

SUPPORTING INFORMATION

Title: Three-Component Indium-Mediated Domino Allylation of 1*H*-Indole-3-carbaldehyde with Electron-Rich (Hetero)arenes: Highly Efficient Access to Variously Functionalized Indolylbutenes

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General

^1H NMR and ^{13}C NMR spectra were recorded on a Bruker Avance 400 instrument (400 MHz for ^1H and 100 MHz for ^{13}C). Multiplicities were determined by DEPT (distortionless enhancement by polarization transfer) or by APT (attached proton test) measurements. Chemical shifts are reported in ppm using either TMS (0.00 ppm) or DMSO as internal standard. CI-MS (positive mode, isobutane as reagent gas) were performed on a Finnigan MAT TSQ70; ESI Spectra were performed on a Thermo Finnigan LCQ-deca XP-PLUS Instrument; TLC: Merck precoated sheets, 0.25 mm F₂₅₄, visualized by UV inspection and/or spraying with Ehrlich's reagent [1% 4-dimethylaminobenzaldehyde in 12N HCl-MeOH (2:2)] followed by heating to 50°C and spot colours are reported. Flash chromatography: Merck silica gel 60, 230-400 mesh. Column chromatography: Merck silica gel 60 (70-230 mesh). Elemental analyses were performed by Laboratorio di Microanalisi – Dipartimento di Scienze Chimiche e Ambientali- Como with a Perkin Elmer Series II CHNS/O 2400 elemental analyzer. Indium powder (99.99%, 100 mesh) was purchased from Aldrich Chemical Co. and used as received.

Reductive trapping of the intermediate 3-alkylidene-3*H*-indolium cation (3) to 3-but-3-enyl-1*H*-indole (5a)

To a solution in THF-H₂O 1:1 (12mL) of 1*H*-indole-3-carbaldehyde (0.145g, 1mmol) allylbromide (0.176mL, 2mmol), indium powder (0.161g, 1.4mmol) and diethyl 1,4-dihydro 2,6-dimethyl 3,5 pyridine dicarboxylate (Hantzsch ester) (253 mg, 1 mmol) were added. The resulting mixture was stirred at 50°C and stopped after 10h. Distilled water (15mL) was added to the flask and the mixture was extracted with ethyl acetate (3x10mL). The combined organic extracts were washed with water (2x15mL), dried over anhydrous sodium sulphate and evaporated under vacuum. The reaction mixture was purified by flash silica-gel chromatography (Ethyl Acetate-n-hexane 1:1) to give **5a** (77% yield) as a pale pink oil; R_f = 0.61 (Ethyl Acetate-n-hexane 1:1). ^1H – NMR (400MHz, CDCl₃, 25°C); δ = 2.54-2.59 (m, 2H), 2.92-3.00 (m, 2H), 5.09 (d, J_{cis} = 10.1Hz, 1H), 5.18 (d, J_{trans} = 17.1Hz, 1H), 5.99-6.06 (m, 1H), 7.01 (s, 1H), 7.20 (t, J = 7.6Hz, 1H), 7.27 (t, J = 7.6Hz, 1H), 7.38 (d, J = 7.6Hz, 1H), 7.70 (d, J = 7.6Hz, 1H), 7.89 (bs, 1H) ppm. ^{13}C – NMR (100MHz, CDCl₃, 25°C); δ = 25.2 (CH₂), 34.7 (CH₂), 111.6 (CH), 115.2 (CH₂), 116.7 (C), 119.4 (CH), 119.6 (CH), 121.7 (CH), 122.4 (CH), 128.0 (C), 136.8 (C), 139.3 (CH) ppm. MS (CI) m/z 172 (M+H)⁺. C₁₂H₁₃N 171.24): Calcd: C, 84.17; H, 7.65; N, 8.18. Found: C, 84.09; H, 7.68; N, 8.23.

Typical experimental procedure for the synthesis of 5b-45

To a solution in THF-H₂O 1:1 (12mL) of 1*H*-indole-3-carbaldehyde (0.145g, 1mmol) allylbromide (0.176mL, 2mmol), the chosen nucleophile (1 mmol) and indium powder (0.161g, 1.4mmol) were added. The resulting mixture was stirred at 50°C and stopped after 8h. Distilled water (15mL) was added to the flask and the mixture was extracted with ethyl acetate (3x10mL). The combined organic extracts were washed with water (2x15mL), dried over anhydrous sodium sulphate and evaporated under vacuum. Crude products **5-45** were purified by flash silica-gel chromatography.

3-[1-(1*H*-Indol-3-yl)-but-3-enyl]-2-methyl-1*H*-indole (5b)

Brown solid; Mp 165-166°C; R_f = 0.28 (CH₂Cl₂-*n*-hexane 1:1), violet. ¹H - NMR (400MHz, CDCl₃, 25°C); δ = 2.38 (s, 3H), 3.00-3.17 (m, 2H), 4.34-4.41 (m, 1H), 4.95 (d, *J*_{cis} = 10.2Hz, 1H), 5.18 (d, *J*_{trans} = 17.1 Hz, 1H), 5.83-5.95 (m, 1H), 7.02 (t, *J* = 7.9 Hz, 2H), 7.08-7.11 (m+t, *J* = 7.9Hz, 2H), 7.16 (t, *J* = 7.9Hz, 1H), 7.26 (d, *J* = 7.9Hz, 1H), 7.32 (d, *J* = 7.9Hz, 1H), 7.46 (d, *J* = 7.9Hz, 1H), 7.62 (d, *J* = 7.9Hz, 1H), 7.67 (bs, 1H), 7.89 (bs, 1H) ppm. ¹³C - NMR (100MHz, CDCl₃, 25°C); δ = 12.7 (CH₃), 34.4 (CH), 39.4 (CH₂), 110.6 (CH), 111.4 (CH), 114.0 (C) 115.8 (CH₂), 119.2 (CH), 119.5 (CH), 119.8 (CH), 119.9 (CH), 120.3 (C), 120.9 (CH), 121.7 (CH), 122.2 (CH), 127.7 (C), 128.6 (C), 131.4 (C), 135.8 (C), 136.9 (C), 138.4 (CH) ppm. MS (CI) *m/z* 301 (M+H)⁺. C₂₁H₂₀N₂ (300.40): Calcd: C, 83.96; H, 6.71; N, 9.33. Found: C, 83.40; H, 6.52; N, 9.21.

3-[1-(1*H*-Indol-3-yl)-but-3-enyl]-3-methyl-1*H*-indole (7)

Pink oil; R_f = 0.32 (AcOEt-*n*-hexane, 3:7), pink. ¹H - NMR (400MHz, CDCl₃, 25°C); δ = 2.47 (s, 3H), 2.85-3.07 (m, 2H), 4.69 (t, *J* = 7.3 Hz, 1H), 5.06 (d, *J*_{cis} = 10.1 Hz, 1H), 5.18 (d, *J*_{trans} = 17.1 Hz, 1H), 5.84-5.96 (m, 1H), 7.04 (bs, 1H), 7.13-7.19 (m, 4H), 7.21 (d, *J* = 7.7, 1H), 7.36 (d, *J* = 7.7 Hz, 1H), 7.42 (d, *J* = 7.7 Hz, 1H), 7.60 (d, *J* = 7.7 Hz, 1H), 7.69 (bs, 1H), 8.06 (bs, 1H) ppm. ¹³C - NMR (100MHz, CDCl₃, 25°C); δ = 9.3 (CH₃), 30.2 (CH), 39.5 (CH₂), 107.3 (C), 111.0 (CH), 111.6 (C), 117.0 (CH₂), 117.7 (CH), 118.7-122.8 (7CH), 127.3 (C), 130.0 (C), 135.6 (C), 136.9 (C), 137.1 (CH), 137.2 (C) ppm. MS (CI) *m/z* 301 (M+H)⁺.

2-{2-[1-(1*H*-Indol-3-yl)-but-3-enyl]-1*H*-indol-3-yl}-ethanol (9)

Brown solid; Mp 92-93°C; R_f = 0.41 (CH₂Cl₂-AcOEt 85:15), violet. ¹H - NMR (400MHz, CDCl₃, 25°C); δ = 2.65-2.97 (m, 2H), 3.18 (t, *J* = 6.6Hz, 2H), 3.96 (t, *J* = 6.6Hz, 2H), 4.69-4.77 (m, 1H), 5.04 (d, *J*_{cis} = 10.1Hz, 1H), 5.15 (d, *J*_{trans} = 17.1Hz, 1H), 5.80-5.90 (m, 1H), 7.05 (t, *J* = 7.8Hz, 1H), 7.09 (d, *J* = 2.0Hz, 1H), 7.12-7.22 (m, 3H), 7.21 (d, *J* = 7.8Hz, 1H), 7.35 (d, *J* = 7.8Hz, 1H), 7.46 (d, *J* = 7.8Hz, 1H), 7.62 (d, *J* = 7.8Hz, 1H), 7.70 (bs, 1H), 7.92 (bs, 1H) ppm. ¹³C - NMR (100MHz,

CDCl₃, 25°C); δ= 28.4 (CH₂), 34.6 (CH), 39.9 (CH₂), 63.2 (CH₂), 107.7 (C), 111.1 (CH), 111.6 (CH), 117.3 (CH₂), 117.6 (C), 118.8 (CH), 119.6 (CH), 119.7 (CH), 120.2 (CH), 121.7 (CH), 121.9 (CH), 122.8 (CH), 127.0 (C), 129.1 (C), 135.6 (C), 136.8 (C), 136.9 (CH), 138.8 (C) ppm. MS (CI) *m/z* 331 (M+H)⁺ C₂₂H₂₂N₂O (330.43): Calcd: C, 79.97; H, 6.71; N, 8.48. Found: C, 79.80; H, 6.55; N, 8.32.

