

Supporting Information

1-Alkyl-3-alkylindolin-2-imine hydrochlorides as the useful building blocks in copper-catalyzed synthesis of polycyclic indoline scaffolds

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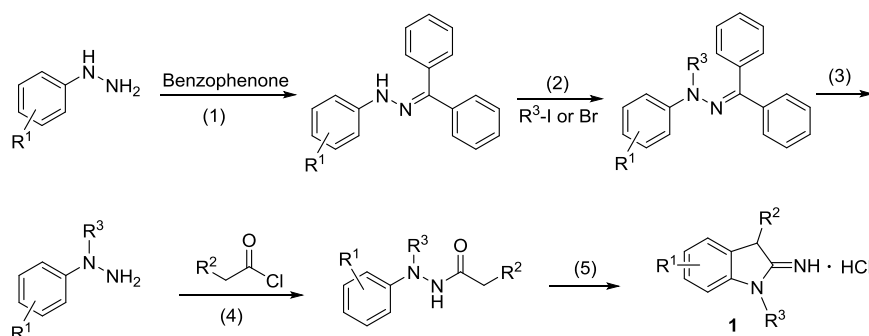
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1. General Procedures

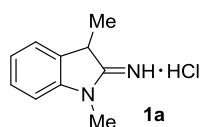
All reactions were carried out under a nitrogen atmosphere in dry solvents. The reactions were monitored by thin layer chromatography (TLC), and the products were isolated by silica gel column chromatography. ^1H , ^{13}C and ^{19}F NMR spectra were recorded on JEOL ECS-400, JNM-ECA 600 or AV-HD-800X spectrometers. Chemical shifts were reported in ppm down field from internal Me_4Si and external CFCl_3 , respectively. ^1H NMR chemical shifts were referenced to the hydrogen signal of tetramethylsilane (TMS) ($\delta = 0.00$ ppm). In ^{13}C measurements the signal of CDCl_3 ($\delta = 77.06$) was used as a reference. The following abbreviations (or combinations thereof) were used to explain the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, quint = quintet, sext = sextet, h = heptet, m = multiplet, dd = doublet of doublets, dt = doublet of triplets, td = triplet of doublets, br = broad.

2. Synthesis and Characterization Data of Substrates 1a-ah

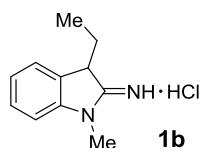
Substrates **1a-ah** were prepared according to the previous procedures.¹



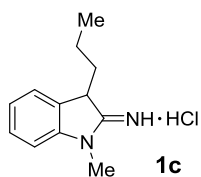
Scheme S1. Synthetic routes of compounds **1a-ah**. Reagents and conditions: (1) *p*-Toluenesulfonic acid (5%), EtOH, 8 h; (2) NaH, CH_2Cl_2 , 0 °C to rt, 3 h; (3) EtOH/HCl, rt or 50 °C, 8 h; (4) NEt_3 , CH_2Cl_2 , 0 °C to rt, 3 h; (5) $POCl_3$ (3.0 eq), 1,4-Dioxane, reflux, 3 h.



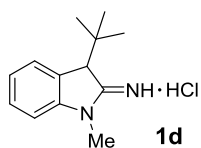
1a: Pale yellow solid, mp = 279 – 281 °C; 1H NMR (800 MHz, Methanol- d_4) δ 7.49 (d, J = 7.4 Hz, 1H), 7.44 (td, J = 7.8, 1.2 Hz, 1H), 7.31 (d, J = 8.0 Hz, 1H), 7.28 (td, J = 7.5, 0.8 Hz, 1H), 3.56 (s, 3H), 1.62 (s, 3H); ^{13}C NMR (201 MHz, MeOD) δ 175.1, 144.3, 132.7, 129.9, 126.4, 124.9, 111.7, 42.7 (m), 30.1, 17.0. Positive ion ESI-MS: Calcd for $C_{10}H_{13}ClN_2$ [$M-Cl$] $^+$: 161.1. Found: 161.2.



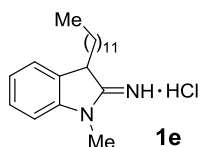
1b: Pale yellow solid, mp = 273 – 276 °C; 1H NMR (400 MHz, DMSO- d_6) δ 10.72 (s, 1H), 10.45 (s, 1H), 7.43 (d, J = 7.4 Hz, 1H), 7.37 (t, J = 7.7 Hz, 1H), 7.28 (d, J = 7.8 Hz, 1H), 7.19 (t, J = 7.5 Hz, 1H), 4.28 (t, J = 4.9 Hz, 1H), 3.55 (s, 3H), 2.16 (dt, J = 12.7, 6.4 Hz, 2H), 0.56 (t, J = 7.4 Hz, 3H); ^{13}C NMR (101 MHz, DMSO- d_6) δ 172.2, 144.3, 129.9, 128.9, 125.1, 124.5, 111.1, 47.3, 30.4, 24.2, 9.1. Positive ion ESI-MS: Calcd for $C_{11}H_{15}ClN_2$ [$M-Cl$] $^+$: 175.1. Found: 175.1.



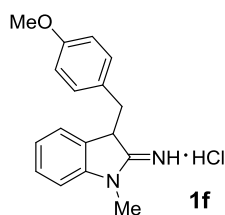
1c: Pale yellow solid, mp = 248 – 250 °C; ^1H NMR (800 MHz, CD_3OD) δ 7.50 (d, J = 7.4 Hz, 1H), 7.46 (td, J = 7.9, 1.1 Hz, 1H), 7.32 (d, J = 8.0 Hz, 1H), 7.31 – 7.28 (m, 1H), 3.56 (s, 3H), 2.24 – 2.16 (m, 1H), 2.08 – 1.99 (m, 1H), 1.32 – 1.23 (m, 1H), 1.16 – 1.08 (m, 1H), 0.92 (t, J = 7.4 Hz, 3H); ^{13}C NMR (201 MHz, CD_3OD) δ 174.3, 144.9, 131.1, 129.9, 126.4, 125.3, 111.8, 47.6 (m), 34.4, 30.0, 19.0, 14.2. Positive ion ESI-MS: Calcd for $\text{C}_{12}\text{H}_{17}\text{ClN}_2$ $[\text{M} - \text{Cl}]^+$: 189.1. Found: 189.2.



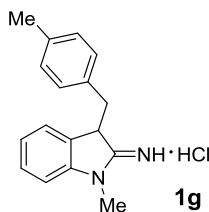
1d: Pale yellow solid, mp = 294 – 297 °C; ^1H NMR (600 MHz, $\text{DMSO}-d_6$) δ 10.46 (s, 1H), 10.03 (s, 1H), 7.48 (d, J = 7.5 Hz, 1H), 7.43 (t, J = 7.7 Hz, 1H), 7.32 (d, J = 7.9 Hz, 1H), 7.21 (t, J = 7.5 Hz, 1H), 3.99 (s, 1H), 3.55 (s, 3H), 0.98 (s, 9H); ^{13}C NMR (151 MHz, $\text{DMSO}-d_6$) δ 171.1, 143.9, 128.7, 128.6, 125.9, 123.8, 110.4, 55.9, 35.6, 29.8, 26.9. Positive ion ESI-MS: Calcd for $\text{C}_{13}\text{H}_{19}\text{ClN}_2$ $[\text{M} - \text{Cl}]^+$: 203.2. Found: 203.2.



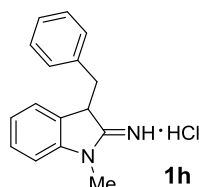
1e: Pale yellow solid, mp = 132 – 134 °C; ^1H NMR (800 MHz, CD_3OD) δ 7.49 (d, J = 7.4 Hz, 1H), 7.46 (td, J = 7.8, 1.1 Hz, 1H), 7.32 (d, J = 8.0 Hz, 1H), 7.30 (td, J = 7.5, 0.7 Hz, 1H), 3.56 (s, 3H), 2.28 – 2.17 (m, 1H), 2.10 – 2.02 (m, 1H), 1.34 – 1.18 (m, 19H), 1.11 – 1.00 (m, 1H), 0.89 (t, J = 7.2 Hz, 3H); ^{13}C NMR (201 MHz, CD_3OD) δ 174.3, 144.9, 131.0, 130.0, 126.4, 125.3, 111.8, 47.7 (m), 33.1, 32.2, 30.7, 30.7, 30.7, 30.6, 30.5, 30.4, 30.3, 30.0, 25.5, 23.7. Positive ion ESI-MS: Calcd for $\text{C}_{21}\text{H}_{35}\text{ClN}_2$ $[\text{M} - \text{Cl}]^+$: 315.3. Found: 315.2.



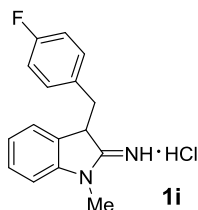
1f: Pale yellow solid, mp = 238 – 241 °C; ¹H NMR (600 MHz, CD₃OD) δ 7.40 (t, *J* = 8.1 Hz, 1H), 7.20 (t, *J* = 7.6 Hz, 1H), 7.17 (d, *J* = 8.1 Hz, 1H), 7.12 (d, *J* = 7.3 Hz, 1H), 6.93 (d, *J* = 8.6 Hz, 2H), 6.75 (d, *J* = 8.5 Hz, 2H), 3.72 (s, 3H), 3.55 (d, *J* = 13.9 Hz, 1H), 3.39 (s, 3H), 3.10 (d, *J* = 14.0 Hz, 1H); ¹³C NMR (151 MHz, CD₃OD) δ 173.4, 160.5, 144.9, 131.5, 130.6, 130.0, 128.5, 126.1, 126.0, 114.8, 111.6, 55.7, 37.5, 29.7. Positive ion ESI-MS: Calcd for C₁₇H₁₉ClN₂O [M–Cl]⁺: 267.1. Found: 267.1.



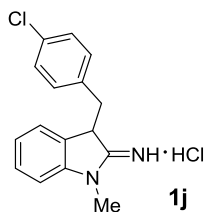
1g: Pale yellow solid, mp = 239 – 242 °C; ¹H NMR (600 MHz, DMSO-*d*₆) δ 10.95 (s, 1H), 10.34 (s, 1H), 7.35 (t, *J* = 7.7 Hz, 1H), 7.21 (d, *J* = 7.9 Hz, 1H), 7.12 (t, *J* = 7.5 Hz, 1H), 7.01 (t, *J* = 9.0 Hz, 3H), 6.96 (d, *J* = 8.0 Hz, 2H), 4.62 (dd, *J* = 8.0, 4.2 Hz, 1H), 3.64 (dd, *J* = 13.8, 4.3 Hz, 1H), 3.42 (s, 3H), 3.17 (dd, *J* = 13.8, 8.4 Hz, 1H), 2.22 (s, 3H); ¹³C NMR (151 MHz, DMSO-*d*₆) δ 181.2, 153.5, 145.9, 143.2, 139.3, 139.1, 138.8, 138.4, 134.3, 134.2, 120.5, 57.1, 45.6, 39.6, 30.7. Positive ion ESI-MS: Calcd for C₁₇H₁₉ClN₂ [M–Cl]⁺: 251.2. Found: 251.1.



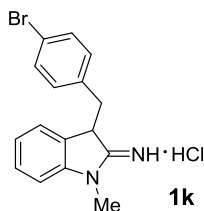
1h: Pale yellow solid, mp = 237 – 239 °C; ¹H NMR (800 MHz, CD₃OD) δ 7.39 (td, *J* = 7.8, 1.2 Hz, 1H), 7.22 – 7.15 (m, 5H), 7.08 – 7.02 (m, 3H), 3.63 (d, *J* = 13.9 Hz, 1H), 3.40 (s, 3H), 3.15 (d, *J* = 13.9 Hz, 1H); ¹³C NMR (201 MHz, CD₃OD) δ 173.3, 144.8, 136.8, 130.5, 130.1, 129.4, 128.4, 126.1, 126.0, 111.6, 38.3, 29.7 (m). Positive ion ESI-MS: Calcd for C₁₆H₁₇ClN₂ [M–Cl]⁺: 237.1. Found: 237.1.



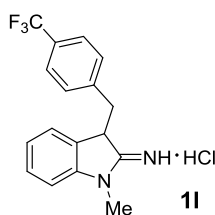
1i: Pale yellow solid, mp = 242 – 245 °C; ¹H NMR (600 MHz, CD₃OD) δ 7.41 (t, *J* = 8.0 Hz, 1H), 7.24 – 7.17 (m, 2H), 7.13 (d, *J* = 7.4 Hz, 1H), 7.05 (dd, *J* = 8.2, 5.5 Hz, 2H), 6.93 (t, *J* = 8.7 Hz, 2H), 3.61 (d, *J* = 13.9 Hz, 1H), 3.41 (s, 3H), 3.19 (d, *J* = 13.9 Hz, 1H); ¹³C NMR (151 MHz, CD₃OD) δ 173.25, 163.53 (d, *J* = 244.5 Hz), 144.83, 132.68 (d, *J* = 2.3 Hz), 132.26 (d, *J* = 8.2 Hz), 130.3, 130.2, 126.2, 125.9, 116.1 (d, *J* = 21.6 Hz), 111.7, 37.4, 29.8; ¹⁹F NMR (565 MHz, CD₃OD) δ -117.1. Positive ion ESI-MS: Calcd for C₁₆H₁₆ClFN₂ [M – Cl]⁺: 255.1. Found: 255.1.



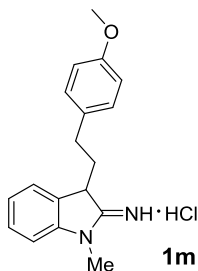
1j: Pale yellow solid, mp = 283 – 287 °C; ¹H NMR (600 MHz, CD₃OD) δ 7.44 – 7.38 (m, 1H), 7.25 – 7.17 (m, 4H), 7.14 (d, *J* = 7.3 Hz, 1H), 7.03 (d, *J* = 8.3 Hz, 2H), 3.61 (d, *J* = 14.0 Hz, 1H), 3.41 (s, 3H), 3.18 (d, *J* = 13.9 Hz, 1H); ¹³C NMR (151 MHz, CD₃OD) δ 173.2, 144.8, 135.5, 134.4, 132.1, 130.2, 129.5, 126.3, 125.9, 111.8, 37.5, 29.7. Positive ion ESI-MS: Calcd for C₁₆H₁₆Cl₂N₂ [M – Cl]⁺: 271.1. Found: 271.2.



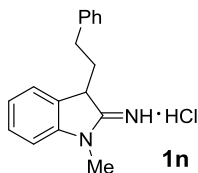
1k: Pale yellow solid, mp = 232 – 236 °C; ¹H NMR (600 MHz, DMSO-*d*₆) δ 10.82 (s, 1H), 10.20 (s, 1H), 7.42 (d, *J* = 8.4 Hz, 2H), 7.38 – 7.35 (m, 1H), 7.23 (d, *J* = 7.9 Hz, 1H), 7.15 (t, *J* = 7.5 Hz, 1H), 7.04 (t, *J* = 7.4 Hz, 3H), 4.67 (dd, *J* = 7.8, 4.3 Hz, 1H), 3.64 (dd, *J* = 13.8, 4.3 Hz, 1H), 3.41 (s, 3H), 3.21 (dd, *J* = 13.8, 8.2 Hz, 1H); ¹³C NMR (151 MHz, DMSO-*d*₆) δ 171.0, 143.5, 135.7, 131.4, 131.2, 129.0, 128.6, 124.4, 124.3, 120.2, 110.6, 46.8, 35.3, 29.5. Positive ion ESI-MS: Calcd for C₁₆H₁₆BrClN₂ [M – Cl]⁺: 315.0. Found: 315.0.



