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Copper-catalyzed synthesis of five-membered heterocycles via double C–N bond formation: an efficient synthesis of pyrroles, dihydropyrroles, and carbazoles

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ABSTRACT

An efficient copper-catalyzed double C–N bond forming reaction using diiodides and nitrogen-centered nucleophiles including amides and carbamates is reported. The reactions proceed to afford di- or tri-substituted *N*-acylpyrroles, dihydropyrroles, and carbazoles in good to excellent yields when different diiodides such as 1,4-diiodo-1,3-butadienes, 1,4-dihalobut-1-enes, and 2,2′-diiodobiphenyls were employed, respectively. It is crucial to use CuI as the catalyst with the assistance of proper base and diamine ligand.

1. Introduction

The nitrogen-containing five-membered rings are an important class of heterocyclic compounds[1] because they represent useful building blocks in the synthesis of natural products or key structural unit in compounds that exhibit remarkable pharmacological activities.[2,3] They have also found broad applications in the field of material science.[4] As a consequence, much attention has been paid to the development of efficient methodologies for their preparation. The known methods for the construction of these five-membered rings proceed either by traditional methods or by transition-metal-catalyzed reactions. Among the transition-metal-catalyzed reactions, palladium was demonstrated to be highly efficient for the construction of C–N bonds toward five-membered rings. For examples, palladium-catalyzed tandem alkenyl and aryl–C–N bond formation to indoles was reported by Willis et al.,[5] double N-arylation of amines to carbazoles by Nozaki et al.[6] Buchwald reported the direct N-arylation of amides to carbazoles.[7] Larock showed the synthetic route to carbazoles through hydroamination and cyclization.[8] In the past few years, copper-catalyzed aryl C–X bond (X=N, O, S, etc.) formation reactions through coupling between aryl halides and heterocentered nucleophiles have drawn considerable attention,[9] which provide an excellent complement to the Pd-catalyzed reactions. More recently, this methodology was successfully extended to the synthesis of allenamides,[9g] enamides,[10] and lactams[9h] by coupling of amides with allenyl halides, vinyl halides, and iodoenamides via intramolecular vinylation, respectively. In the course of our ongoing study on the development of transition metal catalyzed new selective heterocycle forming protocols,[11] we found that a variety of five-membered ring compounds such as pyrroles[11a] and dihydropyrroles[11c] could be efficiently prepared by the reaction of dihalides and nitrogen-centered nucleophiles.[12,13] Here we'd like to report the full detail of nitrogen-containing five-membered ring formation reactions.

2. Results and discussion

2.1. Synthesis of pyrrole derivatives through double alkenylation reactions

We began our investigation with (1*Z*,3*Z*)-2,3-dibutyl-1,4-diiodo-1,3-butadiene **1a**, which was synthesized according to the reported method.[14] The reaction of **1a** with valeramide **2a** was selected as the prototypical case to screen the experimental conditions (Table 1). It was demonstrated that certain copper ligands play important roles for rate accelerations in the coupling reactions. These ligands are thought to increase catalyst solubility, stability and to prevent aggregation of the metal. We thus first carried out ligand screen using CuI (20 mol %) as the catalyst and Cs_2CO_3 (2 equiv) as the base in dioxane at refluxing temperature. The results are summarized in Table 1. Five commercially available ligands were evaluated for the coupling reaction, among them, the ligand of *trans*-*N*,*N*′-dimethylcyclohexane-1,2-diamine (**L1**) gave the most promising results. Thus, heating a mixture of diiodide **1a** and amide **2a** together with CuI catalyst in the presence of 20 mol % **L1** in dioxane at 100 °C afforded the expected pyrrole **3a** in 98% yield (Table 1, entry 5). The yield was rather low under ligandless condition (Table 1, entry 6). Switching

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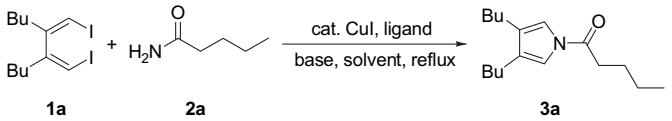
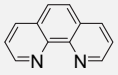
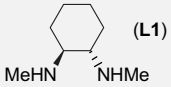
Table 1
Optimization of reaction conditions for the formation of **3a**



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

Entry	Ligand (20 mol %)	Base (2 equiv)	Solvent	Temp (°C)	Yield[a] (%)
1	2,2′-Bipyridine	Cs_2CO_3	1,4-Dioxane	100	20
2	Ethane-1,2-diol	Cs_2CO_3	1,4-Dioxane	100	54
3	L-Proline	Cs_2CO_3	1,4-Dioxane	100	27
4		Cs_2CO_3	1,4-Dioxane	100	43
5	 (**L1**)	Cs_2CO_3	1,4-Dioxane	100	98
6	None	Cs_2CO_3	1,4-Dioxane	100	15
7	**L1**	K_2CO_3	1,4-Dioxane	100	28
8	**L1**	K_3PO_4	1,4-Dioxane	100	25
9	**L1**	KOH	1,4-Dioxane	100	45
10	**L1**	Cs_2CO_3	Toluene	110	95

[a] Yields were determined by GC after hydrolysis. All the reactions were carried out with 20 mol % of CuI and kept for 24 h.

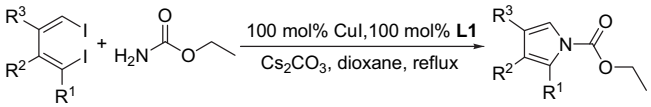
to other bases such as K_2CO_3, K_3PO_4, and KOH afforded lower yields of the product (entries 7–9). When the solvent was changed to toluene, the product yield was similar to that of dioxane (entry 10). It was cleared that the optimized reaction condition was to use 20 mol % of CuI in combination of 20 mol % of *rac-trans-N,N′*-dimethylcyclohexane-1,2-diamine (**L1**) as the ligand, Cs_2CO_3 as the base, and dioxane as the solvent.

