Supporting Information

Aerobic Ru-catalyzed direct C2-olefination of N-heteroarenes with alkenes directed by a removable N-dimethylcarbamoyl group

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I. General remarks

NMR spectra were obtained on a Bruker AV II-400 MHz spectrometer. The ¹H NMR (400 MHz) chemical shifts were measured relative to CDCl₃ or DMSO-*d*₆ as the internal reference (CDCl₃: $\delta = 7.26$ ppm, DMSO-*d*₆: $\delta = 2.50$ ppm). The ¹³C NMR (100 MHz) chemical shifts were given using CDCl₃ or DMSO-*d*₆ as the internal standard (CDCl₃: $\delta = 77.16$ ppm, DMSO-*d*₆: $\delta = 39.52$ ppm). High resolution mass spectra (HRMS) were obtained with a Waters-Q-TOF-Premier (ESI). Melting points were determined with XRC-1 and are uncorrected.

Unless otherwise noted, all reagents were obtained from commercial suppliers and used without further purification. *N*-Dimethylcarbamoyl indoles, pyrrole and carbazole were prepared according to the literature procedures.^{1,2} 1,2-Dichloroethane was dried over CaH₂ and distilled prior to use.

II. Optimization of the Ru-catalyzed C2-olefination of indoles with alkenes

A sealable tube with a magnetic stir bar was charged with Cu(OAc)₂, additive (if required), indole **1** (0.25 mmol), [RuCl₂(*p*-cymene)]₂ (4.0 mg, 6.25 µmol, 2.5 mol%), and silver salt (25 µmol, 10 mol%) under an N₂ atmosphere. The system was evacuated and backfilled with O₂ for three times. Then butyl acrylate **2a** (53.5 µL, 0.375 mmol, 1.5 equiv) and DCE (1.0 mL) were added through syringes and the tube was sealed with a teflon-coated screw cap. The reaction mixture was first stirred at room temperature for 15 min and then heated at the indicated temperature for 15 or 24 h. The resulting solution was subsequently diluted with 5 mL of dichloromethane, filtered through a celite pad and washed with 10-20 mL of dichloromethane. The combined organic phases were evaporated, and the resulting residue was purified by column chromatography on silica gel to provide the desired product.

Table S1: Optimization of the reaction of 1 with butyl acrylate 2a.^a



Entry	R	Silver salt	Cu(OAc) ₂ (mol%)	Atmos- phere	Additive	Solvent	Tempera- ture (°C)	Yield $(\%)^b$
1	Dmc	AgSbF ₆	150	N_2	-	Toluene	130	87
2 ^c	Dmc	AgBF ₄	150	N_2	-	Toluene	130	52
3	Dmc	AgOAc	150	N_2	-	Toluene	130	32
4	Dmc	-	150	N_2	-	Toluene	130	23
5	Dmc	AgSbF ₆	-	O_2	-	Toluene	130	36
6	Dmc	AgSbF ₆	20	O_2	-	Toluene	130	63
7	Dmc	AgSbF ₆	20	O_2	-	<i>t</i> -AmylOH	130	68
8	Dmc	AgSbF ₆	20	O_2	-	THF	130	45
9	Dmc	AgSbF ₆	20	O_2	-	DCE	130	73
10	Dmc	AgSbF ₆	20	O_2	NaOAc	DCE	130	82
11	Dmc	AgSbF ₆	20	O ₂	MesCO ₂ H	DCE	130	78
12	Dmc	AgSbF ₆	20	O ₂	PivOH	DCE	130	75
13	Dmc	AgSbF ₆	20	O ₂	NaOAc	DCE	100	90
14 ^c	Dmc	AgSbF ₆	20	O_2	NaOAc	DCE	100	93
15 ^{<i>c,d</i>}	Dmc	AgSbF ₆	20	O ₂	NaOAc	DCE	100	28
16 ^c	Dmc	AgSbF ₆	20	O ₂	NaOAc	DCE	80	63
17^{c}	Ac	AgSbF ₆	20	O ₂	NaOAc	DCE	100	trace
18 ^c	PhCO	AgSbF ₆	20	O_2	NaOAc	DCE	100	trace
19 ^c	Pym	AgSbF ₆	20	O_2	NaOAc	DCE	100	trace
20^c	Ts	AgSbF ₆	20	O_2	NaOAc	DCE	100	trace

^{*a*} Reaction conditions: **1a** (0.25 mmol, 1.0 equiv), **2a** (1.5 equiv), $[RuCl_2(p-cymene)]_2$ (2.5 mol%), silver salt (10 mol%), oxidant, additive (30 mol%), and solvent (1.0 mL) at 130 °C. ^{*b*} Isolated yields. ^{*c*} 15 h. ^{*d*} [RuCl_2(*p*-cymene)]_2 (1 mol%) and AgSbF₆ (4 mol%) were used. Dmc = dimethylcarbamoyl, Ac = acetyl, Pym = 2-pyrimidyl, Ts = 4-toluenesulfonyl, PivOH = pivalic acid, MesCO₂H = 2,4,6-trimethylbenzoic acid, THF = tetrahydrofuran, DCE = 1,2-dichloroethane.

III. General procedure for the Ru-catalyzed olefination of N-heteroarenes

A sealable tube with a magnetic stir bar was charged with $Cu(OAc)_2$ (9.1 mg, 50 µmol, 20 mol%), NaOAc (6.2 mg, 75 µmol, 30 mol%), *N*-heteroarenes **1** (0.25 mmol), [RuCl₂(*p*-cymene)]₂ (4.0 mg, 6.25 µmol, 2.5 mol%), and AgSbF₆ (8.6 mg, 25 µmol,

10 mol%) under an N_2 atmosphere. The system was evacuated and backfilled with O_2 for three times. Then alkenes **2** (0.375 mmol, 1.5 equiv) and DCE (1.0 mL) were added through syringes and the tube was capped with a teflon-coated screw cap. The reaction mixture was first stirred at room temperature for 15 min and then heated at 100 °C for 15 h. The resulting solution was subsequently diluted with 5 mL of dichloromethane, filtered through a celite pad, and washed with 10-20 mL of dichloromethane. The combined organic phases were evaporated, and the resulting residue was purified by column chromatography on silica gel to provide the desired product.

