Supporting Information for

Gold-catalyzed Deacylative Cycloisomerization Reactions of 3-Acrylindole/ynes: A New Approach for Carbazole Synthesis

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Experimental section

General Methods. All reactions were carried out under nitrogen. DCE and DCM were distilled from P₂O₅. THF was distilled from sodium and benzophenone. Unless noted, all commercial reagents were used as purchased without further purification. (p-CF₃C₆H₄)₃PAuCl¹ and PPh₃AuCl² were prepared according to published methods. AgOTf was purchased from Acros Chemical Company. (Acetonitrile)[(2-biphenyl)di-tert-butylphosphine]gold(I) hexafluoroantimonate was purchased from Aldrich Chemical Company. AgOTf was used as a 0.05 M solution in THF. 1,2-Dimethyl-1H-indole³ and acetylenic aldehydes⁴ were prepared by modified procedures according to published methods.

¹H and ¹³C NMR spectra were recorded at room temperature in CDCl₃ (containing
0.03% TMS) solutions on Varian XL-300 MHz spectrometer or Varian XL-400 MHz spectrometer. \(^1\)H NMR spectra was recorded at 300 or 400 MHz, \(^{13}\)C NMR spectra was recorded at 75.4 or 100.6 MHz. \(^1\)H NMR spectra was recorded with tetramethylsilane (\(\delta=0.00\) ppm) as internal reference; \(^{13}\)C NMR spectra was recorded with CDCl\(_3\) (\(\delta = 77.00\) ppm) as internal reference. High-resolution mass spectra was obtained by using Waters Micromass GCT mass spectrometer. Elemental analyses were performed on an Italian Carlo-Erba 1106 analyzer. Melting points were measured using a SGW-4 microscopic melting point apparatus and were uncorrected. Single crystal X-ray diffraction data was collected in Bruker SMART APEX diffractiometers with molybdenum cathodes.

**General procedure for the synthesis of 3-acylindoles 1a-1g.**

\[
\begin{align*}
\text{R}^1 & \quad \text{N} \\
\text{R}^2 & \quad \text{R}^3 \\
\end{align*}
\]

1) 1.5 equiv Et\(_2\)AlCl, in DCM, 0 °C, 30 min
2) 2.0 equiv \(\text{R}^3\)COCl, 0 °C, 3-4 h

**Typical procedure for the synthesis of 3-acylindole 1a:** To a CH\(_2\)Cl\(_2\) solution (30 mL) of 1,2-dimethyl indole (3.19 g, 22 mmol) was added 33 mL (33 mmol) of Et\(_2\)AlCl (1.0 M in hexane) at 0 °C. The mixture was stirred at 0 °C for 30 min. To this solution was added dropwise a CH\(_2\)Cl\(_2\) solution (15 mL) of isobutyryl chloride (4.6 mL, 44 mmol) at 0 °C. The resulting solution was stirred at 0 °C for 4 h, and pH 7 aqueous buffer was added to quench the reaction. Then the mixture was extracted with CH\(_2\)Cl\(_2\) and dried over Na\(_2\)SO\(_4\). The crude product was purified by chromatography on silica gel (petroleum: ethyl acetate = 20:1 to 10:1 to 5:1) to afford the 3-acylindole 1a (3.74 g, 79% yield) as a yellow solid.

\[
\begin{align*}
\text{N} & \quad \text{Pr} \\
\end{align*}
\]

**1-(1,2-Dimethyl-1H-indol-3-yl)-2-methylpropan-1-one (1a).** \(^1\)H NMR (CDCl\(_3\), Me\(_4\)Si, 400 MHz): \(\delta 1.27\) (d, \(J = 6.4\) Hz, 6H), 2.76 (s, 3H), 3.50-3.56 (m, 1H), 3.67 (s, 3H),
7.23-7.27 (m, 2H), 7.30-7.32 (m, 1H), 7.89-7.91 (m, 1H); \(^{13}\)C NMR (CDCl\(_3\), Me\(_4\)Si, 100 MHz): \(\delta\) 12.69, 18.86, 29.37, 38.71, 109.48, 112.82, 120.50, 121.72, 121.80, 125.55, 136.58, 145.60, 201.62. HRMS (EI) for C\(_{14}\)H\(_{17}\)NO: calcd 215.1310, found 215.1307.

(1,2-Dimethyl-1\(H\)-indol-3-yl)(phenyl)methanone (1b). Column chromatography on silica gel (eluent: petroleum ether / ethyl acetate = 20:1 to 3:1) afforded the title product in 91% yield as a pink solid. \(^1\)H NMR (CDCl\(_3\), Me\(_4\)Si, 400 MHz): \(\delta\) 2.55 (s, 3H), 3.69 (s, 3H), 7.03-7.08 (m, 1H), 7.17-7.21 (m, 1H), 7.28-7.32 (m, 2H), 7.41-7.45 (m, 2H), 7.50-7.55 (m, 1H), 7.73-7.76 (m, 2H); \(^{13}\)C NMR (CDCl\(_3\), Me\(_4\)Si, 100 MHz): \(\delta\) 12.45, 29.59, 109.07, 113.49, 120.85, 121.33, 121.95, 126.97, 128.14, 128.95, 131.35, 136.45, 141.37, 144.67, 192.81. The \(^1\)H NMR data is in agreement with that previously reported.\(^6\)

1-(1-Benzyl-2-methyl-1\(H\)-indol-3-yl)-2-methylpropan-1-one (1c). Column chromatography on silica gel (eluent: petroleum ether / ethyl acetate = 20:1 to 3:1) afforded the title product in 72% yield as a yellow solid. M.p. 72-74 °C. \(^1\)H NMR (CDCl\(_3\), Me\(_4\)Si, 400 MHz): \(\delta\) 1.29 (d, \(J = 6.8\) Hz, 6H), 2.73 (s, 3H), 3.52-3.62 (m, 1H), 5.35 (s, 2H), 6.98 (d, \(J = 6.4\) Hz, 2H), 7.19-7.29 (m, 6H), 7.95 (d, \(J = 7.6\) Hz, 2H); \(^{13}\)C NMR (CDCl\(_3\), Me\(_4\)Si, 100 MHz): \(\delta\) 12.77, 18.90, 38.84, 46.28, 109.97, 113.40, 120.66, 121.99, 122.05, 125.72, 125.85, 127.64, 128.91, 136.06, 136.45, 145.42, 201.90. HRMS (EI) for C\(_{20}\)H\(_{21}\)NO: calcd 291.1623, found 291.1620.
1-(5-Methoxy-1,2-dimethyl-1H-indol-3-yl)-2-methylpropan-1-one (1d). Column chromatography on silica gel (eluent: petroleum ether / ethyl acetate = 50:1 to 20:1 to 5:1) afforded the title product in 69% yield as a white solid. M.p. 58-60 °C. \(^1\)H NMR (CDCl\(_3\), Me\(_4\)Si, 400 MHz): \(\delta 1.27 (d, J = 6.8 \text{ Hz}, 6\text{H}), 2.75 (s, 3\text{H}), 3.41-3.51 (m, 1\text{H}), 3.67 (s, 3\text{H}), 3.89 (s, 3\text{H}), 6.89 (dd, \(J = 8.8, 2.4 \text{ Hz}, 1\text{H}\)), 7.21 (d, \(J = 8.8, 1\text{H}\)), 7.48 (d, \(J = 2.0 \text{ Hz}, 1\text{H}\)); \(^{13}\)C NMR (CDCl\(_3\), Me\(_4\)Si, 100 MHz): \(\delta 12.90, 18.87, 29.54, 38.44, 55.82, 103.97, 109.92, 110.71, 112.72, 126.49, 131.79, 145.42, 155.71, 201.30. HRMS (EI) for C\(_{15}\)H\(_{19}\)NO\(_2\): calcd 245.1416, found 245.1411.

2-Methyl-1-(2-methyl-1H-indol-3-yl)propan-1-one (1e). Column chromatography on silica gel (eluent: petroleum ether / ethyl acetate = 50:1 to 20:1 to 5:1) afforded the title product in 77% yield as a light yellow solid. \(^1\)H NMR (CDCl\(_3\), Me\(_4\)Si, 400 MHz): \(\delta 1.30 (d, J = 6.8 \text{ Hz}, 6\text{H}), 2.76 (s, 3\text{H}), 3.51-3.58 (m, 1\text{H}), 7.16-7.26 (m, 2\text{H}), 7.33-7.35 (m, 1\text{H}), 7.98 (d, \(J = 8.0 \text{ Hz}, 1\text{H}\)), 9.66 (s, 1\text{H}); \(^{13}\)C NMR (CDCl\(_3\), Me\(_4\)Si, 100 MHz): \(\delta 15.61, 18.93, 38.48, 111.23, 113.03, 120.65, 121.93, 122.14, 126.41, 134.84, 144.87, 202.43. LRMS (EI) \(m/z\) 201 (M\(^+\)).

1-(1,2-Dimethyl-1H-indol-3-yl)-3-methylbutan-1-one (1f). Column chromatography on
silica gel (eluent: petroleum ether / ethyl acetate = 15:1 to 10:1) afforded the title product in 76% yield as a white solid. M.p. 82-84 °C. ¹H NMR (CDCl₃, Me₄Si, 400 MHz): δ 1.03 (d, J = 6.8 Hz, 6H), 2.32-2.42 (m, 1H), 2.76 (s, 3H), 2.87 (d, J = 6.8 Hz, 2H), 3.67 (s, 3H), 7.23-7.26 (m, 2H), 7.30-7.33 (m, 1H), 7.92-7.94 (m, 1H); ¹³C NMR (CDCl₃, Me₄Si, 100 MHz): δ 12.65, 22.86, 24.75, 29.38, 52.25, 109.46, 114.18, 120.63, 121.72, 121.76, 125.88, 136.53, 144.96, 197.09; HRMS (EI) for C₁₅H₁₉NO: calcd 229.1467, found 229.1466.

1-(1-Allyl-2-methyl-1H-indol-3-yl)-2-methylpropan-1-one (1g). It was prepared from 1-allyl-2-methyl-1H-indole (containing small amount of impurity) according to the procedure described for 1a. Column chromatography on silica gel (eluent: petroleum ether / ethyl acetate = 50:1 to 20:1 to 5:1) afforded the title product in 51% yield as a light yellow oil. ¹H NMR (CDCl₃, Me₄Si, 400 MHz): δ 1.28 (d, J = 6.4 Hz, 6H), 2.74 (s, 3H), 3.51-3.58 (m, 1H), 4.71-4.73 (m, 2H), 4.84 (dd, J = 16.8, 0.8 Hz, 1H), 5.15 (dd, J = 10.4, 0.8 Hz, 1H), 5.87-5.95 (m, 1H), 7.20-7.29 (m, 3H), 7.91-7.93 (m, 1H); ¹³C NMR (CDCl₃, Me₄Si, 100 MHz): δ 12.43, 18.56, 38.75, 44.95, 109.74, 113.13, 116.93, 120.57, 121.84, 125.64, 131.61, 136.02, 145.23, 201.78; HRMS (EI) for C₁₆H₁₉NO: calcd 241.1467, found 241.1464.

General procedure for the synthesis of 3-acylindole/ynes 3a-3q.

Typical procedure for the synthesis of 1-(2-(2-hydroxy-4-phenylbut-3-ynyl)-1-methyl-1H-indol-3-yl)-2-methylpropan-1-one (3a): To a solution of diisopropylamine (5.25 mmol, 0.74 mL) in THF (15 mL) was added n-BuLi (5.25 mmol, 2.2 mL, 2.4 M in
hexane) slowly at -78 °C. The reaction mixture was stirred at the same temperature for 40 min, then 1-(1,2-dimethyl-1H-indol-3-yl)-2-methylpropan-1-one (1a) (5.0 mmol, 1.08 g) was added and stirred at -78 °C for 40 min. 3-Phenylpropionaldehyde (6 mmol, 0.78 g) was added and the reaction mixture was warmed up to room temperature. After stirring for 4 hours, the reaction mixture was quenched with a saturated aqueous solution of NH₄Cl, and extracted with Et₂O. The extract was washed with brine and dried over Na₂SO₄. The solvent was evaporated in vacuo and the residue was purified by chromatography on silica gel (petroleum ether/ethyl acetate = 20:1 to 10:1 to 5:1) followed by recrystallization to afford 3-acylindole/yne 3a as a light yellow solid in 69% yield.

