Supporting Information
for
Synthesis of 2-substituted tryptophans via a C3- to C2-alkyl migration

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Experimental Procedures and NMR Spectra

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Materials and Methods

All reactions were run in air unless otherwise noted. Column chromatography purifications were performed in flash conditions using Merck 230–400 mesh silica gel. Analytical thin layer chromatography (TLC) was carried out on Merck silica gel plates (silica gel 60 F₂₅₄), that were visualized by exposure to ultraviolet light and an aqueous solution of p-anisaldehyde. ¹H NMR and ¹³C NMR spectra were recorded on a Bruker Avance 200 spectrometer, using CDCl₃ as a solvent. Chemical shifts (δ scale) are reported in parts per million (ppm) relative to the central peak of the solvent. Coupling constants (J values) are given in Hertz (Hz). ESI-MS spectra were taken on a Waters Micromass ZQ instrument, only molecular ions (M + 1 or M − 1) are given. IR spectra were obtained on a Nicolet Avatar 360 FT-IR spectrometer, absorbance values are reported in cm⁻¹. Melting points were determined on a Buchi SMP-510 capillary melting point apparatus and are uncorrected. Elemental analyses were performed on a Carlo Erba analyzer and the results are within ±0.3 of the theoretical values (C,H,N). Methyl 2-acetamidoacrylate (2a) and bis(1H-indol-3-yl)methane (1h) are commercially available. Starting materials 3-benzyl-1H-indole (1a), 3-(4-methoxybenzyl)-1H-indole (1b), 3-(4-chlorobenzyl)-1H-indole (1c), 3-(4-nitrobenzyl)-1H-indole (1d), 3-benzyldihydro-1H-indole (1e), 3-((furan-2-yl)methyl)-1H-indole (1g), 3-benzyl-1-methyl-1H-indole (1i), 3-allyl-1H-indole (1k), 3-(3-methylbut-2-enyl)-1H-indole (1l), 3-((E)-3,7-dimethylocta-2,6-dienyl)-1H-indole (1m), 3-(2-methylbut-3-en-2-yl)-1H-indole (1n), 3-(methylthio)-1H-indole (1o) and methyl 2-(1,3-dioxoisooindolin-2-yl)acrylate (2b) were prepared as previously described.
Compounds Characterization and Synthetic Methods

3-(1,2,3,4-tetrahydronaphthalen-1-yl)-1H-indole (1f)

Compound 1f was prepared according to the procedure reported in literature. Colorless Oil, TLC: \( R_f = 0.47 \) (cyclohexane/ethyl acetate, 9:1; UV, p-anisaldehyde). FTIR (nujol): \( \tilde{\nu} \text{ max} = 3417 \text{ cm}^{-1} \). \(^1\)H NMR (200 MHz, CDCl\(_3\)): \( \delta = 1.76-2.04 \text{ (m, 2H)}, 2.16-2.25 \text{ (m, 2H)}, 2.84-3.09 \text{ (m, 1H)}, 4.48-4.54 \text{ (m, 1H)}, 6.67 \text{ (d, } J=2.5 \text{ Hz, 1H)}, 7.08-7.30 \text{ (m, 6H)}, 7.37-7.42 \text{ (m, 1H)}, 7.57-7.61 \text{ (m, 1H)}, 7.85 \text{ (br s, 1H)} \text{ ppm.} \(^{13}\)C NMR (50 MHz, CDCl\(_3\)): \( \delta = 20.8, 29.8, 30.9, 36.5, 111.3, 119.2, 119.5, 121.9, 122.3, 123.1, 125.6, 125.8, 126.7, 129.0, 130.1, 136.6, 137.4, 139.7 \text{ ppm. MS (ESI): } m/z (\%) = 246 [M-H]-. C\(_{18}\)H\(_{17}\)N (247.14): calcd. C 87.41, H 6.93, N 5.66; found C 87.31, H 6.98, N 5.69.

