Supporting Information for

**Heteroannulation of Arynes with N-Aryl-α-Aminoketones for the Synthesis of Unsymmetrical N-Aryl-2,3-Disubstituted Indoles: An Aryne Twist of Bischler-Möhlau Indole Synthesis**

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General Information

All reactions were carried out in oven dried glasswares. All chemicals were purchased from Acros, Aldrich, Fluka, VWR, AppliChem or Merck and used directly unless stated otherwise. CH$_3$CN, toluene, and DMF were dried by passage over activated alumina under nitrogen atmosphere (H$_2$O content < 30 ppm, Karl-Fischer titration). DMSO was bought from Fischer Bioreagent (>99.7% pure) and used directly. DCE and i-PrCN were distilled on CaH$_2$. Chromatographic purification was conducted with technical grade solvents and silica gel 40-63 μm. TLC was performed on Merck silica gel 60 F254 TLC aluminium plates and visualized with UV light (254 nm), permanganate stain, CAN stain or anisaldehyde stain. Melting points were measured on a Stuart SMP30 melting point apparatus using open glass capillaries (uncorrected). $^1$H NMR spectra were recorded on a Brucker AVIII-400 400 MHz spectrometer and a DPX-600 600 MHz spectrometer in CDCl$_3$ or [D$_6$]DMSO (all signals are reported in ppm with the internal chloroform signal at 7.26 ppm, or the internal DMSO signal at 2.50 ppm as standard). $^{13}$C NMR spectra were recorded with $^1$H-decoupling on a Brucker AVIII-400 101 MHz spectrometer and a DPX-600 125 MHz spectrometer in CDCl$_3$ or [D$_6$]DMSO (all signals are reported in ppm with the internal chloroform signal at 77.2 ppm, or the internal DMSO signal at 39.5 ppm as standard). Infrared spectra were recorded on a JASCO FT/IR-4100 spectrometer with MIRacle ATR and a diamond/ZnSe crystal plate and were reported as cm$^{-1}$. Low resolution mass spectrometric measurements were performed on Waters ACQUITY™ UPLC/MS System. High resolution mass spectrometric measurements were performed by the mass spectrometry service of ISIC at the EPFL on a MICROMASS (ESI) Q-TOF Ultima API.
I. Synthesis of α-N-arylamino ketones 2:

A) Procedure A: Synthesis of α-N-arylamino ketones starting from α-hydroxyketones

**General procedure A1.** α-N-arylamino ketones 2a-2c were synthesized according to the procedure reported previously.\(^1\)

**General procedure A2.** α-N-arylamino ketones 2d-2g, 2k were synthesized according to modified procedure reported previously:\(^1\) To a solution of α-hydroxyketone 10 (2.0 equiv) and aniline 6 (1.0 equiv) in toluene (c = 1.0 M) were added two drops of concentrated HCl. The reaction mixture was stirred at 120 °C in a sealed tube until total consumption of aniline 6 (1-12 h). After cooling the reaction mixture to room temperature, the solvent was evaporated under vacuum and the resulting residue was purified by flash column chromatography to afford the desired α-N-arylamino ketone 2.

Analytical and spectroscopic data of the products synthesized according to general procedures A1 and A2 are described below:

**3-(phenylamino)butan-2-one (2a)**

Following the general procedure A1 after purification by flash chromatography (silica gel, petroleum ether/AcOEt 90:10) the product was obtained as a yellow solid (1.9 g, 11.6 mmol, 58%). The \(^1\)H NMR spectroscopic data were identical to those reported in the literature.\(^1\)

\(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.18 (t, \(J = 7.8\) Hz, 2H), 6.72 (t, \(J = 7.8\) Hz, 1H), 6.56 (d, \(J = 7.8\) Hz, 2H), 4.38 (br s, 1H), 4.07 (quint, \(J = 7.0\) Hz, 1H), 2.21 (s, 3H), 1.42 (d, \(J = 7.0\) Hz, 3H).

**3-((4-nitrophenyl)amino)butan-2-one (2b)**

Following the general procedure A1 after purification by flash chromatography (silica gel, petroleum ether/AcOEt 90:10 then 60:40) the product was obtained as a yellow solid (3.3 g, 15.8 mmol, 79%).

M.p. 101 °C; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 8.09 (d, \(J = 9.1\) Hz, 2H), 6.52 (d, \(J = 9.1\) Hz, 2H), 5.42 (br s, 1H), 4.22 (quint, \(J = 7.0\) Hz, 1H), 2.28 (s, 3H), 1.48 (d, \(J = 7.0\) Hz, 3H); \(^13\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 207.0, 151.5, 138.4, 126.5, 111.6, 57.6, 26.2, 17.5; HRMS (ESI): calcd for C\(_{10}\)H\(_{13}\)N\(_2\)O\(_3\) + [M+H]\(^+\) 209.0921, found 209.0915; ATR-FTIR [cm\(^{-1}\)]: 3291, 1717, 1587, 1528, 1470, 1300, 1282, 1141, 1111, 842, 755.

Following the general procedure A1 after purification by flash chromatography (silica gel, petroleum ether/AcOEt 90:10 then 80:20) the product was obtained as a yellow solid (2.5 g, 12.9 mmol, 65%).

**3-((4-methoxyphenyl)amino)butan-2-one (2c)**

 Following the general procedure A1 after purification by flash chromatography (silica gel, petroleum ether/AcOEt 90:10 then 80:20) the product was obtained as a yellow solid (2.5 g, 12.9 mmol, 65%).

**M.p.** 42 °C; $^1$H NMR (400 MHz, CDCl$_3$) δ 6.77 (d, $J = 8.9$ Hz, 2H), 6.53 (d, $J = 8.9$ Hz, 2H), 3.99 (q, $J = 7.0$ Hz, 1H), 3.88 (br s, 1H), 3.73 (s, 3H), 2.19 (s, 3H), 1.39 (d, $J = 7.0$ Hz, 3H); $^{13}$C NMR (101 MHz, CDCl$_3$) δ 210.9, 152.5, 140.8, 115.1, 114.5, 59.6, 55.9, 25.9, 18.2; HRMS (ESI): calcd for C$_{11}$H$_{16}$NO$_2$ [M+H] 194.1181, found 194.1175; ATR-FTIR [cm$^{-1}$]: 3354, 1695, 1511, 1239, 1030, 825, 816, 646.

Following the general procedure A2 after purification by flash chromatography (silica gel, petroleum ether/AcOEt 96:4 then 92:8) the product was obtained as a yellow oil (764.6 mg, 3.96 mmol, 79%).

$^1$H NMR (400 MHz, CDCl$_3$) δ 6.83 (td, $J = 7.8$, 1.5 Hz, 1H), 6.79 (dd, $J = 7.8$, 1.5 Hz, 1H), 4.81 (br s, 1H), 4.00 (q, $J = 7.1$ Hz, 1H), 3.87 (s, 3H), 2.19 (s, 3H), 1.44 (d, $J = 7.1$ Hz, 3H); $^{13}$C NMR (101 MHz, CDCl$_3$) δ 211.4, 146.9, 136.6, 121.36, 117.4, 109.9, 109.8, 58.8, 55.6, 25.5, 18.1; HRMS (ESI): calcd for C$_{11}$H$_{16}$NO$_2$ [M+H] 194.1181, found 194.1175; ATR-FTIR [cm$^{-1}$]: 3413, 2974, 2364, 1602, 1513, 1458, 1248, 1222, 1145, 1028, 734.

Following the general procedure A2 after purification by flash chromatography (silica gel, petroleum ether/AcOEt 96:4 then 92:8) the product was obtained as a yellow oil (524.0 mg, 2.96 mmol, 59%).

