1,4-dilithio-1,3-diene **1**, which was monitored by GC analysis or by TLC. HMPA (2.0 mmol) was then added, and the reaction mixture was stirred at room temperature for 0.5 h. After addition of nitrile (4.0 mmol), the mixture was stirred at room temperature for 3 h. The reaction mixture was then quenched with saturated aqueous $NaHCO_3$ and extracted with diethyl ether. The extract was washed with brine and dried over $MgSO_4$. The solvent was evaporat-

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ed in vacuo to give a yellow oil, which was purified by column chromatography (neutral Al_2O_3, hexane/Et_2O = 4:1) to afford pyridines **2a–j**.

2a: Light yellow liquid, 62% yield (200 mg); ^{1}H NMR (300 MHz, $CDCl_3$, TMS, 25°C): δ = 0.78 (t, J = 7.2 Hz, 3H), 1.00 (t, J = 7.2 Hz, 3H), 1.03–1.20 (m, 6H), 1.31–1.42 (m, 2H), 1.48–1.64 (m, 4H), 1.68–1.81 (m, 2H), 2.47 (t, J = 8.1 Hz, 2H), 2.54–2.69 (m, 4H), 2.74 (t, J = 7.5 Hz, 2H), 7.23–7.60 ppm (m, 5H); ^{13}C NMR (75 MHz, $CDCl_3$, TMS, 25°C): δ = 14.4, 14.6, 14.9, 15.0, 23.7, 24.5, 24.6, 31.0, 31.4, 31.5, 37.5, 127.1, 128.0, 128.9, 131.2, 132.4, 142.4, 148.2, 156.5, 157.1 ppm; HRMS calcd for $C_{23}H_{33}N$: 323.2613, found: 323.2604.

2b: Light yellow liquid, 63% yield (212 mg); ^{1}H NMR (300 MHz, $CDCl_3$, TMS, 25°C): δ = 0.79 (t, J = 7.2 Hz, 3H), 0.99 (t, J = 7.2 Hz, 3H), 1.03–1.12 (m, 6H), 1.32–1.41 (m, 2H), 1.49–1.62 (m, 4H), 1.67–1.78 (m, 2H), 2.38 (s, 3H), 2.48 (t, J = 8.1 Hz, 2H), 2.53–2.66 (m, 4H), 2.73 (t, J = 8.1 Hz, 2H), 7.18 (d, J = 7.8 Hz, 2H), 7.18 ppm (d, J = 8.1 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$, TMS, 25°C): δ = 14.43, 14.57, 14.90, 15.02, 21.25, 23.65, 24.53, 24.58, 24.62, 30.98, 31.43, 31.48, 37.41, 128.62, 128.77, 131.24, 132.19, 136.66, 139.53, 148.18, 156.52, 157.08 ppm; HRMS calcd for $C_{24}H_{35}N$: 337.2770, found: 337.2755.

2c: Light yellow liquid, 80% yield (282 mg); ^{1}H NMR (300 MHz, $CDCl_3$, TMS, 25°C): δ = 0.79 (t, J = 7.2 Hz, 3H), 0.98 (t, J = 7.2 Hz, 3H), 1.03–1.13 (m, 6H), 1.32–1.44 (m, 2H), 1.49–1.62 (m, 4H), 1.67–1.80 (m, 2H), 2.44–2.54 (m, 2H), 2.55–2.68 (m, 4H), 2.69–2.79 (m, 2H), 3.82 (s, 3H), 6.92 (d, J = 8.4 Hz, 2H), 7.32 ppm (d, J = 8.4 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$, TMS, 25°C): δ = 14.4, 14.6, 14.9, 15.0, 23.6, 24.5, 24.6, 31.0, 31.47, 31.51, 31.6, 37.5, 55.3, 113.4, 130.1, 131.3, 132.1, 135.2, 148.2, 156.2, 157.1, 158.8 ppm; HRMS calcd for $C_{24}H_{35}NO$: 353.2719, found: 353.2729.

2d: Light yellow liquid, 60% yield (202 mg); ^{1}H NMR (300 MHz, $CDCl_3$, TMS, 25°C): δ = 0.79 (t, J = 7.2 Hz, 3H), 0.97–1.10 (m, 9H), 1.34–1.40 (m, 2H), 1.51–1.61 (m, 4H), 1.69–1.77 (m, 2H), 2.37 (s, 3H), 2.44–2.49 (m, 2H), 2.57–2.63 (m, 4H), 2.72–2.77 (m, 2H), 7.12–7.26 ppm (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$, TMS, 25°C): δ = 14.4, 14.6, 14.91, 15.0, 21.5, 23.8, 24.5, 24.60, 24.63, 31.0, 31.4, 31.5, 37.5, 125.8, 127.8, 127.9, 129.7, 131.2, 132.2, 137.4, 142.3, 148.2, 156.7, 157.1 ppm; HRMS calcd for $C_{24}H_{35}N$: 337.2770, found: 337.2782.

