Supporting Information
for DOI: 10.1055/s-0035-1560976
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1. General informations

All reactions were carried out under argon atmosphere in oven-dried glassware with magnetic stirring. Commercially available chemicals were used without further purification. Solvents were distilled prior to use by Solvent Purification System, Mbraun MB-SPS-800. Analytical thin-layer chromatography (TLC) was performed on silica gel 60 with fluorescent indicator UV\(_{254}\) TLC plates. The spots were visualized with UV light (254 nm) and staining with a solution of \(p\)-anisaldehyde, followed by heat. Flash column chromatography was performed using silica gel 60 (particle size 0.040–0.063 mm) typically using a \(n\)-hexane/ethyl acetate eluent system. FT-IR spectra were recorded with Thermo Scientific™ Nicolet™ iST™ 50 FT-IR spectrometer. NMR spectra were measured at room temperature on a Agilent Mercury 400 MHz spectrometer. NMR spectra were calibrated to the solvent residual signals of CDCl\(_3\). \(^1\)H NMR spectra were recorded at 400 MHz. Data are reported as follows: chemical shift, multiplicity (s: singlet, d: doublet, t: triplet, q: quartet, qui: quintuplet, m: multiplet), coupling constant (\(J\) in Hz) and integration. \(^{13}\)C NMR spectra were recorded at 100 MHz using broadband proton decoupling and chemical shifts are reported in ppm using residual solvent peaks as reference. Carbon multiplicities were assigned by DEPT techniques. High resolution mass spectra were recorded on a MS (ESI) spectra LCMS-IT TOF Shimadzu. Melting points were measured using open capillary tubes on a MPM-HV2 analyzer.

2. The hydroamination reaction

**General procedure for the synthesis of gold(I) complexes\(^1\)**

A mixture of silver(I) oxide (1 eq) and corresponding imidazolium or imidazolinium salt (1.6 eq) in dichloromethane (0.05 mol/L) was stirred overnight in dark. The mixture was filtered through Celite and evaporated under reduce pressure. The residue was dissolved in dichloromethane (0.09 mol/L) and (dimethyl sulfide)gold(I) complex (1 eq) was added. The resulting mixture was stirred overnight and filtered through Celite, the solvent was removed in vacuo. The obtained Au(NHC)Cl complex was crystallized form pentane.

**General procedure for the synthesis of 2-alkynylanilines\(^2\)**

Under argon gas, a mixture of 2-iodoaniline (1 eq), alkyne (1.1–1.3 eq), CuI (3 mol%), PdCl\(_2\)(PPh\(_3\))\(_2\) and Et\(_3\)N ([substrate] = 0.45 mol/L) as solvent was stirred for 2h at 50 °C. The reaction mixture was next diluted in water and extracted with CH\(_2\)Cl\(_2\). The organic phase was dried over MgSO\(_4\) and the solvent was evaporated under reduce pressure. The crude product

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\(^1\) Analogous as described in Nolan et al. Organometallics 2005 10 2411.

was purified by chromatography on silica gel with n-hexane/ethyl acetate as the eluent to afford the expected 2-ethynylanilines.

**General procedure for the gold(I)-catalyzed formation of indole derivatives**

To a solution of aniline derivative in hexane ([substrate] = 0.125 mol/L) in a Schlenk tube equipped with a Teflon-coated magnetic stirring bar, (IPr)AuCl followed by AgBF₄ were added. The reaction mixture was then stirred at 40 °C in an oil bath. At the end of the reaction (¹H NMR or TLC monitoring), the solvent was removed in vacuo. The resulting crude product was directly purified by flash column chromatography on silica gel (n-hexane/ethyl acetate) to afford the corresponding indole.

2. 1.List of the Au(NHC)Cl

**[Au(IPr)Cl]**

Following the general procedure Au(IPr)Cl was obtained as a white solid (94% yield); ¹H NMR (400 MHz, CDCl₃, 20 °C) δ 7.50 (t, J = 7.8 Hz, 2H), 7.28 (d, J = 8.0 Hz, 4H), 7.17 (s, 2H), 2.59–2.52 (m, 4H), 1.34 (d, J = 6.9 Hz, 12H), 1.22 (d, J = 6.9 Hz, 12H); ¹³C NMR (100 MHz, CDCl₃, 20 °C) δ 175.3 (C_{carbene}), 145.5 (C₉), 133.9 (C₉), 130.7 (CH), 124.2 (CH), 123.0 (CH), 28.8 (CH₃), 24.5 (CH₃), 24.0 (CH₃);

Analyses were in accordance with previously reported.⁴

**[Au(SIPr)Cl]**

Following the general procedure Au(SIPr)Cl was obtained as a white solid (94% yield); ¹H NMR (400 MHz, CDCl₃, 20 °C) δ 7.53–7.35 (m, 2H), 7.25–7.22 (m, 4H), 4.05 (d, J = 7.4 Hz, 4H), 3.08–3.02 (m, 4H), 1.41 (d, J = 6.8 Hz, 12H), 1.33 (d, J = 6.9Hz, 12H); ¹³C NMR (100 MHz, CDCl₃, 20 °C) δ 196.0 (C_{carbene}), 146.5 (C₉), 134.0 (C₉), 130.0 (C₉), 124.7 (CH), 53.8 (CH₂), 28.9 (CH), 25.4 (CH₃), 24.0 (CH₃);