$^1$H NMR (400 MHz, CDCl$_3$) δ 7.14 – 7.06 (m, 2H), 6.69 (td, $J = 7.4$, 0.8 Hz, 1H), 6.46 (d, $J = 7.4$ Hz, 1H), 4.36 (br s, 1H), 4.12 (q, $J = 7.0$ Hz, 1H), 2.23 (s, 3H), 2.22 (s, 3H), 1.47 (d, $J = 7.0$ Hz, 3H); $^{13}$C NMR (101 MHz, CDCl$_3$) δ 210.2, 144.5, 130.5, 127.2, 122.4, 117.6, 110.9, 109.8, 58.6, 25.8, 18.3, 17.6; HRMS (ESI): calcd for C$_{11}$H$_{16}$NO$_2$ [M+H] 178.1232, found 178.1236; ATR-FTIR [cm$^{-1}$]: 3412, 2980, 2364, 1602, 1513, 1458, 1248, 1222, 1145, 1028, 734.

Following the general procedure A2 after purification by flash chromatography (silica gel, petroleum ether/AcOEt 98:2) the product was obtained as a yellow oil (680.0 mg, 2.65 mmol, 53%).

$^1$H NMR (400 MHz, CDCl$_3$) δ 7.45 (dd, $J = 7.6$, 1.5 Hz, 1H), 7.16 (dd, $J = 7.6$ 1.5 Hz, 1H), 6.61 (td, $J = 7.6$, 1.4 Hz, 1H), 6.47 (dd, $J = 7.6$, 1.4 Hz, 1H), 5.04 (d, $J = 6.8$ Hz, 1H), 4.07 (quint, $J = 6.8$ Hz, 1H), 2.21 (s, 3H), 1.48 (d, $J = 6.8$ Hz, 3H); $^{13}$C NMR (101 MHz, CDCl$_3$) δ 209.7, 143.5, 132.9, 128.7, 118.7, 111.4, 110.0, 58.8, 25.5, 18.0; HRMS (ESI): calcd
for C_{10}H_{13}^{79}BrNO [M+H] 242.0181, found 242.0180; ATR-FTIR [cm^{-1}]: 3381, 2975, 2325, 1500, 1424, 1317, 1019, 738.

3-((2,6-dimethylphenyl)amino)butan-2-one (2g)

Following the general procedure A2 after purification by flash chromatography (silica gel, petroleum ether/AcOEt 97:3 then 93:7) the product was obtained as a yellow oil (550.4 mg, 2.87 mmol, 58%).

{\text{\textsuperscript{1}}H NMR (400 MHz, CDCl}_{3} \delta 6.97 (d, J = 7.5 Hz, 2H), 6.80 (t, J = 7.5 Hz, 1H), 4.10 (q, J = 7.0 Hz, 1H), 2.29 (s, 6H), 2.20 (s, 3H), 1.23 (d, J = 7.0 Hz, 3H); \text{\textsuperscript{13}}C NMR (101 MHz, CDCl}_{3} \delta 209.8, 144.2, 128.9, 128.8, 121.5, 61.0, 27.4, 19.0, 18.4; \text{HRMS (ESI)}: calcd for C_{12}H_{18}NO [M+H] 192.1388, found 178.1381; ATR-FTIR [cm^{-1}]: 3374, 2973, 2324, 1717, 1475, 1435, 1264, 1127, 766.

1,2-diphenyl-2-(phenylamino)ethanone (2k)

Following the general procedure A2 after purification by flash chromatography (silica gel, petroleum ether/AcOEt 95:5) the product was obtained as a white solid (680.0 mg, 2.36 mmol, 47%). M.p. 96 °C; \text{\textsuperscript{1}}H NMR (400 MHz, CDCl}_{3} \delta 8.23 – 7.82 (m, 2H), 7.60 – 7.51 (m, 1H), 7.50 – 7.39 (m, 4H), 7.34 – 7.27 (m, 2H), 7.25 – 7.19 (m, 1H), 7.19 – 7.12 (m, 2H), 6.82 – 6.56 (m, 3H), 6.06 (d, J = 5.7 Hz, 1H), 5.45 (d, J = 5.6 Hz, 1H); \text{\textsuperscript{13}}C NMR (101 MHz, CDCl}_{3} \delta 197.2, 146.2, 137.8, 135.1, 133.6, 129.3, 129.2, 129.0, 128.8, 128.3, 128.2, 117.9, 113.60, 62.8; \text{HRMS (ESI)}: calcd for C_{20}H_{18}NO [M+H] 288.1383, found 288.1376; ATR-FTIR [cm^{-1}]: 3301, 1717, 1588, 1470, 1302, 1282, 1111, 988, 842, 755, 636.

B) Procedure B: Synthesis of α-N-arylaminoketones starting from α-bromoketones

General procedure B1. To a solution of aniline 6 (1.0 equiv) and Et\textsubscript{3}N (2.0 equiv) in THF (c = 0.4 M) was added dropwise α-bromoketone 11 (1.0 equiv) in THF (c = 2.0 M) at 0 °C. The resulting reaction mixture was refluxed for 48 h, then cooled down to room temperature. The white solid formed was filtered off then to the filtrate were added ethyl acetate and water. The aqueous phase was extracted with ethyl acetate. The combined organic layers were washed with brine, dried over anhydrous sodium sulfate and concentrated under reduced pressure. The resulting residue was purified by flash chromatography to afford the desired α-N-aminoketone 2.

General procedure B2. α-Bromoketone 11 (1.0 equiv) was added to the mixture of aniline
(2.0 equiv) and Na₂CO₃ (2.0 equiv). The resulting reaction mixture was stirred at 140 °C under argon atmosphere in a sealed tube until total consumption of α-bromoketone 11 (1-4 h). After cooling the reaction mixture to room temperature ethyl acetate and water were added. The aqueous phase was extracted with ethyl acetate. The combined organic layers were washed with brine, dried over anhydrous sodium sulfate and concentrated under reduced pressure. The resulting residue was purified by flash column chromatography to afford the desired α-N-aminoketone 2.

Analytical and spectroscopic data of the products synthesized according to general procedure B1 and B2 are described below:

**1-phenyl-2-(phenylamino)butan-1-one (2h)**

Following the general procedure B1 after purification by flash chromatography (silica gel, petroleum ether/AcOEt 98:2) the product was obtained as a yellow solid (201.0 mg, 0.84 mmol, 42%). **M.p. 74 °C.** ¹H NMR (400 MHz, CDCl₃) δ 8.01 (d, J = 7.3 Hz, 2H), 7.62 (t, J = 7.3 Hz, 1H), 7.51 (t, J = 7.6 Hz, 2H), 7.18 (t, J = 7.3 Hz, 2H), 6.87 – 6.47 (m, 3H), 5.09 (t, J = 5.4 Hz, 1H), 4.74 (s, 1H), 2.09 (dqd, J = 14.4, 7.4, 5.4 Hz, 1H), 1.86 – 1.65 (m, 1H), 0.91 (t, J = 7.4 Hz, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 200.3, 146.9, 135.2, 133.5, 129.3, 128.8, 128.3, 117.7, 113.5, 58.6, 25.82, 9.12; HRMS (ESI): calcd for C₁₆H₁₈NO⁺ [M+H]⁺ 240.1383, found 254.1376; ATR-FTIR [cm⁻¹]: 3361, 1680, 1598, 1524, 1497, 1324, 1165, 989, 747, 691.

