Supporting Information for

Base-catalyzed controllable reaction of 3-ylideneoxindoles and O-Boc hydroxycarbamates for the synthesis of amidoacrylates and spiroaziridine oxindoles

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1. General information

Unless otherwise noted, materials were purchased from commercial suppliers and used without further purification. All the solvents were treated according to general methods. Flash column chromatography was performed using 200-300 mesh silica gel. 1H NMR spectra were recorded on 400 or 600 MHz spectrometers. Chemical shifts were reported on the delta (δ) scale in parts per million (ppm) relative to the singlet (0 ppm) for tetramethylsilane (TMS). Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, dd = doublet of doublets, m = multiplet), coupling constants (Hz) and integration. 13C NMR spectra were recorded at 100 MHz with complete proton decoupling. Chemical shifts are reported in ppm relative to the central line of the triplet at 77.0 ppm for CDCl₃. Mass spectra were measured on a MS spectrometer (EI).
2. Preparation of substrates

2.1 General procedure for the preparation of 3-ylideneoxindoles

![Chemical structure]

**Step 1**: To a 250 mL 3-necked-round bottom flask equipped with a silicone oil bubbler was added commercially available isatin (7.7 g, 50 mmol) and anhydrous DMF (80 mL). And the mixture was cooled down to 0 °C. To this solution was added NaH (1.32 g, 55 mmol), then CH₃I was added 10 min later (without gas bubbling), and stirred at 0 °C for 15 min. Upon completion of the reaction (monitored by TLC), the mixture was diluted with saturated NH₄Cl solution and extracted with ethyl acetate, the ethyl acetate layer was washed with water and brine. The combined organic layer was then dried over MgSO₄, filtered, and concentrated to yield the crude N-methylindoline-2, 3-dione (7.6 g, 94% yield), which was used directly in the next step[1].

**Step 2**: To a stirred solution of ethyl 2-(triphenyl phosphoranylidene) acetate (18.0 g, 51.7 mmol) in anhydrous THF (100 mL), the N-methylindoline-2, 3-dione (7.58 g, 47 mmol) was added at 0 °C. The mixture was stirred at the same temperature until the reaction was completed monitored by TLC analysis. The crude product was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate 5:1). Compound 1a was obtained as a red solid (9.45 g, 87% yield)[2].

The other 3-ylideneoxindoles were prepared according to the above procedure.

2.2 General procedure for the preparation of O-Boc hydroxycarbamates

![Chemical structure]

**Step 1**: Sodium bicarbonate (21.0 g, 250 mmol) was added to a 500 mL round bottom flask and dissolved in H₂O (120 mL). Then, hydroxylamine hydrochloride (13.9 g, 200 mmol) was added into this solution. After this, the solution of benzyl chloroformate (8.8 g, 50 mmol) in CH₂Cl₂ (60 mL) was added to the mixture dropwisely and the mixture stirred at room temperature. Upon completion of the reaction (monitored by TLC), the system was acidized to pH 4-5 with 1M HCl solution. The aqueous layer was extracted with CH₂Cl₂. The combined organic layer was then dried over MgSO₄, filtered, and concentrated to yield the crude white solid benzyl hydroxycarbamate (8.3 g, 99% yield), which was used directly in the next step.
**Step 2**: benzyl hydroxycarbamate (8.3 g, 49.6 mmol) and ditertbutyl dicarbonate (10.8 g, 49.6 mmol) were dissolved into THF (60 mL) and the mixture stirred vigorously at RT. Then, aqueous NaOH solution (1M, 60 mL) was added to the mixture dropwise. Upon completion of the reaction, the crude product was diluted with ether and brine, the aqueous layer was extracted with ether, the combined organic layer was washed with brine and dried over MgSO₄. The crude product was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate 10:1 to 5:1). Compound 2a was obtained as a colorless oil (4.64 g, 35% yield)[3].

The other N-protected carbamates were prepared according to the above procedure.

References:

3. Representative procedure for preparation of the products.
3.1 Representative procedure for preparation of the amidoacrylates 3.

![Diagram](https://via.placeholder.com/150)

The compound 2 (xx mg, 0.24 mmol) and DABCO (4.5 mg, 0.04 mmol) were dissolved in CH₂Cl₂ (1 mL). Then, compound 1 (xx mg, 0.20 mmol) was added to the mixture. Upon the completion of the reaction (monitored by TLC), the crude product was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate 8:1 to 5:1) to give the desired product 3 as a yellow or red solid.

3.2 Representative procedure for preparation of the spiroaziridine 4.

![Diagram](https://via.placeholder.com/150)

The compound 2 (xx mg, 0.36 mmol) and TMG (6.9 mg, 0.06 mmol) were dissolved in CH₂Cl₂ (5 mL). Then, compound 1 (0.30 mmol) was added to the mixture at 0 °C. Upon the completion of the...
reaction (monitored by TLC), The crude product was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate 5:1 to 3:1) to give the desired product 4 as a white solid.

3.3 Representative procedure for preparation of the bispirooxindole 5.

![Chemical structure](image)

**The compound 2 (91.3 mg, 0.24 mmol) and DBU (6.1 mg, 0.04 mmol) were dissolved in CH₂Cl₂ (1 mL). Then compound 1 (46.3 mg, 0.20 mmol) was added to the mixture and stirred at room temperature, Upon the completion of the reaction (monitored by TLC), The crude product was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate 3:1 to 2:1), Compound 5 was obtained as a white solid (91.7 mg, 75% yield, 1.6:1 dr.).**

![Chemical structure](image)

**The compound 1 (46.3 mg, 0.20 mmol) and compound 4a (91.3 mg, 0.24 mmol) were dissolved in CH₂Cl₂ (1 mL). Then DBU (6.1 mg, 0.04 mmol) was added to the mixture. Upon the completion of the reaction (monitored by TLC), The crude product was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate 3:1 to 2:1), Compound 5 was obtained as a white solid (73.4 mg, 60% yield, 1.6:1 dr.).**

4. Control experiments.

![Chemical structure](image)

**The compound 3a (76.1 mg, 0.20 mmol) was dissolved in CH₂Cl₂ (1 mL). And either DABCO (4.5 mg, 0.04 mmol) or TMG (4.6 mg, 0.04 mmol) was added. The mixture were allowed to stirred at room temperature for 48 h, and no transformation was observed, and substrate 3a was fully remained. This result proves the amidoacrylate is not the intermediote for the generation of spiroaziridine 4a.**

![Chemical structure](image)
The compound 4a (76.1 mg, 0.20 mmol) was dissolved in CH₂Cl₂ (1 mL). And DABCO (4.5 mg, 0.04 mmol) or TMG (4.6 mg, 0.04 mmol) was added. The mixture were allowed to stirred at room temperature for 48 h, however, no amidoacrylate 3a; instead, the isomer 4a' was isolated in 30% and 64% yield, respectively. This result rules out the possibility that the amidoacrylate product 3a was formed through the spiroaziridine oxindole 4a.

