Supporting Information

Substrate Selective Synthesis of Indole, Tetrahydroquinoline and Quinoline Derivatives via Intramolecular Addition of Hydrazones and Imines

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1. General Information

Melting points were determined by a capillary melting point apparatus and are uncorrected. All the compounds were fully characterized by $^1$H, $^{13}$C, IR and further confirmed through ESI-MS and ESI-HRMS analysis. $^1$H NMR spectra were recorded on 400 and 500 MHz in CDCl$_3$ and DMSO-$d_6$ and $^{13}$C NMR spectra recorded on 100 and 125 MHz in CDCl$_3$ and DMSO-$d_6$. Multiplicities are reported as follows: singlet (s), doublet (d), broad singlet (br s), doublet of doublets (dd), triplet (t), doublet of triplet (dt), triplet of doublet (td) multiplet (m) and quintet (quint). Chemical shift ($\delta$) and coupling constants ($J$) are reported in parts per million (ppm) relative to the residual signal of TMS in deuterated solvents and hertz, respectively. IR spectra were recorded using an FT-IR spectrophotometer and values are reported in cm$^{-1}$. HRMS were recorded using a Q-TOF mass spectrometer. Column chromatography was performed over silica gel (60-120, 100-200 and 230-400 mesh) by using EtOAc-$n$-hexane as eluent. All chemicals and reagents were purchased from commercial vendors and used without further purification.
2. Experimental Procedures

General Experimental Procedure for the Preparation of Starting Materials 1.

The starting materials hydrazones of 2-aminobenzophenones 1a, 1b, 1d, 1f and 1e’ (known compounds)\(^1\) and 1c, 1e, 1b’-1d’ (unknown) were prepared by using known literature procedure.\(^{1a,1b}\) Most of the substrates were prepared by the experimental procedure mentioned below.

Experimental procedure for the synthesis of 2-aminobenzophenone phenylhydrazone substrates (1a-1c, 1e’).

To a well-stirred solution of phenylhydrazine (2.0 mL; 1 equiv) in MeOH (30% acetic acid, 20 mL) was added 2-aminobenzophenones (1.0 equiv) at room temperature. The resulting mixture was allowed to stir for 24 h at room temperature. After completion of the reaction (monitored by TLC), MeOH was evaporated under reduced pressure and the residue was treated with saturated aq. NaHCO\(_3\) solution (20 mL) and extracted with DCM (50 mL x 3). The organic layer was washed with brine (20 mL) and dried over anhydrous Na\(_2\)SO\(_4\). Evaporation of the solvent under reduced pressure gave a crude product which was purified by column chromatography on silica gel (60-120 mesh) eluting with EtOAc-n-Hexane (3:97) to afford the solid products 1. The Trans-geometry of 1a was confirmed with the help of 2D-NOESY experiment.
Experimental procedure for the synthesis of 2, 3-diaryl indole (3).

\[ \text{R}_1^1 \text{R}_2^1 \text{NH}_{2} + \text{H} \overset{\text{O}}{\text{O}} \text{R}_3 \text{R}_4 \overset{\text{BF}_3\text{OEt}_2 (20 \text{ mol})}{\text{DMSO, 120 °C, 24 h}} \rightarrow \text{R}_1^2 \text{R}_2^2 \text{NH} \]

\((E)-2-(\text{phenyl}(2\text{-phenylhydrazono})\text{methyl})\text{aniline 1 (300 mg, 1 equiv})\) was added to a well-stirred solution of benzaldehyde \(2\text{a (1.1 equiv), BF}_3\text{OEt}_2 (0.2 \text{ equiv})\) and DMSO (10 mL) in 100 mL round bottom flask. The reaction mixture was allowed to stir for 24 h at 120 °C. The completion of the reaction was monitored by TLC. The reaction mixture was allowed to cool at room temperature and quenched with saturated aq. NaHCO\(_3\) (10 mL) solution and extracted with EtOAc (50 x 3 mL). The organic layer was washed with brine (10 mL) and dried over anhydrous Na\(_2\)SO\(_4\). Evaporation of the solvent under reduced pressure gave a crude product which was purified by silica gel (100-200 mesh) column chromatography by using EtOAc-\(n\)-hexane (2:98) as an eluent to afford the respective products (3).

Experimental procedure for the synthesis of 2-aryl-4-(2-phenylhydrazono)-1, 2, 3, 4-tetrahydroquinoline (4).

\[ \text{R}_1^1 \text{N}^2 \text{N}^3 \text{Ph} + \text{O} \overset{\text{H}}{\text{O}} \text{R}_1 \overset{\text{BF}_3\text{OEt}_2 (20 \text{ mol})}{\text{DMSO RT, 48 h}} \rightarrow \text{R}_1^2 \text{N}^4 \]

\((E)-2-(1-(2\text{-phenylhydrazono})\text{ethyl})\text{aniline 1 (300 mg, 1equiv})\) was added to a well-stirred solution of benzaldehyde \(2 (1.1 \text{ equiv}), \text{BF}_3\text{OEt}_2 (0.2 \text{ equiv})\) and DMSO (10 mL) in 100 mL round bottom flask. The reaction mixture was allowed to stir for 48 h at room temperature.
The completion of the reaction was monitored by TLC. The reaction mixture was quenched with 10 mL of saturated aq. NaHCO₃ solution and extracted with EtOAc (50 x 3 mL). The organic layer was washed with brine (10 mL) and dried over anhydrous Na₂SO₄. Evaporation of the solvent under reduced pressure gave a crude product which was purified by silica gel (100-200 mesh) column chromatography by using EtOAc-ₙ-Hexane (2: 98) as an eluent to afford respective products (4). The Trans-geometry of 4de was confirmed with the help of 2D-NOESY experiment.

**Experimental procedure for the synthesis of substituted quinoline (6).**

Corresponding (E)-2-(aryl/methyl(2-phenylhydrazono)methyl)aniline 1 (300 mg, 1 equiv) was added to a well-stirred solution of ketone 5 (1.1 equiv), BF₃·OEt₂ (0.2 equiv) and DMSO (10 mL) in 100 mL round bottom flask. The reaction mixture was allowed to stir for 48 h at room temperature. The completion of the reaction was monitored by TLC. The reaction mixture was quenched with 10 mL of saturated aq. NaHCO₃ solution and extracted with EtOAc (50 x 3 mL). The organic layer was washed with brine (10 mL) and dried over anhydrous Na₂SO₄. Evaporation of the solvent under reduced pressure gave a crude product which was purified by silica gel (100-200 mesh) column chromatography by using EtOAc-ₙ-Hexane (1: 99) as an eluent to afford respective products (6).
Experimental procedure for three component synthesis of 3aa in one pot via successive addition:

2-aminobenzophenone (300 mg, 1 equiv) and phenylhydrazine (1 equiv) was stirred in DMSO (10 mL) at 120 ºC for 5 h in 100 mL round bottom flask followed by addition of aldehyde (1.1 equiv) and BF₃.OEt₂ (0.2 equiv) and subsequent stirring of reaction mixture at 120 ºC for another 19 h. The progress of the reaction was monitored by TLC. The reaction mixture was allowed to cool at room temperature and quenched with saturated aq. NaHCO₃ (10 mL) solution and extracted with EtOAc (50 x 3 mL). The organic layer was washed with brine (10 mL) and dried over anhydrous Na₂SO₄. Evaporation of the solvent under reduced pressure gave a crude mixture of products which was further analyzed by ESI-MS data.

Experimental procedure for the synthesis of 1, 5-diazocine side product (7):

To a well stirred solution of 2-amino-5-chlorobenzophenone (300 mg, 1 equiv) in DMSO (10 mL) was added BF₃.OEt₂ (0.2 equiv) in 100 mL round bottom flask. The reaction mixture was allowed to stir for 24 h at 120 ºC. The completion of the reaction was monitored by TLC. The reaction mixture was allowed to cool at room temperature and quenched with saturated aq. NaHCO₃.
NaHCO₃ (10 mL) solution and extracted with EtOAc (50 x 3 mL). The organic layer was washed with brine (10 mL) and dried over anhydrous Na₂SO₄. Evaporation of the solvent under reduced pressure gave a crude product which was purified by silica gel (100-200 mesh) column chromatography by using EtOAc-n-hexane (1:99) as an eluent to afford the respective products (7) in 40% yield.

3. Characterization data for compounds

2-(Phenyl(2-phenylhydrazono)methyl)aniline (1a): White solid (816 mg, 56%), mp 160-163 °C; ¹H NMR (400 MHz, DMSO-d₆): δ 8.29 (s, 1H), 7.61 (t, 2H, J = 6.9 Hz), 7.56-7.52 (m, 1H), 7.30-7.28 (m, 2H), 7.21 (t, 2H, J = 8.3 Hz), 7.05 (d, 2H, J = 7.72 Hz), 7.00-6.96 (m, 1H), 6.91 (s, 2H), 6.80-6.75 (m, 2H), 6.46 (dd, 1H, J = 7.9, 1.3 Hz), 6.39-6.35 (m, 1H) ppm. ¹³C NMR (100 MHz, DMSO-d₆): δ 148.9 (C), 147.4 (C), 145.5 (C), 134.1 (C), 130.4 (CH), 129.9 (2xCH), 129.5 (2xCH), 129.38 (CH), 129.31 (2xCH), 128.7 (CH), 119.6 (CH), 119.2 (C), 116.2 (CH), 115.1 (CH), 112.9 (2xCH). FT-IR (KBr, vmax/cm⁻¹) 3465, 3332, 1602, 1501, 1448, 1252, 1119, 1068, 750; HRMS (ESI): calcd for C₁₉H₁₈N₃ [M+H]⁺ 288.1501, found: 288.1493.

(E)-4-Chloro-2-(phenyl(2-phenylhydrazono)methyl)aniline (1b): White solid (241 mg, 58%), mp 151-153 °C; ¹H NMR (400 MHz, DMSO-d₆): δ 8.52 (s, 1H), 7.61-7.51 (m, 3H), 7.28-7.21 (m, 4H), 7.08-7.05 (m, 2H), 7.21 (t, 2H, J = 8.0, 1.5 Hz), 6.37-6.33 (m, 1H). ¹³C NMR (100 MHz, CDCl₃): δ 146.7 (C), 145.7 (C), 144.8 (C), 132.9 (C), 129.6 (2xCH), 129.2 (CH), 129.0 (2xCH), 128.8 (2xCH), 128.5 (CH), 127.6 (CH), 120.0 (C), 119.4 (CH), 117.7 (C), 117.2 (CH), 112.5
(E)-4-Chloro-2-((2-fluorophenyl)(2-phenylhydrazono)methyl)aniline (1c): Yellow solid (159 mg, 39%), mp 155-157 °C; ¹H NMR (400 MHz, CDCl₃): δ 7.63-7.57 (m, 1H), 7.41 (dt, 1H, J = 7.5, 1.0), 7.37-7.26 (m, 4H), 7.21 (br s, 1H), 6.82 (br s, 2H) 7.04 (dd, 1H, J = 8.6, 2.4 Hz), 6.96-6.88 (m, 3H), 6.72 (d, 1H, J = 8.6 Hz), 6.64 (dd, 1H, J = 2.3, 0.5 Hz), 6.11 (br s, 1H). ¹³C NMR (100 MHz, DMSO-d₆): δ 159.2 (d, J = 244 Hz, C), 144.5 (C), 144.8 (C), 140.6 (C), 131.9 (d, J = 8.0 Hz, CH), 131.1 (d, J = 4.0 Hz, CH), 129.0 (2xCH), 127.7 (CH), 127.5 (CH), 125.7 (d, J = 3.0 Hz, CH), 120.2 (d, J = 18 Hz, C), 119.6 (CH), 119.4 (CH), 118.1 (C), 117.3 (CH), 116.7 (d, J = 21 Hz, C), 112.6 (2xCH). FT-IR (KBr, vmax/cm⁻¹) 3471, 3334, 3056, 1603, 1501, 1403, 1252, 1222, 1176, 1096, 756; HRMS (ESI): calcd for C₁₉H₁₆ClFN₃ [M+H]⁺ 340.1017, found: 340.1006.