**3-methyl-1-phenyl-2-(phenylamino)butan-1-one (2i)**

Following the general procedure B2 after purification by flash chromatography (silica gel, petroleum ether/AcOEt 96:4 then 92:8) the product was obtained as yellow oil (573.0 mg, 2.26 mmol, 91%). ¹H NMR (400 MHz, CDCl₃) δ 8.13 – 7.97 (m, 2H), 7.68 – 7.59 (m, 1H), 7.55 – 7.49 (m, 2H), 7.22 – 7.11 (m, 2H), 6.78 – 6.65 (m, 3H), 5.11 (dd, J = 6.8, 4.6 Hz, 1H), 4.68 (s, 1H), 2.06 – 1.89 (m, 1H), 1.76 – 1.59 (m, 1H), 1.58 – 1.32 (m, 2H), 0.91 (t, J = 7.3 Hz, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 201.2, 147.6, 135.7, 134.0, 129.8, 129.3, 128.8, 118.3, 114.0, 58.2, 35.8, 19.0, 14.4; HRMS (ESI): calcd for C₁₇H₂₀NO⁺ [M+H]⁺ 254.1545, found 254.1540; ATR-FTIR [cm⁻¹]: 3365, 2959, 2323, 1680, 1598, 1524, 1497, 1324, 1165, 989, 747, 691.

**3-methyl-1-phenyl-2-(phenylamino)butan-1-one (2j)**

Following the general procedure B2 after purification by flash chromatography (silica gel, petroleum ether/dichloromethane 90:10 then 60:40) the product was obtained as a yellow solid (453.0 mg, 1.79 mmol, 71%). **M.p. 89 °C.** ¹H NMR (400 MHz, CDCl₃) δ 8.00 – 7.92 (m, 2H), 7.70 – 7.52 (m, 1H), 7.54 – 7.46 (m, 2H), 7.22 – 7.10 (m, 2H), 6.80 – 6.67 (m, 3H), 4.91 (d, J = 4.1 Hz, 1H), 2.24 (sept, J = 6.8, 1H), 1.12 (d, J = 6.8 Hz, 3H), 0.89 (d, J = 6.8 Hz, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 201.4, 148.3, 136.1, 133.6, 129.4, 129.0, 128.5, 118.2, 114.2, 63.5, 32.0, 20.5, 17.2; HRMS (ESI): calcd for C₁₇H₂₀NO⁺ [M+H]⁺
254.1540, found 254.1532; ATR-FTIR [cm\(^{-1}\)]: 3377, 2962, 1683, 1597, 1253, 991, 748, 686.

### 1,3-diphenyl-2-(phenylamino)propan-1-one (2l)

Following the general procedure B\(^2\) after purification by flash chromatography (silica gel, petroleum ether/AcOEt 95:5) the product was obtained as a white solid (166.4 mg, 0.55 mmol, 55%). **M.p.** 120 °C; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta 7.53 - 7.47\) (m, 2H), 7.43 (t, \(J = 7.3\) Hz, 2H), 7.40 – 7.34 (m, 1H), 7.34 – 7.22 (m, 3H), 7.15 – 7.08 (m, 2H), 7.09 – 7.02 (m, 2H), 6.68 (t, \(J = 7.5\) Hz, 1H), 6.55 (d, \(J = 7.5\) Hz, 2H), 5.45 (br s, 1H), 5.14 (br s, 1H), 3.77 – 3.70 (m, 2H); \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta 203.8, 146.0, 137.7, 133.5, 129.5, 129.4, 129.3, 128.8, 128.7, 128.3, 127.3, 117.8, 113.4, 67.0, 45.9; HRMS (ESI): calcd for C\(_{21}\)H\(_{20}\)NO [M+H] 302.1545, found 302.1547; ATR-FTIR [cm\(^{-1}\)]: 3393, 3029, 1709, 1600, 1511, 1317, 1061, 751, 694.

### 3-(phenylamino)heptan-4-one (2m)

Following the general procedure B\(^3\) after purification by flash chromatography (silica gel, petroleum ether/AcOEt 97:3) the product was obtained as a yellow oil (80.6 mg, 0.39 mmol, 39%). \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta 7.19\) (d, \(J = 7.3\) Hz, 2H), 6.73 (t, \(J = 7.3\) Hz, 1H), 6.60 (d, \(J = 7.3\) Hz, 2H), 4.41 (s, 1H), 4.03 (t, \(J = 6.0\) Hz, 1H), 2.52 (t, \(J = 7.4\) Hz, 2H), 1.96 (dqd, \(J = 14.9, 7.5, 5.8\) Hz, 1H), 1.75 (dqd, \(J = 14.9, 7.5, 5.8\) Hz, 1H), 1.67 (q, \(J = 6.0\) Hz, 1H), 1.50 – 1.17 (m, 4H), 0.95 (t, \(J = 7.4\) Hz, 2H), 1.95 – 1.77 (m, 1H), 1.71 – 1.62 (m, 1H), 1.62 – 1.52 (m, 2H), 1.50 – 1.17 (m, 4H), 0.95 (t, \(J = 7.3\) Hz, 3H), 0.90 (t, \(J = 7.3\) Hz, 3H); \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta 211.9, 147.0, 129.5, 117.8, 113.1, 63.8, 40.8, 24.9, 17.0, 13.8, 9.6; HRMS (ESI): calcd for C\(_{13}\)H\(_{20}\)NO [M+H] 206.1545, found 206.1541; ATR-FTIR [cm\(^{-1}\)]: 3395, 3052, 2963, 2934, 2875, 1709, 1600, 1511, 1317, 1061, 749, 694.

### 4-(phenylamino)nonan-5-one (2n)

Following the general procedure B\(^3\) after purification by flash chromatography (silica gel, petroleum ether/AcOEt 97:3) the product was obtained as a yellow oil (81.1 mg, 0.35 mmol, 35%). \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta 7.18\) (d, \(J = 7.7\) Hz, 2H), 6.73 (t, \(J = 7.7\) Hz, 1H), 6.59 (d, \(J = 7.7\) Hz, 2H), 4.34 (s, 1H), 4.03 (t, \(J = 6.0\) Hz, 1H), 2.52 (t, \(J = 7.4\) Hz, 2H), 1.95 – 1.77 (m, 1H), 1.71 – 1.62 (m, 1H), 1.62 – 1.52 (m, 2H), 1.50 – 1.17 (m, 4H), 0.95 (t, \(J = 7.3\) Hz, 3H), 0.90 (t, \(J = 7.3\) Hz, 3H); \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta 212.6, 147.1, 129.4, 117.8, 113.1, 62.8, 38.5, 34.3, 25.7, 22.4, 18.8, 14.1, 13.9; HRMS (ESI): calcd for C\(_{15}\)H\(_{24}\)NO [M+H] 234.1858, found 234.1850; ATR-FTIR [cm\(^{-1}\)]: 3396, 2958, 2933, 2870, 1709, 1603, 1504, 1316, 1257, 750, 694.

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\(^2\) The reaction was carried out at room temperature.

\(^3\) 1 equiv of aniline was used.
C) Procedure C: Synthesis of α-N-arylamino ketones starting from α-amino Weinreb amide

**General procedure C.** α-N-arylamino ketones 2o-2r were synthesized according to the procedure reported previously. Analytical and spectroscopic data of the products synthesized according to general procedure are described below:

**5-methyl-4-(phenylamino)hexan-3-one (2o)**

Following the general procedure after purification by flash chromatography (silica gel, petroleum ether/AcOEt 96:4) the product was obtained as a white solid (88.3 mg, 0.430 mmol, 86%). The $^1$H NMR spectroscopic data were identical to those reported in the literature. $^1$H NMR (400 MHz, CDCl$_3$) δ 7.18 – 7.13 (m, 2H), 6.73 – 6.69 (m 1H), 6.61 – 6.57 (m, 2H), 4.24 (br s, 1H), 3.82 – 3.76 (m, 1H), 2.60 – 2.34 (m, 2H), 2.15 – 2.10 (m, 1H), 1.06 – 0.99 (m, 6H), 0.97 (dd, $J = 6.8$, 0.3 Hz, 3H).

