

Supporting Information

Rhodium(III)-catalyzed vinylic sp² C-H Bond Functionalization: Efficient Synthesis of Pyrido[1,2- α]benzimidazoles and Imidazo[1,2- α]pyridines

Lin Dong*[a], Ji-Rong Huang^[a], Chuan-Hua Qu^[a], Qian-Ru Zhang^[a], Wei Zhang^[a], Bo Han^[b],
and Cheng Peng*[b]

E-mail: dongl@scu.edu.cn

Key laboratory of Drug-Targeting and Drug Delivery System of the Education Ministry

Department of Medicinal Chemistry, West China School of Pharmacy, Sichuan University

Chengdu, 610041 (China)

Table of Contents

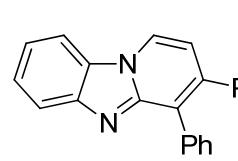
- 1. General Methods**
- 2. General Procedure for Synthesis of Aza-Fused Polycyclic Quinolines**
- 3. Competition Experiments**
- 4. NMR Spectra**

1. General Methods

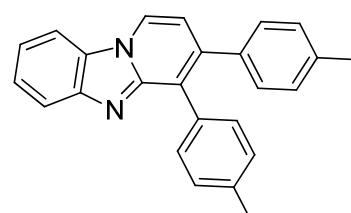
NMR data were obtained for ^1H at 400 MHz, and for ^{13}C at 100 MHz. Chemical shifts were reported in ppm from tetramethylsilane with the solvent resonance as the internal standard in CDCl_3 or DMSO-d_6 solution. ESI HRMS was recorded on a Bruker Apex-2. Infrared spectra were recorded on a VECTOR 22. UV detection was monitored at 220 nm. TLC was performed on glass-backed silica plates. Column chromatography was performed on silica gel (200-300 mesh), eluting with methanol, ethyl acetate, methylene dichloride and petroleum ether (EtOAc/PE or MeOH/DCM). All chemicals were used without purification as commercially available unless otherwise noted. *N*-vinyl azoles substrates were prepared according to the literature procedures.^[1] Alkynes **2b-2e**,^[2] **2j**,^[3] **2k**,^[4] **2l**,^[5] were synthesized according to the literature procedures.

2. General Procedure for Synthesis of pyrido[1,2- α]benzimidazole and imidazo[1,2- α]pyridines

N-vinyl benzimidazole **1a** (14.4 mg, 0.1 mmol, 1.0 equiv), diphenyl acetylene **2a** (35.6 mg, 0.2 mmol, 2.0 equiv), $[\text{Cp}^*\text{RhCl}_2]_2$ (3.1 mg, 5 mol %, 0.05 equiv) and $\text{Cu}(\text{OAc})_2 \cdot \text{H}_2\text{O}$ (24 mg, 0.12 mmol, 1.2 equiv) were stirred in toluene (1.0 mL) under Ar at 110 °C for 12 h. TLC analyses of the mixture confirmed formation of **3aa**. The reaction mixture was neutralized with K_2CO_3 , and flash chromatography on silica gel ($\text{EtOAc/PE} = 1/10$) to give the product **3aa** as a yellow solid (29.1 mg, 91%).



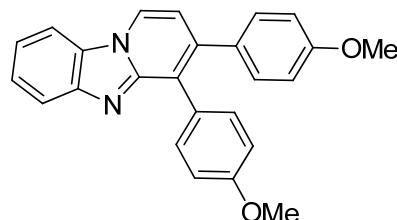
3,4-diphenylbenzo[4,5]imidazo[1,2- α]pyridine (3aa). 12 h, 91% yield; ^1H NMR (400 MHz, CDCl_3): δ 8.48 (d, $J = 7.2$ Hz, 1H), 7.99 (d, $J = 8.0$ Hz, 1H), 7.92 (d, $J = 8.0$ Hz, 1H), 7.52 (t, $J = 7.6$ Hz, 1H), 7.44-7.20 (m, 11H), 7.00 (d, $J = 7.2$ Hz, 1H) ppm; ^{13}C NMR (100 MHz, CDCl_3): δ 148.8, 145.1, 139.3, 135.1, 131.0, 129.6, 128.9, 128.1, 128.0, 127.7, 127.4, 125.4, 123.5, 121.0, 120.4, 113.7, 110.2 ppm. IR (KBr): ν 3052, 1497, 1482, 1228, 760, 737, 699 cm^{-1} . ESI HRMS: calcd. for $\text{C}_{23}\text{H}_{16}\text{N}_2 + \text{H}$ 321.1392, found 321.1395.



3,4-di-p-tolylbenzo[4,5]imidazo[1,2- α]pyridine (3ab). 7 h, 99% yield; ^1H NMR (400 MHz, CDCl_3): δ 8.43 (d, $J = 6.8$ Hz, 1H), 7.98 (d, $J = 8.4$ Hz, 1H), 7.89 (d, $J = 8.4$ Hz, 1H), 7.49 (t, $J = 8.0$ Hz, 1H), 7.36 (d, $J = 7.6$ Hz, 1H), 7.32 (d, $J = 8.0$ Hz, 2H), 7.16-7.06 (m, 6H), 6.97 (d, $J = 6.8$ Hz, 1H), 2.36 (s, 3H), 2.33 (s, 3H) ppm; ^{13}C NMR (100 MHz, CDCl_3): δ 149.1, 145.1, 139.9, 137.2, 137.1, 136.5, 132.3, 130.8, 129.5, 128.9, 128.8, 128.0, 125.2, 123.2, 120.8, 120.4,

113.8, 110.1, 21.4, 21.2 ppm. IR (KBr): ν 3052, 3021, 2919, 1481, 1440, 820, 780, 736 cm^{-1} . ESI HRMS: calcd. for $\text{C}_{25}\text{H}_{20}\text{N}_2\text{H}$ 349.1705, found 349.1706.

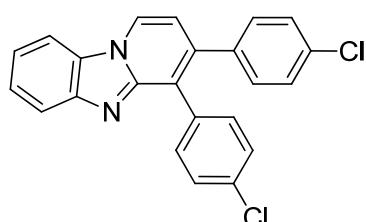
3,4-bis(4-methoxyphenyl)benzo[4,5]imidazo[1,2- α]pyridine (3ac). 7 h, 69% yield; ^1H NMR (400



MHz, CDCl_3): δ 8.42 (d, $J = 7.2$ Hz, 1H), 7.96 (d, $J = 8.4$ Hz, 1H), 7.89 (d, $J = 8.0$ Hz, 1H), 7.51-7.47 (m, 1H), 7.37-7.34 (m, 3H), 7.14 (d, $J = 8.8$ Hz, 2H), 6.97 (d, $J = 7.2$ Hz, 1H), 6.89 (d, $J = 8.8$ Hz, 2H), 6.79 (d, $J = 8.4$ Hz, 2H), 3.82 (s, 3H), 3.79 (s, 3H) ppm; ^{13}C NMR (100 MHz, CDCl_3): δ 158.9, 158.8, 149.2, 145.1, 139.5, 132.3, 131.8, 130.9, 129.0,

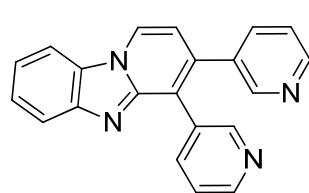
127.6, 127.4, 125.3, 123.1, 120.8, 120.3, 113.9, 113.8, 113.6, 110.2, 55.2 ppm. IR (KBr): ν 3003, 2961, 2935, 2838, 1607, 1248, 1030, 835, 788, 742 cm^{-1} . ESI HRMS: calcd. for $\text{C}_{25}\text{H}_{20}\text{N}_2\text{O}_2\text{H}$ 381.1603, found 381.1605.