2e: Light yellow liquid, 53% yield (213 mg); ^{1}H NMR (300 MHz, $CDCl_3$, TMS, 25°C): δ = 0.81 (t, J = 7.2 Hz, 3H), 0.98–1.10 (m, 9H), 1.35–1.38 (m, 2H), 1.50–1.60 (m, 4H), 1.71–1.73 (m, 2H), 2.43–2.48 (m, 2H), 2.57–2.62 (m, 4H), 2.71–2.76 (m, 2H), 7.26–7.55 ppm (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$, TMS, 25°C): δ = 14.4, 14.5, 14.9, 15.0, 23.7, 24.51, 24.53, 24.6, 31.0, 31.3, 31.4, 37.4, 122.2, 127.6, 129.5, 130.3, 131.2, 132.1, 132.9, 144.4, 148.5, 154.9, 157.4 ppm; HRMS calcd for $C_{23}H_{32}N^{79}Br$: 401.1718, found: 401.1723.

2f: Light yellow liquid, 58% yield (231 mg); ^{1}H NMR (300 MHz, $CDCl_3$, TMS, 25°C): δ = 0.82 (t, J = 7.2 Hz, 3H), 1.01–1.11 (m, 9H), 1.39–1.47 (m, 2H), 1.52–1.62 (m, 4H), 1.72–1.80 (m, 2H), 2.25–2.45 (m, 2H), 2.52–2.64-(m, 4H), 2.74–2.79 (m, 2H), 7.41–7.49 (m, 5H), 7.61–7.65 ppm (m, 3H); ^{13}C NMR (75 MHz, $CDCl_3$, TMS, 25°C): δ = 14.5, 14.6, 14.9, 15.0, 23.7, 24.5, 24.6, 24.7, 31.0, 31.44, 31.5, 37.5, 126.8, 127.1, 128.7, 129.3, 131.3, 132.4, 139.9, 141.2, 141.5, 148.3, 156.1, 157.3 ppm; HRMS calcd for $C_{29}H_{37}N$: 399.2926, found: 399.2939.

2g: Light yellow liquid, 55% yield (227 mg); ^{1}H NMR (300 MHz, $CDCl_3$, TMS, 25°C): δ = 0.65 (t, J = 7.2 Hz, 3H), 0.84 (t, J = 7.2 Hz, 3H), 0.94 (t, J = 7.2 Hz, 3H), 1.04 (t, J = 7.2 Hz, 3H), 1.11–1.19 (m, 4H), 1.50–1.54 (m, 2H), 1.64–1.67 (m, 2H), 1.99–2.04 (m, 2H), 2.22 (s, 3H), 2.39–2.42 (m, 2H), 2.46–2.56 (m, 2H), 2.75 (brs, 2H), 6.87–6.96 (m, 4H), 7.39 ppm (s, 4H); ^{13}C NMR (75 MHz, $CDCl_3$, TMS, 25°C): δ = 14.1, 14.4, 14.5, 14.7, 20.9, 23.9, 24.0, 24.1, 24.7, 30.8, 30.9, 31.2, 37.2, 127.0, 127.7, 128.1, 129.27, 129.31, 130.0, 131.9, 132.1, 135.7, 138.5, 140.7, 140.8, 147.8, 156.1, 156.7 ppm; HRMS calcd for $C_{30}H_{39}N$: 413.3083, found: 413.3093.

2h: Light yellow liquid, 57% yield (213 mg); ^{1}H NMR (300 MHz, $CDCl_3$, TMS, 25°C): δ = 0.60 (t, J = 7.2 Hz, 3H), 0.98 (t, J = 7.2 Hz, 3H), 1.06–1.14 (m, 6H), 1.20–1.27 (m, 2H), 1.56–1.75 (m, 6H), 2.06–2.16 (m, 1H), 2.35–2.45 (m, 1H), 2.61–2.69 (m, 4H), 2.74–2.79 (m, 2H), 7.32–7.50 (m, 5H), 7.82–7.86 ppm (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$, TMS, 25°C): δ = 14.4, 14.6, 14.9, 15.0, 24.0, 24.62, 24.63, 24.7, 31.1, 31.5, 31.8, 37.5, 125.2, 125.5, 125.8, 126.0, 126.5, 127.7, 128.1, 132.3, 132.5, 132.7, 133.8, 139.6, 148.3, 155.2, 157.4 ppm; HRMS calcd for $C_{27}H_{35}N$: 373.2770, found: 373.2768.

2i: Light yellow liquid, 55% yield (178 mg); ^{1}H NMR (300 MHz, $CDCl_3$, TMS, 25°C): δ = 0.78 (t, J = 7.2 Hz, 3H), 1.00 (t, J = 7.2 Hz, 3H), 1.04–1.12 (m, 6H), 1.35–1.41 (m, 2H), 1.47–1.63 (m, 4H), 1.69–1.79 (m, 2H), 2.57–2.80 (m, 8H), 7.20–7.28 (m, 1H), 7.54–7.61 (m, 1H), 7.71–7.79 (m, 1H), 8.59–8.65 ppm (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$, TMS, 25°C): δ = 14.4, 14.6, 14.9, 15.0, 23.5, 24.4, 24.5, 29.7, 30.6, 31.0, 31.3, 37.4, 122.1, 124.4, 132.0, 133.4, 136.4, 148.3, 148.7, 154.2, 157.1, 160.6 ppm; HRMS calcd for $C_{22}H_{32}N_2$: 324.2566, found: 324.2570.