Analyses were in accordance with previously reported.⁴

**[Au(IMes)Cl]**

Following the general procedure Au(IMes)Cl was obtained as a white solid (91% yield); ¹H NMR (400 MHz, CDCl₃, 20 °C) δ 7.09 (s, 2H), 6.99 (s, 4H), 2.34 (s, 6H), 2.10 (s, 12H); ¹³C NMR (100 MHz, CDCl₃, 20 °C) δ 173.3 (C_{carbene}), 139.7 (C₉), 134.7 (C₉), 134.6 (C₉), 129.5 (CH), 122.1 (CH), 21.1 (CH₃), 17.7 (CH₃);

³The [(IPr)Au]BF₄ (0.0025 equiv.) in situ formed by mixing (IPr)AuCl and AgBF₄ (1:3 molar)

Analyses were in accordance with previously reported.  

[Au(SIMes)Cl]

Following the general procedure, Au(SIMes)Cl was obtained as a white solid (94% yield); \(^1\)H NMR (400 MHz, CDCl\(_3\), 20 °C) \(\delta 6.94\) (s, 4H), \(3.99\) (d, \(J = 4.6\) Hz, 4H), \(2.31–2.29\) (m, 18H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\), 20 °C) \(\delta 194.9\) (C\(_{\text{carbene}}\)), 138.9 (C\(_d\)), 135.5 (C\(_q\)), 134.5 (C\(_q\)), 129.8 (CH), 50.7 (CH\(_3\)), 21.1 (CH\(_3\)), 17.9 (CH\(_3\)); Analyses were in accordance with previously reported.  

[Au(IMesCl)Cl] (L\(^1\))

Following the general procedure, L\(^1\) was obtained as a white solid (73% yield); \(^1\)H NMR (400 MHz, CDCl\(_3\), 20 °C) \(\delta 6.98\) (s, 4H), \(2.33\) (s, 6H), \(2.03\) (s, 12H), \(1.90\) (s, 6H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\), 20 °C) \(\delta 169.3\) (C\(_q\)), 139.4 (C\(_q\)), 134.9 (C\(_H\)), 133.1 (C\(_q\)), 129.5 (CH), 125.3 (CH), 21.2 (CH\(_3\)), 17.7 (CH\(_3\)), 9.2 (CH\(_3\)); MS (MALDI TOF m/z) for C\(_{21}\)H\(_{28}\)AuCl\(_3\)N\(_2\) (M+H): 605.06; Elem analysis, calculated for C\(_{21}\)H\(_{28}\)AuCl\(_3\)N\(_2\): C, 48.90; H, 5.00; Cl, 6.28; N, 4.96; found: C, 47.82; H, 5.12; Cl, 6.26; N, 4.83.

[Au(IMesCl)Cl] (L\(^2\))

Following the general procedure, L\(^2\) was obtained as a white solid (49% yield); IR (neat)/\(\nu\) cm\(^{-1}\): 2911, 1578, 1388, 863 cm\(^{-1}\); \(^1\)H NMR (400 MHz, CDCl\(_3\), 20 °C) \(\delta 7.02\) (s, 4H), \(2.36\) (s, 6H), \(2.10\) (s, 9H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\), 20 °C) \(\delta 173.68\) (C\(_{\text{carbene}}\)), 140.8 (C\(_q\)), 135.1 (C\(_q\)), 131.8 (C\(_H\)), 118.0 (C\(_q\)), 21.2 (CH\(_3\)), 17.7 (CH\(_3\)), 9.2 (CH\(_3\)); MS (MALDI TOF m/z) for C\(_{21}\)H\(_{28}\)AuCl\(_3\)N\(_2\) (M+H): 605.06; Elem analysis, calculated for C\(_{41}\)H\(_{22}\)AuCl\(_3\)N\(_2\): C, 41.64; H, 3.66; Cl, 7.37; N, 5.83; found: C, 41.88; H, 3.64; Cl, 7.56; N, 5.78.

[Au(Io-Tol)Cl] (L\(^3\))

