Supporting Information

Synthesis and Anticholinesterase Activity of 2-Substituted-N-Alkynylindoles

Thaís Prochnow,1 Adriano Maroneze,1 Davi F. Back2 Natalia S. Jardim,1 Cristina W. Nogueira1 and Gilson Zeni*.1

aLaboratório de Síntese, Reatividade, Avaliação Farmacológica e Toxicológica de Organocalcogênios CCNE, UFSM, Santa Maria, Rio Grande do Sul, Brazil 97105-900.
E-mail: gzeni@ufsm.br; Fax: (+55)55-3220-8978; Tel: (+55)55-3220-9611.

bLaboratório de Materias Inorgânicos, Departamento de Química, UFSM, Santa Maria, Rio Grande do Sul. Brazil 97105-900.

Table of Contents

Materials and Methods S1

Figure S1. ORTEP structure of compound 3q. S3

Table S1. Crystal data and structure refinement for 3q. S3

General procedure for the synthesis of 2-substituted N-alkynylindoles 3 S4

General procedure for the synthesis of 2-(2,2-dibromovinyl)-1-(phenylethynyl)-1H-indole 4a S9

General procedure for the synthesis of 3-phenyl-1-(1-(phenylethynyl)-1H-indol-2-yl)prop-2-yn-1-ol 4b S10

General procedure for the synthesis of (Z)-(1-(2-phenyl-2-(phenyltellanyl)vinyl)-1H-indol-2-yl)(p-tolyl)methanol 4c S10

NMR Spectra S12

Materials and Methods

Proton nuclear magnetic resonance spectra (¹H NMR) were obtained on a NMR spectrometer at 400 MHz. Spectra were recorded in CDCl₃ solutions. Chemical shifts
are reported in ppm, referenced to the solvent peak of CDCl$_3$ or tetramethylsilane (TMS) as the external reference. Data are reported as follows: chemical shift ($\delta$), multiplicity, coupling constant ($J$) in Hertz and integrated intensity. Carbon-13 nuclear magnetic resonance spectra ($^{13}$C NMR) were obtained on a 400 NMR spectrometer at 100 MHz. Spectra were recorded in CDCl$_3$ solutions. Chemical shifts are reported in ppm, referenced to the solvent peak of CDCl$_3$. Abbreviations to denote the multiplicity of a particular signal are s (singlet), d (doublet), t (triplet), quart (quartet), quint (quintet), sex (sextet), dd (double doublet) and m (multiplet). High resolution mass spectra were recorded on a mass spectrometer using electrospray ionization (ESI). Column chromatography was performed using Silica Gel (230-400 mesh) following the methods described by Still.[1] Thin layer chromatography (TLC) was performed using Gel GF254, 0.25 mm thickness. For visualization, TLC plates were either placed under ultraviolet light, or stained with iodine vapor, or acidic vanillin. Most reactions were monitored by TLC for disappearance of starting material. The following solvents were dried and purified by distillation from the reagents indicated: tetrahydrofuran from sodium with a benzophenone ketyl indicator. All other solvents were ACS or HPLC grade unless otherwise noted. Air- and moisture-sensitive reactions were conducted in flame-dried or oven dried glassware equipped with tightly fitted rubber septa and under a positive atmosphere of dry nitrogen or argon. Reagents and solvents were handled using standard syringe techniques. The $n$-Butyllithium 2.5 M in hexanes purchased from commercial suppliers.
Figure S1. ORTEP structure of compound 3q (CCDC 1862618).

: 0.102 g Crystal data and structure refinement for 3q.

<table>
<thead>
<tr>
<th></th>
<th>3q</th>
</tr>
</thead>
<tbody>
<tr>
<td>Empirical formula</td>
<td>C$<em>{38}$H$</em>{38}$N$_2$Si$_2$</td>
</tr>
<tr>
<td>Formula weight</td>
<td>578.88</td>
</tr>
<tr>
<td>Temperature (K)</td>
<td>110 (2)</td>
</tr>
<tr>
<td>Wavelength. $\lambda$ (Å)</td>
<td>0.71073</td>
</tr>
<tr>
<td>Crystal system, space group</td>
<td>Triclinic, P-1</td>
</tr>
<tr>
<td>Unit cell dimensions</td>
<td></td>
</tr>
<tr>
<td>$a$ (Å)</td>
<td>11.0160 (4)</td>
</tr>
<tr>
<td>$b$ (Å)</td>
<td>11.9919 (4)</td>
</tr>
<tr>
<td>$c$ (Å)</td>
<td>13.0752 (5)</td>
</tr>
<tr>
<td>$\alpha$ (°)</td>
<td>89.5180 (10)</td>
</tr>
<tr>
<td>$\beta$ (°)</td>
<td>75.5500 (10)</td>
</tr>
<tr>
<td>$\gamma$ (°)</td>
<td>80.3100 (10)</td>
</tr>
<tr>
<td>Volume (Å$^3$)</td>
<td>1647.74 (10)</td>
</tr>
<tr>
<td>Z, Calculated density (Mg m$^{-3}$)</td>
<td>2, 1.167</td>
</tr>
<tr>
<td>Absorption coefficien (mm$^{-1}$)</td>
<td>0.136</td>
</tr>
<tr>
<td>F (000)</td>
<td>616</td>
</tr>
<tr>
<td>Crystal size (mm)</td>
<td>0.50 x 0.33 x 0.21</td>
</tr>
</tbody>
</table>
Theta range for data collection $\theta^{\circ}$ 2.32 a 27.93