IV. General procedure for the deprotection of the N-dimethylcarbamoyl group³

A sealable tube with a magnetic stir bar was charged with 2-alkenylated indoles (0.25 mmol), EtOH (2.8 mL) and saturated aqueous KOH solution (0.9 mL). The tube was then capped and the mixture was stirred at 80 °C. After the completion of the reaction as monitored by TLC, the solution was cooled to ambient temperature, diluted with water, acidified to pH = 5 using 1N HCl, and extracted with ethyl acetate for 5-6 times. The combined organic phases were dried over anhydrous Na₂SO₄. The solvent was concentrated and the residue was purified by column chromatography on silica gel to provide the desired products.

V. Experimental data for the described substances



(E)-Butyl 3-(1-(dimethylcarbamoyl)-1*H*-indol-2-yl)acrylate (3a)

Following the general procedure. *N*,*N*-Dimethyl-1*H*-indole-1-carboxamide **1a** (47 mg, 0.25 mmol) and *n*-butyl acrylate **2a** (53.5 μ L, 0.375 mmol) were used. Purification via column chromatography on silica gel (petroleum ether/CH₂Cl₂/Et₂O = 5/2/1, v/v/v) afforded **3a** as yellow oil (73 mg, 93% yield). ¹H NMR (400 MHz, CDCl₃): δ = 0.97 (t, *J* = 7.2 Hz, 3H), 1.39-1.48 (m, 2H), 1.65-1.72 (m, 2H), 3.04 (br. s, 6H), 4.21 (t, *J* =

6.8 Hz, 2H), 6.36 (d, J = 16.0 Hz, 1H), 7.00 (s, 1H), 7.19 (t, J = 8.0 Hz, 1H), 7.29-7.34 (m, 2H), 7.61 (d, J = 8.0 Hz, 1H), 7.69 (d, J = 16.0 Hz, 1H) ppm. ¹³C NMR (100 MHz, CDCl₃): $\delta = 13.8$, 19.2, 30.8, 37.7, 64.6, 108.4, 111.6, 118.7, 121.7, 122.1, 125.3, 128.0, 133.0, 134.0, 137.2, 153.4, 166.9 ppm. HRMS (ESI): calcd for C₁₈H₂₂N₂NaO₃ [M+Na]⁺ 337.1528, found 337.1527.

The structure of 3a was further confirmed by ¹H-¹H NOESY spectrum.



(E)-Butyl 3-(1-(dimethylcarbamoyl)-5-methyl-1H-indol-2-yl)acrylate (3b)

Following the general procedure. 5-Methyl-*N*,*N*-dimethyl-1*H*-indole-1-carboxamide **1b** (50.5 mg, 0.25 mmol) and *n*-butyl acrylate **2a** (53.5 µL, 0.375 mmol) were used. Purification via column chromatography on silica gel (petroleum ether/EtOAc = 5/1, v/v) afforded **3b** as yellow oil (70 mg, 86% yield). ¹H NMR (400 MHz, CDCl₃): δ = 0.97 (t, *J* = 7.2 Hz, 3H), 1.39-1.48 (m, 2H), 1.65-1.72 (m, 2H), 2.43 (s, 3H), 3.01 (br. s, 6H), 4.20 (t, *J* = 6.8 Hz, 2H), 6.34 (d, *J* = 16.0 Hz 1H), 6.91 (s, 1H), 7.13 (dd, *J* = 8.8 Hz, 0.8 Hz, 1H), 7.22 (d, *J* = 8.8 Hz, 1H), 7.39 (s, 1H), 7.67 (d, *J* = 16.0 Hz, 1H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 13.8, 19.3, 21.4, 30.9, 37.7, 64.6, 108.1, 111.3, 118.4, 121.2, 127.0, 128.2, 131.6, 133.1, 134.1, 135.7, 153.6, 166.9 ppm. HRMS (ESI): calcd for C₁₉H₂₄N₂NaO₃ [M+Na]⁺ 351.1685, found 351.1680.



(E)-Butyl 3-(1-(dimethylcarbamoyl)-7-methyl-1H-indol-2-yl)acrylate (3c)

Following the general procedure. 7-Methyl-*N*,*N*-dimethyl-1*H*-indole-1-carboxamide **1c** (50.5 mg, 0.25 mmol) and *n*-butyl acrylate **2a** (53.5 μ L, 0.375 mmol) were used. Purification via column chromatography on silica gel (petroleum ether/EtOAc = 5/1, v/v) afforded **3c** as brown oil (63 mg, 77% yield). ¹H NMR (400 MHz, CDCl₃): δ = 0.97 (t, J = 7.2 Hz, 3H), 1.39-1.48 (m, 2H), 1.65-1.73 (m, 2H), 2.43 (s, 3H), 2.62 (s, 3H), 3.25 (s, 3H), 4.21 (td, J = 6.8 Hz, 0.8 Hz, 2H), 6.40 (d, J = 16.0 Hz, 1H), 6.98 (s, 1H), 7.04-7.10 (m, 2H), 7.47 (dd, J = 7.2 Hz, 1.2 Hz, 1H), 7.57 (d, J = 16.0 Hz, 1H) ppm. ¹³C NMR (100 MHz, CDCl₃): $\delta = 13.8$, 17.5, 19.3, 30.8, 36.8, 37.9, 64.6, 107.6, 118.4, 119.6, 121.5, 122.0, 127.1, 128.2, 132.2, 132.9, 136.1, 154.3, 166.9 ppm. HRMS (ESI): calcd for C₁₉H₂₄N₂NaO₃ [M+Na]⁺ 351.1685, found 351.1690.



(E)-Butyl 3-(1-(dimethylcarbamoyl)-5-methoxy-1H-indol-2-yl)acrylate (3d)

Following the general procedure. 5-Methoxy-*N*,*N*-dimethyl-1*H*-indole-1-carboxamide **1d** (54.5 mg, 0.25 mmol) and *n*-butyl acrylate **2a** (53.5 µL, 0.375 mmol) were used. Purification via column chromatography on silica gel (petroleum ether/EtOAc = 5/1, v/v) afforded **3d** as yellow oil (76 mg, 88% yield). ¹H NMR (400 MHz, CDCl₃): δ = 0.96 (t, *J* = 7.2 Hz, 3H), 1.39-1.48 (m, 2H), 1.65-1.72 (m, 2H), 3.01 (br. s, 6H), 3.84 (s, 3H), 4.20 (t, *J* = 6.8 Hz, 2H), 6.34 (d, *J* = 16.0 Hz, 1H), 6.92 (s, 1H), 6.95 (dd, *J* = 8.8 Hz, 2.4 Hz, 1H), 7.02 (d, *J* = 2.4 Hz, 1H), 7.23 (d, *J* = 8.8 Hz, 1H), 7.66 (d, *J* = 16.0 Hz, 1H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 13.7, 19.3, 30.8, 37.8, 55.8, 64.6, 102.6, 107.9, 112.5, 115.8, 118.4, 128.6, 132.4, 133.0, 134.5, 153.5, 155.6, 166.9 ppm. HRMS (ESI): calcd for C₁₉H₂₄N₂NaO₄ [M+Na]⁺ 367.1634, found 367.1627.