Methyl 2-acetamido-3-(2-benzyl-1H-indol-3-yl)propanoate (3a)

White solid (245 mg, 70%). mp: 168-169 °C (from ether-hexane); TLC: \( R_f = 0.26 \) (cyclohexane/ethyl acetate, 6:4; UV, p-anisaldehyde). FTIR (nujol): \( \tilde{\nu} \text{ max} = 3398, 3397, 1740, 1655 \text{ cm}^{-1} \). \(^1\)H NMR (200 MHz, CDCl\(_3\)): \( \delta = 1.78 \text{ (s, 3H)}, 3.36 \text{ (d, } J=5.5 \text{ Hz, 2H)}, 3.65 \text{ (s, 3H)}, 4.08 \text{ (s, 2H)}, 4.93 \text{ (ddd, } J_1=J_2=5.5 \text{ Hz, } J_3=8.0 \text{ Hz, 1H)}, 6.09 \text{ (br d, } J=8.0 \text{ Hz, 1H)}, 7.06-7.38 \text{ (m, 8H)}, 7.47-7.53 \text{ (m, 1H)}, 8.22 \text{ (br s, 1H)}. \(^{13}\)C NMR (50 MHz, CDCl\(_3\)): \( \delta = 23.0, 26.9, 32.0, 52.4, 53.1, 106.6, 110.8, 118.2, 119.6, 121.7, 126.8, 128.6, 128.7, 128.9, 130.0, 135.0, 135.6, 138.5, 169.9, 172.6. MS (ESI): \( m/z (\%) = 351 [M+H]^+; 349 [M-H]^-. C_{23}H_{22}N_{2}O_{3} (350.16): \) calcd. C 71.98, H 6.33, N 7.99; found C 72.06, H 6.31, N 7.94.

Methyl 3-(2-(4-methoxybenzyl)-1H-indol-3-yl)-2-acetamidopropanoate (3b)

Brown solid (281 mg, 74%). mp: 108-110 °C (from ether-hexane); TLC: \( R_f = 0.24 \) (cyclohexane/ethyl acetate, 1:1; UV, p-anisaldehyde). FTIR (nujol): \( \tilde{\nu} \text{ max} = 3397, 3293, 1736, 1655 \text{ cm}^{-1} \). \(^1\)H NMR (200 MHz, CDCl\(_3\)): \( \delta = 1.83 \text{ (s, 3H)}, 3.35 \text{ (d, } J=5.5 \text{ Hz, 2H)}, 3.65 \text{ (s, 3H)}, 3.79 \text{ ppm.} \)
Methyl 3-(2-(4-chlorobenzyl)-1H-indol-3-yl)-2-acetimidopropanoate (3c)

Brown solid (204 mg, 53%). mp: 89-90 °C (from ether-hexane); TLC: Rf = 0.31 (cyclohexane/ethyl acetate, 1:1; UV, p-anisaldehyde). FTIR (nujol): ν max = 3383, 3292, 1737, 1657 cm⁻¹. ¹H NMR (200 MHz, CDCl₃): δ = 1.87 (s, 3H), 3.35 (d, J=5.5 Hz, 2H), 3.64 (s, 3H), 4.06 (s, 2H), 4.93 (dd, J₁=J₂= 5.5 Hz, J₃= 8.0 Hz, 1H), 6.03 (d, J=8.0 Hz, 1H), 7.07-7.16 (m, 4H), 7.22-7.32 (m, 3H), 7.47-7.52 (m, 1H), 7.85 (br s, 1H). ¹³C NMR (50 MHz, CDCl₃): δ = 23.1, 26.9, 31.4, 52.5, 53.1, 107.0, 110.7, 118.2, 119.8, 121.9, 128.7, 129.0, 129.9, 132.7, 134.3, 135.6, 136.8, 169.7, 172.5. MS (ESI): m/z (%) = 385 [M+H]⁺; 383 [M-H]⁻. C₂₂H₂₄N₂O₄ (380.17): calcd. C 69.46, H 6.36, N 7.36; found C 69.35, H 6.47, N 7.37.