(3a). M.p. 134-136 °C. ¹H NMR (CDCl₃, Me₄Si, 300 MHz): δ 1.28 (d, J = 6.9 Hz, 3H), 1.29 (d, J = 6.3 Hz, 3H), 3.58-3.67 (m, 3H), 3.85 (s, 3H), 5.07 (q, J = 5.4 Hz, 1H), 5.40 (d, J = 4.8 Hz, 1H), 7.25-7.33 (m, 5H), 7.36-7.39 (m, 3H), 7.82-7.85 (m, 1H); ¹³C NMR (CDCl₃, Me₄Si, 75 MHz): δ 18.79, 19.01, 30.28, 34.00, 38.75, 62.40, 84.77, 89.89, 110.21, 115.08, 120.38, 122.30, 122.42, 122.52, 125.04, 128.20, 128.33, 131.55, 137.09, 144.25, 203.47; Anal. calcd for C₂₃H₂₃NO₂: C, 79.97; H, 6.71; N, 4.05; found C, 79.84; H, 6.74; N, 3.86.

(2-(2-Hydroxy-4-phenylbut-3-ynyl)-1-methyl-1H-indol-3-yl)(phenyl)methanone  (3b). Recrystallization (ethyl acetate/petroleum ether) afforded the title product in 70% yield as a light yellow solid. M.p. 160-162 °C. ¹H NMR (CDCl₃, Me₄Si, 400 MHz): δ 3.58-3.72 (m, 2H), 3.89 (s, 3H), 5.07-5.09 (m, 1H), 5.98 (d, J = 4.8 Hz, 1H), 6.95 (d, J = 8.0 Hz, 1H),
7.02 (t, J = 8.0 Hz, 1H), 7.20-7.29 (m, 4H), 7.34-7.46 (m, 5H), 7.57 (t, J = 7.6 Hz, 1H),
7.81 (d, J = 7.6 Hz, 2H); $^{13}$C NMR (CDCl$_3$, Me$_4$Si, 100 MHz): δ 30.46, 33.80, 62.20, 84.80,
90.00, 109.82, 115.52, 120.96, 122.48, 122.62, 126.54, 128.20, 128.32, 129.81,
131.59, 132.26, 136.92, 139.93, 143.97, 193.26; HRMS (EI) for C$_{26}$H$_{21}$NO$_2$: calcd
379.1572, found 379.1574.

1-(2-(2-Hydroxy-4-$p$-tolylbut-3-ynyl)-1-methyl-$1H$-indol-3-yl)-2-methylpropan-1-one (3c).
Recrystallization (ethyl acetate/petroleum ether) afforded the title product in 66% yield as a light yellow solid. M.p. 172-174 °C. $^1$H NMR (CDCl$_3$, Me$_4$Si, 400 MHz): δ 1.27
d (d, J = 6.8 Hz, 3H), 1.28 (d, J = 6.8 Hz, 3H), 2.30 (s, 3H), 3.59-3.64 (m, 3H), 3.81 (s, 3H),
5.04-5.08 (m, 1H), 5.26 (d, J = 4.8 Hz, 1H), 7.06 (d, J = 7.6 Hz, 2H), 7.24-7.29 (m, 4H),
7.34-7.36 (m, 1H), 7.81-7.83 (m, 1H); $^{13}$C NMR (CDCl$_3$, Me$_4$Si, 100 MHz): δ 18.77, 18.96,
21.34, 30.20, 34.12, 38.70, 62.40, 84.90, 89.25, 110.16, 114.92, 119.37, 120.34, 122.21,
122.42, 125.06, 128.92, 131.41, 137.08, 138.36, 144.38, 203.22; HRMS (EI) for
C$_{24}$H$_{25}$NO$_2$: calcd 359.1885, found 359.1886.

1-(2-(4-(4-Chlorophenyl)-2-hydroxybut-3-ynyl)-1-methyl-$1H$-indol-3-yl)-2-methylpropan-1-one (3d).
Column chromatography on silica gel (petroleum ether/ethyl acetate = 20:1 to 3:1) followed by recrystallization afforded the title product in 48% yield as a white solid. M.p. 126-127 °C. $^1$H NMR (CDCl$_3$, Me$_4$Si, 400 MHz): δ 1.28 (d, J = 6.4 Hz, 3H),
1.29 (d, J = 6.8 Hz, 3H), 3.58-3.70 (m, 3H), 3.84 (s, 3H), 5.02-5.06 (m, 1H), 5.29 (d, J =
4.8 Hz, 1H), 7.24-7.32 (m, 6H), 7.36-7.39 (m, 1H), 7.81-7.84 (m, 1H); $^{13}$C NMR (CDCl$_3$,
Me₄Si, 100 MHz): δ 18.80, 19.03, 30.25, 34.02, 38.81, 62.42, 83.73, 90.96, 110.20, 115.19, 120.44, 120.99, 122.38, 122.62, 125.09, 128.60, 132.83, 134.41, 137.14, 144.12, 203.51; HRMS (EI) for C₂₃H₂₂NO₂Cl: calcd 379.1339, found 379.1344.

1-(2-(4-(4-Bromophenyl)-2-hydroxybut-3-ynyl)-1-methyl-1H-indol-3-yl)-2-methylpropan-1-one (3e). Column chromatography on silica gel (petroleum ether/ethyl acetate = 20:1 to 10:1 to 3:1) followed by recrystallization afforded the title product as a light yellow solid in 55% yield. M.p. 153-155 °C. ¹H NMR (CDCl₃, Me₄Si, 300 MHz): δ 1.27 (d, J = 6.6 Hz, 6H), 3.56-3.70 (m, 3H), 3.82 (s, 3H), 5.04 (q, J = 4.8 Hz, 1H), 5.44 (d, J = 5.1 Hz, 1H), 7.20 (d, J = 8.4 Hz, 2H), 7.28-7.39 (m, 5H), 7.81-7.84 (m, 1H); ¹³C NMR (CDCl₃, Me₄Si, 75 MHz): δ 18.79, 19.03, 30.25, 33.97, 38.80, 62.42, 83.78, 91.14, 110.20, 115.19, 120.44, 121.44, 122.38, 122.62, 122.64, 125.07, 131.52, 133.03, 137.12, 144.09, 203.53; HRMS (EI) for C₂₃H₂₂BrNO₂: calcd 423.0834, found 423.0837.

1-(2-(2-Hydroxy-4-(thien-2-yl)but-3-ynyl)-1-methyl-1H-indol-3-yl)-2-methylpropan-1-one (3f). Column chromatography on silica gel (petroleum ether/ethyl acetate = 20:1 to 10:1 to 3:1) followed by recrystallization afforded the title product as a light yellow solid in 55% yield. M.p. 98-100 °C. ¹H NMR (CDCl₃, Me₄Si, 300 MHz): δ 1.29 (d, J = 6.6 Hz, 3H), 1.30 (d, J = 6.3 Hz, 3H), 3.61-3.67 (m, 3H), 3.87 (s, 3H), 5.06-5.12 (m, 1H), 5.43 (d, J = 4.8 Hz, 1H), 6.95 (q, J = 3.6 Hz, 1H), 7.17 (d, J = 3.3 Hz, 1H), 7.23-7.25 (m, 1H), 7.29-7.34 (m, 2H), 7.38-7.42 (m, 1H), 7.83-7.86 (m, 1H); ¹³C NMR (CDCl₃, Me₄Si, 75
MHz): δ 18.81, 19.01, 30.28, 33.98, 38.75, 78.25, 93.73, 110.25, 115.15, 120.41, 122.33, 122.40, 122.57, 125.08, 126.90, 127.19, 132.20, 137.16, 144.07, 203.46; HRMS (EI) for C_{21}H_{21}NO_{2}S: calcd 351.1293, found 351.1295.

![Image of 3g](image-url)

1-(2-(2-Hydroxydec-3-ynyl)-1-methyl-1H-indol-3-yl)-2-methylpropan-1-one (3g). Column chromatography on silica gel (petroleum ether/ethyl acetate = 20:1 to 10:1 to 3:1) afforded the title product in 77% yield as a light yellow solid. M.p. 95-97 °C. ^1H NMR (CDCl₃, Me₄Si, 400 MHz): δ 0.87 (t, J = 6.4 Hz, 3H), 1.25-1.35 (m, 12H), 1.42-1.50 (m, 2H), 2.15-2.20 (m, 2H), 3.48-3.64 (m, 3H), 3.82 (s, 3H), 4.80-4.82 (m, 1H), 4.91 (d, J = 4.8 Hz, 1H), 7.26-7.29 (m, 2H), 7.36-7.38 (m, 1H), 7.80-7.83 (m, 1H); ^13C NMR (CDCl₃, Me₄Si, 100 MHz): δ 14.00, 18.74, 18.77, 19.00, 22.44, 28.45, 28.54, 30.23, 31.26, 34.42, 38.72, 62.11, 80.88, 85.64, 110.12, 114.88, 120.38, 122.19, 122.38, 125.12, 137.07, 144.67, 203.15; HRMS (EI) for C_{23}H_{31}NO_{2}: calcd 353.2355, found 353.2356.

![Image of 3h](image-url)

1-(2-(2-Hydroxy-4-phenylbut-3-ynyl)-5-methoxy-1-methyl-1H-indol-3-yl)-2-methylpropan-1-one (3h). Column chromatography on silica gel (petroleum ether/ethyl acetate = 50:1 to 20:1 to 10:1 to 3:1) afforded the title product as a light yellow solid in 54% yield. M.p. 142-144 °C. ^1H NMR (CDCl₃, Me₄Si, 400 MHz): δ 1.28 (d, J = 6.8 Hz, 3H), 1.29 (d, J = 6.8 Hz, 3H), 3.52-3.67 (m, 3H), 3.82 (s, 3H), 3.89 (s, 3H), 5.03-5.08 (m, 1H), 5.27 (d, J = 4.8 Hz, 1H), 6.94 (dd, J = 8.8, 2.0 Hz, 1H), 7.25-7.30 (m, 5H), 7.36-7.39 (m, 2H); ^13C NMR (CDCl₃, Me₄Si, 100 MHz): δ 18.73, 18.92, 30.35, 34.21, 38.55, 55.88, 62.43, 84.77, 89.98, 103.83, 110.77, 111.29, 114.79, 122.49, 125.82, 128.19, 128.29, 131.55, 132.38,
144.62, 155.93, 202.97; HRMS (EI) for C_{24}H_{25}NO_{3}: calcd 375.1834, found 375.1832.

1-(1-Allyl-2-(2-hydroxy-4-phenylbut-3-ynyl)-1H-indol-3-yl)-2-methylpropan-1-one (3i). Column chromatography on silica gel (petroleum ether/ethyl acetate = 50:1 to 20:1 to 10:1 to 5:1) afforded the title product as a yellow sticky oil in 68% yield. \(^1\)H NMR (CDCl\textsubscript{3}, Me\textsubscript{4}Si, 300 MHz): \(\delta\) 1.28 (d, \(J = 6.8\) Hz, 3H), 1.29 (d, \(J = 6.4\) Hz, 3H), 3.52-3.68 (m, 3H), 4.79-4.89 (m, 2H), 5.01-5.08 (m, 2H), 5.16 (d, \(J = 8.1\) Hz, 1H), 5.26 (d, \(J = 4.8\) Hz, 1H), 5.90-5.99 (m, 1H), 7.24-7.34 (m, 6H), 7.38-7.40 (m, 2H), 7.83-7.85 (m, 1H); \(^{13}\)C NMR (CDCl\textsubscript{3}, Me\textsubscript{4}Si, 100 MHz): \(\delta\) 18.76, 19.04, 33.95, 38.79, 45.50, 62.44, 84.80, 90.01, 110.58, 115.33, 117.05, 120.48, 122.30, 122.48, 122.60, 125.19, 128.18, 128.31, 131.59, 131.85, 136.40, 143.98, 203.50; HRMS (EI) for C_{25}H_{25}NO_{2}: calcd 371.1885, found 371.1887.

