Supporting Information

Copper-Catalyzed N-arylation of Iminodibenzyls and Iminostilbenes Using Unactivated Aryl Halides

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1. General considerations

1.1 Materials

Unless otherwise specified, all manipulations were carried out using standard Schlenk, high vacuum, and glovebox techniques. Glassware was dried in a 140 °C oven over 4 hours before use. The 2-(3-butenyl)bromobenzene was synthesized according to literature procedures. Iminodibenzyl and iminostilbene derivatives were purchased from Accela ChemBio Co., Ltd, China and used as received. Flash column chromatography was performed on silica gel (particle size 300-400 mesh ASTM), purchased from Yantai, China. Hg (99.999% metals basis) and PMe₃ (97%) were purchased from Aladdin Industrial Corporation. The all solvents, bases and aryl halides were obtained from commercial sources and dried and degassed according to known procedure to ensure in absence of water and oxygen.

1.2 Analytical Methods

NMR spectra data were obtained on AVANCE (III) HD 400 MHz instruments. H NMR spectra were referenced to residual protio solvent peaks or TMS signal (0 ppm) and C NMR spectra were referenced to the solvent resonance. Data for H NMR are recorded as follows: chemical shift (δ, ppm), multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet or unresolved, br = broad singlet, coupling constant (s) in Hz, integration). Data for C NMR are reported in terms of chemical shift (δ, ppm). High resolution mass spectrometer (HRMS) were carried out by Jiyun Biotech using the Thermo Scientific LTQ Orbitrap XL. GC was performed on a Shimadzu GC-2010 plus spectrometer. GC/MS was performed on a Shimadzu GCMS-QP2010 Plus spectrometer.
2. Typical procedures for N-arylation of dibenzazepines

2.1 Cu-catalytic system

In an argon filled glovebox, a 5 mL dried schlenk tube equipped with a magnetic stir bar was charged with the CuO (4.0 mg, 50.0 µmol, 5.0 mol %), iminodibenzyl (0.2 g, 1.0 mmol, 1.0 equiv.), bromobenzene (210 µL, 2.0 mmol, 2.0 equiv.), KOtBu (0.2 g, 2.0 mmol, 2.0 equiv.), DMSO (2.0 mL), then stirred at 80 °C oil bath for 18 h. After that, the reaction mixture was cooled to room temperature, and dissolved in ethyl acetate and filtrated though celite. The filtrate was collected and the volatiles were removed under reduced pressure and the crude product was analyzed by GC analysis, with mesitylene (139 µL, 1.0 mmol, 1.0 equiv) as internal standard to obtain the GC yields (95%). After that, the total crude products were purified by silica gel column chromatography using petroleum ether to afford the product as pale yellow solid (258 mg, 90%).

2.2 Ni-catalytic system

In an argon filled glovebox, a 5 mL dried schlenk tube equipped with a magnetic stir bar was charged with the NiO (3.7 mg, 50.0 µmol, 5.0 mol %), PPh₃ (26.2 mg, 0.1 mmol, 10.0 mol %), iminodibenzyl (0.2 g, 1.0 mmol, 1.0 equiv.), bromobenzene (210 µL, 2.0 mmol, 2.0 equiv.), KOtBu (0.2 g, 2.0 mmol, 2.0 equiv.), THF (2.0 mL), then stirred at 100 °C oil bath for 24 h. After that, the reaction mixture was cooled to room temperature, and dissolved in ethyl acetate and filtrated though celite. The filtrate was collected and the volatiles were removed under reduced pressure and the crude product was analyzed by GC analysis, with mesitylene (139 µL, 1.0 mmol, 1.0 equiv) as internal standard to obtain the GC yields (86%). After that, the total crude products were purified by silica gel column chromatography using petroleum ether to afford the product as pale yellow solid (229 mg, 80%).
### 3. Optimization of catalysts and reaction conditions (Ni) $^a$