Following the general procedure, L\(^3\) was obtained as a white solid (71% yield); IR (neat)/\(\nu\) cm\(^{-1}\): 3157, 766, 743 cm\(^{-1}\); \(^1\)H NMR (400 MHz, CDCl\(_3\), 20 °C) \(\delta 7.44–7.39\) (m, 8H), \(7.18\) (s, 2H), \(2.23\) (s, 6H), \(2.10\) (s, 9H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\), 20 °C) \(\delta 172.8\) (C\(_{\text{carbene}}\)), 137.9 (C\(_d\)), 134.3 (C\(_q\)), 131.4 (CH), 130.0 (CH), 127.5 (CH), 127.2 (CH), 122.2(CH), 17.9 (CH\(_3\)); MS (MALDI TOF m/z) for C\(_{17}\)H\(_{16}\)AuCl\(_3\)N\(_2\) (M+H): 481.07; Elem analysis, calculated for C\(_{17}\)H\(_{16}\)AuCl\(_3\)N\(_2\): C, 42.47; H, 3.35; Cl, 7.37; N, 5.83; found: C, 42.48; H, 3.28; Cl, 7.56; N, 5.78.
[Au(IMesBn)Cl] (L$^4$) Following the general procedure L$^4$ was obtained as a white solid (47% yield); IR (neat)/ν cm$^{-1}$: 3127, 1240, 691 cm$^{-1}$; $^1$H NMR (400 MHz, CDCl$_3$, 20 °C) δ 7.40–7.33 (m, 5H), 7.06 (d, $J = 1.9$ Hz, 1H), 6.97 (d, $J = 0.5$ Hz, 2H), 6.88 (d, $J = 1.9$ Hz, 1H), 5.51 (s, 2H), 2.33 (s, 3H), 2.03 (s, 6H); $^{13}$C NMR (100 MHz, CDCl$_3$, 20 °C) δ 172.3 (C$_{\text{carbene}}$), 139.7 (C$_q$), 135.1 (CH), 134.7 (C$_q$), 129.4 (CH), 129.2 (CH), 128.7 (CH), 127.8 (CH), 122.7 (C$_q$), 120.4 (C$_q$), 55.0 (CH$_2$), 21.1 (CH$_3$), 17.8 (CH$_3$); MS (MALDI TOF m/z) for C$_{19}$H$_{20}$AuClN$_2$ (M+H)$^+$: 509.10; Elem anal, calculated for C$_{19}$H$_{20}$AuClN$_2$: C, 44.85; H, 3.96; Cl, 6.97; N, 5.51; found: C, 44.70; H, 3.98; Cl, 6.72; N, 5.40;

2.2. List of the 2-alkynylanilines used as indole derivative precursors in the paper

2-(hex-1-yn-1-yl)aniline (1a)

Following the general procedure 1a was obtained as a pale yellow oil (95% yield); $R_f$ = 0.54 [n-hexane/EtOAc (9/1)]; $^1$H NMR (400 MHz, CDCl$_3$, 20 °C) δ 7.25 (dd, $J = 1.6$, 7.6 Hz, 1H), 7.10–7.06 (m, 1H), 6.71–6.66 (m, 2H), 4.27 (br. s, 2H), 2.47 (t, $J = 6.8$ Hz, 2H), 2.21 (s, 3H), 2.15 (s, 3H), 2.62–2.62 (m, 2H), 2.55–2.49 (m, 2H), 0.98 (t, $J = 7.6$ Hz, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$, 20 °C) δ 147.6 (C$_q$), 132.0 (CH), 128.8 (CH), 117.8 (CH), 114.1 (CH), 109.0 (C$_q$), 96.7 (C$_q$), 7.0 (C$_q$), 31.0 (CH$_2$), 19.3 (CH$_3$), 13.7 (CH$_3$);

Analyses were in accordance with previously reported.$^5$

2-(hex-1-yn-1-yl)-4,6-dimethylaniline (1b)

Following the general procedure 1b was obtained as a yellow oil (99% yield); $R_f$ = 0.4 [cyclohexane/CH$_2$Cl$_2$ (1/1)]; IR (neat)/ν cm$^{-1}$: 3472, 3377, 1479, 858 cm$^{-1}$; $^1$H NMR (400 MHz, CDCl$_3$, 20 °C) δ 7.00 (s, 1H), 6.83 (s, 1H), 4.01 (br. s, 2H) 2.50 (t, $J = 6.8$ Hz, 2H), 2.21 (s, 3H), 2.15 (s, 3H), 2.62–2.62 (m, 2H), 2.55–2.49 (m, 2H), 0.98 (t, $J = 7.6$ Hz, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$, 20 °C) δ 143.4 (C$_q$), 130.9 (CH), 129.8 (CH), 126.6 (C$_q$), 121.7 (C$_q$), 108.7 (C$_q$), 95.1 (C$_q$), 77.5 (C$_q$), 31.1 (CH$_2$), 22.0 (CH$_2$), 20.2 (CH$_3$), 19.3 (CH$_3$), 17.6 (CH$_3$), 13.7 (CH$_3$); HRMS (EI) calculated for C$_{14}$H$_{19}$N (M+H)$^+$: 202.1590; found 202.1596; Elem analysis, calculated for C$_{14}$H$_{19}$N: C, 83.53; H, 9.51; N, 6.96; found: C, 83.76; H, 9.53; N, 6.8;