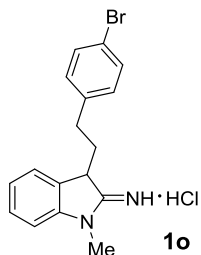
1l: Pale yellow solid, mp = 259 – 261 °C; ¹H NMR (600 MHz, CD₃OD) δ 7.52 (d, *J* = 8.1 Hz, 2H), 7.41 (t, *J* = 8.1 Hz, 1H), 7.27 (d, *J* = 8.0 Hz, 2H), 7.24 – 7.17 (m, 2H), 7.12 (d, *J* = 7.4 Hz, 1H), 3.73 (d, *J* = 13.9 Hz, 1H), 3.43 (s, 3H), 3.29 (d, *J* = 14.2 Hz, 1H); ¹³C NMR (151 MHz, CD₃OD) δ 173.13, 144.81, 141.49, 131.23, 130.65 (q, *J* = 32.4 Hz), 130.3, 130.1, 126.3, 126.3, 125.9, 125.6 (q, *J* = 271.2 Hz), 111.8, 37.8, 29.8; ¹⁹F NMR (565 MHz, CD₃OD) δ -63.91. Positive ion ESI-MS: Calcd for C₁₇H₁₆ClF₃N₂ [M – Cl]⁺: 305.1. Found: 305.1.



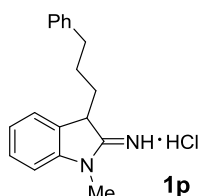
1m: Pale yellow solid, mp = 254 – 257 °C; ¹H NMR (600 MHz, CD₃OD) δ 7.55 (d, *J* = 7.4 Hz, 1H), 7.50 (t, *J* = 7.9 Hz, 1H), 7.35 (t, *J* = 7.5 Hz, 1H), 7.30 (d, *J* = 7.9 Hz, 1H), 6.87 (d, *J* = 8.6 Hz, 2H), 6.78 (d, *J* = 8.7 Hz, 2H), 3.75 (s, 3H), 3.35 (s, 3H), 2.63 – 2.55 (m, 1H), 2.50 – 2.43 (m, 2H), 2.37 – 2.30 (m, 1H); ¹³C NMR (151 MHz, CD₃OD) δ 173.9, 159.9, 145.1, 133.0, 130.7, 130.3, 130.1, 126.5, 125.5, 114.8, 111.8, 55.7, 32.9, 31.0, 29.8. Positive ion ESI-MS: Calcd for C₁₈H₂₁ClN₂O [M – Cl]⁺: 281.2. Found: 281.2.



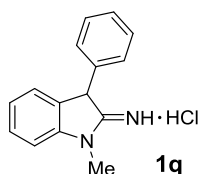
1n: Pale yellow solid, mp = 236 – 238 °C; ¹H NMR (400 MHz, DMSO-*d*₆) δ 10.83 (s, 1H), 10.38 (s, 1H), 7.52 (d, *J* = 7.4 Hz, 1H), 7.39 (t, *J* = 7.7 Hz, 1H), 7.28 (d, *J* = 7.9 Hz, 1H), 7.25 – 7.15 (m, 3H), 7.13 – 7.04 (m, 3H), 4.37 (t, *J* = 4.8 Hz, 1H), 3.48 (s, 3H), 2.55 – 2.41 (m, 2H), 2.41 – 2.30 (m, 1H), 2.29 – 2.18 (m, 1H); ¹³C NMR (101 MHz, DMSO-*d*₆) δ 172.1, 144.3, 140.9, 129.9, 129.0, 128.8, 128.8, 126.6, 125.1, 124.7, 111.1, 46.4, 32.1, 31.0, 30.4. Positive ion ESI-MS: Calcd for C₁₇H₁₉ClN₂ [M – Cl]⁺: 251.2. Found: 251.2.



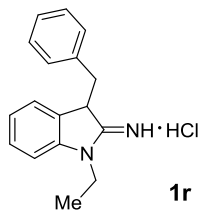
1o: Pale yellow solid, mp = 259 – 261 °C; ^1H NMR (600 MHz, CD_3OD) δ 7.55 (d, J = 7.4 Hz, 1H), 7.53 – 7.47 (m, 1H), 7.41 – 7.28 (m, 4H), 6.94 (d, J = 8.3 Hz, 2H), 3.41 (s, 3H), 2.65 – 2.55 (m, 1H), 2.50 – 2.39 (m, 3H); ^{13}C NMR (151 MHz, CD_3OD) δ 173.8, 145.0, 140.6, 132.5, 131.6, 130.2, 130.2, 126.6, 125.5, 121.2, 111.9, 47.3 (m), 32.7, 31.2, 29.8. Positive ion ESI-MS: Calcd for $\text{C}_{17}\text{H}_{18}\text{BrClN}_2$ $[\text{M} - \text{Cl}]^+$: 329.1. Found: 329.2.



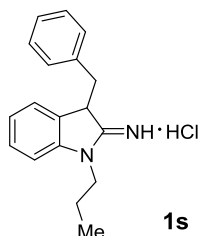
1p: Pale yellow solid, mp = 203 – 205 °C; ^1H NMR (600 MHz, $\text{DMSO}-d_6$) δ 10.61 (s, 1H), 10.38 (s, 1H), 7.43 – 7.34 (m, 2H), 7.27 (d, J = 7.9 Hz, 1H), 7.23 – 7.15 (m, 3H), 7.11 (t, J = 7.3 Hz, 1H), 7.06 (d, J = 7.5 Hz, 2H), 4.33 (t, J = 5.1 Hz, 1H), 3.52 (s, 3H), 2.53 – 2.43 (m, 2H), 2.27 – 2.16 (m, 1H), 2.15 – 2.05 (m, 1H), 1.46 – 1.32 (m, 1H), 1.27 – 1.14 (m, 1H); ^{13}C NMR (151 MHz, $\text{DMSO}-d_6$) δ 171.9, 143.6, 141.4, 129.7, 128.4, 128.3, 128.2, 125.8, 124.5, 124.0, 110.6, 45.9, 35.0, 30.3, 29.8, 26.2. Positive ion ESI-MS: Calcd for $\text{C}_{18}\text{H}_{21}\text{ClN}_2$ $[\text{M} - \text{Cl}]^+$: 265.2. Found: 265.2.



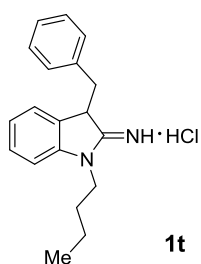
1q: Pale yellow solid, mp = 274 – 277 °C; ^1H NMR (800 MHz, CD_3OD) δ 7.48 (td, J = 8.0, 1.2 Hz, 1H), 7.44 – 7.36 (m, 4H), 7.29 – 7.26 (m, 2H), 7.23 (td, J = 7.5, 0.9 Hz, 1H), 7.21 – 7.18 (m, 1H), 3.67 (s, 3H); ^{13}C NMR (201 MHz, CD_3OD) δ 173.6, 144.5, 136.7, 132.6, 130.6, 130.3, 129.8, 129.7, 126.8, 125.7, 112.0, 30.4. Positive ion ESI-MS: Calcd for $\text{C}_{15}\text{H}_{15}\text{ClN}_2$ $[\text{M} - \text{Cl}]^+$: 223.1. Found: 223.0.



1r: Pale yellow solid, mp = 255 – 258 °C; ¹H NMR (800 MHz, CD₃OD) δ 7.41 (td, *J* = 7.8, 1.2 Hz, 1H), 7.31 (d, *J* = 7.4 Hz, 1H), 7.25 (td, *J* = 7.5, 0.7 Hz, 1H), 7.19 – 7.12 (m, 4H), 6.93 (d, *J* = 7.2 Hz, 2H), 3.90 – 3.83 (m, 2H), 3.61 (d, *J* = 13.9 Hz, 1H), 3.27 (d, *J* = 13.9 Hz, 1H), 1.00 (t, *J* = 7.3 Hz, 3H); ¹³C NMR (201 MHz, CD₃OD) δ 172.4, 143.9, 136.2, 130.8, 130.5, 130.2, 129.3, 128.5, 126.2, 126.1, 111.7, 38.7, 38.2, 11.6. Positive ion ESI-MS: Calcd for C₁₇H₁₉ClN₂ [M – Cl]⁺: 251.2. Found: 251.1.

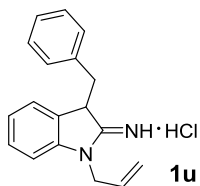


1s: Pale yellow solid, mp = 239 – 241 °C; ¹H NMR (800 MHz, CD₃OD) δ 7.40 (t, *J* = 7.7 Hz, 1H), 7.34 (d, *J* = 7.3 Hz, 1H), 7.25 (t, *J* = 7.5 Hz, 1H), 7.19 – 7.10 (m, 4H), 6.94 (d, *J* = 7.5 Hz, 2H), 3.86 – 3.80 (m, 1H), 3.80 – 3.74 (m, 1H), 3.63 (d, *J* = 14.0 Hz, 1H), 3.31 – 3.28 (m, 1H), 1.45 (m, 2H), 0.75 (t, *J* = 7.3 Hz, 3H); ¹³C NMR (201 MHz, CD₃OD) δ 172.6, 144.5, 136.2, 130.6, 130.6, 130.1, 129.3, 128.5, 126.2, 126.1, 112.0, 45.2, 38.0, 21.0, 11.1. Positive ion ESI-MS: Calcd for C₁₈H₂₁ClN₂ [M – Cl]⁺: 265.2. Found: 265.2.

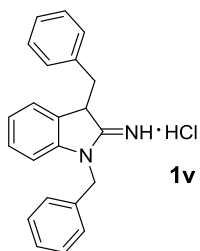


1t: Pale yellow solid, mp = 235 – 237 °C; ¹H NMR (800 MHz, CD₃OD) δ 7.41 (td, *J* = 7.8, 1.2 Hz, 1H), 7.38 (d, *J* = 7.5 Hz, 1H), 7.27 (td, *J* = 7.5, 0.8 Hz, 1H), 7.18 – 7.09 (m, 4H), 6.92 (d, *J* = 7.2 Hz, 2H), 3.87 – 3.77 (m, 2H), 3.62 (d, *J* = 14.0 Hz, 1H), 3.33 (d, *J* = 14.0 Hz, 1H), 1.41 – 1.29 (m, 2H), 1.15 – 1.04 (m, 2H), 0.84 (t, *J* = 7.4 Hz, 3H); ¹³C NMR (201 MHz, CD₃OD) δ 172.5, 144.5, 136.1,

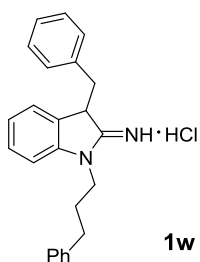
130.6, 130.6, 130.1, 129.3, 128.5, 126.2, 126.1, 112.0, 43.7, 37.9, 29.8, 20.7, 14.2. Positive ion ESI-MS: Calcd for $C_{19}H_{23}ClN_2$ $[M-Cl]^+$: 279.2. Found: 279.1.



1u: Pale yellow solid, mp = 237 – 240 °C; 1H NMR (800 MHz, CD_3OD) δ 7.38 (td, J = 7.8, 1.1 Hz, 1H), 7.34 (d, J = 7.0 Hz, 1H), 7.25 (t, J = 7.9 Hz, 1H), 7.19 – 7.16 (m, 1H), 7.13 (t, J = 7.4 Hz, 2H), 7.07 (d, J = 8.0 Hz, 1H), 6.96 (d, J = 7.3 Hz, 2H), 5.66 – 5.58 (m, 1H), 5.02 (d, J = 10.6 Hz, 1H), 4.62 – 4.52 (m, 2H), 4.52 – 4.45 (m, 1H), 3.66 (d, J = 14.0 Hz, 1H), 3.34 (d, J = 14.0 Hz, 1H); ^{13}C NMR (201 MHz, CD_3OD) δ 172.9, 144.2, 136.3, 130.7, 130.4, 130.1, 129.4, 129.2 (d, J = 3.4 Hz), 128.5, 126.2, 126.0, 118.2 (d, J = 3.2 Hz), 112.1, 45.8, 37.9. Positive ion ESI-MS: Calcd for $C_{18}H_{19}ClN_2$ $[M-Cl]^+$: 263.2. Found: 263.2.

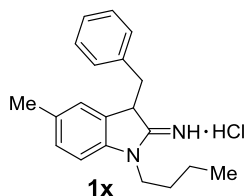


1v: Pale yellow solid, mp = 233 – 237 °C; 1H NMR (400 MHz, CD_3OD) δ 7.50 – 7.42 (m, 1H), 7.33 – 7.10 (m, 8H), 7.01 – 6.94 (m, 2H), 6.93 – 6.86 (m, 1H), 6.77 – 6.61 (m, 2H), 5.23 (d, J = 17.0 Hz, 1H), 5.05 (d, J = 17.0 Hz, 1H), 3.73 (d, J = 14.0 Hz, 1H), 3.46 (d, J = 14.1 Hz, 1H); ^{13}C NMR (101 MHz, CD_3OD) δ 173.43, 144.36, 136.32, 133.64, 130.82, 130.48, 130.14, 130.07, 129.60, 129.05, 128.68, 127.29, 126.38, 126.06, 112.53, 47.31, 37.41. Positive ion ESI-MS: Calcd for $C_{22}H_{21}ClN_2$ $[M-Cl]^+$: 313.2. Found: 313.2.

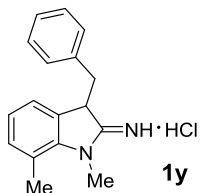


1w: Pale yellow solid, mp = 230 – 232 °C; 1H NMR (600 MHz, CD_3OD) δ 7.37 (t, J = 8.1 Hz, 1H), 7.34 (d, J = 7.0 Hz, 1H), 7.29 – 7.22 (m, 3H), 7.19 (t, J = 7.3 Hz, 1H), 7.13 – 7.03 (m, 5H),

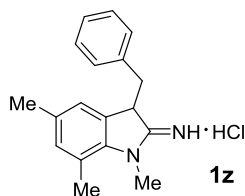
6.98 (d, $J = 7.9$ Hz, 1H), 6.91 (d, $J = 6.9$ Hz, 2H), 3.95 – 3.77 (m, 2H), 3.60 (d, $J = 13.9$ Hz, 1H), 3.27 (d, $J = 13.9$ Hz, 1H), 2.55 – 2.45 (m, 2H), 1.73 – 1.59 (m, 2H); ^{13}C NMR (151 MHz, CD_3OD) δ 172.7, 144.3, 141.8, 136.1, 130.7, 130.5, 130.1, 129.5, 129.3, 128.6, 127.3, 126.3, 126.1, 111.8, 43.4, 38.0, 33.3, 28.9. Positive ion ESI-MS: Calcd for $\text{C}_{24}\text{H}_{25}\text{ClN}_2$ $[\text{M}-\text{Cl}]^+$: 341.2. Found: 341.1.