(E)-2-(1-(2-Phenylhydrazono)ethyl)aniline (1d): Yellow solid (375 mg, 75%), mp 102-103 °C; ¹H NMR (400 MHz, DMSO-d₆): δ 9.09 (s, 1H), 7.34(d, 1H, J = 7.9 Hz), 7.22 (t, 2H, J = 7.4 Hz), 7.08 (d, 2H, J = 8.4 Hz), 6.99 (t, 1H, J = 8.0 Hz), 6.76 (t, 1H, J = 7.2 Hz) 6.71 (d, 1H, J = 8.0 Hz), 6.63 (br s, 2H), 6.56 (t, 1H, J = 7.9 Hz), 2.29 (s, 3H). ¹³C NMR (100 MHz, CDCl₃): δ 146.7 (C), 146.0 (C), 145.7 (C), 129.0 (2xCH), 128.1 (CH), 128.0 (CH), 119.8 (C), 118.7 (CH), 115.7 (CH), 115.1 (CH), 112.3 (2xCH), 14.4. FT-IR (KBr, vmax/cm⁻¹) 3453, 1603, 1496, 1252, 1216, 1159, 751; HRMS (ESI): calcd for C₁₄H₁₆N₃ [M+H]⁺ 226.1344, found: 226.1336.

2, 3-Diphenyl-1H-indole (3aa):² White solid (227 mg, 81%), mp 113-114 (lit.⁵e 108-110 °C); ¹H NMR (400 MHz, CDCl₃): δ = 8.24 (br s, 1H), 7.69 (d, 1H, J = 8.0 Hz), 7.47-7.42 (m, 5H),
7.40-7.24 (m, 7H), 7.18-7.14 (m, 1H). 13C NMR (100 MHz, CDCl3): δ = 136.0 (C), 135.2 (C), 134.2 (C), 132.8 (C), 130.3 (2xCH), 128.9 (C), 128.8 (2xCH), 128.6 (2xCH), 128.3 (2xCH), 127.8 (CH), 126.3 (CH), 122.8 (CH), 120.5 (CH), 119.8 (CH), 115.2 (C), 111.0 (CH). FT-IR (KBr, \( \nu_{\text{max/cm}^{-1}} \)) 3398, 3019, 2399, 1645, 1403, 1156, 1069, 928, 669; HRMS (ESI): calcd for C_{20}H_{16}N [M+H]^+ 270.1283, found: 270.1273.

2-(4-Fluorophenyl)-3-phenyl-1H-indole (3ab):3 White solid (230 mg, 77%), mp 176-180 \(^\circ\)C; \(^1\)H NMR (400 MHz, CDCl3): δ 8.19 (br s, 1H), 7.68 (d, 1H, \( J = 8.0 \) Hz), 7.44-7.36 (m, 7H), 7.31-7.24 (m, 2H), 7.18-7.14 (m, 1H), 7.06-7.00 (m, 2H). 13C NMR (100 MHz, CDCl3): δ 162.4 (d, \( J = 246 \) Hz, C), 136.0 (C), 134.9 (C), 133.3 (C), 130.2 (2xCH), 130.0 (d, \( J = 8 \) Hz, CH), 129.0 (d, \( J = 2.8 \) Hz, C), 128.8 (C), 128.7 (2xCH), 126.4 (CH), 122.9 (CH), 120.6 (CH), 119.8 (CH), 115.9 (d, \( J = 22 \) Hz, CH), 115.2 (C), 111.0 (CH). FT-IR (KBr, \( \nu_{\text{max/cm}^{-1}} \)) 3745, 3392, 3019, 2924, 1645, 1512, 1403, 1158, 1047, 928, 839, 669; HRMS (ESI): calcd for C_{20}H_{15}FN [M+H]^+ 288.1189, found: 288.1191.

2-(4-Chlorophenyl)-3-phenyl-1H-indole (3ac):4 White solid (253 mg, 80%), mp 197-200 \(^\circ\)C; \(^1\)H NMR (400 MHz, CDCl3): δ 8.20 (br s, 1H), 7.67 (d, 1H, \( J = 8.0 \) Hz), 7.44-7.24 (m, 11H), 7.18-7.14 (m, 1H). 13C NMR (100 MHz, CDCl3): δ = 136.1 (C), 134.8 (C), 133.7 (C), 132.9 (C), 131.3 (C), 130.2 (2xCH), 129.4 (2xCH), 129.0 (2xCH), 128.7 (CH), 126.6 (CH), 123.1 (CH), 120.7 (CH), 119.9 (CH), 115.7 (C), 111.0 (CH). FT-IR (KBr, \( \nu_{\text{max/cm}^{-1}} \)) 3399, 3019, 1644, 1215, 1155, 1069, 928, 669; HRMS (ESI): calcd for C_{20}H_{15}ClN [M+H]^+ 304.0893, found: 304.0888.

2-(4-Bromophenyl)-3-phenyl-1H-indole (3ae):3 White solid (272 mg, 75%), mp 140-143 \(^\circ\)C; \(^1\)H NMR (400 MHz, CDCl3): δ 8.19 (br s, 1H), 7.67 (d, 1H, \( J = 8.0 \) Hz), 7.46-7.37 (m, 7H), 7.33-7.24 (m, 4H), 7.18-7.14 (m, 1H). 13C NMR (100 MHz, CDCl3) δ = 136.1 (C), 134.8 (C),
132.9 (C), 132.0 (2xCH), 131.7 (C), 130.2 (2xCH), 129.7 (2xCH), 128.88 (C), 128.80 (2xCH), 126.6 (CH), 123.2 (CH), 121.9 (C), 120.7 (CH), 119.9 (CH), 115.8 (C), 111.0 (CH).FT-IR (KBr, \( \nu_{\text{max}}/\text{cm}^{-1} \)) 3399, 3019, 1644, 1402, 1216, 1155, 1068, 669; HRMS (ESI): calcd for \( \text{C}_{20}\text{H}_{15}\text{BrN} \ [\text{M+H}]^+ \) 348.0388, found: 348.0375.

2-(3-Bromophenyl)-3-phenyl-1H-indole (3af):\(^a\) White solid (254 mg, 70\%), mp 124-126 °C; \(^1\)H NMR (400 MHz, CDCl\(_3\)): \( \delta \) 8.24 (br s, 1H), 7.67 (d, 1H, \( J = 6.4 \) Hz), 7.61 (t, 1H, \( J = 1.4 \) Hz), 7.44-7.38 (m, 6H), 7.33-7.25 (m, 3H), 7.18-7.13 (m, 2H). \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \( \delta \) 136.1 (C), 134.9 (C), 134.6 (C), 132.4 (C), 130.7 (CH), 130.6 (CH), 130.28 (CH), 130.24 (2xCH), 128.7 (2xCH), 127.1 (CH), 126.7 (CH), 123.3 (CH), 122.8 (C), 120.7 (CH), 120.0 (CH), 116.1 (C), 111.1 (CH). FT-IR (KBr, \( \nu_{\text{max}}/\text{cm}^{-1} \)) 3399, 3019, 2400, 1644, 1402, 1215, 1155, 1069, 928, 669; HRMS (ESI): calcd for \( \text{C}_{20}\text{H}_{15}\text{BrN} \ [\text{M+H}]^+ \) 348.0388, found: 348.0380.

2-(2, 4-Dichlorophenyl)-3-phenyl-1H-indole (3ag): White solid (254 mg, 72\%), mp 128-130 °C; \(^1\)H NMR (400 MHz, CDCl\(_3\)): \( \delta \) 8.35 (br s, 1H), 7.80 (d, 1H, \( J = 8.0 \) Hz), 7.50 (d, 1H, \( J = 1.8 \) Hz), 7.45 (d, 1H, \( J = 8.1 \) ), 7.35-7.25 (m, 6H), 7.23-7.13 (m, 3H). \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \( \delta \) 136.0 (C), 134.9 (C), 134.6 (C), 134.4 (C), 134.1 (CH), 130.4 (C), 130.3 (C), 130.2 (CH), 129.7 (2xCH), 128.6 (2xCH), 127.3 (CH), 126.4 (CH), 123.3 (CH), 120.6 (CH), 120.0 (CH), 117.6 (C), 111.1 (CH). FT-IR (KBr, \( \nu_{\text{max}}/\text{cm}^{-1} \)) 3393, 3019, 1644, 1216, 1155, 1069, 1023, 928, 771, 669; HRMS (ESI): calcd for \( \text{C}_{20}\text{H}_{14}\text{Cl}_2\text{N} \ [\text{M+H}]^+ \) 338.0503, found: 338.0512.

2-(2, 3-Dichlorophenyl)-3-phenyl-1H-indole (3ah): White solid (250 mg, 71\%), mp 137-139 °C; \(^1\)H NMR (400 MHz, CDCl\(_3\)): \( \delta \) 8.36 (br s, 1H), 7.81 (d, 1H, \( J = 7.9 \) Hz), 7.46 (d, 2H, \( J = 8.6 \) Hz), 7.34-7.28 (m, 5H), 7.26-7.16 (m, 3H), 7.10 (t, 1H, \( J = 7.8 \) Hz). \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \( \delta \) 135.9 (C), 134.6 (C), 134.2 (C), 133.9 (C), 132.4 (C), 131.7 (CH), 131.0 (C), 130.5
(CH), 129.7 (2xCH), 128.6 (2xCH), 127.4 (CH), 127.2 (C), 126.3 (CH), 123.3 (CH), 120.6 (CH), 120.1 (CH), 117.4 (C), 111.2 (CH). FT-IR (KBr, $\nu_{\text{max}}$/cm$^{-1}$) 3461, 3019, 2343, 1602, 1522, 1475, 1021, 848, 669; HRMS (ESI): calcd for C$_{20}$H$_{14}$Cl$_2$N $[M+H]^+$ 338.0503, found: 338.0506.

