Electronic Supplementary Information

From *N*-Benzoylpyridinium Imides to Pyrazolo[1,5-*a*]pyridines: A Mechanistic Discussion on a Stoichiometric Cu Protocol

Lin Ling[‡,b] Jingqing Chen,[‡,a] Jiahui Song,[a] Yuhai Zhang,[a] Xinqian Li,[b] Lijuan Song,[a] Feng Shi[*,a], Yuxue Li[*,b] and Chunrui Wu[*,a]

[a] *Key Laboratory of Natural Medicine and Immuno-Engineering of Henan Province, Henan University, Jinming Campus, Kaifeng, Henan 475004, China PR. E-mail: fshi@henu.edu.cn, cwu@henu.edu.cn.*

[b] *State Key Laboratory of Organometallic Chemistry, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, 345 Ling Ling Road, Shanghai 200032, China. E-mail: liyuxue@sioc.ac.cn.*

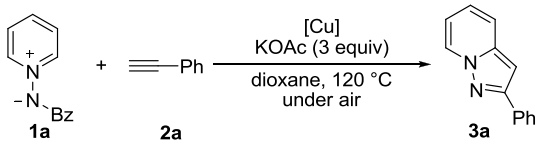
[‡] *Equal contributors*

Part 1. Synthetic Section

Table of Contents

Additional results in the survey of reaction conditions:

Table ESI1[a]



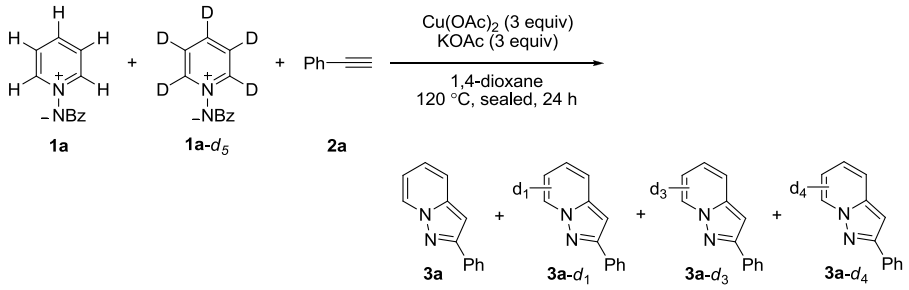
1a **2a** **3a**

Entry	[Cu]/equiv	Addition of **2a**	Additional additive	Additional oxidant	Yield (%)[b]
1	$Cu(OTf)_2$/3.0	2.0 equiv in one batch, 16 h	-	-	trace
2	$CuCl_2$/3.0	2.0 equiv in one batch, 16 h	-	-	trace
3	$CuSO_4 \cdot 5H_2O$/3.0	2.0 equiv in one batch, 16 h	-	-	0
4	$CuBr_2$/3.0	2.0 equiv in one batch, 16 h	-	-	0
5	CuI/3.0	2.0 equiv in one batch, 16 h	-	-	0
6	$Cu(OAc)_2$/3.0	2.0 equiv in one batch, 16 h	py/3.0	-	32
7	$Cu(OAc)_2$/3.0	2.0 equiv in one batch, 16 h	2,6-lutidine/3.0	-	36
8	$Cu(OAc)_2$/3.0	2.0 equiv in one batch, 16 h	3,5-lutidine/3.0	-	7
9	$Cu(OAc)_2$/3.0	2.0 equiv in one batch, 16 h	3-(MeO_2C)py/3.0	-	26
10	$Cu(OAc)_2$/0.2	1.0 equiv, 12 h, another 1.0 equiv, 12 h	-	BQ/2.0	0
11	$Cu(OAc)_2$/0.2	1.0 equiv, 12 h, another 1.0 equiv, 12 h	-	DDQ/2.0	0
12	$Cu(OAc)_2$/0.2	1.0 equiv, 12 h, another 1.0 equiv, 12 h	-	$Fe(acac)_3$/2.0	0
13	$Cu(OAc)_2$/0.2	1.0 equiv, 12 h, another 1.0 equiv, 12 h	-	$Fe(NO_3)_3 \cdot 9H_2O$/2.0	0
14	$Cu(OAc)_2$/0.2	1.0 equiv, 12 h, another 1.0 equiv, 12 h	-	TEMPO/2.0	17
15	$Cu(OAc)_2$/1.0	1.0 equiv, 12 h, another 1.0 equiv, 12 h	-	TEMPO/2.0	36
16	$Cu(OAc)_2$/1.1	1.0 equiv, 12 h, another 1.0 equiv, 12 h	-	-	39