2j: Light yellow liquid, 73% yield (234 mg); ^{1}H NMR (300 MHz, $CDCl_3$, TMS, 25°C): δ = 0.76 (t, J = 6.9 Hz, 3H), 0.93 (t, J = 7.2 Hz, 3H), 1.16–1.26 (m, 2H), 1.29–1.51 (m, 4H), 1.59–1.72 (m, 2H), 1.76–1.94 (m, 4H), 2.47 (t, J = 7.5 Hz, 2H), 2.62–2.97 (m, 6H), 7.21–7.49 ppm (m, 5H); ^{13}C NMR (75 MHz, $CDCl_3$, TMS, 25°C): δ = 13.6, 14.1, 22.6, 23.0, 23.1, 26.0, 26.6, 28.4, 31.4, 32.0, 35.1, 127.1, 128.0, 128.8, 129.0, 131.2, 142.2, 144.6, 155.5, 157.3 ppm; HRMS calcd for $C_{23}H_{31}N$: 321.2457, found: 321.2455.

Typical procedure for the preparation of pyridines 6a–h from 2,3-disubstituted 1,4-diiodo-1,3-dienes: *t*BuLi (4.0 mmol, 1.5 M in pentane) was added to a solution of 2,3-disubstituted 1,4-diiodo-1,3-diene (1.0 mmol) in diethyl ether (5 mL) at −78°C. The reaction mixture was then stirred at −78°C for 1 h to generate 1,4-dilithio-1,3-diene **5**, which was monitored by GC analysis or by TLC. HMPA (2.0 mmol) was then added, and the reaction mixture was stirred at room temperature for 0.5 h. After addition of nitrile (4.0 mmol), the mixture was stirred at room temperature for 3 h. The reaction mixture was then quenched with saturated aqueous $NaHCO_3$ and extracted with diethyl ether. The extract was washed with brine and dried over $MgSO_4$. The solvent was evaporated in vacuo to give a yellow oil, which was purified by column chromatography (neutral Al_2O_3, hexane/Et_2O = 4:1) to afford pyridines **6a–h**.

6a: Light yellow liquid, 60% yield (194 mg); ^{1}H NMR (300 MHz, $CDCl_3$, TMS, 25°C): δ = 0.88–0.92 (m, 6H), 1.32–1.67 (m, 16H), 2.60–2.62 (m, 4H), 7.24–7.49 (m, 4H), 7.94–7.98 (m, 2H), 8.42 ppm (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$, TMS, 25°C): δ = 14.1, 22.61, 22.64, 29.3, 29.4, 29.8, 30.4, 31.0, 31.7, 32.2, 120.7, 126.7, 128.4, 128.6, 134.6, 139.7, 150.0, 150.3, 155.0 ppm. The NMR data are consistent with the reported data.[7b]

6b: Light yellow liquid, 59% yield (199 mg); ^{1}H NMR (300 MHz, $CDCl_3$, TMS, 25°C): δ = 0.87–0.92 (m, 6H), 1.32–1.67 (m, 16H), 2.37 (s, 3H), 2.59–2.65 (m, 4H), 7.23–7.25 (m, 2H), 7.46 (s, 1H), 7.85–7.88 (m, 2H), 8.39 ppm (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$, TMS, 25°C): δ = 14.1, 21.2, 22.6, 22.6, 29.3, 29.4, 29.8, 30.4, 31.1, 31.7, 32.2, 120.3, 126.5, 129.3, 134.3, 136.9, 138.3, 149.9, 150.2, 155.0 ppm. The NMR data are consistent with the reported data.[7b]

6c: Light yellow liquid, 57% yield (175 mg); ^{1}H NMR (300 MHz, $CDCl_3$, TMS, 25°C): δ = 7.16–7.28 (m, 10H), 7.41–7.50 (m, 3H), 7.76 (s, 1H), 8.06 (d, J = 3.6 Hz, 2H), 8.72 ppm (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$, TMS, 25°C): δ = 121.5, 126.9, 127.2, 127.8, 128.2, 128.3, 128.8, 129.0, 129.3, 129.8, 134.2, 137.6, 139.0, 148.5, 150.9, 156.4 ppm; HRMS calcd for $C_{23}H_{17}N$: 307.1361, found: 307.1352.

