Supporting Information

For

One-pot synthesis of 2,3-difunctionalized indoles via

Rh(III)-catalyzed carbenoid insertion C–H activation/cyclization

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General methods and materials:
All commercial materials were used as received unless otherwise noted. $^1$H and $^{13}$C NMR spectra were recorded with Varian Mercury-Plus 400 NMR and Varian Mercury-Plus 500 NMR spectrometer as solutions ($^1$H 400 or 500 MHz; $^{13}$C 100 or 125 MHz) in CDCl$_3$ or CD$_3$OD or $d_6$-DMSO. Chemical shifts are expressed in parts per million (ppm, $\delta$) and are referenced to CHCl$_3$ ($\delta = 7.26$ ppm; $\delta = 77.16$ ppm) or CD$_3$OD ($\delta = 3.31$ ppm; $\delta = 49.0$ ppm) or $d_6$-DMSO ($\delta = 5.50$ ppm; $\delta = 39.52$ ppm) as an internal standard. All coupling constants are absolute values and are expressed in Hz. The description of the signals include: s = singlet, d = doublet, t = triplet, m = multiplet and dd = doublet of doublets, at = apparent triplet, br = broad.
High-resolution mass spectra were measured on an agilent TOF-G6230B mass spectrometer. Thin-layer chromatographies were done on pre-coated silica gel 60 F254 plates (Merck). Silica gel 60H (200-300 mesh) manufactured by Qingdao Haiyang Chemical Group Co. (China) was used for general chromatography.
General procedure for the synthesis of the starting materials:

(a) General experimental procedure for the synthesis of N-arylureas.\textsuperscript{1-4}

\textbf{Scheme 1.} List of known N-arylurea substrates

Aniline derivatives (10 mmol) and triethylamine (2.9 mL, 20 mmol) were dissolved in anhydrous CH\textsubscript{2}Cl\textsubscript{2} (10 mL) in a 50 mL three neck round bottom flask. After cooling to 0 °C, dimethylcarbamic chloride (1.8 mL, 20 mmol) was added slowly by using a syringe and the mixture was allowed to warm to room temperature and stirred 24 h. After completion, the reaction was diluted with CH\textsubscript{2}Cl\textsubscript{2} (30 mL), washed by sat. NaHCO\textsubscript{3} (30 mL), 2N HCl (30 mL), brine (20 mL) and dried over MgSO\textsubscript{4}. The organic solvent was removed by evaporation. Purification by re-crystallization in
diethyl ester afforded the corresponding N-arylurea as an off-white solid.  

(b) General experimental procedure for the synthesis of α-diazo β-keto esters:

To a solution of 1,3-dione (10.62 mmol) and p-acetamidobenzenesulfonyl azide (p-ABSA) (2.5 g, 10.41 mmol) in anhydrous CH₃CN (30 mL) at 0 °C, triethylamine (Et₃N) (4.43 mL, 31.23 mmol) was added dropwise. After stirring at room temperature for 24 h, the reaction mixture was concentrated in vacuo. Water (20 mL) was added. The resulting mixture was extracted with diethyl ether (2 × 20 mL). The combined organic layer was washed with brine (20 mL) and dried over MgSO₄. The solvent was removed under reduced pressure, and the residue was purified by a silica gel column chromatography with petroleum ether/ethyl acetate as the eluent to give the entitled diazo compounds 2a-e and 2g-i in 70-90% yields.  

Scheme 2. List of known α-diazo β-keto esters
Dimethyl 2-oxopropylphosphonate (3.53 g, 21.3 mmol) was dissolved in 60 mL of dry toluene and NaH (0.76 g, 31.9 mmol) was added portion wise, after stirred for 1 h at the 0 °C, a solution of p-ABSA (5.0 g, 21 mmol) in 25 mL of dry THF was added dropwise. Then, the reaction mixture was stirred at room temperature for 24 h, after the reaction was completed (monitored by TLC analysis), 50 mL petroleum ether was added, then the precipitate was filtered off, and the filter cake was washed with ether (3 x 50 mL), the filtrate was evaporated and the residue was purified by column chromatography on silica gel (PE/EA = 2:1 to 1:2), give the 2f (3.76 g) as yellow liquid, yield 92%.  