**N-benzyl-2-(hex-1-yn-1-yl)aniline (1d)**

Following the general procedure 1d was obtained as a yellow oil (93% yield); $R_f = 0.25$ [n-hexane/DCM (9/1)]; $^1$H NMR (400 MHz, CDCl$_3$, 20 °C) δ 7.39–7.33 (m, 3H), 7.30–7.28 (m, 2H), 7.13-7.09 (m, 1H), 6.63–6.59 (m, 1H), 6.55 (dd, $J = 0.8$, 8.4 Hz, 1H), 5.03 (br. s, 2H), 4.41 (s, 2H), 2.46 (t, $J = 6.8$ Hz, 2H), 1.58–1.53 (m, 2H), 1.46–1.40 (m, 2H), 0.9 (t, $J = 7.2$ Hz, 3H); $^1$H NMR (400 MHz, CDCl$_3$, 20 °C) δ 7.27–7.24 (m, 1H), 7.20–7.16 (m, 1H), 6.63–6.56 (m, 2H), 4.60 (br. s, 2H), 2.89 (s, 2H), 2.48 (t, $J = 7.1$ Hz, 2H), 1.62–1.60 (m, 2H), 1.50-1.48 (m, 2H), 0.96 (t, $J = 7.3$ Hz, 3H); $^1$H NMR (400 MHz, CDCl$_3$, 20 °C) δ 148.6 (C$_q$), 139.2 (C$_q$), 131.9 (CH), 129.0 (CH), 128.6 (CH*$^2$), 127.2 (CH*$^2$), 127.1 (CH), 116.4 (CH), 109.6 (CH), 108.6 (C$_q$), 96.3 (C$_q$), 47.8 (CH$_2$), 30.9 (CH$_2$), 22.0 (CH$_2$), 19.3 (CH$_2$), 13.6 (CH$_3$); Analyses were in accordance with previously reported.6

**2-(hex-1-yn-1-yl)-N-methylaniline (1e)**

Following the general procedure 1e was obtained as a yellow oil (91% yield); $R_f = 0.34$ [n-hexane/EtOAc (98/2)]; $^1$H NMR (400 MHz, CDCl$_3$, 20 °C) δ 7.56-7.54 (m, 2H), 7.36–7.34 (m, 4H), 7.14 (dt, $J = 1.6$, 8.0 Hz, 1H), 6.74–6.72 (m, 2H), 4.29 (br. s, 2H); $^1$H NMR (400 MHz, CDCl$_3$, 20 °C) δ 149.7 (C$_q$), 131.8 (CH), 129.1 (CH), 116.4 (CH), 108.7 (CH), 108.3 (C$_q$), 96.0 (CH), 77.0 (C$_q$), 31.1 (CH$_2$), 30.3 (CH$_3$), 22.1 (CH$_2$), 19.4 (CH$_2$), 13.7 (CH$_3$); HRMS (EI) calculated for C$_{13}$H$_{17}$N (M+H)$^+$: 188.1434; found 188.1443; Elem anal, calculated for C$_{13}$H$_{17}$N: C, 83.37; H, 9.15; N, 7.48; found: C, 83.27; H, 9.20; N, 7.41;

**2-(phenylethynyl)aniline (1g)**

Following the general procedure 1g was obtained as a white solid (63% yield); $R_f = 0.28$ [n-hexane/DCM (1/1)]; $^1$H NMR (400 MHz, CDCl$_3$, 20 °C) δ 7.56-7.54 (m, 2H), 7.36–7.34 (m, 4H), 7.14 (dt, $J = 1.6$, 8.0 Hz, 1H), 6.74–6.72 (m, 2H), 4.29 (br. s, 2H); $^1$C NMR (100 MHz, CDCl$_3$, 20 °C) δ 147.8 (C$_q$), 132.1 (CH), 131.5 (CH), 129.7 (CH), 128.4 (CH), 128.2 (CH), 123.3 (C$_q$), 118.0 (CH), 114.3 (CH), 107.9 (C$_q$), 94.7(C$_q$), 85.9 (C$_q$); Analyses were in accordance with previously reported.7

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Diethyl 2-allyl-2-(3-(2-aminophenyl)prop-2-yn-1-yl)malonate (1h)

Following the general procedure 1h was obtained as a yellow oil (90%); $R_f = 0.20$ [n-hexane/EtOAc (9/1)]; IR (neat)/ν cm$^{-1}$: 3384, 2976, 1725, 748 cm$^{-1}$; $^1$H NMR (400 MHz, CDCl$_3$, 20 °C) δ 7.20 (dd, $J = 1.5$, 7.6 Hz, 1H), 7.09–7.05 (m, 1H), 6.66–6.60 (m, 2H), 5.70–5.62 (m, 1H), 5.23–5.13 (m, 2H), 4.26–4.19 (m, 4H), 3.05 (s, 2H), 2.78 (d $J = 7.5$, 2H), 1.25 (dt, $J = 7.1$, 3.4 Hz, 6H);

$^{13}$C NMR (100 MHz, CDCl$_3$, 20 °C) δ 170.1 (C$_{q}$), 169.4 (C$_{q}$), 148.2 (C$_{q}$), 132.0 (C$_{H}$), 131.7 (C$_{H}$), 131.6 (C$_{q}$), 129.6 (CH), 120.0 (CH), 119.9 (CH), 117.4 (CH), 114.1 (CH), 107.7 (C$_{q}$), 89.3 (C$_{q}$), 80.3 (C$_{q}$), 61.8 (C$_{H}$), 2.78 (d $J = 7.5$, 2H), 1.25 (dt, $J = 7.1$, 3.4 Hz, 6H);

HRMS (EI) calculated for C$_{19}$H$_{23}$NO$_{4}$(M+H)$^+$: 330.1700; found 330.1709;

2-(4-(benzyloxy)but-1-yn-1-yl)aniline (1i)