2-(2, 6-Dichlorophenyl)-3-phenyl-1H-indole (3ai): White solid (240 mg, 68%), mp 194-197 °C; $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 8.11 (br s, 1H), 7.85 (dd, 1H, $J$ = 7.9, 0.8 Hz), 7.47-7.45 (m, 1H), 7.38-7.36 (m, 4H), 7.32-7.27 (m, 4H), 7.25-7.19 (m, 2H). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ = 137.2 (2xC), 136.2 (C), 134.8 (C), 131.6 (C), 130.7 (CH), 128.8 (2xCH), 128.6 (C), 128.4 (2xCH), 128.2 (2xCH), 127.1 (C), 126.2(CH), 123.0 (CH), 120.4 (CH), 120.1 (CH), 118.1 (C), 111.3 (CH). FT-IR (KBr, $\nu_{\text{max}}$/cm$^{-1}$) 3390, 1643, 1402, 1068, 831, 769; HRMS (ESI): calcd for C$_{20}$H$_{14}$Cl$_2$N $[M+H]^+$ 338.0503, found: 338.0495.

2-(2-Chloro-6-fluorophenyl)-3-phenyl-1H-indole (3aj): White solid (218 mg, 65%), mp 137-139 °C; $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 8.21 (br s, 1H), 7.84 (d, 1H, $J$ = 8.0 Hz), 7.46 (d, 1H, $J$ = 8.1 Hz), 7.38-7.18 (m, 9H), 7.04-7.00 (m, 1H). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 161.5 (d, $J$ = 250 Hz, C), 136.3 (C), 134.9 (C), 130.9 (d, $J$ = 10 Hz, C), 128.9 (2xCH), 128.5 (2xCH), 127.1 (C), 126.3 (CH), 125.6 (d, $J$ = 3 Hz, CH), 124.6 (C), 123.1 (CH), 121.0 (d, $J$ = 19 Hz, C), 120.4 (CH), 120.0 (CH), 118.9 (C), 114.5 (d, $J$ = 23 Hz, CH), 111.2 (CH). FT-IR (KBr, $\nu_{\text{max}}$/cm$^{-1}$) 3399, 3021, 1611, 1216, 1068, 767, 670; HRMS (ESI): calcd for C$_{20}$H$_{14}$ClFN $[M+H]^+$ 322.0799, found: 322.0794.

4-(3-Phenyl-1H-indol-2-yl)benzonitrile (3ak): Yellow solid (252 mg, 82%), mp 176-179 (lit.$^5a$ 168-170 °C); $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 8.30 (br s, 1H), 7.61 (d, 1H, $J$ = 8.1), 7.55-7.53 (m, 2H), 7.48-7.45 (m, 2H), 7.42 (d, 1H, $J$ = 8.2), 7.38-7.35 (m, 4H), 7.33-7.29 (m, 1H), 7.28-7.22 (m, 1H), 7.15-7.11 (m, 1H). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 137.3 (C), 136.5 (C),...
134.3 (C), 132.5 (2xCH), 131.7 (C), 130.2 (2xCH), 129.0 (2xCH), 128.9 (C), 128.3 (2xCH), 127.1 (CH), 123.9 (CH), 121.0 (CH), 120.3 (CH), 118.8 (C), 117.7 (C), 111.2 (CH), 110.8 (C). FT-IR (KBr, $\nu_{\text{max}}$/cm$^{-1}$) 3745, 3390, 3019, 2227, 1607, 1511, 1329, 1216, 1155, 1070, 928, 842, 669; HRMS (ESI): calcd for C$_{21}$H$_{15}$N$_2$ [M+H]$^+$ 295.1235, found: 295.1233

2-(4-Nitrophenyl)-3-phenyl-1H-indole (3al):$^6$ Red solid (239 mg, 73%), mp 168-171 °C (lit.$^2$g 173-175 °C); $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 8.36 (br s, 1H), 8.17-8.14 (m, 2H), 7.65 (d, 1H, $J$ = 7.9), 7.57-7.54 (m, 2H), 7.48-7.34 (m, 6H), 7.33-7.29 (m, 1H), 7.20-7.16 (m, 1H). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 146.7 (C), 139.2 (C), 136.7 (C), 134.2 (C), 131.4 (C), 130.2 (2xCH), 129.0 (2xCH), 128.9 (C), 128.3 (2xCH), 127.2 (CH), 124.24 (CH), 124.21 (CH), 121.1 (CH), 120.4 (CH), 118.4 (C), 111.3 (CH). FT-IR (KBr, $\nu_{\text{max}}$/cm$^{-1}$) 3390, 1645, 1402, 1068, 770; HRMS (ESI): calcd for C$_{20}$H$_{15}$N$_2$O$_2$ [M+H]$^+$ 315.1134, found: 315.1134.

3-Phenyl-2-(p-tolyl)-1H-indole (3am):$^6b$ Yellow oil (236 mg, 59%); $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 8.18 (br s, 1H), 7.71 (d, 1H, $J$ = 7.9), 7.49-7.14 (m, 12H), 2.38 (s, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ = 137.7 (C), 135.9 (C), 135.3 (C), 134.3 (C), 130.3 (2xCH), 129.9 (C), 129.5 (2xCH), 128.9 (C), 128.6 (2xCH), 128.1 (2xCH), 126.2 (CH), 122.6 (CH), 120.5 (CH), 119.7 (CH), 114.7 (C), 110.9 (CH), 21.3. FT-IR (neat, $\nu_{\text{max}}$/cm$^{-1}$) 3400, 3019, 1642, 1402, 1216, 1069, 669; HRMS (ESI): calcd for C$_{21}$H$_{18}$N [M+H]$^+$ 284.1439, found: 284.1428.

Ethyl-2-(4-(3-phenyl-1H-indol-2-yl)phenoxy)acetate (3an): White solid (217 mg, 56%), mp 141-144 °C; $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 8.21 (br s, 1H), 7.67 (d, 1H, $J$ = 7.6 Hz), 7.43-7.12 (m, 10H), 6.86 (d, 2H, $J$ = 8.2 Hz), 4.62 (s, 2H), 4.27 (q, 2H, $J$ = 6.7 Hz), 1.30 (t, 3H, $J$ = 6.9 Hz). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 168.9 (C), 157.5 (C), 153.9 (C), 135.2 (C), 133.9 (C), 130.2 (2xCH), 129.6 (2xCH), 128.9 (C), 128.6 (2xCH), 126.4 (C), 126.2 (CH), 122.6 (CH), 120.5 (CH), 119.6 (CH), 115.0 (2xCH), 114.5 (C), 110.9 (CH), 65.5 (CH$_2$), 61.6 (CH$_2$),
14.3. FT-IR (KBr, \( \nu_{\text{max}}/\text{cm}^{-1} \)) 3390, 3019, 1642, 1402, 1216, 1069, 668; HRMS (ESI): calcld for C\(_{24}H_{22}NO_3\) [M+H]\(^+\) 372.1600, found: 372.1595.

**3-Phenyl-2-(3, 4, 5-trimethoxyphenyl)-1H-indole (3aq):**\(^5\) White solid (232 mg, 62%), mp 235-238 °C; \(^1\)H NMR (400 MHz, CDCl\(_3\)): \( \delta \) 8.34 (br s, 1H), 7.65 (d, 1H, \( J = 7.9 \) Hz), 7.48-7.37 (m, 5H), 7.32-7.24 (m, 2H), 7.18-7.14 (m, 1H), 6.64 (s, 2H), 3.88 (s, 3H), 3.67 (s, 6H).

\(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \( \delta \) 153.4 (2xCH), 137.8 (C), 135.9 (C), 135.3 (C), 134.0 (C), 130.5 (2xCH), 129.0 (C), 128.6 (2xCH), 128.1 (C), 126.4 (CH), 122.8 (CH), 120.6 (CH), 119.7 (CH), 115.2 (C), 110.9 (CH), 105.4 (2xCH), 61.0, 56.0. FT-IR (KBr, \( \nu_{\text{max}}/\text{cm}^{-1} \)) 3684, 3019, 1602, 1407, 1128, 1032, 928, 669; HRMS (ESI): calcld for C\(_{23}H_{22}NO_3\) [M+H]\(^+\) 360.1600, found: 360.1586.

**2-(Furan-2-yl)-3-phenyl-1H-indole(3ar):**\(^3\) Yellow Oil (108 mg, 40%); \(^1\)H NMR (400 MHz, CDCl\(_3\)): \( \delta \) 8.64 (br s, 1H), 7.60-7.57 (m, 3H), 7.50 (t, 2H, \( J = 7.4 \) Hz), 7.44-7.38 (m, 3H), 7.27-7.23 (m, 1H), 7.14 (t, 1H, \( J = 7.4 \) Hz), 6.39-6.37 (m, 2H). \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \( \delta \) = 147.2 (C), 141.4 (CH), 135.6 (C), 134.7 (C), 130.3 (2xCH), 128.9 (C), 128.7 (2xCH), 127.0 (CH), 125.3 (C), 123.0 (CH), 120.5 (CH), 119.6 (CH), 114.6 (C), 111.9 (CH), 110.9 (CH), 106.9 (CH). FT-IR (neat, \( \nu_{\text{max}}/\text{cm}^{-1} \)) 3391, 3019, 1644, 1403, 1215, 1069, 928, 669; HRMS (ESI): calcld for C\(_{18}H_{14}NO\) [M+H]\(^+\) 260.1075, found: 260.1068.

**3-Phenyl-2-(thiophen-2-yl)-1H-indole (3as):**\(^3, 8\) White solid (195 mg, 68%), mp 120-123 °C; \(^1\)H NMR (400 MHz, CDCl\(_3\)): \( \delta \) 8.23 (br s, 1H), 7.59 (d, 1H, \( J = 8.0 \) Hz), 7.55-7.53 (m, 2H), 7.48-7.37 (m, 4H), 7.29-7.26 (m, 2H), 7.18-7.14 (m, 1H), 7.12 (d, 1H, \( J = 3.5 \) Hz), 7.03-7.01 (m, 1H). \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \( \delta \) 135.8 (C), 134.68 (C), 134.61 (C), 130.6 (2xCH), 129.1 (C), 128.6 (2xCH), 128.4 (C), 127.6 (CH), 126.9 (CH), 125.49 (CH), 125.43 (CH), 123.1 (CH), 120.6 (CH), 119.8 (CH), 115.9 (C), 110.8 (CH). FT-IR (KBr, \( \nu_{\text{max}}/\text{cm}^{-1} \)) 3399,
3019, 1652, 1402, 1215, 1068, 668; HRMS (ESI): calcd for C\textsubscript{18}H\textsubscript{14}NS [M+H]\textsuperscript{+} 276.0847, found: 276.0838.