Limiting indices

-14 $\leq$ h $\leq$ 14
-13 $\leq$ k $\leq$ 15
-17 $\leq$ l $\leq$ 17

Reflections collected 26553
Reflections unique [R (int)] 7884 [0.0230]
Completeness to theta = 22.61 99.6 %
Absorption correction Semi-empirical from equivalents
Max. and min. transmission 0.9720 and 0.9351
Refinement method Full-matrix least-squares on $F^2$
Data / restraints / parameters 7884/0/379
Goodness-of-fit em $F^2$ 1.051
Final $R$ indices [l$>\sigma(l)$] $R1 = 0.0355$
$wR2 = 0.0903$
R indices (all data)* $R1 = 0.0435$
$wR2 = 0.0946$
Largest diff. peak and hole (e Å$^{-3}$) 0.308 and -0.295

* $R1 = |F_o - F_c|/|F_o|$; $wR2 = [\sum w(F_o^2 - F_c^2)^2/(\sum wF_o^2)]^{1/2}$.

General procedure for the synthesis of 2-substituted N-alkynylindoles 3. To a Schlenck tube, under an ambient atmosphere, containing 1-(phenylethynyl)-1$H$-indolederivatives 1 (0.5 mmol) in THF (3mL) were added n-BuLi (0.65 mmol, 2.5 M in hexane) was added dropwise over 5 min at -78 ºC. The resultant yellow/orange solution was stirred for another 10 min and then warmed to 0 ºC over 30 min. The solution was recooled to -78 ºC, and the electrophile (0.6 mmol) in 1 mL of THF was added dropwise. The mixture was stirred for 1 h, the room temperature. After quenching with H$_2$O and extraction with ethyl acetate (3 × 2 mL), the combined organic layers were dried over MgSO$_4$, and concentrated at reduced pressure to give. The residue was purified by column chromatography over silica gel to provide 2-substituted N-alkynylindoles 3. (Phenylethynyl)-1$H$-indol-2-yl)(p-tolyl)methanol (3a). The product was isolated by column chromatography (hexane/ethyl acetate 97:3 as eluent) as a light yellow solid. Yield: 0.101 g (60%); mp 60-63 ºC. $^1$H NMR (CDCl$_3$, 400 MHz): $\delta$ (ppm) 7.56-7.53 (m, 1H), 7.52-7.49 (m, 1H), 7.43-7.40 (m, 2H), 7.34-7.25 (m, 5H), 7.19-7.10 (m, 4H), 6.43 (s, 1H); 6.09 (s, 1H); 2.73 (s, 1H); 2.32 (s, 3H). $^{13}$C {$^1$H} NMR (CDCl$_3$,
100 MHz): δ (ppm) 143.1, 138.8, 137.9, 131.3, 129.1, 128.4, 128.0, 127.3, 126.9, 123.5, 122.4, 122.2, 121.1, 111.1, 103.8, 79.1, 74.1, 69.8, 21.1. MS (EI, 70 eV. m/z (relative intensity)): 338 (26), 337 (100), 219 (21), 204 (95), 90 (10), 77 (3). HRMS (ESI-TOF) m/z calcd for C_{24}H_{20}NO [M + H]^+: 338.1545. Found: 338.1552.

Phenyl (phenylethynyl)-1H-indol-2-yl)metanol (3b). The product was isolated by column chromatography (hexane/ethyl acetate 97:3 as eluent) as a light yellow solid. Yield: 0.105 g (65%); mp 79-82 °C. ¹H NMR (CDCl₃, 400 MHz): δ (ppm) 7.64-7.54 (m, 4H), 7.50-7.33 (m, 9H), 7.29-7.23 (m, 1H), 6.50-6.49 (m, 1H), 6.24 (s, 1H), 2.69 (s, 1H). ¹³C {¹H} NMR (CDCl₃, 100 MHz): δ (ppm) 142.9, 140.7, 138.9, 131.4, 128.5, 128.4, 128.2, 128.1, 127.3, 127.0, 123.6, 122.4, 122.3, 121.2, 111.2, 104.2, 79.1, 74.2, 70.0. MS (EI, 70 eV. m/z (relative intensity)): 324 (26), 323 (100), 306 (35), 227 (45), 204 (20), 156 (16), 105 (24). HRMS (ESI-TOF) m/z calcd for C_{23}H_{18}N [M + H]^+: 324.1388. Found: 324.1392.