Following the general procedure 1i was obtained as a yellow oil (86%); $R_f = 0.23$ [n-hexane/EtOAc (9/1)]; IR (neat)/ν cm$^{-1}$: 3470, 3367, 1612, 1491, 1095 cm$^{-1}$; $^1$H NMR (400 MHz, CDCl$_3$, 20 °C) δ 7.40–7.30 (m, 4H), 7.25–7.22 (m, 1H), 7.08 (ddd, $J = 1.6$, 7.4, 8.1 Hz, 1H), 6.68–6.63 (m, 2H), 4.60 (br. s, 2H), 4.17 (br. s, 2H), 3.71 (t, $J = 7.2$ Hz, 2H), 2.79 (t, $J = 6.8$ Hz, 2H);

$^{13}$C NMR (100 MHz, CDCl$_3$, 20 °C) δ 147.3 (C$_{q}$), 138.0 (C$_{q}$), 131.9 (CH), 129.0 (CH), 128.4 (CH), 127.7 (CH), 118.1 (CH), 114.4 (CH), 92.4 (C$_{q}$), 78.1 (C$_{q}$), 73.0 (CH$_{2}$), 68.5 (CH$_{2}$), 21.1 (CH$_{2}$); HRMS (EI) calculated for C$_{17}$H$_{17}$NO (M+H)$^+$: 252.1383; found 252.1389;

4-bromo-2-(hex-1-yn-1-yl)aniline (1j)

Following the general procedure 1j was obtained as a yellow oil (84%); $R_f = 0.37$ [n-hexane/DCM (1/1)]; IR (neat)/ν cm$^{-1}$: 3474, 3379, 2931, 1657, 1483 cm$^{-1}$; $^1$H NMR (400 MHz, CDCl$_3$, 20 °C) δ 7.34 (d, $J = 2.4$ Hz, 1H), 7.15 (dd, $J = 2.4$, 8.4 Hz, 1H), 6.56 (d $J = 8.8$, 1H), 4.16 (br. s, 2H), 2.46 (t, $J = 7.2$ Hz, 2H), 1.62–1.58 (m, 2H), 1.51–1.47 (m, 2H), 0.95 (t, $J = 7.6$ Hz, 3H);

$^{13}$C NMR (100 MHz, CDCl$_3$, 20 °C) δ 146.6 (C$_{q}$), 134.2 (CH), 131.5 (CH), 115.5 (CH), 110.9 (C$_{q}$), 108.9 (C$_{q}$), 97.0 (C$_{q}$), 75.8 (C$_{q}$), 30.8 (CH$_{2}$), 22.0 (CH$_{2}$), 19.3 (CH$_{2}$), 13.6 (CH$_{3}$); HRMS (EI) calculated for C$_{12}$H$_{14}$NBr(M+H)$^+$: 252.0382; found 252.0378; Elem analysis, calculated for C$_{12}$H$_{14}$NBr: C, 57.16; H, 5.60; Br, 31.69; N, 5.55; found: C, 57.40; H, 5.68; Br, 31.71; N, 5.64;
4-(2-aminophenyl)but-3-yn-1-yl benzoate (1k)

Following the general procedure 1k was obtained as a white solid. (93% yield); \( R_f = 0.33 \) [n-hexane/EtOAc (8/2)]; m.p. 59 °C; IR (neat)/\( \nu \) cm\(^{-1}\): 3440, 3362, 1712, 1616, 1311, 708 cm\(^{-1}\); ^1H NMR (400 MHz, CDCl\(_3\), 20 °C) \( \delta \) 8.09–8.08 (m, 2H), 7.59–7.55 (m, 1H), 7.47–7.43 (m, 2H) 7.56–7.24 (m, 1H), 7.23–7.22 (m, 1H), 6.67–6.63 (m, 2H), 4.54 (t, \( J = 6.8 \) Hz, 2H), 4.17 (br. s, 2H), 2.96 (t, \( J = 6.8 \) Hz, 2H); ^13C NMR (100 MHz, CDCl\(_3\), 20 °C) \( \delta \) 166.4 (C\( _q \)), 147.9 (CH), 133.1 (CH), 132.1 (CH), 129.9 (C\( _q \)), 129.6 (CH), 129.3 (CH), 128.4 (CH), 117.8 (CH), 114.2 (CH), 108.0 (C\( _q \)), 90.8 (C\( _q \)), 78.7 (C\( _q \)), 62.9 (CH\(_2\)), 20.4 (CH\(_2\)); HRMS (EI) calculated for C\(_{17}\)H\(_{15}\)NO\(_2\) (M+H): 266.1176; found 266.1176; Elem analysis, calculated for C\(_{17}\)H\(_{15}\)NO\(_2\): C, 76.96; H, 5.70; N, 5.28; found: C, 76.83; H, 5.78; N, 5.02;

4-(2-aminophenyl)but-3-yn-1-yl 3-nitrobenzoate (1l)