6d: Light yellow liquid, 86% yield (279 mg); ^{1}H NMR (300 MHz, $CDCl_3$, TMS, 25°C): δ = 0.87–0.92 (m, 6H), 1.26–1.71 (m, 16H), 2.64–2.71 (m, 4H), 7.24–7.28 (m, 1H), 7.75–7.81 (m, 1H), 8.18 (brs, 1H), 8.35–8.41 (m, 2H), 8.65–8.68 ppm (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$, TMS, 25°C): δ = 14.1, 22.60, 22.62, 29.3, 29.5, 30.0, 30.5, 31.0, 31.7, 32.3, 120.8, 121.1, 123.3, 136.5, 136.8, 149.1, 150.0, 150.5, 153.7, 156.6 ppm. The NMR data are consistent with the reported data.[7b]

6e: Light yellow solid, 60% yield (185 mg); m.p. 123–124°C;; ^{1}H NMR (300 MHz, $CDCl_3$, TMS, 25°C): δ = 7.18–7.30 (m, 11H), 7.77–7.83 (m, 1H), 8.46–8.49 (m, 2H), 8.67–8.71 ppm (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$, TMS, 25°C): δ = 121.1, 122.1, 127.3, 127.8, 128.2, 128.3, 129.4, 129.8, 135.7, 136.9, 137.6, 138.8, 148.7, 149.2, 150.5, 155.1, 155.9 ppm; HRMS calcd for $C_{22}H_{16}N_2$: 308.1314, found: 308.1308.

6f: Orange liquid, 58% yield (122 mg); ^{1}H NMR (300 MHz, $CDCl_3$, TMS, 25°C): δ = 1.77–1.79 (m, 4H), 2.73–2.79 (m, 4H), 7.19–8.64 ppm (m, 6H); ^{13}C NMR (75 MHz, $CDCl_3$, TMS, 25°C): δ = 22.2, 22.4, 26.0,

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28.7, 120.6, 120.9, 123.0, 133.2, 136.6, 146.8, 148.8, 149.7, 152.7, 156.3 ppm; HRMS calcd for $C_{14}H_{14}N_2$: 210.1152, found: 210.1157.

6g: Orange liquid, 56% yield (125 mg); ^{1}H NMR (300 MHz, $CDCl_3$, TMS, 25°C): δ=1.63 (brs, 4H), 1.82–1.84 (m, 2H), 2.75–2.80 (m, 4H), 7.34–7.44 (m, 4H), 7.93–7.97 (m, 2H), 8.36 ppm (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$, TMS, 25°C): δ=27.6, 28.0, 32.6, 32.9, 36.5, 120.7, 126.7, 128.4, 128.6, 137.2, 139.6, 149.2, 152.7, 155.6 ppm; HRMS calcd for $C_{16}H_{17}N$: 223.1361, found: 223.1351.

6h: Orange solid, 60% yield (122 mg); m.p. 91–92°C; ^{1}H NMR (300 MHz, $CDCl_3$, TMS, 25°C): δ=1.35 (s, 9H), 1.61–1.65 (m, 4H), 1.81–1.86 (m, 2H), 2.72–2.76 (m, 4H), 7.04 (s, 1H), 8.24 ppm (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$, TMS, 25°C): δ=27.7, 28.1, 30.3, 32.7, 32.9, 36.7, 36.8, 119.2, 135.3, 148.1, 152.0, 167.2 ppm; HRMS calcd for $C_{14}H_{21}N$: 203.1674, found: 203.1670.

Typical procedure for the preparation of pyridines 6i,j and Δ^1-bipyrrolines 7a,b from 2,3-disubstituted 1,4-diiodo-1,3-dienes: *t*BuLi (4.0 mmol, 1.5 M in pentane) was added to a solution of 2,3-disubstituted 1,4-diiodo-1,3-diene (1.0 mmol) in diethyl ether (5 mL) at −78°C. The reaction mixture was then stirred at −78°C for 1 h to generate 1,4-dilithio-1,3-diene **5**, which was monitored by GC analysis or by TLC. HMPA (2.0 mmol) was then added, and the reaction mixture was stirred at room temperature for 0.5 h. After addition of nitrile (4.0 mmol), the mixture was stirred at room temperature for 3 h. The reaction mixture was then quenched with saturated aqueous $NaHCO_3$ and extracted with diethyl ether. The extract was washed with brine and dried over $MgSO_4$. The solvent was evaporated in vacuo to give a yellow oil, which was purified by column chromatography (neutral Al_2O_3, hexane/Et_2O=4:1) to afford pyridines **6i,j** and Δ^1-bipyrrolines **7a,b**.

6i: Light yellow liquid, 29% yield (88 mg); ^{1}H NMR (300 MHz, $CDCl_3$, TMS, 25°C): δ=0.88–0.92 (m, 6H), 1.29–1.43 (m, 9H, CH_3; 12H, CH_2), 1.51–1.62 (m, 4H), 2.54–2.60 (m, 4H), 7.07 (s, 1H), 8.28 ppm (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$, TMS, 25°C): δ=14.0, 14.1, 22.6, 29.3, 29.4, 29.7, 30.3, 30.5, 31.0, 31.6, 31.7, 32.3, 36.8, 119.1, 132.7, 149.1, 149.3, 166.5 ppm; HRMS calcd for $C_{21}H_{37}N$: 303.2926, found: 303.2932.