5. Spectral data of products

(Z)-ethyl 2-(((benzyloxy)carbonyl)amino)-2-(1-methyl-2-oxoindolin-3-ylidene)acetate (3a)

![Chemical structure of 3a](image)

Yellow solid; 99% yield in 24 h, mp 112-114 °C. ¹H NMR (600 MHz, CDCl₃): δ = 11.27 (s, 1H), 7.42 – 7.31 (m, 5H), 7.27 – 7.19 (m, 2H), 7.01 (t, J = 7.7 Hz, 1H), 6.86 (d, J = 7.5 Hz, 1H), 5.22 (s, 2H), 4.52 (s, 2H), 3.26 (d, J = 4.1 Hz, 3H), 1.42 (t, J = 6.8 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃): δ = 168.5, 162.4, 152.1, 140.6, 137.9, 134.8, 128.4, 128.2, 127.6, 122.1, 120.0, 119.6, 108.3, 104.1, 68.1, 62.6, 25.6, 13.7; HRMS (ESI): for C₂₁H₂₀N₂O₅ [M⁺]: calcld 380.1372, found 380.1370.

(Z)-ethyl 2-(((benzyloxy)carbonyl)amino)-2-(2-oxoindolin-3-ylidene)acetate (3b)

![Chemical structure of 3b](image)

Yellow solid; 98% yield in 24 h, mp 155-157 °C. ¹H NMR (600 MHz, CDCl₃): δ = 11.13 (d, J = 19.5 Hz, 1H), 8.43 (s, 1H), 7.39 (d, J = 6.1 Hz, 3H), 7.37 (d, J = 4.0 Hz, 1H), 7.21 (d, J = 7.8 Hz, 1H), 7.17 (t, J = 7.7 Hz, 1H), 6.99 (t, J = 7.8 Hz, 1H), 5.23 (s, 2H), 4.52 (s, 2H), 1.41 (t, J = 7.1 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃): δ = 170.8, 162.5, 152.2, 138.6, 138.2, 134.8, 128.6, 128.5, 127.8, 122.3, 120.4, 120.4, 110.3, 104.5, 68.4, 62.9, 13.8; HRMS (ESI): for C₂₀H₁₈N₂O₅ [M⁺]: calcld 366.1216, found 366.1215.

(Z)-ethyl 2-(1-acetyl-2-oxoindolin-3-ylidene)-2-(((benzyloxy)carbonyl)amino)acetate (3c)

![Chemical structure of 3c](image)

Yellow solid; 95% yield in 24 h, mp 104-107 °C. ¹H NMR (600 MHz, CDCl₃): δ = 11.01 (s, 1H), 8.27 (d, J = 8.2 Hz, 1H), 7.40 (s, 4H), 7.36 (d, J = 2.4 Hz, 1H), 7.29 (d, J = 7.3 Hz, 1H), 7.23 (d, J = 7.7 Hz, 1H), 7.16 (d, J = 7.5 Hz, 1H), 5.24 (s, 2H), 4.54 (d, J = 6.3 Hz, 2H), 2.71 (d, J = 1.8 Hz, 3H), 1.42 (t, J = 6.8 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃): δ = 170.4, 169.7, 162.0, 151.8, 139.8, 137.0, 134.4, 128.8, 128.6, 128.2, 124.9, 120.4, 119.3, 116.5, 102.9, 68.74, 63.1, 26.9, 13.7; HRMS (ESI): for C₂₂H₂₀N₂O₆ [M⁺]: calcld 408.1321, found 408.1321.

(Z)-tert-butyl 3-(1-(((benzyloxy)carbonyl)amino)-2-ethoxy-2-oxoethylidene)-2-oxoindoline-1-carboxylate (3d)

![Chemical structure of 3d](image)

Yellow solid; 94% yield in 24 h, mp 99-102 °C. ¹H NMR (600 MHz, CDCl₃): δ = 11.17 (s, 1H), 7.87 (d, J = 8.2 Hz, 1H), 7.42 – 7.33 (m, 5H), 7.30 – 7.25 (m, 2H), 7.22 (d, J = 7.7 Hz, 1H), 7.11 (t, J = 7.6 Hz, 1H), 5.22 (s, 2H), 4.53 (d, J = 5.7 Hz, 2H), 1.65 (s, 9H), 1.42 (t, J = 7.1 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃): δ = 168.0, 162.2, 151.9, 148.7, 139.4, 136.8, 134.6, 128.6, 128.5, 128.3, 127.9, 124.2, 120.0, 119.5, 114.9, 103.0, 84.6, 68.5, 63.0, 28.0, 13.7; HRMS (ESI): for C₂₅H₂₆N₂O₇ [M⁺]: calcld 466.1740, found 466.1741.

(Z)-ethyl 2-(((benzyloxy)carbonyl)amino)-2-(1-(4-methoxybenzyl)-2-oxoindolin-3-ylidene)acetate (3e)

![Chemical structure of 3e](image)

Yellow solid; 98% yield in 24 h, mp 97-100 °C. ¹H NMR (600 MHz, CDCl₃): δ = 11.31 (s, 1H), 7.41 – 7.31 (m, 5H), 7.21 (dd, J = 17.7, 8.1 Hz, 3H), 7.13 (t, J = 7.7 Hz, 1H), 6.97 (t, J = 7.6 Hz, 1H), 6.80 (dd, J = 11.8, 8.4 Hz, 3H), 5.26 – 5.17 (m, 2H), 4.90 (d, J = 17.3 Hz, 2H), 4.53 (s, 2H), 3.78 – 3.68 (m, 3H), 1.41 (t, J = 6.7 Hz, 3H); ¹³C NMR
(100 MHz, CDCl3): $\delta = 168.8, 162.5, 159.0, 152.2, 140.0, 138.3, 134.8, 128.6, 128.4, 127.7, 127.6, 122.3, 120.2, 120.0, 114.1, 109.2, 104.0, 68.3, 62.8, 55.2, 42.8, 13.8; HRMS (ESI): for C$_{28}$H$_{26}$N$_{2}$O$_{6}$ [M]$^+$: calcd 486.1791, found 486.1787.

**Z)**-ethyl 2-(1-benzyl-2-oxoindolin-3-ylidine)-2-(((benzyloxy)carbonyl)amino)acetate (3f)

eyellow solid; 98% yield in 24 h, mp 118-121 °C. $^1$H NMR (600 MHz, CDCl3): $\delta = 11.31 (s, 1H), 7.43 – 7.30 (m, 5H), 7.30 – 7.19 (m, 6H), 7.12 (t, $J = 7.6$ Hz, 1H), 6.97 (t, $J = 7.6$ Hz, 1H), 6.76 (d, $J = 7.9$ Hz, 1H), 5.21 (s, 2H), 4.94 (s, 2H), 4.53 (s, 2H), 1.41 (t, $J = 6.9$ Hz, 3H); $^{13}$C NMR (100 MHz, CDCl3): $\delta = 168.7, 162.4, 152.1, 139.8, 138.3, 135.5, 134.7, 128.7, 128.5, 128.3, 127.6, 127.0, 126.7, 126.0, 122.3, 120.2, 119.9, 109.2, 103.9, 68.2, 62.8, 43.2, 13.7; HRMS (ESI): for C$_{27}$H$_{24}$N$_{2}$O$_{5}$ [M]$^+$: calcd 456.1685, found 456.1681.