2-{1-[1-(1*H*-Indol-3-yl)-but-3-enyl]-1*H*-indol-3-yl}-ethanol (10)

Pink solid; Mp 66-67°C; R_f= 0.27 (CH₂Cl₂-AcOEt 85:15), violet. ¹H – NMR (400MHz, CDCl₃, 25°C); δ= 2.98 (t, *J* = 6.3Hz, 2H), 2.90-3.00 (m, 1H), 3.20-3.40 (m, 2H), 3.83 (t, *J* = 6.3Hz, 2H), 5.02 (d, *J*_{cis} = 10.2Hz, 1H), 5.15 (d, *J*_{trans} = 17.1Hz, 1H), 5.70-5.85 (m, 1H), 5.88 (t, *J* = 7.3Hz, 1H), 6.98 (t, *J* = 8.0Hz, 1H), 7.02 (bs, 1H), 7.12-7.27 (m, 3H), 7.21 (d, *J* = 2.2Hz, 1H), 7.27 (d, *J* = 8.0Hz, 1H), 7.36 (d, *J* = 8.0Hz, 1H), 7.53 (d, *J* = 8.0Hz, 1H), 7.63 (d, *J* = 8.0Hz, 1H), 8.16 (bs, 1H) ppm. ¹³C – NMR (100MHz, CDCl₃, 25°C); δ= 29.2 (CH₂), 39.7 (CH₂), 52.9 (CH), 62.9 (CH₂), 110.3 (CH), 111.2 (C), 111.6 (CH), 111.7 (CH), 116.5 (C), 117.3 (C), 118.0 (CH₂), 119.4 (CH), 120.4 (CH), 122.1 (CH), 122.6 (CH), 122.6 (CH), 123.0 (CH), 124.7 (CH), 126.7 (C), 128.4 (C), 135.0 (CH), 136.8 (C) ppm. MS (CI) *m/z* 331 (M+H)⁺ C₂₂H₂₂N₂O (330.43): Calcd: C, 79.97; H, 6.71; N, 8.48. Found: C, 79.73; H, 6.62; N, 8.69.

9-[1-(1*H*-Indol-3-yl)-but-3-enyl]-2,3,4,9-tetrahydro-1*H*-carbazole (11)

Yellow solid; Mp 141-142°C; R_f= 0.27 (CH₂Cl₂-*n*-hexane 4:6), red. ¹H – NMR (400MHz, CDCl₃, 25°C); δ= 1.96-1.94 (m, 4H), 2.58-2.67 (m, 1H), 2.75-2.88 (m, 3H), 3.21-3.25 (m, 2H), 5.01 (d, *J*_{cis} = 10.1Hz, 1H), 5.13 (d, *J*_{trans} = 17.0Hz, 1H), 5.65-5.72 (m, 1H), 5.82-5.85 (m, 1H), 6.94 (t, *J* = 7.6Hz, 1H), 7.02 (t, *J* = 7.6Hz, 1H), 7.04 (d, *J* = 7.6Hz, 1H), 7.05 (t, *J* = 7.6Hz, 1H), 7.14 (t, *J* = 7.6Hz, 1H), 7.18 (bs, 1H), 7.34 (d, *J* = 7.6Hz, 1H), 7.50 (d, *J* = 7.6Hz, 1H), 7.32 (d, *J* = 7.6Hz, 1H), 8.01 (bs, 1H) ppm. ¹³C – NMR (100MHz, CDCl₃, 25°C); δ= 21.6 (CH₂), 23.5 (CH₂), 24.0 (2CH₂), 38.1 (CH₂), 52.3 (CH), 110.1 (C), 111.1 (CH), 111.4 (CH), 116.9 (C), 117.8 (C+CH₂), 118.0 (CH), 118.6 (CH), 119.7 (CH), 120.3 (CH), 120.5 (CH), 122.2 (CH), 122.7 (CH), 126.9 (C), 128.4 (C), 135.3 (CH), 136.2 (C), 136.8 (C) ppm. MS (CI) *m/z* 341 (M+H)⁺ C₂₄H₂₄N₂ (340.47): Calcd: C, 84.67; H, 7.11; N, 8.23. Found: C, 84.51; H, 7.06; N, 8.15.

3-[1-(1*H*-Pyrrol-2-yl)-but-3-enyl]-1*H*-indole (12)

Brown solid; Mp 129-130°C; R_f= 0.21 (CH₂Cl₂-*n*-hexane 7:3). ¹H – NMR (400MHz, CDCl₃, 25°C); δ= 2.99-2.94 (m, 2H), 4.41 (t, *J* = 7.4Hz, 1H), 5.08 (dd, *J*_{cis} = 10.2Hz, *J*_{gem} = 1.8Hz, 1H), 5.18 (dd, *J*_{trans} = 17.2Hz, *J*_{gem} = 1.8Hz, 1H), 5.97-5.90 (m, 1H), 6.29-6.26 (m, 2H), 6.62-6.60 (m, 1H), 6.97 (d,

$J = 2.4\text{Hz}$, 1H), 7.16 (t, $J = 8.0\text{Hz}$, 1H), 7.28 (t, $J = 8.0\text{Hz}$, 1H), 7.38 (d, $J = 8.0\text{Hz}$, 1H), 7.54 (d, $J = 8.0\text{Hz}$, 1H), 7.87 (bs, 2H) ppm. ^{13}C – NMR (100MHz, CDCl_3 , 25°C); $\delta = 36.3$ (CH), 39.8 (CH_2), 105.2 (CH), 108.4 (CH), 111.5 (CH), 116.5 (CH_2), 116.6 (CH), 118.1 (C), 119.8 (CH), 119.9 (CH), 122.4 (CH), 122.5 (CH), 127.1 (C), 135.2 (C), 137.0 (C), 137.6 (CH) ppm. MS (CI) m/z 237 ($\text{M}+\text{H}$) $^+$ $\text{C}_{16}\text{H}_{16}\text{N}_2$ (236.32): Calcd: C, 81.32; H, 6.82; N, 11.85. Found: C, 81.04; H, 6.79; N, 11.67.

3-[1-(5-Allyl-1H-pyrrol-2-yl)-but-3-enyl]-1H-indole (13)

Brown oil; $R_f = 0.33$ (CH_2Cl_2 -*n*-hexane 7:3). ^1H – NMR (400MHz, CDCl_3 , 25°C); $\delta = 2.91$ -2.93 (m, 2H), 3.30 (d, $J = 6.4\text{Hz}$, 2H), 4.33-4.38 (m, 2H), 5.03-5.16 (m, 4H), 5.88-5.96 (m, 2H), 6.10 (t, $J = 2.7\text{Hz}$, 1H), 7.01 (s, 1H), 7.13 (t, $J = 7.1$ Hz, 1H), 7.25 (t, $J = 7.1\text{Hz}$, 1H), 7.39 (d, $J = 7.1\text{Hz}$, 1H), 7.56 (d, $J = 7.1\text{Hz}$, 1H), 7.66 (bs, 1H), 7.96 (bs, 1H) ppm. MS (CI) m/z 293 ($\text{M}+\text{H}$) $^+$

Bis-adduct (14)

Brown oil; $R_f = 0.16$ (CH_2Cl_2 -*n*-hexane 7:3). ^1H – NMR (400MHz, CDCl_3 , 25°C); $\delta = 2.91$ -2.93 (m, 2H), 3.30 (d, $J = 6.4\text{Hz}$, 2H), 4.33-4.38 (m, 2H), 5.03-5.16 (m, 4H), 5.88-5.96 (m, 2H), 6.10 (t, $J = 2.7\text{Hz}$, 1H), 7.01 (s, 1H), 7.13 (t, $J = 7.1$ Hz, 1H), 7.25 (t, $J = 7.1\text{Hz}$, 1H), 7.39 (d, $J = 7.1\text{Hz}$, 1H), 7.56 (d, $J = 7.1\text{Hz}$, 1H), 7.66 (bs, 1H), 7.96 (bs, 1H) ppm. MS (CI) m/z 438 ($\text{M}+\text{H}$) $^+$

3-[1-(1-tert-Butyl-1H-pyrrol-3-yl)-but-3-enyl]-1H-indole (15)

