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Rh(I)-catalyzed decarbonylation synthesis of carbazoles via C–N cleavage

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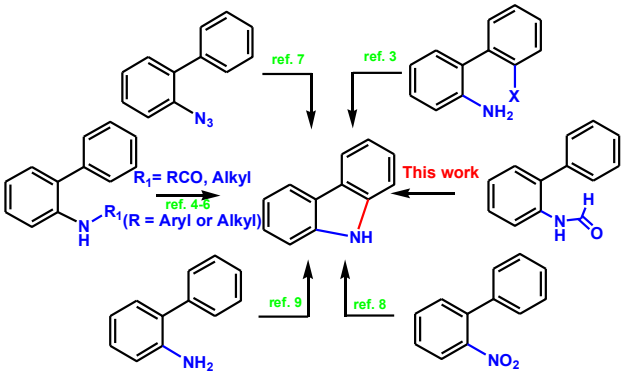
ABSTRACT

A one-pot Rh(I)-catalyzed synthesis of 9-*H* carbazoles via C–N bond cleavage by activation of aldehyde C–H bonds is reported. This protocol offers good yields and tolerates a broad range of functional groups. Based on the extensive control experiments, we propose a plausible decarbonylation mechanism.

1. Introduction

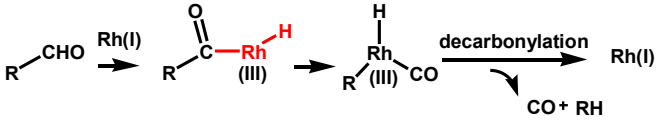
Carbazole and its derivatives are important organic structural motifs found in natural products and biologically active molecules.[1,2] Representative synthetic protocols involving intramolecular C–N coupling are summarized in Scheme 1, including transition-metal-catalyzed C–N formation with halide-functionalized arenas,[3] metal-catalyzed or organocatalytic intramolecular C–H amination to form carbazoles,[4–6] rhodium-catalyzed carbazole formation from biaryl azides,[7] transition-metal-free cyclization of 2-nitrobiaryls,[8] thermal cyclization (550 °C),[9] photostimulated cyclization[10] and Rh(III) or Ir(III) catalyzed C–H amination of nonprotected 2-aminobiaryls.[11]



Scheme 1. Intramolecular C–H amination to form N-substituted carbazoles.

Despite the numerous useful synthetic procedures to prepare these compounds, several limitations still need to be overcome to synthesize 9-H carbazoles directly in one-pot reaction,[3–11] such as using pre-activated substrates (synthesized by many steps),[3,7,8,10] high temperature (>250 °C),[9] special B_2pin_2 additive[11] or additional hydrolysis.[4–6] Herein, we aimed to trigger C–N bond cleavage by activation of aldehyde C–H bonds using Rh-catalysis via one-pot decarbonylation to synthesis 9-H carbazoles.

During the past decades, many successful Rh(I) or Rh(III) catalysis of decarbonylation from aldehydes were reported.[12–15] The general mechanism always included the most important oxidative addition process to form Rh(III)-hydride intermediate along with decarbonylation[16] (Scheme 2). Besides this, the proper ligand for the Rh-catalysts also plays the important roles.[12c,16]



Scheme 2. The general decarbonylation mechanism.

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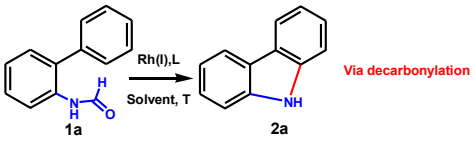
0040-4020/

2. Results and discussion

Encouraged by these, our initial studies were carried out with $Rh(PPh_3)_3Cl$ and *N*-formyl 2-aminobiaryls. Unfortunately, we got very poor yield of **2a** (<5%, Table 1, entry 1), even in harsh conditions (in DMSO, 180 °C). Subsequently screening the other catalysts, $[Rh(COD)OTf]_2$ showed the best catalytic activity to get 58% yield of **2a** (Table 1, entries 2–6). Addition of some bidentate ligands, such as dppe, dppf, Binap or Xantphos (Table 1, entries 7–10), the yield was further increased the yields to 75% (Table 1, entry 9). The scanning of different solvents such as DMSO, Diglyme, NMP, Mesitylene as well as different temperatures (Table 1, entries 11–13, SD-Table 1, entries 16–23), revealed that NMP at 190 °C was the best combination (Table 1, entry 12). As expectedly, we could not detect any **2a** without Rh-catalyst. An increased loading of the Rh-catalyst or increasing the time of transformation had no significant improvement on the yield (SD-Table 1, entries 25–29).

