Supporting Information
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Metal-Free Synthesis 6-Benzylphenanthridines via Radical Addition/Cyclization of 2-Isocyanobiaryl

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1. kinetic isotope effect (KIE) experiment

1.1 intramolecular KIE experiment.

A dry Schlenck tube with stir bar was charged with d\textsubscript{1}-1a (0.25 mmol), DTBP (0.5 mmol), toluene (2.0 mL), which was then charged and filled with argon for three times. The reaction mixture was then stirred at 120°C for 2.0 hours. The reaction mixture was cooled down to room temperature and was subjected to a silica gel column. The column was eluted with petroleum ether/acetyl acetate to give the desired product. As is shown in the \textsuperscript{1}H NMR spectra, the integration of the peak at chemical shift 8.61-8.64 is 0.57. Therefore, \(k_H:k_D = 0.57/0.43 = 1.3\) (Figure S-1).

![Figure S-1](image1.png)

\textbf{Figure S-1} \textsuperscript{1}H NMR spectra of the product of intramolecular KIE experiment

1.2 intermolecular KIE experiment

A dry Schlenck tube with stir bar was charged with d\textsubscript{5}-1a (0.125 mmol), 1a (0.125 mmol), DTBP (0.5 mmol), toluene (2.0 mL), which was then charged and filled with argon for three times. The reaction mixture was then stirred at 120°C for 2h. The reaction mixture was cooled down to room temperature and was subjected to a silica gel column. The column was eluted with petroleum ether/acetyl acetate to give the desired product. As is shown in the \textsuperscript{1}H NMR spectra, the integration of the peak at \(\delta\) 8.61-8.64 is 0.53. Therefore, \(k_H:k_D = 0.53/0.47 = 1.1\). (Figure S-2)
1.3 intermolecular KIE experiment of toluene

A dry Schlenck tube with stir bar was charged with 1a (0.25 mmol), DTBP (0.5 mmol), toluene (1.0 mL), d₈-toluene (1.0 mL), which was then charged and filled with argon for three times. The reaction mixture was then stirred at 120°C for 2h. The reaction mixture was cooled down to room temperature and was subjected to a silica gel column. The column was eluted with petroleum ether/acetyl acetate to give the desired product. As is shown in the ¹H NMR spectra, the integration of the peak at δ 4.74-4.80 is 1.65. Therefore, $k_H: k_D = \frac{1.65}{(2-1.65)} = 4.7$ (Figure S-3).
2. Copies for $^1$H NMR and $^{13}$C NMR spectra for all the products

![Figure S-1 $^1$H NMR (400 MHz) spectra of 3a (rt, CDCl$_3$).](image1)

![Figure S-2 $^{13}$C NMR (100 MHz) spectra of 3a (rt, CDCl$_3$).](image2)
Figure S-3 $^1$H NMR (400 MHz) spectra of 3b (rt, CDCl$_3$).

Figure S-4 $^{13}$C NMR (100 MHz) spectra of 3b (rt, CDCl$_3$).
Figure S-5 $^1$H NMR (400 MHz) spectra of 3c (rt, CDCl$_3$).
Figure S-6 $^{13}$C NMR (100 MHz) spectra of 3c (rt, CDCl$_3$).

Figure S-7 $^1$H NMR (400 MHz) spectra of 3d (rt, CDCl$_3$).

Figure S-8 $^{13}$C NMR (100 MHz) spectra of 3d (rt, CDCl$_3$).
Figure S-9 $^1$H NMR (400 MHz) spectra of 3e (rt, CDCl$_3$).

Figure S-10 $^{13}$C NMR (100 MHz) spectra of 3e (rt, CDCl$_3$).
Figure S-11 $^1$H NMR (400 MHz) spectra of 3f (rt, CDCl$_3$).

Figure S-12 $^{13}$C NMR (100 MHz) spectra of 3f (rt, CDCl$_3$).
Figure S-13 $^1$H NMR (400 MHz) spectra of 3g (rt, CDCl$_3$).

Figure S-14 $^{13}$C NMR (100 MHz) spectra of 3g (rt, CDCl$_3$).
Figure S-15 $^1$H NMR (400 MHz) spectra of 3h (rt, CDCl$_3$).

Figure S-16 $^{13}$C NMR (100 MHz) spectra of 3h (rt, CDCl$_3$).
Figure S-17 $^1$H NMR (400 MHz) spectra of 3i (rt, CDCl$_3$).
Figure S-18 $^{13}$C NMR (100 MHz) spectra of 3i (rt, CDCl$_3$).

Figure S-19 $^1$H NMR (400 MHz) spectra of 3j (rt, CDCl$_3$).
Figure S-20 $^{13}$C NMR (100 MHz) spectra of 3j (rt, CDCl$_3$).

Figure S-21 $^1$H NMR (400 MHz) spectra of 3k (rt, CDCl$_3$).

Figure S-22 $^{13}$C NMR (100 MHz) spectra of 3k (rt, CDCl$_3$).
Figure S-23 $^1$H NMR (400 MHz) spectra of 3l (rt, CDCl$_3$).

Figure S-24 $^{13}$C NMR (100 MHz) spectra of 3l (rt, CDCl$_3$).
Figure S-25 $^1$H NMR (400 MHz) spectra of 4a (rt, CDCl$_3$).

Figure S-26 $^{13}$C NMR (100 MHz) spectra of 4a (rt, CDCl$_3$).
Figure S-27 $^1$H NMR (400 MHz) spectra of 4b (rt, CDCl$_3$).

Figure S-28 $^{13}$C NMR (100 MHz) spectra of 4b (rt, CDCl$_3$).
**Figure S-29** $^1$H NMR (400 MHz) spectra of 4c (rt, CDCl$_3$).

**Figure S-30** $^{13}$C NMR (100 MHz) spectra of 4c (rt, CDCl$_3$).
Figure S-31 $^1\text{H}$ NMR (400 MHz) spectra of 4d (rt, CDCl$_3$).

Figure S-32 $^{13}\text{C}$ NMR (100 MHz) spectra of 4d (rt, CDCl$_3$).
Figure S-33 $^1$H NMR (400 MHz) spectra of 4e (rt, CDCl$_3$).

Figure S-34 $^{13}$C NMR (100 MHz) spectra of 4e (rt, CDCl$_3$).
Figure S-35: H NMR (400 MHz) spectra of 4f (rt, CDCl₃).

Figure S-36: C NMR (100 MHz) spectra of 4f (rt, CDCl₃).
Figure S-37 $^1$H NMR (400 MHz) spectra of 4i (rt, CDCl$_3$).

Figure S-38 $^{13}$C NMR (100 MHz) spectra of 4i (rt, CDCl$_3$).
Figure S-39: $^1$H NMR (400 MHz) spectra of 4j (rt, CDCl$_3$).

Figure S-40: $^{13}$C NMR (100 MHz) spectra of 4j (rt, CDCl$_3$).
Figure S-41 $^1$H NMR (400 MHz) spectra of 3aa (rt, CDCl$_3$).