Thionyl chloride (1.31 mL, 0.018 mmol) was added dropwise to anhydrous DMF (1.39 mL, 0.018 mmol) and the mixture heated at 40 °C for 2 h. The mixture was concentrated in vacuo to give a solid. The solid was dissolved in chloroform (8.0 mL) and ethyl diazoacetate (3.68 mL, 0.036 mmol) added at 0 °C dropwise during a period of 1 h. The mixture was stirred at room temperature for 16 h. The solvent was removed under reduced pressure and ether (8.0 mL) added. The colorless precipitate was filtered off and the solid dissolved in acetic acid (8.0 mL). The suspension was stirred at room temperature for 16 h. The aqueous solution was extracted with ether (3×30 mL) and the combined extracts were washed with aqueous sodium hydrogen carbonate (20%; 3×30 mL), hydrochloric acid (10%; 3 × 30 mL), water (3 × 30 mL) and brine (3 × 30 mL). The extract was dried over anhydrous MgSO₄ and concentrated in vacuo to give the 2j as yellow oil (1.25 g, 49%). The product was used without further purification.
**General procedure for C–H activation/cyclization:**

$$\text{HN} R_2 + R_3 R_4 N_2 O O N R_3 O R_2 O R_4 [\text{RhCp}^*(\text{MeCN})_3][\text{SbF}_6]_2 \text{ (5 mol\%)}$$

$$\text{DCE, 50 °C, 18 h}$$

To a screw capped vial with magnetic stirrer were added substrate 1a-s (0.15 mmol, 1.0 equiv.), 2a-j (0.225 mmol, 1.5 equiv.), [RhCp*(MeCN)_3][SbF_6]_2 (5 mol%) and DCE (0.5 mL) under air. The reaction mixture was stirred at 50 °C for 18 h. After cooling to room temperature, the resulting mixture was diluted with dichloromethane (DCM) and then filtered through a pad of celite and silica gel. The filtrate was concentrated, and the resulting crude mixture was purified through a silica gel column chromatography to give the corresponding desired products 3a-s and 4a-i.

**Characterizations of indole products:**

**Methyl 1-(dimethylcarbamoyl)-2-methyl-1\textit{H}-indole-3-carboxylate (3a)**

R_f = 0.6, 25% EtOAc in Hex; compound 3a was obtained as a colorless oil in 89% yield. $^1$H NMR (400 MHz, CDCl_3) δ 8.12 – 8.10 (m, 1H), 7.27 - 7.20 (m, 3H), 3.95 (s, 3H), 3.26 (s, 3H), 2.76 (s, 3H), 2.76 (s, 3H); $^{13}$C NMR (100 MHz, CDCl_3) δ 166.1, 152.7, 143.7, 134.3, 126.6, 123.5, 122.8, 121.9, 110.6, 106.8, 51.1, 38.4, 36.9, 12.7; HRMS (ESI) calcd for 261.1239 ([M+H]^+), found 261.1241 ([M+H]^+).

**Methyl 1-(dimethylcarbamoyl)-2,7-dimethyl-1\textit{H}-indole-3-carboxylate (3b)**
R\text{f} = 0.6, 25\%\text{ EtOAc in Hex}; compound 3b was obtained as a colorless oil in 82\% yield. \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}) \(\delta\) 7.99 (d, \(J = 7.7\) Hz, 1H), 7.15 (t, \(J = 7.7\) Hz, 1H), 7.01 (d, \(J = 7.7\) Hz, 1H), 3.93 (s, 3H), 3.24 (s, 3H), 2.69 (s, 3H), 2.63 (s, 3H), 2.40 (s, 3H); \textsuperscript{13}C NMR (100 MHz, CDCl\textsubscript{3}) \(\delta\) 166.3, 153.9, 142.5, 133.3, 126.9, 125.5, 122.7, 120.6, 119.7, 106.1, 51.1, 37.9, 36.7, 17.2, 12.0; HRMS (ESI) calcd for 275.1396 ([M+H]\textsuperscript{+}), found 275.1392 ([M+H]\textsuperscript{+}).

Methyl 1-(dimethylcarbamoyl)-2,6-dimethyl-1H-indole-3-carboxylate (3c)

R\text{f} = 0.6, 25\%\text{ EtOAc in Hex}; compound 3c was obtained as a white solid in 87\% yield. Mp: 93-94 °C; \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}) \(\delta\) 7.96 (d, \(J = 8.2\) Hz, 1H), 7.08 (d, \(J = 8.2\) Hz, 1H), 7.01 (s, 1H), 3.93 (s, 3H), 3.27 (s, 3H), 2.78 (s, 3H), 2.72 (s, 3H), 2.45 (s, 3H); \textsuperscript{13}C NMR (100 MHz, CDCl\textsubscript{3}) \(\delta\) 166.3, 152.9, 142.9, 134.7, 133.5, 124.4, 124.3, 121.5, 110.6, 106.7, 51.1, 38.4, 36.9, 21.8, 12.7; HRMS (ESI) calcd for 275.1396 ([M+H]\textsuperscript{+}), found 275.1393 ([M+H]\textsuperscript{+}).