Having established an effective catalytic system for the coupling reactions, we next synthesized a variety of diiodo dienes to explore the scope of double alkenylation under the optimized conditions. The representative results are shown in Table 2. The reaction was applicable to various amides and dienyl diiodo compounds. Coupling of **1a** with 2-phenylacetamide **2b** gave the corresponding pyrrole derivative **3b** in 95% yield (Table 2, entry 2). The aryl amide of 4-methylbenzamide **2c** reacted with **1a** to produce **3c** in 80% yield (Table 2, entry 3). Likewise, the coupling of **1a** with 4-aminobenzamide **2d** furnished the expected pyrrole **3d** in 92% yield, in which $-NH_2$ group was well tolerated during the reaction (entry 4). When 2,3-diphenyl-substituted dienyl diiodide **1b** was employed, the reaction with benzyl amide was completed within 4 h to give the desired product **3f** in 48% isolated yield, along with 24% deacylation product of 3,4-diphenyl-1*H*-pyrrole[15] (**4a**) (entry 6). To our delight, the crystal of **3f** was suitable for single crystal analysis, and its structure was fully characterized by X-ray diffraction analysis[16] (Fig. 1). Interestingly, when **1b** reacted with 2 equiv of benzamide **2e** for 20 h, the product of **4a** was obtained in 95% yield as the only pyrrole product, at the meantime, *N*-benzoylbenzamide[17] was isolated in 51% yield (entry 7). This result indicated that the acyl C–N bond of the initially formed pyrrole was cleaved during the reaction. It might be due to the delocalization of the nitrogen lone pair into the pyrrole ring of the pyrrole amide. The reduced electrodensity on the *N*-acylpyrrole carbonyl favors nucleophilic attack.

In order to make an insight into this reaction, we stopped the reaction in 3 h, the corresponding acyl pyrrole **3g** was obtained in 54% yield along with **4a** (22%) and *N*-benzoylbenzamide (30%) (entry 8). This reaction provides a useful method for synthesis of pyrroles with two aryl groups on adjacent positions, which frequently display interesting biological and pharmacological properties.[2d]

When a diiodide fused with a six-membered ring of **1c** was used, the reaction smoothly occurred to afford bicyclic pyrrole **3h** in 89% yield (entry 9). Interestingly, this method is also effective for trisubstituted dienyl diiodide compounds. The reaction of (1*Z*,3*Z*)-2-butyl-1,4-diiodo-3-propylhepta-1,3-diene (**1d**) and amide **2d** led to the formation of **3i** in 70% isolated yield (entry 10). The substrate of **1d** also reacted with benzamide to give the tri-substituted acyl pyrrole **3j** in moderated yield (entry 11). However, the diiodide **1e** bearing a phenyl group at C1 reacted with **2e** gave the pyrrole **4b** in only 32% isolated yield after 20 h (entry 12). When tetrasubstituted dienyl diiodide such as (3*Z*,5*Z*)-4,5-diethyl-3,6-diiodoocta-3,5-diene was treated with **2e** under the optimized reaction condition, no coupling product was observed.

The scope of this reaction was further examined by applying the optimized conditions to carbamate. Treatment of dienyl diiodide **1a** with ethyl carbamate using a catalytic amount (20%) of CuI resulted in the formation of **3k** only in 20% yield. Reasonable yield (68%) was obtained when 1.0 equiv of ligand and 1.0 equiv of CuI was employed (Eq 1).



3k:R^1=H, R^2 = R^3 = Bu, 68%

3l:R^1=H, R^2 = R^3 = Ph, 80%

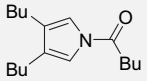
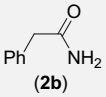
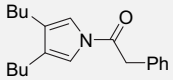
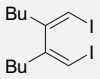
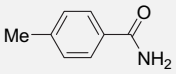
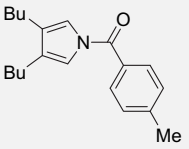
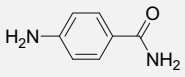
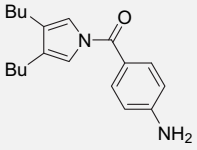
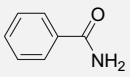
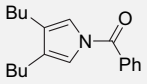
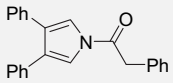
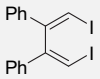
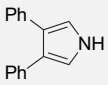
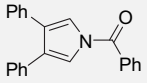
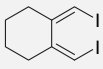
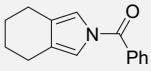
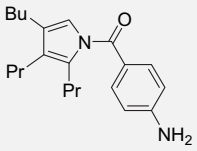
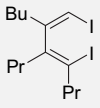
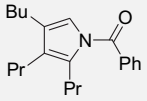
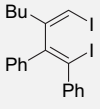
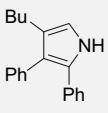
(1)

2.2. Synthesis of dihydropyrrole derivatives through N-alkenylation and N-alkylation reactions

We envisaged that the dihydropyrrole derivatives could be accessible by the combination of N-alkylation and N-alkenylation starting from amides and 1,4-dihalobut-1-ene derivatives under the similar conditions as for pyrroles. Initial studies were performed in toluene using (*Z*)-3-propyl-1,4-diiodohept-3-ene (**6a**) and valeramide (**2a**) as model substrates under the optimized reaction conditions for pyrrole formation. Interestingly, the desired dihydropyrrole **8a** was obtained in 53% yield with 38% of (Z)-4-idodo-5-vinyloct-4-ene (**9**) (Table 3, entry 2). These results indicated the formation of **9** through elimination of HI presumably due to the strong basicity of Cs_2CO_3. As expected, 80% yield of **8a** was generated when a mild base such as K_2CO_3 was used in the reaction, and no formation of **9** was observed (Table 3, entry 3). When the amount of CuI and **L1** was lowered to 10 mol % using K_2CO_3 as the base, the yield of **8a** dropped substantially to 55% with 29% of **6a** remained (Table 3, entry 4). Changing the solvent to 1,4-dioxane, only 35% of **8a** was observed (Table 3, entry 5). Switching to a weaker base such as $NaHCO_3$, or organic base like triethylamine resulted in no coupling reaction or very low yield of the product (Table 3, entries 7 and 8). Other copper salts such as CuCN, CuCl, CuBr gave the desired compound **8a** in 68%, 57%, and 48% yields, respectively (Table 3, entries 9–11). Three commercially available ligands, namely, L-proline (**L2**), *N,N′*-dimethylethane-1,2-diamine (**L3**), and 1,10-phenanthroline (**L4**) were also evaluated for the coupling reaction, and the yields of the corresponding product were 0%, 63%, and 61%, respectively (Table 3, entries 12–14). It was clear that the optimized reaction condition for dihydropyrrole formation was to use 20 mol % CuI in combination of 20 mol % *rac-trans-N,N′*-dimethylcyclohexane-1,2-diamine (**L1**), K_2CO_3 as the base in toluene.