**Z)**-ethyl 2-(1-allyl-2-oxoindolin-3-ylidine)-2-(((benzyloxy)carbonyl)amino)acetate (3g)

yellow solid; 99% yield in 24 h, mp 80-83 °C. $^1$H NMR (600 MHz, CDCl3): $\delta = 11.27 (s, 1H), 7.38 – 7.32 (m, 5H), 7.24 (d, $J = 7.7$ Hz, 1H), 7.20 (t, $J = 7.8$, 0.8 Hz, 1H), 7.00 (dd, $J = 17.2$, 9.5 Hz, 1H), 6.87 – 6.81 (m, 1H), 5.86 – 5.75 (m, 1H), 5.20 (d, $J = 4.7$ Hz, 2H), 5.20 – 5.14 (m, 2H), 4.52 (s, 2H), 4.42 – 4.33 (m, 2H), 1.41 (t, $J = 7.0$ Hz, 3H); $^{13}$C NMR (100 MHz, CDCl3): $\delta = 168.5, 162.5, 152.2, 139.9, 138.3, 134.8, 131.0, 128.5, 128.3, 127.7, 122.3, 120.2, 119.9, 117.5, 109.1, 104.0, 68.2, 62.8, 41.9, 13.8; HRMS (ESI): for C$_{23}$H$_{22}$N$_{2}$O$_{5}$ [M]$^+$: calcd 406.1529, found 406.1526.

**Z)**-ethyl 2-(((benzyloxy)carbonyl)amino)-2-(4-bromo-1-methyl-2-oxoindolin-3-ylidene)acetate (3h)

yellow solid; 98% yield in 24 h, mp 118-120 °C. $^1$H NMR (600 MHz, CDCl3): $\delta = 11.96 (s, 1H), 7.43 – 7.32 (m, 5H), 7.23 (d, $J = 8.1$ Hz, 1H), 7.09 (s, 1H), 6.82 (d, $J = 7.8$ Hz, 1H), 5.21 (s, 2H), 4.46 (d, $J = 7.2$ Hz, 2H), 3.28 (s, 3H), 1.36 (t, $J = 7.2$ Hz, 3H); $^{13}$C NMR (100 MHz, CDCl3): $\delta = 168.9, 162.5, 152.2, 142.5, 142.5, 140.8, 134.8, 128.5, 128.4, 128.2, 127.9, 120.6, 116.1, 107.0, 105.2, 68.1, 62.8, 26.0, 13.5; HRMS (ESI): for C$_{21}$H$_{19}$BrN$_{2}$O$_{5}$ [M]$^+$: calcd 458.0477, found 458.0475.

**Z)**-ethyl 2-(((benzyloxy)carbonyl)amino)-2-(5-bromo-1-methyl-2-oxoindolin-3-ylidene)acetate (3i)

yellow solid; 98% yield in 24 h, mp 121-124 °C. $^1$H NMR (600 MHz, CDCl3): $\delta = 11.23 (s, 1H), 7.41 – 7.30 (m, 6H), 7.29 (s, 1H), 6.70 (d, $J = 8.3$ Hz, 1H), 5.22 (s, 2H), 4.54 (s, 2H), 3.22 (s, 3H), 1.44 (t, $J = 7.0$ Hz, 3H); $^{13}$C NMR (100 MHz, CDCl3): $\delta = 168.3, 162.1, 152.1, 139.6, 139.3, 134.7, 130.2, 128.7, 128.6, 128.4, 123.2, 121.7, 115.1, 109.6, 103.1, 68.4, 63.1, 25.9, 13.8; HRMS (ESI): for C$_{21}$H$_{19}$BrN$_{2}$O$_{5}$ [M]$^+$: calcd 458.0477, found 458.0461.

**Z)**-ethyl 2-(((benzyloxy)carbonyl)amino)-2-(6-bromo-1-methyl-2-oxoindolin-3-ylidene)acetate (3j)

yellow solid; 99% yield in 24 h, mp 130-132 °C. $^1$H NMR (600 MHz, CDCl3): $\delta = 11.18 (s, 1H), 7.45 – 7.30 (m, 5H), 7.15 (d, $J = 8.2$ Hz, 1H), 7.07 (d, $J = 8.2$ Hz, 1H), 7.02 (s, 1H), 5.22 (s, 2H), 4.51 (s, 2H), 3.26 (s, 3H), 1.40 (t, $J = 7.1$ Hz, 3H); $^{13}$C NMR (100 MHz, CDCl3): $\delta = 168.4, 162.3, 152.0, 141.7, 138.6, 134.7, 128.5, 128.4, 128.3, 128.2, 125.0, 121.1, 118.7, 111.7, 103.3, 68.3, 62.9, 25.8, 13.7; HRMS (ESI): for C$_{21}$H$_{19}$BrN$_{2}$O$_{5}$ [M]$^+$: calcd 458.0477, found 458.0477.
(Z)-ethyl 2-(((benzyloxy)carbonyl)amino)-2-(4-chloro-1-methyl-2-oxoindolin-3-ylidene)acetate (3k)
yellow solid; 99% yield in 24 h, mp 129-131°C. ¹H NMR (600 MHz, CDCl₃): δ = 12.15 (s, 1H), 7.43 – 7.32 (m, 5H), 7.18 (t, J = 8.0 Hz, 1H), 7.04 (d, J = 7.6 Hz, 1H), 6.79 (d, J = 7.6 Hz, 1H), 5.21 (s, 2H), 4.44 (d, J = 7.2 Hz, 2H), 3.29 (s, 3H), 1.38 (t, J = 7.2 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃): δ = 167.0, 162.6, 152.1, 142.1, 141.6, 134.8, 128.5, 128.4, 128.3, 128.2, 127.8, 124.5, 118.5, 106.6, 103.5, 68.1, 62.5, 26.1, 13.6; HRMS (ESI): for C₂₁H₁₉ClN₂O₅ [M]+: calcd 414.0982, found 414.0967.

(Z)-ethyl 2-(((benzyloxy)carbonyl)amino)-2-(5-chloro-1-methyl-2-oxoindolin-3-ylidene)acetate (3l)
yellow solid; 98% yield in 24 h, mp 152-155°C. ¹H NMR (600 MHz, CDCl₃): δ = 11.16 (s, 1H), 7.45 – 7.31 (m, 5H), 7.13 (d, J = 8.3 Hz, 1H), 6.86 (d, J = 1.6 Hz, 1H), 5.22 (s, 2H), 4.51 (s, 2H), 3.25 (s, 3H), 1.40 (t, J = 7.1 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃): δ = 168.7, 162.3, 152.1, 141.7, 138.5, 134.7, 133.4, 128.6, 128.4, 122.2, 121.0, 118.3, 108.9, 103.4, 68.4, 62.9, 25.9, 13.8; HRMS (ESI): for C₂₁H₁₉ClN₂O₅ [M]+: calcd 414.0982, found 414.0974.