Following the general procedure 1l was obtained as a pale yellow solid (33% yield); \( R_f = 0.4 \) [n-hexane/EtOAc (7/3)]; m.p. 115 °C; IR (neat)/\( \nu \) cm\(^{-1}\): 3461, 3369, 1715, 772 715 cm\(^{-1}\); ^1H NMR (400 MHz, CDCl\(_3\), 20 °C) \( \delta \) 8.89 (m, 1H), 8.41 (t, \( J = 8.0 \) Hz, 2H), 7.66 (t, \( J = 8.0 \) Hz, 1H), 7.24 (dd, \( J = 1.6, 7.6 \) Hz, 1H), 2.99 (t, \( J = 8.0 \) Hz, 2H), 2.76 (t, \( J = 6.4 \) Hz, 2H), 4.19 (br. s, 2H), 2.99 (t, \( J = 6.4 \) Hz, 2H); ^13C NMR (100 MHz, CDCl\(_3\), 20 °C) \( \delta \) 164.3 (C\( _q \)), 148.2 (C\( _q \)), 147.8 (C\( _q \)), 135.4 (CH), 132.1 (CH), 131.7 (C\( _q \)), 129.7 (CH), 129.4 (CH), 127.5 (CH), 124.6 (CH), 117.8 (CH), 114.2 (CH), 107.8 (C\( _q \)), 90.2 (C\( _q \)), 79.1 (C\( _q \)), 63.7 (CH\(_2\)), 20.3 (CH\(_2\)); HRMS (EI) calculated for C\(_{17}\)H\(_{14}\)N\(_2\)O\(_4\) (M+H): 311.1026; found 311.1032; Elemt analysis, calculated for C\(_{17}\)H\(_{14}\)N\(_2\)O\(_4\), C, 65.80; H, 4.55; N, 9.03; found: C, 65.67; H, 4.73; N, 8.90;

2.2. The hydroamination reaction products

2-butyl-1H-indole (2a)

Following the general procedure 2a was obtained as a colorless oil (85% yield); \( R_f = 0.56 \) [n-hexane/DCM (1/1)]; ^1H NMR (400 MHz, CDCl\(_3\), 20 °C) \( \delta \) 7.85 (br. s, 1H), 7.57–7.55 (m, 1H), 7.32–7.30 (m, 1H), 6.27 (s, 1H), 4.60 (t, \( J = 6.8 \) Hz, 2H), 2.99 (t, \( J = 6.4 \) Hz, 2H); ^13C NMR (100 MHz, CDCl\(_3\), 20 °C) \( \delta \) 140.0 (C\( _q \)), 135.8 (C\( _q \)), 128.8 (C\( _q \)), 120.9 (CH), 119.7 (CH), 119.6 (CH), 100.2 (C\( _q \)), 99.4 (CH), 31.3 (CH\(_2\)), 27.9 (CH\(_2\)), 22.4 (CH\(_2\)), 13.9 (CH\(_3\));
Analyses were in accordance with previously reported.  

2-butyl-5,7-dimethyl-1H-indole (2b)

Following the general procedure 2b was obtained as a yellow solid (97% yield) $R_f = 0.27$ [n-hexane/EtOAc (9/1)]; IR (neat)/$\nu$ cm$^{-1}$: 3301, 2956, 2926, 1681 cm$^{-1}$; $^1$H NMR (400 MHz, CDCl$_3$, 20 °C) δ 7.68 (br. s, 1H), 7.19 (s 1H), 6.78 (s, 1H), 6.18 (s, 1H), 2.79–2.76 (m, 2H), 2.46 (s, 3H), 2.42 (s, 3H), 1.75–1.71 (m, 2H), 1.48–1.44 (m, 2H), 0.98 (t, $J = 7.2$ Hz, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$, 20 °C) δ 139.7 (C$q$), 133.6 (C$q$), 128.9 (C$q$), 128.6 (C$q$), 123.2 (CH), 119.0 (C$q$), 117.1 (CH), 99.5 (CH), 31.4 (CH$_2$), 28.1 (CH$_2$), 21.4 (CH$_2$), 16.7 (CH$_3$), 13.9 (CH$_3$); HRMS (EI) calculated for C$_{14}$H$_{19}$N (M+H)$^+$: 202.1590; found 202.1591;

1-benzyl-2-butyl-1H-indole (2d)

Following the general procedure 2d was obtained as a pale yellow solid (95% yield) $R_f = 0.43$ [n-hexane/EtOAc (99/1)]; $^1$H NMR (400 MHz, CDCl$_3$, 20 °C) δ 7.64–7.62 (m, 1H), 7.30–7.21 (m, 4H), 7.14–7.12 (m, 2H), 7.01–6.99 (m, 2H), 6.40 (s, 1H), 5.35 (s, 2H), 2.73–2.69 (m, 2H), 1.74–1.70 (m, 2H), 1.48–1.42 (m, 2H), 0.96 (t, $J = 7.4$ Hz, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$, 20 °C) δ 141.4 (C$q$), 138.0 (C$q$), 137.2 (C$q$), 128.7 (CH), 128.2 (C$q$), 127.2 (CH), 125.9 (CH), 120.8 (CH), 119.8 (CH), 119.5 (CH), 109.3 (CH), 99.4 (CH), 46.4 (CH$_2$), 30.6 (CH$_2$), 26.5 (CH$_2$), 22.5 (CH$_2$), 13.9 (CH$_3$);