1-(1-Benzyl-2-(2-hydroxy-4-phenylbut-3-ynyl)-1H-indol-3-yl)-2-methylpropan-1-one (3j). Column chromatography on silica gel (petroleum ether/ethyl acetate = 50:1 to 20:1 to 10:1) afforded the title product as a yellow solid in 76% yield. M.p. 144-146 °C. \(^1\)H NMR (CDCl\textsubscript{3}, Me\textsubscript{4}Si, 300 MHz): \(\delta\) 1.30 (d, \(J = 6.4\) Hz, 3H), 1.31 (d, \(J = 6.8\) Hz, 3H), 3.54-3.68 (m, 3H), 4.94-4.96 (m, 1H), 5.24 (d, \(J = 4.4\) Hz, 1H), 5.56 (abq, \(J = 17.6\) Hz, 2H), 6.93 (d, \(J = 6.0\) Hz, 2H), 7.18-7.30 (m, 9H), 7.36-7.38 (m, 2H), 7.86 (d, \(J = 8.0\) Hz, 1H); \(^{13}\)C NMR (CDCl\textsubscript{3}, Me\textsubscript{4}Si, 100 MHz): \(\delta\) 18.75, 19.03, 34.14, 38.79, 46.70, 62.32, 84.77, 90.01, 110.77, 115.40, 120.48, 122.35, 122.42, 122.72, 125.20, 125.64, 127.66, 128.14, 128.25, 128.89, 131.52, 135.94, 136.67, 144.24, 203.48; HRMS (EI) for C_{29}H_{27}NO_{2}: calcd 421.2042, found 421.2037.
1-(2-(2-Hydroxy-4-phenylbut-3-ynyl)-1H-indol-3-yl)-2-methylpropan-1-one (3k). 2.0 equiv of LDA was used. Column chromatography on silica gel (petroleum ether/ethyl acetate/DCM = 10:1:1 to 6:1:1 to 4:1:1 to 2:1:1 to 1:1:1) afforded the title product as a brown solid in 60% yield. M.p. 178-180 °C. $^1$H NMR spectra was recorded with CD$_3$COCD$_3$ ($\delta = 2.09$ ppm) as internal reference; $^{13}$C NMR spectra was recorded with CD$_3$COCD$_3$ ($\delta = 205.87$ ppm) as internal reference. $^1$H NMR (CD$_3$COCD$_3$, 400 MHz): $\delta$ 1.27 (d, $J = 6.4$ Hz, 3H), 1.271 (d, $J = 6.8$ Hz, 3H), 3.60-3.72 (m, 3H), 5.08-5.13 (m, 1H), 5.26 (d, $J = 5.6$ Hz, 1H), 7.21-7.28 (m, 2H), 7.34-7.41 (m, 5H), 7.55-7.57 (m, 1H), 7.95-7.97 (m, 1H), 11.11 (s, 1H); $^{13}$C NMR (CD$_3$COCD$_3$, 100 MHz): $\delta$ 18.79, 37.66, 38.84, 61.85, 84.34, 91.23, 112.19, 113.78, 120.80, 121.96, 122.42, 123.36, 126.29, 128.72, 128.81, 131.84, 136.02, 144.50, 201.39, 205.87; HRMS (EI) for C$_{22}$H$_{21}$NO$_2$: calcld 331.1572, found 331.1575.

(2-(2-Hydroxydec-3-ynyl)-1-methyl-1H-indol-3-yl)(phenyl)methanone (3l). Column chromatography on silica gel (petroleum ether/ethyl acetate = 20:1 to 10:1 to 5:1 to 2:1) afforded the title product as a yellow solid in 69% yield. M.p. 93-95 °C. $^1$H NMR (CDCl$_3$, Me$_4$Si, 400 MHz): $\delta$ 0.87 (t, $J = 6.4$ Hz, 3H), 1.26-1.37 (m, 6H), 1.42-1.51 (m, 2H), 2.19 (t, $J = 6.8$ Hz, 2H), 3.46-3.61 (m, 2H), 3.88 (s, 3H), 4.83 (s, 1H), 5.55 (d, $J = 3.6$ Hz, 1H), 6.94 (d, $J = 8.0$ Hz, 1H), 7.01 (t, $J = 7.6$ Hz, 1H), 7.20-7.25 (m, 1H), 7.35 (d, $J = 8.4$ Hz, 1H), 7.45 (t, $J = 7.6$ Hz, 2H), 7.58 (t, $J = 7.2$ Hz, 1H), 7.80 (d, $J = 7.2$ Hz, 2H); $^{13}$C NMR (CDCl$_3$, Me$_4$Si, 100Mz) : $\delta$ 13.99, 18.76, 22.44, 28.47, 28.55, 30.42, 31.27, 34.19, 61.91,
80.97, 85.69, 109.74, 115.37, 120.97, 121.52, 122.51, 126.60, 128.19, 129.77, 132.18, 136.88, 140.08, 144.34, 193.18; HRMS (EI) for C_{26}H_{29}NO_{2}: calcd 387.2198, found 387.2200.

1-(2-(2-Hydroxydec-3-ynyl)-1-methyl-1H-indol-3-yl)-3-methylbutan-1-one (3m).

Column chromatography on silica gel (petroleum ether/ethyl acetate = 20:1 to 10:1 to 5:1) afforded the title product as a light yellow solid in 79% yield. M.p. 63-64 °C. \(^1^H\) NMR (CDCl\(_3\), Me\(_4\)Si, 400 MHz): δ 0.86 (t, \(J = 6.4\) Hz, 3H), 1.01 (d, \(J = 6.8\) Hz, 3H), 1.02 (d, \(J = 6.4\) Hz, 3H), 1.18-1.35 (m, 6H), 1.42-1.49 (m, 2H), 2.18 (td, \(J = 2.0, 6.8\) Hz, 2H), 2.32-2.39 (m, 1H), 2.88-2.98 (m, 2H), 3.48-3.59 (m, 2H), 3.81 (s, 3H), 4.80-4.84 (m, 1H), 4.95 (d, \(J = 4.8\) Hz, 1H), 7.25-7.30 (m, 2H), 7.34-7.38 (m, 1H), 7.80-7.84 (m, 1H); \(^1^3^C\) NMR (CDCl\(_3\), Me\(_4\)Si, 100 MHz): δ 13.97, 18.70, 22.41, 22.74, 22.76, 24.83, 28.42, 28.51, 30.15, 31.23, 34.34, 51.86, 62.10, 80.85, 85.62, 110.09, 115.98, 120.48, 122.08, 122.36, 125.41, 137.00, 144.16, 198.56; HRMS (EI) for C_{24}H_{33}NO_{2}: calcd 367.2511, found 367.2518.

1-(2-(2-Hydroxyhept-3-ynyl)-1-methyl-1H-indol-3-yl)-2-methylpropan-1-one (3n).

Column chromatography on silica gel (petroleum ether/ethyl acetate = 20:1 to 15:1 to 10:1 to 5:1) afforded the title product as a light yellow solid in 78% yield. M.p. 65-67 °C. \(^1^H\) NMR (CDCl\(_3\), Me\(_4\)Si, 400 MHz): δ 0.92 (t, \(J = 7.6\) Hz, 3H), 1.26 (d, \(J = 6.6\) Hz, 3H), 1.27 (d, \(J = 6.8\) Hz, 3H), 1.45-1.54 (m, 2H), 2.16 (td, \(J = 1.6, 6.8\) Hz, 2H), 3.44-3.64 (m, 3H),
3.81 (s, 3H), 4.79-4.83 (m, 1H), 4.95 (d, $J = 4.8$ Hz, 1H), 7.26-7.30 (m, 2H), 7.35-7.39 (m, 1H), 7.79-7.83 (m, 1H); $^{13}$C NMR (CDCl$_3$, Me$_4$Si, 100 MHz): $\delta$ 13.43, 18.72, 18.95, 20.65, 21.84, 30.18, 34.42, 38.67, 62.04, 81.03, 85.34, 110.08, 114.75, 120.31, 122.13, 122.32, 125.06, 137.02, 144.68, 203.06; HRMS (EI) for C$_{20}$H$_{25}$NO$_2$: calcd 311.1885, found 311.1883.

1-(2-(2-Hydroxy-6-phenylhex-3-ynyl)-1-methyl-1H-indol-3-yl)-2-methylpropan-1-one (3o). Column chromatography on silica gel (petroleum ether/ethyl acetate = 20:1 to 7:1) afforded the title product as a light yellow solid in 74% yield. M.p. 90-92 °C. $^1$H NMR (CDCl$_3$, Me$_4$Si, 400 MHz): $\delta$ 1.26 (d, $J = 6.8$ Hz, 3H), 1.27 (d, $J = 6.8$ Hz, 3H), 2.48 (td, $J = 2.0$, 8.0 Hz, 2H), 2.80 (t, $J = 7.6$ Hz, 2H), 3.44-3.54 (m, 2H), 3.56-3.63 (m, 1H), 3.70 (s, 3H), 4.79-4.80 (m, 1H), 4.96 (d, $J = 3.2$ Hz, 1H), 7.17-7.21 (m, 3H), 7.24-7.30 (m, 4H), 7.33-7.35 (m, 1H), 7.80-7.83 (m, 1H); $^{13}$C NMR (CDCl$_3$, Me$_4$Si, 100Mz): $\delta$ 18.71, 18.93, 20.83, 29.99, 34.30, 34.71, 38.64, 61.95, 81.65, 84.62, 110.13, 114.68, 120.28, 122.13, 122.30, 125.01, 126.14, 128.22, 128.28, 136.96, 140.42, 144.56, 203.03; HRMS (EI) for C$_{25}$H$_{27}$NO$_2$: calcd 373.2042, found 373.2043.

1-(2-(6-(Benzyloxy)-2-hydroxyhex-3-ynyl)-1-methyl-1H-indol-3-yl)-2-methylpropan-1-one (3p). Column chromatography on silica gel (petroleum ether/ethyl acetate = 10:1 to 8:1 to 6:1 to 4:1 to 2:1 to 1:1) afforded the title product as a yellow sticky oil in 59% yield. $^1$H NMR (CDCl$_3$, Me$_4$Si, 300Mz): $\delta$ 1.25 (d, $J = 6.6$ Hz, 3H), 1.26 (d, $J = 6.9$ Hz, 3H), 2.48-2.52 (m, 2H), 3.50-3.61 (m, 5H), 3.76 (s, 3H), 4.48 (s, 2H), 4.80 (d, $J = 3.9$ Hz, 1H),
5.03 (d, J = 4.2 Hz, 1H), 7.25-7.31 (m, 8H), 7.79-7.82 (m, 1H); $^{13}$C NMR (CDCl$_3$, Me$_4$Si, 75Mz): $\delta$ 18.73, 18.94, 20.05, 30.15, 34.22, 38.65, 61.96, 68.10, 72.77, 82.02, 82.08, 110.12, 114.74, 120.28, 122.13, 122.32, 125.03, 127.56, 127.58, 128.28, 137.01, 137.88, 144.52, 203.05; HRMS (EI) for C$_{26}$H$_{29}$NO$_3$: calcd 403.2147, found 403.2151.

**General procedure for the synthesis of 3-acylindoleynes 5a-5o.**

![General procedure for the synthesis of 3-acylindoleynes](image)

**Typical procedure for the synthesis of 1-(3-Benzoyl-1-methyl-1H-indol-2-yl)-4-phenylbut-3-yn-2-one (5b):** To a solution of (2-(2-hydroxy-4-phenylbut-3-ynyl)-1-methyl-1H-indol-3-yl)(phenyl)methanone (3b) (0.38 g, 1.0 mmol) in CH$_2$Cl$_2$ (5 mL) was added a solution of DMP (0.47 g, 1.1 mmol) in CH$_2$Cl$_2$ (5 mL) at room temperature. The reaction mixture was stirred until 3b was disappeared. Then the reaction was quenched by water and filtered. The mixture was extracted with CH$_2$Cl$_2$ and dried over Na$_2$SO$_4$. The solvent was evaporated in vacuo and the residue was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 5:1 to 3:1 to 2:1 to 1:1 to 2:1) to afford 5b as an orange solid in 74% yield.