[a] Reactions are carried out on ~0.2 mmol scale. [b] Isolated yield.

Isotope labeling experiments:

Procedures:



To an oven-dried 30 mL seal-tube equipped with a stir bar were added **1a** (119 mg, 0.60 mmol, 3 equiv), **1a-*d*$_5$** (122 mg, 0.60 mmol, 3 equiv), phenylacetylene (11 μL, 0.10 mmol), $Cu(OAc)_2$ (109 mg, 0.6 mmol, 3 equiv), KOAc (59 mg, 0.6 mmol, 3 equiv), and 1,4-dioxane (4 mL). The mixture was stirred at 120 ºC for 12 h before being cooled to room temperature. Another batch of phenylacetylene (11 μL, 0.1 mmol) was added and reaction continued for 12 h at 120 ºC. The mixture was then cooled to room temperature and diluted with EtOAc. The insolubles were filtered off and washed with EtOAc. Combined EtOAc solution was washed with water and dried over Na_2SO_4, concentrated under reduced pressure, and purified via column chromatography to afford the mixture, which was analyzed by MS and NMR spectroscopy.

Spectra:

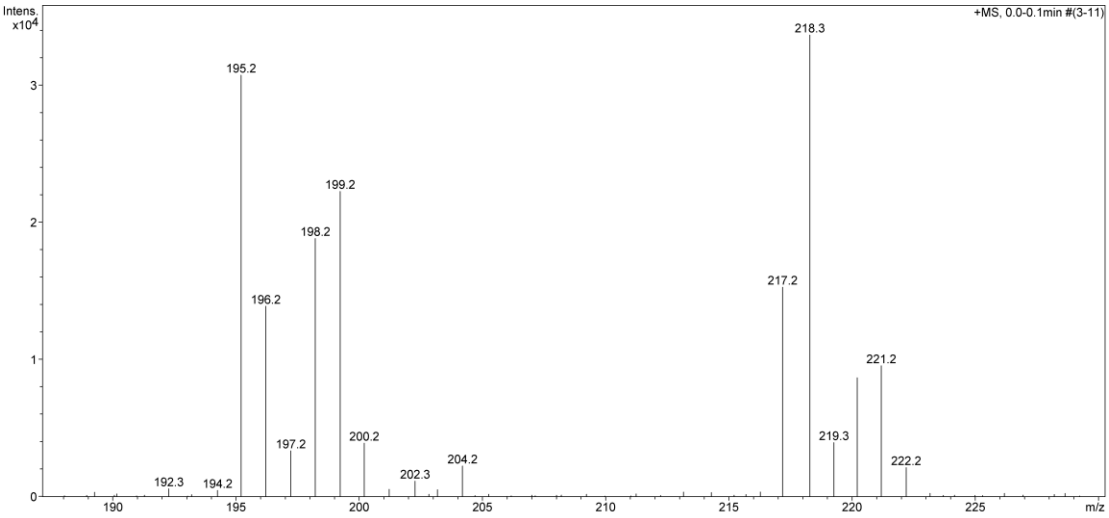


Figure ESI1-1. LRMS spectra for the isotope labeling experiment

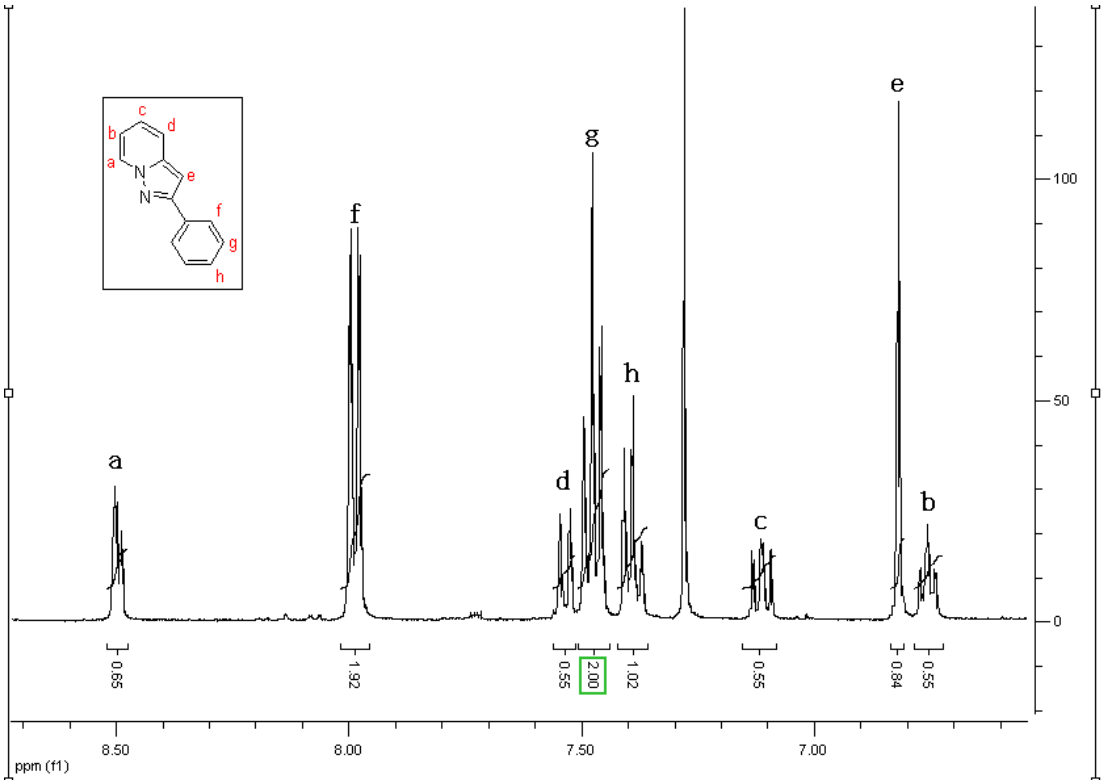


Figure ESI1-2 ^{1}H NMR spectra for the isotope labeling experiment

Analysis:

Figure ESI1:

Signals 195 and 217 belong to **3a**-d_0; signals 196 and 218 belong to **3a**-d_1; signals 198 and 220 belong to **3a**-d_3; signals 199 and 221 belong to **3a**-d_4. Signals 197 and 219 are relatively small (after discounting the added weight of natural ^{13}C).

Since these MS intensities are not calibrated to discount the natural ^{13}C isotope, the ratio deduced from the MS spectrum may not reflect the true value. We therefore used the MS spectrum to determine the presence of certain isotopic products, and referred to the NMR spectrum to determine the ratio.

Figure ESI2:

Since H^b, H^c, and H^d integrate the same but much less than H^a, it appears that H-D scrambling occurs selectively at 2- and 6-positions or **1**.[Note] Thus, it appears that **3a**-d_0 corresponds to H at position-a through -d; **3a**-d_1 corresponds to D at position-a and H at position-b through d; **3a**-d_3 corresponds to H at position-a and D at position-b through d; **3a**-d_4 corresponds to D at position-a through d.