(E)-Butyl 3-(5-chloro-1-(dimethylcarbamoyl)-1H-indol-2-yl)acrylate (3e)

Following the general procedure. 5-Chloro-*N*,*N*-dimethyl-1*H*-indole-1-carboxamide **1e** (56 mg, 0.25 mmol) and *n*-butyl acrylate **2a** (53.5 μ L, 0.375 mmol) were used. Purification via column chromatography on silica gel (petroleum ether/EtOAc = 5/1, v/v) afforded **3e** as a yellow solid (71 mg, 82% yield). M.p.: 80-81 °C. ¹H NMR (400 MHz, CDCl₃): $\delta = 0.97$ (t, J = 7.2 Hz, 3H), 1.39-1.48 (m, 2H), 1.65-1.73 (m, 2H), 3.02 (br. s, 6H), 4.21 (t, J = 6.8 Hz, 2H), 6.39 (d, J = 16.0 Hz, 1H), 6.92 (s, 1H), 7.23-7.28 (m, 2H), 7.58 (s, 1H), 7.64 (d, J = 16.0 Hz, 1H) ppm. ¹³C NMR (100 MHz, CDCl₃): $\delta = 13.8$, 19.2, 30.8, 37.7, 64.7, 107.1, 112.7, 119.7, 120.9, 125.4, 127.7, 128.9, 132.4, 135.2, 135.4, 152.9, 166.5 ppm. HRMS (ESI): calcd for C₁₈H₂₁ClN₂NaO₃ [M+Na]⁺ 371.1138, found 371.1141.



(E)-Butyl 3-(5-bromo-1-(dimethylcarbamoyl)-1H-indol-2-yl)acrylate (3f)

Following the general procedure. 5-Bromo-*N*,*N*-Dimethyl-1*H*-indole-1-carboxamide **1f** (67 mg, 0.25 mmol) and *n*-butyl acrylate **2a** (53.5 µL, 0.375 mmol) were used. Purification via column chromatography on silica gel (petroleum ether/EtOAc = 5/1, v/v) afforded **3f** as a yellow solid (73 mg, 74% yield). M.p.: 98-99 °C. ¹H NMR (400 MHz, CDCl₃): $\delta = 0.97$ (t, J = 7.2 Hz, 3H), 1.38-1.48 (m, 2H), 1.65-1.72 (m, 2H), 3.01 (br. s, 6H), 4.21 (t, J = 6.8 Hz, 2H), 6.39 (d, J = 16.0 Hz, 1H), 6.91 (s, 1H), 7.21 (d, J = 8.8 Hz, 1H), 7.38 (dd, J = 8.8 Hz, 1.6 Hz, 1H), 7.64 (d, J = 16.0 Hz, 1H), 7.74 (d, J = 1.6 Hz, 1H) ppm. ¹³C NMR (100 MHz, CDCl₃): $\delta = 13.8$, 19.3, 30.8, 37.8, 64.8, 107.0, 113.1, 115.3, 119.9, 124.1, 128.0, 129.6, 132.4, 135.1, 135.7, 152.9, 166.6 ppm. HRMS (ESI): calcd for C₁₈H₂₁BrN₂NaO₃ [M+Na]⁺ 415.0633, found 415.0634.



(E)-Butyl 3-(1-(dimethylcarbamoyl)-5-nitro-1H-indol-2-yl)acrylate (3g)

Following the general procedure. *N*,*N*-Dimethyl-5-nitro-1*H*-indole-1-carboxamide **1g** (58.3 mg, 0.25 mmol) and *n*-butyl acrylate **2a** (53.5 μ L, 0.375 mmol) were used. Purification via column chromatography on silica gel (petroleum ether/EtOAc = 3/1,

v/v) afforded **3g** as a yellow solid (57 mg, 63% yield). M.p.: 80-81 °C. ¹H NMR (400 MHz, CDCl₃): $\delta = 0.97$ (t, J = 7.2 Hz, 3H), 1.39-1.48 (m, 2H), 1.66-1.73 (m, 2H), 3.02 (br. s, 6H), 4.23 (t, J = 6.8 Hz, 2H), 6.47 (d, J = 16.0 Hz, 1H), 7.13 (s, 1H), 7.41 (d, J = 9.2 Hz, 1H), 7.64 (d, J = 16.0 Hz, 1H), 8.20 (dd, J = 9.2 Hz, 2.4 Hz, 1H), 8.57 (d, J = 2.4 Hz, 1H) ppm. ¹³C NMR (100 MHz, CDCl₃): $\delta = 13.8$, 19.3, 30.8, 37.9, 65.0, 108.5, 111.8, 118.5, 120.2, 121.4, 127.3, 131.6, 137.1, 139.6, 143.5, 152.2, 166.3 ppm. HRMS (ESI): calcd for C₁₈H₂₁N₃NaO₅ [M+Na]⁺ 382.1379, found 382.1382.



(E)-Butyl 3-(5-cyano-1-(dimethylcarbamoyl)-1H-indol-2-yl)acrylate (3h)

Following the general procedure. 5-Cyano-*N*,*N*-dimethyl-1*H*-indole-1-carboxamide **1h** (53.3 mg, 0.25 mmol) and *n*-butyl acrylate **2a** (53.5 µL, 0.375 mmol) were used. Purification via column chromatography on silica gel (petroleum ether/EtOAc = 3/1, v/v) afforded **3h** as a white solid (45 mg, 54% yield). M.p.: 87-88 °C. ¹H NMR (400 MHz, CDCl₃): $\delta = 0.97$ (t, J = 7.2 Hz, 3H), 1.39-1.48 (m, 2H), 1.65-1.73 (m, 2H), 3.02 (br. s, 6H), 4.22 (t, J = 6.8 Hz, 2H), 6.44 (d, J = 16.0 Hz 1H), 7.03 (s, 1H), 7.41 (d, J = 8.4 Hz, 1H), 7.52 (dd, J = 8.4 Hz, 1.2 Hz, 1H), 7.63 (d, J = 16.0 Hz, 1H), 7.97 (s, 1H) ppm. ¹³C NMR (100 MHz, CDCl₃): $\delta = 13.9$, 19.3, 30.8, 37.9, 65.0, 105.7, 107.4, 112.6, 119.7, 127.0, 121.1, 127.0, 127.68, 127.74, 136.2, 138.4, 152.3, 166.3 ppm. HRMS (ESI): calcd for C₁₉H₂₁N₃NaO₃ [M+Na]⁺ 362.1481, found 362.1476.