**1-cyclopropyl-3-methyl-2-(phenylamino)butan-1-one (2p)**

Following the general procedure after purification by flash chromatography (silica gel, petroleum ether/AcOEt 96:4 then 60:40) the product was obtained as a white solid (80.4 mg, 0.370 mmol, 74%). **M.p.** 46 °C; $^1$H NMR (400 MHz, CDCl$_3$) δ 7.18 – 7.13 (m, 2H), 6.73 – 6.69 (m, 1H), 6.64 – 6.61 (m, 2H), 4.40 (br s, 1H), 4.01 (d, $J = 4.9$ Hz, 1H), 2.32 – 2.24 (m, 1H), 2.12 – 2.08 (m, 1H), 1.10 – 0.97 (m, 8H), 0.90 (dd, $J = 7.7$, 4.0 Hz, 2H); $^{13}$C NMR (101 MHz, CDCl$_3$) δ 121.0, 148.0, 129.4, 117.9, 113.6, 69.3, 31.0, 20.0, 19.0, 11.9, 11.7; HRMS (ESI): calcd for C$_{14}$H$_{20}$NO$^+$ [M+H]$^+$ 218.1539, found 218.1543; ATR-FTIR [cm$^{-1}$]: 3391, 2962, 2923, 2875, 1693, 1602, 1506, 1463, 1385, 1317, 1267, 1177, 1064, 1024, 896, 750, 689.

**8-methyl-6-(phenylamino)non-1-en-5-one (2q)**

Following the general procedure after purification by flash chromatography (silica gel, petroleum ether/AcOEt 98:2 then 80:20) the product was obtained as a light orange solid (83.4 mg, 0.340 mmol, 68%). **M.p.** 67 °C; $^1$H NMR (400 MHz, CDCl$_3$) δ 7.1 – 7.15 (m, 2H), 6.75 – 6.71 (m, 1H), 6.57 – 6.54 (m, 2H), 5.76 (ddt, $J = 16.8$, 10.1, 6.5 Hz, 1H), 5.03 – 4.93 (m, 2H), 4.07 – 4.01 (m, 2H), 2.64 – 2.57 (m, 2H), 2.33 – 2.25 (m, 2H), 1.83 – 1.76 (m, 1H), 1.63 – 1.47 (m, 2H), 0.99 –

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93 (m, 6H); \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 213.0, 147.2, 137.2, 129.5, 118.2, 115.4, 113.1, 61.9, 41.5, 37.6, 27.5, 25.0, 23.2, 22.2; HRMS (ESI): calcd for C\(_{16}\)H\(_{24}\)NO \([\text{M+H}]^+\) 246.1852, found 246.1856; ATR-FTIR \([\text{cm}^{-1}]\): 3398, 2956, 2928, 2870, 1711, 1603, 1506, 1469, 1431, 1316, 1264, 995, 915, 750, 694.

II. Synthesis of N-arylindoles 3

Following the general procedure after purification by flash chromatography (silica gel, petroleum ether/AcOEt 97:3 then 92:8) the product was obtained as a yellow solid (59.0 mg, 0.255 mmol, 51%).

General procedure for the synthesis of N-arylindole. To a solution of \(\alpha\)-N-arylaminoketone 2 (0.21 mmol, 1.0 equiv) and 18-Crown ether-6 (0.23 mmol, 1.1 equiv) in \(i\)-PrCN/DCE (2/8) (1.5 mL, \(c = 0.14\) M) was added silylaryl triflate 1 (0.29 mmol, 1.4 equiv). Then anhydrous CsF (0.63 mmol, 3.0 equiv) and anhydrous Cs\(_2\)CO\(_3\) (0.22 mmol, 2.0 equiv) were added. The resulting reaction mixture was stirred at room temperature until total consumption of 2 (2-6 h). The progress of the reaction was monitored by TLC. After the reaction went to completion, ethyl acetate and water were added. The aqueous phase was extracted with ethyl acetate. The combined organic layers were washed with brine, dried over anhydrous sodium sulfate and concentrated under reduced pressure. To the resulting residue were added MeOH/DCM/AcOH (1/1/1) and silica gel. The resulting mixture was kept at 40 °C until the alcohol intermediate was completely converted to the N-arylindole (monitored by TLC). The crude mixture was purified by flash column chromatography on silica gel to give the desired
compound N-arylindole 3.

Analytical and spectroscopic data of the products synthesized according to general procedure are described below:

2,3-dimethyl-1-phenyl-1H-indole (3a)

Following the general procedure after purification by flash chromatography (silica gel, petroleum ether/toluene 95:5) the product was obtained as a colorless oil (21.9 mg, 0.099 mmol, 71%). The 1H NMR spectroscopic data were identical to those reported in the literature. 1H NMR (400 MHz, CDCl3) δ 7.94 – 7.83 (m, 3H), 7.80 – 7.75 (m, 1H), 7.70 – 7.65 (m, 2H), 7.51 – 7.42 (m, 3H), 2.68 (s, 3H), 2.59 (s, 3H).

2,3-dimethyl-1-(4-nitrophenyl)-1H-indole (3b)

Following the general procedure after purification by flash chromatography (silica gel, petroleum ether/toluene 100:0 then 90:1) the product was obtained as an orange solid (11.7 mg, 0.044 mmol, 21%). Mp. 137°C; 1H NMR (400 MHz, CDCl3) δ 8.40 (d, J = 8.9 Hz, 2H), 7.68 – 7.46 (m, 3H), 7.21 – 7.13 (m, 3H), 2.32 (s, 3H), 2.30 (s, 3H); 13C NMR (101 MHz, CDCl3) δ 146.1, 144.4, 136.7, 132.0, 129.6, 127.9, 125.1, 122.2, 120.7, 118.5, 110.7, 109.6, 11.4, 9.0; HRMS (ESI): calcd for C16H15N2O2 [M+H]+ 267.1133, found 267.1136; ATR-FTIR [cm⁻¹]: 3674, 2987, 2910, 1593, 1499, 1461, 1327, 1220, 1066, 855, 743, 696.

1-(4-methoxyphenyl)-2,3-dimethyl-1H-indole (3c)

Following the general procedure after purification by flash chromatography (silica gel, petroleum ether/toluene 100:0 then 80:20) the product was obtained as a white solid (33.1 mg, 0.132 mmol, 63%). Mp: 101 °C; 1H NMR (400 MHz, CDCl3) δ 7.55 (d, J = 6.8 Hz, 1H), 7.26 (d, J = 8.9 Hz, 2H), 7.14-7.10 (m, 1H), 7.08 – 6.97 (m, 4H), 3.91 (s, 3H), 2.34 (s, 3H), 2.23 (s, 3H); 13C NMR (101 MHz, CDCl3) δ 157.9, 136.7, 132.3, 130.2, 128.4, 127.7, 120.1, 118.4, 116.9, 113.6, 108.8, 106.5, 54.7, 9.0, 8.0; HRMS (ESI): calcd for C17H18NO+ [M+H]+ 252.1383, found 252.1376; ATR-FTIR [cm⁻¹]: 3674, 2928, 2162, 1681, 1598, 1510, 1461, 1239, 1030, 833, 744, 693.

5 Dehydration occurred on silica gel, DCM, 40 °C.
6 The reaction was carried out on 0.14 mmol scale of 3-(phenylamino)butan-2-one.
1-(2-methoxyphenyl)-2,3-dimethyl-1H-indole (3d)

Following the general procedure after purification by flash chromatography (silica gel, petroleum ether/toluene 100:0 then 80:20) the product was obtained as a colorless oil (35.3 mg, 0.141 mmol, 67%). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.55 (dd, $J = 8.0$, 1.2 Hz, 1H), 7.45 (td, $J = 8.0$, 1.2 Hz, 1H), 7.28 (dd, $J = 8.1$, 1.7 Hz, 1H), 7.16 – 7.06 (m, 4H), 6.94 (d, $J = 8.0$ Hz, 1H), 3.74 (s, 3H), 2.35 (s, 3H), 2.17 (s, 3H); $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 156.3, 137.4, 133.9, 130.5, 129.4, 128.9, 126.9, 120.9, 119.2, 117.9, 112.4, 109.8, 107.2, 55.7, 10.5, 9.1; HRMS (ESI): calcd for C$_{17}$H$_{18}$NO $[M+H]^+$ 252.1388, found 252.1394; ATR-FTIR [cm$^{-1}$]: 2917, 1593, 1504, 1462, 1366, 1248, 1026, 738.