Comparing the integration of $H^{b\text{-}d}$ vs $H^{f\text{-}h}$, it appears that (**3a**-d_0 + **3a**-d_1) occupies

55% of all product, and (**3a**-d_3 + **3a**-d_4) 45%. Their ratio is about 1.22.

H^a integrates more than H^{b-d} likely because the presence of trace water and the deprotonation of alkyne introduce sources of proton.

Note:

Since H^b, H^c, and H^d integrate the same, it appears that either all these positions undergo H-D scrambling, or none of them do. As it is hard to believe that 3-, and 5-positions ($H^{b,d}$) could undergo significant H-D scrambling (Charette did not observe it in his Cu-catalyzed 2-vinylation reaction), it is more likely that none of H^b, H^c, and H^d scrambles with D to a noticeable level.

Experimental details and product characterization

General information

All reagents purchased from commercial sources were used as received. Pyridinium imides were prepared according to literature procedures.[1] Solvent 1,4-dioxane was dried over 4Å molecular sieves. Reactions were set up without precautions to exclude air. All melting points are uncorrected. The ^{1}H and ^{13}C NMR spectra are referenced to the residual solvent signals (7.26 ppm for ^{1}H in $CDCl_3$ and 77.0 ppm for ^{13}C in $CDCl_3$, 29.8 ppm for ^{13}C in acetone-d_6, and 39.5 ppm for ^{13}C in DMSO-d_6).

General procedures

To an oven-dried seal-tube equipped with a stir bar were added *N*-benzoylpyridinium imide (0.20 mmol), alkyne (0.20 mmol, 1 equiv), $Cu(OAc)_2$ (109 mg, 0.6 mmol, 3 equiv), KOAc (59 mg, 0.6 mmol, 3 equiv), and 1,4-dioxane (4 mL). The mixture was stirred at 120 ºC for 12 h before being cooled to room temperature. Another batch of alkyne (0.2. mmol, 1 equiv) was added and reaction continued for 12 h at 120 ºC. The mixture was then cooled to room temperature and diluted with EtOAc. The insolubles were filtered off and washed with EtOAc. Combined EtOAc solution was washed with water and dried over Na_2SO_4, concentrated under reduced pressure, and purified via column chromatography to afford the product.

Product characterization data

2-Phenylpyrazolo[1,5-*a*]pyridine (3a): starting from 39.6 mg of **1a** and 44 μL of **2a** (added in two batches), 22 mg of **3a** was obtained following the general procedures as off-white solid; mp 105–106 ºC (lit.[2] 110–113 ºC, lit.[3] 106–108 ºC); ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.48 (dd, *J* = 7.0, 1.0 Hz, 1 H), 8.00–7.95 (m, 2 H), 7.55–7.41 (m, 3 H), 7.40–7.34 (m, 1 H), 7.09 (ddd, *J* = 8.9, 6.7, 1.1 Hz, 1 H), 6.80 (d, *J* = 0.7 Hz, 1 H), 6.73 (td, *J* = 6.9, 1.4 Hz, 1 H); ^{13}C NMR (125 MHz, acetone-d_6) δ 153.9, 142.5, 134.4, 129.5, 129.4, 129.1, 127.0, 124.4, 118.8, 112.8, 94.2; HRMS (ESI) calcd for $C_{13}H_{11}N_2$ (M+H) 195.0917, found 195.0916.

2-(*p*-Tolyl)pyrazolo[1,5-*a*]pyridine (3b): starting from 39.6 mg of **1a** and 51 μL of

2b (added in two batches), 24 mg of **3b** was obtained following the general procedures as white solid; mp 117–118 ºC (lit.[2] 117–118 ºC); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.47 (d, *J* = 6.7 Hz, 1 H), 7.87 (d, *J* = 8.0 Hz, 2 H), 7.49 (d, *J* = 8.9 Hz, 1 H), 7.27 (d, *J* = 8.0 Hz, 2 H), 7.08 (t, *J* = 8.0 Hz, 1 H), 6.76 (s, 1 H), 6.71 (t, *J* = 6.8 Hz, 1 H), 2.41 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.6, 141.6, 138.2, 130.3, 129.4, 128.4, 126.3, 123.3, 117.8, 111.5, 93.4, 21.3; HRMS (ESI) calcd for $C_{14}H_{13}N_2$ (M+H) 209.1073, found 209.1071.