1x: Pale yellow solid, mp = 237 – 239 °C; ^1H NMR (600 MHz, $\text{DMSO}-d_6$) δ 10.85 (s, 1H), 10.20 (s, 1H), 7.17 – 7.11 (m, 5H), 7.07 (d, $J = 8.5$ Hz, 1H), 6.96 – 6.90 (m, 2H), 4.67 – 4.58 (m, 1H), 3.96 – 3.89 (m, 1H), 3.81 – 3.75 (m, 1H), 3.62 – 3.55 (m, 1H), 3.47 – 3.41 (m, 1H), 2.30 (s, 3H), 1.27 – 1.18 (m, 2H), 1.03 – 0.92 (m, 2H), 0.73 (t, $J = 7.3$ Hz, 3H); ^{13}C NMR (151 MHz, $\text{DMSO}-d_6$) δ 170.1, 140.8, 135.6, 133.6, 129.4, 129.3, 128.8, 128.0, 126.9, 125.2, 110.4, 47.1, 42.0, 35.6, 28.4, 20.8, 18.9, 13.8. Positive ion ESI-MS: Calcd for $\text{C}_{20}\text{H}_{25}\text{ClN}_2$ $[\text{M}-\text{Cl}]^+$: 293.2. Found: 293.1.

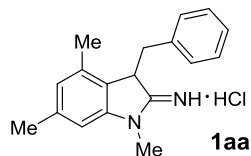


1y: Pale yellow solid, mp = 257 – 259 °C; ^1H NMR (600 MHz, CD_3OD) δ 7.22 – 7.16 (m, 3H), 7.13 (d, $J = 7.6$ Hz, 1H), 7.06 (t, $J = 7.6$ Hz, 1H), 7.03 – 6.99 (m, 2H), 6.94 (d, $J = 7.3$ Hz, 1H), 3.61 – 3.57 (m, 4H), 3.16 (d, $J = 13.8$ Hz, 1H), 2.54 (s, 3H); ^{13}C NMR (151 MHz, CD_3OD) δ 173.8, 142.6, 136.7, 134.0, 131.2, 130.5, 129.4, 128.4, 126.1, 123.9, 123.7, 38.7, 33.5, 19.0. Positive ion ESI-MS: Calcd for $\text{C}_{17}\text{H}_{19}\text{ClN}_2$ $[\text{M}-\text{Cl}]^+$: 251.2. Found: 251.1.

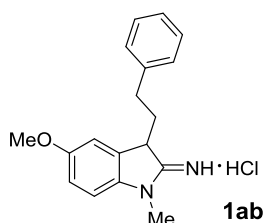


1z: Pale yellow solid, mp = 258 – 260 °C; ^1H NMR (600 MHz, CD_3OD) δ 7.26 – 7.15 (m, 3H), 7.04 – 6.97 (m, 2H), 6.95 (s, 1H), 6.76 (s, 1H), 3.60 – 3.51 (m, 4H), 3.14 (d, $J = 13.8$ Hz, 1H), 2.49 (s, 3H), 2.25 (s, 3H); ^{13}C NMR (151 MHz, CD_3OD) δ 173.5, 140.3, 136.7, 136.2, 134.4,

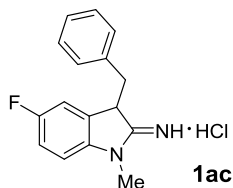
131.3, 130.5, 129.4, 128.4, 124.5, 123.3, 38.6, 33.3, 20.9, 18.8. Positive ion ESI-MS: Calcd for $C_{18}H_{21}ClN_2$ $[M-Cl]^+$: 265.2. Found: 265.2.



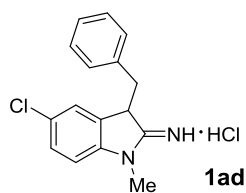
1aa: Pale yellow solid, mp = 262 – 264 °C; 1H NMR (600 MHz, DMSO- d_6) δ 11.05 (s, 1H), 10.32 (s, 1H), 7.12 – 7.04 (m, 3H), 6.84 (s, 1H), 6.82 – 6.77 (m, 2H), 6.75 (s, 1H), 4.66 (s, 1H), 3.63 – 3.59 (m, 1H), 3.54 – 3.48 (m, 1H), 3.24 (s, 3H), 2.36 (s, 3H), 2.26 (s, 3H); ^{13}C NMR (151 MHz, DMSO- D_6) δ 171.3, 143.6, 138.2, 135.3, 134.1, 128.8, 127.9, 126.9, 126.9, 124.0, 108.6, 46.6, 34.4, 29.4, 21.1, 18.1. Positive ion ESI-MS: Calcd for $C_{18}H_{21}ClN_2$ $[M-Cl]^+$: 265.2. Found: 265.2.



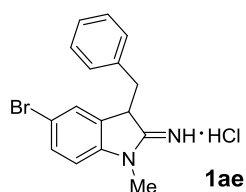
1ab: Pale yellow solid, mp = 255 – 257 °C; 1H NMR (600 MHz, DMSO- d_6) δ 10.44 (s, 1H), 10.00 (s, 1H), 7.27 – 7.21 (m, 3H), 7.20 – 7.15 (m, 2H), 7.10 (d, J = 7.3 Hz, 2H), 6.99 (dd, J = 8.6, 2.4 Hz, 1H), 4.39 (t, J = 4.8 Hz, 1H), 3.78 (s, 3H), 3.45 (s, 3H), 2.56 – 2.45 (m, 2H), 2.40 – 2.34 (m, 1H), 2.31 – 2.24 (m, 1H); ^{13}C NMR (151 MHz, DMSO- d_6) δ 170.9, 157.1, 140.4, 137.1, 130.7, 128.3, 128.3, 126.1, 113.0, 111.2, 111.0, 55.8, 46.1, 31.2, 30.2, 29.7. Positive ion ESI-MS: Calcd for $C_{18}H_{21}ClN_2O$ $[M-Cl]^+$: 281.2. Found: 281.2.



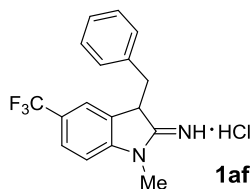
1ac: Pale yellow solid, mp = 260 – 263 °C; 1H NMR (600 MHz, CD_3OD) δ 7.25 – 7.22 (m, 3H), 7.19 – 7.16 (m, 1H), 7.15 – 7.11 (m, 1H), 7.10 – 7.07 (m, 2H), 6.80 (dd, J = 8.1, 2.5 Hz, 1H), 3.64 (d, J = 14.0 Hz, 1H), 3.40 (s, 3H), 3.16 (d, J = 13.8 Hz, 1H); ^{13}C NMR (151 MHz, CD_3OD) δ 173.4, 161.7 (d, J = 242.6 Hz), 141.0, 136.5, 132.6 (d, J = 9.3 Hz), 130.5, 129.6, 128.6, 116.4 (d, J = 24.5 Hz), 113.9 (d, J = 26.5 Hz), 112.8 (d, J = 8.8 Hz), 38.1, 30.0; ^{19}F NMR (565 MHz, CD_3OD) δ -119.3. Positive ion ESI-MS: Calcd for $C_{16}H_{16}ClFN_2$ $[M-Cl]^+$: 255.1. Found: 255.1.



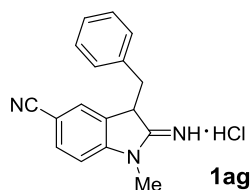
1ad: Pale yellow solid, mp = 250 – 253 °C; ¹H NMR (800 MHz, CD₃OD) δ 7.40 (dd, *J* = 8.4, 2.1 Hz, 1H), 7.28 – 7.22 (m, 3H), 7.17 (d, *J* = 8.5 Hz, 1H), 7.09 – 7.05 (m, 2H), 7.01 (d, *J* = 2.0 Hz, 1H), 3.62 (d, *J* = 13.9 Hz, 1H), 3.39 (s, 3H), 3.13 (d, *J* = 13.9 Hz, 1H); ¹³C NMR (201 MHz, CD₃OD) δ 173.5, 143.6, 136.5, 132.5, 131.6, 130.4, 130.0, 129.6, 128.7, 126.4, 112.9, 38.1, 29.9. Positive ion ESI-MS: Calcd for C₁₆H₁₆Cl₂N₂ [M – Cl]⁺: 271.1. Found: 271.1.



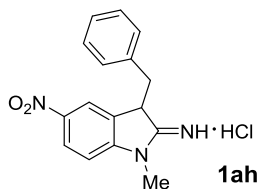
1ae: Pale yellow solid, mp = 248 – 250 °C; ¹H NMR (800 MHz, CD₃OD) δ 7.55 (dd, *J* = 8.4, 2.0 Hz, 1H), 7.28 – 7.23 (m, 3H), 7.14 (d, *J* = 1.9 Hz, 1H), 7.12 (d, *J* = 8.4 Hz, 1H), 7.09 – 7.05 (m, 2H), 3.62 (d, *J* = 13.9 Hz, 1H), 3.39 (s, 3H), 3.12 (d, *J* = 13.9 Hz, 1H); ¹³C NMR (201 MHz, CD₃OD) δ 173.4, 144.1, 136.5, 133.0, 132.8, 130.5, 129.6, 129.2, 128.7, 118.9, 113.3, 38.1, 29.9. Positive ion ESI-MS: Calcd for C₁₆H₁₆BrClN₂ [M – Cl]⁺: 315.0. Found: 315.1.



1af: Pale yellow solid, mp = 248 – 251 °C; ¹H NMR (600 MHz, CD₃OD) δ 7.72 (d, *J* = 8.2 Hz, 1H), 7.37 (d, *J* = 8.3 Hz, 1H), 7.28 – 7.22 (m, 3H), 7.19 (s, 1H), 7.11 – 7.05 (m, 2H), 3.71 (d, *J* = 13.7 Hz, 1H), 3.48 (s, 3H), 3.13 (d, *J* = 13.7 Hz, 1H); ¹³C NMR (151 MHz, CD₃OD) δ 174.4, 147.9, 136.6, 131.6, 130.5, 129.7, 128.7, 128.0 (d, *J* = 33.2 Hz), 126.4 (q, *J* = 4.7 Hz), 125.5 (q, *J* = 270.9 Hz), 121.8 (q, *J* = 4.0 Hz), 112.1, 38.2, 30.1; ¹⁹F NMR (565 MHz, CD₃OD) δ –63.5. Positive ion ESI-MS: Calcd for C₁₇H₁₆ClF₃N₂ [M – Cl]⁺: 305.1. Found: 305.1.



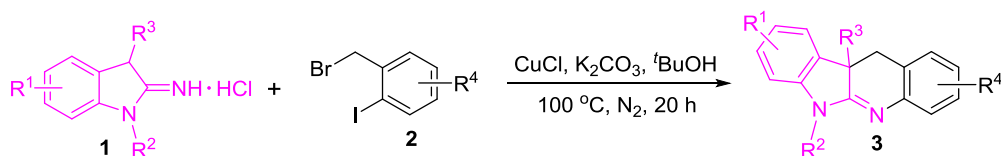
1ag: Pale yellow solid, mp = 242 – 245 °C; ¹H NMR (800 MHz, CD₃OD) δ 7.78 (dd, *J* = 8.3, 1.6 Hz, 1H), 7.36 (d, *J* = 8.3 Hz, 1H), 7.30 (d, *J* = 1.4 Hz, 1H), 7.28 – 7.22 (m, 3H), 7.11 – 7.05 (m, 2H), 3.68 (d, *J* = 13.9 Hz, 1H), 3.45 (s, 3H), 3.19 (d, *J* = 13.9 Hz, 1H); ¹³C NMR (201 MHz, CD₃OD) δ 174.6, 148.6, 136.4, 135.2, 131.9, 130.5, 129.7, 129.4, 128.8, 119.3, 112.7, 109.3, 38.0, 30.1. ESI-MS: Calcd for C₁₇H₁₆ClN₃ [M – Cl]⁺: 262.1. Found: 262.0.



1ah: Pale yellow solid, mp = 189 – 192 °C; ¹H NMR (800 MHz, CD₃OD) δ 8.34 (dd, *J* = 8.7, 2.2 Hz, 1H), 7.84 – 7.79 (m, 1H), 7.39 (d, *J* = 8.7 Hz, 1H), 7.30 – 7.24 (m, 3H), 7.12 – 7.07 (m, 2H), 3.71 (d, *J* = 13.9 Hz, 1H), 3.49 (s, 3H), 3.17 (d, *J* = 13.9 Hz, 1H); ¹³C NMR (201 MHz, CD₃OD) δ 175.3, 149.9, 146.4, 136.3, 131.9, 130.5, 129.8, 128.9, 126.7, 121.5, 112.1, 38.1, 30.3. Positive ion ESI-MS: Calcd for C₁₆H₁₆ClN₃O₂ [M – Cl]⁺: 282.1. Found: 282.2.

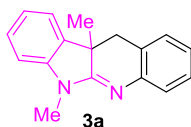
3. Synthesis and Characterization Data of 3a-an, 4, 5a-f.

3.1. General Procedures for Preparation of 3a-an

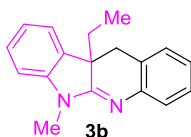


An oven-dried Schlenk tube equipped with a Teflon screw seal was charged with a magnetic stirbar, CuCl (30 μmol , 10 mol%), **1** (0.33 mmol, 1.1 equiv), **2** (0.3 mmol, 1.0 equiv) and K_2CO_3 (1.2 mmol, 4.0 equiv). The tube was evacuated and backfilled with argon; this procedure was carried out three times. The solids were dissolved in $t\text{BuOH}$ (3.0 mL), the tube was sealed, and the reaction mixture was stirred in a pre-heated oil-bath at $100\text{ }^\circ\text{C}$ for 20 h. The solvent was then removed under vacuum, and the residue was purified by column chromatography on silica to give the desired product **3**.

3.2. Characterization of 3a-an

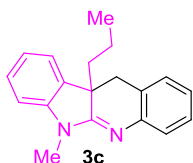


3a: Pale yellow solid, mp = $187 - 189\text{ }^\circ\text{C}$; Eluent: petroleum ether/EtOAc 10:1; $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.27 – 7.18 (m, 4H), 7.14 (d, $J = 7.2\text{ Hz}$, 1H), 7.02 – 6.93 (m, 2H), 6.80 (d, $J = 7.8\text{ Hz}$, 1H), 3.35 (s, 3H), 3.05 – 2.94 (m, 2H), 1.17 (s, 3H); $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 171.0, 145.7, 145.6, 135.3, 128.6, 128.1, 127.8, 124.2, 123.4, 123.1, 122.1, 121.2, 107.6, 41.1, 35.4, 27.6, 22.5. ESI-MS: Calcd for $\text{C}_{17}\text{H}_{17}\text{N}_2$ $[\text{M}+\text{H}]^+$: 249.1. Found: 249.0. HRMS (ESI $^+$): Calcd for $\text{C}_{17}\text{H}_{17}\text{N}_2$, $[\text{M}+\text{H}]^+ m/z$ 249.1392. Found 249.1389.