Methyl 6-chloro-1-(dimethylcarbamoyl)-2-methyl-1H-indole-3-carboxylate (3d)

R\text{f} = 0.5, 25\%\text{ EtOAc in Hex}; compound 3d was obtained as a white solid in 85\% yield. Mp: 104-105 °C; \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}) \(\delta\) 8.05 – 7.97 (m, 1H), 7.25 – 7.19 (m, 2H), 3.93 (s, 3H), 3.26 (s, 3H), 2.79 (s, 3H), 2.73 (s, 3H); \textsuperscript{13}C NMR (100 MHz, CDCl\textsubscript{3}) \(\delta\) 165.7, 152.2, 144.3, 134.7, 129.4, 125.2, 123.5, 122.9, 110.7, 106.9, 51.3, 38.4, 37.0, 12.8; HRMS (ESI) calcd for 295.0849, 297.0820 ([M+H]\textsuperscript{+}), found 295.0840, 297.0820 ([M+H]\textsuperscript{+}).

Dimethyl 1-(dimethylcarbamoyl)-2-methyl-1H-indole-3,6-dicarboxylate (3e)
R_f = 0.45, 40% EtOAc in Hex; compound 3e was obtained as a white solid in 82% yield. Mp: 125-126 °C; ^1H NMR (400 MHz, CDCl_3) δ 8.13 (d, J = 8.9 Hz, 1H), 7.94 – 7.93 (m, 2H), 3.95 (s, 3H), 3.93 (s, 3H), 3.29 (s, 3H), 2.78 (s, 3H), 2.77 (s, 3H); ^13C NMR (100 MHz, CDCl_3) δ 167.6, 165.6, 152.1, 146.6, 133.8, 130.3, 125.3, 123.9, 121.5, 112.5, 107.1, 52.3, 51.3, 38.4, 37.1, 12.9; HRMS (ESI) calcd for 319.1294 ([M+H]^+), found 319.1297 ([M+H]^+).

Methyl 1-(dimethylcarbamoyl)-2,5-dimethyl-1H-indole-3-carboxylate (3f)

R_f = 0.5, 25% EtOAc in Hex; compound 3f was obtained as a colorless oil in 92% yield. ^1H NMR (400 MHz, CDCl_3) δ 7.90 (s, 1H), 7.12 – 7.03 (m, 2H), 3.94 (s, 3H), 3.24 (s, 3H), 2.77 (s, 3H), 2.73 (s, 3H), 2.46 (s, 3H); ^13C NMR (100 MHz, CDCl_3) δ 166.3, 152.9, 143.7, 132.7, 132.3, 126.8, 124.9, 121.7, 110.3, 106.5, 51.1, 38.3, 36.9, 21.7, 12.8; HRMS (ESI) calcd for 275.1396 ([M+H]^+), found 275.1393 ([M+H]^+).

Methyl 1-(dimethylcarbamoyl)-5-isopropyl-2-methyl-1H-indole-3-carboxylate (3g)

R_f = 0.5, 25% EtOAc in Hex; compound 3g was obtained as a colorless oil in 90% yield. ^1H NMR (400 MHz, CDCl_3) δ 7.95 (s, 1H), 7.14 – 7.12 (m, 2H), 3.95 (s, 3H), 3.25 (s, 3H), 3.11 – 2.96 (m, 1H), 2.79 (s, 3H), 2.73 (s, 3H), 1.31 (d, J = 8 Hz, 6H). ^13C NMR (100 MHz, CDCl_3) δ 166.3, 152.9, 143.7, 132.9, 126.8, 122.4, 119.1, 110.4,
106.7, 51.2, 38.5, 36.9, 34.5, 24.7, 12.8; HRMS (ESI) calcd for 303.1709 ([M+H]+), found 303.1708 ([M+H]+).

**Methyl 1-(dimethylcarbamoyl)-5-methoxy-2-methyl-1H-indole-3-carboxylate (3h)**

![Structure of 3h](image)

R_f = 0.5, 25% EtOAc in Hex; compound 3h was obtained as a yellow oil in 93% yield. ^1H NMR (400 MHz, CDCl_3) δ 7.63 (d, J = 2.4 Hz, 1H), 7.11 (d, J = 8.9 Hz, 1H), 6.89 (dd, J = 8.9, 2.4 Hz, 1H), 3.95 (s, 3H), 3.89 (s, 3H), 3.24 (s, 3H), 2.78 (s, 3H), 2.74 (s, 3H); ^13C NMR (100 MHz, CDCl_3) δ 166.2, 156.3, 152.8, 143.9, 129.2, 127.6, 113.1, 111.4, 106.7, 104.0, 55.9, 51.2, 38.5, 36.9, 13.0; HRMS (ESI) calcd for 291.1345 ([M+H]+), found 291.1344 ([M+H]+).