(Z)-ethyl 2-(((benzyloxy)carbonyl)amino)-2-(5-fluoro-1-methyl-2-oxoindolin-3-ylidene)acetate (3m)
yellow solid; 98% yield in 24 h, mp 123-125°C. ¹H NMR (600 MHz, CDCl₃): δ = 11.29 (s, 1H), 7.38 (d, J = 8.5 Hz, 5H), 6.96 (d, J = 7.4 Hz, 2H), 6.82 – 6.73 (m, 1H), 5.23 (s, 2H), 4.53 (s, 2H), 3.26 (s, 3H), 1.42 (t, J = 6.7 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃): δ = 168.5, 162.1, 160.0, 157.6, 152.0, 139.1, 136.8, 134.7, 128.5, 128.3, 120.9, 114.0, 113.8, 108.6, 108.6, 108.0, 107.7, 103.8, 68.3, 62.9, 25.8, 13.7; HRMS (ESI): for C₂₁H₁₉FN₂O₅ [M]+: calcd 398.1278, found 398.1266.

(Z)-ethyl 2-(((benzyloxy)carbonyl)amino)-2-(7-fluoro-1-methyl-2-oxoindolin-3-ylidene)acetate (3n)
yellow solid; 98% yield in 24 h, mp 131-134°C. ¹H NMR (600 MHz, CDCl₃): δ = 11.32 (s, 1H), 7.44 – 7.31 (m, 5H), 6.96 (d, J = 3.1 Hz, 3H), 1.41 (t, J = 6.9 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃): δ = 168.5, 162.1, 160.0, 157.6, 152.0, 139.1, 136.8, 134.7, 128.5, 128.3, 127.3, 127.2, 122.7, 122.6, 115.9, 115.2, 115.0, 103.4, 68.3, 62.9, 28.2, 13.7; HRMS (ESI): for C₂₁H₁₉FN₂O₅ [M]+: calcd 398.1278, found 398.1271.

(Z)-ethyl 2-(((benzyloxy)carbonyl)amino)-2-(1,5-dimethyl-2-oxoindolin-3-ylidene)acetate (3o)
yellow solid; 98% yield in 24 h, mp 98-101°C. ¹H NMR (600 MHz, CDCl₃): δ = 11.28 (s, 1H), 7.38 (d, J = 3.8 Hz, 3H), 7.36 (t, J = 3.6 Hz, 2H), 7.16 – 6.92 (m, 2H), 7.23 (s, 2H), 4.52 (s, 2H), 3.49 (d, J = 2.4 Hz, 3H), 1.41 (t, J = 6.9 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃): δ = 168.7, 162.6, 152.3, 142.3, 139.7, 138.7, 137.7, 134.9, 131.6, 128.5, 128.3, 128.2, 120.9, 119.8, 108.0, 104.4, 68.2, 62.7, 25.8, 21.3, 13.8; HRMS (ESI): for C₂₂H₂₂N₂O₅ [M]+: calcd 394.1529, found 394.1512.

(Z)-ethyl 2-(((benzyloxy)carbonyl)amino)-2-(1-methyl-2-oxo-5-(trifluoromethoxy)indolin-3-ylidene)acetate (3p)
yellow solid; 98% yield in 24 h, mp 77-80°C. ¹H NMR (600 MHz, CDCl₃): δ = 11.23 (s, 1H), 7.46 – 7.33 (m, 5H), 7.17 – 7.06 (m, 2H), 6.85 (d, J = 8.5 Hz, 1H), 5.23 (s, 2H), 4.51 (s, 2H), 3.29 (s, 3H), 1.41 (t, J = 7.1 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃): δ = 168.7, 162.1, 152.1, 144.4, 139.7, 139.2, 134.7, 128.6, 128.4, 121.8, 121.0, 120.7, 119.2, 113.9, 108.6, 103.3, 68.5, 63.1, 26.0, 13.7; HRMS (ESI): for C₂₂H₁₉F₃N₂O₆ [M]+: calcd 464.1195, found 464.1189.
(Z)-benzyl (1-(1-methyl-2-oxoindolin-3-ylidene)-2-oxopropyl)carbamate (3q)

Yellow solid; 98% yield in 24 h, mp 139-141 °C. $^1$H NMR (600 MHz, CDCl$_3$): $\delta = 11.39$ (s, 1H), 7.37 (d, $J = 8.9$ Hz, 5H), 7.24 (d, $J = 7.7$ Hz, 1H), 7.18 (d, $J = 7.7$ Hz, 1H), 7.00 (t, $J = 7.6$ Hz, 1H), 6.87 (d, $J = 7.8$ Hz, 1H), 5.22 (s, 2H), 3.29 (s, 3H), 2.61 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta =$ 196.8, 186.2, 168.9, 152.8, 145.8, 140.7, 134.7, 128.6, 128.6, 127.4, 122.4, 120.3, 119.6, 108.3, 102.1, 68.4, 30.0, 25.7; HRMS (ESI-TOF) for C$_{20}$H$_{18}$N$_2$NaO$_4$ [M+Na]$^+$: calcd 373.1159, found 373.1161.

(Z)-benzyl (1-(1-methyl-2-oxoindolin-3-ylidene)-2-oxo-2-phenylethyl)carbamate (3r)

Red solid; 98% yield in 24 h, mp 165-167 °C. $^1$H NMR (600 MHz, CDCl$_3$): $\delta = 11.65$ (s, 1H), 8.05 (s, 2H), 7.62 (s, 1H), 7.50 (s, 2H), 7.33 – 7.25 (m, 5H), 7.15 (s, 1H), 6.89 – 6.75 (m, 3H), 5.10 (d, $J = 12.5$ Hz, 2H), 3.31 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta =$ 189.7, 168.7, 152.3, 144.5, 140.6, 134.9, 134.7, 134.3, 129.1, 128.7, 128.5, 128.3, 127.4, 122.2, 121.0, 119.8, 108.2, 104.3, 68.3, 25.8; HRMS (ESI-TOF) for C$_{25}$H$_{20}$N$_2$NaO$_4$ [M+Na]$^+$: calcd 435.1315, found 435.1304.