\textbf{3-Phenyl-1H, 1'H-2, 3'-biiindole (3at):}\textsuperscript{4a,9} Yellow solid (206 mg, 64%), mp 212-214 °C (lit.\textsuperscript{10} 220-221 °C); \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}): \(\delta\) 9.80 (br s, 1H), 9.52 (br s, 1H), 7.66 (d, 1H, \(J = 7.3\) Hz), 7.47-6.96 (m, 13H). \textsuperscript{13}C NMR (100 MHz, CDCl\textsubscript{3}): \(\delta\) 136.2 (C), 136.0 (C), 130.2 (C), 129.6 (2xCH), 128.1 (3xCH), 125.9 (C), 125.3 (CH), 124.5 (CH), 121.8 (CH), 121.3 (C), 120.1 (CH), 119.7 (CH), 119.6 (CH), 118.5 (CH), 113.2 (C), 111.4 (CH), 110.9 (CH), 108.2 (C). FT-IR (KBr, \(\nu_{\text{max}}$/cm\textsuperscript{-1}) 3464, 3019, 1602, 1406, 1334, 1156, 1053, 928, 669; HRMS (ESI): calcd for C\textsubscript{22}H\textsubscript{17}N\textsubscript{2} [M+H]\textsuperscript{+} 309.1392, found: 309.1384.

\textbf{1-Benzyl-2, 3-diphenyl-1H-indole (3ea):} White solid (154 mg, 54%), mp 155-158 °C; \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}): \(\delta\) 7.85-7.83 (m, 1H), 7.36-7.17 (m, 16H), 7.03 (d, 2H, \(J = 6.8\) Hz), 5.31 (s, 2H). \textsuperscript{13}C NMR (100 MHz, CDCl\textsubscript{3}): \(\delta\) 138.2 (C), 138.0 (C), 137.1 (C), 135.2 (C), 131.9 (C), 131.2 (2xCH), 130.0 (2xCH), 128.8 (2xCH), 128.5 (2xCH), 128.3 (3xCH), 127.5 (C), 127.3 (CH), 126.2 (2xCH), 125.7 (CH), 122.5 (CH), 120.5 (CH), 119.8 (CH), 115.8 (C), 110.6 (CH), 47.7 (CH\textsubscript{2}). FT-IR (KBr, \(\nu_{\text{max}}$/cm\textsuperscript{-1}) 3399, 3019, 1660, 1601, 1475, 1420, 1027, 928, 669; HRMS (ESI): calcd for C\textsubscript{27}H\textsubscript{22}N [M+H]\textsuperscript{+} 360.1752, found: 360.1778.

\textbf{5-Chloro-2, 3-diphenyl-1H-indole (3ba):} White solid (243 mg, 86%), mp 113-114 °C (lit.\textsuperscript{22a} 110-112 °C); \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}): \(\delta\) 8.26 (br s, 1H), 7.64 (d, 1H, \(J = 1.4\) Hz), 7.42-7.39 (m, 6H), 7.34-7.32 (m, 5H), 7.19 (dd, 1H, \(J = 8.6, 1.9\) Hz). \textsuperscript{13}C NMR (100 MHz, CDCl\textsubscript{3}): \(\delta\) 135.5 (C), 134.5 (C), 134.3 (C), 132.3 (C), 130.1 (2xCH), 130.0 (C), 128.89 (2xCH), 128.81 (2xCH), 128.2 (2xCH), 128.1 (CH), 126.6 (CH), 126.3 (C), 123.0 (CH), 119.2 (CH), 114.9 (C), 112.0 (CH). FT-IR (KBr, \(\nu_{\text{max}}$/cm\textsuperscript{-1}) 3391, 3019, 1644, 1404, 1215, 1156, 1026, 929, 669; HRMS (ESI): calcd for C\textsubscript{20}H\textsubscript{15}ClN [M+H]\textsuperscript{+} 304.0893, found: 304.0886.
5-Chloro-2-(2-chlorophenyl)-3-phenyl-1H-indole (3bd): White solid (262 mg, 83%), mp 202-205 °C; 1H NMR (400 MHz, CDCl₃): δ 8.44 (br s, 1H), 7.77 (d, 1H, J = 1.8 Hz), 7.49 (dd, 1H, J = 8.0, 0.9 Hz), 7.38 (d, 1H, J = 8.6 Hz), 7.34-7.31 (m, 4H), 7.30-7.23 (m, 4H), 7.19 (td, 1H, J = 7.6, 1.1 Hz). 13C NMR (100 MHz, CDCl₃): δ 134.29 (C), 134.22 (C), 133.7 (C), 133.3 (CH), 132.8 (C), 131.3 (C), 130.3 (CH), 129.9 (CH), 129.6 (2xCH), 128.6 (2xCH), 128.5 (C), 126.9 (CH), 126.5 (CH), 126.3 (C), 123.3 (CH), 119.4 (CH), 116.8 (C), 112.1 (CH). FT-IR (KBr, νmax/cm⁻¹) 3461, 3019, 1457, 1334, 1067, 929, 668; HRMS (ESI): calcd for C₂₀H₁₄Cl₂N [M+H]⁺ 338.0503, found: 338.0505.

5-Chloro-2-(2, 3-dichlorophenyl)-3-phenyl-1H-indole (3bh): White solid (281 mg, 81%), mp 137-139 °C; 1H NMR (400 MHz, CDCl₃): δ 8.41 (br s, 1H), 7.77 (d, 1H, J = 1.8 Hz), 7.50 (dd, 1H, J = 7.8, 1.8 Hz), 7.40-7.31 (m, 5H), 7.30-7.25 (m, 2H), 7.19-7.11 (m, 2H). 13C NMR (100 MHz, CDCl₃): δ 134.24 (C), 134.0 (C), 133.9 (C), 133.6 (C), 132.3 (C), 131.5 (CH), 130.8 (CH), 129.6 (2xCH), 128.7 (2xCH), 128.3 (C), 127.4 (CH), 126.7 (CH), 126.4 (C), 123.6 (CH), 119.5 (CH), 117.2 (C), 112.2 (CH). FT-IR (KBr, νmax/cm⁻¹) 3390, 3019, 1645, 1403, 1215, 1155, 669; HRMS (ESI): calcd for C₂₀H₁₃Cl₃N [M+H]⁺ 372.0111, found: 372.0114.

4-(5-Chloro-3-phenyl-1H-indol-2-yl)benzonitrile (3bk): Yellow solid (257 mg, 84%), mp 236-240 °C; 1H NMR (400 MHz, CDCl₃): δ 8.39 (br s, 1H), 7.59-7.57 (m, 3H), 7.50-7.48 (m, 2H), 7.44-7.40 (m, 2H), 7.38-7.34 (m, 4H), 7.26-7.22 (m, 2H). 13C NMR (100 MHz, CDCl₃): δ 136.8 (C), 134.8 (C), 133.7 (C), 133.0 (C), 132.6 (2xCH), 130.1 (2xCH), 129.9 (C), 129.1 (2xCH), 128.4 (2xCH), 127.4 (CH), 126.8 (C), 124.2 (CH), 119.7 (CH), 118.7 (C), 117.3 (C), 112.3 (CH), 111.2 (C). FT-IR (KBr, νmax/cm⁻¹) 3391, 3019, 2229, 1607, 1403, 1215, 1068, 669; HRMS (ESI): calcd for C₂₁H₁₅N₂ [M+H]⁺ 329.0846, found: 329.0846.
**5-Chloro-2-(4-nitrophenyl)-3-phenyl-1H-indole (3bl):** Yellow solid (282 mg, 87%), mp 242-244 °C; \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta\) 12.07 (br s, 1H), 8.22 (d, 2H, \(J = 8.9\) Hz), 7.67 (d, 2H, \(J = 8.9\) Hz), 7.51 (d, 1H, \(J = 8.6\) Hz), 7.47-7.42 (m, 3H), 7.39-7.34 (m, 3H), 7.23 (dd, 1H \(J = 8.6, 2.0\) Hz). \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \(\delta\) 146.3 (C), 138.4 (C), 135.0 (C), 133.7 (C), 133.1 (C), 129.7 (2×CH), 129.0 (2×CH), 128.9 (C), 128.8 (2×CH), 127.0 (CH), 124.8 (C), 123.8 (2×CH), 123.2 (CH), 118.0 (CH), 115.7 (C), 113.5 (CH). FT-IR (KBr, \(\nu_{\max}/\text{cm}^{-1}\)) 3398, 3019, 1644, 1403, 1216, 1068, 669; HRMS (ESI): calcd for C\(_{20}\)H\(_14\)ClN\(_2\)O\(_2\) [M+H]\(^{+}\) 349.0744, found: 349.0744.

**5-Chloro-3-phenyl-2-(p-tolyl)-1H-indole (3bm):**\(^7b\) Yellow solid (201 mg, 68%), mp 142-143 °C (lit.\(^7b\) 140-142 °C); \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta\) 8.22 (br s, 1H), 7.62 (d, 1H, \(J = 1.9\) Hz), 7.41-7.36 (m, 4H), 7.33-7.29 (m, 4H), 7.19-7.13 (m, 3H), 2.36 (s, 3H). \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \(\delta\) 138.1 (C), 135.7 (C), 134.6 (C), 134.2 (C), 130.1 (2×CH), 129.6 (2×CH), 129.4 (C), 128.7 (2×CH), 128.1 (2×CH), 126.6 (CH), 126.2 (C), 122.8 (CH), 119.1 (CH), 114.5 (C), 111.9 (CH), 21.4. FT-IR (KBr, \(\nu_{\max}/\text{cm}^{-1}\)) 3391, 3019, 1644, 1403, 1215, 1068, 669; HRMS (ESI): calcd for C\(_{21}\)H\(_{17}\)ClN [M+H]\(^{+}\) 318.1050, found: 318.1045.

**5-Chloro-2-(2, 4-dimethoxyphenyl)-3-phenyl-1H-indole (3bp):** White solid (248 mg, 73%), mp 187-190 °C; \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta\) 8.96 (br s, 1H), 7.62 (s, 1H), 7.39-7.25 (m, 6H), 7.15-7.12 (m, 2H), 6.55 (s, 1H), 6.34 (d, 1H, \(J = 7.9\) Hz), 3.84 (s, 3H) 3.80 (s, 3H). \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \(\delta\) 160.9 (C), 158.0 (C), 135.5 (C), 133.7 (C), 132.87 (C), 132.80 (CH), 130.1 (2×CH), 129.2 (C), 128.7 (2×CH), 126.3 (CH), 125.7 (C), 122.3 (CH), 118.6 (CH), 114.6 (C), 113.3 (C), 111.7 (CH), 105.1 (CH), 99.3 (CH), 55.8, 55.5. FT-IR (KBr, \(\nu_{\max}/\text{cm}^{-1}\)) 3391, 3019, 1610, 1522, 1215, 1028, 928, 669; HRMS (ESI): calcd for C\(_{22}\)H\(_{19}\)ClNO\(_2\) [M+H]\(^{+}\) 364.1104, found: 364.1091.
**5-Chloro-3-phenyl-2-(3, 4, 5-trimethoxyphenyl)-1H-indole (3bq):** White solid (253 mg, 69%), mp 235-237 °C; $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 8.36 (br s, 1H), 7.58 (s, 1H), 7.44-7.38 (m, 4H), 7.35-7.28 (m, 2H), 7.18 (d, 1H, $J$ = 8.2 Hz), 6.60 (s, 2H), 3.86 (s, 3H), 3.66 and 3.65 (s, 6H). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 153.4 (2xCH), 138.0 (C), 135.4 (C), 134.6 (C), 134.2 (C), 130.3 (2xCH), 130.1 (C), 128.7 (2xCH), 127.6 (C), 126.8 (CH), 126.3 (C), 123.0 (CH), 119.1 (CH), 114.9 (C), 112.0 (CH), 105.4 (2xCH), 61.0, 56.0. FT-IR (KBr, $\nu_{\text{max}}$/cm$^{-1}$) 3369, 3019, 1651, 1403, 1217, 1068, 668; HRMS (ESI): calcd for C$_{23}$H$_{21}$ClNO$_3$ [M+H]$^+$ 394.1210, found: 394.1205.

