Supplementary Content

Aluminium Chloride Catalyzed Synthesis of 4-Benzyl Cinnolines from Aryl Hydrazones

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General Information All solvents and chemicals were purchased commercially and used without further purification. Melting points were determined by open glass capillary method and are uncorrected. NMR spectra were recorded on a **FT-NMR** Bruker Avance II 400 MHz (400 MHz for ^1H NMR, 100 MHz for ^{13}C NMR) using CDCl_3 as solvent and TMS as an internal reference. Infrared spectra were recorded on a Nicolet Impact 410 FT-IR spectrometer. Solid samples were examined as a thin film between KBr salt plates. Mass spectra were recorded on a **LC-MS** Waters ZQ – 4000. Elemental analyses were carried out in Perkin Elmer Model 240 analyzer.

4-benzyl cinnoline (**3a**)

Yellowish solid; **mp**: 103 $^{\circ}\text{C}$ (lit.²⁴ 104.5 $^{\circ}\text{C}$); IR ν /(KBr) cm^{-1} : 3089 cm^{-1} (Ar-H), 2846 cm^{-1} (C-H), 1592 cm^{-1} (N=N), 1280 cm^{-1} (-C-N=N), 1195 cm^{-1} (-N=N-C). ^1H NMR (400 MHz, CDCl_3) δ 8.69 (s, 1H), 7.97 (d, $J = 7.8\text{Hz}$, 1H), 7.81 (d, $J = 7.5\text{Hz}$, 1H), 7.67 (t, $J = 7.8\text{Hz}$, 1H) 7.44 -7.38 (m, 5H), 7.26 (s, 1H) 4.62 (s, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 152.2, 148.1, 138.6, 137.3, 135.5, 132.8, 131.2, 129.1, 128.7, 126.3, 125.2, 120.2, 54.4; Mass: m/z 221.1 $[\text{M}+\text{H}]^+$. Anal. calcd for $\text{C}_{15}\text{H}_{12}\text{N}_2$ (220): C, 81.79; H, 5.49; N, 12.72. Found: C, 81.43; H, 5.55; N, 12.75.

4-benzyl-8-ethyl cinnoline (**3b**)

Yellowish solid; mp: 156 °C; IR ν /(KBr) cm^{-1} : 3040 cm^{-1} (Ar-H), 1589 cm^{-1} (N=N), 1282 cm^{-1} (-C-N=N), 1140 cm^{-1} (-N=N-C), 1610 cm^{-1} (C=C). ^1H NMR (400 MHz, CDCl_3) δ 8.55 (s, 1H), 7.47 (d, $J = 7.6\text{Hz}$, 1H), 7.40 (d, $J = 7.8\text{Hz}$, 1H), 7.28 (s, 1H), 7.06 -6.91 (m, 5H), 4.54 (s, 2H), 2.64 (q, $J = 7.12\text{Hz}$, 2H), 1.29 (t, $J = 7.0\text{Hz}$, 3H) ^{13}C NMR (100 MHz, CDCl_3) δ 154.6, 144.2, 139.8, 136.7, 134.1, 129.3, 128.9, 128.0, 127.6, 126.7, 125.2, 120.2, 53.7, 38.2, 17.6; Mass: m/z 249.0 $[\text{M}+\text{H}]^+$. Anal. calcd for $\text{C}_{17}\text{H}_{16}\text{N}_2$ (248): C, 82.22; H, 6.49; N, 11.28. Found: C, 82.75; H, 6.44; N, 11.12.

4-benzyl-6-p-tolyl cinnoline (**3c**)

Yellowish solid; mp: 126 °C; IR ν /(KBr) cm^{-1} : 3045 cm^{-1} (Ar-H), 1503 cm^{-1} (N=N), 1299 cm^{-1} (-C-N=N), 1140 cm^{-1} (-N=N-C), 1618 cm^{-1} (C=C). ^1H NMR (400 MHz, CDCl_3) δ 8.81 (s, 1H), 7.68 (d, $J = 7.8\text{Hz}$, 1H), 7.58 (s, 1H), 7.39 (d, $J = 7.5\text{Hz}$, 1H), 7.30 (d, $J = 7.6\text{Hz}$, 1H), 7.21 (d, $J = 7.3\text{Hz}$, 2H), 6.96-6.78 (m, 6H), 4.51 (s, 2H), 2.62 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 156.6, 155.3, 140.4, 136.5, 134.6, 134.0, 130.3, 130.1, 129.3, 129.1, 128.9, 128.5,

128.4, 127.6, 126.2, 125.8, 56.7, 29.1; Mass: m/z 311.1 $[M+H]^+$. Anal. calcd for $C_{22}H_{18}N_2$ (310): C, 85.13, H, 5.85; N, 9.03. Found: C, 85.31; H, 5.84; N, 9.19.