Yellow oil; $R_f = 0.36$ (AcOEt-*n*-hexane, 2:8), violet. ^1H – NMR (400MHz, CDCl_3 , 25°C); $\delta = 1.57$ (s, 9H), 2.79-2.84 (m, 1H), 2.92-3.04 (m, 1H), 4.45 (t, $J = 7.4\text{Hz}$, 1H), 5.07 (d, $J_{cis} = 9.3$ Hz, 1H), 5.22 (d, $J_{trans} = 17.1$ Hz, 1H), 5.95-6.03 (m, 1H), 6.27 (bs, 1H), 6.87 (bs, 1H), 6.95 (bs, 1H), 7.03 (bs, 1H), 7.17-7.30 (m, 2H), 7.39 (d, $J = 7.6$ Hz, 1H), 7.76 (d, $J = 7.6$ Hz, 1H), 7.81 (bs, 1H) ppm. ^{13}C – NMR (100MHz, CDCl_3 , 25°C); $\delta = 31.8$ (3 CH_3), 34.6 (CH), 40.8 (C), 41.6 (CH_2), 107.4 (CH), 111.6 (CH), 113.7 (CH), 115.6 (CH_2), 115.7 (CH), 115.8 (C), 117.5 (CH), 119.2 (CH), 120.1 (CH), 122.2 (CH), 121.3 (C), 127.6 (C), 137.0 (C), 138.16 (CH) ppm. MS (CI) m/z 293 ($\text{M}+\text{H}$) $^+$

3-[1-(1-tert-Butyl-1H-pyrrol-2-yl)-but-3-enyl]-1H-indole (16)

Brown oil; $R_f = 0.32$ (AcOEt-*n*-hexane, 2:8), violet. ^1H – NMR (400MHz, CDCl_3 , 25°C); $\delta = 1.70$ (s, 9H), 2.79-2.87 (m, 1H), 2.97-3.04 (m, 1H), 4.77-4.81 (m, 1H), 5.14 (d, $J_{cis} = 9.3$ Hz, 1H), 5.27 (d, $J_{trans} = 17.3$ Hz, 1H), 5.90-6.01 (m, 1H), 6.27 (t, $J = 3.2$ Hz, 1H), 6.43 (bs, 1H), 6.75 (bs, 1H), 6.91 (bs, 1H), 7.22-7.38 (m, 2H), 7.73-7.85 (m, 3H) ppm. ^{13}C – NMR (100MHz, CDCl_3 , 25°C); $\delta = 31.2$ (3 CH_3), 36.04 (CH), 41.6 (C), 43.2 (CH_2), 105.6 (CH), 109.2 (CH), 111.5 (CH), 115.7 (C), 116.3

(CH₂), 117.8 (CH), 119.2 (CH), 121.6 (CH), 122.2 (CH), 123.4 (CH), 126.7 (C), 135.6 (C), 137.7 (C), 138.8 (CH) ppm. MS (CI) *m/z* 293 (M+H)⁺.

{2-[1-(1*H*-Indol-3-yl)-but-3-enyl]-pyrrol-1-yl}-phenyl-acetic acid methyl ester (17)

Mixture of diastereoisomers (ca 1:1) as brown solid; *R*_f = 0.31 (CH₂Cl₂-*n*-hexane, 7:3), dark pink. ¹H – NMR (400MHz, CDCl₃, 25°C); δ = 2.87-3.03 (m, 2H), 3.75 (s, 3H), 4.27 (t, *J* = 7.4Hz, 1H), 5.03 (d, *J*_{cis} = 10.3Hz, 1H), 5.12 (d, *J*_{trans} = 17.1Hz, 1H), 5.87-5.96 (m, 1H), 5.91 (bs, 1H), 6.19 (t, *J* = 3.2Hz, 1H), 6.30 (bs, 1H), 6.54 (bs, 1H), 6.76 (d, *J* = 7.6, 2H), 6.81 (d, *J* = 2.2Hz, 1H), 7.09 (t, *J* = 7.6Hz, 1H), 7.17 (t, *J* = 7.6Hz, 1H), 7.19 (t, *J* = 7.6, 2H), 7.20-7.25 (m, 1H), 7.35 (d, *J* = 7.6Hz, 1H), 7.51 (d, *J* = 7.6Hz, 1H), 7.95 (bs, 1H) ppm. ¹³C – NMR (100MHz, CDCl₃, 25°C); δ = 35.4 (CH), 40.1 (CH₂), 53.0 (CH), 61.9 (CH₃), 107.1 (CH), 107.5 (CH), 111.6 (CH), 116.0 (C), 116.5 (CH₂), 118.9 (C), 119.4 (CH), 119.7 (CH), 120.0 (CH), 122.5 (CH), 122.8 (2CH), 126.9 (C), 128.5 (CH), 128.7 (CH), 128.9 (2CH), 135.5 (C), 136.9 (C), 137.7 (CH), 171.03 (C) ppm. MS (CI) *m/z* 385 (M+H)⁺ C₂₅H₂₄N₂O₂ (384.48) Calcd: C, 78.10; H, 6.29; N, 7.29. Found: C, 78.10; H, 6.29; N, 7.29.

2-[1-(1*H*-Indol-3-yl)-but-3-enyl]-octamethylcalix[4]pyrrole (18)

Yellow glass; *R*_f = 0.35 (AcOEt-*n*-hexane, 2:8), violet. ¹H – NMR (400MHz, CDCl₃, 25°C); δ = 1.54-1.70 (m, 24H), 2.71-2.93 (m, 2H), 4.61 (t, *J* = 6.3 Hz, 1H), 5.04 (d, *J*_{cis} = 10.2 Hz, 1H), 5.13 (d, *J*_{trans} = 14.5 Hz, 1H), 5.85-6.09 (m, 8H), 6.66 (s, 1H), 7.05-7.25 (m, 6H), 7.40 (d, *J* = 8.0 Hz, 1H), 7.66 (d, *J* = 8.0 Hz, 1H), 8.01 (bs, 1H) ppm. MS (ESI) *m/z* 596.1 (M-H)⁻, 628.1 (M-H+CH₃OH)⁻.

3-[1-(5-Methyl-furan-2-yl)-but-3-enyl]-1*H*-indole (19)

Yellow oil; *R*_f = 0.20 (CH₂Cl₂-*n*-hexane, 7:3). ¹H – NMR (400MHz, CDCl₃, 25°C); δ = 2.30 (s, 3H), 2.88-2.96 (m, 2H), 4.36 (t, *J* = 7.5Hz, 1H), 5.04 (d, *J*_{cis} = 10.2Hz, 1H), 5.14 (d, *J*_{trans} = 17.1Hz, 1H), 5.83-5.87 (m, 1H), 5.92 (bs, 1H), 6.00 (d, *J* = 2.9Hz, 1H), 7.05 (d, *J* = 2.2Hz, 1H), 7.15 (t, *J* = 7.8Hz, 1H), 7.24 (t, *J* = 7.8Hz, 1H), 7.36 (d, *J* = 7.8Hz, 1H), 7.67 (d, *J* = 7.8Hz, 1H), 7.92 (bs, 1H) ppm. ¹³C – NMR (100MHz, CDCl₃, 25°C); δ = 14.1 (CH₃), 37.1 (CH), 39.1 (CH₂), 106.2 (CH), 106.5 (CH), 111.6 (CH), 116.5 (CH₂), 117.64 (C), 119.7 (CH), 119.9 (CH), 122.2 (CH), 122.3 (CH), 127.1 (C), 136.8 (C), 137.4 (CH), 150.89 (C), 156.20 (C) ppm. MS (CI) *m/z* 252 (M+H)⁺.

3-[1-(2-Phenyl-indolizin-3-yl)-but-3-enyl]-1*H*-indole (20)

Brown solid; Mp 140-141°C; *R*_f = 0.25 (CH₂Cl₂-*n*-hexane 5:7). ¹H - NMR (400MHz, DMSO-*d*₆, 25°C); δ = 2.90-3.33 (m, 2H), 4.91-4.95 (m, 2H), 5.00-5.10 (m, 2H), 5.60-5.75 (m, 2H), 6.32-3.66 (m, 1H), 6.54 (bs, 1H), 6.57-6.60 (m, 1H), 6.62 (d, *J* = 7.7 Hz, 1H), 6.91 (t, *J* = 7.7 Hz, 1H), 7.26 (d,

$J = 7.7$ Hz, 1H), 7.37 (t, $J = 7.7$ Hz, 1H), 7.44-7.52 (m, 4H), 7.56 (d, $J = 7.8$ Hz, 1H), 7.95 (d, $J = 7.8$ Hz, 1H), 10.96 (bs, 1H) ppm. ^{13}C – NMR (100MHz, DMSO- d_6 , 25°C); $\delta = 43.9$ (CH), 45.2 (CH₂), 96.7 (CH), 111.6 (CH), 112.3 (CH), 115.1 (C), 116.8 (CH₂), 117.5 (CH), 118.3 (CH), 119.7 (CH), 120.3 (CH), 121.6 (C), 122.0 (CH), 123.1 (CH), 124.7 (CH), 127.2 (C), 127.5 (2CH), 128.8 (CH), 129.3 (2CH), 131.1 (C), 133.9 (C), 134.2 (CH), 136.3 (C), 136.4 (C) ppm. MS (ESI⁺) m/z 363 (M+H)⁺ C₂₆H₂₂N₂ (362.47) Calcd: C, 86.15; H, 6.12; N, 7.73. Found: C, 86.26; H, 6.21; N, 7.84.