(4-Chlorophenyl)(1-(phenylethynyl)-1H-indol-2-yl)methanol (3c). The product was isolated by column chromatography (hexane/ethyl acetate 97:3 as eluent) as a light yellow oil. Yield: 0.118 g (66%). ¹H NMR (CDCl₃, 400 MHz): δ (ppm) 7.56-7.52 (m, 1H), 7.51-7.48 (m, 1H), 7.45-7.39 (m, 4H), 7.38-7.26 (m, 6H), 7.23-7.18 (m, 1H), 6.40 (t, J = 0.8 Hz, 1H), 6.13 (s, 1H), 2.85 (s, 1H). ¹³C {¹H} NMR (CDCl₃, 100 MHz): δ (ppm) 142.3, 139.1, 138.8, 133.9, 131.4, 128.6, 128.5, 128.3, 128.3, 127.1, 123.8, 122.4, 122.1, 121.2, 111.2, 104.2, 78.9, 74.2, 69.2. MS (EI, 70 eV. m/z (relative intensity)): 358 (31), 357 (100), 219 (21), 338 (44), 217 (60), 204 (40), 77 (30). HRMS (ESI-TOF) m/z calcd for C_{23}H_{17}ClNO [M + H]^+: 358.0999. Found: 358.1006.

(4-Nitrophenyl)(1-(phenylethynyl)-1H-indol-2-yl)methanol (3d). The product was isolated by column chromatography (hexane/ethyl acetate 97:3 as eluent) as an orange oil. Yield: 0.120 g (65%). ¹H NMR (CDCl₃, 400 MHz): δ (ppm) 8.22-8.19 (m, 2H), 7.70-7.66 (m, 2H), 7.59-7.52 (m, 2H), 7.47-7.43 (m, 2H), 7.39-7.31 (m, 4H), 7.24-7.20 (m, 1H), 6.39-6.38 (m, 1H), 6.28 (s, 1H), 3.03 (s, 1H). ¹³C {¹H} NMR (CDCl₃, 100 MHz): δ (ppm) 147.7, 147.4, 141.3, 138.8, 131.3, 128.5, 128.4, 127.5, 126.9, 124.1, 123.5, 122.6, 121.8, 121.3, 111.2, 104.7, 78.5, 74.4, 68.7. MS (EI, 70 eV. m/z (relative intensity)): 369 (26), 368 (100), 246 (18), 217 (41), 254 (18), 151 (15), 145 (18). HRMS (ESI-TOF) m/z calcd for C_{23}H_{17}N₂O₃ [M + H]^+: 369.1239. Found: 369.1247.
(2-Fluoro-6-methoxyphenyl)(1-(phenylethynyl)-1H-indol-2-yl)methanol (3e). The product was isolated by column chromatography (hexane/ethyl acetate 97:3 as eluent) as a white solid. Yield: 0.115 g (62%); mp 128-130 °C. 1H NMR (CDCl₃, 400 MHz): δ (ppm). 7.63-7.55 (m, 3H), 7.51-7.48 (m, 1H), 7.38-7.24 (m, 5H), 7.18-7.14 (m, 1H), 6.78-6.73 (m, 2H), 6.54 (d, J = 10.5 Hz, 1H), 6.35 (s, 1H), 3.85 (s, 1H), 3.83 (s, 3H). 13C {1H} NMR (CDCl₃, 100 MHz): δ (ppm) 160.7 (d, J = 245.9 Hz), 158.7 (d, J = 7.4 Hz), 141.9, 139.1, 131.4, 129.8 (d, J = 10.8 Hz), 128.3, 127.9, 127.3, 123.5, 122.9, 122.1, 120.9, 116.6 (d, J = 15.5 Hz), 111.3, 108.8 (d, J = 23.1 Hz), 107.2 (d, J = 3.0 Hz), 103.7, 79.1, 73.9, 62.4 (d, J = 6.1 Hz), 56.09. MS (EI. 70 eV. m/z (relative intensity)): 372 (28), 371 (100), 340 (52), 254 (18), 217 (34), 154 (18), 144 (51), 91(25). HRMS (ESI-TOF) m/z calcd for C₂₄H₁₉FNO₂ [M + H]^+: 372.1400. Found: 372.1411.