Methyl 2-acetamido-3-(2-(1,2,3,4-tetrahydronaphthalen-1-yl)-1H-indol-3-yl)propanoate (3f)

Brown solid (43 mg, 11%). mp: 153-154 °C (from ether-hexane); TLC: Rf = 0.27 (cyclohexane/ethyl acetate, 1:1; UV, p-anisaldehyde). FTIR (nujol): ν max = 3351, 3281, 1735, 1655 cm⁻¹. ¹H NMR (200 MHz, CDCl₃): δ = 1.80-1.94 (m, 2H+2H), 1.90 (s, 3H), 2.01-2.19 (m, 2H+2H), 2.04 (s, 3H), 2.88-3.08 (m, 2H+2H), 3.11-3.43 (m, 2H+2H), 3.75 (s, 3H), 3.77 (s, 3H), 4.16-4.29 (m, 1H+1H), 4.85-4.99 (m, 2H+2H), 6.12 (d, J=7.5, 1H), 6.22 (d, J=7.5, 1H), 6.80-7.16 (m, 1H), 7.42-7.62 (m, 4H), 7.81-7.85 (m, 2H), 8.58 (br s, 1H+1H). ¹³C NMR (50 MHz, CDCl₃): δ = 23.0, 23.1, 23.2, 23.3, 29.2, 29.4, 30.0, 30.1, 31.9, 32.0, 36.6, 36.7, 52.1, 52.2, 52.9, 52.9, 110.8, 110.8, 118.2, 118.2, 118.9, 118.9, 120.0, 120.2, 121.5, 121.5, 125.7, 125.8, 126.6, 126.8, 128.3, 128.3, 128.7, 128.9, 129.0, 130.1, 130.1, 136.1, 136.2, 137.0, 137.3, 139.3, 139.7, 170.2, 170.2, 172.4, 172.5. MS (ESI): m/z (%) = 391 [M+H]⁺; 389 [M-H]⁻. C₂₄H₂₆N₂O₅ (390.19): calcd. C 73.82, H 6.71, N 7.17; found C 73.94, H 6.80, N 7.10.
Methyl 3-(2-((1H-indol-3-yl)methyl)-1H-indol-3-yl)-2-acetamidopropanoate (3h)

Brown solid (261 mg, 67%). mp: 145-146 °C (from ether-hexane); TLC: \(R_f = 0.24\) (cyclohexane/ethyl acetate, 1:1; UV, p-anisaldehyde). FTIR (nujol): \(v\) max = 3398, 3277, 1735, 1655 cm\(^{-1}\). \(^1\)H NMR (200 MHz, CDCl\(_3\)): \(\delta = 1.71\) (s, 3H), 3.41 (d, \(J=5.5\) Hz, 2H), 3.64 (s, 3H), 4.17 (s, 2H), 4.96 (ddd, \(J_1=J_2=5.5\) Hz, \(J_3=8.0\) Hz, 1H), 6.05 (d, \(J=8.0\) Hz, 1H), 6.92 (d, \(J=2.5\) Hz, 1H), 7.07-7.26 (m, 5H), 7.36-7.52 (m, 3H), 8.01 (br s, 1H), 8.26 (br s, 1H). \(^{13}\)C NMR (50 MHz, CDCl\(_3\)): \(\delta = 22.3, 22.9, 26.9, 52.4, 53.0, 105.5, 110.7, 111.4, 112.5, 118.0, 118.7, 119.5, 119.9, 121.4, 122.5, 122.8, 127.0, 128.9, 135.2, 135.5, 136.4, 169.9, 172.7. MS (ESI): \(m/z\) (%) = 390 [M+H]\(^+\); 388 [M-H]. \(C_{23}H_{23}N_3O_3\) (389.17): calcd. C 70.93, H 5.95, N 10.79; found C 70.81, H 6.03, N 10.89.

Methyl 2-acetamido-3-(2-benzyl-1-methyl-1H-indol-3-yl)propanoate (3i)

Yellow oil (186 mg, 51%). TLC: \(R_f = 0.25\) (cyclohexane/ethyl acetate, 6:4; UV, p-anisaldehyde). FTIR (nujol): \(v\) max = 3281, 1744, 1659 cm\(^{-1}\). \(^1\)H NMR (200 MHz, CDCl\(_3\)): \(\delta = 1.69\) (s, 3H), 3.37 (d, \(J=5.5\) Hz, 2H), 3.49 (s, 3H), 3.61 (s, 3H), 4.19 (s, 2H), 4.90 (ddd, \(J_1=J_2=5.5\) Hz, \(J_3=7.5\) Hz, 1H), 5.99 (br d, \(J=7.5\) Hz, 1H), 7.04-7.08 (m, 2H), 7.10-7.22 (m, 2H), 7.25-7.35 (m, 4H), 7.52-7.56 (m, 1H). \(^{13}\)C NMR (50 MHz, CDCl\(_3\)): \(\delta = 22.9, 27.2, 30.1, 30.3, 52.4, 53.2, 106.9, 109.0, 118.34, 119.4, 121.5, 126.6, 127.8, 127.9, 128.9, 135.9, 137.0, 138.5, 169.8, 172.5. MS (ESI): \(m/z\) (%) = 365 [M+H]\(^+\). \(C_{21}H_{22}N_2O_3\) (364.18): calcd. C 72.50, H 6.64, N 7.69; found C 72.61, H 6.58, N 7.61.