**5-Chloro-3-(2-fluorophenyl)-2-phenyl-1H-indole (3ca):** White solid (165 mg, 58%), mp 142-144 °C; $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 8.37 (br s, 1H), 7.47 (s, 1H), 7.40-7.31 (m, 8H), 7.20-7.13 (m, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 160.5 (d, $J$ = 246 Hz, C), 136.7 (C), 134.2 (C), 132.8 (CH), 132.3 (C), 130.2 (C), 129.0 (CH), 128.9 (2xCH), 128.3 (CH), 127.5 (2xCH), 126.3 (C), 124.4 (CH), 123.1 (CH), 122.1 (d, $J$ = 16 Hz, C), 119.4 (CH), 116.2 (d, $J$ = 22 Hz, CH), 112.0 (CH), 108.3 (C). FT-IR (KBr, $\nu_{\text{max}}$/cm$^{-1}$) 3390, 3019, 1644, 1402, 1215, 1067, 669; HRMS (ESI): calcd for C$_{20}$H$_{14}$ClFN [M+H]$^+$ 322.0799, found: 322.0789.

**5-Chloro-2-(4-chlorophenyl)-3-(2-fluorophenyl)-1H-indole (3cc):** White solid (163 mg, 52%), mp 166-169 °C; $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 8.34 (br s, 1H), 7.46 (s, 1H), 7.37-7.28 (m, 7H), 7.21-7.13 (m, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 160.4 (d, $J$ = 246 Hz, C), 135.5 (C) 134.3 (d, $J$ = 7 Hz, C), 132.7 (d, $J$ = 3 Hz, C), 130.8 (C), 130.1 (C), 129.2 (3xCH), 128.7 (3xCH), 126.5 (C), 124.5 (d, $J$ = 3 Hz, CH), 123.4 (CH), 121.8 (d, $J$ = 16 Hz, C), 119.4 (CH), 116.3 (d, $J$ = 22 Hz, CH), 112.1 (CH), 108.7 (C). FT-IR (KBr, $\nu_{\text{max}}$/cm$^{-1}$) 3749, 3399, 3019, 1644, 1216, 1154, 1066, 669; HRMS (ESI): calcd for C$_{20}$H$_{13}$Cl$_2$FN [M+H]$^+$ 356.0409, found: 356.0413.
4-(5-Chloro-3-(2-fluorophenyl)-1H-indol-2-yl)benzonitrile (3ck): White solid (171 mg, 56%), mp 195-197 °C; 1H NMR (400 MHz, CDCl3): \( \delta \) 8.47 (br s, 1H), 7.60 (s, 2H, \( J = 8.4 \) Hz), 7.49-7.47 (m, 3H), 7.41-7.34 (m, 3H), 7.26-7.22 (m, 2H), 7.20-7.14 (m, 1H). 13C NMR (100 MHz, CDCl3): \( \delta \) 160.2 (d, \( J = 246 \) Hz, C), 136.8 (C) 134.7 (C), 134.2 (C), 132.7 (2xCH), 132.5 (d, \( J = 3 \) Hz, CH), 130.0 (C), 129.6 (d, \( J = 8 \) Hz, CH), 127.7 (2xCH), 126.9 (CH), 124.7 (d, \( J = 4 \) Hz, CH), 124.3 (CH), 121.3 (d, \( J = 16 \) Hz, C), 119.7 (d, \( J = 2 \) Hz, CH), 118.7 (C), 116.5 (d, \( J = 22 \) Hz, CH) 112.4 (CH), 111.5 (C), 110.4 (C). FT-IR (KBr, \( \nu_{\text{max}}/\text{cm}^{-1} \)) 3388, 3021, 2400, 1608, 1418, 1216, 1066, 671; HRMS (ESI): calcd for C21H13ClFN2 [M+H]+ 347.0751, found: 347.0748.

(E)-2-Phenyl-4-(2-phenylhydrazono)-1, 2, 3, 4-tetrahydroquinoline (4da): White solid (209 mg, 50%), mp 188-190 °C; 1H NMR (400 MHz, CDCl3): \( \delta \)7.34-7.33 (m, 4H), 7.29-7.24 (m, 2H), 7.21-7.15 (m, 3H), 7.14-7.09 (m, 2H), 6.98 (d, 2H, \( J = 7.8 \) Hz), 6.83-6.77 (m, 2H), 6.73-6.69 (m, 1H), 5.18 (dd, 1H, \( J = 12.2, 7.3 \) Hz), 3.94 (dd, 1H, \( J = 16.8, 12.2 \) Hz), 3.26 (dd, 1H, \( J = 16.8, 7.3 \) Hz). 13C NMR (100 MHz, CDCl3): \( \delta \) 149.0 (C), 145.3 (C), 144.7 (C), 142.6 (C), 129.5 (CH), 129.2 (2xCH), 129.1 (2xCH), 128.4 (CH), 127.7 (CH), 126.0 (2xCH), 119.2 (CH), 117.4 (CH), 116.4 (CH), 115.4 (C), 113.3 (2xCH), 63.2 (CH), 45.17 (CH2). FT-IR (KBr, \( \nu_{\text{max}}/\text{cm}^{-1} \)) 3391, 3019, 1613, 1499, 1326, 1155, 1068, 669; HRMS (ESI): calcd for C21H20N3 [M+H]+ 314.1657, found: 314.1650.

(E)-2-(4-Chlorophenyl)-4-(2-phenylhydrazono)-1, 2, 3, 4-tetrahydroquinoline (4dc): White solid (280 mg, 60%), mp 202-203 °C; 1H NMR (400 MHz, DMSO-d6): \( \delta \) 7.81 (d, 2H, \( J = 8.1 \) Hz), \( \delta \) = 7.48 (d, 2H, \( J = 8.1 \) Hz), 7.20-7.13 (m, 3H), 7.08 (t, 1H, \( J = 7.8 \) Hz), 6.89 (d, 2H, \( J = 8.1 \) Hz), 6.81 (d, 2H, \( J = 8.1 \) Hz), 6.75-6.72 (m, 3H), 5.54 (t, 1H, \( J = 7.4 \) Hz), 5.49 (dd, 1H, \( J = 12.0, 6.0 \) Hz), 4.01 (dd, 1H, \( J = 17.2, 12.1 \) Hz), 3.21 (dd, 1H, \( J = 17.2, 6.1 \) Hz). 13C NMR
(100 MHz, DMSO-\textsubscript{d}\textsubscript{6}): $\delta$ 149.8 (C), 147.0 (C), 144.0 (C), 141.5 (C), 131.8 (C), 129.3 (CH), 129.0 (2xCH), 128.9 (2xCH), 128.7 (CH), 127.9 (2xCH), 118.5 (CH), 115.1 (CH), 115.0 (CH) 113.0 (C), 112.6 (2xCH), 60.7 (CH), 44.3 (CH\textsubscript{2}). FT-IR (KBr, $\nu_{\text{max/cm}^{-1}}$) 3387, 2361, 1597, 1512, 1450, 1342, 1265, 748; HRMS (ESI): calcd for C\textsubscript{21}H\textsubscript{19}ClN\textsubscript{3} [M+H]\textsuperscript{+} 348.1268, found: 348.1259.

\textit{(E)-2-(2, 4-Dichlorophenyl)-4-(2-phenylhydrazono)-1, 2, 3, 4-tetrahydroquinoline (4dg):}
White solid (296 mg, 58%), mp 209-210 °C; $^1$H NMR (400 MHz, DMSO-\textsubscript{d}\textsubscript{6}): $\delta$ 7.72 (d, 1H, $J$ = 2.1 Hz), 7.34 (dd, 1H, $J$ = 8.4, 2.1 Hz), 7.23-7.19 (m, 2H), 7.14 (dd, 1H, $J$ = 7.9, 1.4 Hz), 7.10-7.05 (m, 2H), 6.83-6.80 (m, 3H), 6.77-6.73 (m, 3H), 6.56-6.52 (m, 1H), 5.55 (dd, 1H, $J$ = 12.1, 6.0 Hz), 4.08 (dd, 1H, $J$ = 17.2, 12.2 Hz), 3.18 (dd, 1H, $J$ = 17.2, 6.1 Hz). $^{13}$C NMR (100 MHz, DMSO-\textsubscript{d}\textsubscript{6}): $\delta$ 150.1 (C), 147.0 (C), 143.6 (C), 138.0 (C), 132.8 (C), 132.2 (C), 129.49 (CH), 129.45 (CH), 129.2 (2xCH), 128.8 (CH), 128.6 (CH), 128.0 (CH), 118.7 (CH), 115.1 (CH), 115.0 (CH), 112.8 (C), 112.3 (2xCH), 58.4 (CH), 42.8 (CH\textsubscript{2}). FT-IR (KBr, $\nu_{\text{max/cm}^{-1}}$) 2361, 2353, 1597, 1497, 1389, 1327, 833; HRMS (ESI): calcd for C\textsubscript{21}H\textsubscript{18}Cl\textsubscript{2}N\textsubscript{3} [M+H]\textsuperscript{+} 382.0878, found: 382.0867.

\textit{(E)-2-(3, 4-Dichlorophenyl)-4-(2-phenylhydrazono)-1, 2, 3, 4-tetrahydroquinoline (4dv):}
White solid (293 mg, 57%), mp 184-185 °C; $^1$H NMR (400 MHz, DMSO-\textsubscript{d}\textsubscript{6}): $\delta$ 7.60-7.56 (m, 2H), 7.24-7.17 (m, 3H), 7.14 (dd, 1H, $J$ = 7.8, 1.0 Hz), 7.10-7.06 (m, 1H), 6.91 (d, 2H, $J$ = 7.8 Hz), 6.82 (d, 2H, $J$ = 8.1 Hz), 6.76-6.72 (m, 3H), 6.57-6.53 (m, 1H), 5.41 (dd, 1H, $J$ = 11.9, 6.1 Hz), 3.97 (dd, 1H, $J$ = 17.2, 12.0 Hz), 3.24 (dd, 1H, $J$ = 17.3, 6.2 Hz).$^{13}$C NMR (100 MHz, DMSO-\textsubscript{d}\textsubscript{6}): $\delta$ 150.03 (C), 147.0 (C), 143.9 (C), 143.6 (C), 131.3 (C), 131.2 (CH), 129.8 (C), 129.4 (CH), 129.0 (2xCH), 128.7 (CH), 128.1 (CH), 126.2 (CH), 118.7 (CH), 115.1
(CH), 115.0 (CH) 112.9 (C), 112.6 (2xCH), 60.3 (CH), 44.1 (CH2). FT-IR (KBr, \( \nu_{\text{max}}/\text{cm}^{-1} \))
3387, 2924, 2361, 1597, 1327, 1265, 1126, 748; HRMS (ESI): calcd for C\(_{21}\)H\(_{18}\)Cl\(_2\)N\(_3\) [M+H]\(^+\)
382.0878, found: 382.0869.