2-(3-Chlorophenyl)pyrazolo[1,5-*a*]pyridine (3c): starting from 39.6 mg of **1a** and 49 μL of 3-chlorophenylacetylene (added in two batches), 25 mg of **3c** was obtained following the general procedures as off-white solid; mp 106–108 ºC; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.47 (dd, *J* = 7.0, 0.9 Hz, 1 H), 7.98–7.97 (m, 1 H), 7.85 (dt, *J* = 7.3, 1.6 Hz, 1 H), 7.53 (d, *J* = 8.9 Hz, 1 H), 7.41–7.32 (m, 2 H), 7.15–7.09 (m, 1 H), 6.79–6.75 (m, 2 H); ^{13}C NMR (125 MHz, acetone-d_6) δ 152.5, 142.8, 136.7, 135.2, 131.4, 129.7, 129.1, 126.9, 125.7, 124.8, 119.2, 113.5, 94.9; HRMS (ESI) calcd for $C_{13}H_{10}{}^{35}ClN_2$ (M+H) 229.0527, found 229.0525.

2-(3-Methoxyphenyl)pyrazolo[1,5-*a*]pyridine (3d): starting from 39.6 mg of **1a** and 48 μL of 3-methoxyphenylacetylene (added in two batches), 30 mg of **3d** was obtained following the general procedures as yellow solid; mp 53–55 ºC (lit.[2] 43–45 ºC); ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.47 (d, *J* = 6.3 Hz, 1 H), 7.56–7.49 (m, 3 H), 7.36 (t, *J* = 8.1 Hz, 1 H), 7.11–7.06 (m, 1 H), 6.94–6.91 (m, 1 H), 6.79 (s, 1 H), 6.73 (dt, *J* = 1.3, 6.9 Hz, 1 H), 3.90 (s, 3 H); ^{13}C NMR (125 MHz, acetone-d_6) δ 161.1, 153.9, 142.6, 135.8, 130.6, 129.5, 124.5, 119.6, 118.9, 114.9, 112.9, 112.4, 94.5, 55.6; HRMS (ESI) calcd for $C_{14}H_{13}N_2O$ (M+H) 225.1022, found 225.1019.

2-(Thiophen-3-yl)pyrazolo[1,5-*a*]pyridine (3e): starting from 39.6 mg of **1a** and 39 μL of 3-ethynylthiophene (added in two batches), 20 mg of **3e** was obtained following the general procedures as off-white solid; mp 124–126 ºC (lit.[3] 115–118 ºC); ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.45 (dd, *J* = 7.0, 1.0 Hz, 1 H), 7.77 (dd, *J* = 3.0, 1.2 Hz, 1 H), 7.60 (dd, *J* = 5.0, 1.2 Hz, 1 H), 7.49 (dt, *J* = 8.9, 1,2 Hz, 1 H), 7.40 (dd, *J* = 5.0, 3.0 Hz, 1 H), 7.09 (ddd, *J* = 8.9, 6.7, 1.1 Hz, 1 H), 6.73, (td, *J* = 6.9, 1.4 Hz, 1 H), 6.68 (d, *J* = 0.8 Hz, 1 H); ^{13}C NMR (125 MHz, acetone-d_6) δ 150.6, 142.4, 136.5, 129.5, 127.3,

127.1, 124.5, 122.8, 118.8, 112.8, 94.7; HRMS (ESI) calcd for $C_{11}H_9N_2S$ (M+H) 201.0481, found 201.0480.