Methyl 3-(2-benzyl-1H-indol-3-yl)-2-(1,3-dioxoisindolin-2-yl)propanoate (3j)

Compound 3j was prepared according to the general procedure by using methyl 2-(1,3-dioxoisindolin-2-yl)acrylate 2b (1.2 equiv.) instead of 2a. Yellow solid (223 mg, 51%). mp: 125-126 °C (from ether-hexane); TLC: \(R_f = 0.21\) (cyclohexane/ethyl acetate, 1:1; UV, p-anisaldehyde). FTIR (nujol): \(v\) max = 3394, 1774, 1716 cm\(^{-1}\)
1. $^1$H NMR (200 MHz, CDCl$_3$): $\delta$ = 3.79 (s, 3H), 3.74-3.83 (m, 2H), 4.01-4.18 (m, 2H), 5.28 (dd, $J_1$= 6.5 Hz, $J_2$=9.0 Hz, 1H), 6.95-7.22 (m, 8H), 7.53-7.73 (m, 6H) ppm. $^{13}$C NMR (50 MHz, CDCl$_3$): $\delta$ = 24.2, 32.0, 52.5, 52.8, 107.5, 110.5, 118.1, 119.5, 121.5, 123.4, 126.6, 128.1, 128.6, 131.7, 133.9, 134.8, 135.4, 167.5, 169.6 ppm. MS (ESI): $m/z$ (%) = 439 [M+H]$^+$; 437 [M-H]$^-$.

Methyl 2-acetamido-3-(2-allyl-1H-indol-3-yl)propanoate (3k)

![Methyl 2-acetamido-3-(2-allyl-1H-indol-3-yl)propanoate (3k)](image)

Brown solid (183 mg, 61%). mp: 100-101 °C (from ether-hexane); TLC: $Rf$ = 0.31 (cyclohexane/ethyl acetate, 1:1; UV, p-anisaldehyde). FTIR (nujol): $\tilde{\nu}$ max = 3403, 3303, 1737, 1662 cm$^{-1}$. $^1$H NMR (200 MHz, CDCl$_3$): $\delta$ = 1.94 (s, 3H), 3.29 (d, $J$=5.5 Hz, 2H), 3.45-3.49 (m, 2H), 3.68 (s, 3H), 4.91 (ddd, $J_1$= $J_2$=5.5 Hz, $J_3$=8.0 Hz, 1H), 5.16-5.20 (m, 1H), 5.24-5.26 (m, 1H), 5.85-6.05 (m, 2H), 7.05-7.19 (m, 2H), 7.29 (dd, $J_1$=2.0 Hz, $J_2$=6.0 Hz, 1H), 7.46 (dd, $J_1$=2.0 Hz, $J_2$=6.0 Hz, 1H), 8.00 (br s, 1H). $^{13}$C NMR (50 MHz, CDCl$_3$): $\delta$ = 23.3, 26.7, 30.5, 52.4, 53.0, 106.0, 110.6, 117.7, 118.1, 119.6, 121.6, 128.9, 134.0, 134.9, 135.4, 169.7, 172.5. MS (ESI): $m/z$ (%) = 301 [M+H]$^+$; 299 [M-H]$^-$.