3,4-bis(4-chlorophenyl)benzo[4,5]imidazo[1,2- α]pyridine (3ad). 7 h, 75% yield; ^1H NMR (400 MHz,



CDCl_3): δ 8.48 (d, $J = 6.8$ Hz, 1H), 7.97 (d, $J = 8.4$ Hz, 1H), 7.92 (d, $J = 8.0$ Hz, 1H), 7.52 (t, $J = 8.0$ Hz, 1H), 7.41-7.31 (m, 5H), 7.26 (d, $J = 8.4$ Hz, 2H), 7.12 (d, $J = 8.4$ Hz, 2H), 6.94 (d, $J = 6.8$ Hz, 1H) ppm; ^{13}C NMR (100 MHz, CDCl_3): δ 148.3, 145.0, 138.9, 137.4, 133.9, 133.8, 133.3, 132.4, 130.9, 128.9, 128.6, 127.1, 125.7, 123.0, 121.4, 120.4, 113.2, 110.3

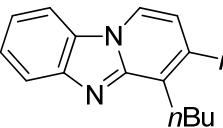
ppm. IR (KBr): ν 3060, 2924, 1499, 1090, 832, 778, 745 cm^{-1} . ESI HRMS: calcd. for $\text{C}_{23}\text{H}_{14}\text{Cl}_2\text{N}_2\text{H}$ 389.0612, found 389.0612.

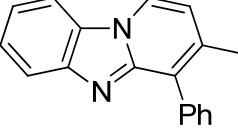


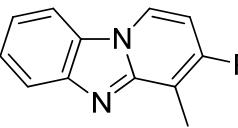
3,4-di(pyridin-3-yl)benzo[4,5]imidazo[1,2- α]pyridine (3ae). 7 h, 99% yield; ^1H NMR (400 MHz, CDCl_3): δ 8.59-8.53 (m, 5H), 7.98-7.92 (m, 3H), 7.55 (t, $J = 8.0$ Hz, 1H), 7.48 (d, $J = 8.0$ Hz, 1H), 7.43 (t, $J = 7.6$ Hz, 1H), 7.37-7.34 (m, 1H), 7.24-7.21 (m, 1H), 7.00 (d, $J = 7.2$ Hz, 1H) ppm; ^{13}C NMR (100 MHz,

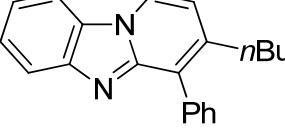
CDCl_3): δ 151.5, 150.1, 149.0, 148.9, 147.9, 145.0, 138.6, 137.2, 136.9, 128.8, 126.0, 125.4, 124.7, 123.3, 123.1, 121.8, 120.4, 112.8, 110.4 ppm. IR (KBr): ν 3054, 3036, 2923, 1493, 1406, 800, 743, 712 cm^{-1} . ESI HRMS: calcd. for $\text{C}_{21}\text{H}_{14}\text{N}_4\text{Na}$ 345.1116, found 345.1116.

3,4-dibutylbenzo[4,5]imidazo[1,2- α]pyridine (3af). 7 h, 86% yield; ^1H NMR (400 MHz, CDCl_3): δ

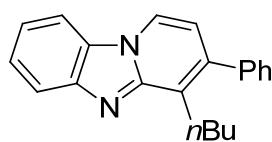
 8.20 (d, $J = 6.8$ Hz, 1H), 7.96 (d, $J = 8.4$ Hz, 1H), 7.80 (d, $J = 8.0$ Hz, 1H), 7.47 (td, $J = 8.4, 1.2$ Hz, 1H), 7.29 (t, $J = 8.0$ Hz, 1H), 6.66 (d, $J = 7.2$ Hz, 1H), 3.11 (t, $J = 8.0$ Hz, 2H), 2.71 (t, $J = 8.0$ Hz, 2H), 1.78-1.70 (m, 2H), 1.67-1.59 (m, 2H), 1.55-1.42 (m, 4H), 1.00-0.95 (m, 6H) ppm; ^{13}C NMR (100 MHz, CDCl_3): δ 149.5, 144.5, 140.6, 129.2, 128.3, 125.0, 121.8, 120.2, 119.6, 113.2, 110.1, 32.8, 32.0, 31.7, 27.4, 23.1, 22.7, 14.1, 14.0 ppm. IR (KBr): ν 2958, 2866, 1638, 1609, 1493, 1466, 764, 739 cm^{-1} . ESI HRMS: calcd. for $\text{C}_{19}\text{H}_{24}\text{N}_2+\text{H}$ 281.2018, found 281.2019.

 **3-methyl-4-phenylbenzo[4,5]imidazo[1,2- α]pyridine (3ag).** 9 h, 59.1% yield; ^1H NMR (400 MHz, CDCl_3): δ 8.32 (d, $J = 6.8$ Hz, 1H), 7.93 (d, $J = 8.4$ Hz, 1H), 7.85 (d, $J = 8.0$, 1H), 7.56-7.45 (m, 6H), 7.33 (t, $J = 7.6$ Hz, 1H), 6.78 (d, $J = 7.2$ Hz, 1H), 2.30 (s, 3H) ppm; ^{13}C NMR (100 MHz, CDCl_3): δ 149.0, 144.8, 136.9, 135.5, 129.9, 129.0, 128.8, 128.5, 127.9, 125.1, 123.0, 120.5, 120.1, 114.0, 110.0, 20.0 ppm. IR (KBr): ν 3054, 2946, 2916, 1630, 1605, 1488, 1433, 777, 736 cm^{-1} . ESI HRMS: calcd. for $\text{C}_{18}\text{H}_{14}\text{N}_2+\text{H}$ 259.1235, found 259.1237.

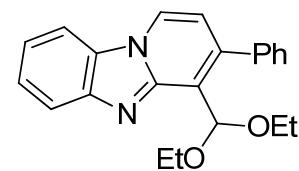
 **4-methyl-3-phenylbenzo[4,5]imidazo[1,2- α]pyridine (3ag').** 9 h, 31.9% yield; ^1H NMR (400 MHz, CDCl_3): δ 8.33 (d, $J = 6.8$ Hz, 1H), 7.99 (d, $J = 8.0$ Hz, 1H), 7.87 (d, $J = 8.4$ Hz, 1H), 7.54-7.47 (m, 4H), 7.43-7.40 (m, 2H), 7.36 (t, $J = 7.6$ Hz, 1H), 6.83 (d, $J = 7.2$ Hz, 1H), 2.67 (s, 3H) ppm; ^{13}C NMR (100 MHz, CDCl_3): δ 149.5, 144.7, 140.4, 139.4, 129.1, 128.4, 127.8, 125.4, 124.0, 121.8, 120.9, 119.8, 113.4, 110.4, 15.0 ppm. IR (KBr): ν 3056, 2925, 1631, 1602, 1501, 1483, 765, 742, 704 cm^{-1} . ESI HRMS: calcd. for $\text{C}_{18}\text{H}_{14}\text{N}_2+\text{H}$ 259.1235, found 259.1236.

 **3-butyl-4-phenylbenzo[4,5]imidazo[1,2- α]pyridine (3ah).** 7 h, 63% yield; ^1H NMR (400 MHz, CDCl_3): δ 8.37 (d, $J = 7.2$ Hz, 1H), 7.90 (d, $J = 8.4$ Hz, 1H), 7.86 (d, $J = 8.0$ Hz, 1H), 7.54-7.50 (m, 2H), 7.47-7.42 (m, 4H), 7.34-7.30 (m, 1H), 6.83 (d, $J = 6.8$ Hz, 1H), 2.56 (t, $J = 8.0$ Hz, 2H), 1.59-1.51 (m, 2H), 1.31-1.21 (m, 2H), 0.82 (t, $J = 7.6$ Hz, 3H) ppm; ^{13}C NMR (100 MHz, CDCl_3): δ 149.2, 144.8, 141.8, 135.5, 130.0, 129.0, 128.8, 128.5, 127.9, 125.1, 123.4, 120.6, 120.2, 112.8, 110.0, 32.8, 32.5, 22.4, 13.8 ppm. IR (KBr): ν 2953, 2919, 2863, 1631, 1605, 1489, 733, 701 cm^{-1} . ESI HRMS: calcd. for $\text{C}_{21}\text{H}_{20}\text{N}_2+\text{H}$ 301.1705, found 301.1705.