(E)-2-(4-Bromophenyl)-4-(2-phenylhydrazono)-1, 2, 3, 4-tetrahydroquinoline (4de): White
solid (302 mg, 58%), mp 203-205 °C; \(^1\)H NMR (400 MHz, DMSO-d\(_6\)): \( \delta \) 7.52 (d, 2H, \( J = 8.3 \)
Hz), 7.24 (d, 2H, \( J = 8.3 \) Hz), 7.18-7.12 (m, 3H), 7.08-7.04 (m, 1H), 6.89 (d, 2H, \( J = 8.2 \) Hz),
6.80 (d, 1H, \( J = 8.1 \) Hz), 6.73-6.69 (m, 3H), 6.54 (t, 1H, \( J = 7.4 \) Hz), 5.37 (dd, 1H, \( J = 12.0, \)
6.1 Hz), 3.97 (dd, 1H, \( J = 17.2, 12.1 \) Hz), 3.17 (dd, 1H, \( J = 17.2, 6.2 \) Hz). \(^{13}\)C NMR (100
MHz, DMSO-d\(_6\)): \( \delta \) 149.8 (C), 146.9 (C), 144.0 (C), 141.9 (C), 131.8 (2xCH), 129.3 (CH),
129.0 (2xCH), 128.7 (CH), 128.2 (2xCH), 120.3 (C), 118.5 (CH), 115.1 (CH), 115.0 (CH),
113.0 (C), 112.6 (2xCH), 60.8 (CH), 44.26 (CH\(_2\)). FT-IR (KBr, \( \nu_{\text{max}}/\text{cm}^{-1} \)) 3389, 3020, 2401,
1595, 1494, 1384, 1120, 1067, 929, 670; HRMS (ESI): calcd for C\(_{21}\)H\(_{19}\)BrN\(_3\) [M+H]\(^+\)
392.0762, found: 392.0760.

(E)-4-(4-(2-Phenylhydrazono)-1, 2, 3, 4-tetrahydroquinolin-2-yl)benzonitrile (4dk): Yellow
(318 mg, 70%), mp 193-194 °C; \(^1\)H NMR (400 MHz, DMSO-d\(_6\)): \( \delta \) 7.39 (d, 2H, \( J = 8.5 \) Hz),
7.30 (d, 2H, \( J = 8.5 \) Hz), 7.19-7.13 (m, 3H), 7.09-7.05 (m, 1H), 6.90 (d, 2H, \( J = 7.9 \) Hz), 6.82-
6.70 (m, 4H), 6.55 (t, 1H, \( J = 7.8 \) Hz) 5.39 (dd, 1H, \( J = 11.9, 6.1 \) Hz), 3.97 (dd, 1H, \( J = 17.2, \)
12.0 Hz), 3.18 (dd, 1H, \( J = 17.2, 6.2 \) Hz). \(^{13}\)C NMR (100 MHz, DMSO-d\(_6\)): \( \delta \) 149.9 (C), 148.1
(C), 147.0 (C), 143.9 (C), 132.9 (2xCH), 129.4 (CH), 129.1 (2xCH), 128.7 (CH), 127.1
(2xCH), 118.7 (CH), 118.6 (C), 115.1 (CH), 115.0 (CH), 112.9 (C), 112.6 (2xCH), 110.2 (C),
61.0 (CH), 44.1 (CH\(_2\)). FT-IR (KBr, \( \nu_{\text{max}}/\text{cm}^{-1} \)) 3397, 3294, 2361, 1597, 1497, 1327, 1265,
748; HRMS (ESI): calcd for C\(_{22}\)H\(_{19}\)N\(_4\) [M+H]\(^+\) 339.1610, found: 339.1604.
(E)-2-(4-Nitrophenyl)-4-(2-phenylhydrazono)-1, 2, 3, 4-tetrahydroquinoline (4dl): Orange solid (327 mg, 68%), mp 155-156 °C; \(^1\)H NMR (400 MHz, DMSO-\textit{d}\textsubscript{6}): \(\delta\) 8.21 (d, 2H, \(J = 8.7\) Hz), 7.57 (d, 2H, \(J = 8.7\) Hz), 7.20-7.10 (m, 3H), 7.08 (t, 1H, \(J = 8.1\) Hz), 6.90 (d, 2H, \(J = 8.0\) Hz), 6.82 (d, 1H, \(J = 8.1\) Hz), 6.76-6.72 (m, 3H), 5.55 (t, 1H, \(J = 7.7\) Hz), 5.56 (dd, 1H, \(J = 12.0, 6.2\) Hz), 4.04 (dd, 1H, \(J = 17.2, 12.2\) Hz), 3.24 (dd, 1H, \(J = 17.3, 6.3\) Hz).\(^{13}\)C NMR (100 MHz, DMSO-\textit{d}\textsubscript{6}): \(\delta\) 150.1 (C), 149.9 (C), 147.0 (C), 146.8 (C), 143.9 (C), 129.4 (CH), 129.0 (2xCH), 128.7 (CH), 127.3 (2xCH), 124.2 (2xCH), 118.7 (CH), 115.1 (CH), 115.0 (CH) 112.8 (C), 112.6 (2xCH), 60.8(CH), 44.1 (CH\textsubscript{2}). FT-IR (KBr, \(\nu_{\text{max}}/\text{cm}^{-1}\)) 3387, 2924, 2361, 1597, 1443, 1350, 1342, 1119, 748; HRMS (ESI): calcd for C\textsubscript{22}H\textsubscript{19}N\textsubscript{4}O\textsubscript{2} [M+H]\(^{+}\) 359.1508, found: 359.1498.

(E)-4-(2-Phenylhydrazono)-2-(p-tolyl)-1, 2, 3, 4-tetrahydroquinoline (4dm): White solid (183 mg, 42%), mp 155-156 °C; \(^1\)H NMR (400 MHz, DMSO-\textit{d}\textsubscript{6}): \(\delta\) 6.16-7.14 (m, 7H), 7.07 (t, 1H, \(J = 7.8\) Hz), 6.91 (d, 1H, \(J = 7.8\) Hz), 7.08 (t, 1H, \(J = 8.1\) Hz), 6.90 (d, 2H, \(J = 8.0\) Hz), 6.82 (d, 1H, \(J = 8.1\) Hz), 6.70(t, 1H, \(J = 7.2\) Hz), 6.55 (t, 1H, \(J = 7.3\) Hz), 5.24 (dd, 1H, \(J = 11.6, 6.1\) Hz), 3.95 (dd, 1H, \(J = 17, 12.1\) Hz), 3.14 (dd, 1H, \(J = 17.0, 6.1\) Hz). \(^{13}\)C NMR (100 MHz, DMSO-\textit{d}\textsubscript{6}): \(\delta\) = 149.7 (C), 146.7 (C), 144.2 (C), 139.6 (C), 136.4 (C), 129.4 (2xCH), 129.2 (CH), 128.8 (2xCH), 128.6 (CH), 125.8 (2xCH), 118.3 (CH), 115.2 (CH), 115.0 (CH) 113.3 (C), 112.6 (2xCH), 61.2(CH), 44.5 (CH\textsubscript{2}), 20.6. FT-IR (KBr, \(\nu_{\text{max}}/\text{cm}^{-1}\)) 3672, 3394, 3032, 2908, 1597, 1497, 1327, 1018, 879; HRMS (ESI): calcd for C\textsubscript{22}H\textsubscript{22}N\textsubscript{3} [M+H]\(^{+}\) 328.1814, found: 328.1817.

(E)-2-(4-Methoxyphenyl)-4-(2-phenylhydrazono)-1, 2, 3, 4-tetrahydroquinoline (4do): White solid (201 mg, 44%), mp 168-170 °C; \(^1\)H NMR (400 MHz, CDCl\textsubscript{3}): \(\delta\) 7.26-7.24 (m,
2H), 7.21-7.17 (m, 2H), 7.15-7.09 (m, 2H), 6.98 (d, 2H, J = 7.8 Hz), 6.86 (d, 2H, J = 8.7 Hz), 6.80-6.76 (m, 2H), 6.70-6.66 (m, 1H), 5.95 (br s, 2H), 5.13 (dd, 1H, J = 12.1, 7.2 Hz), 3.91 (dd, 1H, J = 16.8, 12.2 Hz), 3.23 (dd, 1H, J = 16.8, 7.3 Hz). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 159.1 (C), 149.2 (C), 146.1 (C), 144.9 (C), 134.7 (C), 129.4 (CH), 129.0 (2xCH), 128.4 (CH), 127.2 (2xCH), 119.1 (CH), 116.8 (CH), 115.9 (CH), 115.0 (C), 114.6 (2xCH), 113.3 (2xCH), 62.7 (CH), 55.4, 45.2 (CH$_2$). FT-IR (KBr, $\nu_{\text{max}}$/cm$^{-1}$) 3400, 3019, 1644, 1402, 1216, 1068, 669; HRMS (ESI): calcd for C$_{22}$H$_{22}$N$_3$O [M+H]$^+$ 344.1763, found: 344.1759.

**(E)-2-(2, 4-Dimethoxyphenyl)-4-(2-phenylhydrazineylidene)-1, 2, 3, 4-tetrahydroquinoline (4dp):** Yellow oil (215 mg, 43%); $^1$H NMR (400 MHz, DMSO-$d_6$): $\delta$ 7.18-7.12 (m, 3H), 7.07-7.03 (m, 1H), 6.85-6.78 (m, 4H), 6.71-6.68 (m, 3H), 6.63 (d, 1H, J = 2.3 Hz), 6.55-6.51 (m, 1H), 6.39 (dd, 1H, J = 8.5, 2.4 Hz), 5.42 (dd, 1H, J = 11.9, 5.8 Hz), 3.94-3.87 (m, 4H), 3.70 (s, 3H), 3.05 (dd, 1H, J = 17.1, 5.8 Hz). $^{13}$C NMR (100 MHz, DMSO-$d_6$): $\delta$ 159.8 (C), 157.0 (C), 150.1 (C), 146.8 (C), 144.0 (C), 129.1 (CH), 128.9 (CH), 129.45 (2xCH), 128.6 (CH), 126.7 (CH), 121.4 (C), 118.0 (CH), 115.1 (CH), 114.9 (CH), 113.3 (C), 112.2 (2xCH), 105.0 (CH), 98.8 (CH), 55.7, 55.6 (CH), 55.1, 42.8 (CH$_2$). FT-IR (neat, $\nu_{\text{max}}$/cm$^{-1}$) 3379, 2924, 2361, 1612, 1504, 1203, 1119, 748; HRMS (ESI): calcd for C$_{23}$H$_{24}$N$_3$O$_2$ [M+H]$^+$ 374.1869, found: 374.1860.