Methyl 2-acetamido-3-(2-(3-methylbut-2-enyl)-1H-indol-3-yl)propanoate (3l)

![Methyl 2-acetamido-3-(2-(3-methylbut-2-enyl)-1H-indol-3-yl)propanoate (3l)](image)

Yellow solid (282 mg, 86%). mp: 87-88 °C (from ether-hexane); TLC: $Rf$ = 0.33 (cyclohexane/ethyl acetate, 1:1; UV, p-anisaldehyde). FTIR (nujol): $\tilde{\nu}$ max = 3403, 3315, 1736, 1659 cm$^{-1}$. $^1$H NMR (200 MHz, CDCl$_3$): $\delta$ = 1.77 (s, 3H), 1.79 (s, 3H), 1.92 (s, 3H), 3.28 (dd, $J_1$=2.0 Hz, $J_2$=5.5 Hz, 2H), 3.41 (d, $J$=7.0 Hz, 2H), 3.68 (s, 3H), 4.91 (ddd, $J_1$=$J_2$=5.5 Hz, $J_3$=7.5 Hz, 1H), 5.25-5.32 (m, 1H), 6.12 (d, $J$=7.5 Hz, 1H), 7.03-7.16 (m, 2H), 7.25-7.29 (m, 1H), 7.42-7.47 (m, 1H), 8.20 (br s, 1H). $^{13}$C NMR (50 MHz, CDCl$_3$): $\delta$ = 17.9, 23.1, 25.0, 25.8, 26.7, 52.4, 53.0, 104.9, 110.6, 117.9, 119.5, 120.2, 121.3, 129.0, 135.0, 135.3, 136.2, 169.9, 172.6. MS (ESI): $m/z$ (%) = 329 [M+H]$^+$; 327 [M-H]$^-$.

C$_{19}$H$_{24}$N$_2$O$_3$ (328.18): calcd. C 69.49, H 7.37, N 8.53; found C 69.62, H 7.31, N 8.62.
Methyl 2-acetamido-3-((E)-3,7-dimethylocta-2,6-dienyl)-1H-indol-3-yl)propanoate (3m)

Yellow solid (277 mg, 70%). mp: 84-85 °C (from ether-hexane); TLC: Rf = 0.42 (cyclohexane/ethyl acetate, 1:1; UV, p-anisaldehyde). FTIR (nujol): v max = 3471, 3297, 1736, 1658 cm⁻¹. ¹H NMR (200 MHz, CDCl₃): δ = 1.65 (s, 3H), 1.75 (s, 6H), 1.95 (s, 3H), 2.09-2.18 (m, 4H) 3.30 (d, J=5.5 Hz, 2H), 3.44 (d, J=7.0 Hz, 2H), 3.70 (s, 3H), 4.92 (ddd, J₁=J₂=5.5 Hz, J₃=7.5 Hz, 1H), 5.10-5.13 (m, 1H), 5.27-5.34 (m, 1H), 6.07 (d, J=7.5 Hz, 1H), 7.05-7.17 (m, 2H), 7.26-7.30 (m, 1H), 7.43-7.47 (m, 1H), 7.97 (br s, 1H). ¹³C NMR (50 MHz, CDCl₃): δ = 16.2, 17.8, 23.2, 24.8, 25.8, 26.3, 26.8, 39.6, 52.4, 52.9, 104.9, 110.5, 117.9, 119.5, 119.9, 121.3, 123.9, 129.1, 132.0, 135.1, 136.0, 138.9, 169.6, 172.6. MS (ESI): m/z (%) = 397 [M+H]⁺; 395 [M-H]⁻. C₂₄H₃₂N₂O₃ (396.2): calcd. C 72.70, H 8.13, N 7.06; found C 72.55, H 8.05, N 7.0.

Methyl 2-acetamido-3-((methylthio)-1H-indol-3-yl)propanoate (3o)

Brown solid (208 mg, 68%). mp: 118-119 °C (from ether-hexane); TLC: Rf = 0.25 (cyclohexane/ethyl acetate, 1:1; UV, p-anisaldehyde). FTIR (nujol): v max = 3379, 3277, 1748, 1659 cm⁻¹. ¹H NMR (200 MHz, CDCl₃): δ = 1.96 (s, 3H), 2.38 (s, 3H), 3.38 (dd, J₁=4.5 Hz, J₂=5.5 Hz, 2H), 3.70 (s, 3H), 4.93 (ddd, J₁=J₂=5.5 Hz, J₃=8.0 Hz, 1H), 6.24 (d, J=8.0 Hz, 1H), 7.06-7.25 (m, 3H), 7.50 (d, J=7.5 Hz, 1H), 8.77 (br s, 1H). ¹³C NMR (50 MHz, CDCl₃): δ = 19.7, 23.2, 27.3, 52.5, 53.0, 110.8, 114.1, 118.6, 120.0, 123.0, 128.0, 128.4, 136.6, 169.9, 172.4. MS (ESI): m/z (%) = 307 [M+H]⁺; 305 [M-H]⁻. C₁₅H₁₈N₂O₃S (306.10): calcd. C 58.80, H 5.92, N 9.14; found C 58.96, H 5.88, N 9.05.