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$^a$Reaction conditions: 4a (1.0 mmol), bromobenzene (2.0 mmol), NiO (50 µmol, 5 mol %), Ligand (0.1 mmol, 10 mol %), KO$t$Bu (2.0 mmol) and Solvent (2.0 mL) under Ar at 80-100 °C for 24 h; $^b$Yields determined by GC; The value in parentheses is the isolated yield.
4. NMR spectra data of dibenzazepines

5-phenyl-10,11-dihydro-5H-dibenzo[b,f]azepine. Purification by silica gel column chromatography using petroleum ether gave pale yellow solid (217 mg, 80%, from 3a-Cl; 244 mg, 90%, from 3a-Br; 239 mg, 88%, from 3a-I; 217 mg, 80%, from 6a-Br; 220 mg, 81%, from 6a-I). $^1$H NMR (400 MHz, CDCl$_3$) δ 7.41 (d, $J = 8.0$ Hz, 2H), 7.32-7.16 (m, 7H), 7.14-7.05 (m, 2H), 6.75-6.68 (m, 1H), 6.58 (d, $J = 8.0$ Hz, 2H), 2.99 (s, 4H). These spectroscopic data correspond to reported data.$^2$

5-(4-fluorophenyl)-10,11-dihydro-5H-dibenzo[b,f]azepine. Purification by silica gel column chromatography using petroleum ether gave colorless oil (191 mg, 66%, from 3b-Cl; 237 mg, 82%, from 3b-Br; 225 mg, 78%, from 3b-I; 211 mg, 73%, from 6b-Br; 179 mg, 62%, from 6b-I). $^1$H NMR (400 MHz, CDCl$_3$) δ 7.38 (d, $J = 8.0$ Hz, 2H), 7.28-7.20 (m, 6H), 7.01(q, $J = 12.0$ Hz, $J = 8.0$ Hz, 1H), 6.78 (t, $J = 8.0$ Hz, 1H), 6.51-6.47 (m, 1H), 6.41-6.23 (m, 1H), 2.98 (s, 4H). These spectroscopic data correspond to reported data.$^2$

5-[4-(trifluoromethyl)phenyl]-10,11-dihydro-5H-dibenzo[b,f]azepine. Purification by silica gel column chromatography using petroleum ether gave colorless oil (176 mg, 52%, from 3c-Cl; 231 mg, 68%, from 3c-Br; 224 mg, 66%, from 3c-I; 248 mg, 73%, from 6c-Br; 210 mg, 62%, from 6c-I). $^1$H NMR (400 MHz, CDCl$_3$) δ 7.39-7.34 (m, 2H), 7.32-7.27 (m, 2H), 7.25-7.22 (m, 3H), 7.15 (t, $J = 8.0$ Hz, 1H), 6.92 (d, $J = 8.0$ Hz, 1H), 6.78 (s, 1H), 6.70 (d, $J = 8.0$ Hz, 1H), 6.58 (d, $J = 8.0$ Hz, 1H), 2.97 (s, 4H); $^{13}$C NMR (101 MHz, CDCl$_3$) δ 151.5, 149.4, 142.9 (d, $J = 6.1$ Hz), 138.2 (d, $J = 9.5$ Hz), 131.3, 129.7 (d, $J = 9.1$ Hz), 129.5, 127.6, 126.4 (d, $J = 3.7$ Hz), 121.3 (q, $J = 366.6$ Hz, $J = 30.3$ Hz), 115.6, 114.1, 112.1, 108.9 (d, $J = 5.1$ Hz), 30.8; HRMS (ESI) m/z calcd for C$_{21}$H$_{17}$F$_3$N (M+H)$^+$ 340.13076, found 340.13086.
5-(p-tolyl)-10,11-dihydro-5H-dibenzo[b,f]azepine. Purification by silica gel column chromatography using petroleum ether gave pale yellow oil (231 mg, 81%, from 3d-Cl; 257 mg, 90%, from 3d-Br; 237 mg, 83%, from 3d-I; 240 mg, 84%, from 6d-Br; 225 mg, 79%, from 6d-I). \(^1^H\) NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.42 (d, \(J = 4.0\) Hz, 2H), 7.27-7.19 (m, 6H), 7.00 (t, \(J = 8.0\) Hz, 1H), 6.92 (d, \(J = 8.0\) Hz, 1H), 6.54 (m, 1H), 6.40 (d, \(J = 8.0\) Hz, 1H), 3.00 (s, 4H), 2.20 (s, 3H). These spectroscopic data correspond to reported data.\(^2\)