This CuI catalyzed one-pot N-heterocyclization reaction was applicable to a variety of amides and diiodides to furnish dihydropyrroles in good to high yields. The representative results are depicted in Table 4. Coupling of **6a** with benzamide **2e** gave the corresponding dihydropyrroles **8b** in 64% yield (Table 4, entry 2). Diphenyl substituted diiodide **6b** reacted with **2e** to produce **8c** in 83% yield (Table 4, entry 3). The coupling of **6b** with 4-methylbenzamide (**2c**) furnished the

Table 2
Preparation of pyrroles from amides and dienyl diiodides

Entry	Dienyl diiodide	Amide	Time (h)	Product		Yield[a] (%)
1		 (**2a**)	24		**3a**	98(95)
2		 (**2b**)	18		**3b**	95(73)
3	 (**1a**)	 (**2c**)	24		**3c**	80(68)
4		 (**2d**)	18		**3d**	92(71)
5		 (**2e**)	24		**3e**	63(54)
6		**2b**	4		**3f**	(48)[b]
7	 (**1b**)	**2e**	20		**4a**	(95)[c]
8		**2e**	3		**3g**	(54)[d]
9	 (**1c**)	**2e**	20		**3h**	(89)
10		**2d**	24		**3i**	(70)
11	 (**1d**)	**2e**	24		**3j**	(54)
12	 (**1e**)	**2e**	20		**4b**	(32)

[a] GC yields. Isolated yields are given in parentheses.
[b] 3,4-Diphenyl-1*H*-pyrrole **4a** was obtained in 24% yield.
[c] Compound **2e** (2 equiv) was used. *N*-Benzoylbenzamide was isolated in 51% yield.
[d] Compound **4a** and *N*-benzoylbenzamide were isolated in 22% and 30% yields, respectively.

expected dihydropyrroles in 59% yield (Table 4, entry 4). Reaction of diethyl substituted diiodide **6c** with **2a** afforded **8e** in high yield (Table 4, entry 5). Likewise, the coupling of **6c** with **2c** gave the desired product in 75% yield (Table 4, entry 6).

When a diiodide **6d** fused with a six-membered ring was used, the reaction with **2a** or 4-methoxybenzamide (**2g**) occurred smoothly to produce the desired bicyclic dihydropyrroles in 69% or 59% yield, respectively (Table 4, entries 7 and 8). The coupling of (*E*)-(1,4-diiodo-3,4-diphenylbut-3-enyl)trimethylsilane (**6e**) with **2a** furnished the expected dihydropyrroles in 59% yield, in which the trimethylsilyl group was well tolerated during the reaction (Table 4, entry 9).

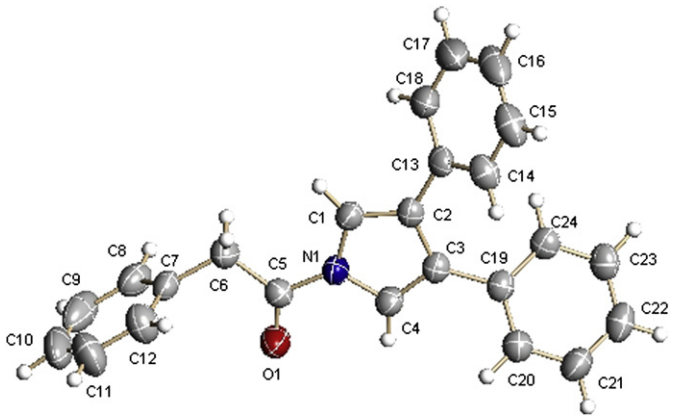
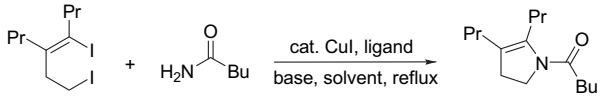
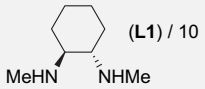
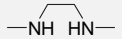
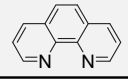


Figure 1. The X-ray crystal structure of **3f**.

Table 3
Optimization of reaction conditions for the formation of **8a**

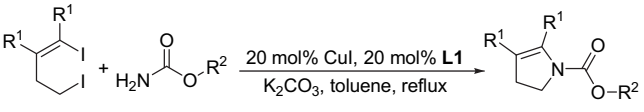


6a **2a** **8a**

Entry	Ligand/mol %	CuX/mol %	Base (2 equiv)	Yield[a] (%)
1	 (**L1**) / 10	CuI/10	Cs_2CO_3	27[b]
2	(**L1**)/20	CuI/20	Cs_2CO_3	53[c]
3	(**L1**)/20	CuI/20	K_2CO_3	80
4	(**L1**)/10	CuI/10	K_2CO_3	55
5	(**L1**)/10	CuI/10	K_2CO_3	35[d]
6	None	CuI/20	K_2CO_3	49
7	(**L1**)/20	CuI/20	$NaHCO_3$	0
8	(**L1**)/20	CuI/20	Triethylamine	4
9	(**L1**)/20	CuCN/20	K_2CO_3	68
10	(**L1**)/20	CuCl/20	K_2CO_3	57
11	(**L1**)/20	CuBr/20	K_2CO_3	48
12	L-Proline (**L2**)/20	CuI/20	K_2CO_3	0
13	 (**L 3**) / 20	CuI/20	K_2CO_3	63
14	 (**L 4**) / 20	CuI/20	K_2CO_3	61

[a] Yields were determined by GC after hydrolysis. All the reactions were done for 48 h. Unless noted, all the reactions were carried out in toluene.
[b] (Z)-4-Iodo-5-vinyloct-4-ene(**9**) was obtained in 53% yield.
[c] Compound **9** was obtained in 38% yield.
[d] 1,4-Dioxane was used as solvent.