(E)-Butyl 3-(6-chloro-1-(dimethylcarbamoyl)-1H-indol-2-yl)acrylate (3i)

Following the general procedure. 6-Chloro-N,N-dimethyl-1H-indole-1-carboxamide **1i** (56 mg, 0.25 mmol) and *n*-butyl acrylate **2a** (53.5 μ L, 0.375 mmol) were used.

Purification via column chromatography on silica gel (petroleum ether/EtOAc = 5/1, v/v) afforded **3i** as yellow oil (78 mg, 90% yield). ¹H NMR (400 MHz, CDCl₃): δ = 0.97 (t, *J* = 7.2 Hz, 3H), 1.38-1.48 (m, 2H), 1.65-1.72 (m, 2H), 3.02 (br. s, 6H), 4.21 (t, *J* = 6.8 Hz, 2H), 6.35 (d, *J* = 16.0 Hz 1H), 6.95 (s, 1H), 7.16 (dd, *J* = 8.4 Hz, 2.0 Hz, 1H), 7.35 (s, 1H), 7.52 (d, *J* = 8.4 Hz, 1H), 7.63 (d, *J* = 16.0 Hz, 1H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 13.9, 19.3, 30.9, 37.8, 64.8, 108.0, 111.7, 119.3, 122.6, 123.1, 126.5, 131.2, 132.5, 134.7, 137.5, 152.9, 166.7 ppm. HRMS (ESI): calcd for C₁₈H₂₁ClN₂NaO₃ [M+Na]⁺ 371.1138, found 371.1141.



(*E*)-Methyl 2-(3-butoxy-3-oxoprop-1-en-1-yl)-1-(dimethylcarbamoyl)-1*H*-indole-6-carboxylate (3j)

Following the general procedure. Methyl 1-(dimethylcarbamoyl)-1*H*-indole-6carboxylate **1j** (47 mg, 0.25 mmol) and *n*-butyl acrylate **2a** (53.5 µL, 0.375 mmol) were used. Purification via column chromatography on silica gel (petroleum ether/EtOAc = 5/1, v/v) afforded **3j** as yellow oil (89 mg, 96% yield). ¹H NMR (400 MHz, CDCl₃): $\delta = 0.96$ (t, J = 7.2 Hz, 3H), 1.38-1.48 (m, 2H), 1.65-1.72 (m, 2H), 3.05 (br. s, 6H), 3.94 (s, 3H), 4.21 (t, J = 6.8 Hz, 2H), 6.44 (d, J = 16.0 Hz, 1H), 7.01 (s, 1H), 7.64 (d, J = 9.2 Hz, 1H), 7.67 (d, J = 16.8 Hz, 1H), 7.87 (d, J = 8.4 Hz, 1H), 8.04 (s, 1H) ppm. ¹³C NMR (100 MHz, CDCl₃): $\delta = 13.8$, 19.3, 30.8, 37.9, 52.3, 64.8, 107.5, 113.6, 120.6, 121.3, 123.1, 126.7, 131.4, 132.3, 136.5, 136.9 152.8, 166.5, 167.4 ppm. HRMS (ESI): calcd for C₂₀H₂₄N₂NaO₅ [M+Na]⁺ 395.1583, found 395.1582.





Following the general procedure. 3-Methyl-*N*,*N*-dimethyl-1*H*-indole-1-carboxamide **1k** (50.5 mg, 0.25 mmol) and *n*-butyl acrylate 2**a** (53.5 µL, 0.375 mmol) were used. Purification via column chromatography on silica gel (petroleum ether/EtOAc = 10/1, v/v) afforded the desired product **3k** as yellow oil (54 mg, 66% yield). ¹H NMR (400 MHz, CDCl₃): $\delta = 0.97$ (t, J = 7.2 Hz, 3H), 1.39-1.48 (m, 2H), 1.66-1.73 (m, 2H), 2.46 (s, 3H), 3.02 (s, 3H), 3.06 (s, 3H), 4.21 (t, J = 6.8 Hz, 2H), 6.09 (d, J = 16.4 Hz, 1H), 7.20 (t, J = 7.2 Hz, 1H), 7.28-7.35 (m, 2H), 7.59 (d, J = 8.0 Hz, 1H), 7.80 (d, J =16.0 Hz, 1H) ppm. ¹³C NMR (100 MHz, CDCl₃): $\delta = 10.0$, 13.9, 19.4, 31.0, 37.8, 64.6, 111.3, 117.5, 120.1, 120.8, 121.6, 126.0, 129.1, 130.1, 131.9, 137.0, 154.1, 167.3 ppm. HRMS (ESI): calcd for C₁₉H₂₄N₂NaO₃ [M+Na]⁺ 351.1685, found 351.1686.



(E)-tert-Butyl 3-(1-(dimethylcarbamoyl)-1H-indol-2-yl)acrylate (3l)

Following the general procedure. *N*,*N*-Dimethyl-1*H*-indole-1-carboxamide **1a** (47 mg, 0.25 mmol) and *tert*-butyl acrylate **2b** (54.4 µL, 0.375 mmol) were used. Purification via column chromatography on silica gel (petroleum ether/CH₂Cl₂/Et₂O = 5/2/1, v/v/v) afforded **3l** as yellow oil (68 mg, 87% yield). ¹H NMR (400 MHz, CDCl₃): δ = 1.53 (s, 9H), 3.03 (br. s, 6H), 6.30 (d, *J* = 16.0 Hz, 1H), 6.96 (s, 1H), 7.18 (td, *J* = 7.6 Hz, 1.2 Hz, 1H), 7.27-7.34 (m, 2H), 7.59 (d, *J* = 16.0 Hz, 1H), 7.60 (d, *J* = 7.6 Hz, 1H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 28.3, 37.8, 80.8, 107.9, 111.6, 120.7, 121.6, 122.1, 125.1, 128.0, 132.0, 134.2, 137.1, 153.5, 166.1 ppm. HRMS (ESI): calcd for C₁₈H₂₂N₂NaO₃ [M+Na]⁺ 337.1528, found 337.1533.