2,3-dimethyl-1-(o-tolyl)-1H-indole (3e)

Following the general procedure after purification by flash chromatography (silica gel, petroleum ether/toluene 95:5) the product was obtained as a white solid (37.2 mg, 0.157 mmol, 75%). M.p.: 82 °C; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.57 (d, $J = 7.2$ Hz, 1H), 7.43 – 7.37 (m, 2H), 7.35 – 7.32 (m, 1H), 7.22 (d, $J = 7.3$ Hz, 1H), 7.13 (td, $J = 7.2$, 1.2 Hz, 1H), 7.08 (td, $J = 7.2$, 1.2 Hz, 1H), 6.82 (d, $J = 7.2$ Hz, 1H), 2.36 (s, 3H), 2.13 (s, 3H), 1.95 (s, 3H); $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 137.7, 137.3, 137.1, 133.0, 131.1, 129.7, 128.8, 128.6, 127.0, 121.0, 119.2, 117.9, 109.8, 107.3, 17.5, 10.6, 9.1; HRMS (ESI): calcd for C$_{17}$H$_{18}$NO $[M+H]^+$ 236.1439, found 236.1432; ATR-FTIR [cm$^{-1}$]: 3675, 2970, 2913, 1499, 1462, 1365, 1227, 1044, 742, 722.

1-(2-bromophenyl)-2,3-dimethyl-1H-indole (3f)

Following the general procedure after purification by flash chromatography (silica gel, petroleum ether/toluene 97:3) the product was obtained as a white solid (50.5 mg, 0.168 mmol, 80%). M.p.: 88 °C; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.80 (dd, $J = 7.9$, 1.2 Hz, 1H), 7.58 (d, $J = 7.8$ Hz, 1H), 7.48 (td, $J = 7.9$, 1.2 Hz, 1H), 7.42 – 7.32 (m, 2H), 7.16 (td, $J = 7.8$, 1.3 Hz, 1H), 7.11 (td, $J = 7.8$, 1.3 Hz, 1H), 6.84 (dt, $J = 7.8$, 1.3 Hz, 1H), 2.36 (s, 3H), 2.17 (s, 3H); $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 137.83, 137.1, 133.8, 133.0, 131.4, 130.0, 129.0, 128.5, 124.6, 121.3, 119.6, 118.1, 109.7, 108.0, 10.7, 9.0; HRMS (ESI): calcd for C$_{16}$H$_{15}$BrN$^+$ [M+H]$^+$ 300.0382, found 300.0379; ATR-FTIR [cm$^{-1}$]: 2914, 1585, 1481, 1374, 1225, 1013, 859, 741, 663.

1-(2,6-dimethylphenyl)-2,3-dimethyl-1H-indole (3g)

Following the general procedure after purification by flash chromatography (silica gel, petroleum ether/toluene 97:3) the product was obtained as a light pink solid (45.5 mg, 0.182 mmol,
2-ethyl-1,3-diphenyl-1H-indole (3h)

Following the general procedure after purification by flash chromatography (silica gel, petroleum ether/toluene 97:3) the product was obtained as a colorless oil (48.6 mg, 0.163 mmol, 78%).

$^1$H NMR (400 MHz, CDCl$_3$) δ 7.75 – 7.66 (m, 1H), 7.64 – 7.55 (m, 3H), 7.57 – 7.48 (m, 4H), 7.48 – 7.44 (m, 2H), 7.41 – 7.34 (m, 1H), 7.20 – 7.14 (m, 2H), 7.14 – 7.08 (m, 1H) 2.85 (q, $J = 7.5$ Hz, 2H), 0.96 (t, $J = 7.5$ Hz, 3H); $^{13}$C NMR (101 MHz, CDCl$_3$) δ 139.6, 138.2, 138.0, 135.7, 129.9, 129.7, 128.6, 128.5, 128.2, 127.5, 126.2, 121.8, 120.4, 118.9, 115.1, 110.2, 18.4, 14.7; HRMS (ESI): calcd for C$_{22}$H$_{20}$N$^+$ [M+H]$^+$ 298.1590, found 298.1582; ATR-FTIR [cm$^{-1}$]: 3048, 2970, 1596, 1498, 1373, 1221, 1022, 751, 698.

1,3-diphenyl-2-propyl-1H-indole (3i)

Following the general procedure after purification by flash chromatography (silica gel, petroleum ether/toluene 97:3) the product was obtained as a white solid (52.9 mg, 0.169 mmol, 81%).

M.p.: 69 °C; $^1$H NMR (400 MHz, CDCl$_3$) δ 7.73 – 7.65 (m, 1H), 7.62 – 7.55 (m, 4H), 7.54 – 7.47 (m, 3H), 7.48 – 7.43 (m, 2H), 7.39 – 7.34 (m, 1H), 7.20 – 7.14 (m, 2H), 7.13 – 7.09 (m, 1H), 2.84 – 2.75 (m, 2H), 1.41 – 1.27 (m, 2H), 0.70 (t, $J = 7.3$ Hz, 3H); $^{13}$C NMR (101 MHz, CDCl$_3$) 138.3, 138.1, 137.9, 135.8, 130.0, 129.6, 128.6, 128.5, 128.1, 127.6, 126.2, 121.8, 120.4, 118.9, 115.8, 110.2, 27.1, 23.1, 14.0; HRMS (ESI): calcd for C$_{23}$H$_{22}$N$^+$ [M+H]$^+$ 312.1747 found 312.1741; ATR-FTIR [cm$^{-1}$]: 2956, 1496, 1456, 1377, 1019, 747, 699.

2-isopropyl-1,3-diphenyl-1H-indole (3j)

Following the general procedure after purification by flash chromatography (silica gel, petroleum ether/toluene 97:3) the product was obtained as a white solid (56.1 mg, 0.180 mmol, 86%).

M.p.: 107 °C; $^1$H NMR (400 MHz, CDCl$_3$) δ 7.98 – 7.86 (m, 5H), 7.89 – 7.79 (m, 5H), 7.79 – 7.70 (m, 1H), 7.52 – 7.44 (m, 2H), 7.35 – 7.25 (m, 1H), 3.59 (sept, $J = 7.1$ Hz, 1H), 1.51 (d, $J = 7.1$ Hz, 6H); $^{13}$C NMR (101 MHz, CDCl$_3$) 143.1, 138.8, 138.1, 136.1, 129.8, 129.5, 128.6, 128.5, 128.3, 126.5, 121.7, 120.1, 118.8, 114.9.
110.2, 26.7, 23.0; **HRMS (ESI):** calcd for C\textsubscript{23}H\textsubscript{22}N\textsuperscript{+} [M+H]\textsuperscript{+} 312.1747, found 312.1742; **ATR-FTIR [cm\textsuperscript{-1}]:** 2963, 1596, 1495, 1455, 1239, 1078, 743, 701.

1,2,3-triphenyl-1H-indole (3k)

Following the general procedure after purification by flash chromatography (silica gel, petroleum ether/toluene 97:3) the product was obtained as a white solid (65.6 mg, 0.189 mmol, 90%).