The scope of the copper-catalyzed N-alkenylation and N-alkylation reaction could also be extended to carbamates under the optimized conditions. Treatment of **6a** with ethylcarbamate led to 63% yield of **8j** (Eq. 2). The reaction of **6b** with benzyl carbamate resulted in the formation of **8k** in 38% yield.



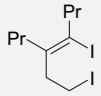
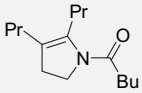
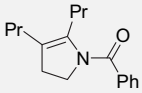
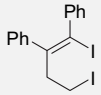
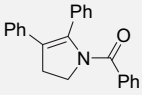
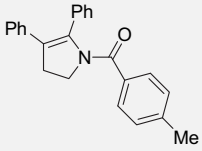
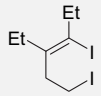
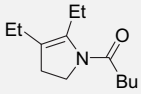
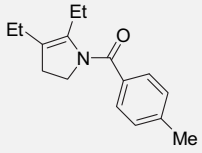
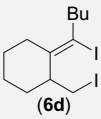
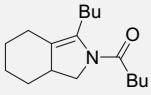
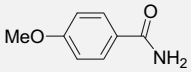
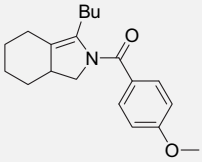
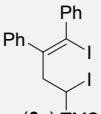
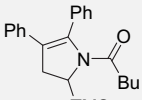
8j: R^1 = Pr, R^2 = Et, 63%

8k: R^1 = Ph, R^2 = Benzyl, 38%

(2)

When alkyl 1,4-diidodide like 1-iodo-3-(iodomethyl)nonane was treated with benzamide **2e** under the same reaction conditions, no desired product was observed.

Table 4
Preparation of dihydropyrroles from amides and diiodobutenes

Entry	Diiodide	Amide	Product	Yield[a] (%)
1	 (**6a**)	**2a**		**8a** 80(69)
2	(**6a**)	**2e**		**8b** 64(46)
3	 (**6b**)	**2e**		**8c** 83(65)
4	(**6b**)	**2c**		**8d** 59(47)
5	 (**6c**)	**2a**		**8e** 84(70)
6	(**6c**)	**2c**		**8f** 75(64)
7	 (**6d**)	**2a**		**8g** 69(57)
8	(**6d**)	 (**2g**)		**8h** 59(32)
9	 (**6e**) TMS	**2a**		**8i** 59(41)

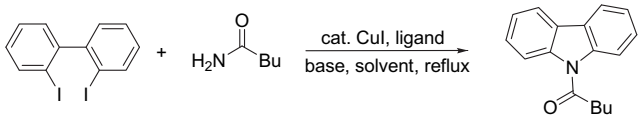
[a] GC yields. Isolated yields are given in parentheses.

2.3. Synthesis of carbazole derivatives through double arylation reactions

Carbazoles are very important in material science. The Pd-catalyzed synthesis of carbazoles is known.[6,7,17] However, Cu-catalyzed carbazole formation through double arylation of amides is rare.[12] We reasoned that this Cu-catalyzed N–C coupling system could be effective for their synthesis. Thus, the coupling reaction of 2,2′-diiodobiphenyl (**10a**) and valeramide **2a** was carried out under the same reaction conditions as for dihydropyrrole formation. As expected the desired carbazole **12a** was obtained in 47% yield (Table 5, entry 4), along with ca. 30% of **10a** recovered.

Double amount of **2a** resulted in the formation of **10a** in 73% yield (Table 5, entry 5). Changing the ligand to *N*,*N*′-dimethylethane-1,2-diamine (**L3**) furnished **10a** in 98% yield (Table 5, entry 8). All results of the reaction condition screening were depicted in Table 5. Thus, the optimized reaction condition for carbazole

Table 5
Optimization of reaction conditions for the formation of **12a**



10a **2a** **12a**

Entry	Ligand/mol %	CuX/mol %	**2a** (equiv)	Base (2 equiv)	Yield[a] (%)
1	**L1**/10	CuI/10	1.0	K_2CO_3	60
2	**L1**/10	CuI/10	1.0	K_2CO_3	58
3	**L1**/10	CuBr/10	1.0	K_2CO_3	55
4	**L1**/20	CuI/20	1.0	K_2CO_3	47
5	**L1**/20	CuI/20	2.0	K_2CO_3	73(56)
6	**L3**/10	CuI/10	1.0	K_2CO_3	63
7	**L3**/10	CuI/10	1.5	K_2CO_3	68
8	**L3**/20	CuI/20	2.0	K_2CO_3	98(85)
9	**L3**/20	CuI/20	2.0	KOH	—
10	**L3**/20	CuI/20	2.0	Cs_2CO_3	—
11	**L3**/20	CuI/20	2.0	Na_2CO_3	—

[a] GC yields, isolated yields were given in parentheses. All the reactions were done for 48 h. Unless noted, all the reactions were carried out in toluene.

forming was to use 20 mol % of CuI in combination of 20 mol % of *N*,*N*′-dimethylethane-1,2-diamine (**L3**) as the ligand, K_2CO_3 as the base, and toluene as the solvent.