**Methyl 1-(dimethylcarbamoyl)-5-fluoro-2-methyl-1H-indole-3-carboxylate (3i)**

![Structure of 3i](image)

R_f = 0.5, 25% EtOAc in Hex; compound 3i was obtained as a colorless oil in 85% yield. ^1H NMR (400 MHz, CDCl_3) δ 7.76 (dd, J = 9.8, 2.4 Hz, 1H), 7.14 (dd, J = 8.9, 4.3 Hz, 1H), 6.97 (ddd, J = 9.8, 8.9, 2.4 Hz, 1H), 3.93 (s, 3H), 3.24 (s, 3H), 2.77 (s, 3H), 2.73 (s, 3H); ^13C NMR (100 MHz, CDCl_3) δ 165.8, 159.6 (d, J = 237.7 Hz), 152.5, 145.1, 130.7, 127.5 (d, J = 11.1 Hz), 111.6 (d, J = 31.0 Hz), 111.4 (d, J = 15.0 Hz), 107.6 (d, J = 25.5 Hz), 107.0 (d, J = 4.0 Hz), 51.3, 38.4, 37.0, 12.9; ^19F NMR (500 MHz, CDCl_3) δ -120.67 (td, J = 9.2, 4.2 Hz); HRMS (ESI) calcd for 279.1145 ([M+H]+), found 279.1146 ([M+H]+).

**Methyl 5-chloro-1-(dimethylcarbamoyl)-2-methyl-1H-indole-3-carboxylate (3j)**
R_f = 0.5, 25% EtOAc in Hex; compound 3j was obtained as a colorless oil in 88% yield. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 8.07 (s, 1H), 7.20 (d, \(J = 8.7\) Hz, 1H), 7.12 (d, \(J = 8.7\) Hz, 1H), 3.93 (s, 3H), 3.24 (s, 3H), 2.75 (s, 3H), 2.73 (s, 3H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 165.7, 152.3, 144.9, 132.7, 128.7, 127.7, 123.8, 121.6, 111.6, 106.5, 51.3, 38.4, 37.0, 12.8; HRMS (ESI) calcd for 295.0849, 297.0820 (\([\text{M+H}]^+\)), found 295.0842, 297.0820 (\([\text{M+H}]^+\)).

**Methyl 5-bromo-1-(dimethylcarbamoyl)-2-methyl-1H-indole-3-carboxylate (3k)**

R_f = 0.5, 25% EtOAc in Hex; compound 3k was obtained as a colorless oil in 90% yield. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 8.24 (s, 1H), 7.33 (d, \(J = 8.6\) Hz, 1H), 7.08 (d, \(J = 8.6\) Hz, 1H), 3.93 (s, 1H), 3.24 (s, 1H), 2.79-2.69 (m, 6H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 165.6, 152.2, 144.8, 133.0, 128.2, 126.4, 124.6, 116.4, 112.0, 106.4, 51.4, 38.4, 37.0, 12.8; HRMS (ESI) calcd for 339.0344, 341.0324 (\([\text{M+H}]^+\)), found 339.0348, 341.0327 (\([\text{M+H}]^+\)).

**Dimethyl 1-(dimethylcarbamoyl)-2-methyl-1H-indole-3,5-dicarboxylate (3l)**

R_f = 0.5, 40% EtOAc in Hex; compound 3l was obtained as a white solid in 80% yield. Mp: 121.5-122.5 °C; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 8.80 (d, \(J = 1.2\) Hz, 1H), 7.96 (dd, \(J = 8.6, 1.2\) Hz, 1H), 7.24 (d, \(J = 8.6\) Hz, 1H), 3.97 (s, 3H), 3.94 (s, 3H), 3.27 (s, 3H), 2.77 (s, 3H), 2.76 (s, 3H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 167.8, 165.7, 152.2, 145.1,
136.8, 126.2, 125.0, 124.9, 124.4, 110.4, 107.6, 52.2, 51.4, 38.4, 37.0, 12.8; HRMS (ESI) calcd for 319.1294 ([M+H]+), found 319.1302 ([M+H]+).

**Methyl 5-acetyl-1-(dimethylcarbamoyl)-2-methyl-1H-indole-3-carboxylate (3m)**

\[
\text{R}_{f} = 0.5, \text{ 40\% EtOAc in Hex; compound 3m was obtained as a white solid in 78\% yield. Mp: 129-130 °C; } ^{1} \text{H NMR (400 MHz, CDCl}_{3} \text{) } \delta 8.74 (d, J = 1.7 Hz, 1H), 7.92 (dd, J = 8.6, 1.7 Hz, 1H), 7.25 (d, J = 8.6 Hz, 1H), 3.97 (s, 3H), 3.27 (s, 3H), 2.78 (s, 3H), 2.76 (s, 3H), 2.69 (s, 3H); } ^{13} \text{C NMR (100 MHz, CDCl}_{3} \text{) } \delta 198.4, 183.1, 165.6, 152.1, 145.1, 136.8, 132.5, 126.3, 123.7, 110.6, 107.7, 51.4, 38.4, 37.0, 26.9, 12.8; \text{ HRMS (ESI) calcd for 303.1345 ([M+H]+), found 303.1348 ([M+H]+).}
\]