(Z)-benzyl (1-(1-methyl-2-oxoindolin-3-ylidene)-2-oxo-2-(thiophen-2-yl)ethyl)carbamate (3s)

Yellow solid; 99% yield in 24 h, mp 146-148 °C. $^1$H NMR (600 MHz, CDCl$_3$): $\delta = 11.56$ (s, 1H), 7.78 (d, $J = 4.7$ Hz, 1H), 7.70 (d, $J = 3.5$ Hz, 1H), 7.33 (d, $J = 3.3$ Hz, 5H), 7.17 (t, $J = 7.7$ Hz, 1H), 7.12 – 7.08 (m, 1H), 7.01 (d, $J = 7.5$ Hz, 1H), 6.85 (t, $J = 7.3$ Hz, 2H), 5.14 (s, 2H), 3.31 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta =$ 186.2, 181.5, 168.7, 152.1, 143.6, 142.0, 140.7, 135.8, 134.5, 128.6, 128.5, 128.3, 127.5, 122.3, 121.1, 119.7, 108.2, 104.5, 68.3, 25.8; HRMS (ESI-TOF) for C$_{23}$H$_{18}$N$_2$NaO$_4$S [M+Na]$^+$: calcd 441.0879, found 441.0879.

(Z)-ethyl 2-((benzoyloxy)amino)-2-(1-methyl-2-oxoindolin-3-ylidene)acetate (3t)

Yellow solid; 99% yield in 24 h. $^1$H NMR (600 MHz, CDCl$_3$): $\delta = 11.54$ (s, 1H), 7.39 (t, $J = 8.0$ Hz, 2H), 7.29 – 7.23 (m, 4H), 7.23 – 7.19 (m, 2H), 7.05 (d, $J = 7.6$ Hz, 1H), 6.89 (d, $J = 7.8$ Hz, 1H), 4.51 (q, $J = 7.2$ Hz, 2H), 3.31 (s, 3H), 1.39 (t, $J = 7.2$ Hz, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta =$ 168.7, 162.0, 150.7, 150.0, 140.9, 137.5, 129.4, 128.0, 126.1, 122.4, 121.2, 120.3, 119.6, 108.4, 105.1, 62.9, 25.8, 13.8; HRMS (ESI-TOF) for C$_{20}$H$_{18}$N$_2$NaO$_5$ [M+Na]$^+$: calcd 389.1108, found 389.1105.

(Z)-ethyl 2-((benzoyloxy)amino)-2-(1-methyl-2-oxoindolin-3-ylidene)acetate (3u)

Yellow solid; 99% yield in 24 h. $^1$H NMR (600 MHz, CDCl$_3$): $\delta = 11.51$ (s, 1H), 7.29 – 7.25 (m, 2H), 7.18 (d, $J = 8.2$ Hz, 2H), 7.08 (d, $J = 8.3$ Hz, 2H), 7.04 (s, 1H), 6.89 (d, $J = 7.8$ Hz, 1H), 4.50 (q, $J = 7.2$ Hz, 2H), 3.31 (s, 3H), 1.39 (t, $J = 7.2$ Hz, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta =$ 168.8, 162.3, 151.0, 147.9, 141.0, 137.7, 135.8, 129.4, 128.0, 126.1, 122.4, 121.2, 120.3, 119.6, 108.4, 105.1, 62.9, 25.8, 13.8; HRMS (ESI-TOF) for C$_{21}$H$_{20}$N$_2$NaO$_5$ [M+Na]$^+$: calcd 403.1264, found 403.1257.

1-benzyl 3-ethyl 1'-methyl-2'-oxospiro[aziridine-2,3'-indoline]-1,3-dicarboxylate (4a)

White solid; 82% yield in 2.5 h, >95:5 d.r. mp 120-122 °C. $^1$H NMR (600 MHz, CDCl$_3$): $\delta =$ 7.38 – 7.24 (m, 5H), 7.16 (dd, $J =$ 7.7 Hz, 1.6, 2H), 6.92 – 6.83 (m, 2H), 6.55 (d, $J =$ 7.4 Hz, 1H), 5.18 – 5.03 (m, 2H), 3.31 (s, 3H), 2.34 (s, 3H), 1.39 (t, $J =$ 7.2 Hz, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta =$ 168.8, 162.3, 151.0, 147.9, 141.0, 137.7, 135.8, 129.9, 128.0, 122.4, 120.9, 120.4, 119.7, 108.4, 105.0, 62.9, 25.8, 20.8, 13.8; HRMS (ESI-TOF) for C$_{21}$H$_{20}$N$_2$NaO$_5$ [M+Na]$^+$: calcd 403.1264, found 403.1257.

1-benzyl 3-ethyl 1'-methyl-2'-oxospiro[aziridine-2,3'-indoline]-1,3-dicarboxylate (4a)
1-benzyl 3-methyl 1'-methyl-2'-oxospiro[aziridine-2,3'-indoline]-1,3-dicarboxylate (4b)
white solid; 75% yield in 2 h, >95:5 d.r. 1H NMR (600 MHz, CDCl3): δ = 7.42 – 7.21 (m, 4H), 7.17 (s, 2H), 6.87 (t, J = 8.6 Hz, 2H), 6.55 (d, J = 7.3 Hz, 1H), 5.10 (dd, J = 28.5, 11.7 Hz, 2H), 3.91 (s, 1H), 3.84 (s, 3H), 3.21 (s, 3H); 13C NMR (100 MHz, CDCl3): δ = 167.8, 164.6, 158.2, 144.8, 134.5, 130.4, 128.7, 128.5, 128.4, 122.6, 120.7, 119.7, 109.1, 69.1, 52.8, 48.7, 46.7, 26.6; HRMS (ESI-TOF) for C20H18N2NaO5 [M+Na]+: calcd 389.1108, found 389.1104.

1-benzyl 3-tert-butyl 1'-methyl-2'-oxospiro[aziridine-2,3'-indoline]-1,3-dicarboxylate (4c)
white solid; 74% yield in 2 h, >95:5 d.r. mp 139-142 °C. 1H NMR (600 MHz, CDCl3): δ = 7.28 (dt, J = 12.8, 6.8 Hz, 5H), 7.20 – 7.11 (m, 2H), 6.92 – 6.82 (m, 2H), 6.54 (d, J = 7.4 Hz, 1H), 5.08 (dd, J = 28.4, 12.0 Hz, 2H), 3.80 (s, 1H), 3.23 (d, J = 8.3 Hz, 3H), 1.54 – 1.49 (m, 9H); 13C NMR (100 MHz, CDCl3): δ = 168.0, 162.9, 158.5, 157.8, 144.9, 134.7, 130.2, 128.6, 128.4, 128.3, 122.4, 120.7, 120.3, 108.9, 83.2, 68.9, 48.7, 47.5, 27.9, 26.6; HRMS (ESI-TOF) for C23H24N2NaO5 [M+Na]+: calcd 431.1577, found 431.1559.