A variety of 2,2′-diiodobiphenyl and amide analogs were subjected to the modified reaction conditions to define the reaction scope. As shown in Table 6, not only amides but also carbamates were applicable to the coupling reaction to afford the corresponding carbazoles in good to high yields. When 2,2′-diiodobiphenyl (**10a**) was employed, it coupled with carbamate **2f** and amides (**2g**, **2d**) to give the desired compounds in 69–89% yields (Table 6, entries 3–5), in which $-NH_2$ and –OMe groups were well tolerated during the reaction. It is worthy to note that the reaction of **10a** with benzyl amide furnished the deacylation product **12b** in 78% yield (Table 6, entry 2). Substituted diiodobiphenyles, for example, 2,2′-diiodo-4,4′,5,5′-tetramethylbiphenyl (**10b**) reacted with benzamide (**2e)** gave the corresponding carbazole **12g** in 61% yield (Table 6, entry 7). Compound **10b** also coupled with ethyl carbamate (**2f**) to produce **12f** in 63% yield (Table 6, entry 6). Likewise, the coupling of 2,2′-diiodo-4,4′,5,5′-tetramethoxybiphenyl (**10c**) with **2a** and **2f** furnished the expected carbazoles **12h** and **12i** in 62% and 53% yields, respectively (Table 6, entries 8 and 9). When diaryl dibromide such as 2,2′-dibromobiphenyl was treated with **2a** under the optimized reaction condition, no coupling product was observed.

3. Conclusion

We have reported an efficient copper-catalyzed double C–N bond forming reaction using diiodides and nitrogen-centered nucleophiles including amides and carbamates. This methodology provided a facile route for the synthesis of di- or trisubstituted *N*-acylpyrroles, dihydropyrroles, tetrahydropyrroles, and carbazoles in good to excellent yields when different diiodides such as 1,4-diiodo-1,3-butadienes, 1,4-dihalobut-1-enes, and 2,2′-diiodobiphenyles were employed, respectively. It is crucial to use CuI as the catalyst with the assistance of proper base and diamine ligand in order to achieve reasonable yields, the optimized reaction conditions are: *rac-trans-N*,*N*′-dimethylcyclohexane-1,2-diamine (**L1**) and Cs_2CO_3 for pyrroles, *rac-trans-N*,*N*′-dimethylcyclohexane-1,2-diamine, and K_2CO_3 for dihydropyrroles, and *N*,*N*′-dimethylethane-1,2-diamine (**L3**) and K_2CO_3 for carbazoles.

4. Experimental

4.1. General

All reactions were carried out in 1 mmol scale unless noted using standard Schlenk techniques under nitrogen. 1,4-Dioxane and toluene were distilled from sodium and benzophenone. All commercial reagents such as *rac-trans-N*,*N*′-dimethylcyclohexane-1,2-diamine, cesium carbonate, and alkynes were used without further purification. (1*Z*,3*Z*)-1,4-Diiodo-1,3-dienes were prepared according to the published methods.[14] ^1H and ^{13}C NMR spectra were recorded at 300 and 75.4 MHz, or 400 and 100 MHz, respectively, in $CDCl_3$ (containing 1% TMS) solutions. GC yields were determined using suitable hydrocarbons as internal standards. The product characterization data, and ^1H and ^{13}C NMR spectra for compounds **3a**–**3l** and **4b** can be found in Supplementary data of our previous communication.[11a]

4.2. General procedure for products synthesis

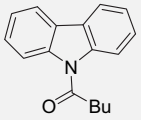
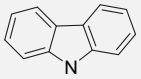
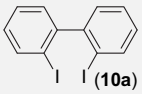
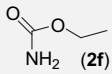
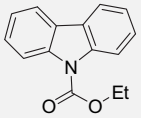
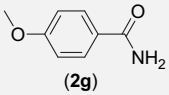
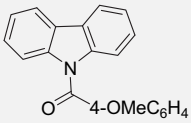
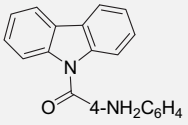
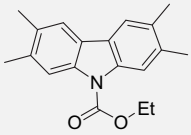
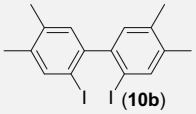
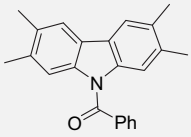
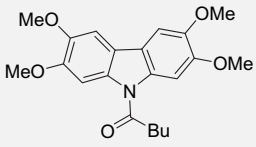
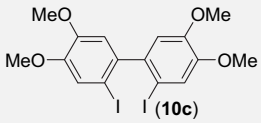
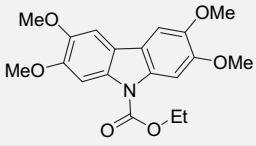
4.2.1. A typical procedure for the formation of pyrroles. A 20 mL Schlenk tube was charged with valeramide (101 mg, 1.0 mmol), CuI (38 mg, 0.2 mmol), and Cs_2CO_3 (652 mg, 2 mmol). After that 1,4-dioxane (8 mL) was added followed by *trans-N*,*N*′-dimethylcyclohexane-1,2-diamine (0.032 mL, 0.2 mmol) and (1*Z*,3*Z*)-2,3-dibutyl-1,4-diiodo-1,3-butadiene **1a** (418 mg, 1.0 mmol). The reaction mixture was heated to 100 °C for 24 h and then cooled down to room temperature. The mixture was quenched with aqueous $NaHCO_3$ and extracted with ethyl acetate (3×10 mL). The extract was washed with brine and dried over magnesium sulfate. The solvent was evaporated in vacuo and the residue was purified by chromatography on silica gel to afford 250 mg (95%) pyrrole derivative **3a** as a light-yellow oil. GC yield: 98%.

4.2.2. A typical procedure for the formation of dihydropyrroles. A 20 mL Schlenk tube was charged with valeramide (101 mg, 1.0 mmol), CuI(38 mg, 0.2 mmol), and K_2CO_3(276 mg, 2 mmol). After that toluene (8 mL) was added, followed by *rac-trans-N*,*N*′-dimethylcyclohexyldiamine (0.032 mL, 0.2 mmol) and (*Z*)-3-propyl-1,4-diiodohept-3-ene (1.0 mmol). The reaction mixture was heated to 110 °C for 48 h. The reaction mixture was cooled and quenched with aqueous $NaHCO_3$, extracted with ether (3×10 mL), washed with brine, dried over sodium sulfate, and concentrated under vacuum. Column chromatography on silica gel afforded the corresponding products. An orange oil of dihydropyrrole derivative **8a** (164 mg, 69%) was obtained. GC yield: 80%.