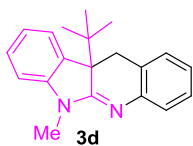


3b: Light yellow oil, Eluent: petroleum ether/EtOAc 10:1; $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.26 (td, $J = 7.7, 1.2\text{ Hz}$, 1H), 7.23 – 7.16 (m, 3H), 7.12 (d, $J = 7.5\text{ Hz}$, 1H), 7.01 – 6.94 (m, 2H), 6.80 (d, $J = 7.8\text{ Hz}$, 1H), 3.35 (s, 3H), 3.07 (d, $J = 15.6\text{ Hz}$, 1H), 2.99 (d, $J = 15.6\text{ Hz}$, 1H), 1.75 – 1.63 (m,

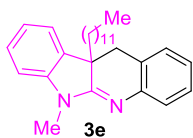
1H), 1.55 – 1.43 (m, 1H), 0.61 (t, $J = 7.4$ Hz, 3H); ^{13}C NMR (101 MHz, CDCl_3) δ 170.6, 146.7, 145.9, 133.4, 128.6, 128.2, 127.9, 124.2, 123.4, 123.1, 122.8, 121.1, 107.4, 45.5, 33.9, 27.7, 27.6, 8.3. ESI-MS: Calcd for $\text{C}_{18}\text{H}_{19}\text{N}_2$ $[\text{M}+\text{H}]^+$: 263.1. Found: 263.0. HRMS (ESI $^+$): Calcd for $\text{C}_{18}\text{H}_{19}\text{N}_2$, $[\text{M}+\text{H}]^+$ m/z 263.1548. Found 263.1545.



3c: Light yellow oil; Eluent: petroleum ether/EtOAc 10:1; ^1H NMR (400 MHz, CDCl_3) δ 7.29 – 7.20 (m, 3H), 7.18 (d, $J = 7.3$ Hz, 1H), 7.12 (d, $J = 7.2$ Hz, 1H), 7.02 – 6.92 (m, 2H), 6.79 (d, $J = 7.8$ Hz, 1H), 3.34 (s, 3H), 3.09 – 2.96 (m, 2H), 1.65 (td, $J = 12.8, 4.5$ Hz, 1H), 1.40 (td, $J = 12.8, 4.5$ Hz, 1H), 1.16 – 1.02 (m, 1H), 0.99 – 0.85 (m, 1H), 0.66 – 0.59 (m, 3H); ^{13}C NMR (101 MHz, CDCl_3) δ 170.5, 146.5, 145.8, 133.7, 128.5, 128.1, 127.8, 124.1, 123.3, 123.0, 122.6, 121.2, 107.3, 45.1, 37.0, 34.4, 27.5, 17.0, 14.0. ESI-MS: Calcd for $\text{C}_{19}\text{H}_{21}\text{N}_2$ $[\text{M}+\text{H}]^+$: 277.2. Found: 277.0. HRMS (ESI $^+$): Calcd for $\text{C}_{19}\text{H}_{21}\text{N}_2$, $[\text{M}+\text{H}]^+$ m/z 277.1705. Found 277.1704.

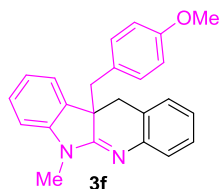


3d: Light yellow oil; Eluent: petroleum ether/EtOAc 10:1; ^1H NMR (400 MHz, CDCl_3) δ 7.27 – 7.22 (m, 1H), 7.21 – 7.14 (m, 3H), 7.08 (d, $J = 7.3$ Hz, 1H), 6.99 – 6.89 (m, 2H), 6.77 (d, $J = 7.8$ Hz, 1H), 3.45 (d, $J = 16.9$ Hz, 1H), 3.35 (s, 3H), 3.01 (d, $J = 16.8$ Hz, 1H), 0.73 (s, 9H); ^{13}C NMR (101 MHz, CDCl_3) δ 169.5, 147.5, 146.5, 134.8, 128.0, 127.7, 127.3, 124.7, 124.1, 123.9, 120.1, 107.0, 49.8, 38.7, 31.8, 28.0, 26.3. ESI-MS: Calcd for $\text{C}_{20}\text{H}_{23}\text{N}_2$ $[\text{M}+\text{H}]^+$: 291.2. Found: 291.0. HRMS (ESI $^+$): Calcd for $\text{C}_{20}\text{H}_{23}\text{N}_2$, $[\text{M}+\text{H}]^+$ m/z 291.1861. Found 291.1860.

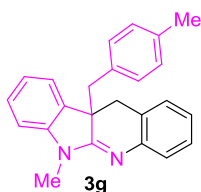


3e: Light yellow oil; Eluent: petroleum ether/EtOAc 10:1; ^1H NMR (600 MHz, CDCl_3) δ 7.25 (td, $J = 7.7, 1.0$ Hz, 1H), 7.23 – 7.20 (m, 2H), 7.18 (d, $J = 7.2$ Hz, 1H), 7.12 (d, $J = 7.3$ Hz, 1H), 7.00 – 6.94 (m, 2H), 6.80 (d, $J = 7.8$ Hz, 1H), 3.35 (s, 3H), 3.06 (d, $J = 15.5$ Hz, 1H), 2.99 (d, $J = 15.5$ Hz, 1H), 1.63 (td, $J = 12.9, 4.4$ Hz, 1H), 1.43 (td, $J = 12.7, 4.2$ Hz, 1H), 1.29 – 0.95 (m, 20H), 0.86 (t,

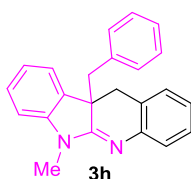
$J = 7.1$ Hz, 3H); ^{13}C NMR (151 MHz, CDCl_3) δ 170.7, 146.7, 145.9, 133.8, 128.6, 128.2, 127.9, 124.2, 123.4, 123.1, 122.8, 121.1, 107.4, 45.1, 34.8, 34.5, 32.0, 29.7, 29.6, 29.5, 29.4, 29.4, 27.6, 23.7, 22.8, 14.2. ESI-MS: Calcd for $\text{C}_{28}\text{H}_{39}\text{N}_2$ $[\text{M}+\text{H}]^+$: 403.3. Found: 403.1. HRMS (ESI $^+$): Calcd for $\text{C}_{28}\text{H}_{39}\text{N}_2$, $[\text{M}+\text{H}]^+$ m/z 403.3113. Found 403.3128.



3f: Light yellow oil; Eluent: petroleum ether/EtOAc 10:1; ^1H NMR (600 MHz, CDCl_3) δ 7.32 (d, $J = 7.5$ Hz, 1H), 7.27 (t, $J = 7.5$ Hz, 1H), 7.22 – 7.16 (m, 2H), 7.05 (t, $J = 7.2$ Hz, 1H), 6.90 (d, $J = 4.3$ Hz, 2H), 6.66 – 6.59 (m, 3H), 6.57 (d, $J = 8.5$ Hz, 2H), 3.70 (s, 3H), 3.14 (s, 3H), 3.10 (d, $J = 15.7$ Hz, 1H), 2.95 (d, $J = 15.6$ Hz, 1H), 2.73 – 2.60 (m, 2H); ^{13}C NMR (151 MHz, CDCl_3) δ 169.7, 158.2, 146.2, 145.8, 132.4, 131.0, 128.7, 128.2, 127.9, 127.7, 124.4, 123.5, 122.9, 120.5, 112.7, 107.2, 55.0, 46.2, 39.0, 33.1, 27.2. ESI-MS: Calcd for $\text{C}_{24}\text{H}_{23}\text{N}_2\text{O}$ $[\text{M}+\text{H}]^+$: 355.2. Found: 355.1. HRMS (ESI $^+$): Calcd for $\text{C}_{24}\text{H}_{23}\text{N}_2\text{O}$, $[\text{M}+\text{H}]^+$ m/z 355.1810. Found 355.1814.

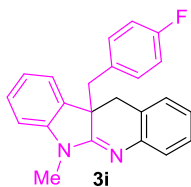


3g: Pale yellow solid; mp = 154 – 156 $^{\circ}\text{C}$; Eluent: petroleum ether/EtOAc 10:1; ^1H NMR (400 MHz, CDCl_3) δ 7.35 – 7.24 (m, 2H), 7.23 – 7.16 (m, 2H), 7.05 (td, $J = 7.3, 1.4$ Hz, 1H), 6.94 – 6.83 (m, 4H), 6.61 (d, $J = 7.8$ Hz, 1H), 6.55 (d, $J = 7.9$ Hz, 2H), 3.15 (s, 3H), 3.11 (d, $J = 15.7$ Hz, 1H), 2.94 (d, $J = 15.7$ Hz, 1H), 2.68 (s, 2H), 2.24 (s, 3H); ^{13}C NMR (101 MHz, CDCl_3) δ 169.9, 146.4, 145.94, 136.0, 132.6, 132.5, 130.1, 128.8, 128.3, 128.2, 128.1, 124.5, 123.8, 123.7, 123.1, 120.5, 107.3, 46.3, 39.5, 33.2, 27.3, 21.1. ESI-MS: Calcd for $\text{C}_{24}\text{H}_{23}\text{N}_2$ $[\text{M}+\text{H}]^+$: 339.2. Found: 339.0. HRMS (ESI $^+$): Calcd for $\text{C}_{24}\text{H}_{23}\text{N}_2$, $[\text{M}+\text{H}]^+$ m/z 339.1861. Found 339.1886.

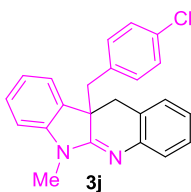


3h: Light yellow oil; Eluent: petroleum ether/EtOAc 10:1; ^1H NMR (400 MHz, CDCl_3) δ 7.35 – 7.31 (m, 1H), 7.28 (t, $J = 7.5$ Hz, 1H), 7.24 – 7.16 (m, 2H), 7.14 – 7.04 (m, 4H), 6.94 – 6.87 (m,

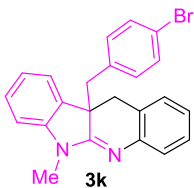
2H), 6.65 (dd, $J = 7.7, 1.4$ Hz, 2H), 6.58 (d, $J = 7.8$ Hz, 1H), 3.16 – 3.09 (m, 4H), 2.98 (d, $J = 15.7$ Hz, 1H), 2.77 (d, $J = 12.8$ Hz, 1H), 2.69 (d, $J = 12.8$ Hz, 1H); ^{13}C NMR (101 MHz, CDCl_3) δ 169.6, 146.4, 145.9, 135.7, 132.3, 130.2, 128.9, 128.4, 128.1, 127.4, 126.6, 124.6, 123.7, 123.7, 123.0, 120.6, 107.3, 46.3, 40.0, 33.4, 27.2. ESI-MS: Calcd for $\text{C}_{23}\text{H}_{21}\text{N}_2$ $[\text{M}+\text{H}]^+$: 325.2. Found: 325.1. HRMS (ESI $^+$): Calcd for $\text{C}_{23}\text{H}_{21}\text{N}_2$, $[\text{M}+\text{H}]^+$ m/z 325.1705. Found 325.1712.



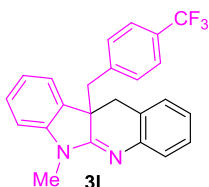
3i: Pale yellow solid, mp = 138 – 140 °C; Eluent: petroleum ether/EtOAc 10:1; ^1H NMR (600 MHz, CDCl_3) δ 7.35 – 7.26 (m, 2H), 7.24 – 7.16 (m, 2H), 7.05 (t, $J = 7.2$ Hz, 1H), 6.97 (d, $J = 7.0$ Hz, 1H), 6.93 (t, $J = 7.4$ Hz, 1H), 6.75 (t, $J = 8.6$ Hz, 2H), 6.58 (t, $J = 6.6$ Hz, 3H), 3.09 (d, $J = 13.2$ Hz, 4H), 3.01 (d, $J = 15.7$ Hz, 1H), 2.79 (d, $J = 13.1$ Hz, 1H); ^{13}C NMR (151 MHz, CDCl_3) δ 169.1, 161.7 (d, $J = 244.4$ Hz), 146.2, 145.7, 132.0, 131.3 (d, $J = 7.2$ Hz), 128.7, 128.4, 128.1, 124.5, 123.7, 123.3, 122.8, 120.7, 114.1 (d, $J = 20.9$ Hz), 107.2, 46.3, 39.2, 33.5, 27.1. ESI-MS: Calcd for $\text{C}_{23}\text{H}_{20}\text{FN}_2$ $[\text{M}+\text{H}]^+$: 343.2. Found: 343.1. HRMS (ESI $^+$): Calcd for $\text{C}_{23}\text{H}_{20}\text{FN}_2$, $[\text{M}+\text{H}]^+$ m/z 343.1611. Found 343.1628.



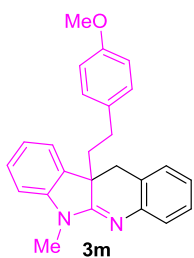
3j: Light yellow oil; Eluent: petroleum ether/EtOAc 10:1; ^1H NMR (600 MHz, CDCl_3) δ 7.34 – 7.26 (m, 2H), 7.22 – 7.17 (m, 2H), 7.07 – 7.01 (m, 3H), 6.96 (d, $J = 6.7$ Hz, 1H), 6.92 (t, $J = 7.4$ Hz, 1H), 6.59 (d, $J = 7.8$ Hz, 1H), 6.55 (d, $J = 8.3$ Hz, 2H), 3.09 (d, $J = 23.8$ Hz, 4H), 3.00 (d, $J = 15.7$ Hz, 1H), 2.77 (d, $J = 13.0$ Hz, 1H), 2.62 (d, $J = 13.0$ Hz, 1H); ^{13}C NMR (151 MHz, CDCl_3) δ 169.0, 146.2, 145.6, 134.1, 132.4, 131.9, 131.2, 128.7, 128.5, 128.1, 127.4, 124.5, 123.7, 123.3, 122.7, 120.7, 107.3, 46.1, 39.3, 33.5, 27.2. ESI-MS: Calcd for $\text{C}_{23}\text{H}_{20}\text{ClN}_2$ $[\text{M}+\text{H}]^+$: 359.1. Found: 359.1. HRMS (ESI $^+$): Calcd for $\text{C}_{23}\text{H}_{20}\text{ClN}_2$, $[\text{M}+\text{H}]^+$ m/z 359.1315. Found 359.1327.



3k: Pale yellow solid, mp = 138 – 140 °C; Eluent: petroleum ether/EtOAc 10:1; ¹H NMR (600 MHz, CDCl₃) δ 7.32 (d, *J* = 7.6 Hz, 1H), 7.28 (t, *J* = 7.5 Hz, 1H), 7.22 – 7.16 (m, 4H), 7.05 (t, *J* = 7.2 Hz, 1H), 6.96 (d, *J* = 7.0 Hz, 1H), 6.92 (t, *J* = 7.3 Hz, 1H), 6.59 (d, *J* = 7.8 Hz, 1H), 6.49 (d, *J* = 8.2 Hz, 2H), 3.11 (s, 3H), 3.07 (d, *J* = 15.7 Hz, 1H), 2.99 (d, *J* = 15.7 Hz, 1H), 2.75 (d, *J* = 13.0 Hz, 1H), 2.60 (d, *J* = 13.0 Hz, 1H); ¹³C NMR (151 MHz, CDCl₃) δ 169.0, 146.2, 145.7, 134.7, 131.9, 131.6, 130.4, 128.7, 128.5, 128.1, 124.5, 123.7, 123.3, 122.7, 120.7, 120.6, 107.3, 46.1, 39.4, 33.5, 27.2. ESI-MS: Calcd for C₂₃H₂₀BrN₂ [M+H]⁺: 403.1. Found: 403.1. HRMS (ESI⁺): Calcd for C₂₃H₂₀BrN₂, [M+H]⁺ *m/z* 403.0810. Found 403.0817.