![Typical procedure for the synthesis of 1-(3-Benzoyl-1-methyl-1H-indol-2-yl)-4-phenylbut-3-yn-2-one](image)

**1-(3-Benzoyl-1-methyl-1H-indol-2-yl)-4-phenylbut-3-yn-2-one (5b).** M.p. 180-182 °C. $^1$H NMR (CDCl$_3$, Me$_4$Si, 400 MHz): $\delta$ 3.76 (s, 3H), 4.57 (s, 2H), 7.07 (t, J = 7.6 Hz, 1H), 7.20-7.29 (m, 4H), 7.34-7.43 (m, 6H), 7.53 (t, J = 7.2 Hz, 1H), 7.78 (d, J = 6.8 Hz, 2H); $^{13}$C NMR (CDCl$_3$, Me$_4$Si, 100 MHz): $\delta$ 30.17, 42.33, 87.28, 93.12, 109.63, 115.15, 119.34, 121.29, 121.59, 122.73, 126.58, 128.24, 128.49, 129.15, 130.93, 131.74, 133.22, 136.93, 139.01, 140.83, 182.08, 192.60; HRMS (EI) for C$_{26}$H$_{19}$NO$_2$: calcd 377.1416, found
1-(3-Isobutryl-1-methyl-1H-indol-2-yl)-4-phenylbut-3-yn-2-one (5a). 1.8 equiv DMP was used. Column chromatography on silica gel (petroleum ether/ethyl acetate = 20:1 to 10:1 to 5:1) afforded the title product as a light red solid in 62% yield. M.p. 143-145 °C. $^1$H NMR (CDCl$_3$, Me$_4$Si,400 MHz): $\delta$ 1.27 (d, $J = 6.8$ Hz, 6H), 3.54-3.61 (m, 1H), 3.71 (s, 3H), 4.77 (s, 2H), 7.28-7.32 (m, 4H), 7.39-7.42 (m, 4H), 7.89-7.91 (m, 1H); $^{13}$C NMR (CDCl$_3$, Me$_4$Si, 100 MHz): $\delta$ 18.70, 29.77, 38.98, 42.73, 87.44, 92.51, 110.07, 114.10, 119.54, 120.75, 122.17, 122.49, 124.98, 130.82, 133.15, 137.09, 140.09, 182.29, 201.45; HRMS (EI) for C$_{23}$H$_{21}$NO$_2$: calcd 343.1572, found 343.1577.

1-(3-Isobutryl-1-methyl-1H-indol-2-yl)-4-p-tolybut-3-yn-2-one (5c). Column chromatography on silica gel (petroleum ether/ethyl acetate = 20:1 to CH$_2$Cl$_2$) afforded the title product as an orange solid in 75% yield. M.p. 150-152 °C. $^1$H NMR (CDCl$_3$, Me$_4$Si, 400 MHz): $\delta$ 1.27 (d, $J = 7.2$ Hz, 6H), 2.34 (s, 3H), 3.54-3.61 (m, 1H), 3.71 (s, 3H), 4.76 (s, 2H), 7.11 (d, $J = 8.0$ Hz, 2H), 7.27-7.32 (m, 4H), 7.38-7.41 (m, 1H), 7.89-7.91 (m, 1H); $^{13}$C NMR (CDCl$_3$, Me$_4$Si, 100 MHz): $\delta$ 18.71, 21.67, 29.79, 38.97, 42.70, 87.32, 93.30, 110.06, 114.09, 116.41, 120.74, 122.14, 122.46, 125.01, 129.30, 133.21, 137.08, 140.23, 141.62, 182.32, 201.45; HRMS (EI) for C$_{24}$H$_{23}$NO$_2$: calcd 357.1729, found 357.1733.
4-(4-Chlorophenyl)-1-(3-isobutyryl-1-methyl-1H-indol-2-yl)but-3-yn-2-one (5d). Column chromatography on silica gel (petroleum ether/ethyl acetate = 20:1 to 10:1 to 5:1) afforded the title product as a light red solid in 74% yield. M.p. 137-139 °C. $^1$H NMR (CDCl$_3$, Me$_4$Si, 400 MHz): $\delta$ 1.26 (d, $J = 6.8$ Hz, 6H), 3.53-3.63 (m, 1H), 3.72 (s, 3H), 4.75 (s, 2H), 7.27-7.33 (m, 6H), 7.39-7.41 (m, 1H), 7.89-7.91 (m, 1H); $^{13}$C NMR (CDCl$_3$, Me$_4$Si, 100 MHz): $\delta$ 18.70, 29.79, 38.99, 42.70, 88.09, 91.02, 110.09, 114.09, 118.02, 120.76, 122.24, 122.56, 124.93, 128.98, 134.33, 137.08, 137.25, 139.97, 182.14, 201.47; HRMS (EI) for C$_{23}$H$_{20}$ClNO$_2$: calcd 377.1183, found 377.1185.

1-(3-Isobutyryl-1-methyl-1H-indol-2-yl)-4-(thien-2-yl)but-3-yn-2-one (5e). Column chromatography on silica gel (petroleum ether/DCM = 1:1 to 1:2 to 1:3) afforded the title product as a khaki solid in 82% yield. M.p. 170-172 °C. $^1$H NMR (CDCl$_3$, Me$_4$Si, 400 MHz): $\delta$ 1.28 (d, $J = 7.2$ Hz, 6H), 3.53-3.64 (m, 1H), 3.72 (s, 3H), 4.74 (s, 2H), 7.00 (dd, $J = 3.6$, 4.8 Hz, 1H), 7.30-7.32 (m, 3H), 7.39-7.42 (m, 1H), 7.45 (dd, $J = 1.2$, 5.2 Hz, 1H), 7.89-7.92 (m, 1H); $^{13}$C NMR (CDCl$_3$, Me$_4$Si, 100 MHz): $\delta$ 18.73, 29.79, 39.00, 42.45, 86.63, 92.10, 110.09, 114.12, 119.38, 120.76, 122.18, 122.50, 124.98, 127.66, 132.10, 137.05, 137.10, 140.02, 181.80, 201.47; HRMS (EI) for C$_{21}$H$_{19}$NO$_2$S: calcd 349.1136, found 349.1133.
**1-(3-Isobutyryl-1-methyl-1H-indol-2-yl)dec-3-yn-2-one (5f).** Column chromatography on silica gel (petroleum ether/ethyl acetate = 10:1 to 6:1) afforded the title product as a light red solid in 82% yield. M.p. 57-59 °C. \(^1^H\) NMR (CDCl\(_3\), Me\(_4\)Si, 400 MHz): \(\delta\) 0.87 (t, \(J = 6.4\) Hz, 3H), 1.18-1.30 (m, 12H), 1.42-1.49 (m, 2H), 2.29 (t, \(J = 7.6\) Hz, 2H), 3.51-3.61 (m, 1H), 3.67 (s, 3H), 4.64 (s, 2H), 7.26-7.30 (m, 2H), 7.36-7.39 (m, 1H), 7.86-7.89 (m, 1H); \(^1^C\) NMR (CDCl\(_3\), Me\(_4\)Si, 100 MHz): \(\delta\) 13.95, 18.70, 18.95, 22.33, 27.43, 28.39, 29.72, 31.07, 38.94, 42.74, 80.38, 96.33, 109.98, 113.96, 120.70, 122.07, 122.37, 124.97, 137.01, 140.25, 182.46, 201.41; HRMS (El) for C\(_{23}\)H\(_{29}\)NO\(_2\): calcd 351.2198, found 351.2197.

**1-(3-Isobutyryl-5-methoxy-1-methyl-1H-indol-2-yl)-4-phenylbut-3-yn-2-one (5g).** Column chromatography on silica gel (petroleum ether/ethyl acetate = 10:1 to 6:1) afforded the title product as a yellow solid in 20% yield. M.p. 148-150 °C. \(^1^H\) NMR (CDCl\(_3\), Me\(_4\)Si, 400 MHz): \(\delta\) 1.27 (d, \(J = 6.8\) Hz, 6H), 3.45-3.55 (m, 1H), 3.67 (s, 3H), 3.89 (s, 3H), 4.72 (dd, \(J = 2.4, 8.8\) Hz, 1H), 7.26-7.32 (m, 3H), 7.37-7.42 (m, 4H); \(^1^C\) NMR (CDCl\(_3\), Me\(_4\)Si, 100 MHz): \(\delta\) 18.60, 29.81, 38.74, 42.81, 55.82, 87.38, 92.42, 103.94, 110.62, 111.42, 113.80, 119.46, 125.64, 128.44, 130.78, 132.31, 133.08, 140.26, 155.80, 182.20, 201.01; HRMS (El) for C\(_{24}\)H\(_{23}\)NO\(_3\): calcd 373.1678, found 373.1679.
1-(1-Allyl-3-isobutyryl-1H-indol-2-yl)-4-phenylbut-3-yn-2-one (5h). Column chromatography on silica gel (petroleum ether/ethyl acetate = 10:1 to 6:1) afforded the title product as a yellow solid in 64% yield. M.p. 90-92 °C. \(^1\)H NMR (CDCl\(_3\), Me\(_4\)Si, 400 MHz): \(\delta\) 1.27 (d, \(J = 6.8\) Hz, 6H), 3.54-3.64 (m, 1H), 4.67 (s, 2H), 4.74-4.77 (m, 2H), 4.89-4.94 (m, 1H), 5.00-5.19 (m, 1H), 5.87-5.96 (m, 1H), 7.25-7.32 (m, 4H), 7.35-7.41 (m, 4H), 7.89-7.94 (m, 1H); \(^13\)C NMR (CDCl\(_3\), Me\(_4\)Si, 100 MHz): \(\delta\) 18.64, 38.92, 42.64, 45.35, 87.48, 92.26, 110.38, 114.33, 117.35, 119.52, 120.74, 122.18, 122.53, 124.97, 128.42, 130.74, 131.65, 133.06, 136.43, 139.86, 182.21, 201.32; HRMS (EI) for C\(_{25}\)H\(_{23}\)NO\(_2\): calcd 369.1729, found 369.1726.

1-(1-Benzyl-3-isobutyryl-1H-indol-2-yl)-4-phenylbut-3-yn-2-one (5i). Column chromatography on silica gel (petroleum ether/CH\(_2\)Cl\(_2\) = 1:1 to 1:2 to 1:3) afforded the title product as a yellow solid in 45% yield. M.p. 144-146 °C. \(^1\)H NMR (CDCl\(_3\), Me\(_4\)Si, 400 MHz): \(\delta\) 1.29 (d, \(J = 6.4\) Hz, 6H), 3.56-3.66 (m, 1H), 4.63 (s, 2H), 5.37 (s, 2H), 6.99-7.01 (m, 2H), 7.22-7.34 (m, 8H), 7.37-7.41 (m, 3H), 7.94 (d, \(J = 8.4\) Hz, 1H); \(^13\)C NMR (CDCl\(_3\), Me\(_4\)Si, 100 MHz): \(\delta\) 18.68, 39.01, 42.76, 46.64, 87.52, 92.29, 110.59, 114.65, 119.58, 120.84, 122.31, 122.75, 125.08, 125.90, 127.80, 128.44, 128.94, 130.75, 133.10, 135.71, 136.88, 140.11, 182.07, 201.41; HRMS (EI) for C\(_{29}\)H\(_{25}\)NO\(_2\): calcd 419.1885, found 419.1887.
1-(3-Benzoyl-1-methyl-1H-indol-2-yl)dec-3-yn-2-one (5j). Column chromatography on silica gel (petroleum ether/ethyl acetate/CH$_2$Cl$_2$ = 20:1:2 to 20:1:4 to 10:1:4) afforded the title product as a light yellow solid in 86% yield. M.p. 104-106 °C. $^1$H NMR (CDCl$_3$, Me$_4$Si, 400 MHz): δ 0.86 (t, $J = 6.8$ Hz, 3H), 1.17-1.26 (m, 6H), 1.38-1.44 (m, 2H), 2.23 (t, $J = 7.2$ Hz, 2H), 3.71 (s, 3H), 4.43 (s, 2H), 7.06 (t, $J = 7.6$ Hz, 1H), 7.18-7.25 (m, 2H), 7.35 (d, $J = 8.4$ Hz, 1H), 7.44 (t, $J = 7.6$ Hz, 2H), 7.55 (t, $J = 7.2$ Hz, 1H), 7.77 (d, $J = 7.2$ Hz, 2H); $^{13}$C NMR (CDCl$_3$, Me$_4$Si, 100 MHz): δ 13.93, 18.95, 22.32, 27.37, 28.39, 30.09, 31.06, 42.34, 80.23, 96.99, 109.55, 115.00, 121.22, 121.50, 122.62, 126.55, 128.20, 129.12, 131.69, 136.87, 139.16, 140.87, 182.21, 192.51; HRMS (EI) for C$_{26}$H$_{27}$NO$_2$: calcd 385.2042, found 385.2037.