2-Cyclohexenylpyrazolo[1,5-a]pyridine (3f): starting from 39.6 mg of **1a** and 48 μL of 1-ethynylcyclohexene (added in two batches), 22 mg of **3f** was obtained following the general procedures as yellow solid; mp 48–50 ºC (lit.[3] 44–45 ºC); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.39 (d, *J* = 7.0 Hz, 1 H), 7.42 (d, J = 8.9 Hz, 1 H), 7.04–7.01 (m, 1 H), 6.67–6.63 (m, 1 H), 6.57–6.55 (m, 1 H), 6.48 (s, 1 H), 2.56–2.52 (m, 2 H), 2.27–2.22 (m, 2 H), 1.83–1.67 (m, 4 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.7, 141.1, 130.4, 128.4, 126.8, 123.2, 117.7, 111.2, 92.6, 26.3, 25.7, 22.8, 22.6; HRMS (ESI) calcd for $C_{13}H_{15}N_2$ (M+H) 199.1230, found 199.1226.

2-Phenylpyrazolo[1,5-a]pyridin-3-yl acetate (4): starting from 42.4 mg of **1b** and 44 μL of **2a** (added in two batches), 12 mg of **4** was obtained following the general procedures as beige solid; mp 95–96 ºC (lit.[4,5] 66–67 ºC); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.37 (d, *J* = 7.0 Hz, 1 H), 7.92 (d, *J* = 7.3 Hz, 2 H), 7.47 (t, *J* = 7.5 Hz, 2 H), 7.41–7.37 (m, 1 H), 7.31 (d, *J* = 9.1 Hz, 1 H), 7.14–7.03 (m, 1 H), 6.74 (t, *J* = 6.4 Hz, 1 H), 2.41 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.8, 143.3, 133.1, 131.4, 128.7, 128.5, 128.4, 127.2, 123.1, 121.9, 116.0, 112.0, 20.7; HRMS (ESI) calcd for $C_{15}H_{13}N_2O_2$ (M+H) 253.0972, found 253.0966.

5-Methyl-2-phenylpyrazolo[1,5-*a*]pyridine (3i): starting from 42.4 mg of **1d** and 44 μL of **2a** (added in two batches), 20 mg of **3i** was obtained following the general procedures as off-white solid; mp 154–156 ºC; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.35 (d, *J* = 7.1 Hz, 1 H), 7.97–7.93 (m, 2 H), 7.47–7.26 (m, 4 H), 6.66 (s, 1 H), 6.56 (dd, *J* = 7.1, 1.9 Hz, 1 H), 2.37 (s, 3 H); ^{13}C MR (125 MHz, acetone-d_6) δ 154.2, 142.9, 135.2, 134.8, 129.6, 129.2, 128.9, 127.2, 117.2, 115.4, 93.2, 21.2; HRMS (ESI) calcd for $C_{14}H_{13}N_2$ (M+H) 209.1073, found 209.1070.

Methyl 2-phenylpyrazolo[1,5-*a*]pyridine-5-carboxylate (3j): starting from 51.3 mg of **1f** and 44 μL of **2a** (added in two batches), 37 mg of **3j** was obtained following the general procedures as off-white solid; mp 181–183 ºC; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.49 (dt, *J* = 7.3, 0.9 Hz, 1 H), 8.29 (dd, *J* = 1.7, 0.9 Hz, 1 H), 7.99–7.96 (m, 2 H), 7.50–7.44 (m, 2 H), 7.42–7.36 (m, 1 H), 7.32 (dd, *J* = 7.3, 1.9 Hz, 1 H), 7.00 (d, *J* =

0.6 Hz, 1 H), 3.96 (s, 3 H); ^{13}C NMR (125 MHz, DMSO-d_6) δ 165.0, 153.6, 140.2, 132.2, 128.92, 128.90, 128.8, 126.1, 124.8, 120.6, 110.6, 97.2, 52.5; HRMS (ESI) calcd for $C_{15}H_{13}N_2O_2$ (M+H) 253.0972, found 253.0972.