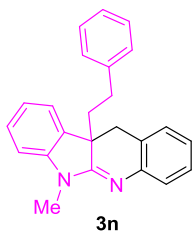


3l: Light yellow oil; Eluent: petroleum ether/EtOAc 10:1; ¹H NMR (600 MHz, CDCl₃) δ 7.35 – 7.27 (m, 4H), 7.23 – 7.18 (m, 2H), 7.06 (t, *J* = 7.3 Hz, 1H), 6.98 (d, *J* = 7.1 Hz, 1H), 6.94 (t, *J* = 7.2 Hz, 1H), 6.72 (d, *J* = 7.8 Hz, 2H), 6.56 (d, *J* = 7.8 Hz, 1H), 3.09 (d, *J* = 15.6 Hz, 1H), 3.07 (s, 3H), 3.01 (d, *J* = 15.7 Hz, 1H), 2.87 (d, *J* = 12.9 Hz, 1H), 2.69 (d, *J* = 12.9 Hz, 1H); ¹³C NMR (151 MHz, CDCl₃) δ 168.7, 146.2, 145.6, 139.8, 131.7, 130.2, 128.7, 128.7 (d, *J* = 32.4 Hz), 128.6, 128.2, 124.6, 124.2 (q, *J* = 272.0 Hz), 124.1 (q, *J* = 3.7 Hz), 123.8, 123.3, 122.7, 120.8, 107.4, 46.2, 39.8, 33.6, 27.1. ESI-MS: Calcd for C₂₄H₂₀F₃N₂ [M+H]⁺: 393.2. Found: 393.1. HRMS (ESI⁺): Calcd for C₂₄H₂₀F₃N₂, [M+H]⁺ *m/z* 393.1579. Found 393.1596.

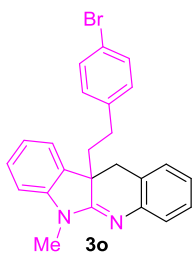


3m: Light yellow oil; Eluent: petroleum ether/EtOAc 10:1; ¹H NMR (600 MHz, CDCl₃) δ 7.28 (t, *J* = 7.7 Hz, 1H), 7.26 – 7.18 (m, 3H), 7.09 (d, *J* = 7.2 Hz, 1H), 7.01 (t, *J* = 7.5 Hz, 1H), 6.96 (t, *J* =

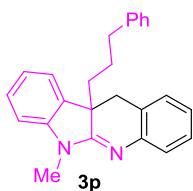
7.2 Hz, 1H), 6.82 (d, $J = 7.8$ Hz, 1H), 6.77 (d, $J = 7.7$ Hz, 2H), 6.68 – 6.61 (m, 2H), 3.66 (s, 3H), 3.35 (s, 3H), 3.12 – 2.99 (m, 2H), 2.34 – 2.24 (m, 1H), 2.17 – 2.08 (m, 1H), 2.04 – 1.94 (m, 1H), 1.72 – 1.63 (m, 1H); ^{13}C NMR (151 MHz, CDCl_3) δ 169.8, 157.6, 146.5, 145.4, 133.1, 133.0, 129.0, 128.5, 128.3, 127.9, 124.0, 123.5, 122.7, 122.6, 121.3, 113.5, 107.5, 55.1, 45.0, 36.7, 34.5, 29.2, 27.6. ESI-MS: Calcd for $\text{C}_{25}\text{H}_{25}\text{N}_2\text{O}$ $[\text{M}+\text{H}]^+$: 369.2. Found: 369.1. HRMS (ESI $^+$): Calcd for $\text{C}_{25}\text{H}_{25}\text{N}_2\text{O}$, $[\text{M}+\text{H}]^+$ m/z 369.1967. Found 369.1980.



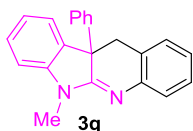
3n: Light yellow oil; Eluent: petroleum ether/EtOAc 10:1; ^1H NMR (400 MHz, CDCl_3) δ 7.38 – 7.24 (m, 4H), 7.19 – 7.00 (m, 6H), 6.95 – 6.84 (m, 3H), 3.40 (s, 3H), 3.19 – 3.05 (m, 2H), 2.42 (td, $J = 12.8, 5.1$ Hz, 1H), 2.26 (td, $J = 12.7, 4.5$ Hz, 1H), 2.10 (td, $J = 12.7, 12.3, 5.2$ Hz, 1H), 1.77 (td, $J = 12.7, 4.5$ Hz, 1H); ^{13}C NMR (101 MHz, CDCl_3) δ 169.9, 146.7, 145.8, 141.2, 133.2, 128.6, 128.4, 128.2, 128.2, 128.0, 125.9, 124.3, 123.6, 122.8, 122.7, 121.3, 107.6, 45.0, 36.6, 34.7, 30.3, 27.7. ESI-MS: Calcd for $\text{C}_{24}\text{H}_{23}\text{N}_2$ $[\text{M}+\text{H}]^+$: 339.2. Found: 339.0. HRMS (ESI $^+$): Calcd for $\text{C}_{24}\text{H}_{23}\text{N}_2$, $[\text{M}+\text{H}]^+$ m/z 339.1861. Found 339.1872.



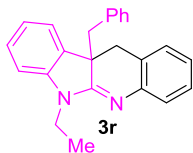
3o: Light yellow oil; Eluent: petroleum ether/EtOAc 10:1; ^1H NMR (600 MHz, CDCl_3) δ 7.29 (t, $J = 7.7$ Hz, 1H), 7.27 – 7.18 (m, 5H), 7.10 (d, $J = 7.2$ Hz, 1H), 7.01 (t, $J = 7.4$ Hz, 1H), 6.97 (t, $J = 7.2$ Hz, 1H), 6.83 (d, $J = 7.8$ Hz, 1H), 6.69 (d, $J = 8.4$ Hz, 2H), 3.35 (s, 3H), 3.09 – 3.01 (m, 2H), 2.28 (td, $J = 12.8, 5.2$ Hz, 1H), 2.12 (td, $J = 13.2, 12.8, 4.4$ Hz, 1H), 2.01 (td, $J = 12.7, 5.2$ Hz, 1H), 1.66 (td, $J = 12.7, 4.4$ Hz, 1H); ^{13}C NMR (151 MHz, CDCl_3) δ 169.5, 146.4, 145.2, 139.9, 132.7, 131.1, 129.8, 128.5, 128.0, 124.0, 123.6, 122.6, 122.5, 121.4, 119.4, 107.6, 44.9, 36.2, 34.6, 29.6, 27.7. ESI-MS: Calcd for $\text{C}_{24}\text{H}_{22}\text{BrN}_2$ $[\text{M}+\text{H}]^+$: 417.1. Found: 417.1. HRMS (ESI $^+$): Calcd for $\text{C}_{24}\text{H}_{22}\text{BrN}_2$, $[\text{M}+\text{H}]^+$ m/z 417.0966. Found 417.0981.



3p: Light yellow oil; Eluent: petroleum ether/EtOAc 10:1; ^1H NMR (600 MHz, CDCl_3) δ 7.26 – 7.19 (m, 3H), 7.17 – 7.12 (m, 3H), 7.11 – 7.06 (m, 2H), 7.00 – 6.90 (m, 4H), 6.77 (d, $J = 7.8$ Hz, 1H), 3.32 (s, 3H), 3.03 (d, $J = 15.5$ Hz, 1H), 2.98 (d, $J = 15.5$ Hz, 1H), 2.40 – 2.30 (m, 1H), 2.29 – 2.20 (m, 1H), 1.74 (td, $J = 12.6, 4.2$ Hz, 1H), 1.49 (td, $J = 12.6, 3.9$ Hz, 1H), 1.45 – 1.36 (m, 1H), 1.30 – 1.17 (m, 1H); ^{13}C NMR (151 MHz, CDCl_3) δ 170.4, 146.6, 145.8, 141.9, 133.5, 128.6, 128.3, 128.2, 127.9, 125.7, 124.3, 123.5, 123.0, 122.7, 121.2, 107.5, 44.9, 35.7, 34.5, 34.5, 27.7, 25.6. ESI-MS: Calcd for $\text{C}_{25}\text{H}_{25}\text{N}_2$ $[\text{M}+\text{H}]^+$: 353.2. Found: 353.1. HRMS (ESI $^+$): Calcd for $\text{C}_{25}\text{H}_{25}\text{N}_2$, $[\text{M}+\text{H}]^+$ m/z 353.2018. Found 353.2039.

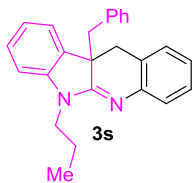


3q: Light yellow oil; Eluent: petroleum ether/EtOAc 10:1; ^1H NMR (400 MHz, CDCl_3) δ 7.33 – 7.28 (m, 3H), 7.22 – 7.17 (m, 1H), 7.15 (dd, $J = 7.8, 1.1$ Hz, 1H), 7.12 – 7.07 (m, 3H), 7.05 – 6.99 (m, 2H), 6.90 (td, $J = 7.5, 0.8$ Hz, 1H), 6.85 (td, $J = 7.3, 1.3$ Hz, 1H), 6.79 (d, $J = 7.8$ Hz, 1H), 3.65 (d, $J = 15.6$ Hz, 1H), 3.46 (s, 3H), 3.24 (d, $J = 15.5$ Hz, 1H); ^{13}C NMR (101 MHz, CDCl_3) δ 168.8, 146.1, 146.0, 139.7, 134.9, 128.6, 128.4, 128.2, 127.9, 127.1, 125.7, 124.2, 123.7, 123.3, 123.0, 121.5, 107.9, 49.4, 35.9, 28.0. ESI-MS: Calcd for $\text{C}_{22}\text{H}_{19}\text{N}_2$ $[\text{M}+\text{H}]^+$: 311.2. Found: 311.0. HRMS (ESI $^+$): Calcd for $\text{C}_{22}\text{H}_{19}\text{N}_2$, $[\text{M}+\text{H}]^+$ m/z 311.1548. Found 311.1542.

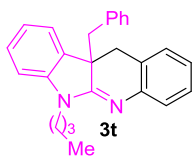


3r: Light yellow oil; Eluent: petroleum ether/EtOAc 10:1; ^1H NMR (400 MHz, Chloroform- d) δ 7.37 – 7.24 (m, 2H), 7.23 – 7.14 (m, 2H), 7.13 – 6.96 (m, 5H), 6.91 (t, $J = 7.4$ Hz, 1H), 6.64 – 6.50 (m, 3H), 3.92 – 3.73 (m, 1H), 3.58 – 3.41 (m, 1H), 3.11 (d, $J = 15.6$ Hz, 1H), 3.00 (d, $J = 15.7$ Hz, 1H), 2.84 (d, $J = 12.8$ Hz, 1H), 2.65 (d, $J = 12.9$ Hz, 1H), 0.96 (t, $J = 7.2$ Hz, 3H); ^{13}C NMR (101 MHz, CDCl_3) δ 168.5, 146.2, 145.6, 135.8, 132.6, 130.1, 128.8, 128.3, 128.1, 127.4, 126.5, 124.5, 123.6, 123.5, 123.0, 120.5, 107.4, 46.2, 40.1, 35.3, 33.9, 12.7. ESI-MS: Calcd for

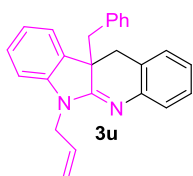
$C_{24}H_{23}N_2$ $[M+H]^+$: 339.2. Found: 339.1. HRMS (ESI⁺): Calcd for $C_{24}H_{23}N_2$, $[M+H]^+$ m/z 339.1861. Found 339.1869.



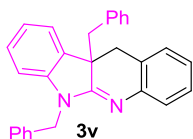
3s: Light yellow oil; Eluent: petroleum ether/EtOAc 10:1; ¹H NMR (400 MHz, CDCl₃) δ 7.32 (d, J = 6.9 Hz, 1H), 7.27 (t, J = 7.5 Hz, 1H), 7.22 – 7.13 (m, 2H), 7.12 – 7.01 (m, 4H), 6.98 (d, J = 6.7 Hz, 1H), 6.90 (t, J = 7.4 Hz, 1H), 6.65 – 6.53 (m, 3H), 3.79 (dt, J = 14.4, 7.1 Hz, 1H), 3.35 (dt, J = 14.3, 7.6 Hz, 1H), 3.09 (d, J = 15.7 Hz, 1H), 2.98 (d, J = 15.6 Hz, 1H), 2.82 (d, J = 12.8 Hz, 1H), 2.66 (d, J = 12.8 Hz, 1H), 1.45 (sext, J = 7.3 Hz, 2H), 0.80 (t, J = 7.4 Hz, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 168.9, 146.2, 135.8, 132.5, 130.1, 128.8, 128.3, 128.0, 127.5, 126.5, 124.6, 123.6, 123.5, 123.0, 120.4, 107.5, 46.1, 42.5, 40.1, 33.9, 20.5, 11.6. ESI-MS: Calcd for $C_{25}H_{25}N_2$ $[M+H]^+$: 353.2. Found: 353.1. HRMS (ESI⁺): Calcd for $C_{25}H_{25}N_2$, $[M+H]^+$ m/z 353.2018. Found 353.2033.



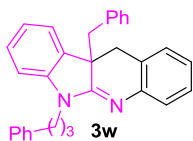
3t: Pale yellow solid, mp = 65-67 °C; Eluent: petroleum ether/EtOAc 10:1; ¹H NMR (600 MHz, CDCl₃) δ 7.34 – 7.26 (m, 2H), 7.24 – 7.18 (m, 2H), 7.13 – 7.09 (m, 1H), 7.08 – 7.02 (m, 3H), 7.00 (d, J = 7.2 Hz, 1H), 6.93 (t, J = 7.3 Hz, 1H), 6.66 – 6.57 (m, 3H), 3.82 (dt, J = 14.3, 7.4 Hz, 1H), 3.41 (dt, J = 14.5, 7.5 Hz, 1H), 3.12 (d, J = 15.6 Hz, 1H), 3.01 (d, J = 15.6 Hz, 1H), 2.83 (d, J = 12.9 Hz, 1H), 2.68 (d, J = 13.0 Hz, 1H), 1.40 (quint, J = 7.5 Hz, 2H), 1.30 – 1.22 (m, 1H), 1.21 – 1.13 (m, 1H), 0.89 (t, J = 7.2 Hz, 3H); ¹³C NMR (151 MHz, CDCl₃) δ 168.8, 146.2, 146.2, 135.8, 132.5, 130.1, 128.8, 128.3, 128.0, 127.5, 126.5, 124.6, 123.6, 123.5, 123.0, 120.4, 107.5, 46.1, 40.7, 40.1, 34.0, 29.3, 20.3, 14.0. ESI-MS: Calcd for $C_{26}H_{27}N_2$ $[M+H]^+$: 367.2. Found: 367.1. HRMS (ESI⁺): Calcd for $C_{26}H_{27}N_2$, $[M+H]^+$ m/z 367.2174. Found 367.2187.