3-{1-[2-(4-Bromo-phenyl)-indolizin-3-yl]-but-3-enyl}-1H-indole (21)

Pale-green solid; Mp 135-136°C; R_f = 0.28 (CH₂Cl₂-*n*-hexane 35:65), blue. ^1H – NMR (400MHz, CDCl₃, 25°C); $\delta = 3.05$ -3.22 (m, 2H), 4.93 (d, $J_{cis} = 9.2$ Hz, 1H), 5.00 (t, $J = 6.1$ Hz, 1H), 5.04 (dd, $J_{trans} = 16.9$ Hz, 1H), 5.66-5.73 (m, 1H), 6.28-6.32 (m, 1H), 6.57 (s, 1H), 6.61-6.64 (m, 1H), 6.94 (t, $J = 7.5$ Hz, 1H), 7.03 (d, $J = 7.5$ Hz, 1H), 7.06 (bs, 1H), 7.16 (t, $J = 7.5$ Hz, 1H), 7.33 (d, $J = 8.0$ Hz, 1H), 7.40 (d, $J = 8.0$ Hz, 1H), 7.43 (d, $J = 8.4$ Hz, 2H), 7.54 (d, $J = 8.4$ Hz, 2H), 7.86 (d, $J = 7.5$ Hz, 1H), 7.99 (bs, 1H) ppm. ^{13}C – NMR (100MHz, DMSO- d_6 , 25°C); $\delta = 43.7$ (CH), 44.9 (CH₂), 97.3 (CH), 111.1 (CH), 112.6 (CH), 115.4 (C), 116.4 (CH₂), 117.2 (CH), 118.9 (CH), 119.8 (CH), 120.1 (CH), 121.8 (C), 122.2 (CH), 122.9 (CH), 123.1 (C), 124.5 (CH), 127.4 (C), 129.8 (2CH), 130.9 (C), 132.1 (2CH), 133.8 (C), 134.3 (CH), 135.3 (C), 136.4 (C) ppm. MS (ESI⁺) m/z 443/441 (M+H)⁺ C₂₆H₂₁BrN₂ (441.37) Calcd: C, 70.75; H, 4.80; N, 6.35. Found: C, 70.73; H, 4.59; N, 6.48.

2-(4-Bromo-phenyl)-3-[1-(1H-indol-3-yl)-but-3-enyl]-imidazo[1,2-*a*]pyridine (22)

Brown solid; Mp 167-168°C; R_f = 0.31 (CH₂Cl₂-AcOEt 9:1), orange. ^1H – NMR (400MHz, CDCl₃, 25°C); $\delta = 2.99$ -3.31 (m, 2H), 4.94 (d, $J_{cis} = 10.2$ Hz, 1H), 5.01 (dd, $J_{trans} = 17.0$ Hz, 1H), 5.10 (dd, $J = 6.7$ Hz, $J = 9.0$ Hz, 1H), 5.67-5.76 (m, 1H), 6.58 (t, $J = 7.3$ Hz, 1H), 6.91 (t, $J = 7.7$ Hz, 1H), 7.06 (d, $J = 7.7$ Hz, 1H), 7.09 (bs, 1H), 7.11 (t, $J = 7.7$ Hz, 1H), 7.13 (t, $J = 7.3$ Hz, 1H), 7.31 (d, $J = 7.7$ Hz, 1H), 7.58 (d, $J = 8.5$ Hz, 2H), 7.61 (d, $J = 7.3$ Hz, 1H), 7.71 (d, $J = 8.5$ Hz, 2H), 7.99 (d, $J = 7.3$ Hz, 1H), 8.85 (bs, 1H) ppm. ^{13}C – NMR (100MHz, CDCl₃, 25°C); $\delta = 33.9$ (CH), 36.0 (CH₂), 111.7 (CH), 112.2 (CH), 115.3 (C), 117.5 (CH₂), 117.9 (CH), 119.5 (CH), 120.1 (CH), 121.9 (C), 122.1 (CH), 122.4 (C), 122.8 (CH), 124.5 (CH), 125.2 (CH), 126.9 (C), 131.2 (2CH), 132.0 (CH), 132.52 (CH), 134.5 (C), 136.0 (CH), 137.2 (C), 143.1 (C), 145.3 (C) ppm. MS (ESI⁺) m/z 444/442 (M+H)⁺ C₂₅H₂₀BrN₃ (442.36) Calcd: C, 67.88; H, 4.56; N, 9.50. Found: C, 67.44; H, 4.37; N, 9.63.

1-[1-(1H-Indol-3-yl)-but-3-enyl]-imidazo[1,5-*a*]pyridine (23)

Colourless solid; Mp 177-178°C; R_f = 0.24 (AcOEt-*n*-hexane 1:1), violet. ^1H - NMR (400MHz, DMSO- d_6 , 25°C); $\delta = 2.91$ -2.98 (m, 1H), 3.16-3.23 (m, 1H), 4.76 (t, $J = 7.6$ Hz, 1H), 4.86 (dd, $J_{cis} =$

10.2 Hz, $J_{gem} = 2.0$ Hz, 1H), 5.00 (dd, $J_{trans} = 17.2$ Hz, $J_{gem} = 2.0$ Hz, 1H), 5.75-5.85 (m, 1H), 6.46 (t, $J = 7.2$ Hz, 1H), 6.60 (t, $J = 7.7$ Hz, 1H), 6.82 (t, $J = 7.7$ Hz, 1H), 6.96 (t, $J = 7.7$ Hz, 1H), 7.27 (bs+d, $J = 7.7$ Hz, 2H), 7.34 (bs, 1H), 7.43 (2d, $J_1 = 7.7$ Hz, $J_2 = 7.2$ Hz, 2H), 8.04 (d, $J = 7.2$ Hz, 1H), 10.84 (bs, 1H) ppm. ^{13}C - NMR (100MHz, DMSO- d_6 , 25°C); $\delta = 35.5$ (CH), 38.6 (CH₂), 112.3 (CH), 112.5 (CH), 114.6 (C), 117.0 (CH₂), 118.7 (CH), 118.9 (CH), 119.2 (CH), 119.9 (CH), 121.8 (2CH), 122.3 (CH), 124.1 (CH), 126.8 (C), 130.7 (C), 137.3 (C), 137.9 (CH), 140.9 (C) ppm. MS (CI) m/z 288 (M+H)⁺ C₁₉H₁₇N₃ (287.38) Calcd: C, 79.41; H, 5.96; N, 14.62. Found: C, 79.53; H, 5.79; N, 14.78.

3-[1-(1*H*-Indol-3-yl)-but-3-enyl]-imidazo[1,5-*a*]pyridine (24)

Brown solid; Mp 177-178°C; $R_f = 0.07$ (AcOEt-*n*-hexane 1:1), violet. ^1H - NMR (400MHz, DMSO- d_6 , 25°C); $\delta = 2.88$ -3.01 (m, 2H), 4.57 (t, $J = 7.4$ Hz, 1H), 4.82 (dd, $J_{cis} = 10.2$ Hz, $J_{gem} = 1.6$ Hz, 1H), 4.96 (dd, $J_{trans} = 17.2$ Hz, $J_{gem} = 1.6$ Hz, 1H), 5.72-5.75 (m, 1H), 6.47 (t, $J = 7.0$ Hz, 1H), 6.53 (dd, $J = 7.0$ Hz, $J = 8.0$ Hz, 1H), 6.83 (t, $J = 7.7$ Hz, 1H), 6.96 (t, $J = 7.7$ Hz, 1H), 7.24 (bs+d, $J = 8.0$ Hz, 2H), 7.40 (d, $J = 7.7$ Hz, 1H), 7.49 (d, $J = 7.7$ Hz, 1H), 8.14 (d, $J = 7.0$ Hz, 1H), 8.22 (s, 1H), 10.74 (bs, 1H) ppm. ^{13}C - NMR (100MHz, DMSO- d_6 , 25°C); $\delta = 35.7$ (CH), 40.0 (CH₂), 112.1 (CH), 112.7 (CH), 116.5 (CH₂), 118.3 (CH), 118.4 (CH), 118.7 (C), 118.9 (CH), 119.0 (CH), 119.8 (CH), 121.6 (CH), 123.0 (CH), 123.8 (CH), 126.2 (C), 127.4 (C), 134.9 (C), 137.1 (C), 138.7 (CH) ppm. MS (CI) m/z 288 (M+H)⁺ C₁₉H₁₇N₃ (287.36) Calcd: C, 79.41; H, 5.96; N, 14.62. Found: C, 79.50; H, 5.81; N, 14.80.

1,3-Bis-[1-(1*H*-indol-3-yl)-but-3-enyl]-imidazo[1,5-*a*]pyridine (25)

Mixture of diastereoisomers (ca 1:1) as yellow solid; $R_f = 0.44$ (AcOEt-*n*-hexane 1:1), red-orange. ^1H - NMR (400MHz, CDCl₃, 25°C); $\delta = 3.04$ -3.33 (m, 4H), 4.67-4.70 (m, 2H), 4.89-4.94 (m, 2H), 5.02-5.09 (m, 2H), 5.84-5.92 (m, 2H), 6.20-6.23 (m, 1H), 6.34-6.36 (m, 1H), 6.92-7.01 (m, 3H), 7.12-7.18 (m, 3H), 7.22-7.29 (m, 3H), 7.46-7.53 (m, 2H), 7.61 (t, $J = 8.3$ Hz, 1H), 8.15 (bs, 2H) ppm. ^{13}C - NMR (100MHz, CDCl₃, 25°C); $\delta = 36.0$ (CH), 36.15 (CH), 38.52 (CH₂), 40.28 (CH₂), 111.50 (CH), 111.63 (CH), 112.09 (CH), 116.06 (CH₂), 116.69 (CH), 116.84 (CH₂), 118.54 (CH), 119.24 (CH), 119.30 (C), 119.40 (C), 119.62 (CH), 119.71 (CH), 119.76 (CH), 119.97 (CH), 121.16 (CH), 121.88 (CH), 121.95 (CH), 122.37 (CH), 126.93 (C), 127.49 (2C), 133.43 (C), 136.86 (C), 136.91 (C), 137.19 (CH), 138.22 (CH), 138.88 (C) ppm. C₃₁H₂₈N₄ (456.59) Calcd: C, 81.55; H, 6.18; N, 12.27. Found: C, 81.35; H, 6.07; N, 12.11.