Table 1
Optimization of the reaction conditions



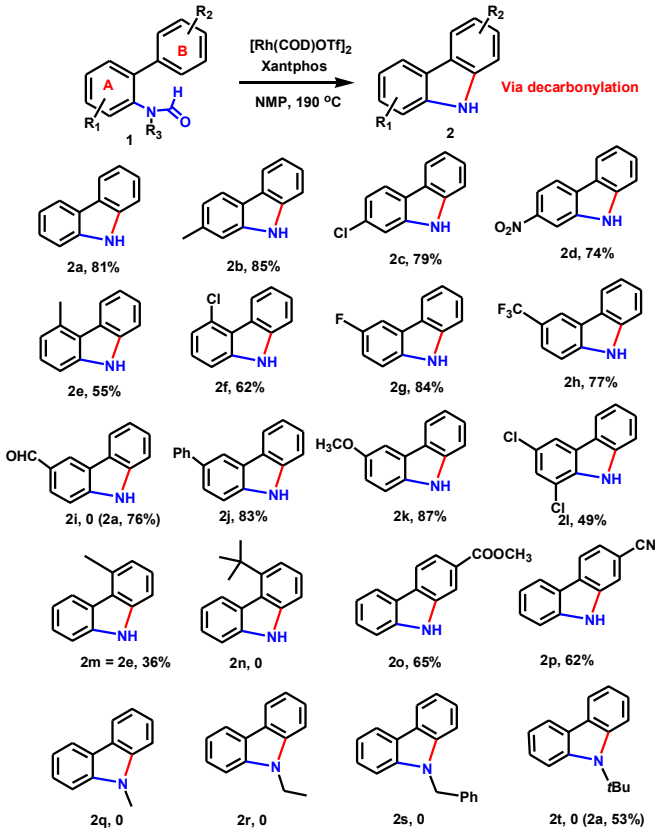
Entry[a]	Catalyst	Ligand	Solvent/T (°C)	Yield (%)[b]
1	$Rh(PPh_3)_3Cl$	—	DMSO/180	<5
2	$Rh(CO)(PPh_3)_2Cl$	—	DMSO/180	<5
3	$[Rh(COD)Cl]_2$	—	DMSO/180	18
4	$[Rh(COD)BF_4]_2$	—	DMSO/180	41
5	$[Rh(COD)OTf]_2$	—	DMSO/180	58
6	$Rh(COE)_2Cl$	—	DMSO/180	35
7	$[Rh(COD)OTf]_2$	dppe	DMSO/180	30
8	$[Rh(COD)OTf]_2$	dppf	DMSO/180	69
9	$[Rh(COD)OTf]_2$	Xantphos	DMSO/180	75
10	$[Rh(COD)OTf]_2$	Binap	DMSO/180	53
11	$[Rh(COD)OTf]_2$	Xantphos	Diglyme/160	48
12	$[Rh(COD)OTf]_2$	Xantphos	NMP/190	81
13	$[Rh(COD)OTf]_2$	Xantphos	Mesitylene/160	27
14	—	Xantphos	NMP/190	0

[a] Conditions: **1a** (0.2 mmol), Rh(I)-catalyst (2 mol %), Ligand (3 mol %), in 4 mL solvent, reacting at proper temperature under Ar atmosphere for 24 h.
[b] Isolated yield.