1-(1-Methyl-3-(3-methylbutanoyl)-1H-indol-2-yl)dec-3-yn-2-one (5k). Column chromatography on silica gel (petroleum ether/ethyl acetate = 20:1 to 10:1 to 5:1) afforded the title product as a yellow solid in 75% yield. M.p. 63-64 °C. $^1$H NMR (CDCl$_3$, Me$_4$Si, 400 MHz): δ 0.87 (t, $J = 7.2$ Hz, 3H), 1.02 (d, $J = 6.8$ Hz, 6H), 1.15-1.31 (m, 6H), 1.41-1.48 (m, 2H), 2.29 (t, $J = 6.8$ Hz, 2H), 2.33-2.40 (m, 1H), 2.90 (d, $J = 7.2$ Hz, 2H), 3.64 (s, 3H), 4.63 (s, 2H), 7.26-7.30 (m, 2H), 7.34-7.37 (m, 1H), 7.87-7.90 (m, 1H); $^{13}$C NMR (CDCl$_3$, Me$_4$Si, 100 MHz): δ 13.92, 18.91, 22.29, 22.76, 24.55, 27.40, 28.35, 29.63, 31.04, 42.58, 52.22, 80.37, 96.34, 109.93, 115.08, 120.73, 121.92, 122.35, 125.29, 136.92, 139.63, 182.40, 196.84; HRMS (EI) for C$_{24}$H$_{31}$NO$_2$: calcd 365.2355, found 365.2358.
1-(3-Isobutyryl-1-methyl-1H-indol-2-yl)hept-3-yn-2-one (5l). Column chromatography on silica gel (petroleum ether/ethyl acetate = 15:1 to 10:1 to 6:1) afforded the title product as a light yellow solid in 72% yield. M.p. 64-66 °C. $^1$H NMR (CDCl$_3$, Me$_4$Si, 400 MHz): δ 0.91 (t, $J = 7.6$ Hz, 3H), 1.27 (d, $J = 6.4$ Hz, 6H), 1.46-1.55 (m, 2H), 2.28 (t, $J = 7.2$ Hz, 2H), 2.53-3.60 (m, 1H), 3.67 (s, 3H), 4.65 (s, 2H), 7.26-7.32 (m, 2H), 7.36-7.40 (m, 1H), 7.86-7.90 (m, 1H); $^{13}$C NMR (CDCl$_3$, Me$_4$Si, 100 MHz): δ 13.33, 18.70, 20.90, 21.02, 29.74, 38.94, 42.76, 80.53, 96.06, 110.00, 113.96, 120.72, 122.08, 122.38, 124.98, 137.03, 140.24, 182.46, 201.44; HRMS (EI) for C$_{20}$H$_{23}$NO$_2$: calcd 309.1729, found 309.1730.

1-(3-Isobutyryl-1-methyl-1H-indol-2-yl)-6-phenylhex-3-yn-2-one (5m). Column chromatography on silica gel (petroleum ether/ethyl acetate = 10:1 to 6:1) afforded the title product as a red solid in 76% yield. M.p. 70-72 °C. $^1$H NMR (CDCl$_3$, Me$_4$Si, 400 MHz): 1.26 (d, $J = 6.8$, 6H), 2.59 (t, $J = 7.2$ Hz, 2H), 2.78 (t, $J = 7.2$ Hz, 2H), 3.52-3.61 (m, 4H), 4.60 (s, 2H), 7.13 (d, $J = 7.2$ Hz, 2H), 7.20-7.29 (m, 5H), 7.35-7.37 (m, 1H), 7.86-7.88 (m, 1H); $^{13}$C NMR (CDCl$_3$, Me$_4$Si, 100Mz): δ 18.68, 21.05, 29.64, 33.68, 38.91, 42.69, 80.86, 94.93, 110.02, 113.93, 120.68, 122.09, 122.37, 124.92, 126.50, 128.19, 128.43, 136.99, 139.46, 140.11, 182.26, 201.36; HRMS (EI) for C$_{25}$H$_{25}$NO$_2$: calcd 371.1885, found 371.1886.
6-(Benzyloxy)-1-(3-isobutyryl-1-methyl-1H-indol-2-yl)hex-3-yn-2-one (5n). Column chromatography on silica gel (petroleum ether/ethyl acetate = 10:1 to 8:1 to 6:1 to 5:1) afforded the title product as an orange solid in 60% yield. M.p. 101-102 °C. $^1$H NMR (CDCl$_3$, Me$_4$Si, 400Mz): $\delta$ 1.25 (d, $J = 6.8$ Hz, 6H), 2.61 (t, $J = 6.4$ Hz, 2H), 3.49-3.56 (m, 3H), 3.62 (s, 3H), 4.45 (s, 2H), 4.61 (s, 2H), 7.26-7.36 (m, 8H), 7.85-7.87 (m, 1H); $^{13}$C NMR (CDCl$_3$, Me$_4$Si, 100Mz): $\delta$ 18.65, 20.38, 29.63, 38.87, 42.66, 66.91, 72.89, 80.93, 92.39, 110.00, 113.89, 120.63, 122.06, 122.35, 124.87, 127.58, 127.68, 128.34, 136.97, 137.57, 140.07, 182.12, 201.32; HRMS (EI) for C$_{26}$H$_{27}$NO$_3$: calcd 401.1991, found 401.1996.

**General procedure for the synthesis of carbazoles 4a-4k.**

To a solution of (p-CF$_3$C$_6$H$_4$)$_3$PAuCl (10.5 mg, 0.015 mmol) in CH$_2$Cl$_2$ (3 mL) was added AgOTf (0.015 mmol, 300 uL, used as a 0.05 M solution in THF), and the mixture was stirred at room temperature for 10 min. Then the 3-acylindole/yne 3 (0.30 mmol) was added. The flask was sealed and the resulting solution was stirred at 60 °C until the reaction was complete as monitored by thin-layer chromatography. Several drops of Et$_3$N were added to quench the reaction. The solvent was evaporated under the reduced pressure and the residue was purified by chromatography on silica gel to afford the desired carbazole 4.
**9-Methyl-4-phenyl-9H-carbazole (4a).** Column chromatography on silica gel (petroleum ether as eluant) afforded the title product as a colorless sticky oil in 73% yield. $^1$H NMR (CDCl$_3$, Me$_4$Si, 400 MHz): $\delta$ 3.78 (s, 3H), 6.94-6.98 (m, 1H), 7.08-7.10 (m, 1H), 7.31-7.39 (m, 3H), 7.42-7.52 (m, 5H), 7.60-7.63 (m, 2H); $^{13}$C NMR (CDCl$_3$, Me$_4$Si, 100 MHz): $\delta$ 29.02, 107.33, 108.20, 118.46, 120.10, 120.55, 122.31, 122.33, 125.37, 125.47, 127.42, 128.34, 129.19, 137.67, 141.11, 141.24, 141.32; HRMS (EI) for C$_{19}$H$_{15}$N: calcd 257.1204, found 257.1207.

**9-Methyl-4-p-tolyl-9H-carbazole (4c).** Column chromatography on silica gel (petroleum ether/ethyl acetate = 25:1) afforded the title product as a light yellow sticky liquid in 86% yield. It can be solidified upon standing. M.p. 98-100 ºC. $^1$H NMR (CDCl$_3$, Me$_4$Si, 400 MHz): $\delta$ 2.47 (s, 3H), 3.82 (s, 3H), 6.95-7.00 (m, 1H), 7.08 (dd, $J$ = 1.2, 7.6 Hz, 1H), 7.30-7.39 (m, 5H), 7.46-7.57 (m, 4H); $^{13}$C NMR (CDCl$_3$, Me$_4$Si, 100 MHz): $\delta$ 21.34, 29.06, 107.16, 108.16, 118.42, 120.17, 120.63, 122.41, 122.44, 125.38, 125.43, 129.07, 137.07, 137.74, 138.37, 141.12, 141.29; HRMS (EI) for C$_{20}$H$_{17}$N: calcd 271.1361, found 271.1360.

**4-(4-Chlorophenyl)-9-methyl-9H-carbazole (4d).** Column chromatography on silica gel (petroleum ether/ethyl acetate = 25:1) afforded the title product as a colorless sticky oil in 69% yield. M.p. 79-81 ºC. $^1$H NMR (CDCl$_3$, Me$_4$Si, 400 MHz): $\delta$ 3.81 (s, 3H), 6.97-7.01 (m,
(1H), 7.03 (dd, $J = 0.8, 7.2$ Hz, 1H), 7.35-7.40 (m, 3H), 7.45-7.50 (m, 4H), 7.52-7.55 (m, 2H); $^{13}$C NMR (CDCl$_3$, Me$_4$Si, 100 MHz): $\delta$ 29.07, 107.67, 108.34, 118.60, 119.94, 120.47, 122.08, 122.14, 125.41, 125.65, 128.56, 130.56, 133.39, 136.27, 139.76, 141.12, 141.26; HRMS (EI) for C$_{19}$H$_{14}$ClN: calcd 291.0815, found 291.0818.

![4e](image)

4-(4-Bromophenyl)-9-methyl-9H-carbazole (4e). Column chromatography on silica gel (petroleum /ethyl acetate = 25:1) afforded the title product as a white sticky liquid in 71% yield. $^1$H NMR (CDCl$_3$, Me$_4$Si, 400 MHz): $\delta$ 3.80 (s, 3H), 6.97-7.30 (m, 2H), 7.33-7.42 (m, 3H), 7.44-7.51 (m, 4H), 7.60-7.62 (m, 2H); $^{13}$C NMR (CDCl$_3$, Me$_4$Si, 100 MHz): $\delta$ 29.06, 107.69, 108.34, 118.61, 119.85, 120.42, 121.57, 122.05, 122.14, 125.41, 125.66, 130.90, 131.50, 136.23, 140.22, 141.12, 141.26; HRMS (EI) for C$_{19}$H$_{14}$BrN: calcd 335.0310, found 335.0308.

![4f](image)

9-Methyl-4-(thien-2-yl)-9H-carbazole (4f). Column chromatography on silica gel (petroleum /ethyl acetate = 25:1) afforded the title product as a colorless sticky oil in 84% yield. $^1$H NMR (CDCl$_3$, Me$_4$Si, 400 MHz): $\delta$ 3.75 (s, 3H), 7.00-7.05 (m, 1H), 7.13-7.33 (m, 2H), 7.30-7.33 (m, 3H), 7.38-7.42 (m, 3H), 7.73 (dd, $J =0.8, 8.0$ Hz, 1H); $^{13}$C NMR (CDCl$_3$, Me$_4$Si, 100 MHz): $\delta$ 29.00, 108.20, 108.28, 118.64, 120.92, 121.88, 122.13, 122.27, 125.12, 125.46, 125.74, 126.61, 127.17, 129.66, 141.08, 141.19, 142.29; HRMS (EI) for C$_{17}$H$_{13}$NS: calcd 263.0769, found 263.0774.
4-Hexyl-9-methyl-9H-carbazole (4g). Column chromatography on silica gel (petroleum /ethyl acetate = 25:1) afforded the title product as a white solid in 76% yield. M.p. 48-50 °C. $^1$H NMR (CDCl$_3$, Me$_4$Si, 400 MHz): δ 0.89 (t, $J = 6.8$ Hz, 3H), 1.32-1.37 (m, 4H), 1.47-1.55 (m, 2H), 1.80-1.87 (m, 2H), 3.21 (t, $J = 8.0$ Hz, 2H), 3.78 (s, 3H), 7.01 (d, $J = 7.6$ Hz, 1H), 7.22-7.26 (m, 2H), 7.36-7.40 (m, 2H), 7.44-7.48 (m, 1H), 8.12 (d, $J = 8.0$ Hz, 1H); $^{13}$C NMR (CDCl$_3$, Me$_4$Si, 100 MHz): δ 14.13, 22.66, 28.97, 29.55, 29.70, 31.81, 34.48, 106.03, 108.20, 118.79, 119.60, 120.53, 122.55, 122.70, 124.94, 125.44, 138.42, 140.89, 141.30; HRMS (EI) for C$_{19}$H$_{23}$N: calcd 265.1830, found 265.1826.