Methyl 1-acetyl-3a-benzyl-1,2,3,3a,8,8a-hexahydro[2,3-b]indole-2-carboxylate (4a)

Compound 4a was prepared according to the general procedure by quenching the reaction after 5 hours. The separation of diastereoisomers was performed on preparative thin layer chromatography (silica gel 60 F254 0.5 mm). The ratio of the diastereoisomers of the exo-endo compounds is 3:1, it
was determined by HPLC [Merck Purospher-Star™ RP 18 column, End-capped (250x4x5 micron) and methanol/water, with 5% of formic acid, as eluent (gradient from 40% to 90% of methanol in 15 minutes, flow of 0.8 mL/min)].

(±)-endo-Methyl 1-acetyl-3a-benzyl-1,2,3,3a,8,8a-hexahydropyrrolo[2,3-b]indole-2-carboxylate

![Structure Image]

Brown solid (25 mg, 7%). mp: 236-238 °C (from ether-hexane); TLC: Rf = 0.26 (cyclohexane/ethyl acetate, 1:1; UV, p-anisaldehyde). HPLC: t = 13.15 min. FTIR (nujol): νmax = 3393, 1736, 1647 cm⁻¹. 1H NMR (200 MHz, CDCl₃): δ = 1.87 (s, 3H), 2.50 (dd, J₁=8.0 Hz, J₂=13.0 Hz, 1H), 2.65 (d, J=13.0 Hz, 1H), 2.83 (d, J=13.5 Hz, 1H), 2.91 (d, J=13.5 Hz, 1H), 3.07 (s, 3H), 4.28 (d, J=8.0 Hz, 1H), 5.17 (br s, 1H), 5.29 (s, 1H), 6.48-6.62 (m, 3H), 6.93-7.02 (m, 3H), 7.17-7.24 (m, 3H). 13C NMR (50 MHz, CDCl₃): δ = 22.1, 29.7, 38.6, 52.3, 55.8, 60.7, 80.5, 109.4, 118.3, 124.4, 126.8, 128.1, 128.9, 129.9, 130.4, 136.7, 150.1, 171.0, 171.0. MS (ESI): m/z (%) = 351 [M+H]+.


(±)-exo-Methyl 1-acetyl-3a-benzyl-1,2,3,3a,8,8a-hexahydropyrrolo[2,3-b]indole-2-carboxylate

![Structure Image]

Brown solid (63 mg, 18%). mp: 182-184 °C (from ether-hexane); TLC: Rf = 0.34 (cyclohexane/ethyl acetate, 1:1; UV, p-anisaldehyde). HPLC: t = 13.67 min. FTIR (nujol): νmax = 3399, 1742, 1642 cm⁻¹. 1H and 13C NMR signals corresponding to major rotamer were indicated with * while the signals corresponding to minor rotamer were indicated with §. 1H NMR (200 MHz, CDCl₃): δ = 1.75 (s, 3H*), 2.09 (s, 1.4H§), 2.26 (dd, J₁=9.0 Hz, J₂=13 Hz, 0.47H§), 2.33 (dd, J₁=8.0 Hz, J₂=12.5 Hz, 1H*), 2.49 (dd, J₁=7.0 Hz, J₂=12.5 Hz, 0.47H§), 2.61 (dd, J₁=8.0 Hz, J₂=13.0 Hz, 1H*), 2.79 (d, J=13.5 Hz, 1H*), 2.94 (d, J=13.5 Hz, 1H*), 2.95 (d, J=13.0 Hz, 0.47H§), 3.07 (d, J=13.0 Hz, 0.47H§), 3.68 (s, 3H*), 3.68 (s, 1.4H§) 4.07 (dd, J₁=7.0 Hz, J₂=9.0 Hz, 0.47H§), 4.09 (dd, J₁=J₂=8.0 Hz, 1H*), 4.22 (br s, 0.47H§), 5.33 (s, 0.47H§), 5.38 (s, 1H*), 5.47 (br s, 1H*), 5.67-7.55 (m, 9H*), 6.47-7.55 (m, 4.2H§). 13C NMR (50 MHz, CDCl₃): δ = 22.4§, 22.6*, 39.6§, 40.3*,42.7*, 44.0§, 52.3§,52.8*, 55.7*, 59.2§, 59.4§, 60.0*, 80.8§, 82.1*, 109.8*, 110.9§, 118.5*, 120.3§, 123.7§, 123.8*, 126.8*, 128.1*, 128.1§, 128.9§, 130.0*, 130.3*, 130.3§, 131.7§, 136.6*, 136.7§, 148.1§, 148.6*, 169.8§, 171.3*, 172.6§, 173.0*. MS (ESI): m/z (%) = 351 [M+H]+.