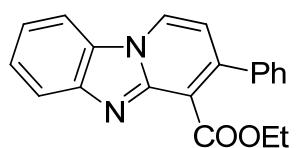
4-butyl-3-phenylbenzo[4,5]imidazo[1,2- α]pyridine (3ah'). 7 h, 36% yield; ^1H NMR (400 MHz, CDCl_3): δ 8.33 (d, $J = 7.2$ Hz, 1H), 8.01 (d, $J = 8.4$ Hz, 1H), 7.89 (d, $J = 8.0$ Hz, 1H), 7.55-7.34 (m, 7H), 6.79 (d, $J = 6.8$ Hz, 1H), 3.07(t, $J = 8.0$ Hz, 2H), 1.78-1.70 (m, 2H), 1.34-1.28 (m, 2H), 0.80 (t, $J = 7.6$ Hz, 3H) ppm; ^{13}C NMR (100 MHz, CDCl_3): δ 140.4, 139.8, 129.1, 128.8, 128.4, 127.7, 125.3, 121.8, 120.8, 119.9, 113.7, 110.3, 31.5, 28.3, 22.7, 13.8 ppm. IR (KBr): ν 3051, 2959, 2927, 2852, 1632, 1602, 1499, 801, 765, 703 cm^{-1} . ESI HRMS: calcd. for $\text{C}_{21}\text{H}_{20}\text{N}_2+\text{H}$ 301.1705, found 301.1706.



3-(diethoxymethyl)-4-phenylbenzo[4,5]imidazo[1,2- α]pyridine (3ai). 7 h, 68.6% yield; ^1H NMR (400 MHz, CDCl_3): δ 8.49 (d, $J = 7.2$ Hz, 1H), 7.94 (d, $J = 8.0$ Hz, 1H), 7.91 (d, $J = 7.6$ Hz, 1H), 7.58-7.47 (m, 6H), 7.39-7.35 (m, 1H), 7.27 (d, $J = 7.6$ Hz, 1H), 5.22 (s, 1H), 3.64-3.57 (m, 2H), 3.44-3.37 (m, 2H), 1.19 (t, $J = 7.2$ Hz, 6H) ppm; ^{13}C NMR (100 MHz, CDCl_3): δ 148.1, 144.7, 137.7, 133.9, 130.2, 129.4, 128.9, 128.4, 125.4, 124.2, 121.3, 120.4, 110.3, 108.9, 99.6, 62.9, 15.1 ppm. IR (KBr): ν 3056, 2973, 2925, 2872, 1489, 1104, 1059, 739, 700 cm^{-1} . ESI HRMS: calcd. for $\text{C}_{22}\text{H}_{22}\text{N}_2\text{O}_2+\text{H}$ 347.1760, found 347.1760.



4-(diethoxymethyl)-3-phenylbenzo[4,5]imidazo[1,2- α]pyridine (3ai'). 7 h, 28.4% yield; ^1H NMR (400 MHz, CDCl_3): δ 8.40 (d, $J = 7.2$ Hz, 1H), 8.06 (d, $J = 8.0$ Hz, 1H), 7.86 (d, $J = 8.4$ Hz, 1H), 7.53-7.42 (m, 6H), 7.35 (t, $J = 7.6$ Hz, 1H), 6.77 (d, $J = 7.2$ Hz, 1H), 5.92 (s, 1H), 3.76-3.70 (m, 2H), 3.50-3.42 (m, 2H), 1.12 (t, $J = 7.2$ Hz, 6H) ppm; ^{13}C NMR (100 MHz, CDCl_3): δ 147.0, 145.1, 141.6, 139.3, 129.1, 128.5, 127.9, 127.9, 125.4, 124.4, 124.0, 120.9, 120.5, 113.6, 110.0, 100.6, 63.6, 15.1 ppm. IR (KBr): ν 2973, 2925, 2872, 1635, 1603, 1108, 1062, 739, 699 cm^{-1} . ESI HRMS: calcd. for $\text{C}_{22}\text{H}_{22}\text{N}_2\text{O}_2+\text{Na}$ 369.1579, found 369.1579.



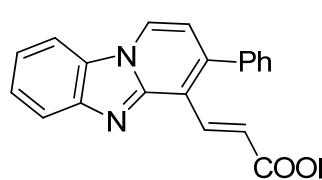
ethyl 3-phenylbenzo[4,5]imidazo[1,2- α]pyridine-4-carboxylate (3aj). 7 h, 49% yield; ^1H NMR (400 MHz, CDCl_3): δ 8.50 (d, $J = 7.2$ Hz, 1H), 7.99 (d, $J = 8.0$ Hz, 1H), 7.94 (d, $J = 8.4$ Hz, 1H), 7.56-7.41 (m, 7H), 7.28 (d, $J = 7.2$ Hz, 1H), 4.09 (q, $J = 7.2$ Hz, 2H), 0.97 (t, $J = 7.6$ Hz, 3H) ppm; ^{13}C NMR (100 MHz, CDCl_3): δ 167.1, 147.7, 145.2, 135.3, 132.6, 130.1, 129.3, 128.9, 128.5, 128.3, 126.0, 123.9, 122.2, 120.9, 110.6, 110.3, 61.5, 13.5 ppm. IR (KBr): ν 3058, 2977, 1712, 1476, 1327, 1230, 1137, 1027, 743, 698 cm^{-1} . ESI HRMS: calcd. for $\text{C}_{20}\text{H}_{16}\text{N}_2\text{O}_2+\text{Na}$ 339.1109, found 339.1109.

diethyl (3-phenylbenzo[4,5]imidazo[1,2- α]pyridin-4-yl)phosphonate (3ak). 7 h, 67% yield; ^1H NMR

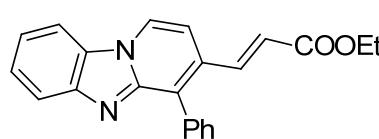


(400 MHz, CDCl_3): δ 8.52 (dd, $J = 7.2$, 3.6 Hz, 1H), 7.97 (d, $J = 8.0$ Hz, 1H), 7.94 (d, $J = 8.4$ Hz, 1H), 7.60-7.58 (m, 2H), 7.54-7.40 (m, 6H), 4.00-3.92 (m, 2H), 3.89-3.83 (m, 2H), 1.17 (t, $J = 7.2$ Hz, 6H) ppm; ^{13}C NMR (100 MHz, CDCl_3): δ 145.1, 137.0, 135.0, 135.0, 130.0, 128.8, 127.9, 126.1, 123.5, 123.4, 122.2, 121.1, 112.6, 112.5, 110.7, 62.3, 62.3, 16.1, 16.1 ppm. IR (KBr): ν 2986, 1481, 1323, 1229, 1048, 1019, 771, 739 cm^{-1} . ESI HRMS: calcd. for $\text{C}_{21}\text{H}_{21}\text{N}_2\text{O}_3\text{P}+\text{Na}$ 403.1187, found 403.1189.