3-[1-(6-Phenyl-imidazo[2,1-*b*]thiazol-5-yl)-but-3-enyl]-1*H*-indole (26)

Yellow solid; Mp 241-242°C; $R_f = 0.34$ (AcOEt- *n*-hexane 3:7). ^1H - NMR (400MHz, DMSO- d_6 , 25°C); $\delta = 3.01$ -3.19 (m, 2H), 4.82-4.93 (m, 1H), 4.95 (dd, $J_{cis} = 10.2$ Hz, $J_{gem} = 2.0$ Hz, 1H), 5.07 (dd, $J_{trans} = 17.1$ Hz, $J_{gem} = 2.0$ Hz, 1H), 5.81-5.87 (m, 1H), 6.64-6.71 (m, 2H), 6.91-6.95 (m, 1H), 7.09 (d, $J = 4.0$ Hz, 1H), 7.26 (d, $J = 8.1$ Hz, 1H), 7.34 (t, $J = 7.5$ Hz, 1H), 7.44 (s, 1H), 7.47 (d, $J = 7.5$ Hz, 2H), 7.68-7.72 (m, 3H), 10.97 (bs, 1H) ppm. ^{13}C - NMR (100MHz, DMSO- d_6 , 25°C); $\delta = 33.7$ (CH), 36.9 (CH₂), 112.3 (CH), 113.4 (CH), 114.9 (C), 117.7 (CH₂), 118.8 (CH), 119.3 (CH), 120.2 (CH), 122.0 (CH), 123.4 (CH), 125.3 (C), 127.1 (C), 127.9 (CH), 128.7 (CH), 128.9 (CH), 129.8 (2CH), 136.1 (C), 137.2 (C), 137.3 (CH), 143.5 (C), 148.6 (C) ppm. MS (ESI⁺) m/z 370 (M+H)⁺ C₂₃H₁₉N₃S (369.48) Calcd: C, 74.77; H, 5.18; N, 11.37. Found: C, 74.82; H, 5.35; N, 11.68.

3-[1-(3,5-Diphenyl-pyrazol-1-yl)-but-3-enyl]-1*H*-indole (27)

Brown thick oil; $R_f = 0.46$ (AcOEt- *n*-hexane 1:1). ^1H - NMR (400MHz, CDCl₃, 25°C); $\delta = 3.00$ -3.05 (m, 1H), 3.41-3.46 (m, 1H), 4.98 (d, $J_{cis} = 10.2$ Hz, 1H), 5.07 (d, $J_{trans} = 17.1$ Hz, 1H), 5.67-5.75 (m, 2H), 6.59 (bs, 1H), 7.11 (t, $J = 7.4$ Hz, 1H), 7.19 (t, $J = 7.4$ Hz, 1H), 7.31-7.52 (m, 11H), 7.75 (d, $J = 7.4$ Hz, 1H), 7.93 (d, $J = 7.4$ Hz, 1H), 8.20 (bs, 1H) ppm. ^{13}C - NMR (100MHz, CDCl₃, 25°C); $\delta = 41.3$ (CH₂), 56.3 (CH), 103.3 (CH), 111.7 (CH), 117.9 (C), 117.9 (CH₂), 119.5 (CH), 120.0 (CH), 122.5 (CH), 126.0 (2CH), 127.8 (CH), 128.8 (CH), 128.9 (CH), 129.0 (2CH), 129.4 (2CH), 129.8 (2CH), 131.5 (C), 134.5 (C), 135.2 (CH), 136.4 (C), 145.7 (C), 149.0 (C), 150.8 (C) ppm. MS (ESI⁺) m/z 390 (M+H)⁺.

1-[1-(1*H*-Indol-3-yl)-but-3-enyl]-1*H*-indazole (28)

Colourless solid; Mp 169-170°C; $R_f = 0.27$ (CH₂Cl₂). ^1H - NMR (400MHz, CDCl₃, 25°C); $\delta = 3.20$ -3.23 (m, 1H), 3.35-3.50 (m, 1H), 4.96 (dd, $J_{cis} = 10.1$ Hz, $J_{gem} = 1.2$ Hz, 1H), 5.10 (dd, $J_{trans} = 17.0$ Hz, $J_{gem} = 1.2$ Hz, 1H), 5.68-5.77 (m, 1H), 6.06 (t, $J = 8.0$ Hz, 1H), 7.01 (t, $J = 8.0$ Hz, 1H), 7.10-7.17 (m, 3H), 7.29 (d, $J = 8.0$ Hz, 1H), 7.34 (t, $J = 8.0$ Hz, 1H), 7.40 (d, $J = 8.0$ Hz, 1H), 7.53 (d, $J = 8.0$ Hz, 1H), 7.72 (d, $J = 8.0$ Hz, 1H), 8.06 (s, 1H), 8.37 (bs, 1H) ppm. ^{13}C - NMR (100MHz, CDCl₃, 25°C); $\delta = 38.9$ (CH₂), 56.1 (CH), 109.6 (CH), 111.4 (CH), 115.9 (2C), 117.7 (CH₂), 119.0 (CH), 119.9 (CH), 120.6 (CH), 121.3 (CH), 122.4 (CH), 122.5 (CH), 124.2 (C), 126.2 (CH), 133.1 (CH), 134.7 (CH), 137.4 (C), 139.7 (C) ppm. MS (ESI⁺) m/z 288 (M+H)⁺ C₁₉H₁₇N₃ (287.36) Calcd: C, 79.41; H, 5.96; N, 14.62. Found: C, 79.31; H, 5.81; N, 14.43.

1-[1-(1*H*-Indol-3-yl)-but-3-enyl]-1*H*-benzimidazole (29)

Yellow solid; Mp 131-132°C; $R_f = 0.27$ (CH_2Cl_2 -AcOEt 6:4). ^1H – NMR (400MHz, CDCl_3 , 25°C); $\delta = 3.15$ -3.20 (m, 1H), 3.22-3.28 (m, 1H), 5.07 (d, $J_{cis} = 10.2\text{Hz}$, 1H), 5.14 (d, $J_{trans} = 17.1\text{Hz}$, 1H), 5.78-5.86 (m, 1H), 5.87 (t, $J = 7.4\text{Hz}$, 1H), 7.02 (t, $J = 7.4\text{Hz}$, 1H), 7.20 (t, $J = 7.4\text{Hz}$, 1H), 7.30 (m, 3H), 7.34 (d, $J = 7.4\text{Hz}$, 1H), 7.40 (d, $J = 7.4\text{Hz}$, 1H), 7.52-7.49 (m, 1H), 7.84-7.82 (m, 1H), 7.97 (s, 1H), 8.58 (bs, 1H) ppm. ^{13}C – NMR (100MHz, CDCl_3 , 25°C); $\delta = 39.2$ (CH_2), 53.5 (CH), 110.9 (CH), 111.9 (CH), 114.2 (C), 114.9 (C), 118.9 (CH), 119.1 (CH_2), 120.5 (CH), 120.7 (CH), 122.7 (CH), 123.0 (CH), 123.2 (CH), 123.3 (CH), 126.2 (C), 133.8 (CH), 136.9 (C), 142.3 (CH), 143.8 (C) ppm. MS (ESI⁺) m/z 288 (M+H)⁺ $\text{C}_{19}\text{H}_{17}\text{N}_3$: (287.36) Calcd: C, 79.41; H, 5.96; N, 14.62. Found: C, 79.38; H, 5.93; N, 14.55.

3-(1-[1,2,3]Triazol-1-yl-but-3-enyl)-1*H*-indole (30)

Pink solid; Mp 124-125°C; $R_f = 0.27$ (CH_2Cl_2 -AcOEt 4:6), violet. ^1H – NMR (400MHz, CDCl_3 , 25°C); $\delta = 3.08$ -3.14 (m, 1H), 3.26-3.33 (m, 1H), 5.02 (d, $J_{cis} = 10.3\text{Hz}$, 1H), 5.12 (d, $J_{trans} = 17.1\text{Hz}$, 1H), 5.30-5.60 (m, 1H), 6.14 (dd, $J = 8.9\text{Hz}$, $J = 6.1\text{Hz}$, 1H), 7.11 (m, 2H), 7.20 (t, $J = 7.5\text{Hz}$, 1H), 7.35 (s, 1H), 7.41 (d, $J = 7.5\text{Hz}$, 1H), 7.63 (m, 2H), 8.27 (s, 1H) ppm. ^{13}C – NMR (100MHz, CDCl_3 , 25°C); $\delta = 39.3$ (CH_2), 62.5 (CH), 111.7 (CH), 118.3 (CH_2), 118.9 (C), 119.6 (2CH), 120.4 (CH), 122.8 (CH), 124.3 (CH), 126.5 (C), 134.0 (CH), 134.1 (CH), 136.5 (C) ppm. MS (ESI⁺) m/z 239 (M+H)⁺ $\text{C}_{14}\text{H}_{14}\text{N}_4$ (238.29) Calcd: C, 70.57; H, 5.92; N, 23.51. Found: C, 70.77; H, 5.84; N, 23.78.