6j: Light yellow liquid, 22% yield (54 mg); ^{1}H NMR (300 MHz, $CDCl_3$, TMS, 25°C): δ=0.92–0.99 (m, 6H), 1.35 (s, 9H), 1.40–1.45 (m, 4H), 1.47–1.61 (m, 4H), 2.55–2.60 (m, 4H), 7.08 (s, 1H), 8.28 ppm (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$, TMS, 25°C): δ=13.9, 14.0, 22.7, 22.8, 29.3, 30.3, 32.0, 32.7, 33.2, 36.8, 119.1, 132.7, 149.1, 149.3, 166.5 ppm; HRMS calcd for $C_{17}H_{29}N$: 247.2300, found: 247.2302.

7a: Light yellow liquid, 34% yield (132 mg); ^{1}H NMR (300 MHz, $CDCl_3$, TMS, 25°C): δ=0.88 (t, J=7.5 Hz, 6H), 1.08 (s, 18H), 1.27–1.77 (m, 20H), 2.50 (d, J=17.1 Hz, 2H), 2.99 ppm (d, J=17.1 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$, TMS, 25°C): δ=14.1, 22.6, 25.1, 28.1, 30.1, 31.7, 35.2, 35.6, 45.9, 83.5, 181.1 ppm; HRMS calcd for $C_{26}H_{48}N_2$: 388.3818, found: 388.3826.

7b: Light yellow liquid, 30% yield (100 mg); ^{1}H NMR (300 MHz, $CDCl_3$, TMS, 25°C): δ=0.89 (t, J=7.8 Hz, 6H), 1.09 (s, 18H), 1.27–1.77 (m, 12H), 2.50 (d, J=17.1 Hz, 2H), 2.99 ppm (d, J=17.1 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$, TMS, 25°C): δ=14.0, 23.5, 27.4, 28.1, 34.9, 35.6, 45.9, 83.5, 181.2 ppm; HRMS calcd for $C_{22}H_{40}N_2$: 332.3192, found: 332.3198.

Typical procedure for preparation of tricyclic Δ^1-bipyrrolines 9 from cyclic 2,3-disubstituted 1,4-diiodo-1,3-dienes: *t*BuLi (4.0 mmol, 1.5 M in pentane) was added to a solution of cyclic 2,3-disubstituted 1,4-diiodo-1,3-diene (1.0 mmol) in diethyl ether (5 mL) at −78°C. The reaction mixture was then stirred at −78°C for 1 h to generate 1,4-dilithio-1,3-diene **5**, which was monitored by GC analysis or by TLC. HMPA (2.0 mmol) was then added, and the reaction mixture was stirred at room temperature for 0.5 h. After addition of nitrile (2.4 mmol), the mixture was stirred at room temperature for 2 h. The above reaction mixture was then quenched with saturated aqueous $NaHCO_3$ and extracted with diethyl ether. The extract was washed with brine and dried over $MgSO_4$. The solvent was evaporated in vacuo to give a yellow oil, which was purified by column chromatography (neutral Al_2O_3, hexane/Et_2O=4:1) to afford tricyclic Δ^1-bipyrrolines **9a–m**.

9a: White solid, 90% yield (247 mg); m.p. 92–93°C; ^{1}H NMR (300 MHz, $CDCl_3$, TMS, 25°C): δ=1.09 (brs, 18H, CH_3; 4H, CH_2), 1.61 (brs, 2H), 2.30 (d, J=6.0 Hz, 2H), 2.66 (d, J=17.1 Hz, 2H), 2.96 ppm (d, J=17.1 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$, TMS, 25°C): δ=20.9, 27.8, 32.6, 35.3, 43.0, 78.8, 181.0 ppm; HRMS calcd for $C_{18}H_{30}N_2$: 274.2409, found: 274.2402.

9aD: White solid, 85% yield (235 mg); m.p. 92–93°C; ^{1}H NMR (300 MHz, $CDCl_3$, TMS, 25°C): δ=1.09 (brs, 18H, CH_3; 4H, CH_2), 1.61–1.64 (m, 2H), 2.29 (d, J=6.0 Hz, 2H), 2.66 (brs, 0.8H, *endo*), 2.96 ppm (brs, 1.2H, *exo*); ^{13}C NMR (75 MHz, $CDCl_3$, TMS, 25°C): δ=21.0, 27.8, 32.6, 35.3, 42.66, 42.92, 43.18 (J_{CD}=19.5 Hz), 78.8, 181.1 ppm; HRMS calcd for $C_{18}H_{28}N_2D_2$: 276.2534, found: 276.2535.