4.2.3. A typical procedure for the formation of carbazoles. A 20 mL Schlenk tube was charged with valeramide (202 mg, 2.0 mmol), CuI(38 mg, 0.2 mmol), and K_2CO_3(276 mg, 2 mmol). After that toluene (8 mL) was added, followed by *N*,*N*′-dimethylethane-1,2-diamine (0.2 mmol) and 2,2′-diiodobiphenyl (1.0 mmol). The reaction mixture was heated to 110 °C for 48 h. The reaction mixture was cooled and quenched with aqueous $NaHCO_3$, extracted with ether (3×10 mL), washed with brine, dried over sodium sulfate, and concentrated under vacuum. Column chromatography on silica gel afforded the corresponding products. A white solid of carbazole derivative **12a** (213 mg, 85%) was obtained. GC yield: 98%.

*4.2.3.1. 1-(4,5-Dipropyl-2,3-dihydropyrrol-1-yl)pentan-1-one (**8a**).* Orange liquid. ^1H NMR ($CDCl_3$, Me_4Si) δ 0.83 (t, *J*=5 Hz, 3H), 0.84 (t, *J*=7 Hz, 3H), 0.86 (t, *J*=8 Hz, 3H), 1.18–1.46 (m, 6H), 1.51–1.61 (m, 2H), 1.98 (t, *J*=7 Hz, 2H), 2.19 (t, *J*=8 Hz, 2H), 2.38 (t, *J*=9 Hz, 2H), 2.52 (t, *J*=7 Hz, 2H), 3.66 (t, *J*=9 Hz, 2H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ 13.67, 13.71, 13.73, 21.03, 22.24, 22.35, 26.83, 28.31, 29.11, 30.41, 35.69, 46.89, 120.87, 138.67, 169.22. HRMS for $C_{15}H_{28}NO$ $[M+H]^+$: calcd 238.2171, found 238.2165.

Table 6
Preparation of carbazole derivatives

Entry	Diiodide	Amide	Product		Yield[a] (%)
1		**2a**		**12a**	98(85)
2		**2b**		**12b**	78(69)
3	 (**10a**)	 (**2f**)		**12c**	69(58)
4		 (**2g**)		**12d**	89(84)
5		**2d**		**12e**	82(65)
6		**2f**		**12f**	63(47)
7	 (**10b**)	**2e**		**12g**	61(41)
8		**2a**		**12h**	62(55)
9	 (**10c**)	**2f**		**12i**	53(47)

[a] GC yields. Isolated yields are given in parentheses.

*4.2.3.2. (4,5-Dipropyl-2,3-dihydropyrrol-1-yl)(phenyl)methanone (**8b**).* Orange liquid. ^{1}H NMR ($CDCl_3$, Me_4Si) δ 0.84 (t, J=7 Hz, 6H), 1.31–1.39 (m, 4H), 2.04 (t, J=7 Hz, 2H), 2.30 (t, J=8 Hz, 2H), 2.52 (br s, 2H), 3.67 (br s, 2H), 7.21–7.46 (m, 5H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ 13.63, 13.84, 21.12, 21.41, 27.85, 29.34, 31.14, 50.70, 124.57, 127.34, 128.06, 128.44, 129.89, 137.61, 168.13. HRMS for $C_{17}H_{24}NO$ $[M+H]^+$: calcd 258.1858, found 258.1852.

*4.2.3.3. (4,5-Diphenyl-2,3-dihydropyrrol-1-yl)(phenyl)methanone (**8c**).* Light yellow solid. ^{1}H NMR ($CDCl_3$, Me_4Si) δ 2.97 (t, J=8 Hz, 2H), 4.14 (t, J=8 Hz, 2H), 6.90–7.35 (m, 15H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ 33.40, 50.86, 124.80, 126.47, 127.20, 127.69, 127.74, 127.90, 128.03, 128.13, 129.07, 130.17, 132.70, 135.70, 136.32, 138.37, 168.89. Mp: 155–158 °C. HRMS for $C_{23}H_{20}NO$ $[M+H]^+$: calcd 326.1545, found 326.1531.

*4.2.3.4. (4,5-Diphenyl-2,3-dihydropyrrol-1-yl)(p-tolyl)methanone (**8d**).* Pale yellow solid. ^{1}H NMR ($CDCl_3$, Me_4Si) δ 2.29 (s, 3H), 3.04 (t, J=8 Hz, 2H), 4.21 (t, J=8 Hz, 2H), 7.00–7.39 (m, 14H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ 21.29, 33.64, 51.09, 124.61, 126.41, 127.21, 127.54, 127.89, 127.99, 128.24, 128.40, 128.95, 132.90, 133.39, 135.80, 138.62, 140.55, 169.07. Mp: 203–205 °C. HRMS calcd for $C_{24}H_{21}NO$ 339.1623, found 339.1621.

*4.2.3.5. 1-(2,3-Diethyl-4,5-dihydropyrrol-1-yl)pentan-1-one (**8e**).* Light yellow liquid. ^{1}H NMR ($CDCl_3$, Me_4Si) δ 0.85 (t, J=8 Hz, 3H), 0.91 (t, J=8 Hz, 3H), 0.98 (t, J=8 Hz, 3H), 1.27–1.32 (m, 2H), 1.54–1.58 (m, 2H), 2.01 (q, J=8 Hz, 2H), 2.04–2.21 (m, 2H), 2.39–2.42 (m, 2H), 2.55–2.58 (m, 2H), 3.67 (t, J=8 Hz, 2H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ 12.83, 13.74, 14.01, 19.63, 19.99, 22.34, 26.81, 30.00, 35.60, 46.87, 121.67, 139.66, 169.17. HRMS calcd for $C_{13}H_{23}NO$ 209.1780, found 209.1777.