3-(1-[1,2,3]Triazol-2-yl-but-3-enyl)-1*H*-indole (31)

Yellow solid; Mp 87-88°C; $R_f = 0.20$ (CH_2Cl_2), violet. ^1H – NMR (400MHz, CDCl_3 , 25°C); $\delta = 3.08$ -3.14 (m, 1H), 3.24-3.31 (m, 1H), 5.03 (d, $J_{cis} = 10.2\text{Hz}$, 1H), 5.13 (dd, $J_{trans} = 17.1\text{Hz}$, 1H), 5.74-5.76 (m, 1H), 6.15 (dd, $J = 8.6\text{Hz}$, $J = 6.2\text{Hz}$, 1H), 7.13 (t, $J = 7.4\text{Hz}$, 1H), 7.21 (t, $J = 7.4\text{Hz}$, 1H), 7.34 (d, $J = 2.5\text{Hz}$, 1H), 7.36 (d, $J = 7.4\text{Hz}$, 1H), 7.61 (s, 2H), 7.63 (d, $J = 7.4\text{Hz}$, 1H), 8.25 (bs, 1H) ppm. ^{13}C – NMR (100MHz, CDCl_3 , 25°C); $\delta = 39.3$ (CH_2), 62.5 (CH), 111.6 (CH), 111.7 (CH), 118.3 (CH_2), 119.0 (C), 119.6 (CH), 119.7 (CH), 120.4 (CH), 122.9 (CH), 123.0 (CH), 126.3 (C), 134.1 (CH), 136.6 (C) ppm. MS (ESI⁺) m/z 239 (M+H)⁺ $\text{C}_{14}\text{H}_{14}\text{N}_4$ (238.29) Calcd.: C, 70.57; H, 5.92; N, 23.51. Found: C, 70.66; H, 5.89; N, 23.63.

3-(1-[1,2,4]Triazol-1-yl-but-3-enyl)-1*H*-indole (32)

Pale yellow solid; Mp 109-110°C; $R_f = 0.35$ (AcOEt-*n*-hexane 8:2), violet. ^1H – NMR (400MHz, CDCl_3 , 25°C); $\delta = 3.08$ -3.14 (m, 1H), 3.27-3.37 (m, 1H), 5.08 (d, $J_{cis} = 10.2\text{Hz}$, 1H), 5.14 (d, $J_{trans} =$

17.1Hz, 1H), 5.72-5.77 (m, 1H), 5.78 (t, $J = 7.5\text{Hz}$, 1H), 7.13 (t, $J = 7.5\text{Hz}$, 1H), 7.25 (t, $J = 7.5\text{Hz}$, 1H), 7.36 (d, $J = 2.0\text{Hz}$, 1H), 7.42 (d, $J = 7.5\text{Hz}$, 1H), 7.45 (d, $J = 7.5\text{Hz}$, 1H), 8.02 (s, 1H), 8.05 (s, 1H), 8.35 (bs, 1H) ppm. ^{13}C – NMR (100MHz, CDCl_3 , 25°C); $\delta = 39.4$ (CH_2), 57.8 (CH), 112.0 (CH), 112.1 (CH), 113.1 (C), 118.9 (CH), 119.0 (CH_2), 120.6 (CH), 123.1 (CH), 123.6 (CH), 123.7 (CH), 126.1 (C), 133.7 (CH), 136.8 (C) ppm. MS (ESI⁺) m/z 239 (M+H)⁺ $\text{C}_{14}\text{H}_{14}\text{N}_4$ (238.29) Calcd.: C, 70.57; H, 5.92; N, 23.51. Found: C, 70.50; H, 5.70; N, 23.42.

1-[1-(1*H*-Indol-3-yl)-but-3-enyl]-1*H*-benzotriazol (33)

Yellow solid; Mp 158-159°C; $R_f = 0.33$ (AcOEt-*n*-hexane 4:6), pink. ^1H – NMR (400MHz, CDCl_3 , 25°C); $\delta = 3.33$ -3.51 (m, 2H), 5.00 (d, $J_{cis} = 10.2\text{Hz}$, 1H), 5.10 (d, $J_{trans} = 17.1\text{Hz}$, 1H), 5.79 (m, 1H), 6.40 (dd, $J = 6.7\text{Hz}$, $J = 2.7\text{Hz}$, 1H), 7.04 (t, $J = 7.6\text{Hz}$, 1H), 7.18 (t, $J = 7.6\text{Hz}$, 1H), 7.29 (bs, 1H), 7.31-7.45 (m, 5H), 8.04 (d, $J = 7.6\text{Hz}$, 1H), 8.47 (bs, 1H) ppm. ^{13}C – NMR (100MHz, CDCl_3 , 25°C); $\delta = 38.8$ (CH_2), 57.4 (CH), 110.6 (CH), 111.8 (CH), 114.3 (C), 118.8 (CH_2), 119.2 (CH), 120.4 (CH), 120.6 (CH), 122.9 (CH), 123.1 (CH), 124.1 (CH), 126.3 (C), 127.3 (CH), 132.9 (C), 133.9 (CH), 136.7 (C), 146.7 (C) ppm. MS (ESI⁺) m/z 289 (M+H)⁺ $\text{C}_{18}\text{H}_{16}\text{N}_4$: (288.35) Calcd: C, 74.98; H, 5.59; N, 19.43. Found: C, 74.70; H, 5.61; N, 19.10.

4-[1-(1*H*-Indol-3-yl)-but-3-enyl]-benzene-1,3-diol (34)

Reddish solid; Mp 143-144°C; $R_f = 0.30$ (CH_2Cl_2 -AcOEt 92:8), violet. ^1H – NMR (400MHz, CDCl_3 , 25°C); $\delta = 2.78$ -2.96 (m, 2H), 4.44 (t, $J = 7.6\text{ Hz}$, 1H), 5.01 (dd, $J_{cis} = 10.2\text{Hz}$, $J_{gem} = 1.3\text{Hz}$, 1H), 5.10 (dd, $J_{trans} = 17.1\text{Hz}$, $J_{gem} = 1.3\text{Hz}$, 1H), 5.68 (bs, 1H), 5.80 (bs, 1H), 5.81-5.89 (m, 1H), 6.21 (d, $J = 2.5\text{Hz}$, 1H), 6.35 (dd, $J = 8.3\text{Hz}$, $J = 2.5\text{Hz}$, 1H), 7.01 (d, $J = 2.5\text{Hz}$, 1H), 7.03 (t, $J = 7.7\text{Hz}$, 1H), 7.09 (d, $J = 8.3\text{Hz}$, 1H), 7.18 (t, $J = 7.7\text{Hz}$, 1H), 7.29 (d, $J = 7.7\text{Hz}$, 1H), 7.45 (d, $J = 7.7\text{Hz}$, 1H), 8.02 (bs, 1H) ppm. ^{13}C – NMR (100MHz, CDCl_3 , 25°C); $\delta = 37.3$ (CH), 39.0 (CH_2), 104.0 (CH), 108.2 (CH), 111.7 (CH), 116.6 (CH_2), 118.8 (C), 120.0 (CH), 120.1 (CH), 122.1 (CH), 122.8 (CH), 127.1 (C), 130.2 (CH), 137.2 (C), 137.4 (C), 137.6 (CH), 155.2 (C), 155.4 (C) ppm. MS (ESI⁺) m/z 280 (M+H)⁺ $\text{C}_{18}\text{H}_{17}\text{NO}_2$ (279.34) Calcd.: C, 77.40; H, 6.13; N, 5.01. Found: C, 77.32; H, 6.09; N, 4.97.

5-[1-(1*H*-Indol-3-yl)-but-3-enyl]-benzene-1,2,4-triol (35)

Reddish thick oil; $R_f = 0.31$ (AcOEt-*n*-hexane 1:1), violet. ^1H – NMR (400MHz, CDCl_3 , 25°C); $\delta = 2.71$ -2.87 (m, 2H), 4.40 (t, $J = 7.5\text{Hz}$, 1H), 4.96 (d, $J_{cis} = 10.3\text{Hz}$, 1H), 5.06 (d, $J_{trans} = 17.1\text{Hz}$, 1H), 5.30, 5.49, 6.03 (3 bs, 3H), 5.77-5.83 (m, 1H), 6.29 (s, 1H), 6.70 (s, 1H), 6.95 (d, $J = 1.9\text{Hz}$, 1H), 7.00 (t, $J = 7.5\text{Hz}$, 1H), 7.14 (t, $J = 7.5\text{Hz}$, 1H), 7.25 (d, $J = 7.5\text{Hz}$, 1H), 7.43 (d, $J = 7.5\text{Hz}$, 1H),

8.04 (bs, 1H) ppm. ^{13}C – NMR (100MHz, CDCl_3 , 25°C); δ = 37.2 (CH), 39.0 (CH_2), 104.8 (CH), 111.6 (CH), 116.3 (CH), 116.7 (CH_2), 118.7 (C), 120.0 (CH), 120.1 (CH), 122.02 (CH), 122.7 (C), 122.8 (CH), 127.1 (C), 137.1 (C), 137.4 (C), 137.5 (CH), 143.0 (C), 148.1 (C) ppm. MS (ESI⁺) m/z 296 (M+H)⁺.