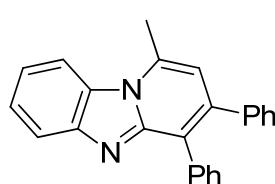
(E)-ethyl 3-(3-phenylbenzo[4,5]imidazo[1,2- α]pyridin-4-yl)acrylate (3al). 12 h, 20.5% yield; ^1H NMR



(400 MHz, CDCl_3): δ 8.44 (d, $J = 6.8$ Hz, 1H), 8.21 (d, $J = 16.0$ Hz, 1H), 8.03 (d, $J = 8.0$ Hz, 1H), 7.90 (d, $J = 8.0$ Hz, 1H), 7.86 (d, $J = 16.0$ Hz, 1H), 7.58-7.39 (m, 7H), 6.90 (d, $J = 6.8$ Hz, 1H), 4.24 (q, $J = 7.2$ Hz, 2H), 1.32 (t, $J = 7.2$ Hz, 3H) ppm; ^{13}C NMR (100 MHz, CDCl_3): δ 168.0, 146.8, 145.3, 144.8, 138.2, 137.7, 129.7, 128.7, 128.6, 128.3, 125.9, 125.2, 124.6, 121.7, 120.5, 120.3, 113.4, 110.2, 60.3, 14.3 ppm. IR (KBr): ν 3058, 2980, 1706, 1601, 1283, 1182, 741, 703 cm^{-1} . ESI HRMS: calcd. for $\text{C}_{22}\text{H}_{18}\text{N}_2\text{O}_2+\text{H}$ 343.1447, found 343.1449

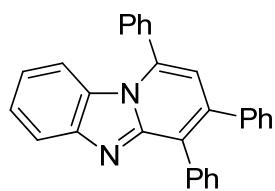


(E)-ethyl 3-(4-phenylbenzo[4,5]imidazo[1,2- α]pyridin-3-yl)acrylate (3al'). 12 h, 55.5% yield; ^1H NMR (400 MHz, CDCl_3): δ 8.42 (d, $J = 7.2$ Hz, 1H), 7.96 (d, $J = 8.4$ Hz, 1H), 7.89 (d, $J = 8.0$ Hz, 1H), 7.69 (d, $J = 16.0$ Hz, 1H), 7.57-7.48 (m, 6H), 7.40 (t, $J = 7.6$ Hz, 1H), 7.13 (d, $J = 7.2$ Hz, 1H), 6.49 (d, $J = 16.0$ Hz, 1H), 4.22 (q, $J = 7.2$ Hz, 2H), 1.29 (t, $J = 7.2$ Hz, 3H) ppm; ^{13}C NMR (100 MHz, CDCl_3): δ 166.3, 148.1, 145.2, 140.8, 133.5, 132.5, 131.8, 130.8, 129.2, 128.9, 128.5, 125.7, 123.8, 122.0, 121.3, 120.7, 110.3, 107.9, 60.7, 14.2 ppm. IR (KBr): ν 3060, 2988, 1705, 1627, 1285, 1183, 786, 740 cm^{-1} . ESI HRMS: calcd. for $\text{C}_{22}\text{H}_{18}\text{N}_2\text{O}_2+\text{H}$ 343.1447, found 343.1449.

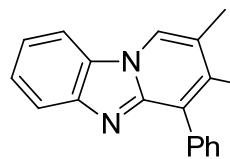


1-methyl-3,4-diphenylbenzo[4,5]imidazo[1,2- α]pyridine (3ba). 8 h, 66% yield; ^1H NMR (400 MHz, CDCl_3): δ 8.18 (d, $J = 8.4$ Hz, 1H), 7.98 (d, $J = 8.0$ Hz, 1H), 7.50 (t, $J = 7.6$ Hz, 1H), 7.41-7.38 (m, 2H), 7.35-7.17 (m, 9H), 6.77 (s, 1H), 3.11 (s, 3H) ppm; ^{13}C NMR (100 MHz, CDCl_3): δ 149.9, 145.6, 140.2, 139.4, 137.2, 135.6, 131.3, 130.2, 129.6, 128.0, 128.0, 127.5, 127.3, 125.6, 124.9, 120.7, 120.3, 114.4, 114.1, 21.4 ppm.

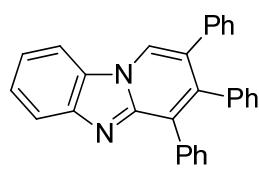
IR (KBr): ν 3049, 2919, 2850, 1632, 1602, 1501, 1440, 763, 733, 698 cm^{-1} . ESI HRMS: calcd. for $\text{C}_{24}\text{H}_{18}\text{N}_2+\text{H}$ 335.1548, found 335.1548.



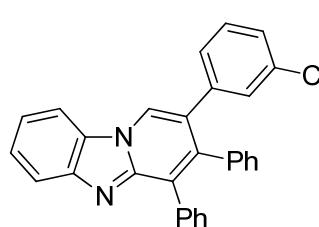
1,3,4-triphenylbenzo[4,5]imidazo[1,2- α]pyridine (3ca). 12 h, 74% yield; ^1H NMR (400 MHz, CDCl_3): δ 7.94 (d, $J = 8.4$ Hz, 1H), 7.67-7.62 (m, 5H), 7.48 (d, $J = 7.2$ Hz, 2H), 7.40-7.31 (m, 4H), 7.26-7.23 (m, 5H), 6.97 (t, $J = 8.0$ Hz, 1H), 6.86 (s, 1H), 6.65 (d, $J = 8.4$ Hz, 1H) ppm; ^{13}C NMR (100 MHz, CDCl_3): δ 149.8, 145.6, 140.0, 139.5, 139.3, 135.5, 134.4, 131.3, 130.0, 129.7, 129.4, 129.1, 129.1, 128.1, 128.0, 127.6, 127.3, 126.9, 124.8, 120.3, 120.2, 115.3, 114.5 ppm. IR (KBr): ν 3059, 3034, 1598, 1482, 1450, 1313, 766, 743 cm^{-1} . ESI HRMS: calcd. for $\text{C}_{29}\text{H}_{20}\text{N}_2+\text{H}$ 397.1705, found 397.1705.



2-methyl-3,4-diphenylbenzo[4,5]imidazo[1,2- α]pyridine (3da). 10 h, 90% yield; ^1H NMR (400 MHz, CDCl_3): δ 8.34 (s, 1H), 7.94 (d, $J = 8.0$ Hz, 1H), 7.91 (d, $J = 8.0$ Hz, 1H), 7.48 (t, $J = 7.6$ Hz, 1H), 7.36 (t, $J = 7.6$ Hz, 1H), 7.31-7.17 (m, 8H), 7.08 (d, $J = 6.8$ Hz, 2H), 2.16 (s, 3H) ppm; ^{13}C NMR (100 MHz, CDCl_3): δ 148.2, 144.8, 142.9, 137.9, 135.4, 130.7, 129.7, 129.2, 128.8, 127.9, 127.8, 127.3, 127.1, 125.1, 121.8, 120.7, 120.3, 120.0, 110.2, 18.6 ppm. IR (KBr): ν 3051, 2958, 2918, 1636, 1600, 1487, 1443, 731, 697 cm^{-1} . ESI HRMS: calcd. for $\text{C}_{24}\text{H}_{18}\text{N}_2+\text{H}$ 335.1548, found 335.1548.

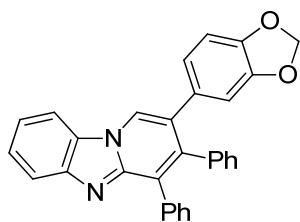


2,3,4-triphenylbenzo[4,5]imidazo[1,2- α]pyridine (3ea). 9 h, 99% yield; ^1H NMR (400 MHz, CDCl_3): δ 8.48 (s, 1H), 7.99 (d, $J = 8.0$, 1H), 7.91 (d, $J = 8.4$ Hz, 1H), 7.53-7.49 (m, 1H), 7.39-7.35 (m, 3H), 7.31-7.23 (m, 6H), 7.16-7.14 (m, 2H), 7.05-6.99 (m, 3H), 6.90-6.87 (m, 2H) ppm; ^{13}C NMR (100 MHz, CDCl_3): δ 148.1, 145.1, 141.0, 137.6, 137.3, 135.5, 131.0, 130.9, 130.0, 129.3, 129.0, 127.9, 127.8, 127.4, 127.3, 127.0, 126.6, 126.6, 125.4, 123.3, 121.0, 120.4, 110.3 ppm. IR (KBr): ν 3056, 3027, 1476, 1319, 1259, 754, 698 cm^{-1} . ESI HRMS: calcd. for $\text{C}_{29}\text{H}_{20}\text{N}_2+\text{H}$ 397.1705, found 397.1707.