**Methyl 1-(dimethylcarbamoyl)-2,5,7-trimethyl-1H-indole-3-carboxylate (3n)**

\[
\text{R}_{f} = 0.5, \text{ 25\% EtOAc in Hex; compound 3n was obtained as a colorless oil in 82\% yield. } ^{1} \text{H NMR (400 MHz, CDCl}_{3} \text{) } \delta 7.84 (s, 1H), 6.98 (s, 1H), 3.93 (s, 3H), 3.25 (s, 3H), 2.77 (s, 3H), 2.71 (s, 3H), 2.36 (s, 3H), 2.34 (s, 3H); } ^{13} \text{C NMR (100 MHz, CDCl}_{3} \text{) } \delta 166.3, 153.0, 142.7, 133.2, 132.6, 131.6, 124.8, 121.9, 111.0, 106.3, 51.1, 38.4, 36.8, 20.5, 20.2, 12.7; \text{ HRMS (ESI) calcd for 289.1552 ([M+H]+), found 289.1556 ([M+H]+).}
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**Methyl 1-(dimethylcarbamoyl)-2,5,6-trimethyl-1H-indole-3-carboxylate (3o)**

\[
\text{R}_{f} = 0.5, 40 \% \text{ EtOAc in Hex; compound 3m was obtained as a white solid in 78\% yield. Mp: 129-130 °C; } ^{1} \text{H NMR (400 MHz, CDCl}_{3} \text{) } \delta 8.74 (d, J = 1.7 Hz, 1H), 7.92 (dd, J = 8.6, 1.7 Hz, 1H), 7.25 (d, J = 8.6 Hz, 1H), 3.97 (s, 3H), 3.27 (s, 3H), 2.78 (s, 3H), 2.76 (s, 3H), 2.69 (s, 3H); } ^{13} \text{C NMR (100 MHz, CDCl}_{3} \text{) } \delta 198.4, 183.1, 165.6, 152.1, 145.1, 136.8, 132.5, 126.3, 123.7, 110.6, 107.7, 51.4, 38.4, 37.0, 26.9, 12.8; \text{ HRMS (ESI) calcd for 303.1345 ([M+H]+), found 303.1348 ([M+H]+).}
\]
Rf = 0.5, 25% EtOAc in Hex; compound 3o was obtained as a colorless oil in 89% yield. ¹H NMR (400 MHz, CDCl₃) δ 7.78 (s, 1H), 6.84 (s, 1H), 3.93 (s, 3H), 3.23 (s, 3H), 2.67 (s, 3H), 2.62 (s, 3H), 2.42 (s, 3H), 2.36 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 166.4, 153.9, 142.5, 132.2, 131.6, 127.2, 127.1, 120.2, 119.4, 105.7, 51.1, 37.8, 36.7, 21.5, 17.1, 12.1; HRMS (ESI) calcd for 289.1552 ([M+H]⁺), found 289.1556 ([M+H]⁺).

**Methyl 1-(dimethylcarbamoyl)-2-methyl-1H-benzo[f]indole-3-carboxylate (3p)**

Rf = 0.5, 25% EtOAc in Hex; compound 3p was obtained as a colorless oil in 83% yield. ¹H NMR (400 MHz, CDCl₃) δ 8.27 (d, J = 8.8 Hz, 1H), 7.95 (d, J = 7.9 Hz, 1H), 7.89 (d, J = 7.9 Hz, 1H), 7.68 (d, J = 8.8 Hz, 1H), 7.52 (t, J = 7.9 Hz, 1H), 7.46 (t, J = 7.9 Hz, 1H), 3.98 (s, 3H), 3.37 (s, 3H), 2.79 (s, 3H), 2.54 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 166.3, 154.2, 140.7, 131.3, 129.4, 128.0, 126.7, 124.5, 123.8, 123.7, 121.2, 120.9, 119.0, 107.2, 51.3, 37.7, 37.1, 12.1; HRMS (ESI) calcd for 311.1396 ([M+H]⁺), found 311.1395 ([M+H]⁺).