3-Methoxy-9-methyl-5-phenyl-9H-carbazole (4h). Column chromatography on silica gel (petroleum /ethyl acetate =100:1-50:1) afforded the title product as a white solid in 80% yield. M.p. 136-138 °C. $^1$H NMR (CDCl$_3$, Me$_4$Si, 400 MHz): δ 3.59 (s, 3H), 3.76 (s, 3H), 6.95 (d, $J = 2.4$ Hz, 1H), 7.02 (dd, $J = 2.4$, 8.8 Hz, 1H), 7.06 (dd, $J = 0.8$, 7.2 Hz, 1H), 7.22 (d, $J = 8.8$ Hz, 1H), 7.31 (dd, $J = 0.8$, 8.0 Hz, 1H), 7.41-7.52 (m, 4H), 7.59-7.62 (m, 2H); $^{13}$C NMR (CDCl$_3$, Me$_4$Si, 100 MHz): δ 29.12, 55.55, 105.37, 107.45, 108.74, 114.51, 119.88, 119.89, 122.54, 125.30, 127.46, 128.22, 129.29, 136.22, 137.60, 141.14, 141.70, 152.83; HRMS (EI) for C$_{20}$H$_{17}$NO: calcd 287.1310, found 287.1314.
9-Allyl-4-phenyl-9H-carbazole (4i). Column chromatography on silica gel (petroleum /ethyl acetate =100:1-20:1) afforded the title product as a light yellow oil in 48% yield. \(^1\)H NMR (CDCl\(_3\), Me\(_4\)Si, 400 MHz): \(\delta\) 4.88-4.90 (m, 2H), 5.03-5.08 (m, 1H), 5.14-5.17 (m, 1H), 5.94-6.01 (m, 1H), 6.94-6.98 (m, 1H), 7.10 (dd, \(J = 0.8, 7.6\) Hz,1H), 7.32-7.38 (m, 3H), 7.44-7.52 (m, 5H), 7.61-7.64 (m, 2H); \(^1^3\)C NMR (CDCl\(_3\), Me\(_4\)Si, 100 MHz): \(\delta\) 45.23, 107.68, 108.54, 116.84, 118.67, 120.31, 120.78, 122.41, 122.53, 125.41, 125.52, 127.44, 128.36, 129.20, 132.16, 132.18, 137.77, 140.53, 140.65, 141.29; HRMS (EI) for C\(_{21}\)H\(_{17}\)N: calcd 283.1361, found 283.1363.

![4j](image)

9-Benzyl-4-phenyl-9H-carbazole (4j). Column chromatography on silica gel (petroleum /ethyl acetate =100:1) afforded the title product as a white solid in 64% yield. M.p. 115-117 °C. \(^1\)H NMR (CDCl\(_3\), Me\(_4\)Si, 400 MHz): \(\delta\) 5.46 (s, 2H), 6.95-6.98 (m, 1H), 7.09-7.13 (m, 3H), 7.19-7.22 (m, 3H), 7.30-7.32 (m, 3H), 7.39-7.53 (m, 5H), 7.62-7.65 (m, 2H); \(^1^3\)C NMR (CDCl\(_3\), Me\(_4\)Si, 100 MHz): \(\delta\) 46.48, 107.79, 108.66, 118.83, 120.38, 120.94, 122.44, 122.61, 125.54, 125.65, 126.36, 127.42, 127.48, 128.37, 128.74, 129.21, 137.05, 137.79, 140.82, 140.92, 141.26; HRMS (EI) for C\(_{25}\)H\(_{19}\)N: calcd 333.1517, found 333.1516.

![4j](image)

4-Phenyl-9H-carbazole (4k). Column chromatography on silica gel (petroleum /ethyl acetate =100:1-25:1) afforded the title product as a yellow solid in 56% yield. M.p. 130-132 °C. \(^1\)H NMR (CDCl\(_3\), Me\(_4\)Si, 400 MHz): \(\delta\) 6.95-7.00 (m, 1H), 7.09-7.12 (m, 1H), 7.32-7.34 (m, 3H), 7.40-7.52 (m, 5H), 7.61-7.63 (m, 2H), 7.98 (bs, 1H); \(^1^3\)C NMR (CDCl\(_3\), Me\(_4\)Si, 100 MHz): \(\delta\) 109.51, 110.39, 119.01, 120.69, 121.06, 122.39, 122.87, 125.58,
General procedure for the synthesis of 2-hydroxycarbazoles 6a-6i.

To a solution of (p-CF₃C₆H₄)₃PAuCl (10.5 mg, 0.015 mmol) in CH₂Cl₂ (3 mL) was added AgOTf (0.015 mmol, 300 μL, used as a 0.05 M solution in THF), and the mixture was stirred at room temperature for 10 min. Then 5.0 equiv H₂O (1.5 mmol, 27 μL) and 3-acylindole/yn (0.30 mmol) was added. The resulting solution was stirred at room temperature until the reaction was complete as monitored by thin-layer chromatography. Four drops of Et₃N were added to quench the reaction. The solvent was evaporated under the reduced pressure and the residue was purified by chromatography on silica gel to afford the desired 2-hydroxycarbazole 6.

9-Methyl-4-phenyl-9H-carbazol-2-ol (6a). Column chromatography on silica gel (petroleum/ethyl acetate = 20:1-10:1) afforded the title product as a sticky yellow liquid in 80% yield. It can be solidified upon standing. M.p. 140-142 °C. ¹H NMR (CDCl₃, Me₄Si, 400 MHz): δ 3.71 (s, 3H), 5.39 (s, 1H), 6.60 (d, J = 2.0 Hz, 1H), 6.79 (d, J = 2.0 Hz, 1H), 6.92-6.96 (m, 1H), 7.28-7.34 (m, 2H), 7.36-7.38 (m, 1H), 7.44-7.50 (m, 3H), 7.55-7.58 (m, 2H); ¹³C NMR (CDCl₃, Me₄Si, 100 MHz): δ 29.06, 93.70, 108.01, 109.54, 114.40, 118.63, 121.29, 122.55, 124.38, 127.63, 128.38, 129.00, 138.70, 140.70, 141.33, 142.85, 154.23; HRMS (EI) for C₁₉H₁₅NO: calcd 273.1154, found 273.1149.
**6a-d.** Column chromatography on silica gel (petroleum /ethyl acetate = 20:1-5:1) afforded the title product as a yellow solid in 82% yield. The deuterium incorporation on C-1 and C-3 are 65% and 37%, respectively (the protons on C-1 and C-3 are distinguished by 2D NOESY spectra). $^1$H NMR (CDCl$_3$, Me$_4$Si, 300 MHz): $\delta$ 3.67 (s, 3H), 5.60 (s, 1H), 6.59 (s), 6.76 (bs), 6.91-6.96 (m, 1H), 7.26-7.39 (m, 3H), 7.43-7.50 (m, 3H), 7.54-7.57 (m, 2H); $^{13}$C NMR (CDCl$_3$, Me$_4$Si, 75 MHz): $\delta$ 29.01, 93.72, 108.01, 109.54, 114.37, 118.60, 121.27, 122.52, 124.37, 127.60, 128.36, 128.98, 138.58, 138.60, 138.65, 138.68, 140.63, 140.67, 141.30, 142.78, 142.81, 154.08, 154.12, 154.17; HRMS (EI) for C$_{19}$H$_{13}$D$_2$NO: calcd 275.1279, found 275.1276.

**6c**

**9-Methyl-4-p-tolyl-9H-carbazol-2-ol (6c).** Column chromatography on silica gel (petroleum /ethyl acetate = 10:1-5:1) afforded the title product as a yellow solid in 86% yield. $^1$H NMR (CDCl$_3$, Me$_4$Si, 400 MHz): $\delta$ 2.47 (s, 3H), 3.76 (s, 3H), 5.20 (s, 1H), 6.59 (d, $J$ = 2.4 Hz, 1H), 6.80 (d, $J$ = 2.4 Hz, 1H), 6.92-6.98 (m, 1H), 7.29-7.36 (m, 4H), 7.43-7.50 (m, 3H); $^{13}$C NMR (CDCl$_3$, Me$_4$Si, 100 MHz): $\delta$ 21.27, 28.91, 93.59, 107.96, 109.60, 114.35, 118.52, 121.32, 122.62, 124.26, 128.82, 129.03, 137.24, 137.71, 138.72, 141.27, 142.84, 154.20; HRMS (EI) for C$_{20}$H$_{17}$NO: calcd 287.1310, found 287.1309.
4-(4-Chlorophenyl)-9-methyl-9H-carbazol-2-ol (6d). Column chromatography on silica gel (petroleum /ethyl acetate = 20:1-10:1-7:1) afforded the title product as a yellow solid in 82% yield. M.p. 88-90 °C. ¹H NMR (CDCl₃, Me₄Si, 400 MHz): δ 3.80 (s, 3H), 5.14 (bs, 1H), 6.58 (d, J = 2.0 Hz, 1H), 6.84 (d, J = 2.4 Hz, 1H), 6.95-7.00 (m, 1H), 7.34-7.39 (m, 3H), 7.47-7.55 (m, 4H); ¹³C NMR (CDCl₃, Me₄Si, 100 MHz): δ 28.97, 94.05, 108.14, 109.46, 114.21, 118.75, 121.09, 122.27, 124.54, 128.55, 130.31, 133.54, 137.23, 139.09, 141.31, 142.84, 154.20; HRMS (EI) for C₁₉H₁₄NOCl: calcd 307.0764, found 307.0765.

9-Methyl-4-(thien-2-yl)-9H-carbazol-2-ol (6e). Column chromatography on silica gel (petroleum /ethyl acetate = 10:1-7:1-5:1) afforded the title product as a yellow solid in 81% yield. M.p. 150-152 °C. ¹H NMR (CDCl₃, Me₄Si, 400 MHz): δ 3.60 (s, 3H), 5.91 (bs, 1H), 6.71 (d, J = 2.4 Hz, 1H), 6.74 (d, J = 2.0 Hz, 1H), 6.98-7.02 (m, 1H), 7.15 (dd, J = 3.6, 5.2 Hz, 1H), 7.24 (d, J = 8.0 Hz, 1H), 7.29-7.34 (m, 2H), 7.38 (dd, J = 1.2, 5.2 Hz, 1H), 7.63-7.66 (m, 1H); ¹³C NMR (CDCl₃, Me₄Si, 100 MHz): δ 28.95, 94.65, 108.10, 110.74, 115.11, 118.74, 121.26, 122.32, 124.62, 125.57, 126.69, 127.19, 130.58, 141.28, 141.59, 142.78, 153.87; HRMS (EI) for C₁₇H₁₃NOS: calcd 279.0718, found 279.0714.

4-Hexyl-9-methyl-9H-carbazol-2-ol (6f). Column chromatography on silica gel (petroleum /ethyl acetate = 20:1-15:1-10:1-7:1) afforded the title product as a white solid in 58% yield. M.p. 120-122 °C. ¹H NMR (CDCl₃, Me₄Si, 400 MHz): δ 0.88 (t, J = 6.8 Hz, 3H), 1.28-1.34 (m, 4H), 1.46-1.49 (m, 2H), 1.74-1.82 (m, 2H), 3.10 (t, J = 7.6 Hz, 2H), 3.66 (s, 3H), 5.25 (s, 1H), 6.51 (d, J = 2.4 Hz, 1H), 6.62 (d, J = 2.0 Hz, 1H), 7.19-7.23 (m,
1H), 7.31 (d, J = 8.0 Hz, 1H), 7.36-7.40 (m, 1H), 7.99 (d, J = 7.6 Hz, 1H); $^{13}$C NMR (CDCl$_3$, Me$_4$Si, 100 MHz): δ 14.08, 22.62, 28.94, 29.47, 29.51, 31.76, 34.30, 92.37, 108.01, 108.56, 114.77, 118.97, 121.47, 122.94, 123.82, 139.80, 141.10, 142.83, 154.35; HRMS (EI) for C$_{19}$H$_{23}$NO: calcd 281.1780, found 281.1783.