1-benzyl 3-methyl 1'-benzyl-2'-oxospiro[aziridine-2,3'-indoline]-1,3-dicarboxylate (4d)
white solid; 84% yield in 2 h, >95:5 d.r. mp 112-114 °C. 1H NMR (600 MHz, CDCl3): δ = 7.31 – 7.22 (m, 9H), 7.11 (d, J = 7.6 Hz, 2H), 6.84 (s, 1H), 6.76 (d, J = 7.9 Hz, 1H), 6.57 (d, J = 7.5 Hz, 1H), 5.10 (dd, J = 43.7, 12.0 Hz, 2H), 4.94 (d, J = 10.5 Hz, 2H), 3.97 (s, 1H), 3.88 (s, 3H); 13C NMR (100 MHz, CDCl3): δ = 168.3, 164.6, 158.2, 144.0, 134.8, 134.5, 130.4, 128.7, 128.5, 128.4, 127.7, 127.1, 122.7, 120.8, 119.9, 110.2, 69.1, 52.9, 48.8, 46.9, 44.2; HRMS (ESI-TOF) for C26H22N2NaO5 [M+Na]+: calcd 465.1421, found 465.1421.

1-benzyl 3-tert-butyl 1'-benzyl-2'-oxospiro[aziridine-2,3'-indoline]-1,3-dicarboxylate (4e)
white solid; 95% yield in 2 h, >95:5 d.r. mp 108-110 °C. 1H NMR (600 MHz, CDCl3): δ = 7.31 – 7.21 (m, 10H), 7.12 (d, J = 7.4 Hz, 2H), 6.83 (d, J = 7.9 Hz, 1H), 6.57 (d, J = 7.5 Hz, 1H), 5.11 (dd, J = 44.0, 12.2 Hz, 2H), 4.95 (d, J = 10.5 Hz, 2H), 3.86 (s, 1H), 1.51 (s, 9H); 13C NMR (100 MHz, CDCl3): δ = 168.3, 162.7, 158.4, 141.6, 135.2, 134.7, 130.7, 128.7, 128.5, 128.4, 128.3, 127.6, 127.0, 122.6, 120.8, 120.4, 110.0, 83.3, 68.9, 48.7, 47.8, 44.0, 27.9, 27.5; HRMS (ESI-TOF) for C29H28N2NaO5 [M+Na]+: calcd 507.1890, found 507.1866.

1-benzyl 3-tert-butyl 1'-benzyl-5'-methyl-2'-oxospiro[aziridine-2,3'-indoline]-1,3-dicarboxylate (4f)
white solid; 96% yield in 2 h, >95:5 d.r. mp 122-124 °C. 1H NMR (600 MHz, CDCl3): δ = 7.25 (d, J = 5.2 Hz, 9H), 7.13 (d, J = 6.8 Hz, 2H), 6.99 (d, J = 7.6 Hz, 1H), 6.63 (d, J = 8.0 Hz, 1H), 6.40 (s, 1H), 5.13 (dd, J = 30.6, 12.1 Hz, 2H), 4.94 (dd, J = 73.8, 15.8 Hz, 2H), 3.82 (s, 1H), 2.11 (s, 3H), 1.51 (s, 9H); 13C NMR (100 MHz, CDCl3): δ = 168.2, 162.7, 158.4, 141.6, 135.2, 134.8, 132.3, 130.5, 128.7, 128.4, 128.3, 127.6, 127.0, 122.6, 120.8, 120.4, 110.0, 83.3, 68.8, 48.8, 47.8, 44.0, 27.9, 20.9; HRMS (ESI-TOF) for C30H30N2NaO5 [M+Na]+: calcd 521.2047, found 521.2036.

1-benzyl 3-tert-butyl 1'-benzyl-5'-methoxy-2'-oxospiro[aziridine-2,3'-indoline]-1,3-dicarboxylate (4g)
white solid; 98% yield in 6 h, >95:5 d.r. mp 136-138 °C. 1H NMR (600 MHz, CDCl3): δ = 7.27 – 7.24 (m, 6H), 7.23 (s, 2H), 7.13 (s, 1H), 7.11 (s, 1H), 6.72 (dd, J = 8.6, 2.4,
1H), 6.64 (d, J = 8.6 Hz, 1H), 6.26 (d, J = 2.4 Hz, 1H), 5.13 (dd, J = 28.7, 12.1 Hz, 2H), 4.93 (dd, J = 65.6, 15.8 Hz, 2H), 3.84 (s, 1H), 3.57 (s, 3H), 1.51 (s, 9H); 13C NMR (100 MHz, CDCl3): δ = 168.0, 162.7, 158.4, 137.2, 134.7, 128.7, 128.4, 128.3, 128.1, 127.6, 127.0, 121.6, 114.8, 110.6, 107.9, 83.3, 68.8, 55.6, 48.9, 47.8, 44.1, 27.9; HRMS (ESI-TOF) for C30H30N2NaO6 [M+Na]+: calcd 537.1996, found 537.1983.

1-benzyl 3-tert-butyl 1'-benzyl-4'-bromo-2'-oxospiro[aziridine-2,3'-indoline]-1,3-dicarboxylate (4h)
white solid; 93% yield in 15 min, >95:5 d.r. mp 159-161 °C. 1H NMR (600 MHz, CDCl3): δ = 7.26 (dd, J = 12.2, 5.8 Hz, 10H), 7.08 (d, J = 5.9 Hz, 2H), 6.71 (dd, J = 6.0, 2.5 Hz, 1H), 5.17 (s, 2H), 5.05 (d, J = 15.9 Hz, 1H), 4.86 (s, 1H), 4.83 (d, J = 16.0 Hz, 1H), 1.52 (s, 9H); 13C NMR (100 MHz, CDCl3): δ = 167.7, 162.3, 156.9, 142.9, 134.6, 133.0, 128.8, 128.7, 128.6, 128.4, 127.8, 126.9, 124.1, 122.5, 115.2, 111.4, 83.5, 69.2, 48.0, 44.1, 27.9; HRMS (ESI-TOF) for C29H27BrN2NaO5 [M+Na]+: calcd 585.0996, found 585.0992.

1-benzyl 3-tert-butyl 1'-benzyl-5'-bromo-2'-oxospiro[aziridine-2,3'-indoline]-1,3-dicarboxylate (4i)
white solid; 92% yield in 15 min, >95:5 d.r. mp 123-126 °C. 1H NMR (600 MHz, CDCl3): δ = 7.32 – 7.24 (m, 8H), 7.21 (d, J = 10.1 Hz, 4H), 6.77 (s, 1H), 6.60 (d, J = 8.3 Hz, 1H), 5.15 (dd, J = 44.1, 12.1 Hz, 2H), 4.93 (dd, J = 81.3, 15.8 Hz, 2H), 3.84 (s, 1H), 1.51 (s, 9H); 13C NMR (100 MHz, CDCl3): δ = 167.7, 162.3, 158.0, 142.9, 134.6, 134.5, 133.0, 128.8, 128.7, 128.6, 128.4, 127.8, 126.9, 124.1, 122.5, 115.2, 114.4, 83.5, 69.2, 48.0, 44.1, 27.9; HRMS (ESI-TOF) for C29H27BrN2NaO5 [M+Na]+: calcd 585.0996, found 585.0990.