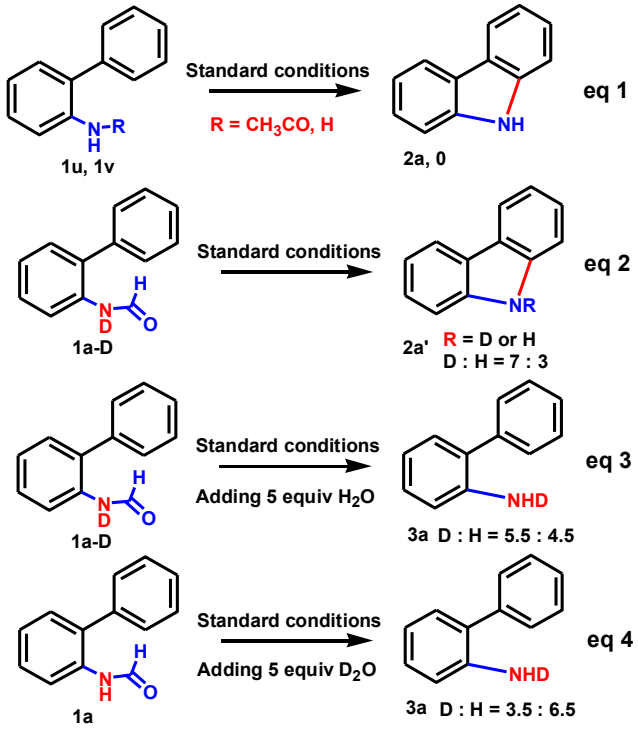
To determine the scope and limitations of the decarbonylation procedure several different *N*-formyl 2-aminobiaryls were subjected to the optimized conditions (Table 2). The 2-aminobiaryl derivatives with either an electron-donating or an electron-withdrawing group (e.g., Ph, OMe, Me, $COCH_3$, CN, F, CF_3) on the aryl rings gave rise to the corresponding N–H carbazole products (**2a**–**2p**, Table 2) in middle to good yields except the big steric substrate of **2n** (0). In general, a substrate that contained an electron-donating group in rings A (See Table 2 for labeling) led to a higher yield (**2b**, **2k** vs **2c**, **2d**, **2h**), but the yields were lower for products containing 3-substituted (See Table 2 for labeling) group in ring A (**2e**, **2f**). 3-Formyl substrates (**1i**) gave only 76% yield of **2a** under the standard conditions. Note that N-substituted biaryl derivatives (**2q**–**2t**) gave no products. However, when R_3 was ^{t}Bu group (**1t**), **2a** was isolated unexpectedly.

To understand the role of each compound in the formation of the N–H carbazole products, control experiments were performed (Scheme 3, SD-3 in the Supplementary data). Firstly, 2-aminobiaryls **1u** (R=CH_3CO) and **1v** (R=H) reacting under standard conditions gave no **2a** (eq 1), which suggested that the CH_3CO or NH_2 groups were more difficult to occur oxidative addition process[16] to form C–Rh species than CHO group. Secondly, using **1a-D** as starting material gave a mixture of **2a′** (D:H=7:3), which suggested forming N–Rh or N=Rh species after

Table 2
Screening the substrates



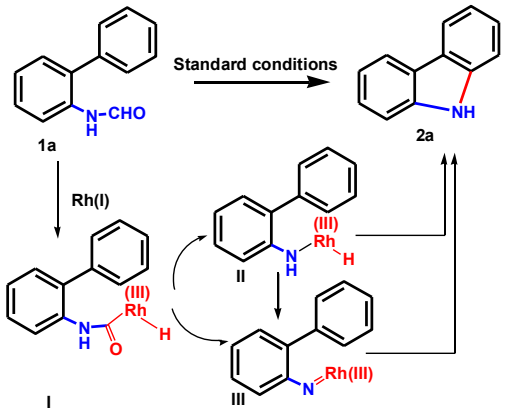
Conditions: **1** (0.2 mmol), Rh-cat (2 mol %), Xantphos (3 mol %), stirring for 24 h in 4 mL NMP at 190 °C under Ar atmosphere.



Scheme 3. Control experiments.

decarbonylation[12–15] (eq 2). Finally, **1a-D** or **1a** reacted with addition 5 equiv H_2O or D_2O under standard conditions affording the mixture of **3a** (D/H=5.5:4.5, D/H=3.5:6.5, respectively). This experiments were also in agreement with the forming N–Rh or N=Rh species.

With these results in hand, a possible mechanism was suggested in Scheme 4. The initial oxidative addition process occurred to form intermediate **I**,[12–15] subsequently decarbonylation to form intermediates **II** or **III**,[16] finally C–H activation to leaving H_2 or Rh(I) species to give **2a**.[16] However, Some of the results in Table 2, such as **2n** and **2t**, can not be explained by the proposed mechanism, which might due to the big steric hindrance making the intermediate **II** or **III** unstable.



Scheme 4. Proposed formation mechanism.

3. Conclusions

In summary, we have developed a one-pot Rh(I)-catalyzed synthesis of 9-H carbazoles via C–N bond cleavage by activation of aldehyde C–H bonds. This direct C–H amination is suitable for a broad range of substrates. The control experiments suggested a possible decarbonylation mechanism. Further studies concerning the detailed mechanism and the broader scope of substrates are currently underway in our laboratory.