5-[4-(tert-butyl)phenyl]-10,11-dihydro-5H-dibenzo[b,f]azepine. Purification by silica gel column chromatography using petroleum ether gave colorless oil (272 mg, 83%, from 3e-Cl; 288 mg, 88%, from 3e-Br; 255 mg, 78%, from 3e-I; 269 mg, 82%, from 6e-Br; 265 mg, 81%, from 6e-I). \(^1^H\) NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.42 (d, \(J = 8.0\) Hz, 2H), 7.22 (m, 4H), 7.12 (d, \(J = 8.0\) Hz, 1H), 7.04 (t, \(J = 8.0\) Hz, 1H), 6.92 (d, \(J = 8.0\) Hz, 1H), 6.54 (m, 1H), 6.42 (d, \(J = 8.0\) Hz, 1H), 3.00 (s, 4H), 1.18 (s, 9H); \(^1^C\) NMR (101 MHz, CDCl\(_3\)) \(\delta\) 152.0, 148.9, 143.8, 138.5, 130.9, 130.2, 128.5, 125.7, 127.0, 114.8, 112.4, 110.1, 34.8, 31.7, 31.4; HRMS (ESI) m/z calcd for C\(_{24}\)H\(_{26}\)N\(^+\) (M+H\(^+\)) 328.20598, found 328.20593.

5-(4-methoxyphenyl)-10,11-dihydro-5H-dibenzo[b,f]azepine. Purification by silica gel column chromatography using petroleum ether gave white solid (262 mg, 87%, from 3f-Cl; 274 mg, 91%, from 3f-Br; 259 mg, 86%, from 3f-I; 274 mg, 91%, from 6f-Br; 248 mg, 87%, from 6f-I). \(^1^H\) NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.43 (m, 2H), 7.28-7.21 (m, 6H), 7.03 (t, \(J = 8.0\) Hz, 1H), 6.72 (d, \(J = 4.0\) Hz, 1H), 6.59 (d, \(J = 4.0\) Hz, 1H), 6.31 (d, \(J = 8.0\) Hz, 1H), 6.21-6.17 (m, 1H), 3.73 (s, 3H), 3.02 (s, 4H).
5-(3-methoxyphenyl)-10,11-dihydro-5H-dibenzo[b,f]azepine. Purification by silica gel column chromatography using petroleum ether gave white solid (238 mg, 79%, from 3g-Cl; 250 mg, 83%, from 3g-Br; 253 mg, 84%, from 3g-I; 250 mg, 83%, from 6g-Br; 262 mg, 87%, from 6g-I). $^1$H NMR (400 MHz, CDCl$_3$) δ 7.40 (d, $J = 8.0$ Hz, 2H), 7.21 (m, 5H), 7.01 (t, $J = 8.0$ Hz, 2H), 6.28 (d, $J = 8.0$ Hz, 1H), 3.67 (s, 3H), 2.99 (s, 4H).