(2-Bromo-6-methoxyphenyl)(1-(phenylethynyl)-1H-indol-2-yl)methanol (3f). The product was isolated by column chromatography (hexane/ethyl acetate 97:3 as eluent) as a yellow oil. Yield: 0.151 g (70%). 1H NMR (CDCl₃, 400 MHz): δ (ppm) 7.62-7.59 (m, 1H), 7.53-7.49 (m, 3H), 7.46 -7.43 (m, 1H), 7.37 -7.29 (m, 4H), 7.26-7.25 (m, 1H), 7.20-7.16 (m, 1H), 6.77 (dd, J = 8.7, 3.1 Hz, 1H), 6.49 -6.47 (m, 1H), 6.27 (t, J = 0.9 Hz, 1H), 3.77 (s, 3H), 2.75 (d, J = 4.5 Hz, 1H). 13C {1H} NMR (CDCl₃, 100 MHz): δ (ppm) 159.3, 141.5, 140.9, 138.9, 133.36, 131.4, 128.4, 128.1, 127.3, 123.8, 122.5, 122.3, 121.3, 115.5, 114.2, 113.3, 111.3, 104.9, 78.8, 77.3, 68.7, 55.5. HRMS (ESI-TOF) m/z calcd for C₂₄H₁₉BrNO₂ [M + H]^+: 432.0599. Found: 432.0589.

p-Tolyl(1-(p-tolylethynyl)-1H-indol-2-yl)methanol (3g). The product was isolated by column chromatography (hexane/ethyl acetate 97:3 as eluent) as a white solid. Yield: 0.114 g (65%); mp 153-157 °C. 1H NMR (CDCl₃, 400 MHz): δ (ppm) 7.56-7.66 (m, 2H), 7.36-7.22 (m, 5H), 7.19-7.11 (m, 5H), 6.41 (s, 1H), 6.08 (s, 1H), 2.83 (s, 1H), 2.35 (s, 3H), 2.32 (s, 3H). 13C {1H} NMR (CDCl₃, 100 MHz): δ (ppm) 143.1, 138.7, 138.2, 137.8, 137.7, 131.3, 129.1, 129.1, 127.2, 126.9, 123.36, 122.1, 121.0, 119.2, 111.1, 103.6, 78.34, 74.02, 69.8, 21.4, 21.1. MS (EI. 70 eV. m/z (relative intensity)): 352 (26), 351 (100), 334 (50), 259 (36), 217 (29), 204 (27), 119 (34), 91(33). HRMS (ESI-TOF) m/z calcd for C₂₅H₂₂NO [M + H]^+: 352.1701. Found: 352.1710.

1-(p-Tolylethynyl)-1H-indole-2-carbaldehyde (3h). The product was isolated by column chromatography (hexane/ethyl acetate 97:3 as eluent) as an orange solid. Yield:
0.158 g (61%); mp 60-62 °C. \(^1\)H NMR (CDCl\(_3\), 400 MHz): \(\delta\) (ppm) 10.12 (s, 1H), 7.76-7.68 (m, 2H), 7.34 (s, 1H), 7.30 (t, \(J = 7.6\) Hz, 1H), 7.19 (d, \(J = 7.8\) Hz, 2H), 2.38 (s, 3H). \(^{13}\)C \(^1\)H NMR (CDCl\(_3\), 100 MHz): \(\delta\) (ppm) 181.0, 140.8, 138.6, 136.3, 131.5, 129.2, 128.0, 126.2, 123.6, 123.4, 119.0, 115.2, 112.3, 77.6, 73.8, 21.5. MS (EI. 70 eV. m/z (relative intensity)): 260 (18), 259 (100), 143 (68), 115 (62), 77 (3). HRMS (ESI-TOF) m/z calcd for C\(_{18}\)H\(_{14}\)NO [M + H]\(^+\): 260.1075. Found: 260.1080.

(1-((4-Chlorophenyl)ethynyl)-1H-indol-2-yl) methanol (3j). The product was isolated by column chromatography (hexane/ethyl acetate 97:3 as eluent) as a white solid. Yield: 0.070 g (50%); mp 80-82 °C. \(^1\)H NMR (CDCl\(_3\), 400 MHz): \(\delta\) (ppm) 7.61-7.57 (m, 2H), 7.50-7.46 (m, 2H), 7.37-7.32 (m, 3H), 7.25-7.21 (m, 1H), 6.58-6.57 (m, 1H), 4.91 (s, 2H), 1.64 (s, 1H). \(^{13}\)C \(^1\)H NMR (CDCl\(_3\), 100 MHz): \(\delta\) (ppm) 139.8, 138.7, 134.1, 132.6, 128.8, 127.4, 123.8, 122.4, 121.2, 120.9, 111.2, 104.8, 79.6, 72.6, 57.2. MS (EI. 70 eV. m/z (relative intensity)): 283 (57), 282 (24), 281 (100), 264 (24), 217 (56), 143 (28), 108 (22), 89 (19), 75 (11). HRMS (ESI-TOF) m/z calcd for C\(_{17}\)H\(_{13}\)ClNO [M + H]\(^+\): 282.0686. Found: 282.0691.