4. Experiment

4.1. General

*4.1.1. Procedure for synthesis of **2a**–**2t**.* A mixture of **1** (0.2 mmol), $[Rh(COD)OTf]_2$ (2 mol %) and Xantphos (3 mol %) in NMP (4 mL) was stirred at 190 °C under Ar atmosphere for 24 h. After the reaction system was cooled to room temperature, saturated NH_4Cl solution (30 mL) and EtOAc (20 mL) were added. The combined organic phases were dried over Na_2SO_4 and then concentrated to give crude products. Further separation by column chromatography on silica gel (eluant with EtOAc and *n*-hexane) gave the corresponding products.

4.2. Characterization data

*4.2.1. **2a**: 9H-Carbazole.*[6c] (81%) mp 243–245 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.11 (d, J=7.8 Hz, 2H), 8.05 (br s, 1H, NH), 7.45–7.40 (m, 4H), 7.27–7.24 (m, 2H); HRMS (EI) m/z calcd for $C_{12}H_9N$ $[M]^+$: 167.0735, found: 167.0736.

*4.2.2. **2b**: 2-Methyl-9H-carbazole.*[7d] (85%) mp 174–175 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.06 (d, J=8.0 Hz, 1H), 7.95 (d, J=8.0 Hz, 1H), 7.86 (br s, 1H), 7.39–7.38 (m, 2H), 7.26–7.20 (m, 2H), 7.07 (d, J=7.6 Hz, 1H), 2.55 (s, 3H); HRMS (EI) m/z calcd for $C_{13}H_{11}N$ $[M]^+$: 181.0891, found: 181.0890.

*4.2.3. **2c**: 2-Chloro-9H-carbazole.*[7d] (79%) mp 236–240 °C; ^{1}H NMR (500 MHz, DMSO-d_6): 11.45 (s, 1H), 8.10 (d, J=8.4 Hz, 2H), 7.56 (d, J=2.0 Hz, 1H), 7.51 (td, J=8.1, 0.7 Hz, 1H), 7.42 (m, 1H), 7.18 (m, 1H), 7.17 (dd, J=8.4, 2.0 Hz, 1H); HRMS (EI) m/z calcd for $C_{12}H_8ClN$ $[M]^+$: 201.0345, found: 201.0344.

*4.2.4. **2d**: 2-Nitro-9H-carbazole.*[7d] (74%) mp 174–175 °C; ^{1}H NMR (500 MHz,DMSO-d_6): δ 8.38–8.35 (m, 2H), 8.28–8.26 (m, 1H), 8.05–8.03 (m, 1H), 7.64–7.62 (m, 1H), 7.55–7.53 (m, 1H), 7.30–7.27 (m, 1H); HRMS (EI) m/z calcd for $C_{12}H_8N_2O_2$ $[M]^+$: 212.0586, found: 212.0583.

*4.2.5. **2e**: 4-Methyl-9H-carbazole.*[7d] (55%) mp 120–122 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.23 (d, J=8.0 Hz, 1H), 8.02 (br s, 1H), 7.45–7.43 (m, 2H), 7.36–7.33 (m, 1H), 7.29–7.25 (m, 2H), 7.04 (dd, J=7.0 Hz, 0.5 Hz, 1H), 2.94 (s, 3H); HRMS (EI) m/z calcd for $C_{13}H_{11}N$ $[M]^+$: 181.0891, found: 181.0890.

*4.2.6. **2f**: 4-Chloro-9H-carbazole.*[7d] (62%) mp 88–92 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.66 (d, J=8.0 Hz, 1H), 7.92 (br s, 1H), 7.50 (dd, J=7.6 Hz, 1.0 Hz, 1H), 7.38–7.33 (m, 3H), 7.25–7.22 (m, 2H); HRMS (EI) m/z calcd for $C_{12}H_8ClN$ $[M]^+$: 201.0345, found: 201.0346.

*4.2.7. **2g**: 3-Fluoro-9H-carbazole.*[7d] (84%) mp 208–209 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.03 (d, J=7.6 Hz, 2H), 7.72 (dd, J=9.0 Hz, 2.5 Hz, 1H), 7.47–7.42 (m, 2H), 7.35 (dd, J=9.0 Hz, 4.0 Hz, 1H), 7.27–7.20 (m, 1H), 7.17 (dt, J=9.0 Hz, 2.6 Hz, 1H); HRMS (EI) m/z calcd for $C_{12}H_8NF$ $[M]^+$: 185.0641, found: 185.0640.