M.p.: 181 °C; \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}) \(\delta\) 7.88 – 7.79 (m, 1H), 7.48 – 7.31 (m, 8H), 7.31 – 7.21 (m, 5H), 7.21 – 7.07 (m, 5H); \textsuperscript{13}C NMR (101 MHz, CDCl\textsubscript{3}) \(\delta\) 138.3, 138.0, 137.2, 135.1, 131.7, 131.3, 130.4, 129.2, 128.4, 128.4, 128.0, 127.7, 127.5, 127.3, 126.1, 122.9, 121.0, 119.7, 116.8, 110.8; **HRMS (ESI):** calcd for C\textsubscript{26}H\textsubscript{20}N\textsuperscript{+} [M+H]\textsuperscript{+} 346.1590, found 346.1581; **ATR-FTIR [cm\textsuperscript{-1}]:** 3052, 2164, 1596, 1499, 1366, 1236, 1029, 741, 698.

3-benzyl-1,2-diphenyl-1H-indole (3l)

Following the general procedure after purification by flash chromatography (silica gel, petroleum ether/dichloromethane 95:5) the product was obtained as a yellow viscous oil (62.3 mg, 0.174 mmol, 83%).

\textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}) \(\delta\) 7.50 (dt, \(J = 7.8, 1.0\) Hz, 1H), 7.38 – 7.33 (m, 3H), 7.30 – 7.16 (m, 14H), 7.12 (dt, \(J = 7.8, 1.0\) Hz, 1H), 4.22 (s, 2H); \textsuperscript{13}C NMR (101 MHz, CDCl\textsubscript{3}) \(\delta\) 141.8, 138.6, 138.2, 138.0, 132.0, 130.7, 129.2, 128.6, 128.5, 128.2, 128.1, 127.6, 126.8, 125.9, 122.6, 120.4, 119.8, 113.5, 110.6, 30.9; **HRMS (ESI):** calcd for C\textsubscript{27}H\textsubscript{22}N [M+H] 360.1752, found 360.1749; **ATR-FTIR [cm\textsuperscript{-1}]:** 2922, 2852, 1453, 1370, 874, 740, 689.

2-ethyl-1-phenyl-3-propyl-1H-indole (3m)

Following the general procedure after purification by flash chromatography (silica gel, petroleum ether/toluene 97:3) the product was obtained as a colorless oil (42.2 mg, 0.160 mmol, 76%).

\textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}) \(\delta\) 7.63 (dd, \(J = 8.1, 1.3\) Hz, 1H), 7.56 (t, \(J = 7.4\) Hz, 2H), 7.47 (t, \(J = 7.4\) Hz, 1H), 7.40 (d, \(J = 7.4\) Hz, 2H), 7.19 – 7.05 (m, 3H), 2.81 (t, \(J = 7.3\) Hz, 2H), 2.75 (q, \(J = 7.5\) Hz, 2H), 1.78 (sext, \(J = 7.3\) Hz, 2H), 1.08 (t, \(J = 7.3\) Hz, 3H), 1.01 (t, \(J = 7.5\) Hz, 3H); \textsuperscript{13}C NMR \(\delta\) 139.1, 138.6, 137.9, 129.5, 128.5, 128.3, 127.5, 127.3, 126.8, 125.9, 122.6, 120.4, 119.8, 113.5, 110.6, 30.9; **HRMS (ESI):** calcd for C\textsubscript{19}H\textsubscript{22}N [M+H] 264.1752, found 264.1741 **ATR-FTIR [cm\textsuperscript{-1}]:** 2922, 2852, 1453, 1370, 874, 740, 689.

3-butyl-1-phenyl-2-propyl-1H-indole (3n)
Following the general procedure after purification by flash chromatography (silica gel, petroleum ether/toluene 97:3) the product was obtained as a colorless oil (42.5 mg, 0.145 mmol, 69%).

\[ ^1H \text{ NMR (400 MHz, CDCl}_3 \text{)} \delta 7.60 (d, J = 7.5 \text{ Hz}, 1H), 7.52 (t, J = 7.4 \text{ Hz}, 2H), 7.44 (t, J = 7.4 \text{ Hz}, 1H), 7.39 – 7.31 (m, 2H), 7.17 – 6.99 (m, 3H), 2.78 (t, J = 7.7 \text{ Hz}, 2H), 2.66 (t, J = 7.7 \text{ Hz}, 2H), 1.70 (quint, J = 7.7 \text{ Hz}, 2H), 1.54 – 1.41 (m, 2H), 1.40 – 1.28 (m, 2H), 0.99 (t, J = 7.7 \text{ Hz}, 3H), 0.79 (t, J = 7.7 \text{ Hz}, 3H); \]

\[ ^13C \text{ NMR } \delta 138.7, 137.9, 137.4, 129.5, 128.5, 128.3, 127.7, 121.1, 119.4, 118.4, 113.5, 110.0, 33.5, 26.9, 24.5, 23.1, 14.3, 14.1; \text{ HRMS (ESI)}: \text{ calcd for C}_{21}\text{H}_{20}\text{N} [M+H]^+ 292.2065, \text{ found 292.2055}; \text{ ATR-FTIR [cm}^{-1}]: 2957, 2927, 1597, 1501, 1458, 1397, 1225, 1055, 672. \]

3-ethyl-2-isopropyl-1-phenyl-1H-indole (3o)

Following the general procedure after purification by flash chromatography (silica gel, petroleum ether/toluene 95:5) the product was obtained as a yellow solid (44.8 mg, 0.174 mmol, 83%).

\[ \text{ M.p. } 144 ^\circ \text{C; } ^1H \text{ NMR (400 MHz, CDCl}_3 \text{)} \delta 7.54 – 7.43 (m, 3H), 7.34 – 7.30 (m, 2H), 7.13 – 7.03 (m, 2H), 6.90 (dt, J = 7.8, 0.9 \text{ Hz}, 1H), 3.06 – 2.99 (m, 1H), 2.92 (q, J = 7.5 \text{ Hz, 2H}), 1.29 (d, J = 7.2 \text{ Hz, 6H}), 1.21 (t, J = 7.5 \text{ Hz, 3H}); \]

\[ ^13C \text{ NMR (101 MHz, CDCl}_3 \text{)} \delta 142.0, 138.9, 137.8, 129.4, 129.3, 128.5, 128.0, 121.1, 119.4, 118.0, 113.7, 110.3, 26.3, 22.7, 18.2, 16.0, 14.3; \text{ HRMS (ESI)}: \text{ calcd for C}_{19}\text{H}_{22}\text{N} [M+H]^+ 264.1747, \text{ found 264.1741}; \text{ ATR-FTIR [cm}^{-1}]: 3627, 3059, 2960, 2924, 2853, 2972, 1597, 1500, 1461, 1369, 1021, 965, 741, 699. \]

3-cyclopropyl-2-isopropyl-1-phenyl-1H-indole (3p)

Following the general procedure after purification by flash chromatography (silica gel, petroleum ether/toluene 95:5 then 90:10) the product was obtained as a light orange solid (48.0 mg, 0.174 mmol, 83%).

\[ \text{ M.p. } 159 ^\circ \text{C; } ^1H \text{ NMR (400 MHz, CDCl}_3 \text{)} \delta 7.74 (dt, J = 8.1, 0.9 \text{ Hz}, 1H), 7.55 – 7.43 (m, 3H), 7.34 – 7.30 (m, 2H), 7.10 – 7.0 (m, 2H), 6.83 (dt, J = 7.9, 0.9 \text{ Hz}, 1H), 3.26 – 3.18 (m, 1H), 1.96 – 1.89 (m, 1H), 1.31 (d, J = 7.3 \text{ Hz, 6H}), 1.03 – 0.97 (m, 2H), 0.88 – 0.83 (m, 2H); \]

\[ ^13C \text{ NMR (101 MHz, CDCl}_3 \text{)} \delta 144.9, 138.9, 137.7, 129.6, 129.4, 128.6, 128.3, 121.0, 119.5, 119.0, 112.2, 110.3, 26.6, 22.0, 6.7, 6.6, 1.2; \text{ HRMS (ESI)}: \text{ calcd for C}_{20}\text{H}_{22}\text{N} [M+H]^+ 276.1747, \text{ found 276.1744}; \text{ ATR-FTIR [cm}^{-1}]: 3731, 3628, 3345, 3297, 1650, 1501, 1458, 1397, 1225, 1055, 672. \]