(1-(Phenylethynyl)-1H-indol-2-yl) methanol (3l). The product was isolated by column chromatography (hexane/ethyl acetate 97:3 as eluent) as a white solid. Yield: 0.069 g (56%); mp 84-87 °C. \(^1\)H NMR (CDCl\(_3\), 400 MHz): \(\delta\) (ppm) 7.61-7.51 (m, 4H); 7.37-7.28 (m, 4H); 7.22-7.17 (m, 1H), 6.53 (s, 1H), 4.88 (s, 2H), 2.11 (s, 1H). \(^{13}\)C \(^1\)H NMR (CDCl\(_3\), 100 MHz): \(\delta\) (ppm) 140.0, 138.8, 131.4, 128.4, 128.2, 127.5, 123.7, 122.4, 122.3, 121.1, 111.2, 104.5, 78.8, 73.7, 57.3. MS (EI. 70 eV. m/z (relative intensity)): 247 (100), 230 (29), 217 (44), 144 (16), 115 (17), 89 (18), 63 (10). HRMS (ESI-TOF) m/z calcd for C\(_{17}\)H\(_{14}\)NO [M + H]\(^+\): 248.1075. Found: 248.1090.

1-(Phenylethynyl)-1H-indole-2-carbaldehyde (3m). The product was isolated by column chromatography (hexane/ethyl acetate 97:3 as eluent) as an orange solid. Yield: 0.074 g (60%); mp 80-83 °C. \(^1\)H NMR (CDCl\(_3\), 400 MHz): \(\delta\) (ppm) 10.09 (s, 1H); 7.74-7.69 (m, 2H), 7.63-7.59 (m, 2H), 7.55-7.49 (m, 1H), 7.41-7.22 (m, 5H). \(^{13}\)C \(^1\)H NMR (CDCl\(_3\), 100 MHz): \(\delta\) (ppm) 180.9, 140.7, 136.2, 131.5, 128.4, 128.3, 128.1, 126.1, 123.6, 123.5, 122.1, 115.7, 112.2, 78.2, 73.6. MS (EI. 70 eV. m/z (relative intensity)): 246 (19), 245 (100), 207 (46), 143 (86), 115 (74), 89 (12), 63 (10). HRMS (ESI-TOF) m/z calcd for C\(_{17}\)H\(_{12}\)NO [M + H]\(^+\): 246.0919. Found: 246.0924.
Diphenyl (1-(phenylethynyl)-1H-indol-2-yl)methanol (3p). The product was isolated by column chromatography (hexane/ethyl acetate 97:3 as eluent) as a white solid. Yield: 0.090 g (45%); mp 151-153 °C. $^1$H NMR (CDCl$_3$, 400 MHz): δ (ppm) 7.59-7.56 (m, 1H), 7.47-7.40 (m, 5H), 7.38-7.29 (m, 7H), 7.25-7.17 (m, 4H), 7.04-7.00 (m, 2H), 5.93 (d, $J = 0.9$ Hz, 1H), 3.88 (s, 1H). $^{13}$C {$^1$H} NMR (CDCl$_3$, 100 MHz): δ (ppm) 145.2, 144.4, 139.4, 132.4, 131.1, 130.0, 128.2, 128.1 (2C), 127.7, 127.4 (2C), 126.6, 124.0, 122.4, 121.9, 121.3, 111.1, 108.8, 79.9, 78.6, 75.8. MS (EI, 70 eV, m/z (relative intensity)): 400 (26), 399 (77), 294 (81), 281 (100), 207 (83), 105 (40), 77 (38). HRMS (ESI-TOF) m/z calcd for C$_{29}$H$_{22}$N0 [M + H]$^+$: 400.1701. Found: 400.1710.