*4.2.3.6. (2,3-Diethyl-4,5-dihydropyrrol-1-yl)(p-tolyl)methanone (**8f**).* Light yellow liquid. ^{1}H NMR ($CDCl_3$, Me_4Si) δ 0.93 (t, J=8 Hz, 6H), 2.06–2.09 (m, 2H), 2.27–2.52 (m, 7H), 3.6 (m, 2H), 7.10 (d, J=8 Hz, 2H), 7.34 (d, J=8 Hz, 2H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ 12.87, 13.24, 19.27, 20.30, 21.29, 30.70, 50.81, 125.03, 127.46, 128.67, 134.74, 139.37, 140.07, 168.26. HRMS calcd for $C_{16}H_{21}NO$ 243.1623, found 243.1625.

*4.2.3.7. 1-(1-Butyl-3a,4,5,6-tetrahydro-1H-isoindol-2(4H)-yl)pentan-1-one (**8g**).* Yellow liquid. ^{1}H NMR ($CDCl_3$, Me_4Si) δ 0.80–0.87 (m, 6H), 0.95–1.03 (m, 2H), 1.24–1.37 (m, 7H), 1.52–1.59 (m, 2H), 1.68–1.89 (m, 4H), 2.18 (br s, 2H), 2.36–2.47 (m, 2H), 2.63 (br s, 2H), 3.14–3.19 (m, 1H), 3.86 (t, J=8 Hz, 1H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ 13.83, 13.91, 22.15, 22.43, 24.62, 25.28, 25.96, 26.81, 26.90, 31.36, 34.31, 35.83, 41.21, 53.81, 123.41, 135.80, 169.28. HRMS calcd for $C_{17}H_{29}NO$ 263.2249, found 263.2255.

*4.2.3.8. (1-Butyl-3a,4,5,6-tetrahydro-1H-isoindol-2(4H)-yl)(4-methoxyphenyl)methanone (**8h**).* Light yellow liquid. ^{1}H NMR ($CDCl_3$, Me_4Si) δ 0.80 (t, J=8 Hz, 3H), 0.91–1.00 (m, 2H), 1.11–1.33 (m, 6H), 1.67–1.82 (m, 4H), 2.34–2.7 (m, 3H), 3.28 (t, J=8 Hz, 1H), 3.76 (s, 3H), 3.70–3.86 (m, 1H), 6.78–6.86 (m, 2H), 7.43–7.48 (m, 2H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ 13.90, 22.17, 24.71, 25.07, 25.50, 26.51, 30.28, 33.87, 41.43, 55.30, 57.75, 113.31, 126.19, 129.55, 129.97, 135.76, 161.00, 168.14. HRMS calcd for $C_{20}H_{27}NO_2$ 313.2042, found 313.2039.

*4.2.3.9. 1-(4,5-Diphenyl-2-(trimethylsilyl)-2,3-dihydropyrrol-1-yl)-pentan-1-one (**8i**).* Orange red liquid. ^{1}H NMR ($CDCl_3$, Me_4Si) δ 0.00 (s, 9H), 0.55 (t, J=8 Hz, 3H), 0.80–0.87 (m, 2H), 1.13–1.28 (m, 2H), 1.29–1.58 (m, 2H), 2.39 (d, J=12 Hz, 1H), 3.46 (t, J=12 Hz, 1H), 4.38 (br s, 1H), 6.76–6.79 (m, 2H), 6.95–6.99 (m, 3H), 7.13–7.20 (m, 5H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ −3.10, 13.53, 22.18, 27.35, 35.02, 35.71, 51.83, 126.04, 126.22, 127.01, 127.88, 128.43, 128.78, 129.01, 133.93, 136.24, 137.12, 171.81. HRMS calcd for $C_{24}H_{31}NOSi$ 377.2175, found 377.2185.

*4.2.3.10. Ethyl 4,5-dipropyl-2,3-dihydropyrrole-1-carboxylate (**8j**).* Yellow liquid. ^{1}H NMR ($CDCl_3$, Me_4Si) δ 1.01 (t, J=7 Hz, 3H), 1.03 (t, J=7 Hz, 3H), 1.39 (t, J=7 Hz, 3H), 1.48–1.63 (m, 4H), 2.16 (t, J=9 Hz, 2H), 2.52 (t, J=9 Hz, 2H), 2.60 (t, J=8 Hz, 2H), 3.85 (t, J=9 Hz, 2H), 4.26 (q, J=7 Hz, 2H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ 13.82, 13.85, 14.64, 21.24, 22.18, 27.67, 29.54, 29.91, 46.35, 60.54, 119.38, 136.41, 152.77. HRMS calcd for $C_{13}H_{23}NO_2$ 225.1729, found 225.1721.

*4.2.3.11. Benzyl 4,5-diphenyl-2,3-dihydropyrrole-1-carboxylate (**8k**).* Yellow solid. ^{1}H NMR ($CDCl_3$, Me_4Si) δ 3.02 (t, J=8 Hz, 2H), 4.10 (t, J=8 Hz, 2H), 4.97 (s, 2H), 6.89–7.29 (m, 15H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ 31.93, 47.36, 66.82, 121.22, 126.02, 126.86, 127.72, 127.77, 127.83, 127.92, 128.10, 128.17, 129.26, 133.62, 135.64, 136.07, 137.57, 152.95. Mp: 90–93 °C. HRMS calcd for $C_{24}H_{21}NO_2$ 355.1572, found 355.1570.

*4.2.3.12. (Z)-4-Iodo-5-vinyloct-4-ene (**9**)*[14c]. Colorless liquid. ^{1}H NMR ($CDCl_3$, Me_4Si) δ 0.93 (t, J=8 Hz, 3H), 0.94 (t, J=8 Hz, 3H), 1.40–1.46 (m, 2H), 1.58–1.63 (m, 2H), 2.35 (t, J=8 Hz, 2H), 2.65 (t, J=8 Hz, 2H), 5.15 (d, J=12 Hz, 1H), 5.26 (d, J=20 Hz, 1H), 6.66 (dd, J=12 Hz, 16 Hz, 1H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ 13.08, 14.12, 22.44, 23.04, 30.53, 43.93, 114.70, 116.09, 140.31, 143.01.