2-butyl-1-methyl-1H-indole (2e)

Following the general procedure 2e was obtained as a pale yellow oil (88% yield) $R_f = 0.45$ [n-hexane/EtOAc (1/1)]; $^1$H NMR (400 MHz, CDCl$_3$, 20 °C) δ 7.63–7.61 (m, 1H), 7.29–7.21 (m, 4H), 7.14–7.12 (m, 2H), 7.01–6.99 (m, 2H), 6.40 (s, 1H), 5.35 (s, 2H), 2.73–2.69 (m, 2H), 1.81–1.77 (m, 2H), 1.58–1.52 (m, 2H), 1.06 (t $J = 7.4$, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$, 20 °C) δ 141.5 (C$q$), 137.4 (C$q$), 128.0 (C$q$), 120.5 (CH), 119.7 (CH), 119.2 (CH), 108.7 (CH), 98.7 (CH), 30.8 (CH$_2$), 29.4 (CH$_3$), 26.6 (CH$_2$), 22.6 (CH$_2$), 14.0 (CH$_3$);

Analyses were in accordance with previously reported.10

2-phenyl-1H-indole (2g)

Following the general procedure 2g was obtained as a pale yellow solid (81% yield); \( R_f = 0.45 \) [cyclohexane/DCM (1/1)]; \(^1\)H NMR (400 MHz, CDCl\(_3\), 20 °C) \( \delta \) 8.31 (br. s, 1H), 7.69–7.66 (m, 3H), 7.48–7.37 (m, 4H), 7.35–7.15 (m, 2H), 6.86 (s, 1H); \(^13\)C NMR (100 MHz, CDCl\(_3\), 20 °C) \( \delta \) 137.9 (C\(_q\)), 136.8 (C\(_q\)), 132.3, (C\(_q\)), 129.2 (C\(_q\)), 129.0 (CH), 127.7 (CH), 125.2 (CH), 122.4 (CH), 120.7 (CH), 120.3 (CH), 110.9 (CH), 100.0;

Analyses were in accordance with previously reported.11

Diethyl 2-((1H-indol-2-yl)methyl)-2-allylmalonate (2h)

Following the general procedure 2c was obtained as a pale yellow solid (89% yield); \( R_f = 0.56 \) [n-hexane/DCM (1/1)]; IR (neat)/\( \nu \) cm\(^{-1}\): 3401, 2981, 1718, 1186 cm\(^{-1}\); \(^1\)H NMR (400 MHz, CDCl\(_3\), 20 °C) \( \delta \) 8.62 (s, 1H), 7.51–7.49 (m, 1H), 7.30–7.28 (m, 1H), 7.13–7.09 (m, 1H), 7.06–7.02 (m, 1H), 6.23 (dd, \( J = 0.8, 2.0 \) Hz, 1H), 5.73–5.65 (m, 1H), 5.18–5.13 (m, 2H), 4.21–4.10 (m, 4H), 3.31 (s, 2H), 2.72 (dt, \( J = 7.4, 4.1 \) Hz, 2H), 1.13 (t, \( J = 7.1 \) Hz, 6H); \(^13\)C NMR (100 MHz, CDCl\(_3\), 20 °C) \( \delta \) 171.3 (C\(_q\)), 136.1 (C\(_q\)), 133.8 (C\(_q\)), 132.3 (CH), 128.2 (C\(_q\)), 121.3 (CH), 119.9 (CH), 119.6 (CH), 119.4 (CH), 110.6 (CH), 102.7 (CH), 61.7 (CH\(_2\)), 58.7 (C\(_q\)), 38.7 (CH\(_2\)), 32.6 (CH\(_2\)), 13.9 (CH\(_3\)); HRMS (EI) calculated for C\(_{19}\)H\(_{23}\)NO\(_4\) (M+H\(^+\)): 330.1700; found 330.1707;

2-(2-(benzyloxy)ethyl)-1H-indole (2i)

Following the general procedure 2i was obtained as a pale yellow solid (68% yield); \( R_f = 0.29 \) [n-hexane/EtOAc (9/1)]; \(^1\)H NMR (400 MHz, CDCl\(_3\), 20 °C) \( \delta \) 8.56 (s, 1H), 7.61–7.59 (m, 1H), 7.44–7.31 (m, 6H) 7.20–7.11 (m, 2H), 6.31–6.30 (m, 1H), 4.63 (s, 2H), 3.84 (t, \( J = 5.8 \) Hz, 2H), 3.11–3.08 (m, 2H); \(^13\)C NMR (100 MHz, CDCl\(_3\), 20 °C) \( \delta \) 138.0 (C\(_q\)), 137.8 (C\(_q\)), 136.0 (C\(_q\)), 128.4 (C\(_q\)), 127.9 (CH), 127.8 (CH), 121.1 (CH), 119.9 (CH), 119.5 (CH), 110.5 (CH), 99.9 (CH), 73.4 (CH\(_2\)), 70.0 (CH\(_2\)), 28.7 (CH\(_2\));

Analyses were in accordance with previously reported.12


5-bromo-2-butyl-1H-indole (2j)