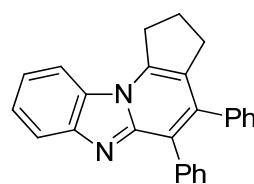


2-(4-chlorophenyl)-3,4-diphenylbenzo[4,5]imidazo[1,2- α]pyridine (3fa). 12 h, 89% yield; ^1H NMR (400 MHz, CDCl_3): δ 8.47 (s, 1H), 7.97 (d, $J = 8.4$ Hz, 1H), 7.92 (d, $J = 8.4$ Hz, 1H), 7.51(t, $J = 8.0$ Hz, 1H), 7.38 (t, $J = 7.2$ Hz, 1H), 7.34-7.32 (m, 2H), 7.28-7.19 (m, 5H), 7.10 (t, $J = 8.8$ Hz, 1H), 7.06-7.02

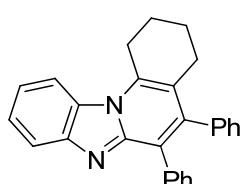
(m, 3H), 6.93 (d, $J = 7.6$ Hz, 1H), 6.87-6.86 (m, 2H) ppm; ^{13}C NMR (100 MHz, CDCl_3): δ 148.0, 145.2, 140.6, 139.5, 137.0, 135.3, 133.8, 130.9, 129.8, 129.6, 129.1, 129.0, 128.3, 127.9, 127.5, 127.2, 126.9, 125.6, 125.3, 123.4, 121.3, 120.6, 110.3 ppm. IR (KBr): ν 3057, 3027, 1599, 1469, 1320, 787, 744, 702 cm^{-1} . ESI HRMS: calcd. for $\text{C}_{29}\text{H}_{19}\text{ClN}_2+\text{H}$ 431.1315, found 431.1315.



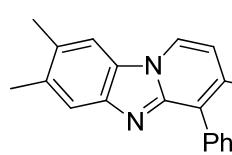
2-(benzo[d][1,3]dioxol-5-yl)-3,4-diphenylbenzo[4,5]imidazo[1,2- α]pyridine (3ga). 8 h, 77% yield; ^1H NMR (400 MHz, CDCl_3): δ 8.44 (s, 1H), 7.97 (d, $J = 8.0$ Hz, 1H), 7.90 (d, $J = 8.0$, 1H), 7.49 (t, $J = 8.0$ Hz, 1H), 7.36 (d, $J = 7.6$ Hz, 1H), 7.33-7.31 (m, 2H), 7.28-7.21 (m, 3H), 7.05-7.03 (m, 3H), 6.89-6.87 (m, 2H), 6.68 (d, $J = 8.0$ Hz, 1H), 6.63 (dd, $J = 8.0, 1.2$ Hz, 1H), 6.56 (d, $J = 1.2$ Hz, 1H), 5.90 (s, 2H) ppm; ^{13}C NMR (100 MHz, CDCl_3): δ 148.1, 147.2, 146.7, 145.1, 141.1, 137.4, 135.5, 131.4, 130.9, 130.9, 129.3, 129.0, 127.8, 127.4, 127.4, 126.7, 126.2, 125.4, 123.6, 123.1, 121.0, 120.5, 110.5, 110.3, 107.9, 101.0 ppm. IR (KBr): ν 3062, 3026, 2895, 2207, 1476, 1232, 1034, 927, 728, 699 cm^{-1} . ESI HRMS: calcd. for $\text{C}_{30}\text{H}_{22}\text{N}_2\text{O}_2+\text{H}$ 441.1603, found 441.1604.



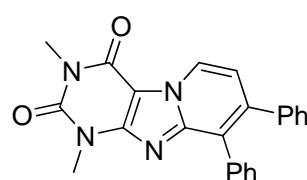
4,5-diphenyl-2,3-dihydro-1H-benzo[4,5]imidazo[1,2- α] cyclopenta [e] pyridine (3ha). 12 h, 53% yield; ^1H NMR (400 MHz, CDCl_3): δ 8.04 (d, $J = 8.0$ Hz, 1H), 7.96 (d, $J = 8.4$ Hz, 1H), 7.47 (t, $J = 7.6$ Hz, 1H), 7.33 (t, $J = 6.8$ Hz, 2H), 7.29-7.19 (m, 7H), 7.12-7.10 (m, 2H), 3.73 (t, $J = 7.6$ Hz, 2H), 2.87 (t, $J = 7.6$ Hz, 2H), 2.41-2.34 (m, 2H) ppm; ^{13}C NMR (100 MHz, CDCl_3): δ 149.7, 145.2, 139.8, 139.0, 138.2, 135.8, 131.3, 129.6, 129.4, 127.8, 127.2, 127.0, 126.1, 124.8, 124.6, 120.5, 120.1, 112.9, 32.2, 30.7, 22.5 ppm. IR (KBr): ν 3057, 3025, 2926, 1500, 1478, 1028, 736, 695 cm^{-1} . ESI HRMS: calcd. for $\text{C}_{26}\text{H}_{20}\text{N}_2+\text{H}$ 361.1705, found 361.1706.



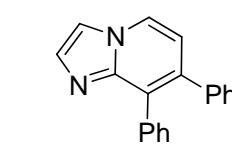
5,6-diphenyl-1,2,3,4-tetrahydrobenzo[4,5]imidazo[1,2- α]quinoline (3ia). 12 h, 60% yield; ^1H NMR (400 MHz, CDCl_3): δ 8.23 (d, $J = 8.8$ Hz, 1H), 7.96 (d, $J = 8.0$ Hz, 1H), 7.46 (t, $J = 8.0$ Hz, 1H), 7.31-7.15 (m, 9H), 7.07-7.05 (m, 2H), 3.56 (t, $J = 6.4$ Hz, 2H), 2.44 (t, $J = 6.0$ Hz, 2H), 2.11-2.05 (m, 2H), 1.84-1.78 (m, 2H) ppm; ^{13}C NMR (100 MHz, CDCl_3): δ 177.1, 145.5, 142.7, 138.1, 136.6, 136.0, 130.9, 130.4, 129.8, 127.8, 127.7, 127.0, 126.9, 124.4, 120.2, 118.5, 115.4, 28.9, 28.0, 22.3, 22.2 ppm. IR (KBr): ν 3055, 3023, 2926, 1494, 1441, 1292, 728, 697 cm^{-1} . ESI HRMS: calcd. for $\text{C}_{27}\text{H}_{22}\text{N}_2+\text{H}$ 375.1861, found 375.1863.



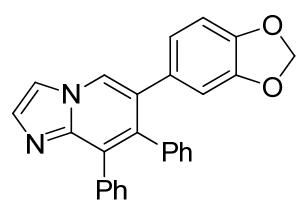
7,8-dimethyl-3,4-diphenylbenzo[4,5]imidazo[1,2- α]pyridine (3ja). 7 h, 80% yield; ^1H NMR (400 MHz, CDCl_3): δ 8.38 (d, $J = 7.2$ Hz, 1H), 7.73 (s, 1H), 7.66 (s, 1H), 7.42-7.40 (m, 2H), 7.34-7.17 (m, 8H), 6.93 (d, $J = 7.2$ Hz, 1H), 2.48 (s, 3H), 2.44 (s, 3H) ppm; ^{13}C NMR (100 MHz, CDCl_3): δ 148.3, 143.8, 139.6, 139.3, 135.3, 134.7, 131.1, 130.5, 129.7, 128.1, 128.0, 127.5, 127.4, 127.2, 123.3, 120.2, 113.3, 110.1, 20.7, 20.6 ppm. IR (KBr): ν 3049, 2968, 2917, 1615, 1498, 1433, 753, 701 cm^{-1} . ESI HRMS: calcd. for $\text{C}_{25}\text{H}_{20}\text{N}_2+\text{H}$ 349.1705, found 349.1706.