*4.2.8. **2h**: 3-Trifluoromethyl-9H-carbazole.*[7d] (77%) mp 158–162 °C; ^{1}H NMR (500 MHz,DMSO-d_6): 10.65 (s, 1H), 8.03 (s, 1H), 7.81 (d, J=9.4 Hz, 1H), 7.32 (d, J=9.4 Hz, 1H), 7.27–7.18 (m, 2H), 7.14 (t, J=9.4 Hz, 1H), 6.85 (t, J=9.4 Hz, 1H); HRMS (EI) m/z calcd for $C_{13}H_8NF_3$ $[M]^+$: 235.0609, found: 235.0610.

*4.2.9. **2j**: 3-Phenyl-9H-carbazole.*[17a] (83%) mp; ^{1}H NMR ($CDCl_3$): 8.33 (t, J=6.8 Hz, 1H), 8.17 (m, 1H), 8.10 (br s, 1H, NH), 7.75–7.71 (m, 2H), 7.70 (m, 1H), 7.55–7.46 (m, 5H), 7.38 (m, 1H), 7.28 (m, 1H); HRMS (EI^+) m/z calcd for $C_{18}H_{13}N$ $[M]^+$: 243.1048, found: 243.1045.

*4.2.10. **2k**: 3-Methoyl-9H-carbazole.*[7d] (87%) mp; ^{1}H NMR ($CDCl_3$): 8.06 (d, J=7.0 Hz, 1H), 8.04 (br s, 1H, NH), 7.58 (d, J=7.2 Hz, 1H), 7.42–7.41 (m, 2H), 7.35 (d, J=9.8 Hz, 1H), 7.22 (m, 1H), 7.07 (dd, J_1=7.2 Hz, J_2=3.0 Hz, 1H), 3.99 (s, 3H, OMe); HRMS (EI^+) m/z calcd for $C_{13}H_{11}NO$ $[M]^+$: 197.0841, found: 197.0840.

*4.2.11. **2l**: 1,3-Dichloro-9H-carbazole.*[17b] (49%) mp; ^{1}H NMR (d^6–acetone): 10.67 (br, 1H, NH), 8.19–8.14 (m, 2H), 7.60 (m, 1H), 7.53–7.47 (m, 2H), 7.25 (td, J_1=7.4 Hz, J_2=1.5 Hz, 1H); HRMS (EI^+) m/z calcd for $C_{12}H_7Cl_2N$ $[M]^+$: 234.9956, found: 234.9958.

*4.2.12. **2o**: Methyl 9H-carbazole-2-carboxylate.*[7d] (65%) mp 180–182 °C; ^{1}H NMR (500 MHz,DMSO-d_6): δ 11.56 (s, 1H), 8.23 (d, J=8.2 Hz, 1H), 8.19 (d, J=7.8 Hz, 1H), 8.14 (d, J=2.8 Hz, 1H), 7.79 (dd, J=8.2, 1.4 Hz, 1H), 7.58 (d, J=8.2 Hz, 1H), 7.45 (m, 1H), 7.20 (m, 1H), 3.90 (s, 3H); HRMS (EI^+) m/z calcd for $C_{14}H_{11}NO_2$ $[M]^+$: 225.0790, found: 225.0791.

*4.2.13. **2p**: 2-Cyano-9H-carbazole.* (62%) mp 248–249 °C; ^{1}H NMR (500 MHz,DMSO-d_6): δ 10.68 (s, 1H), 8.39–8.37 (m, 2H), 8.30–8.25 (m, 1H), 8.08–8.05 (m, 1H), 7.64–7.62 (m, 1H), 7.58–7.57 (m, 1H), 7.30–7.28 (m, 1H); ^{13}C NMR (125 MHz,DMSO-d_6): 167.5, 146.2, 142.5, 138.8, 128.7, 126.2, 124.3, 121.8, 120.4, 119.1, 114.2, 110.8,

106.9; HRMS (EI^+) m/z calcd for $C_{13}H_8N_2$ $[M]^+$: 192.2160, found 192.2163.

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Supplementary data

Supplementary data associated with this article can be found in the online version, at http://dx.doi.org/10.1016/j.tet.2015.04.058. These data include MOL files and InChiKeys of the most important compounds described in this article.

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