(E)-Ethyl 3-(1-(dimethylcarbamoyl)-1H-indol-2-yl)acrylate (3m)

Following the general procedure. N,N-Dimethyl-1H-indole-1-carboxamide 1a (47 mg,

0.25 mmol) and ethyl acrylate **2c** (40.5 µL, 0.375 mmol) were used. Purification via column chromatography on silica gel (petroleum ether/CH₂Cl₂/Et₂O = 5/2/1, v/v/v) afforded the desired product **3m** as yellow oil (64 mg, 89% yield). ¹H NMR (400 MHz, CDCl₃): δ = 1.34 (t, *J* = 7.2 Hz, 3H), 3.02 (br. s, 6H), 4.26 (q, *J* = 7.2 Hz, 2H), 6.36 (d, *J* = 16.0 Hz, 1H), 6.99 (s, 1H), 7.19 (t, *J* = 6.8 Hz, 1H), 7.28-7.34 (m, 2H), 7.61 (d, *J* = 8.0 Hz, 1H), 7.69 (d, *J* = 16.0 Hz, 1H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 14.5, 37.9, 60.8, 108.5, 111.6, 118.7, 121.8, 122.2, 125.3, 128.0, 133.0, 134.1, 137.3, 153.5, 166.8 ppm. HRMS (ESI): calcd for C₁₆H₁₈N₂NaO₃ [M+Na]⁺ 309.1215, found 309.1214.



(E)-Benzyl 3-(1-(dimethylcarbamoyl)-1H-indol-2-yl)acrylate (3n)

Following the general procedure. *N*,*N*-Dimethyl-1*H*-indole-1-carboxamide **1a** (47 mg, 0.25 mmol) and benzylacrylate **2d** (57.7 µL, 0.375 mmol) were used. Purification via column chromatography on silica gel (petroleum ether/EtOAc = 5/1, v/v) afforded **3n** as yellow oil (79 mg, 91% yield). ¹H NMR (400 MHz, CDCl₃): δ = 3.02 (br. s, 6H), 5.25 (s, 2H), 6.41 (d, *J* = 16.0 Hz, 1H), 7.00 (s, 1H), 7.17-7.21 (m, 1H), 7.29-7.43 (m, 7H), 7.61 (d, *J* = 8.0 Hz, 1H), 7.74 (d, *J* = 16.0 Hz, 1H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 37.4, 66.6, 108.8, 111.7, 118.2, 121.8, 122.2, 125.4, 128.0, 128.40, 128.45, 128.7, 133.6, 134.0, 136.1, 137.3, 153.4, 166.6 ppm. HRMS (ESI): calcd for C₂₁H₂₀N₂NaO₃ [M+Na]⁺ 371.1372, found 371.1371.



(*E*)-*N*,*N*-Dimethyl-2-((2-oxodihydrofuran-3(2*H*)-ylidene)methyl)-1*H*-indole-1-car boxamide (30)

Following the general procedure. N,N-Dimethyl-1H-indole-1-carboxamide 1a (47 mg,

0.25 mmol) and 3-methylenedihydro-2(3*H*)-furanone **2e** (32.8 µL, 0.375 mmol) were used. Purification via column chromatography on silica gel (petroleum ether/EtOAc = 2/1, v/v) afforded **3o** as a yellow solid (40 mg, 56% yield). M.p.: 162-163 °C. ¹H NMR (400 MHz, CDCl₃): δ = 2.95 (br. s, 6H), 3.23 (td, *J* = 7.2 Hz, 2.8 Hz, 2H), 4.53 (t, *J* = 7.2 Hz, 2H), 6.88 (s, 1H), 7.19-7.23 (m, 1H), 7.32-7.37 (m, 2H), 7.59 (t, *J* = 2.8 Hz, 1H), 7.65 (d, *J* = 8.0 Hz, 1H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 28.2, 38.0, 65.5, 109.5, 111.7, 121.8, 122.2, 124.4, 124.6, 125.6, 128.2, 133.7, 136.2, 153.0, 171.9 ppm. HRMS (ESI): calcd for C₁₆H₁₆N₂NaO₃ [M+Na]⁺ 307.1059, found 307.1057.

The configuration of **30** was confirmed by ¹H-¹H NOESY spectrum.



(*E*)-Dimethyl (2-(1-(dimethylcarbamoyl)-1*H*-indol-2-yl)vinyl)phosphonate (3p) Following the general procedure. *N*,*N*-Dimethyl-1*H*-indole-1-carboxamide **1a** (47 mg, 0.25 mmol) and dimethyl vinylphosphonate **2f** (44.5 μ L, 0.375 mmol) were used. Purification via column chromatography on silica gel (petroleum ether/EtOAc = 5/2, v/v) afforded **3p** as a white solid (71 mg, 88% yield). M.p.: 81-83 °C. ¹H NMR (400 MHz, CDCl₃): δ = 3.00 (br. s, 6H), 3.76 (s, 3H), 3.79 (s, 3H), 6.12 (t, *J* = 17.6 Hz, 1H), 6.96 (s, 1H), 7.17-7.21 (m, 1H), 7.28-7.31 (m, 2H), 7.52 (dd, *J* = 23.2 Hz, 17.6 Hz, 1H), 7.61 (d, *J* = 7.6 Hz, 1H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 37.8, 52.59, 52.65, 108.3, 111.6, 112.0, 114.0, 121.8, 122.2, 125.3, 127.8, 134.2, 134.5, 137.1, 137.9, 138.0, 153.3 ppm. HRMS (ESI): calcd for C₁₅H₁₉N₂NaO₄P [M+Na]⁺ 345.0980, found 345.0982.



(*E*)-*N*,*N*-Dimethyl-2-(2-(phenylsulfonyl)vinyl)-1*H*-indole-1-carboxamide (3q)

Following the general procedure. *N*,*N*-Dimethyl-1*H*-indole-1-carboxamide **1a** (47 mg, 0.25 mmol) and phenyl vinyl sulfone **2g** (63mg, 0.375 mmol) were used. Purification via column chromatography on silica gel (petroleum ether/EtOAc = 3/1, v/v) afforded the desired product **3q** as a yellow solid (80 mg, 87% yield). M.p.: 48-49 °C. ¹H NMR (400 MHz, CDCl₃): δ = 2.99 (br. s, 6H), 6.77 (d, *J* = 15.6 Hz, 1H), 6.99 (s, 1H), 7.17-7.21 (m, 1H), 7.31-7.36 (m, 2H), 7.55 (t, *J* = 7.6 Hz, 2H), 7.59-7.64 (m, 2H), 7.73 (d, *J* = 15.6 Hz, 1H), 7.95 (d, *J* = 8.0 Hz, 2H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 37.7, 110.5, 111.7, 122.0, 122.4, 126.0, 126.9, 127.63, 127.68, 129.5, 131.3, 131.6, 133.5, 137.5, 140.7, 153.1 ppm. HRMS (ESI): calcd for C₁₉H₁₈N₂NaO₃S [M+Na]⁺ 377.0936, found 377.0936.