1,3-dimethyl-8,9-diphenyl-1,10a-dihydropyrido[2,1-f]purine-2,4(3H,4aH)-dione (3ka). 9 h, 67% yield; ^1H NMR (400 MHz, CDCl_3): δ 9.07 (d, $J = 6.8$ Hz, 1H), 7.36-7.30 (m, 5H), 7.27-7.16 (m, 6H), 3.62 (s, 3H) ppm; ^{13}C NMR (100 MHz, CDCl_3): δ 155.1, 152.0, 151.3, 147.5, 141.6, 138.7, 134.0, 131.2, 129.6, 128.2, 128.0, 127.9, 127.8, 127.4, 125.7, 117.0, 30.2, 27.8 ppm. IR (KBr): ν 3057, 2956, 1700, 1660, 1540, 758, 702 cm^{-1} . ESI HRMS: calcd. for $\text{C}_{23}\text{H}_{18}\text{N}_4\text{O}_2+\text{K}$ 421.1067, found 421.1067.

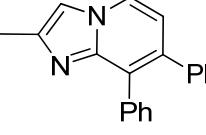


7,8-diphenylimidazo[1,2- α]pyridine (3la). 12 h, 81% yield; ^1H NMR (400 MHz, CDCl_3): δ 8.16 (d, $J = 6.8$ Hz, 1H), 7.67-7.65 (m, 2H), 7.37-7.16 (m, 10H), 6.95 (d, $J = 6.8$, 1H) ppm; ^{13}C NMR (100 MHz, CDCl_3): δ 145.4, 139.4, 135.5, 135.2, 134.3, 130.9, 129.7, 128.3, 128.0, 127.4, 127.0, 124.2, 115.6, 112.4 ppm. IR (KBr): ν 3093, 3060, 1482, 1436, 1310, 1142, 756, 699 cm^{-1} . ESI HRMS: calcd. for $\text{C}_{19}\text{H}_{14}\text{N}_2+\text{H}$ 271.1235, found 271.1235.



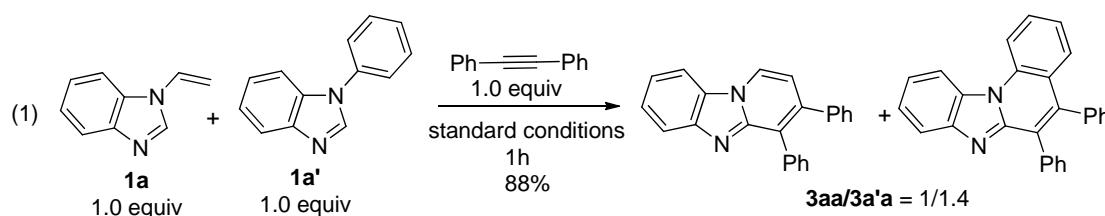
6-(benzo[d][1,3]dioxol-5-yl)-7,8-diphenylimidazo[1,2- α]pyridine (3ma). 13 h, 77% yield; ^1H NMR (400 MHz, CDCl_3): δ 8.14 (s, 1H), 7.66 (d, $J = 13.2$ Hz, 2H), 7.28-7.19 (m, 5H), 7.03-7.00 (m, 3H), 6.87-6.84 (m, 2H), 6.64 (d, $J = 8.0$ Hz, 1H), 6.57 (dd, $J = 8.0, 1.6$ Hz, 1H), 6.51 (d, $J = 1.2$ Hz, 1H), 5.89 (s, 2H) ppm; ^{13}C NMR (100 MHz, CDCl_3): δ 147.1, 146.6, 144.8, 137.4, 136.3, 135.6, 134.6, 131.6, 131.2, 130.7, 129.4, 128.1, 127.7, 127.3, 127.2, 126.5, 123.9, 123.5, 112.4, 110.4, 107.8, 101.0 ppm. IR (KBr): ν 3135, 3057, 3025, 1477, 1323, 1237, 1039, 745, 702 cm^{-1} . ESI HRMS: calcd. for $\text{C}_{26}\text{H}_{18}\text{N}_2\text{O}_2+\text{H}$ 391.1447, found 391.1449.

2-methyl-7,8-diphenylimidazo[1,2-α]pyridine (3na). 8 h, 45% yield; ^1H NMR (400 MHz, CDCl_3): δ

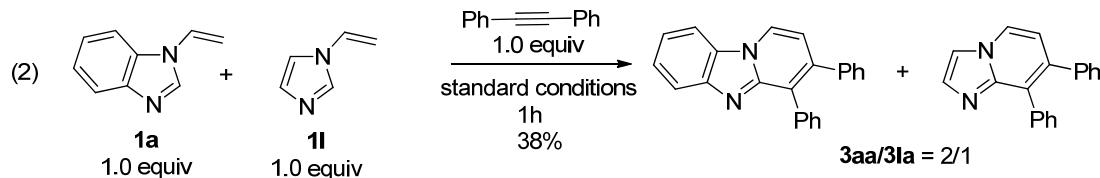
 8.05 (d, $J = 6.8$ Hz, 1H), 7.40 (s, 1H), 7.35-7.34 (m, 2H), 7.29-7.19 (m, 6H), 7.13-7.11 (m, 2H), 6.86 (d, $J = 7.2$ Hz, 1H), 2.45 (s, 3H) ppm; ^{13}C NMR (100 MHz, CDCl_3): δ 144.3, 139.8, 135.4, 135.2, 131.1, 129.8, 127.9, 127.9, 127.4, 126.8, 123.6, 114.9, 109.7, 14.7 ppm. IR (KBr): ν 3025, 2919, 2853, 1319, 1269, 753, 733, 698 cm^{-1} . ESI HRMS: calcd. for $\text{C}_{20}\text{H}_{16}\text{N}_2\text{H}$ 285.1392, found 285.1395.