3u: Pale yellow solid, mp = 71-73 °C; Eluent: petroleum ether/EtOAc 10:1; ¹H NMR (600 MHz, CDCl₃) δ 7.32 (d, *J* = 7.2 Hz, 1H), 7.29 (t, *J* = 7.4 Hz, 1H), 7.23 (d, *J* = 6.8 Hz, 1H), 7.18 (t, *J* = 7.5 Hz, 1H), 7.12 (t, *J* = 7.2 Hz, 1H), 7.09 – 7.05 (m, 3H), 7.03 (d, *J* = 6.9 Hz, 1H), 6.95 (t, *J* = 7.4 Hz, 1H), 6.63 (d, *J* = 7.2 Hz, 2H), 6.60 (d, *J* = 7.8 Hz, 1H), 5.60 – 5.46 (m, 1H), 5.09 – 4.96 (m, 1H), 4.90 – 4.78 (m, 1H), 4.59 – 4.49 (m, 1H), 4.04 (dd, *J* = 16.6, 5.5 Hz, 1H), 3.15 (d, *J* = 15.7 Hz, 1H), 3.03 (d, *J* = 15.6 Hz, 1H), 2.87 (d, *J* = 12.9 Hz, 1H), 2.70 (d, *J* = 13.0 Hz, 1H); ¹³C NMR (101 MHz, CDCl₃) δ 168.7, 145.9, 145.9, 135.8, 132.4, 131.9, 130.2, 128.8, 128.3, 128.1, 127.6, 126.6, 124.6, 123.7, 123.5, 123.1, 120.7, 116.9, 108.4, 46.3, 43.4, 40.1, 34.1. ESI-MS: Calcd for C₂₅H₂₃N₂ [M+H]⁺: 351.2. Found: 351.0. HRMS (ESI⁺): Calcd for C₂₅H₂₃N₂, [M+H]⁺ *m/z* 351.1861. Found 351.1874.

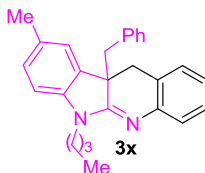


3v: Pale yellow solid, mp = 137-139 °C; Eluent: petroleum ether/EtOAc 10:1; ¹H NMR (400 MHz, CDCl₃) δ 7.34 – 7.23 (m, 3H), 7.21 – 7.14 (m, 4H), 7.12 – 7.03 (m, 5H), 6.93 (t, *J* = 7.4 Hz, 1H), 6.89 – 6.82 (m, 2H), 6.66 (d, *J* = 7.5 Hz, 2H), 6.39 (d, *J* = 7.7 Hz, 1H), 5.19 (d, *J* = 16.2 Hz, 1H), 4.60 (d, *J* = 16.2 Hz, 1H), 3.17 (d, *J* = 15.7 Hz, 1H), 3.08 (d, *J* = 15.6 Hz, 1H), 2.94 (d, *J* = 12.9 Hz, 1H), 2.76 (d, *J* = 12.9 Hz, 1H); ¹³C NMR (101 MHz, CDCl₃) δ 169.2, 146.0, 136.3, 135.9, 132.5, 130.3, 128.9, 128.6, 128.4, 128.2, 127.8, 127.1, 127.0, 126.8, 124.7, 123.8, 123.5, 123.2, 121.0, 108.7, 46.4, 45.0, 40.1, 34.6. ESI-MS: Calcd for C₂₉H₂₅N₂ [M+H]⁺: 401.2. Found: 401.1. HRMS (ESI⁺): Calcd for C₂₉H₂₅N₂, [M+H]⁺ *m/z* 401.2018. Found 401.2025.

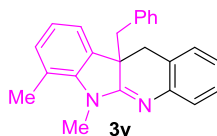


3w: Pale yellow solid, mp = 138-140 °C; Eluent: petroleum ether/EtOAc 10:1; ¹H NMR (600 MHz, CDCl₃) δ 6.47 (d, *J* = 7.7 Hz, 1H), 6.43 – 6.36 (m, 3H), 6.34 – 6.25 (m, 5H), 6.20 – 6.12 (m, 4H), 6.10 (d, *J* = 7.1 Hz, 1H), 6.03 (t, *J* = 7.3 Hz, 1H), 5.77 – 5.71 (m, 2H), 5.58 (d, *J* = 7.8 Hz, 1H), 2.98 (dt, *J* = 14.5, 7.5 Hz, 1H), 2.55 (dt, *J* = 14.5, 7.5 Hz, 1H), 2.22 (d, *J* = 15.6 Hz, 1H), 2.10 (d, *J* = 15.5 Hz, 1H), 1.95 (d, *J* = 12.9 Hz, 1H), 1.79 (d, *J* = 13.0 Hz, 1H), 1.72 – 1.59 (m, 2H), 0.88 (p, *J* = 7.6 Hz, 2H); ¹³C NMR (151 MHz, CDCl₃) δ 168.7, 146.1, 145.9, 141.4, 135.7, 132.4,

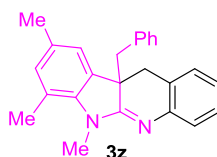
130.0, 128.7, 128.4, 128.3, 128.2, 128.0, 127.4, 126.5, 125.9, 124.5, 123.5, 123.5, 122.9, 120.4, 107.4, 46.0, 40.3, 40.0, 33.9, 32.9, 28.1. ESI-MS: Calcd for C₃₁H₂₉N₂ [M+H]⁺: 429.2. Found: 429.1. HRMS (ESI⁺): Calcd for C₃₁H₂₉N₂, [M+H]⁺ *m/z* 429.2331. Found 429.2342.



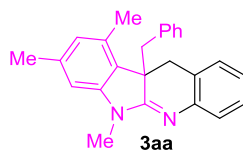
3x: Pale yellow solid, mp = 124-125 °C; Eluent: petroleum ether/EtOAc 10:1; ¹H NMR (600 MHz, CDCl₃) δ 7.31 (d, *J* = 7.5 Hz, 1H), 7.26 (t, *J* = 7.5 Hz, 1H), 7.19 (d, *J* = 7.2 Hz, 1H), 7.12 – 7.00 (m, 4H), 6.98 (d, *J* = 7.6 Hz, 1H), 6.80 (s, 1H), 6.62 (d, *J* = 7.2 Hz, 2H), 6.48 (d, *J* = 7.8 Hz, 1H), 3.79 (dt, *J* = 14.4, 7.2 Hz, 1H), 3.38 (dt, *J* = 14.4, 7.5 Hz, 1H), 3.08 (d, *J* = 15.6 Hz, 1H), 2.97 (d, *J* = 15.5 Hz, 1H), 2.80 (d, *J* = 13.0 Hz, 1H), 2.66 (d, *J* = 13.0 Hz, 1H), 2.31 (s, 3H), 1.46 – 1.31 (m, 2H), 1.26 – 1.11 (m, 2H), 0.87 (t, *J* = 7.4 Hz, 3H); ¹³C NMR (151 MHz, CDCl₃) δ 169.0, 146.4, 143.9, 135.9, 132.7, 130.2, 129.8, 128.8, 128.4, 128.0, 127.4, 126.5, 124.5, 123.3, 123.1, 107.3, 46.2, 40.8, 40.1, 34.1, 29.4, 21.1, 20.4, 14.0. ESI-MS: Calcd for C₂₇H₂₉N₂ [M+H]⁺: 381.2. Found: 381.0. HRMS (ESI⁺): Calcd for C₂₇H₂₉N₂, [M+H]⁺ *m/z* 381.2331. Found 381.2344.



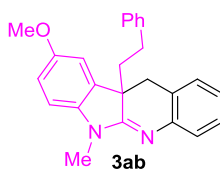
3y: Pale yellow solid, mp = 124-125 °C; Eluent: petroleum ether/EtOAc 10:1; ¹H NMR (800 MHz, CDCl₃) δ 7.34 (d, *J* = 7.7 Hz, 1H), 7.28 (t, *J* = 7.5 Hz, 1H), 7.21 (d, *J* = 7.3 Hz, 1H), 7.11 (t, *J* = 7.3 Hz, 1H), 7.09 – 7.01 (m, 3H), 6.92 (d, *J* = 7.6 Hz, 1H), 6.81 (t, *J* = 7.4 Hz, 1H), 6.76 (d, *J* = 7.1 Hz, 1H), 6.60 (d, *J* = 7.2 Hz, 2H), 3.40 (s, 3H), 3.10 (d, *J* = 15.6 Hz, 1H), 2.96 (d, *J* = 15.5 Hz, 1H), 2.75 (d, *J* = 13.0 Hz, 1H), 2.64 (d, *J* = 13.0 Hz, 1H), 2.38 (s, 3H); ¹³C NMR (201 MHz, CDCl₃) δ 170.3, 144.0, 135.6, 133.0, 132.0, 130.0, 128.7, 128.0, 127.2, 126.5, 124.3, 123.5, 123.0, 121.4, 120.7, 119.1, 45.8, 40.3, 33.4, 30.6, 19.1. ESI-MS: Calcd for C₂₄H₂₃N₂ [M+H]⁺: 339.2. Found: 339.0. HRMS (ESI⁺): Calcd for C₂₄H₂₃N₂, [M+H]⁺ *m/z* 339.1861. Found 339.1872.



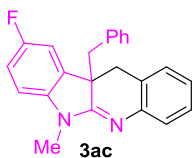
3z: Pale yellow solid, mp = 154-156 °C; Eluent: petroleum ether/EtOAc 10:1; ¹H NMR (600 MHz, CDCl₃) δ 7.31 (d, *J* = 7.7 Hz, 1H), 7.27 (t, *J* = 7.5 Hz, 1H), 7.20 (d, *J* = 7.2 Hz, 1H), 7.14 – 7.05 (m, 3H), 7.03 (t, *J* = 7.3 Hz, 1H), 6.72 (s, 1H), 6.59 (d, *J* = 7.7 Hz, 2H), 6.55 (s, 1H), 3.36 (s, 3H), 3.07 (d, *J* = 15.6 Hz, 1H), 2.93 (d, *J* = 15.6 Hz, 1H), 2.72 (d, *J* = 12.8 Hz, 1H), 2.63 (d, *J* = 12.9 Hz, 1H), 2.34 (s, 3H), 2.24 (s, 3H); ¹³C NMR (151 MHz, CDCl₃) δ 170.4, 146.2, 141.7, 135.7, 133.1, 132.2, 130.1, 129.9, 128.7, 127.9, 127.1, 126.4, 124.3, 123.2, 123.1, 122.2, 118.6, 45.7, 40.2, 33.5, 30.4, 20.7, 18.9. ESI-MS: Calcd for C₂₅H₂₅N₂ [M+H]⁺: 353.2. Found: 353.0. HRMS (ESI⁺): Calcd for C₂₅H₂₅N₂, [M+H]⁺ *m/z* 353.2018. Found 353.2032.



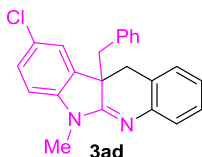
3aa: Light yellow oil; Eluent: petroleum ether/EtOAc 10:1; ¹H NMR (600 MHz, CDCl₃) δ 7.33 (d, *J* = 7.7 Hz, 1H), 7.27 (t, *J* = 7.5 Hz, 1H), 7.20 (d, *J* = 7.2 Hz, 1H), 7.06 – 6.96 (m, 4H), 6.59 (d, *J* = 7.3 Hz, 2H), 6.53 (s, 1H), 6.12 (s, 1H), 3.35 (d, *J* = 15.6 Hz, 1H), 3.15 (d, *J* = 15.6 Hz, 1H), 2.95 (s, 3H), 2.89 (d, *J* = 12.9 Hz, 1H), 2.73 (d, *J* = 13.0 Hz, 1H), 2.24 (s, 3H), 2.23 (s, 3H); ¹³C NMR (151 MHz, CDCl₃) δ 168.7, 146.4, 145.4, 138.1, 136.0, 133.8, 129.4, 128.7, 127.9, 127.1, 126.2, 126.2, 124.1, 123.8, 123.3, 122.9, 105.7, 47.5, 38.1, 34.0, 26.8, 21.5, 18.2. ESI-MS: Calcd for C₂₅H₂₅N₂ [M+H]⁺: 353.2. Found: 353.0. HRMS (ESI⁺): Calcd for C₂₅H₂₅N₂, [M+H]⁺ *m/z* 353.2018. Found 353.2032.



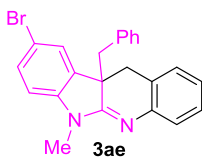
3ab: Light yellow oil; Eluent: petroleum ether/EtOAc 10:1; ¹H NMR (600 MHz, CDCl₃) δ 7.24 – 7.17 (m, 2H), 7.12 – 7.06 (m, 3H), 7.03 (t, *J* = 7.3 Hz, 1H), 6.94 (td, *J* = 7.0, 1.6 Hz, 1H), 6.90 – 6.84 (m, 3H), 6.82 – 6.78 (m, 1H), 6.71 (d, *J* = 8.4 Hz, 1H), 3.79 (s, 3H), 3.31 (s, 3H), 3.03 (s, 2H), 2.35 (td, *J* = 12.8, 5.0 Hz, 1H), 2.18 (td, *J* = 12.8, 4.5 Hz, 1H), 2.06 (td, *J* = 12.8, 5.0 Hz, 1H), 1.69 (td, *J* = 12.9, 4.5 Hz, 1H); ¹³C NMR (151 MHz, CDCl₃) δ 169.7, 155.1, 145.8, 141.1, 140.3, 134.5, 128.4, 128.1, 127.8, 125.7, 124.0, 123.1, 122.6, 112.0, 110.6, 107.5, 55.8, 45.3, 36.5, 34.7, 30.1, 27.7. ESI-MS: Calcd for C₂₅H₂₅N₂O [M+H]⁺: 369.2. Found: 369.1. HRMS (ESI⁺): Calcd for C₂₅H₂₅N₂O, [M+H]⁺ *m/z* 369.1967. Found 369.1974.



3ac: Pale yellow solid, mp = 144-145 °C; Eluent: petroleum ether/EtOAc 10:1; ¹H NMR (600 MHz, CDCl₃) δ 7.35 – 7.26 (m, 2H), 7.24 – 7.19 (m, 1H), 7.16 – 7.04 (m, 4H), 6.89 (td, *J* = 8.8, 2.5 Hz, 1H), 6.72 – 6.63 (m, 3H), 6.50 – 6.44 (m, 1H), 3.09 (d, *J* = 15.5 Hz, 4H), 2.97 (d, *J* = 15.6 Hz, 1H), 2.77 (d, *J* = 13.0 Hz, 1H), 2.68 (d, *J* = 13.0 Hz, 1H); ¹³C NMR (151 MHz, CDCl₃) δ 169.2, 157.9 (d, *J* = 238.9 Hz), 145.5, 142.2, 135.2, 133.8 (d, *J* = 7.9 Hz), 130.0, 128.8, 128.1, 127.5, 126.7, 124.5, 123.7, 122.5, 114.3 (d, *J* = 23.7 Hz), 111.8 (d, *J* = 24.7 Hz), 107.3 (d, *J* = 8.1 Hz), 46.6, 39.8, 33.2, 27.3; ¹⁹F NMR (565 MHz, CDCl₃) δ -123.65. ESI-MS: Calcd for C₂₃H₂₀FN₂ [M+H]⁺: 343.2. Found: 343.0. HRMS (ESI⁺): Calcd for C₂₃H₂₀FN₂, [M+H]⁺ *m/z* 343.1611. Found 343.1622.