**Methyl 2,5-dimethyl-1-(methylcarbamoyl)-1H-indole-3-carboxylate (3q)**

Rf = 0.5, 50% EtOAc in Hex; compound 3q was obtained as a white solid in 85% yield. Mp: 125-126 °C; ¹H NMR (400 MHz, CDCl₃) δ 7.80 (s, 1H), 7.34 (d, J = 8.4 Hz, 1H), 7.03 (d, J = 8.4 Hz, 1H), 6.07 (br, 1H), 3.89 (s, 3H), 3.11 (d, J = 4.8 Hz, 3H), 2.73 (s, 3H), 2.44 (s, 3H); ¹³C NMR (100MHz, CDCl₃) δ 166.4, 152.0, 144.7, 132.8, 132.6, 127.1, 124.8, 121.5, 110.8, 107.1, 51.2, 27.9, 21.6, 13.4; HRMS (ESI) calcd for 261.1239 ([M+H]⁺), found 261.1241 ([M+H]⁺).

**Methyl 5-fluoro-2-methyl-1-(methylcarbamoyl)-1H-indole-3-carboxylate (3r)**
R_f = 0.5, 50% EtOAc in Hex; compound 3r was obtained as a white solid in 80% yield. Mp: 133-134 °C; ^1H NMR (400 MHz, CDCl_3) δ 7.63 (dd, J = 9.7, 2.5 Hz, 1H), 7.40 (dd, J = 9.0, 4.4 Hz, 1H), 6.94 (td, J = 9.0, 2.5 Hz, 1H), 6.13 (br, 1H), 3.88 (s, 3H), 3.13 (d, J = 4.8 Hz, 3H), 2.74 (s, 3H); ^13C NMR (100 MHz, CDCl_3) δ 166.0, 159.5 (d, J = 238.3 Hz), 151.6, 145.8, 130.9, 127.8 (d, J = 10.9 Hz), 112.1 (d, J = 9.5 Hz), 111.4 (d, J = 25.8 Hz), 107.4, 107.2 (d, J = 25.6 Hz), 51.3, 28.0, 13.5; ^19F NMR (500 MHz, CDCl_3) δ -120.22 (td, J = 9.2, 4.2 Hz); HRMS (ESI) calcd for 265.0988 ([M+H]^+), found 265.0992 ([M+H]^+).

Methyl 5-chloro-2-methyl-1-(methylcarbamoyl)-1H-indole-3-carboxylate (3s)

R_f = 0.5, 50% EtOAc in Hex; compound 3s was obtained as a white solid in 83% yield. Mp: 121-122 °C; ^1H NMR (400 MHz, CDCl_3) δ 7.83 (d, J = 2.0 Hz, 1H), 7.30 (d, J = 8.7 Hz, 1H), 7.10 (dd, J = 8.7, 2.0 Hz, 1H), 6.46 (d, J = 4.8 Hz, 1H), 3.85 (s, 3H), 3.11 (d, J = 4.8 Hz, 3H), 2.64 (s, 3H); ^13C NMR (100 MHz, CDCl_3) δ 165.9, 151.4, 145.5, 132.8, 128.7, 127.8, 123.4, 121.0, 112.2, 106.7, 51.3, 28.0, 13.3; HRMS (ESI) calcd for 281.0693, 283.0663 ([M+H]^+), found 281.0697, 283.0664 ([M+H]^+).

Ethyl 1-(dimethylcarbamoyl)-2-methyl-1H-indole-3-carboxylate (4a)

R_f = 0.5, 25% EtOAc in Hex; compound 4a was obtained as a white solid in 88% yield. Mp: 58-59 °C; ^1H NMR (400 MHz, CDCl_3) δ 8.20-8.09 (m, 1H), 7.42 – 7.11 (m, 3H), 4.43 (q, J = 6.7 Hz, 2H), 3.27 (s, 3H), 2.77 (br, 6H), 1.47 (t, J = 6.7 Hz, 3H); ^13C
NMR (100 MHz, CDCl$_3$) $\delta$ 164.7, 151.8, 142.6, 133.3, 125.7, 122.4, 121.7, 120.9, 109.5, 106.0, 58.9, 37.4, 35.9, 13.6, 11.7; HRMS (ESI) calcd for 275.1396 ([M+H]$^+$), found 275.1398 ([M+H]$^+$).

**Benzyl 1-(dimethylcarbamoyl)-2-methyl-1H-indole-3-carboxylate (4b)**

![Structure of Benzyl 1-(dimethylcarbamoyl)-2-methyl-1H-indole-3-carboxylate (4b)]

R$_f$ = 0.5, 30% EtOAc in Hex; compound 4b was obtained as a colorless oil in 86% yield. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.15 – 8.08 (m, 1H), 7.53 – 7.47 (m, 2H), 7.44 – 7.32 (m, 3H), 7.28 – 7.20 (m, 3H), 5.43 (d, $J$ = 2.0 Hz, 2H), 3.26 (s, 3H), 2.78 (s, 3H), 2.77 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 165.5, 152.7, 144.0, 136.7, 134.3, 128.7, 128.2, 128.2, 126.6, 123.5, 122.9, 121.9, 110.6, 106.6, 65.8, 38.4, 36.9, 12.9; HRMS (ESI) calcd for 337.1552 ([M+H]$^+$), found 337.1554 ([M+H]$^+$).