*4.2.3.13. 1-(9H-Carbazol-9-yl)pentan-1-one (**12a**).* White solid. ^{1}H NMR ($CDCl_3$, Me_4Si) δ 0.92 (t, J=8 Hz, 3H), 1.40–1.53 (m, 2H), 1.79–1.83 (m, 2H), 3.00 (t, J=8 Hz, 2H), 7.26 (t, J=8 Hz, 2H), 7.36 (t, J=8 Hz, 2H), 7.86 (d, J=8 Hz, 2H), 8.09 (d, J=8 Hz, 2H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ 13.94, 22.35, 26.71, 38.83, 116.37, 119.72, 123.43, 126.33, 127.22, 138.52, 173.30. Mp 80–82 °C. HRMS calcd for $C_{17}H_{17}NO$ 251.1310, found 251.1321.

*4.2.3.14. 9H-Carbazole (**12b**)*[8b]. White solid. ^{1}H NMR (DMSO, Me_4Si) δ 7.18 (t, J=8 Hz, 2H), 7.41 (t, J=8 Hz, 2H), 7.54 (d, J=8 Hz, 2H), 8.13 (d, J=8 Hz, 2H), 11.34 (s, 1H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ 110.89, 118.42, 120.10, 122.34, 125.44, 139.68.

*4.2.3.15. Ethyl 9H-carbazole-9-carboxylate (**12c**)*[8b]. White solid. ^{1}H NMR ($CDCl_3$, Me_4Si) δ 1.47 (t, J=7 Hz, 3H), 4.50 (q, J=7 Hz, 2H), 7.27 (t, J=8 Hz, 2H), 7.40 (t, J=7 Hz, 2H), 7.85 (d, J=8 Hz, 2H), 8.13 (d, J=8 Hz, 2H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ 14.28, 62.84, 116.07, 119.37, 122.99, 125.66, 126.91, 138.05, 152.17.

*4.2.3.16. (9H-Carbazol-9-yl)(4-methoxyphenyl)methanone (**12d**)*[18]. White solid. ^{1}H NMR ($CDCl_3$, Me_4Si) δ 3.78 (s, 3H), 6.86–6.88 (d, J=8 Hz, 2H), 7.23–7.27 (m, 4H), 7.45–7.47 (m, 2H), 7.59 (d, J=8 Hz, 2H), 7.89–7.97 (m, 2H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ 55.41, 113.99, 115.43, 119.74, 122.95, 125.67, 126.49, 127.42, 131.67, 139.25, 163.11, 168.98. Mp 110–113 °C. HRMS calcd for $C_{20}H_{15}NO_2$ 301.1103, found 301.1111.

*4.2.3.17. (4-Aminophenyl)(9H-carbazol-9-yl)methanone (**12e**).* Light yellow solid. ^{1}H NMR ($CDCl_3$, Me_4Si) δ 4.11 (s, 2H), 6.61–6.64 (d, J=8 Hz, 2H), 7.18–7.27 (m, 4H), 7.52–7.56 (m, 4H), 7.95–7.97 (m, 2H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ 114.06, 115.38, 119.76, 122.67, 124.31, 125.55, 126.42, 132.27, 139.49, 150.98, 169.22. Mp 220–222 °C. HRMS calcd for $C_{19}H_{14}N_2O$ 286.1106, found 286.1119.

*4.2.3.18. Ethyl 2,3,6,7-tetramethyl-9H-carbazole-9-carboxylate (**12f**).* White solid. ^{1}H NMR ($CDCl_3$, Me_4Si) δ 1.43 (t, J=7 Hz, 3H), 2.19 (s, 6H), 2.25 (s, 6H), 4.43 (q, J=7 Hz, 2H), 7.49 (s, 2H), 7.90 (s, 2H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ 14.42, 19.86, 20.81, 62.63, 116.82, 119.66, 123.93, 131.44, 135.21, 136.76, 152.44. Mp 162 °C. HRMS calcd for $C_{19}H_{21}NO_2$ 295.1572, found 295.1578.

*4.2.3.19. Phenyl(2,3,6,7-tetramethyl-9H-carbazol-9-yl)methanone (**12g**).* Light yellow solid. ^{1}H NMR ($CDCl_3$, Me_4Si) δ 2.13 (s, 6H), 2.24 (s, 6H), 7.13 (s, 2H), 7.39 (s, 2H), 7.45–7.55 (m, 5H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ 19.89, 20.68, 116.56, 119.80, 124.19, 128.64, 128.74, 131.80, 131.86, 134.89, 136.11, 137.64, 169.32. Mp 192–193 °C. HRMS calcd for $C_{23}H_{21}NO$ 327.1623, found 327.1624.

*4.2.3.20. 1-(2,3,6,7-Tetramethoxy-9H-carbazol-9-yl)pentan-1-one (**12h**).* Light yellow solid. ^{1}H NMR ($CDCl_3$, Me_4Si) δ 0.95 (t, J=7 Hz, 3H), 1.43–1.46 (m, 2H), 1.77–1.82 (m, 2H), 2.86 (t, J=7 Hz, 2H), 3.88 (s, 6H), 3.91 (s, 6H), 7.07 (s, 2H), 7.59 (s, 2H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ 13.67, 22.15, 26.29, 38.13, 55.79, 55.91, 100.18, 100.57, 118.75, 131.83, 146.09, 147.51, 172.18. Mp 152–154 °C. HRMS calcd for $C_{21}H_{25}NO_5$ 371.1733, found 371.1729.

*4.2.3.21. Ethyl 2,3,6,7-tetramethoxy-9H-carbazole-9-carboxylate (**12i**).* White solid. ^{1}H NMR ($CDCl_3$, Me_4Si) δ 1.46 (t, J=7 Hz, 3H), 3.88 (s, 6H), 3.90 (s, 6H), 4.42 (q, J=7 Hz, 2H), 7.06 (s, 2H), 7.70 (s, 2H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ 14.19, 55.88, 55.99, 62.67, 100.07, 100.33, 118.17, 131.79, 146.08, 147.78, 151.98. Mp 148–150 °C. HRMS calcd for $C_{19}H_{21}NO_6$ 359.1369, found 359.1364.

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