4,6-Dimethyl-2-phenylpyrazolo[1,5-*a*]pyridine (3k): starting from 45.2 mg of **1g** and 44 μL of **2a** (added in two batches), ~12 mg of **3k** was obtained following the general procedures as yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.15 (s, 1 H), 7.98–7.95 (m, 2 H), 7.47–7.32 (m, 3 H), 6.73 (s, 1 H), 6.72 (s, 1 H), 2.46 (s, 3 H), 2.29 (s, 3 H); ^{13}C NMR (125 MHz, acetone-d_6) δ 152.1, 141.1, 133.9, 128.6, 128.0, 126.9, 126.0, 125.3, 124.0, 121.7, 92.0, 17.2, 17.1; HRMS (ESI) calcd for $C_{15}H_{15}N_2$ (M+H) 223.1230, found 223.1228.

6-Bromo-2-phenylpyrazolo[1,5-*a*]pyridine (3l): starting from 55.4 mg of **1i** and 44 μL of **2a** (added in two batches), 21 mg of **3l** (upper spot) was obtained following the general procedures as off-white solid; mp 118–121 ºC; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.63 (dt, *J* = 1.7, 0.8 Hz, 1 H), 7.96–7.92 (m, 2 H), 7.49–7.35 (m, 4 H), 7.18 (d, *J* = 1.7 Hz, 1 H), 6.81 (d, *J* = 0.7 Hz, 1 H); ^{13}C NMR (100 MHz, acetone-d_6) δ 153.7, 140.2, 133.0, 128.8, 128.7, 128.5, 126.8, 126.3, 118.8, 105.8, 94.5; HRMS (ESI) calcd for $C_{13}H_{10}{}^{79}BrN_2$ (M+H) 273.0022, found 273.0017.

4-Bromo-2-phenylpyrazolo[1,5-*a*]pyridine (3l'): 10.6 mg of **3l'** (lower spot) was obtained from the above reaction as off-white solid; mp 111–112 ºC; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.44 (dt, *J* = 7.0 Hz, 0.8 Hz, 1 H), 7.99–7.95 (m, 2 H), 7.50–7.36 (m, 3 H), 7.31 (dd, *J* = 7.3, 0.8 Hz, 1 H), 6.93 (d, *J* = 0.9 Hz, 1 H), 6.63 (t, *J* = 7.1 Hz, 1 H); ^{13}C NMR (125 MHz, acetone-d_6) δ 154.4, 142.6, 133.8, 129.8, 129.7, 129.1, 127.5, 127.4, 113.1, 111.4, 95.9; HRMS (ESI) calcd for $C_{13}H_{10}{}^{79}BrN_2$ (M+H) 273.0022, found 273.0020.

Methyl 2-phenylpyrazolo[1,5-*a*]pyridine-6-carboxylate (3m): starting from 51.3 mg of **1j** and 44 μL of **2a** (added in two batches), 37 mg of **3m** was obtained under the general Cu-mediated conditions as off-white solid; mp 136–138 ºC; ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.21 (s, 1 H), 7.99–7.96 (m, 2 H), 7.66–7.37 (m, 5 H), 6.86 (d, *J* = 0.7 Hz, 1 H), 3.96 (s, 3 H); ^{13}C NMR (100 MHz, acetone-d_6) δ 165.9, 157.0, 143.7, 133.1, 130.0, 129.8, 127.5, 123.7, 118.6, 116.9, 111.9, 96.0, 52.8; HRMS (ESI) calcd for

$C_{15}H_{13}N_2O_2$ (M+H) 253.0972, found 253.0971.