(E)-2-(2-Cyanovinyl)-N,N-dimethyl-1H-indole-1-carboxamide (3r)

Following the general procedure. *N*,*N*-Dimethyl-1*H*-indole-1-carboxamide **1a** (47 mg, 0.25 mmol) and vinyl cyanide **2h** (49.2 µL, 0.75 mmol) were used. Purification via column chromatography on silica gel (petroleum ether/EtOAc = 5/2, v/v) afforded **3r** as a white solid (39 mg, 65% yield). M.p.: 83-86 °C. ¹H NMR (400 MHz, CDCl₃): δ = 3.04 (br. s, 6H), 5.83 (d, *J* = 16.8 Hz, 1H), 7.01 (s, 1H), 7.21 (t, *J* = 8.0 Hz, 1H), 7.29 (d, *J* = 7.6 Hz, 1H), 7.35 (t, *J* = 8.0 Hz, 1H), 7.45 (d, *J* = 16.8 Hz, 1H), 7.63 (d, *J* = 8.0 Hz, 1H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 38.0, 96.3, 108.8, 111.8, 118.2, 122.2, 122.6, 126.1, 127.7, 133.2, 137.3, 138.9, 153.2 ppm. HRMS (ESI): calcd for C₁₄H₁₃N₃NaO [M+Na]⁺ 262.0956, found 262.0951.



(E)-N,N-Dimethyl-2-styryl-1H-indole-1-carboxamide (3s)

Following the general procedure. *N*,*N*-Dimethyl-1*H*-indole-1-carboxamide **1a** (47 mg, 0.25 mmol) and styrene **2i** (43 µL, 0.375 mmol) were used. Purification via column chromatography on silica gel (petroleum ether/EtO₂ = 10/1, v/v) afforded **3s** as yellow oil (49 mg, 68% yield). ¹H NMR (400 MHz, CDCl₃): δ = 3.02 (br. s, 6H), 6.86 (s, 1H), 7.14 (d, *J* = 2.0 Hz, 2H), 7.18 (d, *J* = 7.2 Hz, 1H), 7.23 (d, *J* = 7.2 Hz, 1H), 7.28-7.39 (m, 4H), 7.51 (d, *J* = 7.6 Hz, 2H), 7.59 (d, *J* = 7.6 Hz, 1H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 37.6, 103.1, 111.3, 117.5, 120.8, 121.7, 123.5, 126.6, 128.1, 128.6, 128.8 130.8, 136.3, 136.9, 137.2, 154.1 ppm. HRMS (ESI): calcd for C₁₉H₁₈N₂NaO [M+Na]⁺ 313.1317, found 313.1323.



(E)-2-(4-Fluorostyryl)-N,N-dimethyl-1H-indole-1-carboxamide (3t)

Following the general procedure. *N*,*N*-Dimethyl-1*H*-indole-1-carboxamide **1a** (47 mg, 0.25 mmol) and 4-fluorostyrene **2j** (30.2 µL, 0.375 mmol) were used. Purification via column chromatography on silica gel (petroleum ether/EtOAc = 5/1, v/v) afforded **3t** as a yellow solid (56 mg, 73% yield). M.p.: 120-121 °C. ¹H NMR (400 MHz, CDCl₃): δ = 3.04 (br. s, 6H), 6.85 (s, 1H), 7.05 (t, *J* = 8.4 Hz, 2H), 7.08 (s, 2H), 7.17 (t, *J* =7.2 Hz, 1H), 7.23 (d, *J* = 8.0 Hz, 1H), 7.30 (d, *J* = 8.0 Hz, 1H), 7.46 (d, *J* = 8.8 Hz, 1H), 7.47 (d, *J* = 8.4 Hz, 1H), 7.58 (d, *J* = 8.0 Hz, 1H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 37.9, 103.1, 111.3, 115.7, 115.9, 117.3, 117.4, 120.8, 121.8, 123.5, 128.2, 128.3, 128.6, 129.6, 133.17, 133.21, 136.2, 137.2, 154.1, 161.4, 163.9 ppm. HRMS (ESI): calcd for C₁₉H₁₇FN₂NaO [M+Na]⁺ 331.1223, found 331.1223.



(E)-2-(4-Chlorostyryl)-N,N-dimethyl-1H-indole-1-carboxamide (3u)

Following the general procedure. N,N-Dimethyl-1H-indole-1-carboxamide 1a (47 mg,

0.25 mmol) and 4-chlorostyrene **2k** (45 µL, 0.375 mmol), were used. Purification via column chromatography on silica gel (petroleum ether/EtOAc = 5/1, v/v) afforded **3u** as a white solid (53 mg, 65% yield). M.p.: 121-123 °C. ¹H NMR (400 MHz, DMSO-*d*₆): δ = 3.03 (br. s, 6H), 6.87 (s, 1H), 7.06 (d, *J* = 16.4 Hz, 1H), 7.13 (d, *J* = 16.0 Hz, 1H), 7.18 (d, *J* = 7.2 Hz, 1H), 7.24 (d, *J* = 8.0 Hz, 1H), 7.29 (s, 1H), 7.32 (d, *J* = 8.4 Hz, 2H), 7.42 (d, *J* = 8.4 Hz, 2H), 7.58 (d, *J* = 7.6 Hz, 1H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 37.7, 103.5, 111.4, 118.1, 120.9, 121.8, 123.7, 127.8, 128.5, 129.0, 129.4, 133.6, 135.5, 136.3, 137.0, 154.1 ppm. HRMS (ESI): calcd for C₁₉H₁₇ClN₂NaO [M+Na]⁺ 347.0927, found 347.0930.



(E)-2-(3-Chlorostyryl)-N,N-dimethyl-1H-indole-1-carboxamide (3v)

Following the general procedure. *N*,*N*-Dimethyl-1*H*-indole-1-carboxamide **1a** (47 mg, 0.25 mmol) and 3-chlorostyrene **2l** (45 µL, 0.375 mmol) were used. Purification via column chromatography on silica gel (petroleum ether/EtOAc = 5/1, v/v) afforded **3v** as a yellow solid (75 mg, 93% yield). M.p.: 96-98 °C. ¹H NMR (400 MHz, CDCl₃): δ = 3.03 (br. s, 6H), 6.87 (s, 1H), 7.04 (d, *J* = 16.4 Hz, 1H), 7.13-7.19 (m, 2H), 7.22-7.31 (m, 4H), 7.35 (d, *J* = 7.6 Hz, 1H), 7.48 (s, 1H), 7.58 (d, *J* = 7.6 Hz, 1H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 37.8, 103.8, 111.4, 119.0, 121.0, 121.9, 123.8, 124.9, 126.4, 128.0, 128.5, 129.2, 130.1, 134.8, 136.4, 136.8, 138.9, 154.1 ppm. HRMS (ESI): calcd for C₁₉H₁₇ClN₂NaO [M+Na]⁺ 347.0927, found 347.0933.