3. Competition Experiments

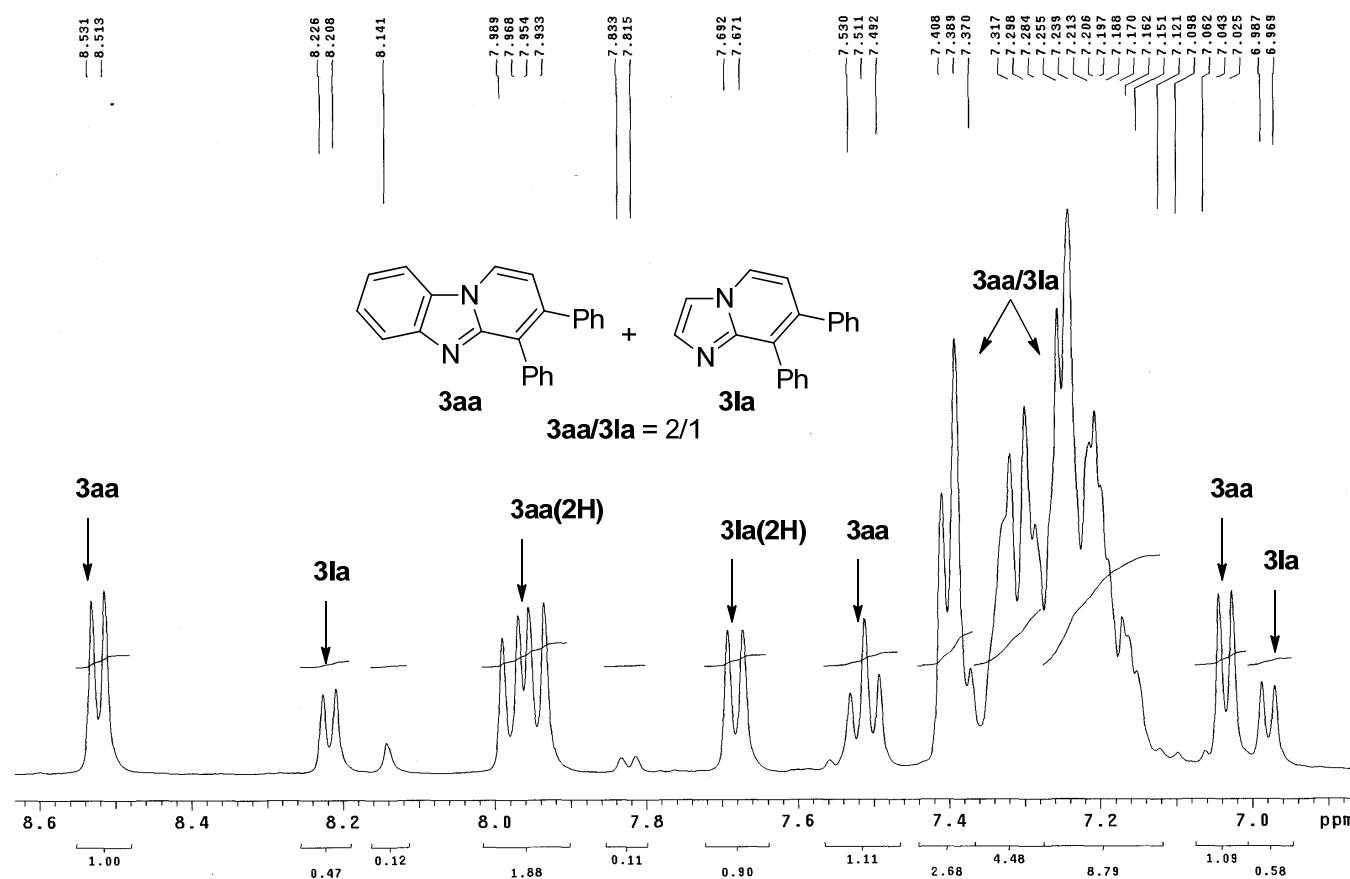
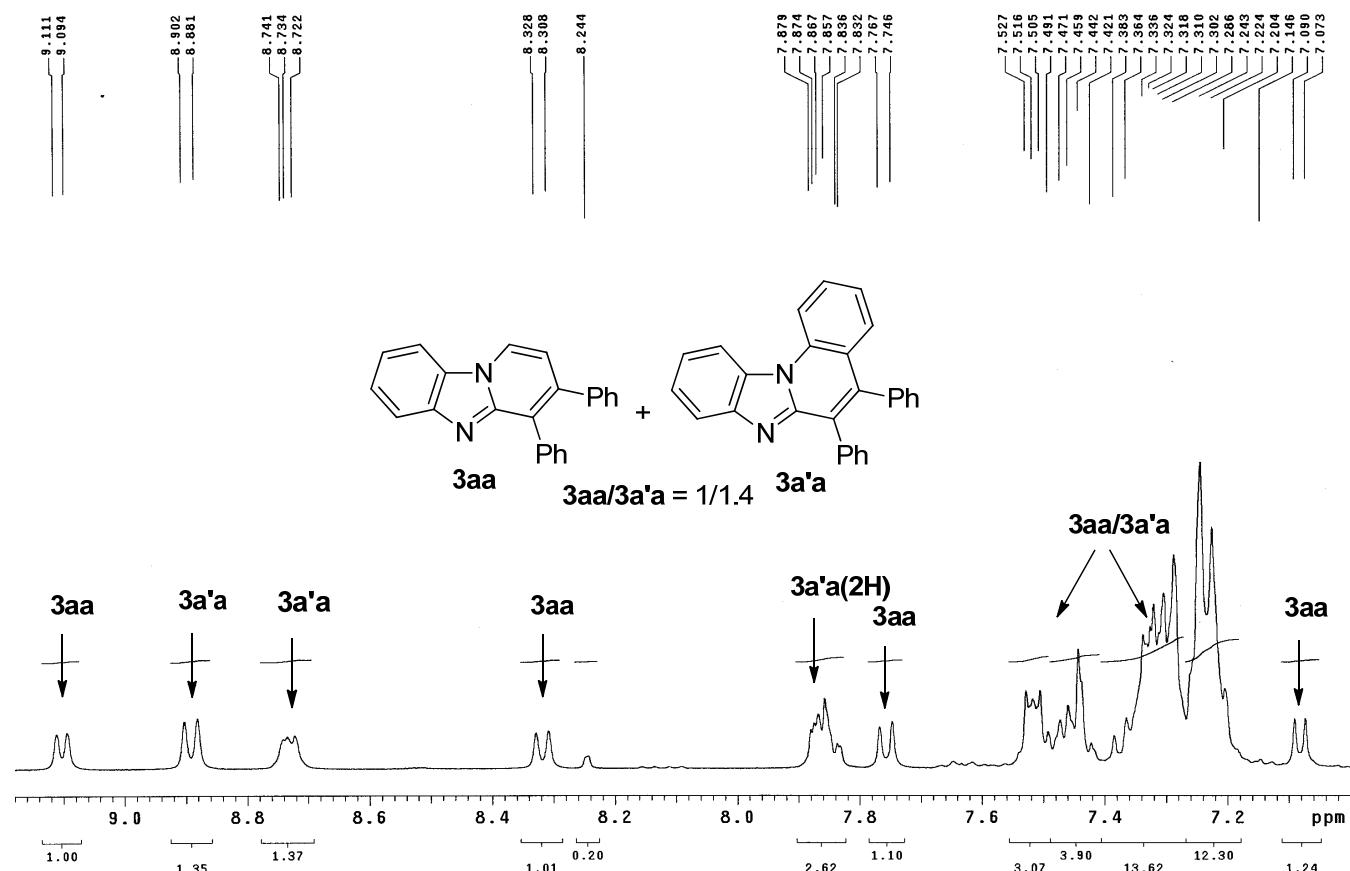
We conducted intermolecular competition experiments with different substituted azoles. Aryl sp^2 C-H exhibit higher reactivity than vinylic sp^2 C-H and the oxidative annulations are favored for benzimidazole derivatives more than imidazoles (eqs 1, 2)



N-vinyl-benzimidazole **1a** (14.4 mg, 0.1 mmol, 1.0 equiv), *N*-phenyl benzimidazole **1a'** (19.5 mg, 0.1 mmol, 1.0 equiv), diphenyl acetylene **2a** (17.8 mg, 0.1 mmol, 1.0 equiv), $[\text{Cp}^*\text{RhCl}_2]_2$ (3.1 mg, 5 mol %, 0.05 equiv) and $\text{Cu}(\text{OAc})_2 \cdot \text{H}_2\text{O}$ (24 mg, 0.12 mmol, 1.2 equiv) were stirred in toluene (1.0 mL) under Ar at 110 °C for 1 h. The reaction mixture was neutralized with K_2CO_3 , and flash chromatography on silica gel ($\text{EtOAc/PE} = 1/10$) to give the product **3aa/3a'a** as a mixture (30.8 mg, 88%)

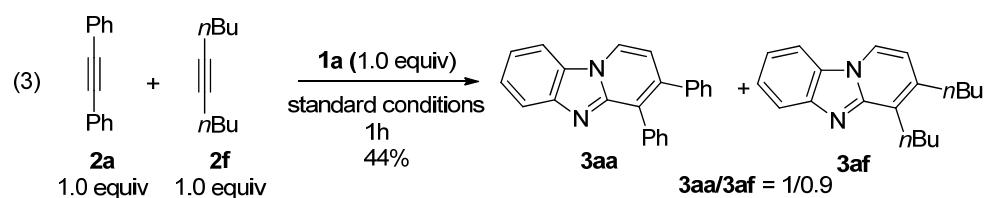


N-vinyl-benzimidazole **1a** (14.4 mg, 0.1 mmol, 1.0 equiv), *N*-vinylimidazole **1l** (9.4 mg, 0.1 mmol, 1.0 equiv), diphenyl acetylene **2a** (17.8 mg, 0.1 mmol, 1.0 equiv), $[\text{Cp}^*\text{RhCl}_2]_2$ (3.1 mg, 5 mol %, 0.05 equiv) and $\text{Cu}(\text{OAc})_2 \cdot \text{H}_2\text{O}$ (24 mg, 0.12 mmol, 1.2 equiv) were stirred in toluene (1.0 mL) under Ar at 110 °C for 1 h. The reaction mixture was neutralized with K_2CO_3 , and flash chromatography on silica gel ($\text{EtOAc/PE} = 1/10$) to give the product **3aa/3la** as a mixture (11.5 mg, 38%)