**Aallyl 1-(dimethylcarbamoyl)-2-methyl-1H-indole-3-carboxylate (4c)**

![Structure of Aallyl 1-(dimethylcarbamoyl)-2-methyl-1H-indole-3-carboxylate (4c)]

R$_f$ = 0.5, 30% EtOAc in Hex; compound 4c was obtained as a colorless oil in 85% yield. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.17 – 8.10 (m, 1H), 7.31 – 7.17 (m, 3H), 6.11 (ddt, $J$ = 17.2, 10.4, 5.5 Hz, 1H), $\delta$ 5.44 (dd, $J$ = 17.2, 1.3 Hz 1H), 5.30 (dd, $J$ = 10.4, 1.3 Hz, 1H), 4.88 (d, $J$ = 5.5 Hz, 2H), 3.26 (s, 3H), 2.78 (s, 3H), 2.76 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 165.4, 152.7, 143.9, 134.3, 132.9, 126.6, 123.5, 122.9, 122.0, 118.1, 110.6, 106.7, 64.7, 38.4, 36.9, 12.8; HRMS (ESI) calcd for 287.1396 ([M+H]$^+$), found 287.1392 ([M+H]$^+$).

$N^1,N^1,N^3,N^3,2$-Pentamethyl-1H-indole-1,3-dicarboxamide (4d)
R\textsubscript{f} = 0.5, 10\% MeOH in CH\textsubscript{2}Cl\textsubscript{2}; compound 4d was obtained as a colorless oil in 80\% yield. \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}) \(\delta\) 7.46 (d, \(J = 7.2\) Hz, 1H), 7.24 – 7.13 (m, 3H), 3.31 – 2.74 (m, 12H), 2.49 (s, 3H). \textsuperscript{13}C NMR (100 MHz, CDCl\textsubscript{3}) \(\delta\) 167.6, 153.6, 136.1, 134.4, 126.4, 123.1, 121.9, 120.0, 112.6, 111.1, 12.1; HRMS (ESI) calcd for 274.1556 ([M+H]+), found 274.1555 ([M+H]+).

**Dimethyl 1-(dimethylcarbamoyl)-2-methyl-1H-indol-3-ylphosphonate (4e)**

R\textsubscript{f} = 0.5, 50\% EtOAc in Hex; compound 4e was obtained as a white solid in 87\% yield. Mp: 116-117 °C; \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}) \(\delta\) 7.75 – 7.80 (m, 1H), 7.25 – 7.17 (m, 3H), 3.74 (s, 6H), 3.23 (s, 3H), 2.78 (s, 3H), 2.70 (d, \(J = 2.0\) Hz, 3H); \textsuperscript{13}C NMR (100 MHz, CDCl\textsubscript{3}) \(\delta\) 152.7, 145.3 (d, \(J = 26.8\) Hz), 135.1 (d, \(J = 14.0\) Hz), 128.5 (d, \(J = 12.1\) Hz), 123.5, 122.5, 120.9, 110.7, 99.2 (d, \(J = 215.8\) Hz), 52.3, 38.4, 36.9, 12.3; HRMS (ESI) calcd for 311.1161 ([M+H]+), found 311.1162 ([M+H]+).

**Methyl 1-(dimethylcarbamoyl)-2-ethyl-1H-indole-3-carboxylate (4f)**

R\textsubscript{f} = 0.5, 30\% EtOAc in Hex; compound 4f was obtained as a colorless oil in 87\% yield. \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}) \(\delta\) 8.20 – 8.05 (m, 1H), 7.31 – 7.12 (m, 3H), 3.95 (s, 3H), 3.26 (s, 3H), 3.42 – 2.99 (m, 2H), 2.76 (s, 3H), 1.29 (t, \(J = 7.4\) Hz, 3H); \textsuperscript{13}C NMR (100 MHz, CDCl\textsubscript{3}) \(\delta\) 165.8, 152.8, 149.8, 134.2, 126.6, 123.5, 122.8, 122.1, 110.5, 105.9, 51.1, 38.4, 36.9, 19.9, 14.0; HRMS (ESI) calcd for 275.1396 ([M+H]+), found 275.1406 ([M+H]+).
Methyl 1-(dimethylcarbamoyl)-2-phenyl-1H-indole-3-carboxylate (4g)

\[ \text{R}_f = 0.5, 35\% \text{ EtOAc in Hex; compound 4g was obtained as a white solid in 71\% yield. Mp: 119-120 °C; } ^1\text{H NMR (400 MHz, CDCl}_3\text{) } \delta 8.25 - 8.19 (m, 1H), 7.63 - 7.56 (m, 2H), 7.50 - 7.43 (m, 3H), 7.43 - 7.39 (m, 1H), 7.37 - 7.30 (m, 2H), 3.82 (s, 3H), 2.94 (s, 3H), 2.49 (s, 3H); ^1^3\text{CNMR (150 MHz, CDCl}_3\text{) } \delta 165.4, 152.6, 144.0, 135.1, 130.5, 130.2, 129.6, 128.0, 126.8, 124.4, 122.4, 111.3, 107.0, 51.2, 38.1, 36.6; HRMS (ESI) calcd for 323.1396 ([M+H]^+), found 323.1399 ([M+H]^+). \]