**(E)-6-(4-Chlorophenyl)-8-(2-phenylhydrazono)-5, 6, 7, 8-tetrahydro- [1, 3]dioxolo [4, 5-g]quinoline (4fc):** Yellow solid (204 mg, 46%), mp 205-206 °C; $^1$H NMR (400 MHz, DMSO-$d_6$): $\delta$ 7.39 (d, 2H, J = 8.4 Hz), 7.29 (d, 2H, J = 8.4 Hz), 7.15 (t, 2H, J = 7.5 Hz), 6.87 (br s, 2H), 6.72 (br s, 4H), 6.45 (s, 1H), 5.87 (br s, 2H), 5.32 (br s, 1H), 3.90 (dd, 1H, J = 17.2, 12.0 Hz), 3.13 (dd, 1H, J = 17.1, 6.0 Hz). $^{13}$C NMR (100 MHz, DMSO-$d_6$): $\delta$ = 150.4 (C), 146.9 (C), 144.5 (C), 140.1 (CH), 130.6 (C), 129.4 (CH), 128.8 (CH), 127.0 (2xCH), 121.3 (C), 118.4 (CH), 114.7 (CH), 113.3 (C), 112.3 (2xCH), 105.2 (CH), 98.8 (CH), 55.7, 55.6 (CH), 55.1, 42.8 (CH$_2$). FT-IR (neat, $\nu_{\text{max}}$/cm$^{-1}$) 3390, 3019, 1645, 1507, 1402, 1216, 1119, 748; HRMS (ESI): calcd for C$_{23}$H$_{19}$N$_3$O$_2$ [M+H]$^+$ 374.1869, found: 374.1860.
149.0 (C), 144.7 (C), 144.4 (C), 142.1 (C), 138.4 (C), 132.2 (C), 129.4 (2xCH), 128.4 (2xCH), 118.7 (CH), 113.0 (2xCH), 107.6 (CH), 105.5 (C), 100.9 (CH), 96.5 (CH), 61.1 (CH), 45.2 (CH). FT-IR (KBr, $\nu_{\text{max}}$/cm$^{-1}$) 3425, 2924, 2361, 1597, 1412, 1234, 741; HRMS (ESI): calcd for C$_{22}$H$_{19}$ClN$_3$O$_2$ [M+H]$^+$ 392.1166, found: 392.1173.

(E)-2-Ethyl-4-(2-phenylhydrazono)-1, 2, 3, 4-tetrahydroquinoline (4dw): White solid (128 mg, 36%), mp 112-113 °C; $^1$H NMR (400 MHz, DMSO-$_d_6$): $\delta$ 7.28-7.22 (m, 3H), 7.09-7.02 (m, 3H), 6.80-6.74 (m, 2H), 6.62-6.58 (m, 1H), 4.37-4.31 (m, 1H), 3.50 (dd, 1H, $J = 17.1$, 11.2 Hz), 3.18-3.13 (m, 1H), 1.76-1.67 (m, 1H), 1.56-1.45 (m, 1H), 0.84 (t, 3H, $J = 7.4$ Hz). $^{13}$C NMR (100 MHz, DMSO-$_d_6$): $\delta$ 150.4 (C), 146.7 (C), 143.9 (C), 129.1 (2xCH), 128.9 (CH), 128.5 (CH), 118.0 (CH), 115.0 (CH), 114.9 (CH) 113.5 (C), 112.5 (2xCH), 58.2 (CH), 38.4 (CH$_2$), 24.3 (CH$_2$), 8.5. FT-IR (KBr, $\nu_{\text{max}}$/cm$^{-1}$) 3371, 3032, 2955, 2361, 1597, 1497, 1388, 1296, 1337, 1134, 748; HRMS (ESI): calcd for C$_{17}$H$_{20}$N$_3$ [M+H]$^+$ 266.1657, found: 266.1658.

9-Phenyl-1, 2, 3, 4-tetrahydroacridine (6aa): $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 8.01 (d, 1H, $J = 8.4$Hz), 7.61-7.57 (m, 1H), 7.54-7.50 (m, 2H), 7.48-7.44 (m, 1H), 7.33-7.30 (m, 2H), 7.24-7.22 (m, 2H), 3.20 (t, 2H, $J = 13.2$, 6.6 Hz), 2.60 (t, 2H, $J = 13.0$, 6.5 Hz), 2.00-1.93 (m, 2H), 1.82-1.76 (m, 2H). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 159.2 (C), 146.6 (C), 146.4 (C), 137.2 (C), 129.2 (2xCH), 128.7 (2xCH), 128.49 (2xCH), 128.46 (C), 127.8 (CH), 126.8 (C), 125.9 (CH), 125.4 (CH), 34.3 (CH$_2$), 28.1 (CH$_2$), 23.1 (CH$_2$), 23.0 (CH$_2$). FT-IR (KBr, $\nu_{\text{max}}$/cm$^{-1}$) 3433, 2924, 2361, 1628, 1481, 1134, 671; HRMS (ESI): calcd for C$_{19}$H$_{18}$N [M+H]$^+$ 260.1439, found: 260.1431.
**2-Methyl-4-phenylquinoline (6ab):** Yellow oil (115 mg, 50%); $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 8.10 (br d, 1H, $J$ = 8.4 Hz), 7.85 (dd, 1H, $J$ = 8.4, 0.9 Hz), 7.68 (ddd, 1H, $J$ = 8.3, 6.8, 1.4 Hz), 7.53-7.47 (m, 5H), 7.42 (ddd, 1H, 8.2, 6.9, 1.2 Hz), 7.23 (s, 1H), 2.77 (s, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 158.5 (C), 148.6 (C), 148.4 (C), 138.2 (C), 129.5 (2xCH), 129.4 (CH), 129.0 (CH), 128.6 (2xCH), 128.4 (CH), 125.8 (CH), 125.7 (CH), 125.1 (C), 122.3 (CH), 25.4. FT-IR (neat, $\nu_{\text{max/cm}^{-1}}$) 3402, 3063, 2361, 1597, 1489, 1404, 1196, 764; HRMS (ESI): calcd for C$_{16}$H$_{14}$N [M+H]$^+$ 220.1126, found: 220.1118.

**9-Phenyl-2, 3-dihydro-1H-cyclopenta [b]quinoline (6ac):** Yellow oil (144 mg, 56%); $^1$H NMR (400 MHz, DMSO-$d_6$): $\delta$ 8.07-8.05 (m, 1H), 7.63-7.59 (m, 2H), 7.54-7.50 (m, 2H), 7.48-7.43 (m, 1H), 7.39-7.35 (m, 3H), 3.23 (t, 2H, $J$ = 7.64 Hz), 2.90 (t, 2H, $J$ = 7.36 Hz), 2.16 (quint, 2H, $J$ = 7.5 Hz). $^{13}$C NMR (100 MHz, DMSO-$d_6$): $\delta$ 167.5 (C), 148.0 (C), 142.8 (C), 136.9 (C), 133.7 (C), 129.4 (2xCH), 128.9 (CH), 128.6 (2xCH), 128.3 (CH), 128.1 (CH), 126.3 (C), 125.7 (CH), 125.6 (CH), 35.3 (CH$_2$), 30.4 (CH$_2$), 23.6 (CH$_2$). FT-IR (neat, $\nu_{\text{max/cm}^{-1}}$) 3433, 2962, 2924, 2361, 1597, 1389, 1342, 1126, 764; HRMS (ESI): calcd for C$_{18}$H$_{16}$N [M+H]$^+$ 246.1283, found: 246.1274.

**6-Chloro-3-methyl-2, 4-diphenylquinoline (6bd):** Yellow oil (169 mg, 55%); $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 8.09 (d, 1H, $J$ = 9.0 Hz), 7.61-7.58 (m, 3H), 7.57-7.54 (m, 2H), 7.52-7.48 (m, 3H), 7.46-7.42 (m, 1H), 7.35 (d, 1H, $J$ = 2.2 Hz), 7.30-7.28 (m, 2H), 2.14 (s, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 161.2 (C), 147.2 (C), 144.7 (C), 141.2 (C), 137.1 (C), 132.2 (C), 131.2 (CH), 129.6 (CH), 129.3 (2xCH), 129.0 (4xCH), 128.5 (2xCH), 128.4 (CH), 128.3 (CH), 127.98 (C), 127.95 (C), 124.8 (CH), 18.8. FT-IR (neat, $\nu_{\text{max/cm}^{-1}}$) 3402, 2932, 2361, 1628,
1381, 1196, 1119, 756; HRMS (ESI): calcd for C_{22}H_{17}ClN [M+H]^+ 330.1050, found: 330.1044.

2, 4-Dimethylquinoline (6da):\textsuperscript{17} Yellow oil (105 mg, 50%); \(^1\)H NMR (400 MHz, DMSO-\(d_6\)): \(\delta\) 8.00 (dd, 1H, \(J = 8.3, 0.5\) Hz), 7.91 (dd, 1H, \(J = 8.3, 1.0\) Hz), 7.64 (ddd, 1H, \(J = 8.3, 6.9, 1.4\) Hz), 7.47 (ddd, 1H, 8.2, 6.9, 1.2 Hz), 7.09 (d, 1H, \(J = 0.6\) Hz), 2.67 (br s, 3H), 2.62 (d, 3H, \(J = 0.9\) Hz). \(^{13}\)C NMR (100 MHz, DMSO-\(d_6\)): \(\delta\) 158.7 (C), 147.7 (C), 144.2 (C), 129.2 (CH), 129.1 (CH), 126.6 (C), 125.4 (CH), 123.6 (CH), 122.7 (CH), 25.2, 18.6. FT-IR (neat, \(\nu_{\text{max}}/\text{cm}^{-1}\) \(\textsuperscript{1})\) 3703, 3402, 3063, 2950, 2361, 1612, 1574, 1389, 1342, 1196, 756; HRMS (ESI): calcd for C\(_{11}\)H\(_{12}\)N [M+H]^+ 158.0970, found: 158.0959.

9-Methyl-1, 2, 3, 4-tetrahydroacridine (6db):\textsuperscript{18} Yellow oil (128 mg, 49%); \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta\) 7.98-7.95 (m, 2H), 7.66-7.57 (m, 1H), 7.48-7.43 (m, 1H), 3.12-3.10 (m, 2H), 2.92-2.89 (m, 2H), 2.56 (s, 3H), 1.95-1.92 (m, 4H). \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \(\delta\) = 158.7 (C), 146.0 (C), 141.4 (C), 129.0 (CH), 128.8 (C), 128.2 (CH), 127.0 (C), 125.4 (CH), 123.4 (CH), 34.6 (CH\(_2\)), 27.2 (CH\(_2\)), 23.3 (CH\(_2\)), 22.9 (CH\(_2\)), 13.6. FT-IR (neat, \(\nu_{\text{max}}/\text{cm}^{-1}\) 3433, 2962, 2361, 1597, 1402, 1226, 764; HRMS (ESI): calcd for C\(_{14}\)H\(_{16}\)N [M+H]^+ 198.1283, found: 198.1284.