6-Methoxy-9-methyl-4-phenyl-9H-carbazol-2-ol (6g). Column chromatography on silica gel (petroleum /ethyl acetate =10:1-5:1) afforded the title product as a yellow solid in 73% yield. M.p. 215-217 °C. $^1$H NMR (CDCl$_3$, Me$_4$Si, 400 MHz): δ 3.62 (s, 3H), 3.76 (s, 3H), 5.00 (br, 1H), 6.59 (d, J = 2.4 Hz, 1H), 6.79 (d, J = 2.0 Hz, 1H), 6.86 (d, J = 2.4 Hz, 1H), 6.97 (dd, J = 8.8, 2.8 Hz, 1H), 7.22 (d, J = 8.8 Hz, 1H), 7.45-7.53 (m, 3H), 7.58-7.61 (m, 2H); $^{13}$C NMR (CDCl$_3$, Me$_4$Si, 100 MHz): δ 29.14, 55.71, 93.67, 105.01, 108.49, 109.10, 112.91, 114.20, 122.90, 127.67, 128.26, 129.05, 136.44, 138.68, 140.48, 143.32, 152.85, 154.30; HRMS (EI) for C$_{20}$H$_{17}$NO: calcd 303.1259, found 303.1260.

9-Allyl-4-phenyl-9H-carbazol-2-ol (6h). Column chromatography on silica gel (petroleum /ethyl acetate =10:1-6:1) afforded the title product as an yellow sticky liquid in 79% yield. $^1$H NMR (CDCl$_3$, Me$_4$Si, 400 MHz): δ 4.79-4.81 (m, 2H), 5.02-5.07 (m, 1H), 5.10 (s, 1H), 5.13-5.17 (m, 1H), 5.90-5.99 (m, 1H), 6.60 (d, J = 2.4 Hz, 1H), 6.78 (d, J = 2.0 Hz, 1H), 6.92-6.96 (m, 1H), 7.26-7.32 (m, 2H), 7.38 (d, J = 8.0 Hz, 1H), 7.43-7.51 (m, 3H), 7.56-7.59 (m, 2H); $^{13}$C NMR (CDCl$_3$, Me$_4$Si, 100 MHz): δ 45.11, 94.14, 108.33, 109.82, 114.51, 116.79, 118.77, 121.33, 122.69, 124.37, 127.58, 128.33, 128.95, 131.86, 138.74, 140.63, 140.68, 142.17, 154.13; HRMS (EI) for C$_{21}$H$_{17}$NO: calcd 299.1310, found
9-Benzyl-4-phenyl-9H-carbazol-2-ol (6i). Column chromatography on silica gel (petroleum /ethyl acetate =5:1) afforded the title product as a yellow solid in 78% yield. M.p. 84-86 °C. $^1$H NMR (CDCl$_3$, Me$_4$Si, 400 MHz): $\delta$ 5.14 (s, 1H), 5.32 (s, 2H), 6.57 (d, $J$ = 2.4 Hz, 1H), 6.70 (d, $J$ = 2.4 Hz, 1H), 6.92-6.96 (m, 1H), 7.08-7.10 (m, 2H), 7.17-7.22 (m, 3H), 7.24-7.26 (m, 2H), 7.40 (d, $J$ = 8.0 Hz, 1H), 7.44-7.49 (m, 3H), 7.56-7.58 (m, 2H); $^{13}$C NMR (CDCl$_3$, Me$_4$Si, 100 MHz): $\delta$ 46.41, 94.19, 108.45, 109.94, 114.62, 118.97, 121.38, 122.76, 124.54, 126.34, 127.41, 127.65, 128.39, 128.73, 129.00, 136.82, 138.80, 140.60, 140.99, 142.42, 154.17; HRMS (EI) for C$_{25}$H$_{19}$NO: calcd 349.1467, found 349.1463.

General procedure for the synthesis of acyl carbazoles 7a-7h and 8a-8h.

To a solution of 3-acylindole/yne 5 (0.20 mmol) in DCM (2 mL) was added gold catalyst (acetonitrile)[(2-biphenyl)di-tert-butylphosphine]gold(I) hexafluoroantimonate (7.7 mg, 0.01 mmol). The resulting solution was stirred at room temperature until the reaction was complete as monitored by thin-layer chromatography. Four drops of Et$_3$N were added to quench the reaction. The solvent was evaporated under the reduced pressure and the
residue was purified by chromatography on silica gel to afford the desired products 7 and 8.

1-(4-Hexyl-2-hydroxy-9-methyl-9\(H\)-carbazol-3-yl)-2-methylpropan-1-one  (7a).
Column chromatography on silica gel (petroleum /ethyl acetate = 200:1-20:1-15:1-10:1-7:1) afforded 7a in 63% yield and 8a in 13% yield (8a was further purified by treatment of a THF solution of crude 8a with a NaOH aqueous solution (0.4 M), and stirred overnight).

**7a**: yellow solid. M.p. 125-127 °C. \(^1^H\) NMR (CDCl\(_3\), Me\(_4\)Si, 400 MHz): \(\delta\) 0.89 (t, \(J = 6.4\) Hz, 3H), 1.25 (d, \(J = 6.8\) Hz, 6H), 1.31-1.33 (m, 4H), 1.44-1.54 (m, 2H), 1.77-1.85 (m, 2H), 3.23-3.27 (m 2H), 3.40-3.47 (m, 1H), 3.68 (s, 3H), 6.70 (s, 1H), 7.23-7.27 (m, 1H), 7.32 (d, \(J = 8.4\) Hz, 1H), 7.40-7.44 (m, 1H), 7.94 (d, \(J =8.0\) Hz, 1H), 9.60 (s, 1H); \(^1^C\) NMR (CDCl\(_3\), Me\(_4\)Si, 100 MHz): \(\delta\) 14.00, 19.68, 22.54, 28.95, 29.70, 30.10, 31.47, 32.82, 41.62, 93.34, 108.40, 115.40, 118.37, 119.88, 121.82, 123.10, 124.70, 139.64, 141.75, 144.40, 157.25, 214.60; HRMS (EI) for C\(_{23}\)H\(_{29}\)NO\(_2\): calcd 351.2198, found 351.2195.

1-(4-Hexyl-2-hydroxy-9-methyl-9\(H\)-carbazol-1-yl)-2-methylpropan-1-one  (8a). White solid. M.p. 70 °C. \(^1^H\) NMR (CDCl\(_3\), Me\(_4\)Si, 400 MHz): \(\delta\) 0.90 (t, \(J = 7.2\) Hz, 3H), 1.17 (d, \(J = 6.8\) Hz, 6H), 1.34-1.38 (m, 4H), 1.48-1.55 (m, 2H), 1.78-1.86 (m, 2H), 3.14 (t, \(J = 7.6\) Hz, 2H), 3.44-3.51 (m, 1H), 3.74 (s, 3H), 6.65 (s, 1H), 7.29-7.33 (m, 1H), 7.40 (d, \(J = 7.2\) Hz, 1H), 7.42-7.46 (m, 1H), 7.99 (d, \(J = 7.6\) Hz, 1H), 10.40 (s, 1H); \(^1^C\) NMR (CDCl\(_3\), Me\(_4\)Si, 100 MHz): \(\delta\) 14.08, 19.62, 22.59, 29.00, 29.43, 31.72, 34.64, 36.63, 40.19, 105.55, 109.77, 115.73, 120.85, 121.37, 123.79, 124.35, 142.32, 142.91, 146.54, 158.91, 210.01;
HRMS (EI) for C_{23}H_{29}NO_{2}: calcd 351.2198, found 351.2195.

![7b](image)

**7b**

*(4-Hexyl-2-hydroxy-9-methyl-9H-carbazol-3-yl)(phenyl)methanone* (7b). Column chromatography on silica gel (petroleum /ethyl acetate = 200:1-20:1-15:1-10:1-7:1) afforded 7b in 58% yield and 8b in 21% yield. 7b: yellow solid. M.p. 108 °C. \(^1\)H NMR (CDCl\(_3\), Me\(_4\)Si, 400 MHz): ð 0.79 (t, J = 6.8 Hz, 3H), 1.04-1.19 (m, 6H), 1.48-1.56 (m, 2H), 2.92 (t, J = 7.6 Hz, 2H), 3.77 (s, 3H), 6.82 (s, 1H), 7.21-7.25 (m, 1H), 7.36-7.38 (m, 1H), 7.42-7.46 (m, 3H), 7.54-7.58 (m, 1H), 7.70-7.72 (m, 2H), 7.91 (d, J = 8.0 Hz, 1H), 9.52 (s, 1H); \(^{13}\)C NMR (CDCl\(_3\), Me\(_4\)Si, 100 MHz): ð 13.99, 22.40, 29.10, 29.16, 30.20, 31.34, 32.69, 93.30, 108.49, 115.48, 116.61, 120.00, 121.94, 123.19, 124.85, 128.56, 129.17, 132.52, 141.31, 141.68, 141.83, 144.99, 158.05, 201.32; HRMS (EI) for C\(_{26}\)H\(_{27}\)NO\(_2\): calcd 385.2042, found 385.2040.

![8b](image)

**8b**

*(4-Hexyl-2-hydroxy-9-methyl-9H-carbazol-1-yl)(phenyl)methanone* (8b). Yellow solid. M.p. 65-67 °C. \(^1\)H NMR (CDCl\(_3\), Me\(_4\)Si, 400 MHz): ð 0.92 (t, J = 7.2 Hz, 3H), 1.34-1.42 (m, 4H), 1.52-1.58 (m, 2H), 1.84-1.92 (m, 2H), 2.98 (s, 3H), 3.20 (t, J = 8.0 Hz, 2H), 6.77 (s, 1H), 7.17 (d, J = 8.0 Hz, 1H), 7.27-7.32 (m, 1H), 7.36-7.40 (m, 3H), 7.51-7.60 (m, 3H), 8.03 (d, J = 7.2 Hz, 1H), 10.70 (s, 1H); \(^{13}\)C NMR (CDCl\(_3\), Me\(_4\)Si, 100 MHz): ð 14.10, 22.61, 29.08, 29.48, 31.75, 34.80, 35.16, 104.39, 109.31, 110.01, 115.00, 120.59, 121.35, 123.28, 124.17, 128.77, 129.38, 132.85, 140.00, 141.96, 147.29, 160.45, 197.04; HRMS (EI) for C\(_{26}\)H\(_{27}\)NO\(_2\): calcd 385.2042, found 385.2044.
1-(4-Hexyl-2-hydroxy-9-methyl-9H-carbazol-3-yl)-3-methylbutan-1-one (7c). Column chromatography on silica gel (petroleum /ethyl acetate =20:1) afforded 7c in 48% yield and 8c in 27% yield (8c was further purified by treatment of a THF solution of crude 8c with a NaOH aqueous solution (0.4 M), and stirred overnight). M.p. 65-66 °C. 7c: yellow solid. \(^1\)H NMR (CDCl\(_3\), Me\(_4\)Si, 400 MHz): \(\delta\) 0.90 (t, \(J = 7.2\text{ Hz}, 3\text{H}), 0.97 (d, J = 6.8 \text{ Hz, 6H}), 1.32-1.38 (m, 4H), 1.50-1.57 (m, 2H), 1.79-1.87 (m, 2H), 2.30-2.40 (m, 1H), 2.91 (d, \(J = 6.8\text{ Hz, 2H}), 3.35-3.39 (m, 2H), 3.71 (s, 3H), 6.72 (s, 1H), 7.24-7.28 (m, 1H), 7.34 (d, \(J = 7.6\text{ Hz, 1H}), 7.41-7.45 (m, 1H), 7.96 (d, J = 8.0 \text{ Hz, 1H}), 11.04 (s, 1H); \(^{13}\)C NMR (CDCl\(_3\), Me\(_4\)Si, 100 MHz): \(\delta\) 14.04, 22.58, 22.61, 27.00, 28.99, 29.67, 30.10, 31.60, 32.58, 53.55, 93.56, 108.45, 115.58, 115.82, 120.03, 121.93, 123.29, 124.85, 140.75, 141.96, 144.93, 159.13, 209.49; HRMS (EI) for C\(_{24}\)H\(_{31}\)NO\(_2\): calcd 365.2355, found 365.2359.