Methyl 1-(dimethylcarbamoyl)-2-(methoxymethyl)-1H-indole-3-carboxylate (4h)

\[ \text{R}_f = 0.5, 40\% \text{ EtOAc in Hex; compound 4h was obtained as a white solid in 89\% yield. Mp: 91-92 °C; } ^1\text{H NMR (400 MHz, CDCl}_3\text{) } \delta 8.19 - 8.11 (m, 1H), 7.35 - 7.21 (m, 3H), 5.39 (d, J = 12.8 Hz, 1H), 4.88 (d, J = 12.8 Hz, 1H), 3.95 (s, 3H), 3.40 (s, 3H), 3.22 (s, 3H), 2.78 (s, 3H); ^1^3\text{CNMR (100 MHz, CDCl}_3\text{) } \delta 165.6, 153.1, 142.7, 134.8, 125.9, 124.3, 122.8, 122.5, 110.6, 107.8, 64.5, 58.9, 51.3, 38.4, 36.9; HRMS (ESI) calcd for 291.1345 ([M+H]^+), found 291.1343 ([M+H]^+). \]

Ethyl 1-(dimethylcarbamoyl)-1H-indole-3-carboxylate (4i)

\[ \text{R}_f = 0.5, 25\% \text{ EtOAc in Hex; compound 4i was obtained as a colorless oil in 83\% yield. } ^1\text{H NMR (400 MHz, CDCl}_3\text{) } \delta 8.26 - 8.12 (m, 1H), 8.01 (s, 1H), 7.62 - 7.58 (m, 1H), 7.46 - 7.28 (m, 2H), 4.40 (q, J = 7.1 Hz, 2H), 3.10 (s, 6H), 1.42 (t, J = 7.1 Hz,} \]
$^3$H; $^{13}$CNMR (100 MHz, CDCl$_3$) $\delta$ 164.5, 153.8, 135.9, 132.2, 126.7, 124.5, 123.4, 122.0, 113.4, 111.3, 60.3, 38.5, 14.6; HRMS (ESI) calcd for 261.1239 ([M+H]$^+$), found 261.1246 ([M+H]$^+$).

**Synthesis of methyl 2-methyl-1H-indole-3-carboxylate:**

A solution of 3a (0.052 g, 0.2 mmol) and TBAF (1mL, 1 M in THF, 1mmol) in dry THF (1 mL) was stirred under argon. The reaction mixture was refluxed for 10 h. After cooling, a solution of NH$_4$Cl satd. (5 mL) was added and the aqueous phase was extracted with EtOAc (3 x 10 mL). The combined organic layers were dried over MgSO$_4$, filtered and the solvent was removed under reduced pressure and the residue was purified by column chromatography (silica gel, hexane/ethyl acetate = 3/1) to afford compound 5 as a white solid (0.034 g, 90%). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.33 (br, 1H), 8.09 (dd, $J = 7.6$Hz, 1.8H, 1H), 7.31 (dd, $J = 7.6$Hz, 1.8H, 1H), 7.25 – 7.16 (m, 1H), 3.94 (s, 3H), 2.75 (s, 3H). This is a known compound reported in the literature.  

**Synthesis of 1H-indole-3-carboxylic acid:**

A solution of 4i (0.2 mmol), aqueous sodium hydroxide solution (50%, 3 mL) and ethanol (5 mL) was stirred at 80 $^\circ$C for 24 h. After cooling, 1N HCl (5 mL) was added and the aqueous phase was extracted with EtOAc (3 x 10 mL). The combined organic
layers were dried over MgSO$_4$, filtered and the solvent was removed under reduced pressure and the residue was purified by column chromatography (silica gel, hexane/ethyl acetate = 2/1) to afford compound 6 as a colorless oil (0.0275 g, 85%).

$^1$H NMR (400 MHz, MeOD) $\delta$ 8.02 (dd, $J = 6.6, 1.9$ Hz, 1H), 7.89 (s, 1H), 7.39 (dd, $J = 6.7, 1.7$ Hz, 1H), 7.17 – 7.07 (m, 2H). This is a known compound reported in the literature.  

**References**

$^1$H and $^{13}$C NMR spectra of indole products

3a
3c
4c
4e