1-(Phenylethynyl)-2-(trimethylsilyl)-1H-indole (3q). The product was isolated by column chromatography (hexane was eluent) as a green solid. Yield: 0.130 g (90%); mp 58-61 °C. $^1$H NMR (CDCl$_3$, 400 MHz): δ (ppm) 8.10-7.96 (m, 4H), 7.84-7.73 (m, 4H), 7.67-7.60 (m, 1H), 7.18 (s, 1H), 0.90 (s, 9H). $^{13}$C {$^1$H} NMR (CDCl$_3$, 100 MHz): δ (ppm) 142.8, 141.3, 130.9, 128.5, 128.2, 127.8, 123.7, 123.0, 121.8, 120.9, 114.9, 111.1, 82.4, 71.6, -1.3. MS (EI, 70 eV, m/z (relative intensity)): 290 (27), 289 (100), 274 (55), 258 (12), 73 (20). HRMS (ESI-TOF) m/z calcd for C$_{19}$H$_{20}$NSi [M + H]$^+$: 290.1365. Found: 290.1377.

1-(Naphthalen-1-ylethynyl)-2-(trimethylsilyl)-1H-indole (3r). The product was isolated by column chromatography (hexane was eluent) as a green oil. Yield: 0.119 g (70%). $^1$H NMR (CDCl$_3$, 400 MHz): δ (ppm) 8.73-8.65 (m, 1H), 8.10-7.92 (m, 4H), 7.83-7.61 (m, 4H), 7.59-7.52 (m, 1H), 7.45-7.36 (m, 1H), 6.99 (d, $J = 0.9$ Hz, 1H), 0.68 (s, 9H). $^{13}$C {$^1$H} NMR (CDCl$_3$,100 MHz): δ (ppm) 142.9, 141.6, 133.4, 133.2, 130.1, 128.4, 126.8, 126.5, 126.2, 125.4, 123.9, 122.0, 121.0, 120.7, 115.2, 111.2, 86.9, 69.8, -1.2. MS (EI, 70 eV, m/z (relative intensity)): 340 (30), 339 (100), 324 (33), 308 (25), 154 (24), 73(35). HRMS (ESI-TOF) m/z calcd for C$_{23}$H$_{22}$NSi [M + H]$^+$: 340.1522. Found: 340.1530.

2-(tert-Butyldimethylsilyl)-1-(phenylethynyl)-1H-indole (3s). The product was isolated by column chromatography (hexane was eluent) as a green solid. Yield: 0.108 g (65%); mp 81-84 °C. $^1$H NMR (CDCl$_3$, 400 MHz): δ (ppm) 7.65-7.63 (m, 1H), 7.61-7.57 (m, 1H), 7.55-7.51 (m, 2H), 7.39-7.29 (m, 4H), 7.22-7.17 (m, 1H), 6.79 (d, $J = 0.9$ Hz, 1H), 1.01 (s, 9H), 0.46 (s, 6H). $^{13}$C {$^1$H} NMR (CDCl$_3$, 100 MHz): δ (ppm) 141.6, 140.7, 131.0, 128.5, 128.2, 127.8, 123.7, 123.1, 121.9, 120.8, 116.7, 111.2, 83.1, 71.6,
26.9, 17.5, -5.2. MS (EI. 70 eV. m/z (relative intensity)): 332 (14), 331 (44), 274 (100), 258 (12), 230 (9), 129 (4). HRMS (ESI-TOF) m/z calcd for C_{22}H_{20}NSi [M + H]^+: 332.1835. Found: 332.1841.

1-(Phenylethynyl)-2-(phenylthio)-1H-indole (3t). The product was isolated by column chromatography (hexane was eluent) as a yellow oil. Yield: 0.081 g (50 %). 1H NMR (CDCl_3, 400 MHz): δ (ppm) 7.59-7.56 (m, 2H), 7.37-7.13 (m, 12H), 6.93 (d, J = 0.8 Hz, 1H). 13C {1H} NMR (CDCl_3, 100 MHz): δ (ppm) 139.9, 135.4, 131.4, 130.6, 129.2, 128.7, 128.4, 128.0, 127.5, 126.7, 124.7, 122.6, 122.6, 121.1, 114.2, 111.7, 78.9, 75.1. MS (EI. 70 eV. m/z (relative intensity)): 326 (26), 325 (100), 291 (18), 204 (8), 146 (11), 89(9). HRMS (ESI-TOF) m/z calcd for C_{22}H_{16}NS [M + H]^+: 326.1003. Found: 326.1011.

1-(Phenylethynyl)-2-(phenylselanyl)-1H-indole (3v). The product was isolated by column chromatography (hexane was eluent) as a yellow oil. Yield: 0.102 g (55 %). 1H NMR (CDCl_3, 400 MHz): δ (ppm) 7.60-7.55 (m, 2H), 7.48-7.44 (m, 2H), 7.40-7.37 (m, 2H), 7.34-7.27 (m, 4H), 7.23-7.18 (m, 4H), 6.91 (d, J = 0.8 Hz, 1H). 13C {1H} NMR (CDCl_3, 100 MHz): δ (ppm) 140.0, 131.4, 131.3, 130.6, 129.3, 128.3, 127.9, 127.9, 127.2, 126.6, 124.2, 122.6, 122.3, 120.8, 114.9, 111.6, 79.6, 74.5. MS (EI. 70 eV. m/z (relative intensity)): 375 (17), 374 (23), 373 (90), 292 (100), 189 (22), 145(49), 89(29). HRMS (ESI-TOF) m/z calcd for C_{22}H_{16}NSe [M + H]^+: 374.0448. Found: 374.0460.