9b: Colorless liquid, 81% yield (267 mg); ^{1}H NMR (300 MHz, $CDCl_3$, TMS, 25°C): δ=0.70–1.62(m, 18H, CH_3; 14H, CH_2), 2.34 (d, J=6.0 Hz, 2H), 2.60 (d, J=17.1 Hz, 2H), 2.97 ppm (d, J=17.1 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$, TMS, 25°C): δ=8.6, 8.7, 20.9, 21.2, 31.9, 32.1, 33.5, 42.3, 43.6, 78.9, 179.8 ppm; HRMS calcd for $C_{22}H_{38}N_2$: 330.3035, found: 330.3040.

9c: White solid, 95% yield (409 mg); m.p. 222–223°C; ^{1}H NMR (300 MHz, $CDCl_3$, TMS, 25°C): δ=0.94–2.04 (m, 6H, CH; 30H, CH_2), 2.27 (d, J=6.0 Hz, 2H), 2.59 (d, J=17.1 Hz, 2H), 2.94 ppm (d, J=17.1 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$, TMS, 25°C): δ=20.9, 28.0, 32.8, 36.6, 37.3, 40.0, 42.5, 78.1, 181.9 ppm; HRMS calcd for $C_{30}H_{42}N_2$: 430.3348, found: 430.3350.

9d: Orange liquid, 64% yield (166 mg); ^{1}H NMR (300 MHz, $CDCl_3$, TMS, 25°C): δ=1.14 (s, 18H), 1.51–1.59 (m, 2H), 1.80–1.96 (m, 4H), 2.71(d, J=18.3 Hz, 2H), 2.83 ppm (d, J=18.3 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$, TMS, 25°C): δ=24.8, 28.3, 35.6, 40.0, 47.0, 91.7, 182.3 ppm; HRMS calcd for $C_{17}H_{38}N_2$: 260.2252, found: 260.2244.

9e: White solid, 54% yield (170 mg); m.p. 182–183°C; ^{1}H NMR (300 MHz, $CDCl_3$, TMS, 25°C): δ=1.21–1.31 (m, 4H), 1.70–1.72 (m, 2H), 2.44–2.48 (m, 2H), 3.20 (d, J=17.1 Hz, 2H), 3.53 (d, J=17.1 Hz, 2H), 7.33–7.40 (m, 6H), 7.78–7.81 ppm (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$, TMS, 25°C): δ=20.8, 33.0, 45.2, 80.3, 127.7, 128.3, 130.5, 134.5, 169.5 ppm; HRMS calcd for $C_{22}H_{22}N_2$: 314.1783, found: 314.1779.

9f: White solid, 53% yield (198 mg); m.p. 165–166°C; ^{1}H NMR (300 MHz, $CDCl_3$, TMS, 25°C): δ=1.28 (brs, 4H), 1.68 (brs, 2H), 2.41–2.44 (m, 2H), 3.14 (d, J=17.1 Hz, 2H), 3.48(d, J=17.1 Hz, 2H), 3.80 (s, 6H), 6.87 (d, J=7.0 Hz, 4H), 7.74 ppm (d, J=7.1 Hz, 4H); ^{13}C NMR (75 MHz, $CDCl_3$, TMS, 25°C): δ=20.8, 33.1, 45.3, 55.3, 80.1, 113.7, 127.4, 129.4, 161.5, 168.9 ppm; HRMS calcd for $C_{24}H_{26}N_2O_2$: 374.1994, found: 374.2003.

9g: White solid, 57% yield (195 mg); m.p. 122–123°C; ^{1}H NMR (300 MHz, $CDCl_3$, TMS, 25°C): δ=1.21–1.37 (m, 4H), 1.72 (brs, 2H), 2.44 (brs, 6H, CH_3; 2H, CH_2), 3.22 (d, J=17.9 Hz, 2H) , 3.39 (d, J=17.9 Hz, 2H), 7.18–7.25 (m, 6H), 7.35–7.37 ppm (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$, TMS, 25°C): δ=20.1, 32.9, 48.5, 80.6, 125.6, 128.3, 129.0, 131.0, 135.3, 136.5, 172.1 ppm; HRMS calcd for $C_{24}H_{26}N_2$: 342.2096, found: 342.2102.

9h: White solid, 52% yield (178 mg); m.p. 167–168°C; ^{1}H NMR (300 MHz, $CDCl_3$, TMS, 25°C): δ=1.27 (brs, 4H), 1.68 (brs, 2H), 2.33(s, 6H), 2.38–2.46 (m, 2H), 3.18 (d, J=17.3 Hz, 2H), 3.51 (d, J=17.3 Hz, 2H), 7.16–7.26 (m, 4H), 7.52–7.55 (m, 2H), 7.66 ppm (s, 2H); ^{13}C NMR (75 MHz, $CDCl_3$, TMS, 25°C): δ=20.8, 21.2, 33.0, 45.3, 80.3, 125.1, 128.1, 128.2, 131.2, 134.5, 138.0, 169.6 ppm; HRMS calcd for $C_{24}H_{26}N_2$: 342.2096, found: 342.2090.