4-(10,11-dihydro-5H-dibenzo[b,f]azepin-5-yl)-N,N-dimethylaniline. Purification by silica gel column chromatography using petroleum ether gave pale yellow solid (185 mg, 59%, from 3h-Cl; 217 mg, 69%, from 3h-Br; 220 mg, 70%, from 3h-I; 179 mg, 57%, from 6h-Br; 154 mg, 49%, from 6h-I). $^1$H NMR (400 MHz, CDCl$_3$) δ 7.42 (d, $J = 8.0$ Hz, 2H), 7.22 (m, 4H), 7.12 (d, $J = 8.0$ Hz, 1H), 6.76 (d, $J = 8.0$ Hz, 1H), 6.54 (d, $J = 8.0$ Hz, 1H), 3.00 (s, 4H), 1.18 (s, 9H); $^{13}$C NMR (101 MHz, CDCl$_3$) δ 151.6, 150.2, 143.9, 138.6, 130.9, 130.4, 129.5, 127.0, 126.9, 102.9, 102.6, 97.8, 40.7, 31.1; HRMS (ESI) m/z calcd for C$_{22}$H$_{23}$N$_2$ (M+H)$^+$ 315.18558, found 315.18552.

5-([1,1'-biphenyl]-4-yl)-10,11-dihydro-5H-dibenzo[b,f]azepine. Purification by silica gel column chromatography using petroleum ether gave pale yellow oil (250 mg, 72%, from 3i-Cl; 278 mg, 80%, from 3i-Br; 260 mg, 75%, from 3i-I; 257 mg, 74%, from 6i-Br; 267 mg, 77%, from 6i-I). $^1$H NMR (400 MHz, CDCl$_3$) δ 7.43 (d, $J = 8.0$, 1H), 7.40-7.34 (m, 3H), 7.31-7.26 (m, 3H), 7.23-7.19 (m, 3H), 7.17-7.14 (m, 2H), 7.12-7.05 (m, 1H), 6.91-6.83 (m, 1H), 6.76-6.71 (m, 1H), 6.62-6.56 (m, 1H), 6.54-6.46 (m, 1H), 2.94 (s, 4H); $^{13}$C NMR (101 MHz, CDCl$_3$) δ 149.6, 148.6, 143.5 (d, $J = 7.1$ Hz), 142.0 (d, $J = 17.2$ Hz), 141.2, 138.5, 131.1, 130.2 (d, $J = 4.0$ Hz), 129.3, 128.71 (d, $J = 9.1$ Hz), 127.65 (s), 127.3 (d, $J = 6.1$ Hz), 126.4, 126.2, 116.8, 113.1, 111.8, 111.5, 31.0; HRMS (ESI) m/z calcd for C$_{26}$H$_{22}$N$_2$ (M+H)$^+$ 348.17468, found 348.17484.
3-chloro-5-phenyl-10,11-dihydro-5H-dibenzo[b,f]azepine. Purification by silica gel column chromatography using petroleum ether gave white solid (260 mg, 85%, from 3j-Cl; 263 mg, 86%, from 3j-Br; 253 mg, 83%, from 3j-I; 275 mg, 90%, from 6j-Br; 275 mg, 90%, from 6j-I). \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.43-7.38 (m, 2H), 7.27-7.25 (m, 3H), 7.18 (d, \(J = 4.0\) Hz, 2H), 7.12 (t, \(J = 8.0\) Hz, 2H), 6.74 (t, \(J = 8.0\) Hz, 1H), 6.58 (d, \(J = 12.0\) Hz, 2H), 2.96 (s, 4H); \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 148.7, 144.4, 143.3, 138.6, 136.8, 132.3, 131.9, 130.9, 130.3, 129.1, 127.6, 127.4 (d, \(J = 8.1\) Hz), 118.2, 112.9, 30.7, 30.6; HRMS (ESI) m/z calcd for C\(_{20}\)H\(_{17}\)NCl\(^+\) (M+H)\(^+\) 306.10440, found 306.10443.