1-(4-Hexyl-2-hydroxy-9-methyl-9H-carbazol-1-yl)-3-methylbutan-1-one (8c). Yellow solid. M.p. 100 °C. \(^1\)H NMR (CDCl\(_3\), Me\(_4\)Si, 400 MHz): \(\delta\) 0.79 (d, \(J = 6.4\text{ Hz, 6H}), 0.89 (t, \(J = 6.8\text{ Hz, 3H}), 1.32-1.38 (m, 4H), 1.46-1.54 (m, 2H), 1.78-1.86 (m, 2H), 2.19-2.26 (m, 1H), 2.77 (d, \(J = 7.2\text{ Hz, 2H}), 3.13 (t, J = 8.0 \text{ Hz, 2H}), 3.73 (s, 3H), 6.65 (s, 1H), 7.30-7.34 (m, 1H), 7.41-7.47 (m, 2H), 7.99 (d, J = 8.0 Hz, 1H), 11.01 (s, 1H); \(^{13}\)C NMR (CDCl\(_3\), Me\(_4\)Si, 100 MHz): \(\delta\) 14.06, 22.36, 22.58, 28.28, 28.97, 29.38, 31.70, 34.66, 36.79, 51.66, 108.19, 109.97, 115.61, 120.96, 121.37, 123.94, 124.31, 142.66, 143.09, 147.13, 158.92, 205.15; HRMS (EI) for C\(_{24}\)H\(_{31}\)NO\(_2\): calcd 365.2355, found 365.2351.
1-(2-Hydroxy-9-methyl-4-propyl-9H-carbazol-3-yl)-2-methylpropan-1-one (7d).

Column chromatography on silica gel (petroleum /ethyl acetate =200:1-20:1-15:1-10:1-7:1) afforded 7d in 67% yield and 8d in 19% yield. 7d: white solid. M.p. 220-222 °C. $^1$H NMR (CDCl$_3$, Me$_4$Si, 400 MHz): $\delta$ 1.08 (t, $J = 7.2$ Hz, 3H), 1.25 (d, $J = 6.8$ Hz, 6H), 1.80-1.89 (m, 2H), 3.22-3.26 (m, 2H), 3.39-3.46 (m, 1H), 3.67 (s, 3H), 6.70 (s, 1H), 7.23-7.27 (m, 1H), 7.32 (d, $J = 7.6$ Hz, 1H), 7.40-7.44 (m, 1H), 7.93 (d, $J = 7.6$ Hz, 1H), 9.56 (s, 1H); $^{13}$C NMR (CDCl$_3$, Me$_4$Si, 100 MHz): $\delta$ 14.38, 19.75, 23.51, 29.00, 34.75, 41.66, 93.40, 108.43, 115.48, 118.38, 119.94, 121.84, 123.13, 124.76, 139.52, 141.79, 144.48, 157.35, 214.65; HRMS (EI) for C$_{20}$H$_{23}$NO$_2$: calcd 309.1729, found 309.1732.

1-(2-Hydroxy-9-methyl-4-propyl-9H-carbazol-1-yl)-2-methylpropan-1-one (8d). White solid. $^1$H NMR (CDCl$_3$, Me$_4$Si, 400 MHz): $\delta$ 1.11 (t, $J = 7.6$ Hz, 3H), 1.18 (d, $J = 6.4$ Hz, 6H), 1.82-1.92 (m, 2H), 3.12 (t, $J = 7.6$ Hz, 2H), 3.45-3.51 (m, 1H), 3.74 (s, 3H), 6.65 (s, 1H), 7.29-7.33 (m, 1H), 7.39-7.46 (m, 2H), 7.99 (d, $J = 8.0$ Hz, 1H), 10.39 (s, 1H); $^{13}$C NMR (CDCl$_3$, Me$_4$Si, 100 MHz): $\delta$ 14.20, 19.62, 22.23, 36.57, 36.62, 40.21, 105.60, 109.77, 109.87, 115.76, 120.86, 121.38, 123.79, 124.37, 142.31, 142.91, 146.22, 158.86, 210.04; HRMS (EI) for C$_{20}$H$_{23}$NO$_2$: calcd 309.1729, found 309.1725.
1-(2-Hydroxy-9-methyl-4-phenethyl-9H-carbazol-3-yl)-2-methylpropan-1-one (7e).

Column chromatography on silica gel (petroleum /ethyl acetate = 200:1-20:1-15:1-10:1-7:1-6:1 -5:1) afforded 7e in 81% yield and 8e in 15% yield. 7e: yellow solid. $^1$H NMR (CDCl$_3$, Me$_4$Si, 400 MHz): $\delta$ 1.24 (d, $J$ = 6.8 Hz, 6H), 3.07-3.11 (m, 2H), 3.43-3.50 (m, 1H), 3.54-3.58 (m, 2H), 3.67 (s, 3H), 6.72 (s, 1H), 7.24-7.29 (m, 4H), 7.33-7.37 (m, 3H), 7.44 (t, $J$ = 8.0 Hz, 1H), 8.09 (d, $J$ = 8.0 Hz, 1H), 9.27 (s, 1H); $^{13}$C NMR (CDCl$_3$, Me$_4$Si, 100 MHz): $\delta$ 19.56, 28.97, 34.31, 36.16, 41.80, 93.68, 108.52, 115.33, 118.94, 119.96, 121.83, 122.88, 124.86, 126.33, 128.13, 128.67, 138.06, 141.14, 141.76, 144.27, 156.76, 214.24; HRMS (EI) for C$_{25}$H$_{25}$NO$_2$: calcd 371.1885, found 371.1889.

1-(2-Hydroxy-9-methyl-4-phenethyl-9H-carbazol-1-yl)-2-methylpropan-1-one (8e).

Yellow solid. $^1$H NMR (CDCl$_3$, Me$_4$Si, 400 MHz): $\delta$ 1.19 (d, $J$ = 6.8 Hz, 6H), 3.11-3.16 (m, 2H), 3.44-3.52 (m, 3H), 3.77 (s, 3H), 6.65 (s, 1H), 7.24-7.38 (m, 6H), 7.41-7.48 (m, 2H), 8.07 (d, $J$ = 7.6 Hz, 1H), 10.33 (s, 1H); $^{13}$C NMR (CDCl$_3$, Me$_4$Si, 100 MHz): $\delta$ 19.58, 35.28, 36.30, 36.60, 40.30, 105.77, 109.79, 109.86, 115.64, 120.97, 121.31, 123.63, 124.51, 126.24, 128.37, 128.57, 141.32, 142.31, 142.91, 145.10, 158.86, 210.05; HRMS (EI) for C$_{25}$H$_{25}$NO$_2$: calcd 371.1885, found 371.1887.
1-(4-(2-(Benzyloxy)ethyl)-2-hydroxy-9-methyl-9H-carbazol-3-yl)-2-methylpropan-1-one (7f). Column chromatography on silica gel (petroleum /ethyl acetate = 20:1-15:1-7:1) afforded 7f in 71% yield and 8f in 20% yield. 7f: light yellow solid. $^1$H NMR (CDCl$_3$, Me$_4$Si, 400 MHz): $\delta$ 1.22 (d, $J = 6.8$ Hz, 6H), 3.38-3.48 (m, 1H), 3.66 (t, $J = 8.4$ Hz, 2H), 3.72 (s, 3H), 3.83-3.87 (m, 2H), 4.53 (s, 2H), 6.74 (s, 1H), 7.22-7.36 (m, 7H), 7.42-7.46 (m, 1H), 8.04 (d, $J = 8.0$ Hz, 1H), 9.56 (s, 1H); $^{13}$C NMR (CDCl$_3$, Me$_4$Si, 100 MHz): $\delta$ 19.66, 29.05, 33.19, 41.56, 69.31, 73.14, 94.01, 108.46, 116.05, 118.76, 120.18, 121.85, 122.94, 125.00, 127.74, 127.76, 128.42, 134.51, 138.06, 141.81, 144.32, 157.51, 214.08; HRMS (EI) for C$_{26}$H$_{27}$NO$_3$: calcd 401.1991, found 401.1989.

1-(4-(2-(Benzyloxy)ethyl)-2-hydroxy-9-methyl-9H-carbazol-1-yl)-2-methylpropan-1-one (8f). Light yellow solid. $^1$H NMR (CDCl$_3$, Me$_4$Si, 400 MHz): $\delta$ 1.17 (d, $J = 6.8$ Hz, 6H), 3.43-3.52 (m, 3H), 3.73 (s, 3H), 3.91 (t, $J = 7.2$ Hz, 2H), 4.59 (s, 2H), 6.69 (s, 1H), 7.26-7.30 (m, 2H), 7.32-7.40 (m, 5H), 7.42-7.46 (m, 1H), 8.01 (d, $J = 8.0$ Hz, 1H), 10.28 (s, 1H); $^{13}$C NMR (CDCl$_3$, Me$_4$Si, 100 MHz): $\delta$ 19.56, 34.86, 36.54, 40.31, 68.89, 73.16, 105.97, 109.76, 110.33, 116.11, 120.98, 121.27, 123.57, 124.54, 127.69, 127.73, 128.42, 138.14, 141.70, 142.15, 142.86, 158.68, 210.10; HRMS (EI) for C$_{26}$H$_{27}$NO$_3$: calcd 401.1991, found 401.1994.
1-(2-Hydroxy-9-methyl-4-phenyl-9H-carbazol-3-yl)-2-methylpropan-1-one (7g) and 1-(2-Hydroxy-9-methyl-4-phenyl-9H-carbazol-1-yl)-2-methylpropan-1-one (8g). Column chromatography on silica gel (petroleum /ethyl acetate = 15:1) afforded the mixture of 7g and 8g in a ratio of 1:1.7 as a yellow solid in 68% yield. $^1$H NMR (CDCl$_3$, Me$_4$Si, 400 MHz): two isomers, δ 0.83 (d, $J = 6.8$ Hz), 1.22 (d, $J = 6.8$ Hz), 2.44-2.51 (m), 3.50-3.57 (m), 3.70 (s), 3.73 (s), 6.57 (dt, $J = 1.2$, 8.0 Hz), 6.72 (s), 6.84-6.88 (m), 6.96-7.02 (m), 7.20-7.34 (m), 7.43-7.58 (m), 10.24 (s), 11.95 (s); $^{13}$C NMR (CDCl$_3$, Me$_4$Si, 100 MHz): two isomers, δ 19.46, 19.53, 29.00, 36.39, 38.96, 40.50, 94.83, 106.42, 108.19, 109.52, 110.73, 115.04, 115.38, 115.63, 119.67, 120.34, 121.05, 121.43, 123.44, 123.46, 124.77, 125.23, 128.21, 128.46, 128.63, 128.92, 129.34, 139.10, 139.73, 139.93, 142.14, 142.96, 144.37, 144.65, 158.19, 160.98, 210.14, 214.31; HRMS (EI) for C$_{23}$H$_{21}$NO$_2$: calcd 343.1572, found 343.1574.

1-(2-Hydroxy-9-methyl-4-(thien-2-yl)-9H-carbazol-3-yl)-2-methylpropan-1-one (7h) and 1-(2-hydroxy-9-methyl-4-(thien-2-yl)-9H-carbazol-1-yl)-2-methylpropan-1-one (8h). Column chromatography on silica gel (petroleum /ethyl acetate = 15:1) afforded the mixture of 7h and 8h in a ratio of 1.1:1 as a yellow solid in 67% yield. $^1$H NMR (CDCl$_3$, Me$_4$Si, 400 MHz): two isomers, δ 0.94 (d, $J = 6.4$ Hz), 1.22 (d, $J = 6.8$ Hz), 2.61-2.68 (m), 3.48-3.55 (m), 3.73 (s), 3.74 (s), 6.82-6.84 (m), 6.92 (s), 6.95-6.99 (m), 7.06-7.10 (m), 7.20-7.29 (m), 7.33-7.41 (m), 7.48 (dd, $J = 0.8$, 5.2 Hz), 7.58 (dd, $J = 0.8$, 5.2 Hz), 7.61 (d, $J = 8.4$ Hz), 10.14 (s), 11.84 (s); $^{13}$C NMR (CDCl$_3$, Me$_4$Si, 100 MHz): two isomers, δ
19.52, 29.07, 36.41, 38.79, 40.61, 96.01, 108.30, 109.60, 111.88, 115.97, 116.21, 117.12, 119.91, 120.52, 121.07, 121.57, 123.14, 123.33, 125.07, 125.64, 126.42, 127.31, 127.35, 127.41, 127.66, 127.98, 130.38, 136.55, 140.26, 140.51, 142.20, 142.24, 142.98, 144.47, 157.84, 160.79, 210.13, 214.00. HRMS (EI) for \( \text{C}_{21}\text{H}_{19}\text{NO}_{2}\text{S} \): calcd 349.1136, found 349.1134.

References:


X-ray crystal structure of 4h.

X-ray crystal structure of 6g.
X-ray crystal structure of 7a.

X-ray crystal structure of 8e.