9i: White solid, 60% yield (205 mg); m.p. 190–191°C; ^{1}H NMR (300 MHz, $CDCl_3$, TMS, 25°C): δ=1.28 (brs, 4H), 1.68 (brs, 2H), 2.34 (s, 6H), 2.43–2.46 (m, 2H), 3.17 (d, J=17.1 Hz, 2H), 3.50 (d, J=17.1 Hz, 2H), 7.16 (d, J=3.6 Hz, 4H), 7.68 ppm (d, J=3.8 Hz, 4H); ^{13}C NMR (75 MHz, $CDCl_3$, TMS, 25°C): δ=20.9, 21.4, 33.1, 45.3, 80.2, 127.7, 129.0, 131.9, 140.6, 169.4 ppm; HRMS calcd for $C_{24}H_{26}N_2$: 342.2096, found: 342.2090.

9j: White solid, 70% yield (329 mg); m.p. 163–164°C; ^{1}H NMR (300 MHz, $CDCl_3$, TMS, 25°C): δ=1.18–1.32 (m, 4H), 1.69 (brs, 2H), 2.43–2.46 (m, 2H), 3.17 (d, J=17.1 Hz, 2H), 3.47 (d, J=17.1 Hz, 2H), 7.20–7.25 (m, 2H), 7.49–7.52 (m, 2H), 7.65–7.68 (m, 2H), 7.98 ppm (s, 2H); ^{13}C NMR (75 MHz, $CDCl_3$, TMS, 25°C): δ=20.6, 32.8, 44.9, 80.5,

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122.6, 126.3, 129.8, 130.4, 133.3, 136.3, 168.3 ppm; HRMS calcd for $C_{22}H_{20}N_2{}^{79}Br_2$: 469.9993, found: 470.0008.

9k: White solid, 55% yield (259 mg); m.p. 190–191°C; ^{1}H NMR (300 MHz, $CDCl_3$, TMS, 25°C): δ = 1.21–1.30 (m, 4H), 1.70 (brs, 2H), 2.42–2.46 (m, 2H), 3.16 (d, J = 17.1 Hz, 2H), 3.46 (d, J = 17.1 Hz, 2H), 7.49 (d, J = 8.4 Hz, 4H), 7.64 ppm (d, J = 8.4 Hz, 4H); ^{13}C NMR (75 MHz, $CDCl_3$, TMS, 25°C): δ = 20.8, 32.9, 45.0, 80.6, 125.1, 129.3, 131.6, 133.3, 168.7 ppm; HRMS calcd for $C_{22}H_{20}N_2{}^{79}Br_2$: 469.9993, found: 469.9980.

9l: Light yellow liquid, 56% yield (277 mg); ^{1}H NMR (300 MHz, $CDCl_3$, TMS, 25°C): δ = 0.96–1.08 (m, 4H), 1.53–1.56 (m, 2H), 2.07–2.11 (m, 2H), 2.39 (s, 6H), 2.38 (d, J = 18.0 Hz, 2H), 2.69 (d, J = 18.0 Hz, 2H), 7.16–7.53 ppm (m, 16H); ^{13}C NMR (75 MHz, $CDCl_3$, TMS, 25°C): δ = 20.5 (2 CH_2), 21.2, 32.2, 47.6, 80.2, 127.1, 128.9, 129.0, 129.2, 130.0, 135.8, 137.2, 138.4, 140.8, 173.4 ppm; HRMS calcd for $C_{36}H_{34}N_2$: 494.2715, found: 494.2722.

9m: White solid, 55% yield (228 mg); m.p. 185–186°C; ^{1}H NMR (300 MHz, $CDCl_3$, TMS, 25°C): δ = 1.40–1.43 (m, 4H), 1.81 (brs, 2H), 2.57–2.61 (m, 2H), 3.46 (d, J = 17.1 Hz, 2H), 3.71 (d, J = 17.1 Hz, 2H), 7.42–7.48 (m, 6H), 7.62–7.65 (m, 2H), 7.81–7.86 (m, 4H), 8.74–8.77 ppm (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$, TMS, 25°C): δ = 21.0, 32.9, 49.0, 80.9, 124.7, 125.9, 126.0, 126.9, 127.0, 128.2, 130.1, 130.9, 132.7, 133.8, 171.6 ppm; HRMS calcd for $C_{30}H_{26}N_2$: 414.2096, found: 414.2099.

Typical procedure for the preparation of siloles 12 from 1,2,3,4-tetrasubstituted 1,4-diiodo-1,3-dienes: *t*BuLi (4.0 mmol, 1.5 M in pentane) was added to a solution of 1,2,3,4-tetrasubstituted 1,4-diiodo-1,3-diene (1.0 mmol) in diethyl ether (5 mL) at −78°C. The reaction mixture was then stirred at −78°C for 1 h to generate 1,4-dilithio-1,3-diene **1**, which was monitored by GC analysis or by TLC. Me_3SiCN (1.0 mmol) was then added, and the reaction mixture was stirred at room temperature for 0.5 h. The reaction mixture was then quenched with saturated aqueous $NaHCO_3$ and extracted with diethyl ether. The extract was washed with brine and dried over $MgSO_4$. The solvent was evaporated in vacuo to give a yellow oil, which was purified by column chromatography (neutral Al_2O_3, hexane) to afford siloles **12**.