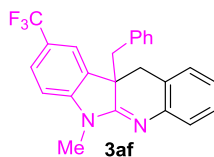
3ad: Pale yellow solid, mp = 172-174 °C; Eluent: petroleum ether/EtOAc 10:1; ¹H NMR (600 MHz, CDCl₃) δ 7.34 – 7.28 (m, 2H), 7.25 – 7.21 (m, 1H), 7.18 – 7.07 (m, 5H), 6.89 (d, *J* = 2.0 Hz, 1H), 6.67 (d, *J* = 6.9 Hz, 2H), 6.49 (d, *J* = 8.3 Hz, 1H), 3.09 (d, *J* = 3.3 Hz, 4H), 2.98 (d, *J* = 15.7 Hz, 1H), 2.77 (d, *J* = 13.0 Hz, 1H), 2.68 (d, *J* = 13.0 Hz, 1H); ¹³C NMR (151 MHz, CDCl₃) δ 168.8, 145.4, 144.9, 135.1, 133.9, 130.0, 128.8, 128.2, 128.1, 127.5, 126.8, 125.6, 124.6, 124.1, 123.9, 122.6, 107.9, 46.5, 39.8, 33.2, 27.3. ESI-MS: Calcd for C₂₃H₂₀ClN₂ [M+H]⁺: 359.1. Found: 359.0. HRMS (ESI⁺): Calcd for C₂₃H₂₀ClN₂, [M+H]⁺ *m/z* 359.1315. Found 359.1327.



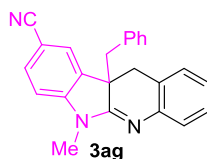
3ae: Pale yellow solid, mp = 209-211 °C; Eluent: petroleum ether/EtOAc 10:1; ¹H NMR (600 MHz, CDCl₃) δ 7.34 – 7.28 (m, 3H), 7.23 (d, *J* = 7.3 Hz, 1H), 7.16 – 7.07 (m, 4H), 7.04 – 6.98 (m, 1H), 6.67 (d, *J* = 6.6 Hz, 2H), 6.45 (d, *J* = 8.3 Hz, 1H), 3.11 – 3.06 (m, 4H), 2.97 (d, *J* = 15.6 Hz, 1H), 2.76 (d, *J* = 13.0 Hz, 1H), 2.67 (d, *J* = 13.0 Hz, 1H); ¹³C NMR (151 MHz, CDCl₃) δ 168.6, 145.4, 135.1, 134.3, 131.0, 130.0, 128.8, 128.2, 127.5, 126.8, 126.8, 124.6, 124.0, 122.6, 112.8,

108.5, 46.4, 39.8, 33.1, 27.2. ESI-MS: Calcd for C₂₃H₂₀BrN₂ [M+H]⁺: 403.1. Found: 403.1.

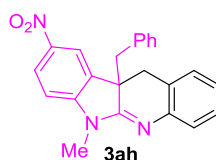
HRMS (ESI⁺): Calcd for C₂₃H₂₀BrN₂, [M+H]⁺ *m/z* 403.0810. Found 403.0818.



3af: Pale yellow solid, mp = 206-208 °C; Eluent: petroleum ether/EtOAc 10:1; ¹H NMR (800 MHz, CDCl₃) δ 7.48 (d, *J* = 9.0 Hz, 1H), 7.34 (dd, *J* = 7.7, 1.1 Hz, 1H), 7.30 (t, *J* = 7.5 Hz, 1H), 7.27 – 7.22 (m, 1H), 7.16 – 7.06 (m, 5H), 6.66 – 6.58 (m, 3H), 3.19 – 3.09 (m, 4H), 2.99 (d, *J* = 15.5 Hz, 1H), 2.77 – 2.68 (m, 2H); ¹³C NMR (201 MHz, CDCl₃) δ 168.9, 149.2, 145.2, 135.0, 132.8, 130.0, 128.9, 128.2, 127.6, 126.9, 126.1 (q, *J* = 4.0 Hz), 124.8, 124.6 (q, *J* = 271.1 Hz), 124.3, 122.6, 122.5 (q, *J* = 32.5 Hz), 120.8 (q, *J* = 3.4 Hz), 106.6, 77.2, 77.1, 76.9, 46.1, 39.7, 33.0, 27.3; ¹⁹F NMR (565 MHz, CDCl₃) δ -62.36. ESI-MS: Calcd for C₂₄H₂₀F₃N₂ [M+H]⁺: 393.2. Found: 393.1. HRMS (ESI⁺): Calcd for C₂₄H₂₀F₃N₂, [M+H]⁺ *m/z* 393.1579. Found 393.1588.

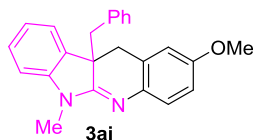


3ag: Pale yellow solid, mp = 246-247 °C; Eluent: petroleum ether/EtOAc 10:1; ¹H NMR (600 MHz, CDCl₃) δ 7.56 – 7.50 (m, 1H), 7.37 – 7.30 (m, 2H), 7.28 – 7.24 (m, 1H), 7.18 – 7.09 (m, 5H), 6.63 (d, *J* = 7.2 Hz, 2H), 6.60 (d, *J* = 8.2 Hz, 1H), 3.16 (d, *J* = 15.8 Hz, 1H), 3.13 (s, 3H), 3.00 (d, *J* = 15.7 Hz, 1H), 2.79 (d, *J* = 13.1 Hz, 1H), 2.67 (d, *J* = 13.1 Hz, 1H); ¹³C NMR (151 MHz, CDCl₃) δ 168.2, 150.1, 144.7, 134.7, 133.9, 133.2, 129.8, 128.9, 128.3, 127.6, 127.0, 126.7, 125.0, 124.7, 122.5, 119.7, 107.4, 103.0, 46.0, 39.8, 33.0, 27.3. ESI-MS: Calcd for C₂₄H₂₀N₃ [M+H]⁺: 350.2. Found: 350.1. HRMS (ESI⁺): Calcd for C₂₄H₂₀N₃, [M+H]⁺ *m/z* 350.1657. Found 350.1669.

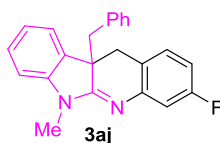


3ah: Light yellow oil; Eluent: petroleum ether/EtOAc 10:1; ¹H NMR (400 MHz, CDCl₃) δ 8.20 (dd, *J* = 8.7, 2.2 Hz, 1H), 7.87 (d, *J* = 2.2 Hz, 1H), 7.38 – 7.26 (m, 3H), 7.19 – 7.04 (m, 4H), 6.63 (d, *J* = 7.1 Hz, 2H), 6.58 (d, *J* = 8.7 Hz, 1H), 3.22 (d, *J* = 15.7 Hz, 1H), 3.15 (s, 3H), 3.06 (d, *J* = 15.7 Hz, 1H), 2.87 (d, *J* = 13.0 Hz, 1H), 2.68 (d, *J* = 13.0 Hz, 1H); ¹³C NMR (101 MHz, CDCl₃) δ

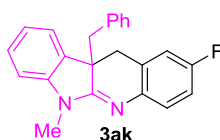
168.3, 152.0, 144.5, 141.5, 134.6, 132.9, 129.7, 129.0, 128.4, 127.7, 127.1, 126.2, 125.1, 125.0, 122.5, 119.4, 106.2, 46.1, 39.9, 33.2, 27.4. ESI-MS: Calcd for C₂₃H₂₀N₃O₂ [M+H]⁺: 370.2. Found: 370.0. HRMS (ESI⁺): Calcd for C₂₃H₂₀N₃O₂, [M+H]⁺ *m/z* 370.1556. Found 370.1561.



3ai: Light yellow oil; Eluent: petroleum ether/EtOAc 10:1; ¹H NMR (400 MHz, CDCl₃) δ 7.26 (d, *J* = 8.4 Hz, 1H), 7.22 – 7.16 (m, 1H), 7.13 – 7.05 (m, 3H), 6.91 – 6.87 (m, 2H), 6.86 – 6.79 (m, 2H), 6.69 – 6.62 (m, 2H), 6.57 (d, *J* = 7.8 Hz, 1H), 3.83 (s, 3H), 3.08 (d, *J* = 14.2 Hz, 4H), 2.96 (d, *J* = 15.7 Hz, 1H), 2.77 (d, *J* = 12.8 Hz, 1H), 2.70 (d, *J* = 12.8 Hz, 1H); ¹³C NMR (101 MHz, CDCl₃) δ 168.3, 156.1, 146.5, 139.4, 135.8, 132.1, 130.2, 128.4, 127.4, 126.6, 125.1, 124.4, 123.7, 120.3, 115.2, 112.2, 107.1, 55.6, 46.2, 39.9, 33.8, 27.2. ESI-MS: Calcd for C₂₄H₂₃N₂O [M+H]⁺: 355.2. Found: 355.0. HRMS (ESI⁺): Calcd for C₂₄H₂₃N₂O, [M+H]⁺ *m/z* 355.1810. Found 355.1818.

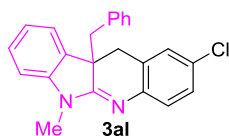


3aj: Pale yellow solid, mp = 118-120 °C; Eluent: petroleum ether/EtOAc 10:1; ¹H NMR (400 MHz, CDCl₃) δ 7.24 – 7.17 (m, 1H), 7.16 – 7.01 (m, 5H), 6.93 (d, *J* = 4.3 Hz, 2H), 6.74 (td, *J* = 8.3, 2.6 Hz, 1H), 6.66 – 6.55 (m, 3H), 3.14 – 3.06 (m, 4H), 2.90 (d, *J* = 15.5 Hz, 1H), 2.76 (d, *J* = 12.9 Hz, 1H), 2.67 (d, *J* = 12.9 Hz, 1H); ¹³C NMR (101 MHz, CDCl₃) δ 170.4, 162.9 (d, *J* = 242.7 Hz), 147.7 (d, *J* = 11.3 Hz), 146.1, 135.5, 132.2, 130.1, 129.4 (d, *J* = 9.3 Hz), 128.5, 127.5, 126.7, 123.7, 121.0, 118.6 (d, *J* = 2.7 Hz), 111.4 (d, *J* = 22.7 Hz), 109.9 (d, *J* = 21.5 Hz), 107.5, 77.48, 77.2, 76.8, 46.6, 40.1, 32.7, 27.2; ¹⁹F NMR (565 MHz, CDCl₃) δ -115.16. ESI-MS: Calcd for C₂₃H₂₀FN₂ [M+H]⁺: 343.2. Found: 343.0. HRMS (ESI⁺): Calcd for C₂₃H₂₀FN₂, [M+H]⁺ *m/z* 343.1611. Found 343.1625.

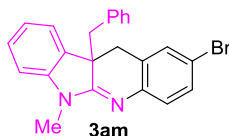


3ak: Light yellow oil; Eluent: petroleum ether/EtOAc 10:1; ¹H NMR (400 MHz, CDCl₃) δ 7.26 (dd, *J* = 8.5, 5.4 Hz, 1H), 7.22 – 7.16 (m, 1H), 7.14 – 7.05 (m, 3H), 7.00 – 6.88 (m, 4H), 6.66 –

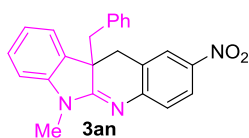
6.61 (m, 2H), 6.58 (d, $J = 7.8$ Hz, 1H), 3.14 – 3.04 (m, 4H), 2.95 (d, $J = 15.8$ Hz, 1H), 2.75 (d, $J = 12.9$ Hz, 1H), 2.67 (d, $J = 12.9$ Hz, 1H); ^{13}C NMR (101 MHz, CDCl_3) δ 169.2, 159.3 (d, $J = 241.7$ Hz), 146.3, 142.0 (d, $J = 2.4$ Hz), 135.5, 131.9, 130.1, 128.5, 127.5, 126.7, 125.4 (d, $J = 8.0$ Hz), 124.7 (d, $J = 7.6$ Hz), 123.7, 120.7, 115.6 (d, $J = 22.9$ Hz), 114.4 (d, $J = 21.8$ Hz), 107.3, 77.5, 77.2, 76.8, 45.9, 40.0, 33.5, 27.2; ^{19}F NMR (565 MHz, CDCl_3) δ -119.4. ESI-MS: Calcd for $\text{C}_{23}\text{H}_{20}\text{FN}_2$ $[\text{M}+\text{H}]^+$: 343.2. Found: 343.0. HRMS (ESI $^+$): Calcd for $\text{C}_{23}\text{H}_{20}\text{FN}_2$, $[\text{M}+\text{H}]^+$ m/z 343.1611. Found 343.1636.



3al: Pale yellow solid, mp = 156-157 °C; Eluent: petroleum ether/EtOAc 10:1; ^1H NMR (400 MHz, CDCl_3) δ 7.28 – 7.16 (m, 4H), 7.13 – 7.04 (m, 3H), 6.92 (d, $J = 4.2$ Hz, 2H), 6.62 (d, $J = 6.5$ Hz, 2H), 6.58 (d, $J = 7.8$ Hz, 1H), 3.13 – 3.04 (m, 4H), 2.94 (d, $J = 15.8$ Hz, 1H), 2.76 (d, $J = 12.9$ Hz, 1H), 2.66 (d, $J = 12.9$ Hz, 1H); ^{13}C NMR (101 MHz, CDCl_3) δ 169.7, 146.2, 144.6, 135.4, 132.0, 130.1, 128.7, 128.5, 128.1, 128.0, 127.5, 126.7, 125.6, 124.8, 123.7, 120.9, 107.4, 46.2, 40.1, 33.3, 27.2. ESI-MS: Calcd for $\text{C}_{23}\text{H}_{20}\text{ClN}_2$ $[\text{M}+\text{H}]^+$: 359.1. Found: 359.1. HRMS (ESI $^+$): Calcd for $\text{C}_{23}\text{H}_{20}\text{ClN}_2$, $[\text{M}+\text{H}]^+$ m/z 359.1315. Found 359.1529.