3-(but-3-en-1-yl)-2-isobutyl-1-phenyl-1H-indole (3q)

Following the general procedure after purification by flash chromatography (silica gel, petroleum ether/toluene 98:2 then 80:20) the product was obtained as a white solid (54.2 mg, 0.179 mmol, 85%).

\[ \text{ M.p. } 167 ^\circ \text{C; } ^1H \text{ NMR (400 MHz, CDCl}_3 \text{)} \delta 7.63 – 7.59 (m, 1H), 7.56 – 7.49 (m, 2H), 7.47 – 7.41 (m, 1H), 7.35 – 7.32 (m, 2H), \]

s14
Mixture of (E)/(Z)-2-isobutyl-1-phenyl-3-(prop-1-en-1-yl)-1H-indole (3r/3r’~10/1)

Following the general procedure after purification by flash chromatography (silica gel, petroleum ether/toluene 98:2 then 80:20) mixture of Z/E isomers (in ratio 1/10) was obtained (48.0 mg, 0.166 mmol, 79%). Spectral data for (E)-2-isobutyl-1-phenyl-3-(prop-1-en-1-yl)-1H-indole are: \(^1\)H NMR (400 MHz, Chloroform-d) \(\delta\) 7.90 (dt, \(J = 8.1, 0.9\) Hz, 1H), 7.57 – 7.48 (m, 3H), 7.48 – 7.42 (m, 1H), 7.33 – 7.27 (m, 2H), 7.20 – 7.05 (m, 3H), 7.03 – 6.98 (m, 1H), 6.59 (dq, \(J = 15.9, 1.6\) Hz, 1H), 6.28 (dq, \(J = 15.9, 6.5\) Hz, 1H), 2.62 (d, \(J = 7.3\) Hz, 2H), 1.98 (dd, \(J = 6.5, 1.6\) Hz, 3H), 1.68 – 1.57 (m, 1H) 0.75 (d, \(J = 6.7\) Hz, 6H); \(^13\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 139.1, 138.7, 138.1, 136.7, 129.5, 128.6, 127.7, 121.2, 119.5, 118.4, 114.7, 113.3, 110.0, 35.2, 33.9, 28.7, 24.7, 22.5; HRMS (ESI): calcd for C\(_{22}\)H\(_{26}\)N\(^+\) [M+H]\(^+\) 304.2060, found 304.2063; ATR-FTIR [cm\(^{-1}\)]: 3728, 3628, 3600, 2930, 2935, 2852, 1733, 1596, 1501, 1454, 1376, 1135, 1018, 914, 741, 697, 657, 625.

1-(2,6-dimethylphenyl)-2,3-dimethyl-1H-benzo[f]indole (3s)

The naphthyl precursor for 3s is 3-(Trimethylsilyl)-2-naphthyl trifluoromethanesulfonate. Following the general procedure after purification by flash chromatography (silica gel, petroleum ether/toluene 97:3) the product was obtained as a yellow oil (40.6 mg, 0.136 mmol, 65%). \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 8.04 (s, 1H), 8.03 – 7.99 (m, 1H), 7.83 – 7.71 (m, 1H), 7.40 – 7.30 (m, 3H), 7.30 – 7.23 (m, 2H), 7.15 (s, 1H), 2.48 (s, 3H), 2.15 (s, 3H), 1.92 (s, 6H); \(^13\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 138.5, 137.1, 136.7, 136.1, 131.1, 130.13, 128.7, 128.6, 128.6, 128.2, 127.4, 123.3, 122.1, 115.1, 106.4, 104.3, 17.7, 10.7, 9.3; HRMS (ESI): calcd for C\(_{23}\)H\(_{24}\)N\(^+\) [M+H]\(^+\) 300.1752, found 300.1764; ATR-FTIR [cm\(^{-1}\)]: 2914, 1481, 1438, 1374, 1362, 1225, 1013, 758, 741, 663.

5,6-dimethyl-1,2,3-triphenyl-1H-indole (3t)

Following the general procedure after purification by flash chromatography (silica gel, petroleum ether/dichloromethane 95:5) the product was obtained as a white solid (53.3 mg, 0.143 mmol, 68%). M.p.: 181 °C; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.60 (s, 1H),...
Following the general procedure after purification by flash chromatography (silica gel, petroleum ether/dichloromethane 90:10 then 80:0) the product was obtained as a white solid (59.6 mg, 0.153 mmol, 73%). M.p.: 197 °C; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.43 – 7.30 (m, 7H), 7.29 – 7.19 (m, 4H), 7.17 – 7.10 (m, 3H), 7.10 – 6.99 (m, 2H), 6.82 (s, 1H), 5.96 (s, 2H); $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 145.5, 143.9, 138.4, 135.8, 135.1, 133.3, 131.8, 131.1, 130.2, 129.2, 128.4, 128.3, 127.9, 127.2, 127.1, 126.0, 121.7, 117.0, 100.9, 98.2, 91.8; HRMS (ESI): calcd for C$_{27}$H$_{20}$NO$_2$ [M+H]$^+$ 390.1494, found 390.1499; ATR-FTIR [cm$^{-1}$]: 2935, 1598, 1489, 1447, 1204, 1130, 1022, 755, 714.

5,6-dimethoxy-1,2,3-triphenyl-1H-indole (3v)

Following the general procedure after purification by flash chromatography (silica gel, petroleum ether/AcOEt 95:5 then 90:10) the product was obtained as a yellow solid (57.9 mg, 0.143 mmol, 68%). M.p.: 185 °C; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.49 – 7.31 (m, 7H), 7.31 – 7.21 (m, 4H), 7.18 – 7.10 (m, 3H), 7.10 – 6.99 (m, 2H), 6.85 (s, 1H), 3.95 (s, 3H), 3.88 (s, 3H); $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 147.7, 146.1, 138.5, 135.7, 135.3, 132.4, 131.9, 131.2, 130.2, 129.3, 128.5, 128.2, 127.9, 127.2, 127.1, 126.0, 120.4, 116.6, 101.2, 94.1, 56.6, 56.4; HRMS (ESI): calcd for C$_{28}$H$_{24}$NO$_2$ [M+H]$^+$ 406.1807, found 406.1812; ATR-FTIR [cm$^{-1}$]: 2935, 1598, 1489, 1447, 1204, 1130, 1022, 755, 714.