(E)-2-(3,4-Dimethoxystyryl)-N,N-dimethyl-1H-indole-1-carboxamide (3w) Following the general procedure. N,N-Dimethyl-1H-indole-1-carboxamide 1a (47 mg, 0.25 mmol) and 3,4-dimethoxystyrene 2m (111.0 μL, 0.75 mmol) were used.

Purification via column chromatography on silica gel (petroleum ether/EtOAc = 10/1, v/v) afforded **3w** as a yellow solid (44 mg, 50% yield). M.p.: 43-45 °C. ¹H NMR (400 MHz, CDCl₃): δ = 3.02 (br. s, 6H), 3.91 (s, 3H), 3.95 (s, 3H), 6.81 (s, 1H), 6.86 (d, *J* = 8.4 Hz, 1H), 6.98-7.09 (m, 4H), 7.16 (t, *J* = 7.6 Hz, 1H), 7.23 (t, *J* = 7.6 Hz, 1H), 7.31 (d, *J* = 8.4 Hz, 1H), 7.57 (d, *J* = 7.6 Hz, 1H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 37.7, 56.10, 56.12, 102.7, 109.1, 111.3, 111.4, 115.7, 120.2, 120.7, 121.7, 123.3, 128.7, 130.2, 130.9, 136.2, 137.6, 149.3, 149.5, 154.2 ppm. HRMS (ESI): calcd for C₂₁H₂₂N₂NaO₃ [M+Na]⁺ 373.1528, found 373.1523.

(E)-Butyl 3-(1-(dimethylcarbamoyl)-1H-pyrrol-2-yl)acrylate (4a)

Following the general procedure. *N*,*N*-Dimethyl-1*H*-pyrrole-1-carboxamide **11** (34.5 mg, 0.25 mmol) and *n*-butyl acrylate **2a** (53.5 μ L, 0.375 mmol) were used. Purification via column chromatography on silica gel (petroleum ether/EtOAc = 5/1, v/v) afforded **4a** as yellow oil (58 mg, 87% yield). ¹H NMR (400 MHz, CDCl₃): δ = 0.95 (t, *J* = 7.2 Hz, 3H), 1.37-1.46 (m, 2H), 1.62-1.70 (m, 2H), 2.97 (s, 6H), 4.17 (t, *J* = 6.8 Hz, 2H), 6.13 (d, *J* = 16.0 Hz, 1H), 6.28 (t, *J* = 3.2 Hz, 1H), 6.68 (dd, *J* = 3.6 Hz, 0.9 Hz, 1H), 6.96 (q, *J* = 0.9 Hz, 1H), 7.56 (d, *J* = 16.0 Hz, 1H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 13.9, 19.3, 30.9, 37.9, 64.4, 111.3, 113.8, 115.0, 124.0, 129.3, 132.7, 153.8, 167.5 ppm. HRMS (ESI): calcd for C₁₄H₂₀N₂NaO₃ [M+Na]⁺ 287.1372, found 287.1374.



(2*E*,2'*E*)-Dibutyl 3,3'-(1-(dimethylcarbamoyl)-1*H*-pyrrole-2,5-diyl)diacrylate (4b) A sealable tube with a magnetic stir bar was charged with Ag₂CO₃ (172 mg, 0.625 mmol), NaOAc (12.4 mg, 0.15 mmol), *N*,*N*-dimethyl-1*H*-pyrrole-1-carboxamide **11** (34.5 mg, 0.25 mmol), [RuCl₂(*p*-cymene)]₂ (8.0 mg, 12.5 µmol), AgSbF₆ (17.2 mg, 50 µmol), butyl acrylate **2a** (53.5 µL, 0.375 mmol, 1.5 equiv) and DCE (1.0 mL) under

an N₂ atmosphere. The tube was then sealed with a teflon-coated screw cap. The reaction mixture was first stirred at room temperature for 15 min and then heated at 100 °C for 15 h. The resulting solution was subsequently diluted with 5 mL of dichloromethane, filtered through a celite pad and washed with 10-20 mL of dichloromethane. The combined organic phases were evaporated, and the resulting residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 5/1, v/v) to afford product **4b** as yellow oil (50 mg, 51% yield). ¹H NMR (400 MHz, CDCl₃): δ = 0.95 (t, *J* = 7.2 Hz, 6H), 1.37-1.46 (m, 4H), 1.63-1.70 (m, 4H), 2.61 (s, 3H), 3.23 (s, 3H), 4.17 (t, *J* = 7.2 Hz, 4H), 6.20 (d, *J* = 16.0 Hz, 2H), 6.69 (s, 2H), 7.39 (d, *J* = 16.0 Hz, 2H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 13.9, 19.3, 30.9, 37.2, 37.9, 64.6, 114.1, 117.0, 131.0, 131.6, 152.1, 167.0 ppm. HRMS (ESI): calcd for C₂₁H₃₀N₂NaO₅ [M+Na]⁺ 413.2052, found 413.2051.



(E)-Butyl 3-(9-(dimethylcarbamoyl)-9H-carbazol-1-yl)acrylate (5a)

Following the general procedure. 9-(Dimethylcarbamoy1)carbazole **1m** (59.5 mg, 0.25 mmol) and *n*-butyl acrylate **2a** (53.5 µL, 0.375 mmol) were used. Purification via column chromatography on silica gel (petroleum ether/EtOAc = 15/1, v/v) afforded **5a** as light yellow oil (64 mg, 70% yield). ¹H NMR (400 MHz, CDCl₃): δ = 0.99 (t, *J* = 7.2 Hz, 3H), 1.43-1.52 (m, 2H), 1.69-1.76 (m, 2H), 2.82 (s, 3H), 3.29 (s, 3H), 4.24 (t, *J* = 6.4 Hz, 2H), 6.46 (d, *J* = 15.6 Hz, 1H), 7.33 (t, *J* = 7.2 Hz, 2H), 7.46-7.51 (m, 2H), 7.64 (d, *J* = 7.6 Hz, 1H), 8.01-8.09 (m, 3H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 13.9, 19.3, 30.9, 36.7, 38.2, 64.6, 111.1, 119.6, 120.3, 120.5, 121.65, 121.71, 122.2, 123.7, 125.3, 125.6, 127.2, 137.2, 139.3, 140.0, 154.8, 166.8 ppm. HRMS (ESI): calcd for C₂₂H₂₄N₂NaO₃ [M+Na]⁺ 387.1685, found 387.1685.