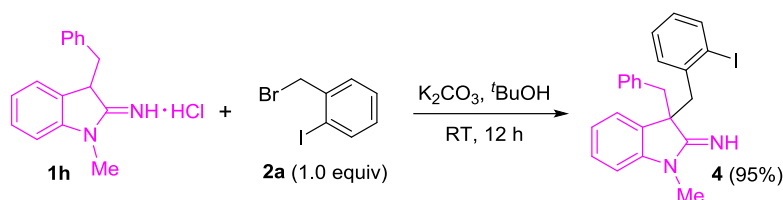
3am: Pale yellow solid, mp = 160-162 °C; Eluent: petroleum ether/EtOAc 10:1; ^1H NMR (400 MHz, CDCl_3) δ 7.41 – 7.32 (m, 2H), 7.24 – 7.16 (m, 2H), 7.14 – 7.04 (m, 3H), 6.96 – 6.90 (m, 2H), 6.66 – 6.54 (m, 3H), 3.13 – 3.06 (m, 4H), 2.97 (d, $J = 15.8$ Hz, 1H), 2.77 (d, $J = 12.9$ Hz, 1H), 2.66 (d, $J = 12.9$ Hz, 1H); ^{13}C NMR (101 MHz, CDCl_3) δ 169.8, 146.2, 145.1, 135.4, 132.0, 131.5, 131.0, 130.0, 128.6, 127.5, 126.7, 126.1, 125.3, 123.7, 120.9, 115.8, 107.5, 46.2, 40.2, 33.3, 27.3. ESI-MS: Calcd for $\text{C}_{23}\text{H}_{20}\text{BrN}_2$ $[\text{M}+\text{H}]^+$: 403.1. Found: 403.1. HRMS (ESI $^+$): Calcd for $\text{C}_{23}\text{H}_{20}\text{BrN}_2$, $[\text{M}+\text{H}]^+$ m/z 403.0810. Found 403.0821.



3an: Pale yellow solid, mp = 224-226 °C; Eluent: petroleum ether/EtOAc 10:1; ¹H NMR (400 MHz, CDCl₃) δ 8.24 – 8.08 (m, 2H), 7.34 (d, *J* = 8.4 Hz, 1H), 7.30 – 7.22 (m, 1H), 7.16 – 7.00 (m, 5H), 6.66 (d, *J* = 7.8 Hz, 1H), 6.60 (d, *J* = 6.9 Hz, 2H), 3.28 (d, *J* = 16.0 Hz, 1H), 3.15 (s, 3H), 3.03 (d, *J* = 16.0 Hz, 1H), 2.79 (d, *J* = 13.0 Hz, 1H), 2.69 (d, *J* = 13.0 Hz, 1H); ¹³C NMR (101 MHz, CDCl₃) δ 172.1, 152.8, 145.5, 143.1, 134.8, 131.9, 129.9, 128.8, 127.6, 127.0, 124.6, 124.5, 124.3, 123.8, 123.5, 122.0, 108.1, 46.5, 40.6, 33.2, 27.4. ESI-MS: Calcd for C₂₃H₂₀N₃O₂ [M+H]⁺: 370.2. Found: 370.1. HRMS (ESI⁺): Calcd for C₂₃H₂₀N₃O₂, [M+H]⁺ *m/z* 370.1556. Found 370.1563.

3.3. Procedure for preparation of compound 4.

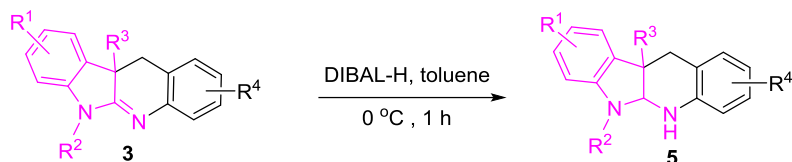
To a dried Schlenk tube were added **1h** (0.3 mmol, 1.0 equiv), **2a** (0.3 mmol, 1.0 equiv) and K₂CO₃ (0.9 mmol, 3.0 equiv) under N₂, 3.0 mL of ^tBuOH was then introduced via syringe. The mixture was stirred at room temperature for 12 h. The solvent was then removed under vacuum, and the residue was purified by column chromatography on silica to give the desired product **4** as a light yellow oil.



4: Eluent: CH₂Cl₂/MeOH 15:1; ¹H NMR (400 MHz, CDCl₃) δ 7.70 (d, *J* = 8.0 Hz, 1H), 7.09 – 6.99 (m, 6H), 6.98 – 6.91 (m, 1H), 6.88 – 6.78 (m, 3H), 6.78 – 6.71 (m, 1H), 6.37 (d, *J* = 7.7 Hz, 1H), 3.49 (d, *J* = 14.5 Hz, 1H), 3.40 (d, *J* = 14.4 Hz, 1H), 3.24 – 3.11 (m, 2H), 2.91 (s, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 172.6, 145.4, 139.5, 139.4, 135.3, 130.2, 130.1, 129.7, 128.3, 128.0, 127.7, 127.4, 126.4, 124.4, 120.0, 106.4, 103.6, 55.3 47.6 45.7, 26.7. ESI-MS: Calcd for C₂₃H₂₂IN₂ [M+H]⁺: 453.1. Found: 453.1. HRMS (ESI⁺): Calcd for C₂₃H₂₂IN₂, [M+H]⁺ *m/z* 453.0828. Found 453.0834.

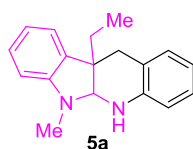
3.4 Procedure for the reductions using DIBAL-H.

(1) General Procedures

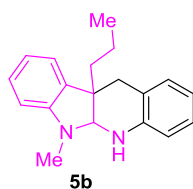


To a solution of **3** (0.2 mmol, 1.0 eq) in 2 mL of anhydrous toluene under Argon atmosphere was added DIBAL-H (1.5 M in toluene, 0.6 mmol, 0.4 mL, 3 equiv) at 0 °C, then the reaction mixture was stirred for 1h. TLC showed the reaction completed. The resulting mixture was extracted with ethyl acetate (2 mL x 2) and water, and the combined organic phase was washed with brine (2 mL), dried over anhydrous Na₂SO₄, concentrated and purified by column chromatography on silica to give the desired product **5**.

(2) Characterizaion Data of compound 5a-f.

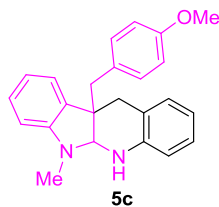


5a: Light yellow oil; Eluent: petroleum ether/EtOAc 15:1; ¹H NMR (600 MHz, CDCl₃) δ 7.11 – 7.04 (m, 2H), 7.01 (t, *J* = 7.5 Hz, 1H), 6.94 (d, *J* = 7.3 Hz, 1H), 6.72 (t, *J* = 7.2 Hz, 1H), 6.65 (t, *J* = 7.2 Hz, 1H), 6.59 (d, *J* = 8.0 Hz, 1H), 6.45 (d, *J* = 7.7 Hz, 1H), 4.56 (br, 1H), 4.35 (s, 1H), 2.83 (d, *J* = 15.1 Hz, 1H), 2.77 (s, 3H), 2.58 (d, *J* = 15.1 Hz, 1H), 1.78 – 1.69 (m, 1H), 1.65 – 1.57 (m, 1H), 0.86 (t, *J* = 7.5 Hz, 3H); ¹³C NMR (151 MHz, CDCl₃) δ 149.9, 141.7, 134.7, 128.8, 127.6, 126.87, 122.4, 122.0, 118.2, 113.6, 107.4, 80.1, 44.6, 37.3, 31.9, 27.6, 9.1. ESI-MS: Calcd for C₁₈H₂₁N₂ [M+H]⁺: 265.2. Found: 265.0. HRMS (ESI⁺): Calcd for C₁₈H₂₁N₂, [M+H]⁺ *m/z* 265.1705. Found 265.1713.

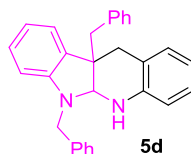


5b: Light yellow oil; Eluent: petroleum ether/EtOAc 15:1; ¹H NMR (600 MHz, CDCl₃) δ 7.11 – 7.04 (m, 2H), 7.01 (t, *J* = 7.5 Hz, 1H), 6.94 (d, *J* = 7.3 Hz, 1H), 6.72 (t, *J* = 7.3 Hz, 1H), 6.65 (t, *J* = 7.3 Hz, 1H), 6.59 (d, *J* = 7.9 Hz, 1H), 6.44 (d, *J* = 7.7 Hz, 1H), 4.55 (br, 1H), 4.34 (s, 1H), 2.82 (d, *J* = 15.1 Hz, 1H), 2.75 (s, 3H), 2.57 (d, *J* = 15.2 Hz, 1H), 1.67 – 1.61 (m, 1H), 1.58 – 1.52 (m,

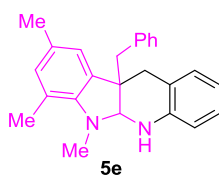
1H), 1.32 – 1.24 (m, 2H), 0.84 (t, $J = 7.3$ Hz, 3H); ^{13}C NMR (151 MHz, CDCl_3) δ 149.7, 141.6, 135.1, 128.8, 127.6, 126.9, 122.3, 121.9, 118.2, 118.1, 113.6, 107.4, 80.5, 44.2, 37.6, 37.5, 31.9, 18.0, 14.7. ESI-MS: Calcd for $\text{C}_{19}\text{H}_{23}\text{N}_2$ $[\text{M}+\text{H}]^+$: 279.2. Found: 279.2.



5c: Light yellow oil; Eluent: petroleum ether/EtOAc 15:1; ^1H NMR (400 MHz, CDCl_3) δ 7.09 – 7.00 (m, 3H), 6.98 (d, $J = 7.3$ Hz, 1H), 6.93 (d, $J = 8.4$ Hz, 2H), 6.75 – 6.65 (m, 4H), 6.61 (d, $J = 7.9$ Hz, 1H), 6.40 (d, $J = 7.8$ Hz, 1H), 4.50 (br, 1H), 4.16 (s, 1H), 3.74 (s, 3H), 3.10 (d, $J = 14.1$ Hz, 1H), 2.83 (d, $J = 15.3$ Hz, 1H), 2.75 – 2.67 (m, 2H), 2.64 (s, 3H); ^{13}C NMR (101 MHz, CDCl_3) δ 158.1, 149.7, 141.8, 134.4, 131.7, 129.7, 129.1, 127.7, 127.1, 122.6, 121.9, 118.2, 118.1, 113.7, 113.3, 107.7, 80.1, 55.2, 45.0, 40.0, 37.0, 31.8; ESI-MS: Calcd for $\text{C}_{24}\text{H}_{25}\text{N}_2\text{O}$ $[\text{M}+\text{H}]^+$: 357.2. Found: 357.1. HRMS (ESI $^+$): Calcd for $\text{C}_{24}\text{H}_{25}\text{N}_2\text{O}$, $[\text{M}+\text{H}]^+$ m/z 357.1967. Found 357.1973.

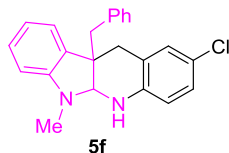


5d: Light yellow oil; Eluent: petroleum ether/EtOAc 15:1; ^1H NMR (600 MHz, CDCl_3) δ 7.27 – 7.16 (m, 6H), 7.10 (d, $J = 7.0$ Hz, 2H), 7.03 (d, $J = 7.2$ Hz, 1H), 7.00 – 6.89 (m, 5H), 6.72 – 6.61 (m, 2H), 6.42 (d, $J = 7.7$ Hz, 1H), 6.15 (d, $J = 7.8$ Hz, 1H), 4.64 (s, 1H), 4.20 – 4.08 (m, 3H), 3.19 (d, $J = 13.5$ Hz, 1H), 2.99 (d, $J = 14.6$ Hz, 1H), 2.90 – 2.82 (m, 2H); ^{13}C NMR (151 MHz, CDCl_3) δ 150.2, 142.9, 138.5, 137.4, 133.2, 130.6, 128.6, 128.5, 127.9, 127.8, 127.3, 127.1, 126.9, 126.4, 124.1, 122.8, 118.9, 117.6, 114.5, 106.5, 79.0, 49.2, 49.0, 44.1, 37.5. ESI-MS: Calcd for $\text{C}_{29}\text{H}_{27}\text{N}_2$ $[\text{M}+\text{H}]^+$: 403.2. Found: 403.1. HRMS (ESI $^+$): Calcd for $\text{C}_{29}\text{H}_{27}\text{N}_2$, $[\text{M}+\text{H}]^+$ m/z 403.2174. Found 403.2181.



5e: Light yellow oil; Eluent: petroleum ether/EtOAc 15:1; ^1H NMR (600 MHz, CDCl_3) δ 7.19 – 7.11 (m, 3H), 7.06 – 6.99 (m, 3H), 6.97 (d, $J = 7.3$ Hz, 1H), 6.84 (s, 1H), 6.71 – 6.63 (m, 2H),

6.60 (d, $J = 7.8$ Hz, 1H), 4.45 (br, 1H), 4.00 (s, 1H), 3.15 (d, $J = 14.0$ Hz, 1H), 2.79 (d, $J = 15.3$ Hz, 1H), 2.73 – 2.64 (m, 5H), 2.26 (s, 3H), 2.25 (s, 3H); ^{13}C NMR (151 MHz, CDCl_3) δ 145.8, 141.7, 137.8, 135.7, 131.7, 130.6, 129.0, 128.8, 127.9, 127.0, 126.2, 121.5, 121.0, 120.8, 118.0, 113.6, 81.1, 44.7, 41.0, 37.7, 36.4, 20.9, 19.5. ESI-MS: Calcd for $\text{C}_{25}\text{H}_{27}\text{N}_2$ $[\text{M}+\text{H}]^+$: 355.2. Found: 355.1. HRMS (ESI $^+$): Calcd for $\text{C}_{25}\text{H}_{27}\text{N}_2$, $[\text{M}+\text{H}]^+$ m/z 355.2174. Found 355.2183.



5f: Light yellow oil; Eluent: petroleum ether/EtOAc 15:1; ^1H NMR (400 MHz, CDCl_3) δ 7.21 – 7.14 (m, 3H), 7.10 – 7.04 (m, 2H), 7.02 – 6.93 (m, 4H), 6.77 – 6.69 (m, 1H), 6.52 (d, $J = 8.1$ Hz, 1H), 6.39 (d, $J = 8.4$ Hz, 1H), 4.49 (br, 1H), 4.18 (s, 1H), 3.15 (d, $J = 14.0$ Hz, 1H), 2.82 (d, $J = 15.4$ Hz, 1H), 2.76 – 2.67 (m, 2H), 2.62 (s, 3H); ^{13}C NMR (101 MHz, CDCl_3) δ 149.6, 140.5, 137.3, 133.8, 130.7, 128.7, 128.0, 128.0, 126.9, 126.4, 123.7, 122.7, 122.6, 118.3, 114.7, 107.8, 80.0, 45.06, 41.15, 36.8, 31.8. ESI-MS: Calcd for $\text{C}_{23}\text{H}_{22}\text{ClN}_2$ $[\text{M}+\text{H}]^+$: 361.1. Found: 361.1. HRMS (ESI $^+$): Calcd for $\text{C}_{23}\text{H}_{22}\text{ClN}_2$, $[\text{M}+\text{H}]^+$ m/z 361.1472. Found 361.1475.

4. References

1. A. N. Kost, G. A. Golubeva, V. G. Zabrodnyaya and Y. N. Portnov, *Chem. Heterocycl. Compd.*, 1975, **12**, 1383; A. N. Kost, Y. N. Portnov, V. G. Zabrodnyaya, V.G. Voronin and A. N. Kost, *Chem. Heterocycl. Compd.*, 1983, **11**, 1175.
2. F. J. Robertson, B. D. Kenimer and J. Wu, *Tetrahedron Lett.*, 2011, **67**, 4327.

5. NMR Spectra of 1a-ah, 3a-an, 4 and 5a-f