12a: Colorless liquid, 92% yield (256 mg); ^{1}H NMR (300 MHz, $CDCl_3$, TMS, 25°C): δ = 0.13 (s, 6H), 0.88–0.95 (m, 12H), 1.28–1.48 (m, 8H), 2.16–2.23 ppm (m, 8H); ^{13}C NMR (75 MHz, $CDCl_3$, TMS, 25°C): δ = −3.26, 14.40, 14.60, 23.40, 23.97, 30.10, 31.84, 137.15, 152.30 ppm. The NMR data are consistent with the reported data.[17]

12b: Colorless liquid, 94% yield (233 mg); ^{1}H NMR (300 MHz, $CDCl_3$, TMS, 25°C): δ = 0.14 (s, 6H), 0.90 (t, J = 7.2 Hz, 6H), 1.39–1.46 (m, 4H), 1.55–1.60 (m, 4H), 2.17 (t, J = 7.8 Hz, 4H), 2.37 ppm (brs, 4H); ^{13}C NMR (75 MHz, $CDCl_3$, TMS, 25°C): δ = −3.5, 14.6, 23.4, 23.7, 27.0, 31.0, 135.7, 148.8 ppm; HRMS calcd for $C_{16}H_{28}Si$: 248.1960, found: 248.1971.

Typical procedure for the preparation of (*Z*,*Z*)-dienylsilanes 13 from 2,3-disubstituted 1,4-diiodo-1,3-dienes: *t*BuLi (4.0 mmol, 1.5 M in pentane) was added to a solution of 2,3-disubstituted 1,4-diiodo-1,3-diene- (1.0 mmol) in diethyl ether (5 mL) at −78°C. The reaction mixture was then stirred at −78°C for 1 h to generate 1,4-dilithio-1,3-diene **5**, which was monitored by GC analysis or by TLC. Me_3SiCN (2.0 mmol) was then added, and the reaction mixture was stirred at room temperature for 0.5 h. The above reaction mixture was then quenched with saturated aqueous $NaHCO_3$ and extracted with diethyl ether. The extract was washed with brine and dried over $MgSO_4$. The solvent was evaporated in vacuo to give a yellow oil, which was purified by column chromatography (neutral Al_2O_3, hexane) to afford (*Z*,*Z*)-dienylsilanes **13**.

13a: Colorless liquid, 92% yield (337 mg); ^{1}H NMR (300 MHz, $CDCl_3$, TMS, 25°C): δ = 0.03 (s, 18H), 0.89 (t, J = 6.6 Hz, 6H), 1.30–1.43 (m, 16H), 2.09–2.13 (m, 4H), 5.18 ppm (s, 2H); ^{13}C NMR (75 MHz, $CDCl_3$, TMS, 25°C): δ = 0.13, 14.1, 22.7, 27.4, 29.3, 31.9, 41.5, 121.5, 161.1 ppm; HRMS calcd for $C_{22}H_{46}Si_2$: 366.3138, found: 366.3136.

13b: Colorless liquid, 91% yield (319 mg); ^{1}H NMR (300 MHz, $CDCl_3$, TMS, 25°C): δ = −0.06 (s, 18H), 6.46 (s, 2H), 7.20–7.28 (m, 6H), 7.52–7.54 ppm (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$, TMS, 25°C): δ = −0.39, 126.5, 127.6, 128.2, 128.9, 142.0, 154.3 ppm; HRMS calcd for $C_{22}H_{30}Si_2$: 350.1886, found: 350.1881.

13c: Colorless liquid, 90% yield (227 mg); ^{1}H NMR (300 MHz, $CDCl_3$, TMS, 25°C): δ = 0.05 (s, 18H), 1.50–1.56 (m, 2H), 1.87–1.91 (m, 2H), 2.17–2.36 (m, 4H), 5.13 ppm (s, 2H); ^{13}C NMR (75 MHz, $CDCl_3$, TMS, 25°C): δ = 0.3, 30.6, 45.1, 121.3, 161.4 ppm; HRMS calcd for $C_{14}H_{28}Si_2$: 252.1730, found: 252.1733.

13d: Colorless liquid, 96% yield (255 mg); ^{1}H NMR (300 MHz, $CDCl_3$, TMS, 25°C): δ = 0.04 (s, 18H), 1.49–1.56 (m, 6H), 1.29–1.34 (m, 4H), 5.24 ppm (s, 2H); ^{13}C NMR (75 MHz, $CDCl_3$, TMS, 25°C): δ = 0.3, 27.5, 28.6, 43.0, 124.9, 160.7 ppm; HRMS calcd for $C_{15}H_{30}Si_2$: 266.1880, found: 266.1886.

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