2-[1-(1*H*-Indol-3-yl)-but-3-enyl]-benzene-1,3,5-triol (36)

Yellow solid; Mp 94-95°C; R_f = 0.29 (CH_2Cl_2 -AcOEt 75:25), red. ^1H - NMR (400MHz, $\text{DMSO-}d_6$, 25°C); δ = 2.84-3.00 (m, 2H), 4.65 (t, J = 7.4Hz, 1H), 4.83 (dd, J_{cis} = 10.1Hz, J_{gem} = 2.1Hz, 1H), 5.02 (dd, J_{trans} = 17.2Hz, J_{gem} = 2.1Hz, 1H), 5.69-5.73 (m, 1H), 5.72 (s, 2H), 6.84 (t, J = 7.6Hz, 1H), 6.96 (t, J = 7.6Hz, 1H), 7.13 (d, J = 1.7Hz, 1H), 7.25 (d, J = 7.6Hz, 1H), 7.54 (d, J = 7.6Hz, 1H), 8.68 (bs, 1H), 8.78 (bs, 2H), 10.57 (bs, 1H) ppm. ^{13}C – NMR (100MHz, $\text{DMSO-}d_6$, 25°C); δ = 31.7 (CH), 37.5 (CH_2), 94.9 (CH), 95.3 (CH), 109.0 (C), 111.7 (CH), 115.3 (CH_2), 118.4 (CH), 119.2 (C), 119.9 (CH), 121.0 (CH), 123.1 (CH), 128.4 (C), 136.6 (C), 140.0 (CH), 156.6 (C), 157.6 (C), 159.8 (C) ppm. MS (ESI⁺) m/z 296 (M+H)⁺ $\text{C}_{18}\text{H}_{17}\text{NO}_3$ (295.34) Calcd.: C, 73.20; H, 5.80; N, 4.74. Found: C, 73.13; H, 5.74; N, 4.79.

1-[1-(1*H*-Indol-3-yl)-but-3-enyl]-naphthalene-2,3-diol (37)

Colourless solid; Mp 89-90°C; R_f = 0.15 (AcOEt-*n*-hexane 3:7). ^1H – NMR (400MHz, CDCl_3 , 25°C); δ = 3.00-3.20 (m, 2H), 4.98 (d, J_{cis} = 10.2 Hz, 1H), 5.15 (d, J_{trans} = 17.0 Hz, 1H), 5.27 (t, J = 7.0 Hz, 1H), 5.88 (bs, 1H), 6.84 (t, J = 7.7 Hz, 1H), 7.00 (d, J = 7.7 Hz, 1H), 7.15 (t, J = 7.7 Hz, 1H), 7.25 (s, 1H), 7.32 (d, J = 7.7 Hz, 1H), 7.37-7.46 (m, 3H), 7.72 (d, J = 7.7 Hz, 1H), 8.20 (d, J = 7.7 Hz, 1H), 8.33 (bs, 1H), 8.80 (bs, 2H) ppm. ^{13}C – NMR (100MHz, CDCl_3 , 25°C); δ = 34.8 (CH), 37.2 (CH_2), 109.3 (CH), 111.7 (CH), 117.0 (CH_2), 120.3 (CH), 120.4 (CH), 121.7 (C), 122.2 (CH), 122.9 (CH), 123.6 (CH), 124.3 (CH), 124.5 (CH), 127.3 (C), 128.0 (CH), 128.2 (C), 130.5 (C), 137.1 (CH), 137.4 (C), 143.7 (C), 145.3 (C), 145.5 (C) ppm. MS (ESI⁺) m/z 330 (M+H)⁺ $\text{C}_{22}\text{H}_{19}\text{NO}_2$ (329.40) Calcd.: C, 80.22; H, 5.81; N, 4.25. Found: C, 80.02; H, 5.64; N, 4.13.

(2*R*,3*S*)-2-(3,4-Dihydroxy-phenyl)-8-[1-(1*H*-indol-3-yl)-but-3-enyl]-chroman-3,5,7-triol (38)

Mixture of diastereoisomers ; pale yellow thick oil; R_f = 0.31 (AcOEt-*n*-hexane 8:2), violet. ^1H - NMR (400MHz, $\text{DMSO-}d_6$, 25°C); δ = 2.45-2.55 (m, 2H), 2.69-2.89 (m, 2H), 2.92-2.99 (m, 1H), 3.70-3.80 (m, 1H), 4.66 (d, J = 6.3 Hz, 1H), 7.78 (d, J = 6.3 Hz, 1H), 5.70 (m, 1H), 5.96 (s, 1H), 6.59-6.97 (m, 7H), 7.22 (m, 1H), 7.56 (m, 1H), 8.80-8.92 (m, 5H), 10.54 (s, 1H) ppm. ^{13}C – NMR (100MHz, $\text{DMSO-}d_6$, 25°C); δ = 28.7 (2 CH_2), 31.2 (2CH), 37.7 (2 CH_2), 67.4 (2CH), 82.4 (2CH), 94.7 (2CH), 95.9 (2CH), 100.4 (2C), 111.7 (2CH), 115.4 (2 CH_2), 115.9 (2CH), 118.5 (2CH), 118.9

(2C), 119.3 (2CH), 119.9 (2CH), 121.0 (2CH), 123.0 (2CH), 128.3 (2C), 131.5 (2C), 136.3 (2C), 139.9 (2CH), 145.6 (2C), 145.8 (2C), 154.2 (2C), 156.2 (2C), 157.1 (2C), 157.3 (2C) ppm. MS (ESI⁺) *m/z* 459 (M+H)⁺.

5-Diethylamino-2-[1-(1*H*-indol-3-yl)-but-3-enyl]-phenol (39)

Brown oil; *R_f* = 0.34 (AcOEt-*n*-hexane 4:6), violet. ¹H – NMR (400MHz, CDCl₃, 25°C); δ = 1.16 (t, *J* = 7.0 Hz, 6H), 1.65 (bs, 1H), 2.83-2.99 (m, 2H), 3.30 (q, *J* = 7.0 Hz, 4H), 4.37 (t, *J* = 7.4 Hz, 1H), 5.01 (d, *J_{cis}* = 10.2 Hz, 1H), 5.12 (d, *J_{trans}* = 17.1 Hz, 1H), 5.84-5.94 (m, 1H), 6.17 (s, 1H), 6.30 (d, *J* = 7.8 Hz, 1H), 7.04 (t, *J* = 7.8 Hz, 1H), 7.11-7.13 (m, 2H), 7.18 (t, *J* = 7.8 Hz, 1H), 7.35 (d, *J* = 7.8 Hz, 1H), 7.49 (d, *J* = 7.8 Hz, 1H), 8.04 (bs, 1H) ppm. ¹³C – NMR (100MHz, CDCl₃, 25°C); δ = 13.0 (2CH₃), 37.6 (CH), 39.2 (2CH₂), 44.8 (CH₂), 111.5 (CH), 116.3 (CH₂), 119.2 (2C), 119.9 (CH), 120.3 (2CH), 122.0 (2CH), 122.8 (CH), 127.3 (2C), 129.9 (CH), 137.2 (C), 138.0 (CH), 155.5 (C) ppm. MS (ESI⁺) *m/z* 335 (M+H)⁺.

4-Hydroxy-3-[1-(1*H*-indol-3-yl)-but-3-enyl]-chromen-2-one (40)

Colourless solid; Mp 144-145°C; *R_f* = 0.28 (CH₂Cl₂-*n*-hexane 8:2). ¹H – NMR (400MHz, CDCl₃, 25°C); δ = 2.85-3.10 (m, 2H), 4.94 (t, *J* = 7.2 Hz, 1H), 5.09 (d, *J_{cis}* = 10.1 Hz, 1H), 5.19 (d, *J_{trans}* = 17.0 Hz, 1H), 5.98-6.03 (m, 1H), 7.07 (t, *J* = 7.7 Hz, 1H), 7.20 (t, *J* = 7.7 Hz, 1H), 7.26 (bs, 1H), 7.28 (t, *J* = 7.7 Hz, 1H), 7.33 (d, *J* = 7.7 Hz, 1H), 7.44 (d, *J* = 7.7 Hz, 1H), 7.47 (s, 1H), 7.50 (d, *J* = 7.7 Hz, 1H), 7.52 (t, *J* = 7.7 Hz, 1H), 7.59 (d, *J* = 7.7 Hz, 1H), 8.40 (bs, 1H) ppm. ¹³C – NMR (100MHz, CDCl₃, 25°C); δ = 36.7 (CH₂), 33.1 (CH), 106.9 (C), 112.0 (CH), 112.1 (CH), 115.9 (C), 116.4 (C), 116.8 (CH), 117.7 (CH₂), 119.9 (CH), 120.7 (CH), 123.4 (CH), 123.9 (CH), 124.3 (CH), 127.1 (C), 132.3 (CH), 136.4 (CH), 137.4 (C), 137.5 (C), 153.0 (C), 164.6 (C) ppm. MS (ESI⁺) *m/z* 332 (M+H)⁺ C₂₁H₁₇NO₃ (331.37) Calcd.: C, 76.12; H, 5.17; N, 4.23. Found: C, 76.01; H, 5.23; N, 4.30.