4-benzyl-6-methyl cinnoline (**3d**)

Yellowish solid; mp: 120 $^{\circ}C$; IR ν /(KBr) cm^{-1} : 3027 cm^{-1} (Ar-H), 1566 cm^{-1} (N=N), 1279 cm^{-1} (-C-N=N), 1133 cm^{-1} (-N=N-C), 1627 cm^{-1} (C=C). 1H NMR (400 MHz, $CDCl_3$) δ 8.45 (s, 1H), 7.56 (d, $J = 7.5Hz$, 1H), 7.39 (d, $J = 7.4Hz$, 1H), 7.29 (t, $J = 7.7Hz$, 1H), 7.19-7.10 (m, 5H), 4.32 (s, 2H), 2.66 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.2, 148.6, 141.5, 140.4, 134.1, 128.2, 128.0, 127.9, 126.1, 125.9, 120.1, 54.6, 23.5; Mass: m/z 235.0 $[M+H]^+$. Anal. calcd for $C_{16}H_{14}N_2$ (234): C, 82.02, H, 6.02; N, 11.96. Found: C, 82.31; H, 6.01; N, 11.87.

4-benzyl-6-chloro cinnoline (**3e**)

Yellowish solid; mp: 140 $^{\circ}C$; IR ν /(KBr) cm^{-1} : 3021 cm^{-1} (Ar-H), 1520 cm^{-1} (N=N), 1240 cm^{-1} (-C-N=N), 1135 cm^{-1} (-N=N-C), 747 cm^{-1} (C-Cl) 1H NMR (400 MHz, $CDCl_3$) δ 8.57 (s, 1H), 8.06 (d, $J = 7.7Hz$, 1H), 7.67 (d, $J = 7.6Hz$, 1H), 7.45 (t, $J = 7.7Hz$, 1H), 7.18-7.06 (m, 5H), 4.48 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.5, 153.6, 142.1, 134.6, 132.1, 131.6,

130.3, 130.2, 128.9, 128.3, 127.1, 122.3, 57.2; Mass: m/z 256.1 $[M+H]^+$. Anal. calcd for $C_{15}H_{11}ClN_2$ (255): C, 70.73, H, 4.35; N, 11.00. Found: C, 70.78; H, 4.33; N, 11.10.

Figure S1: 1H NMR (400 MHz, $CDCl_3$) of compound 3a:

Figure S2: ^{13}C NMR (100 MHz, CDCl_3) of compound 3a:

Figure S3: ^1H NMR (400 MHz, CDCl_3) of compound 3b:

Figure S4: ^{13}C NMR (100 MHz, CDCl_3) of compound **3b**:

Figure S5: ^1H NMR (400 MHz, CDCl_3) of compound 3c:

Figure S6: ^{13}C NMR (100 MHz, CDCl_3) of compound 3c:

Figure S7: ^1H NMR (400 MHz, CDCl_3) of compound 3d:

Figure S8: ^{13}C NMR (100 MHz, CDCl_3) of compound 3d:

Figure S9: ^1H NMR (400 MHz, CDCl_3) of compound 3e:

Figure S10: ^{13}C NMR (100 MHz, CDCl_3) of compound 3e:

Figure S11: ^1H NMR (400 MHz, CDCl_3) of compound 3f:

Figure S12: ^{13}C NMR (100 MHz, CDCl_3) of compound 3f:

Figure S13: ^1H NMR (400 MHz, CDCl_3) of compound 3g:

Figure S14: ^{13}C NMR (100 MHz, CDCl_3) of compound 3g:

Figure S15: ^1H NMR (400 MHz, CDCl_3) of compound 3h:

Figure S16: ^{13}C NMR (100 MHz, CDCl_3) of compound 3h:

Figure S17: ^1H NMR (400 MHz, CDCl_3) of compound **3i**:

Figure S18: ^{13}C NMR (100 MHz, CDCl_3) of compound 3i:

Figure S19: ^1H NMR (400 MHz, CDCl_3) of compound 3j:

Figure S20: ^{13}C NMR (100 MHz, CDCl_3) of compound 3j:

Figure S21: ^1H NMR (400 MHz, CDCl_3) of compound 3k:

Figure S22: ^{13}C NMR (100 MHz, CDCl_3) of compound 3k:

Figure S23: MS of compound 3a:

Figure S24: MS of compound 3b:

Figure S25: *MS of compound 3c:*

Figure S26: MS of compound 3d:

Figure S27: *MS of compound 3e:*