(E)-N,N-dimethyl-1-styryl-9H-carbazole-9-carboxamide (5b)

Following the general procedure. 9-(Dimethylcarbamoy1)carbazole **1m** (59.5 mg, 0.25 mmol) and styrene **2i** (43 µL, 0.375 mmol) were used. Purification via column chromatography on silica gel (petroleum ether/EtOAc = 15/1, v/v) afforded the desired product **5b** as yellow oil (29 mg, 35% yield). ¹H NMR (400 MHz, CDCl₃): δ = 2.60 (s, 3H), 3.12 (s, 3H), 7.08 (d, *J* = 16.0 Hz, 1H), 7.27-7.36 (m, 3H), 7.39 (t, *J* = 7.2 Hz, 2H), 7.46-7.57 (m, 5H), 7.64 (d, *J* = 7.2 Hz, 1H), 8.01 (d, *J* = 7.6 Hz, 1H), 8.06 (d, *J* = 7.6 Hz, 1H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 36.9, 37.9, 111.1, 119.9, 120.4, 121.4, 121.7, 123.6, 123.8, 124.2, 124.8, 124.9, 126.7, 126.9, 128.0, 128.9, 130.8, 136.6, 137.3, 139.2, 155.1 ppm. HRMS (ESI): calcd for C₂₃H₂₀N₂NaO [M+Na]⁺ 363.1473, found 363.1472.



(E)-3-(1H-indol-2-yl)acrylic acid (6a)⁴

(*E*)-Butyl 3-(1-(dimethylcarbamoyl)-1*H*-indol-2-yl) acrylate **3a** (79 mg, 0.25 mmol) was used as the starting material and the reaction time was 5 h. Purification via column chromatography on silica gel (CH₂Cl₂/MeOH = 5/1, v/v) afforded **6a** as a brown solid (43 mg, 91% yield). ¹H NMR (400 MHz, DMSO-*d*₆): δ = 6.46 (d, *J* = 16 Hz, 1H), 6.86 (d, *J* = 1.2 Hz, 1H), 7.01 (t, *J* = 7.2 Hz, 1H), 7.18 (td, *J* = 7.6 Hz, 0.8 Hz, 1H), 7.37 (d, *J* = 8.0 Hz, 1H), 7.55-7.59 (m, 2H), 11.54 (s, 1H), 12.33 (br. s, 1H) ppm. ¹³C NMR (100 MHz, DMSO-*d*₆): δ = 107.9, 111.5, 116.9, 119.8, 121.1, 123.8, 127.9, 133.9, 134.4, 138.0, 167.8 ppm. HRMS (ESI): calcd for C₁₁H₉NNaO₂ [M+Na]⁺ 210.0531, found 210.0532.



(E)-2-((1H-indol-2-yl)methylene)-4-hydroxybutanoic acid (6b)

(*E*)-*N*,*N*-Dimethyl-2-((2-oxodihydrofuran-3(2*H*)-ylidene)methyl)-1*H*-indole-1-carbox amide **30** (71 mg, 0.25 mmol) was used as the starting material and the reaction time was 5 h. Purification via column chromatography on silica gel (CH₂Cl₂/MeOH = 5/1, v/v) afforded **6b** as a yellow solid (52 mg, 89% yield). M.p.: 244-245 °C. ¹H NMR (400 MHz, DMSO-*d*₆): δ = 2.84 (t, *J* = 7.2 Hz, 2H), 3.61 (t, *J* = 7.2 Hz, 2H), 5.00 (br. s, 1H), 6.92 (s, 1H), 7.03 (td, *J* = 7.6 Hz, 0.8 Hz, 1H), 7.15 (td, *J* = 7.6 Hz, 0.8 Hz, 1H), 7.38 (d, *J* = 8.0 Hz, 1H), 7.59 (d, *J* = 8.0 Hz, 1H), 7.67 (s, 1H), 11.38 (s, 1H), 12.45 (br. s, 1H) ppm. ¹³C NMR (100 MHz, DMSO-*d*₆): δ = 31.8, 59.3, 104.8, 111.4, 119.7, 120.7, 122.9, 128.2, 128.4, 129.8, 133.3, 136.6, 169.0 ppm. HRMS (ESI): calcd for C₁₃H₁₃NNaO₃ [M+Na]⁺ 254.0793, found 254.0795.



(E)-2-(3-chlorostyryl)-1H-indole (6c)

(*E*)-2-(3-Chlorostyryl)-*N*,*N*-dimethyl-1*H*-indole-1-carboxamide **3v** (81 mg, 0.25 mmol) was used as the starting material and the reaction time was 20 h. THF (1.0 mL) was added to the reaction system due to the low solubility of **3v** in EtOH/H₂O. Purification via column chromatography on silica gel (petroleum ether/EtOAc = 10/1, v/v) afforded **6c** as a yellow solid (48 mg, 77% yield). M.p.: 151-153 °C. ¹H NMR (400 MHz, CDCl₃): δ = 6.65 (d, *J* = 1.2 Hz, 1H), 6.81 (d, *J* = 16.4 Hz, 1H), 7.09-7.14 (m, 2H), 7.20-7.25 (m, 2H), 7.30 (t, *J* = 7.6 Hz, 1H), 7.35 (d, *J* = 8.0 Hz, 2H), 7.49 (m, 1H), 7.60 (d, *J* = 8.0 Hz, 1H), 8.20 (s, 1H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 104.8, 110.8, 120.49, 120.52, 120.9, 123.3, 124.6, 125.6, 126.2, 127.7, 129.0, 130.1, 134.9, 135.9, 137.2, 138.9 ppm. HRMS (ESI): calcd for C₁₆H₁₃ClN [M+H]⁺ 254.0737, found 254.0734.

VI. References

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VII. ¹H-¹H NOESY spectra of compounds 3a and 3o



fl (ppm)



VIII. Copies of ¹H and ¹³C NMR spectra



























































Electronic Supplementary Material (ESI) for Chemical Communications This journal is The Royal Society of Chemistry 2013







