4-Hydroxy-3-[1-(1*H*-indol-3-yl)-but-3-enyl]-1-methyl-1*H*-quinolin-2-one (41)

Yellow solid; Mp 84-85°C; *R_f* = 0.30 (AcOEt- *n*-hexane 1:1), red. ¹H – NMR (400MHz, CDCl₃, 25°C); δ = 2.07 (bs, 1H), 2.87-3.06 (m, 2H), 3.84 (s, 3H), 5.04 (d, *J_{cis}* = 10.1 Hz, 1H), 5.17 (d, *J_{trans}* = 17.1 Hz, 1H), 5.22 (t, *J* = 7.1 Hz, 1H), 5.95-6.07 (m, 1H), 6.95 (bs, 1H), 7.00 (t, *J* = 7.8 Hz, 1H), 7.15 (t, *J* = 7.8 Hz, 1H), 7.21 (t, *J* = 7.8 Hz, 1H), 7.35 (d, *J* = 7.8 Hz, 1H), 7.39-7.52 (m, 2H), 7.54 (t, *J* = 7.8 Hz, 1H), 7.76 (d, *J* = 7.8 Hz, 1H), 8.50 (bs, 1H) ppm. ¹³C – NMR (100MHz, CDCl₃, 25°C); δ = 30.4 (CH₃), 33.0 (CH), 36.8 (CH₂), 111.9 (CH), 112.7 (C), 114.2 (CH), 116.7 (C), 116.9 (C), 117.0 (CH₂), 120.2 (CH), 120.3 (CH), 121.8 (CH), 122.1 (CH), 123.6 (2CH), 127.4 (C), 130.9 (CH),

137.1 (CH), 137.5 (C), 139.2 (C), 158.4 (C), 163.8 (C) ppm. MS (ESI⁺) *m/z* 345 (M+H)⁺ C₂₂H₂₀N₂O₂ (344.41) Calcd.: C, 76.72; H, 5.85; N, 8.13. Found: C, 76.65; H, 5.76; N, 8.09.

4-Hydroxy-3-[1-(1*H*-indol-3-yl)-but-3-enyl]-5*H*-furan-2-one (42)

Orange glass; R_f = 0.35 (AcOEt- *n*-hexane 6:4), orange. ¹H – NMR (400MHz, CDCl₃, 25°C); δ = 2.81- 2.97 (m, 2H), 4.19 (t, *J* = 7.6 Hz, 1H), 4.38 (d, *J* = 15.0 Hz, 1H), 4.44 (d, *J* = 15.0 Hz, 1H), 5.02 (d, *J*_{cis} = 10.2 Hz, 1H), 5.14 (d, *J*_{trans} = 16.1 Hz, 1H), 5.81-5.88 (m, 1H), 7.09 (t, *J* = 7.5 Hz, 1H), 7.14 (bs, 1H), 7.18 (t, *J* = 7.5 Hz, 1H), 7.28 (d, *J* = 7.5 Hz, 1H), 7.66 (d, *J* = 7.5 Hz, 1H), 8.00 (bs, 1H), 9.50 (bs, 1H) ppm. ¹³C – NMR (100MHz, CDCl₃, 25°C); δ = 30.7 (CH), 36.6 (CH₂), 46.9 (C), 67.6 (CH₂), 103.0 (C), 111.7 (CH), 119.4 (CH), 119.8 (CH), 122.3 (CH), 122.6 (CH), 116.7 (CH₂), 127.0 (C), 136.6 (C), 137.3 (CH), 175.2 (C), 177.6 (C) ppm. MS (ESI⁺) *m/z* 270 (M+H)⁺ C₁₆H₁₅NO₃ (269.30) Calcd.: C, 71.36; H, 5.61; N, 5.20. Found: C, 71.29; H, 5.68; N, 5.16.

5-[1-(1*H*-Indol-3-yl)-but-3-enyl]-1-methyl-pyrimidine-2,4,6-trione (43)

Yellow solid; Mp 100-101°C; R_f = 0.26 (AcOEt-*n*-hexane 3:7), red. ¹H – NMR (400MHz, CDCl₃, 25°C); δ = 2.55-3.07 (m, 2H), 2.86 (s, 3H), 2.97 (s, 3H), 3.84 (d, *J* = 3.0Hz, 1H), 3.97-4.02 (m, 1H), 5.15 (d, *J*_{cis} = 10.1Hz, 1H), 5.29 (d, *J*_{trans} = 17.0Hz, 1H), 5.85-5.90 (m, 1H), 6.90 (d, *J* = 2.4Hz, 1H), 7.09 (t, *J* = 7.5Hz, 1H), 7.17 (t, *J* = 7.5Hz, 1H), 7.28 (d, *J* = 7.5Hz, 1H), 7.43 (d, *J* = 7.5Hz, 1H), 8.44 (bs, 1H) ppm. ¹³C – NMR (100MHz, CDCl₃, 25°C); δ = 28.3 (CH₃), 28.6 (CH₃), 37.4 (CH₂), 42.7 (CH), 53.7 (CH), 111.8 (CH), 113.5 (C), 118.6 (CH₂), 119.1 (CH), 120.2 (CH), 122.2 (CH), 122.9 (CH), 126.6 (C), 136.1 (C), 136.2 (CH), 151.6 (C), 168.4 (C), 170.1 (C) ppm. MS (ESI⁺) *m/z* 326 (M+H)⁺ C₁₈H₁₉N₃O₃ (325.37) Calcd.: C, 66.45; H, 5.89; N, 12.91. Found: C, 66.57; H, 5.76; N, 12.84.

2-[1-(1*H*-Indol-3-yl)-but-3-enyl]-5,5-dimethyl-cyclohexane-1,3-dione (44)

Brown solid; Mp 95-96°C; R_f = 0.23 (AcOEt-*n*-hexane 3:7), red. ¹H – NMR (400MHz, CDCl₃, 25°C); δ = 1.05 (s, 3H), 1.07 (s, 3H), 2.15 (d, *J* = 17.1Hz, 1H), 2.20 (d, *J* = 17.1Hz, 1H), 2.34 (bs, 2H), 2.69-2.73 (m, 1H), 2.83-2.85 (m, 1H), 4.80 (bt, *J* = 7.5Hz, 1H), 5.02 (d, *J*_{cis} = 10.2Hz, 1H), 5.14 (d, *J*_{trans} = 16.9Hz, 1H), 5.87-5.92 (m, 1H), 7.07 (bs+t, *J* = 7.6Hz, 2H), 7.22 (t, *J* = 7.6Hz, 1H), 7.23 (d, *J* = 1.6Hz, 1H), 7.37 (d, *J* = 7.6Hz, 1H), 7.43 (d, *J* = 7.6Hz, 1H), 8.48 (bs, 1H) ppm. ¹³C – NMR (100MHz, CDCl₃, 25°C); δ = 28.5 (CH), 29.9 (CH₃), 30.0 (CH₃), 36.9 (CH₂), 45.4 (CH₂), 45.5 (2CH₂), 110.5 (CH), 116.5 (C), 116.8 (CH₂), 117.1 (C), 118.2 (C), 120.6 (CH), 121.2 (CH), 121.8 (CH), 122.4 (CH), 123.5 (CH), 127.2 (C), 136.8 (CH), 176.1 (C), 176.5 (C) ppm. MS (ESI⁺) *m/z* 310 (M+H)⁺ C₂₀H₂₃NO₂ (309.41) Calcd.: C, 77.64; H, 7.49; N, 4.53. Found: C, 77.40; H, 7.31; N, 4.35.

4-[1-(1*H*-Indol-3-yl)-but-3-enyl]-1,5-dimethyl-2-phenyl-1,2-dihydro-pyrazol-3-one (45)

Pale brown solid; Mp 79-80°C; R_f= 0.24 (AcOEt-*n*-hexane 1:1 violet). ¹H – NMR (400MHz, CDCl₃, 25°C); δ= 2.18 (s, 3H), 2.93-3.05 (m, 2H), 2.97 (s, 3H), 4.22 (t, *J* = 7.9 Hz, 1H), 4.98 (d, *J*_{cis} = 10.1 Hz, 1H), 5.11 (d, *J*_{trans} = 17.1 Hz, 1H), 5.95-5.99 (m, 1H), 7.09 (t, *J* = 7.3 Hz, 1H), 7.17 (t, *J* = 7.3 Hz, 1H), 7.22-7.28 (m, 2H), 7.35 (d, *J* = 7.3 Hz, 1H), 7.40-7.46 (m, 4H), 7.62 (d, *J* = 7.3 Hz, 1H), 8.20 (bs, 1H) ppm. ¹³C – NMR (100MHz, CDCl₃, 25°C); δ= 11.6 (CH₃), 30.1 (CH₃), 36.7 (CH), 37.9 (CH₂), 111.7 (CH), 113.0 (C), 116.2 (CH₂), 118.1 (C), 119.1 (CH), 119.4 (CH), 121.9 (CH), 122.6 (CH), 124.0 (CH), 126.4 (CH), 127.4 (C), 129.4 (CH), 135.9 (C), 136.5 (C), 138.0 (CH), 153.3 (C), 166.0 (C) ppm. MS (ESI⁺) *m/z* 358 (M+H)⁺ C₂₃H₂₃N₃O (357.46) Calcd.: C, 77.28; H, 6.49; N, 11.76. Found: C, 77.24; H, 6.55; N, 11.82.