5-phenyl-5H-dibenzo[b,f]azepine. Purification by silica gel column chromatography using petroleum ether gave white solid (194 mg, 72%, from 3k-Cl; 191 mg, 71%, from 3k-Br; 199 mg, 74%, from 3k-I; 229 mg, 85%, from 6k-Br; 183 mg, 68%, from 6k-I). \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.51-7.49 (m, 4H), 7.45 (d, \(J = 8.0\) Hz, 2H), 7.36-7.34 (m, 2H), 7.04-6.95 (m, 2H), 6.83 (s, 2H), 6.73-6.65 (m, 1H), 6.30-6.24 (m, 2H). These spectroscopic data correspond to reported data. \(^2\)

10-methoxy-5-phenyl-5H-dibenzo[b,f]azepine. Purification by silica gel column chromatography using petroleum ether gave pale yellow solid (177 mg, 59%, from 3l-Cl; 207 mg, 69%, from 3l-Br; 189 mg, 63%, from 3l-I; 189 mg, 63%, from 6l-Br; 171 mg, 57%, from 6l-I). \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.72 (d, \(J = 8.0\) Hz, 1H), 7.44-7.37 (m, 3H), 7.31-7.28 (m, 3H), 7.18 (d, \(J = 8.0\) Hz, 1H), 6.93 (t, \(J = 8.0\) Hz, 2H), 6.60 (t, \(J = 8.0\) Hz, 1H), 6.31 (d, \(J = 8.0\) Hz, 2H), 5.95 (s, 1H), 3.69 (s, 3H); \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 156.3, 148.4, 143.4, 141.7, 136.2, 134.6, 130.8, 130.2, 130.0 (d, \(J = 5.1\) Hz), 128.7, 128.5, 127.6, 127.0 (d, \(J = 17.2\) Hz), 117.9, 111.8, 102.5, 55.5; HRMS (ESI) m/z calcd for C\(_{21}\)H\(_{18}\)NO\(^+\) (M+H)\(^+\) 300.13829, found 300.13821.
5. Reference


6. NMR and HRMS (ESI) spectra

![NMR spectrum](image)

Figure S1. $^1$H NMR (400 MHz, CDCl$_3$, 20 °C) of 3a
Figure S2. $^1$H NMR (400 MHz, CDCl$_3$, 20 °C) of 3b

Figure S3. $^1$H NMR (400 MHz, CDCl$_3$, 20 °C) of 3c
Figure S4. $^{13}$C NMR (101 MHz, CDCl$_3$, 20 °C) of 3c

Figure S5. HRMS (ESI) of 3c
Figure S6. $^1$H NMR (400 MHz, CDCl$_3$, 20 °C) of 3d

Figure S7. $^1$H NMR (400 MHz, CDCl$_3$, 20 °C) of 3e
Figure S8. $^{13}$C NMR (101 MHz, CDCl$_3$, 20 °C) of 3e

Figure S9. HRMS (ESI) of 3e
Figure S10. $^1$H NMR (400 MHz, CDCl$_3$, 20 °C) of 3f

Figure S11. $^1$H NMR (400 MHz, CDCl$_3$, 20 °C) of 3g
Figure S12. $^1$H NMR (400 MHz, CDCl$_3$, 20 °C) of 3h

Figure S13. $^{13}$C NMR (101 MHz, CDCl$_3$, 20 °C) of 3h
Figure S14. HRMS (ESI) of 3h

Figure S15. $^1$H NMR (400 MHz, CDCl$_3$, 20 °C) of 3i
**Figure S16.** $^{13}$C NMR (101 MHz, CDCl$_3$, 20 °C) of 3i

**Figure S17.** HRMS (ESI) of 3i
Figure S18. $^1$H NMR (400 MHz, CDCl$_3$, 20 °C) of 3j

Figure S19. $^{13}$C NMR (101 MHz, CDCl$_3$, 20 °C) of 3j
Figure S20. HRMS (ESI) of 3j

Figure S21. $^1$H NMR (400 MHz, CDCl$_3$, 20 $^\circ$C) of 3k
Figure S22. $^1$H NMR (400 MHz, CDCl$_3$, 20 °C) of 3l

Figure S23. $^{13}$C NMR (101 MHz, CDCl$_3$, 20 °C) of 3l
Figure S24. HRMS (ESI) of 3l