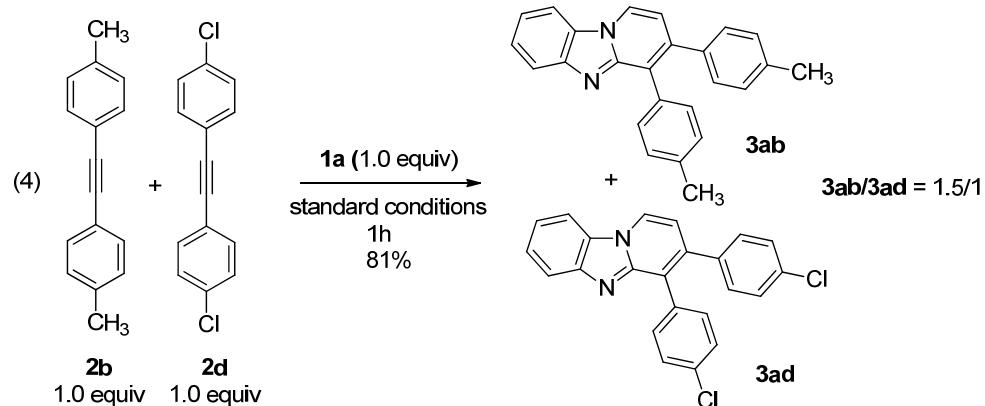


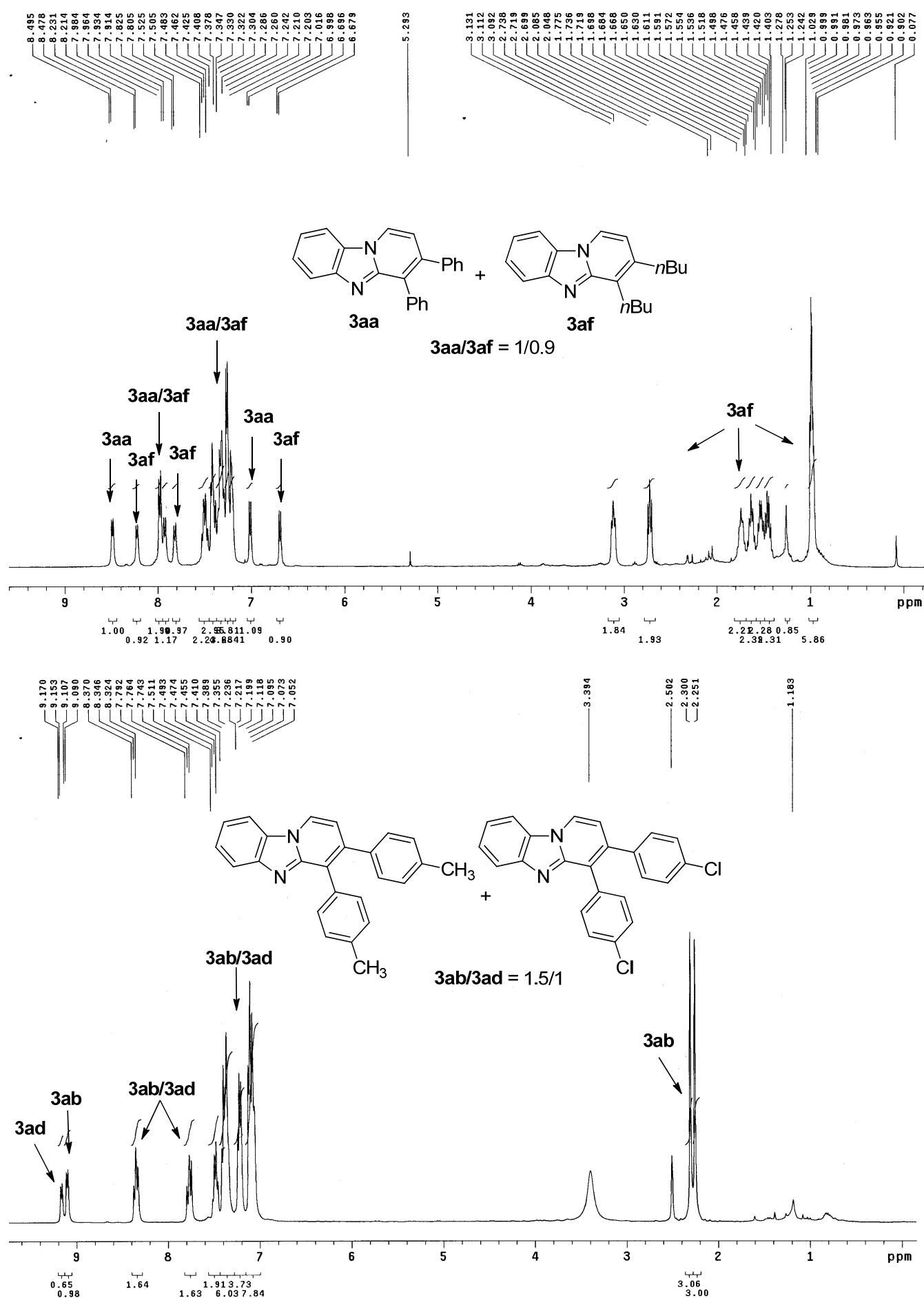
Competition experiments with different alkynes **2** revealed that the diarylalkynes had the similar reactivity as the alkyl-substituted alkynes while electron-donating substituents on the aryl moiety was beneficial for this reaction (eqs 3, 4)

N-vinyl-benzimidazole **1a** (14.4 mg, 0.1 mmol, 1.0 equiv), diphenyl acetylene **2a** (17.8 mg, 0.1 mmol, 1.0 equiv), dec-5-yne **2f** (13.8 mg, 0.1 mmol, 1.0 equiv), $[\text{Cp}^*\text{RhCl}_2]_2$ (3.1 mg, 5 mol %, 0.05 equiv) and $\text{Cu}(\text{OAc})_2 \cdot \text{H}_2\text{O}$ (24 mg, 0.12 mmol, 1.2 equiv) were stirred in toluene (1.0 mL) under Ar at 110 °C for 1 h. The reaction mixture was neutralized with K_2CO_3 , and flash chromatography on silica gel ($\text{EtOAc/PE} = 1/10$) to give the product **3aa/3af** as a mixture (13.1 mg, 44%).



N-vinyl-benzimidazole **1a** (14.4 mg, 0.1 mmol, 1.0 equiv), 1,2-di-*p*-tolylethyne **2b** (20.6 mg, 0.1 mmol, 1.0 equiv), 1,2-bis(4-chlorophenyl)ethyne **2d** (24.7 mg, 0.1 mmol, 1.0 equiv), $[\text{Cp}^*\text{RhCl}_2]_2$ (3.1 mg, 5 mol %, 0.05 equiv) and $\text{Cu}(\text{OAc})_2 \cdot \text{H}_2\text{O}$ (24 mg, 0.12 mmol, 1.2 equiv) were stirred in toluene (1.0 mL) under Ar at 110 °C for 1 h. The reaction mixture was neutralized with K_2CO_3 , and flash chromatography on silica gel ($\text{EtOAc/PE} = 1/10$) to give the product **3ab/3ad** as a mixture (29.4 mg, 81%).





Reference

- [1] a) R.-J. Song, C.-L. Deng, Y.-X. Xie and J.-H. Li, *Tetrahedron Lett.* **2007**, *48*, 7845; b) P. Y. S. Lam, S. Deudon, K. M. Averill, R. Li, M. Y. He, P. DeShong and C. G. Clark, *J. Am. Chem. Soc.* **2000**, *122*, 7600.
- [2] Z. Novák, P. Nemes, A. Kotschy, *Org. Lett.* **2004**, *6*, 4917.
- [3] C. Pan, F. Luo, W. Wang, Z. Ye, J. Cheng, *Tetrahedron Lett.* **2009**, *50*, 5044.
- [4] Y. Gao, G. Wang, L. Chen, P. Xu, Y. Zhao, Y. Zhou, L.-B. Han, *J. Am. Chem. Soc.* **2009**, *131*, 7956.
- [5] I. N. Michaelides, B. Darses and D. J. Dixon, *Org. Lett.* **2011**, *13*, 664.