5,6-difluoro-2,3-dimethyl-1-phenyl-1H-indole (3w)

Following the general procedure after purification by flash chromatography (silica gel, petroleum ether/dichloromethane 95:5) the product was obtained as a colorless oil (15.4 mg, 0.060 mmol, 57%); $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.57 – 7.50 (m, 2H), 7.48 – 7.41 (m, 1H), 7.31 – 7.27 (m, 2H), 7.23 (dd, J = 10.7, 7.7 Hz, 1H), 6.85 (dd, J = 10.9, 6.7 Hz, 1H), 2.26 (s, 3H), 2.20 (s, 3H); $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 146.4 (dd, J = 238.4, 15.9 Hz), 145.3 (dd, J = 237.3, 15.0 Hz), 137.9, 134.4 (d, J = 4.4 Hz), 132.4 (d, J = 9.8 Hz), 129.7, 128.0, 127.9, 124.1 (d, J = 8.0 Hz), 108.0 (d, J = 3.4 Hz), 104.6 (d, J = 19.1 Hz), 98.05 (d, J = 22.4 Hz), 11.3, 9.0; HRMS

8 The reaction was carried out with 0.105 mmol of 3-(phenylamino)butan-2-one and 2.0 equiv of benzyne precursor was used.
Following the general procedure after purification by flash chromatography (silica gel, petroleum ether/toluene 97:3) the mixture of two isomers was obtained as a white solid (50.6 mg, 0.155 mmol, 74%). $^1$H NMR (400 MHz, CDCl$_3$) δ 7.66 – 7.30 (m, 1H), 7.11 – 7.00 (m, 1H), 7.02 – 6.94 (m, 0.6H), 6.94 – 6.86 (m, 1H), 2.73 – 2.37 (m, 2H), 2.17 (s, 1.8H), 1.92 (s, 1.2H), 1.43 – 1.32 (m, 0.8H), 1.29 – 1.18 (m, 1.2H), 0.70 (t, $J = 7.4$ Hz, 1.2H), 0.64 (t, $J = 7.4$ Hz, 1.8H); $^{13}$C NMR (101 MHz, CDCl$_3$) δ 140.2, 139.2, 138.4, 138.3, 137.6, 137.5, 136.1, 135.9, 131.8, 130.5, 130.4, 130.1, 129.6, 128.6, 128.5, 128.4, 128.0, 127.7, 126.6, 126.2, 126.1, 124.6, 121.7, 121.5, 121.4, 120.2, 117.0, 116.6, 115.5, 108.1, 27.1, 26.9, 23.6, 20.5, 19.7, 14.1, 13.9. HRMS (ESI): calcd for C$_{24}$H$_{24}$N [$M+H$] 326.1917, found 326.1909; ATR-FTIR [cm$^{-1}$]: 3393, 3041, 2958, 1708, 1706, 1704, 1598, 1596, 1494, 1454, 1365, 1147, 1024, 750, 701.

Following the general procedure after purification by flash chromatography (silica gel, petroleum ether/AcOEt 98:2) the mixture of two isomers was obtained as a yellow oil (34.6 mg, 0.138 mmol, 66%). $^1$H NMR (400 MHz, CDCl$_3$) δ 7.58 – 7.48 (m, 4H), 7.47 – 7.38 (m, 3H), 7.37 – 7.30 (m, 4H), 7.06 – 6.98 (m, 2H), 6.81 (dd, $J = 8.5$, 2.3 Hz, 1H), 0.76 (dd, $J = 8.5$, 2.3 Hz, 1H), 6.63 (d, $J = 2.3$ Hz, 1H), 3.90 (s, 3H), 3.77 (s, 3H), 2.33 – 2.28 (m, 6H), 2.24 (s, 3H), 2.20 (s, 3H); $^{13}$C NMR (101 MHz, CDCl$_3$) δ 156.2, 154.3, 138.6, 138.5, 138.0, 133.6, 132.6, 131.6, 129.5, 129.4, 129.2, 128.1, 128.0, 127.5, 127.4, 123.4, 118.5, 110.8, 110.6, 108.9, 107.8 (2C), 100.4, 94.1, 56.2, 55.9, 11.2, 11.1, 9.9, 9.0; HRMS (ESI): calcd for C$_{17}$H$_{19}$NO [$M+H$] 252.1388, found 252.1378; ATR-FTIR [cm$^{-1}$]: 2917, 2857, 1596, 1494, 1455, 1376, 1237, 1198, 1160, 1151, 1032, 764, 699, 625.

Following the general procedure after purification by flash chromatography (silica gel, petroleum ether/toluene 97:3) the product was obtained as a white solid (31.1 mg, 0.111 mmol, 53%). M.p.: 56 °C; $^1$H NMR (400 MHz, CDCl$_3$) δ 7.33 – 7.27 (m, 1H), 7.20 (d, $J = 7.9$ Hz, 2H), 6.93 (t, $J = 7.9$ Hz, 1H), 6.50 (dd, $J = 7.8$, 0.7 Hz, 1H), 6.35 (dd, $J = 8.1$, 0.7 Hz, 1H), 3.95 (s, 3H), 2.52 (s, 3H), 2.01 (s, 3H), 1.87 (s, 6H); $^{13}$C NMR (101 MHz, CDCl$_3$) δ 154.4, 138.0, 137.4, 136.3, 130.6, 128.4, 128.3, 121.4, 118.3, 107.4, 103.1.
1-(2,6-dimethylphenyl)-4-methoxy-5-(3-methoxyphenyl)-2,3-dimethyl-1H-indole (3z′)

Following the general procedure after purification by flash chromatography (silica gel, petroleum ether/dichloromethane 95:5 then 50:50) the product was obtained as a grey solid (13.7 mg, 0.036 mmol, 17%). M, p.: 136 °C; ¹H NMR (400 MHz, CDCl₃) δ 7.37 – 7.26 (m, 1H), 7.29 – 7.22 (m, 3H), 7.20 (d, J = 7.7 Hz, 2H), 7.00 (d, J = 8.3 Hz, 1H), 6.86 (ddd, J = 8.1, 2.6, 1.2 Hz, 1H), 6.53 (d, J = 8.3 Hz, 1H), 3.86 (s, 3H), 3.58 (s, 3H), 2.52 (s, 3H), 2.03 (s, 3H), 1.90 (s, 6H); ¹³C NMR (101 MHz, CDCl₃) δ 159.5, 151.1, 141.5, 138.0, 137.7, 136.0, 132.6, 129.0, 128.6, 128.4, 124.7, 123.9, 122.3, 122.0, 115.0, 112.0, 106.9, 105.9, 61.7, 55.4, 17.7, 10.8, 10.2; HRMS (ESI): calcd for C₂₆H₂₈NO₂ [M+H] 386.2120, found 386.2113; ATR-FTIR [cm⁻¹]: 2922, 1605, 1577, 1275, 1043, 982, 785, 698.

3-(diphenylamino)butan-2-one (3aa)

Colorless oil; ¹H NMR (400 MHz, CDCl₃) δ 7.32 – 7.28 (m, 4H), 7.05-7.01 (m, 2H), 6.98 – 6.80 (m, 4H), 4.47 (q, J = 7.0 Hz, 1H), 2.32 (s, 3H), 1.43 (d, J = 7.0 Hz, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 211.0, 147.0, 129.6, 122.5, 122.4, 66.6, 27.2, 13.9; HRMS (ESI): calcd for C₁₆H₁₈NO [M+H] 240.1388, found 240.1383; ATR-FTIR [cm⁻¹]: 2924, 2359, 1715, 1598, 1493, 1371, 1260, 749, 696.

2-(2-(diphenylamino)phenyl)but-3-en-2-ol (3ab)

Colorless oil; ¹H NMR (400 MHz, CDCl₃) δ 7.65 – 7.49 (m, 1H), 7.35 – 7.25 (m, 2H), 7.26 – 7.18 (m, 4H), 7.14 – 7.06 (m, 1H), 7.05 – 6.87 (m, 6H), 5.91 (dd, J = 17.3, 10.6 Hz, 1H), 5.02 (s, 1H), 4.96 (dd, J = 17.3, 1.1 Hz, 1H), 4.72 (dd, J = 10.6, 1.1 Hz, 1H), 1.50 (s, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 148.8, 147.7, 144.5, 144.4, 144.1, 132.8, 129.2, 129.1, 128.8, 128.7, 127.0, 123.2, 122.8, 122.7, 111.4, 75.7, 29.1; HRMS (ESI): calcd for C₂₂H₂₂NO [M+H] 316.1701, found 316.1702; ATR-FTIR [cm⁻¹]: 2919, 2851, 1589, 1489, 1268, 1020, 920, 755, 693, 619.
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