General procedure for the synthesis of 2-(2,2-dibromovinyl)-1-(phenylethynyl)-1H-indole (4a). To a Schlenck tube, under an ambient atmosphere, containing CBr_4 (2.2 mmol) in in CH_2Cl_2 (10 mL) and this solution was cooled to 0 °C. To this solution was added the PPh_3 (4.4 mmol), and the color of the reaction turned orange. After stirring the mixture for 10 minutes at that temperature, the corresponding N-alkynyl-1H-indole-2-carbaldehyde (1 mmol) was added dropwise to the solution at 0 °C. After stirring 2 h, the reaction mixture was diluted with pentane, the residue was purified by column chromatography over silica gel to provide 2-(2,2-dibromovinyl)-1-(phenylethynyl)-1H-indole (4a). 2-(2,2-Dibromovinyl)-1-(phenylethynyl)-1H-indole (4a). Was isolated by column chromatography (hexane was eluent) as a light yellow oil. Yield: 0.299 g (75%). 1H NMR (CDCl_3, 400 MHz): δ (ppm) 7.71-7.58 (m, 1H), 7.51-7.43 (m, 2H), 7.37-7.32 (m, 1H), 7.30-7.09 (m, 5H), 6.80-6.76 (m, 2H). 13C {1H} NMR (CDCl_3,100 MHz): δ (ppm) 137.1, 135.1, 133.0, 132.6, 129.2, 128.9, 128.6, 127.9, 125.6, 124.7, 114.2, 111.7, 78.9, 75.1. MS (EI. 70 eV. m/z (relative intensity)): 326 (26), 325 (100), 291 (18), 204 (8), 146 (11), 89(9). HRMS (ESI-TOF) m/z calcd for C_{22}H_{16}NS [M + H]^+: 326.1003. Found: 326.1011.
122.45, 121.6, 112.9, 111.2, 107.9, 91.4. HRMS (ESI-TOF) m/z calcd for C_{18}H_{12}Br_{2}N [M + H]^+: 399.9336. Found: 399.9345.

**General procedure for the synthesis of 3-phenyl-1-(1-(phenylethynyl)-1H-indol-2-yl)prop-2-yn-1-ol (4b).** To a solution of terminal alkyne (1.2 equiv) in THF (3 mL), was added n-BuLi (1.1 equiv, 2.5 M in hexane) slowly at -78 ºC. The reaction mixture was stirred at the same temperature for 30 min, the N-alkynyl-1H-indole-2-carbaldehyde (1 mmol) was added and the reaction mixture was warmed up to room temperature. After the reaction was completed as monitor by thin-layer chromatography (usually 1 h), the reaction mixture was quenched with H_{2}O and extraction with ethyl acetate (3 × 2 mL), the combined organic layers were dried over MgSO_{4}, and concentrated at reduced pressure to give. The residue was purified by column chromatography over silica gel to provide 3-phenyl-1-(1-(phenylethynyl)-1H-indol-2-yl)prop-2-yn-1-ol (4b). 3-Phenyl-1-(1-(phenylethynyl)-1H-indol-2-yl)prop-2-yn-1-ol (4b). The product was isolated by column chromatography (hexane/ethyl acetate 97:3 as eluent) as a brown solid. Yield: 0.243 g (70%); mp 116-119 ºC. \(^1\)H NMR (CDCl_{3}, 400 MHz): \(\delta\) (ppm) 7.64-7.57 (m, 2H), 7.56-7.52 (m, 2H), 7.48-7.46 (m, 2H), 7.36-7.26 (m, 7H), 7.23-7.19 (m, 1H), 6.81 (d, \(J = 0.9\) Hz, 1H), 6.02 (s, 1H), 2.65 (s, 1H). \(^13\)C \({^1\text{H}}\) NMR (CDCl_{3},100 MHz): \(\delta\) (ppm) 139.6, 139.2, 131.9, 131.5, 128.8, 128.5, 128.4, 128.2, 127.1, 124.2, 122.5, 121.5, 111.4, 104.6, 86.6, 86.45, 78.8, 74.4, 58.63. HRMS (ESI-TOF) m/z calcd for C_{25}H_{18}NO [M + H]^+: 348.1388. Found: 348.1394.