9-Methyl-2, 3-dihydro-1H-cyclopenta [b]quinoline (6dc):\textsuperscript{19} Yellow oil (130 mg, 53%); \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta\) 7.99 (dd, 1H, \(J = 8.4, 0.6\) Hz), 7.88 (dd, 1H, \(J = 8.3, 1.1\) Hz), 7.57 (ddd, 1H, \(J = 8.3, 6.9, 1.4\) Hz), 7.43 (ddd, 1H, \(J = 8.2, 6.9, 1.2\) Hz), 3.13 (t, 2H, \(J = 7.7\) Hz), 2.99 (t, 2H, \(J = 7.5\) Hz), 2.51 (s, 3H), 2.15 (quint, 2H, \(J = 7.6\) Hz). \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \(\delta\) 166.9 (C), 147.4 (C), 138.1 (C), 134.0 (C), 129.1 (CH), 128.0 (CH), 127.0 (C), 125.2 (CH), 123.3 (CH), 35.11 (CH\(_2\)), 29.6 (CH\(_2\)), 22.9 (CH\(_2\)), 14.8. FT-IR (neat, \(\nu_{\text{max}}/\text{cm}^{-1}\) 325
3402, 3063, 2955, 2361, 1612, 1443, 1342, 1119, 756; HRMS (ESI): calcd for C\textsubscript{13}H\textsubscript{14}N\textsubscript{2} [M+H]\^{+} 184.1126, found: 184.1126.

\textbf{2, 8-dichloro-6, 12-diphenyldibenzo[b, f] [1, 5]diazocine (7):} Yellow solid (220 mg, 40%), mp 120-122 °C; \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}): δ 7.75-7.73 (m, 4H), 7.46-7.42 (m, 2H), 7.38-7.34 (m, 4H), 7.31 (dd, 2H, J= 2.4, 8.6 Hz), 7.00-6.96 (m, 4H). \textsuperscript{13}C NMR (100 MHz, CDCl\textsubscript{3}): δ 168.9 (C), 150.3 (C), 137.3 (C), 131.6 (CH), 130.2 (CH), 129.5 (2xCH), 129.2 (C), 128.5 (2xCH), 128.2 (C), 127.3 (CH), 122.6 (CH). HRMS (ESI): calcd for C\textsubscript{26}H\textsubscript{17}Cl\textsubscript{2}N\textsubscript{2} [M+H]\^{+} 427.0769, found: 427.0763.
4. References


Copies of $^1$H, $^{13}$C NMR, HRMS spectra

$^1$H NMR spectrum of 1a

$^{13}$C NMR spectrum of 1a
DEPT 135 spectrum of 1a

Expanded COSY spectrum of 1a
Expanded HSQC spectrum of 1a

Expanded HMBC spectrum of 1a
Expanded NOESY spectrum of 1a

HRMS spectrum of 1a
$^1$H NMR spectrum of 1b

$^{13}$C NMR spectrum of 1b
HRMS spectrum of 1b

\[ \text{\H NMR spectrum of 1c} \]
$^{13}$C NMR spectrum of 1c

HRMS spectrum of 1c
$^1$H NMR spectrum of 1d

$^{13}$C NMR spectrum of 1d
HRMS spectrum of 1d

\[ \text{HRMS spectrum of 1d} \]

\[ \text{\(^1\)H NMR spectrum of 3aa} \]
$^{13}$C NMR spectrum of 3aa

DEPT 135 spectrum of 3aa
Expanded COSY spectrum of 3aa

Expanded HSQC spectrum of 3aa
Expanded HMBC spectrum of 3aa

HRMS spectrum of 3aa
$^1$H NMR spectrum of 3ab

$^{13}$C NMR spectrum of 3ab
HRMS spectrum of 3ab

$^1$H NMR spectrum of 3ac
$^{13}$C NMR spectrum of 3ac

DEPT 135 spectrum of 3ac
Expanded COSY spectrum of 3ac

Expanded HSQC spectrum of 3ac
Expanded HMBC spectrum of 3ac

HRMS spectrum of 3ac
\[ \text{\textsuperscript{1}H NMR spectrum of 3ae} \]

\[ \text{\textsuperscript{13}C NMR spectrum of 3ae} \]
HRMS spectrum of 3ae

$^1$H NMR spectrum of 3af
$^{13}$C NMR spectrum of 3af

HRMS spectrum of 3af
$^1$H NMR spectrum of 3ag

$^{13}$C NMR spectrum of 3ag
HRMS spectrum of 3ag

$^1$H NMR spectrum of 3ah
$^{13}$C NMR spectrum of 3ah

HRMS spectrum of 3ah
$\text{H NMR spectrum of } 3\text{ai}$

$\text{13C NMR spectrum of } 3\text{ai}$
HRMS spectrum of 3ai

\[ \text{\( ^1H \) NMR spectrum of 3aj} \]
$^{13}$C NMR spectrum of 3aj

HRMS spectrum of 3aj
$^{1}$H NMR spectrum of 3ak

$^{13}$C NMR spectrum of 3ak
HRMS spectrum of 3ak

$^1$H NMR spectrum of 3al
$^{13}$C NMR spectrum of 3al

HRMS spectrum of 3al
$^1$H NMR spectrum of 3am

$^{13}$C NMR spectrum of 3am
HRMS spectrum of 3am

$^{1}H$ NMR spectrum of 3an
$^{13}$C NMR spectrum of 3an

HRMS spectrum of 3an
$^1$H NMR spectrum of 3aq

$^{13}$C NMR spectrum of 3aq
HRMS spectrum of 3aq

$^1$H NMR spectrum of 3ar
\( ^{13}\text{C} \) NMR spectrum of 3ar

HRMS spectrum of 3ar
$^1$H NMR spectrum of 3as

$^{13}$C NMR spectrum of 3as
HRMS spectrum of 3as

\[ \overset{\text{IN INDOLE}}{\text{HRMS spectrum of 3as}} \]

\[ \text{1H NMR spectrum of 3at} \]
$^{13}$C NMR spectrum of 3at

HRMS spectrum of 3at
$^1$H NMR spectrum of 3ea

$^{13}$C NMR spectrum of 3ea
HRMS spectrum of 3ea

$^1$H NMR spectrum of 3ba
$^{13}$C NMR spectrum of 3ba

HRMS spectrum of 3ba
$^1$H NMR spectrum of 3bd

$^{13}$C NMR spectrum of 3bd
HRMS spectrum of 3bd

$^1$H NMR spectrum of 3bh
$^{13}$C NMR spectrum of 3bh

HRMS spectrum of 3bh
$^1$H NMR spectrum of 3bk

$^{13}$C NMR spectrum of 3bk
HRMS spectrum of 3bk

$^1$H NMR spectrum of 3bl
$^{13}$C NMR spectrum of 3bl

HRMS spectrum of 3bl
$^1$H NMR spectrum of 3bm

$^{13}$C NMR spectrum of 3bm
HRMS spectrum of 3bm

^1H NMR spectrum of 3bp
$^{13}$C NMR spectrum of 3bp

HRMS spectrum of 3bp
$^1$H NMR spectrum of 3bq

$^{13}$C NMR spectrum of 3bq
HRMS spectrum of 3bq

$^{1}$H NMR spectrum of 3ca
$^{13}$C NMR spectrum of 3ca

HRMS spectrum of 3ca
HRMS spectrum of 3cc

$^1$H NMR spectrum of 3ck
$^{13}$C NMR spectrum of 3ck

HRMS spectrum of 3ck
$^1$H NMR spectrum of 4da

$^{13}$C NMR spectrum of 4da
HRMS spectrum of 4da

$^1$H NMR spectrum of 4dc
$^{13}$C NMR spectrum of 4dc

HRMS spectrum of 4dc
$^{1}H$ NMR spectrum of 4dg

$^{13}C$ NMR spectrum of 4dg
HRMS spectrum of 4dg

\[ ^1H \text{ NMR spectrum of 4dv} \]
$^{13}$C NMR spectrum of 4dv

HRMS spectrum of 4dv
$^1$H NMR spectrum of 4de

$^{13}$C NMR spectrum of 4de
COSY spectrum of 4de

Expanded COSY spectrum of 4de
HSQC spectrum of 4de

Expanded HSQC spectrum of 4de
HMBC spectrum of 4de

NOESY spectrum of 4de
$^{13}$C NMR spectrum of 4dk

HRMS spectrum of 4dk
$^1$H NMR spectrum of 4dl

$^{13}$C NMR spectrum of 4dl
HRMS spectrum of 4dl

$^1$H NMR spectrum of 4dm
$^{13}$C NMR spectrum of 4dm

HRMS spectrum of 4dm
$^{1}H$ NMR spectrum of 4do

$^{13}C$ NMR spectrum of 4do
HRMS spectrum of 4do

^1^H NMR spectrum of 4dp
$\text{HNCH}$

$\text{C NMR spectrum of 4dp}$

HRMS spectrum of 4dp
$^1$H NMR spectrum of 4fc

$^{13}$C NMR spectrum of 4fc
HSQC spectrum of 4fc

Expanded HSQC spectrum of 4fc
$^1$H NMR spectrum of 4dw

$^{13}$C NMR spectrum of 4dw
HRMS spectrum of 4dw

$^{1}$H NMR spectrum of 6aa
$^{13}$C NMR spectrum of 6aa

HRMS spectrum of 6aa
$^{1}H$ NMR spectrum of 6ab

$^{13}C$ NMR spectrum of 6ab
HRMS spectrum of 6ab

\[ ^1H \text{NMR spectrum of 6ac} \]
$^{13}$C NMR spectrum of 6ac

HRMS spectrum of 6ac
$1^1$H NMR spectrum of 6bd

$1^3$C NMR spectrum of 6bd
HRMS spectrum of 6bd

$^1$H NMR spectrum of 6da
\textbf{13C NMR spectrum of 6da}

\textbf{HRMS spectrum of 6da}
$\text{H NMR spectrum of 6db}$

$\text{C NMR spectrum of 6db}$
HRMS spectrum of 6db

\[ \text{1H NMR spectrum of 6dc} \]
$^{13}$C NMR spectrum of 6dc

HRMS spectrum of 6dc
$^1$H NMR Spectra of compound 7

$^{13}$C NMR Spectra of compound 7
HRMS Spectra of compound 7

5. LC-ESIMS of crude reaction of Compound 3ac

LC-ESI-MS spectrum (-ve mode) of Crude Reaction mixture (8 h) of Compound 3ac
LC-ESI-MS spectrum (+ve mode) of Crude Reaction mixture (8 h) of Compound 3ac

6. ESI-MS of crude reaction mixtures of 3aa and 6aa

ESI-MS of crude reaction mixture for the synthesis of 3aa in one pot via successive addition
ESI-MS of crude reaction mixture of 6aa (reaction at RT)

ESI-MS of crude reaction mixture of 6aa (reaction at 120 °C)