Following the general procedure 2j was obtained as a yellow solid (86% yield); 

\[ R_f = 0.5 \text{ [cyclohexane/DCM (1/1)]} \];

IR (neat)/\( \nu \text{ cm}^{-1} \): 3403, 2953, 1453, 796 cm\(^{-1} \);

\(^1\)H NMR (400 MHz, CDCl\(_3\), 20 \(^\circ\)C) \( \delta \) 7.88 (br. s, 1H), 7.65–7.64 (m, 1H), 7.20–7.14 (m, 2H), 6.18 (br. s, 1H), 2.76–2.72 (m, 2H), 1.72–1.66 (m, 2H), 1.44–1.39 (m, 2H), 0.96 (t, \( J = 8.0 \) Hz, 3H);

\(^13\)C NMR (100 MHz, CDCl\(_3\), 20 \(^\circ\)C) \( \delta \) 141.4 (C\(_q\)), 134.4 (C\(_q\)), 130.6 (C\(_q\)), 123.6 (CH), 122.2 (CH), 112.7 (C\(_q\)), 111.6 (CH), 99.2 (CH), 31.3 (CH\(_2\)), 27.9 (CH\(_2\)), 22.3 (CH\(_2\)), 13.8 (CH\(_3\));

HRMS (EI) calculated for C\(_{12}\)H\(_{14}\)NBr: 252.0382; found 252.0384;

(1H-indol-2-yl)methyl benzoate (2k)

Following the general procedure 2k was obtained as a pale yellow solid (78% yield); 

\[ R_f = 0.23 \text{ [n-hexane/EtOAc (9/1)]} \]; m.p. 117 \(^\circ\)C;

IR (neat)/\( \nu \text{ cm}^{-1} \): 3347, 1699, 1658 cm\(^{-1} \);

\(^1\)H NMR (400 MHz, CDCl\(_3\), 20 \(^\circ\)C) \( \delta \) 8.13 (br. s, 1H), 8.08–8.05 (m, 2H), 7.61–7.55 (m, 2H), 7.48–7.44 (m, 2H), 7.32 (dd, \( J = 0.8, 2.0 \) Hz, 1H), 7.17–7.08 (m, 2H), 6.38 (dd \( J = 0.8, 2.0 \) Hz, 1H), 4.65 (t, \( J = 6.6 \) Hz, 2H), 3.25 (t, \( J = 6.6 \) Hz, 2H);

\(^13\)C NMR (100 MHz, CDCl\(_3\), 20 \(^\circ\)C) \( \delta \) 166.5 (C\(_q\)), 136.0 (C\(_q\)), 136.3 (C\(_q\)), 133.2 (C\(_q\)), 130.0 (C\(_q\)), 129.6 (CH), 128.6 (C\(_q\)), 128.5 (CH), 121.5 (CH), 120.0 (CH), 119.8 (CH), 110.5 (CH), 100.8 (CH), 63.9 (CH\(_2\)), 28.1(CH\(_2\));

HRMS (EI) calculated for C\(_{17}\)H\(_{15}\)NO\(_2\): 266.1176; found 266.1182;

Elem analysis, calculated for C\(_{17}\)H\(_{15}\)NO\(_2\): C, 76.96; H, 5.70; N, 5.28; found: C, 76.93; H, 5.82; N, 5.15;

(1H-indol-2-yl)methyl 3-nitrobenzoate (2l)

Following the general procedure 2l was obtained as a pale yellow solid (78% yield); 

\[ R_f = 0.4 \text{ [n-hexane/EtOAc (7/3)]} \]; m.p. 127 \(^\circ\)C;

IR (neat)/\( \nu \text{ cm}^{-1} \): 3369, 1714, 1525, 1347 cm\(^{-1} \);

\(^1\)H NMR (400 MHz, CDCl\(_3\), 20 \(^\circ\)C) \( \delta \) 8.88–8.87 (m, 1H), 8.44–8.42 (m, 1H), 8.36–8.34 (m, 1H), 8.07 (br. s, 1H), 7.66 (t, \( J = 8.0 \) Hz, 1H), 7.56 (d, 7.9 Hz, 1H), 7.34 (dd, \( J = 0.8, 8.0 \) Hz, 1H), 7.18–7.08 (m, 2H), 6.39 (dd, 0.8, 1.9 Hz, 1H), 4.71 (t, \( J = 6.7 \) Hz, 2H), 3.29 (t, \( J = 6.7 \)Hz, 2H);

\(^13\)C NMR (100 MHz, CDCl\(_3\), 20 \(^\circ\)C) \( \delta \) 166.5 (C\(_q\)), 136.0 (C\(_q\)), 136.3 (C\(_q\)), 133.1 (CH), 130.0 (C\(_q\)), 129.6 (CH), 128.6 (C\(_q\)), 128.5 (CH), 121.5 (CH), 120.0 (CH), 119.8 (CH), 110.5 (CH), 100.8 (CH), 63.9 (CH\(_2\)), 28.1(CH\(_2\));

HRMS (EI) calculated for C\(_{17}\)H\(_{14}\)N\(_2\)O\(_4\)(M+H): 311.1026; found 311.1039;