2-Phenylpyrazolo[5,1-*a*]isoquinoline (3n): starting from 49.7 mg of **1k** and 44 μL of **2a** (added in two batches), 36 mg of **3n** was obtained following the general procedures as off-white solid; mp 111–113 ºC (lit.[2] 115–117 ºC); ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.27 (d, *J* = 7.4 Hz, 1 H), 8.15–8.12 (m, 1 H), 8.03–7.99 (m, 2 H), 7.74–7.71 (m, 1 H), 7.61–7.35 (m, 5 H), 7.29 (d, *J* = 0.7 Hz, 1 H), 7.00 (d, *J* = 7.4 Hz, 1 H); ^{13}C NMR (125 MHz, acetone-d_6) δ 152.6, 139.6, 133.5, 128.9, 128.7, 128.2, 128.1, 127.8, 127.4, 126.5, 126.1, 124.5, 123.7, 112.1, 94.6; HRMS (ESI) calcd for $C_{17}H_{13}N_2$ (M+H) 245.1073, found 245.1071.

2-(*p*-Tolyl)-3-(*p*-tolylethynyl)pyrazolo[1,5-*a*]pyridine (5b): to an oven-dried 25 mL round-bottom flask equipped with a stir bar were added 39.6 mg of **1a** (0.20 mmol), $Pd(OAc)_2$ (2.3 mg, 0.01 mmol, 5 mol %), d^{t}bpy (3.2 mg, 0.01 mmol, 5 mol %), Ag_2O (139 mg, 0.6 mmol, 3 equiv), and 1,4-dioxane (5 mL). The mixture was stirred for 5 min at 100 ºC. A solution containing 51 μL of **2b** (0.4 mmol, 2 equiv), $Pd(OAc)_2$ (2.3 mg, 0.01 mmol, 5 mol %), and d^{t}bpy (3.2 mg, 0.01 mmol, 5 mol %) in 1,4-dioxane (5 mL) was added slowly over 5 h using a syringe pump under air. The reaction continued for another 12 h at 100 ºC before being cooled to room temperature. EtOAc was added and the insolubles were filtered off and washed with EtOAc. Combined EtOAc solution was washed with water and dried over Na_2SO_4, concentrated under reduced pressure, and purified via column chromatography to afford 15 mg of **3b** and 15 mg of **5b**. Compound **5b** is a yellow solid and deterioriates upon standing; mp 154–157 ºC; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.46 (d, *J* = 9.3 Hz, 1 H), 8.22 (d, *J* = 10.9 Hz, 2 H), 7.73 (d, *J* = 11.8 Hz, 1 H), 7.46 (d, *J* = 10.7 Hz, 2 H), 7.31 (d, *J* = 10.7 Hz, 2 H), 7.23–7.17 (m, 3 H), 6.83 (td, *J* = 9.1, 1.6 Hz, 1 H), 2.42 (s, 3 H), 2.39 (s, 3 H); ^{13}C NMR (125 MHz, acetone-d_6) δ 153.1, 143.2, 138.9, 138.2, 131.0, 130.2, 129.4, 129.3, 129.2, 127.4, 125.5, 121.1, 117.4, 113.7, 94.4, 90.6, 81.1, 20.7, 20.6; HRMS (ESI) calcd for $C_{23}H_{18}N_2$ (M+H) 323.1543, found 323.1544.

References and notes for the experimental details

1 C. Y. Legault, and A. B. Charette, *J. Org. Chem.*, 2003, **68**, 7119.

2 J. J. Mousseau, A. Fortier and A. B. Charette, *Org. Lett.*, 2010, **12**, 516.

3 S. Ding, Y. Yan, and N. Jiao, *Chem. Commun.*, ASAP doi: 10.1039/c2cc33706a.

4 J. J. Mousseau, J. A. Bull, C. L. Ladd, A. Fortier, D. S. Roman, and A. B. Charette, *J. Org. Chem.*, 2011, **76**, 8243.

5 We are not sure why the literature melting point is much lower than that of our compound. The NMR data are the same. Maybe the forms of crystal are different.