1-benzyl 3-tert-butyl 1'-benzyl-6'-bromo-2'-oxospiro[aziridine-2,3'-indoline]-1,3-dicarboxylate (4j)
white solid; 90% yield in 15 min, >95:5 d.r. mp 72-74 °C. 1H NMR (600 MHz, CDCl3): δ = 7.32 – 7.24 (m, 8H), 7.16 (d, J = 7.5 Hz, 1H), 6.88 (d, J = 6.5 Hz, 2H), 6.31 (d, J = 8.4 Hz, 1H), 5.12 (s, 2H), 5.01 (d, J = 15.8 Hz, 1H), 4.83 (d, J = 15.9 Hz, 1H), 4.71 (s, 1H), 1.52 (s, 9H); 13C NMR (100 MHz, CDCl3): δ = 167.7, 162.3, 158.0, 145.2, 134.7, 134.6, 128.9, 128.7, 128.6, 128.4, 127.8, 126.9, 124.1, 122.5, 115.2, 113.0, 83.5, 69.0, 48.2, 47.8, 44.2, 27.9; HRMS (ESI-TOF) for C29H27BrN2NaO5 [M+Na]+: calcd 585.0996, found 585.0993.

1-benzyl 3-tert-butyl 1'-benzyl-4'-chloro-2'-oxospiro[aziridine-2,3'-indoline]-1,3-dicarboxylate (4k)
white solid; 99% yield in 15 min, >95:5 d.r. mp 149-152 °C. 1H NMR (600 MHz, CDCl3): δ = 7.28 (s, 3H), 7.23 (d, J = 6.7 Hz, 5H), 7.18 – 7.12 (m, 2H), 6.90 (d, J = 8.2 Hz, 1H), 6.68 (d, J = 7.9 Hz, 1H), 5.16 (s, 2H), 5.06 (d, J = 15.9 Hz, 1H), 4.83 (d, J = 15.9 Hz, 1H), 4.71 (s, 1H), 1.52 (s, 9H); 13C NMR (100 MHz, CDCl3): δ = 167.8, 163.1, 157.3, 146.1, 134.8, 134.6, 131.0, 130.0, 128.8, 128.4, 128.3, 127.8, 127.0, 124.0, 116.6, 108.7, 83.4, 69.0, 48.5, 44.2, 43.4, 28.0; HRMS (ESI-TOF) for C29H27ClN2NaO5 [M+Na]+: calcd 541.1501, found 541.1509.

1-benzyl 3-tert-butyl 1'-benzyl-5'-chloro-2'-oxospiro[aziridine-2,3'-indoline]-1,3-dicarboxylate (4l)
white solid; 90% yield in 15 min, >95:5 d.r. mp 128-131 °C. 1H NMR (600 MHz, CDCl3): δ = 7.26 (s, 6H), 7.19 (dd, J = 16.0, 9.9 Hz, 5H), 6.65 (d, J = 8.4 Hz, 1H), 6.60 (s, 1H), 5.15 (dd, J = 38.5, 12.0 Hz, 2H), 4.93 (dd, J = 79.2, 15.9 Hz, 2H), 3.83 (s, 1H), 1.51 (s, 9H); 13C NMR (100 MHz, CDCl3): δ = 167.8, 162.3, 158.0, 142.4, 134.6, 134.5, 130.1, 128.8, 128.61, 128.5, 128.4, 128.2, 127.8, 127.0, 122.2, 121.4, 111.0, 83.6, 69.2, 48.0, 44.2, 27.9;
HRMS (ESI-TOF) for C_{29}H_{27}ClN_{2}NaO_{5} [M+Na]^+: calcd 541.1501, found 541.1500.

1-benzyl 3-tert-butyl 1’-benzyl-7’-fluoro-2’-oxospiro[aziridine-2,3’-indoline]-1,3-dicarboxylate (4m)
white solid; 90% yield in 15 min, >95:5 d.r. mp 92-95°C. $^1$H NMR (600 MHz, CDCl$_3$): $\delta$ = 7.31 – 7.19 (m, 10H), 7.15 (d, $J$ = 6.7 Hz, 2H), 7.00 – 6.92 (m, 1H), 6.75 (d, $J$ = 4.2 Hz, 1H), 6.31 (s, 1H), 5.19 – 5.11 (m, 2H), 5.05 (dd, $J$ = 20.6, 13.7 Hz, 2H), 3.82 (s, 1H), 1.50 (s, 9H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ = 178.2, 174.2, 168.0, 162.3, 158.1, 148.9, 146.4, 136.3, 134.6, 130.6, 128.6, 128.5, 128.4, 127.6, 127.2, 123.3, 118.4, 118.2, 116.7, 83.4, 69.0, 48.4, 48.2, 45.7, 27.9; HRMS (ESI-TOF) for C$_{29}$H$_{27}$FN$_{2}$NaO$_{5}$ [M+Na]$^+$: calcd 525.1796, found 525.1784.

1-benzyl 3-ethyl 1’-methyl-2’-oxospiro[aziridine-2,3’-indoline]-1,3-dicarboxylate (4a’)
white solid; >95:5 d.r. mp 120-122 °C. $^1$H NMR (600 MHz, CDCl$_3$): $\delta$ = 7.41-7.33 (m, 7H), 7.06 (t, $J$ = 7.4 Hz, 1H), 6.90 (d, $J$ = 7.8 Hz, 1H), 5.18 (dd, $J$ = 38.1, 12.0 Hz, 2H), 4.22 (dt, $J$ = 17.8, 10.8 Hz, 2H), 3.90 (s, 1H), 3.26 (s, 3H), 1.25 (t, $J$ = 7.1 Hz, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ =168.1, 164.3, 157.9, 144.6, 134.5, 130.0, 128.2, 128.0, 123.8, 122.6, 120.1, 108.6, 68.8, 61.9, 48.8, 47.8, 26.6, 14.0; HRMS (ESI-TOF) for C$_{21}$H$_{20}$N$_{2}$NaO$_{5}$ [M+Na]$^+$: calcd 402.1264, found 402.1259.