Resubmission of Methyl 1-acetyl-3a-benzyl-1,2,3,3a,8,8a-hexahydropyrrolo[2,3-b]indole-2-carboxylate (4a) to the general procedure.

Compound 4a was resubmitted to the general reaction conditions and after 16 h gave 3a in 89% yield.
COSY and NOESY Spectra of 3a

$^{1}H$ COSY of 3a

No correlation between H-1 (NH) and the other hydrogens of the molecule (no cross peaks), so there are no Hydrogens linked to C-2, that carbon have a substituent.
Nuclear Overhauser effect between H-1 and Ha+Hb, H-4 and Hc+Hd, the cross peaks confirm that those Hydrogens are spatially close demonstrating that the compound was 2-benzyl-N-acetyltryptophan methyl ester.
References

$^{1}$H and $^{13}$C NMR Spectra

$^{1}$H and $^{13}$C NMR Spectrum of 3-(1,2,3,4-Tetrahydronaphthalen-1-yl)-1H-indole (1f)
$^1$H and $^{13}$C NMR Spectrum of Methyl 2-acetamido-3-(2-benzyl-$1^H$-indol-3-yl)propanoate (3a)
$^1$H and $^{13}$C NMR Spectrum of Methyl 3-(2-(4-methoxybenzyl)-1H-indol-3-yl)-2-acetamidopropanoate (3b)
$^1$H and $^{13}$C NMR Spectrum of Methyl 3-(2-(4-chlorobenzyl)-1H-indol-3-yl)-2-acetamidopropanoate (3c)
$^1$H and $^{13}$C NMR Spectrum of Methyl 2-acetamido-3-(2-(1,2,3,4-tetrahydronaphthalen-1-yl)-1H-indol-3-yl)propanoate (3f)
$^1$H and $^{13}$C NMR Spectrum of Methyl 3-(2-((1H-indol-3-yl)methyl)-1H-indol-3-yl)-2-acetamidopropanoate (3h)
$^1$H and $^{13}$C NMR Spectrum of Methyl 2-acetamido-3-(2-benzyl-1-methyl-1H-indol-3-yl)propanoate (3i)
$^{1}$H and $^{13}$C NMR Spectrum of methyl 3-(2-benzyl-1H-indol-3-yl)-2-(1,3-dioxoisindolin-2-yl)propanoate (3j)
$^1$H and $^{13}$C NMR Spectrum of Methyl 2-acetamido-3-(2-allyl-1H-indol-3-yl)propanoate (3k)
$^1$H and $^{13}$C NMR Spectrum of Methyl 2-acetamido-3-(2-(3-methylbut-2-enyl)-1H-indol-3-yl)propanoate (3l)
$^1$H and $^{13}$C NMR Spectrum of Methyl 2-acetamido-3-(2-((E)-3,7-dimethylcta-2,6-dienyl)-1H-indol-3-yl)propanoate (3m)
$^{1}H$ and $^{13}C$ NMR Spectrum of Methyl 2-acetamido-3-(2-(methylthio)-1H-indol-3-yl)propanoate (3o)
$^1$H and $^{13}$C NMR Spectrum of (±)-endo-methyl 1-acetyl-3a-benzyl-1,2,3,3a,8,8a-hexahydropyrrolo[2,3-b]indole-2-carboxylate
$^1$H and $^{13}$C NMR Spectrum of (±)-exo-methyl 1-acetyl-3a-benzyl-1,2,3,3a,8,8a-hexahydropyrrolo[2,3-b]indole-2-carboxylate