**General procedure for the synthesis of (Z)-(1-(2-phenyl-2-(phenyltellanyl)vinyl)-1H-indol-2-yl)(p-tolyl)methanol (4c).** To a solution of (4-chlorophenyl)(1-(phenylethynyl)-1H-indol-2-yl)methanol (3c) (0.25 mmol) in EtOH (3 mL), was added diorganoil diteluret (0.5 equiv), was added and the reaction mixture NaBH\(\_4\) ( 5 equiv) warmed up to room temperature. The reaction was refluxed for 5 h. The reaction mixture was extraction with NaCl\(_4\) and ethyl acetate (3 × 2 mL), the combined organic layers were dried over MgSO\(_4\), and concentrated at reduced pressure to give. The residue was purified by column chromatography over silica gel to provide (Z)-(1-(2-phenyl-2-(phenyltellanyl)vinyl)-1H-indol-2-yl)(p-tolyl)methanol (4c). (Z)-(1-(2-Phenyl-2-(phenyltellanyl)vinyl)-1H-indol-2-yl)(p-tolyl)methanol (4c). The product was isolated by column chromatography (hexane/ethyl acetate 97:3 as eluent) as a white.
solid. Yield: 0.126 g (70%); mp 67-69 °C. $^1$H NMR (CDCl$_3$, 400 MHz): δ (ppm) 7.67 (d, $J = 8.3$ Hz, 1H), 7.57 - 7.52 (m, 2H), 7.38 - 7.30 (m, 6H), 7.27 - 7.05 (m, 8H), 6.92 - 6.85 (m, 1H), 6.85 - 6.55 (m, 1H), 6.33 (s, 1H), 6.02 (s, 1H), 2.42 (s, 1H), 2.35 (s, 3H). $^{13}$C {$^1$H} NMR (CDCl$_3$, 100 MHz): δ (ppm) 141.5, 138.1, 137.9, 136.9, 135.9, 129.2, 129.0, 128.7, 128.5, 128.2, 127.4, 126.7, 126.7, 126.0, 124.3, 122.9, 122.4, 121.1, 120.8, 111.6, 104.3, 69.7, 21.1. HRMS (ESI-TOF) m/z calcd for C$_{30}$H$_{36}$NOTe [M + H]$^+$: 546.1077. Found: 546.1053.
The $^1$H (400 MHz) and $^{13}$C (100 MHz) spectra of 3a in CDCl$_3$. 
The $^1$H (400 MHz) and $^{13}$C (100 MHz) spectra of 3b in CDCl$_3$. 

S13
The $^1$H (400 MHz) and $^{13}$C (100 MHz) spectra of 3c in CDCl$_3$. 
The $^1$H (400 MHz) and $^{13}$C (100 MHz) spectra of 3d in CDCl$_3$. 

S15
The $^1$H (400 MHz) and $^{13}$C (100 MHz) spectra of 3e in CDCl$_3$. 

S16
The $^1$H (400 MHz) and $^{13}$C (100 MHz) spectra of 3f in CDCl$_3$. 
The $^1$H (400 MHz) and $^{13}$C (100 MHz) spectra of 3g in CDCl₃.
The $^1$H (400 MHz) and $^{13}$C (100 MHz) spectra of 3h in CDCl$_3$. 

S19
The $^1$H (400 MHz) and $^{13}$C (100 MHz) spectra of 3j in CDCl$_3$. 
The $^1$H (400 MHz) and $^{13}$C (100 MHz) spectra of 3i in CDCl$_3$. 
The $^1$H (400 MHz) and $^{13}$C (100 MHz) spectra of 3m in CDCl$_3$. 

S22
The $^1$H (400 MHz) and $^{13}$C (100 MHz) spectra of 3p in CDCl$_3$. 
The $^1$H (400 MHz) and $^{13}$C (100 MHz) spectra of 3q in CDCl$_3$. 
The $^1$H (400 MHz) and $^{13}$C (100 MHz) spectra of 3r in CDCl$_3$. 
The $^1$H (400 MHz) and $^{13}$C (100 MHz) spectra of 3s in CDCl$_3$. 
The $^1$H (400 MHz) and $^{13}$C (100 MHz) spectra of 3t in CDCl$_3$. 
The $^1$H (400 MHz) and $^{13}$C (100 MHz) spectra of $3v$ in CDCl$_3$. 
The $^1$H (400 MHz) and $^{13}$C (100 MHz) spectra of 4a in CDCl$_3$. 
The $^1$H (400 MHz) and $^{13}$C (100 MHz) spectra of 4b in CDCl$_3$. 
The $^1$H (400 MHz) and $^{13}$C (100 MHz) spectra of 4c in CDCl$_3$. 