1-benzyl 3-tert-butyl 1’-benzyl-5’-bromo-2’-oxospiro[aziridine-2,3’-indoline]-1,3-dicarboxylate (5)
white solid; 75% yield, 1.6:1 d.r. mp 156-159 °C. $^1$H NMR (600 MHz, CDCl$_3$): $\delta$ = 8.08 (d, $J$ = 6.9 Hz, 1H), 7.95 (d, $J$ = 7.1 Hz, 1H), 7.50 (d, $J$ = 7.8 Hz, 2H), 7.30 (s, 4H), 7.16 (dd, $J$ = 15.1, 7.3 Hz, 5H), 7.09 (t, $J$ = 7.5 Hz, 2H), 6.77 – 6.66 (m, 4H), 6.43 (d, $J$ = 7.1 Hz, 1H), 5.39 (d, $J$ = 9.2 Hz, 2H), 5.05 (dd, $J$ = 39.4, 12.0 Hz, 1H), 4.79 (dd, $J$ = 30.2, 11.5 Hz, 2H), 4.38 (dd, $J$ = 15.0, 7.2 Hz, 2H), 4.29 (dd, $J$ = 17.7, 9.0 Hz, 2H), 4.06 (s, 1H), 3.91 (s, 1H), 3.84 (s, 2H), 3.79 (d, $J$ = 7.6 Hz, 2H), 3.48 (d, $J$ = 6.5 Hz, 1H), 2.98 (d, $J$ = 9.6 Hz, 7H), 2.30 (s, 3H), 1.62 (d, $J$ = 6.9 Hz, 3H), 1.38 (t, $J$ = 6.4 Hz, 3H), 1.21 (t, $J$ = 7.1 Hz, 1H), 1.10 (s, 2H), 0.81 (d, $J$ = 6.1 Hz, 5H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ = 171.4, 171.1, 170.8, 170.5, 166.1, 152.2, 151.7, 142.6, 141.9, 136.9, 134.9, 134.1, 129.8, 129.1, 127.9, 127.6, 127.2, 126.7, 126.2, 125.2, 122.9, 121.5, 121.1, 107.5, 72.0, 71.3, 67.5, 61.4, 60.8, 60.2, 59.4, 53.5, 52.7, 26.1, 25.5, 13.6, 13.4, 13.0; HRMS (ESI-TOF) for C$_{34}$H$_{34}$N$_{3}$O$_{8}$ [M+H]$^+$: calcd 612.2268, found 612.2337.
6. X-Ray single crystal diffraction structures of 3a, 4a, 4a’ and 5.
7. Copies of $^1$H NMR and $^{13}$C NMR spectra

$^1$H NMR (600 MHz, CDCl$_3$) and $^{13}$C NMR (100 MHz, CDCl$_3$) spectra of 3a
$^1$H NMR (600 MHz, CDCl$_3$) and $^{13}$C NMR (100 MHz, CDCl$_3$) spectra of product 3b
$^1$H NMR (600 MHz, CDCl$_3$) and $^{13}$C NMR (100 MHz, CDCl$_3$) spectra of product 3c
$^1$H NMR (600 MHz, CDCl$_3$) and $^{13}$C NMR (100 MHz, CDCl$_3$) spectra of product 3d
$^1$H NMR (600 MHz, CDCl$_3$) and $^{13}$C NMR (100 MHz, CDCl$_3$) spectra of product 3e
$^1$H NMR (600 MHz, CDCl$_3$) and $^{13}$C NMR (100 MHz, CDCl$_3$) spectra of product 3f
$^1$H NMR (600 MHz, CDCl$_3$) and $^{13}$C NMR (100 MHz, CDCl$_3$) spectra of product 3g
$^1$H NMR (600 MHz, CDCl$_3$) and $^{13}$C NMR (100 MHz, CDCl$_3$) spectra of product 3h
$^1$H NMR (600 MHz, CDCl$_3$) and $^{13}$C NMR (100 MHz, CDCl$_3$) spectra of product 3i
$^1$H NMR (600 MHz, CDCl$_3$) and $^{13}$C NMR (100 MHz, CDCl$_3$) spectra of product 3j

![Diagram of 3j with NMR spectra]
$^1$H NMR (600 MHz, CDCl$_3$) and $^{13}$C NMR (100 MHz, CDCl$_3$) spectra of product 3k
$^1$H NMR (600 MHz, CDCl$_3$) and $^{13}$C NMR (100 MHz, CDCl$_3$) spectra of product 3l

![Diagram of molecular structure](image)

![NMR spectra](image)
$^1$H NMR (600 MHz, CDCl$_3$) and $^{13}$C NMR (100 MHz, CDCl$_3$) spectra of product 3m
$^1$H NMR (600 MHz, CDCl$_3$) and $^{13}$C NMR (100 MHz, CDCl$_3$) spectra of product 3n
$^1$H NMR (600 MHz, CDCl$_3$) and $^{13}$C NMR (100 MHz, CDCl$_3$) spectra of product 3o
$^1$H NMR (600 MHz, CDCl$_3$) and $^{13}$C NMR (100 MHz, CDCl$_3$) spectra of product 3p
$^1$H NMR (600 MHz, CDCl$_3$) and $^{13}$C NMR (100 MHz, CDCl$_3$) spectra of product 3q
$^1$H NMR (600 MHz, CDCl$_3$) and $^{13}$C NMR (100 MHz, CDCl$_3$) spectra of product 3r
$^1$H NMR (600 MHz, CDCl₃) and $^{13}$C NMR (100 MHz, CDCl₃) spectra of product 3s
$^1$H NMR (600 MHz, CDCl$_3$) and $^{13}$C NMR (100 MHz, CDCl$_3$) spectra of product 3t
$^1$H NMR (600 MHz, CDCl₃) and $^{13}$C NMR (100 MHz, CDCl₃) spectra of product 3u
$^1$H NMR (600 MHz, CDCl$_3$) and $^{13}$C NMR (100 MHz, CDCl$_3$) spectra of product 4a
$^1$H NMR (600 MHz, CDCl$_3$) and $^{13}$C NMR (100 MHz, CDCl$_3$) spectra of product 4b
$^1$H NMR (600 MHz, CDCl$_3$) and $^{13}$C NMR (100 MHz, CDCl$_3$) spectra of product 4c
$^1$H NMR (600 MHz, CDCl$_3$) and $^{13}$C NMR (100 MHz, CDCl$_3$) spectra of product 4d
$^1$H NMR (600 MHz, CDCl$_3$) and $^{13}$C NMR (100 MHz, CDCl$_3$) spectra of product 4e
$^1$H NMR (600 MHz, CDCl$_3$) and $^{13}$C NMR (100 MHz, CDCl$_3$) spectra of product 4f
$^1$H NMR (600 MHz, CDCl$_3$) and $^{13}$C NMR (100 MHz, CDCl$_3$) spectra of product 4g
$^1$H NMR (600 MHz, CDCl$_3$) and $^{13}$C NMR (100 MHz, CDCl$_3$) spectra of product 4h
$^1$H NMR (600 MHz, CDCl$_3$) and $^{13}$C NMR (100 MHz, CDCl$_3$) spectra of product 4i
$^1$H NMR (600 MHz, CDCl$_3$) and $^{13}$C NMR (100 MHz, CDCl$_3$) spectra of product 4j
$^1$H NMR (600 MHz, CDCl$_3$) and $^{13}$C NMR (100 MHz, CDCl$_3$) spectra of product 4k
$^1$H NMR (600 MHz, CDCl$_3$) and $^{13}$C NMR (100 MHz, CDCl$_3$) spectra of product 4l
$^1$H NMR (600 MHz, CDCl$_3$) and $^{13}$C NMR (100 MHz, CDCl$_3$) spectra of product 4m
$^1$H NMR (600 MHz, CDCl$_3$) and $^{13}$C NMR (100 MHz, CDCl$_3$) spectra of product 4a*
$^1$H NMR (600 MHz, CDCl$_3$) and $^{13}$C NMR (100 MHz, CDCl$_3$) spectra of product 5 (d.r. = 1.6:1)