Supporting Information

Late-Stage Construction of Stapled Peptides through Fujiwara-Moritani Reaction between Tryptophan and Olefins

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1. General Information

All the reagents are obtained from commercial sources without further purification unless indicated. The water used in the laboratory comes from the Milli-Q reference system. Thin-layer chromatography (TLC) and silica gel for column chromatography comes from Qingdao Marine chemical plant (200-300 mesh). The peptide substrates and stapled peptide precursors were synthesized by traditional methods including liquid phase synthesis of peptides and solid synthesis of peptides. The spectra of absorption and fluorescence were analyzed using Molecular Devices SpectraMax M5. $^1$HNMR spectra were obtained on AVANCE III 500 (500 MHz), WNMRI 400MHZ and AVANCE III HD 600 instrument (600 MHz). $^{13}$CNMR spectra were obtained on AVANCE III 500 (126 MHz), WNMRI 400MHZ (101 MHz) and AVANCE III HD 600 instrument (151 MHz). $^1$HNMR spectrum multiplicities as following: s (singlet), br (broad), d (doublet), t (triplet), q (quadruplet), m (multiplet). Cell imaging was performed using Leica TCS SP8. Reactions were detected by thin layer chromatography (TLC) under 254 nm or 365 nm with portable UV lamp and 2% ninhydrin stains in ethanol. Liquid chromatography-mass spectrometry (LC-MS) with Thermo Fisher.

2. Experimental Section

A. General procedure for the synthesis of dipeptides and tripeptides

Scheme S1. Preparation of linear peptides through solution-phase peptide synthesis.

Boc-Trp-OH (304 mg, 1 mmol), EDCI (290 mg, 1.5 mmol), HOBT (202 mg, 1.5 mmol) and H-AA-OMe.HCl (1 mmol) were dissolved in 10mL DMF, then DIEA (390 mg, 3 mmol) was added, stirred in room temperature overnight. Upon completion, 30 mL EtOAc and 30 mL H$_2$O were added, the organic layer was separated and washed with 30 mL 1N HCl, 30 mL saturated sodium bicarbonate, 30 mL saturated sodium chloride and dried with anhydrous sodium sulfate, filtered, concentrated in vacuum to get dipeptides Boc-Trp-AA-OMe. Next, the Boc-Trp-AA-OMe (1 mmol) was dissolved in 10 mL 4M HCl/dioxane for 30 min, then concentrated in vacuum, diluting with ice ether, a lot of solid form, dried in vacuum to get H-Trp-AA-OMe.HCl for the next step. R$_3$-AA-OH (1 mmol), EDCI (290 mg, 1.5 mmol), HOBT (202 mg, 1.5 mmol) and H-Trp-AA-OMe.HCl (1 mmol) were dissolved in 10 mL DMF, then DIEA (390 mg, 3 mmol) was added, stirred in room temperature overnight. Upon completion, 30 mL EtOAc and 30 mL H$_2$O were added, the organic layer was separated and washed with 30 mL 1N HCl, 30 mL saturated sodium bicarbonate, 30 mL saturated sodium chloride and dried with anhydrous sodium sulfate, filtered, concentrated in vacuum to get tripeptides R$_3$-AA-Trp-AA-OMe without further
purified for the next step.

B. General procedure for the synthesis of dipeptides.

\[
\text{R}_1 \text{H} \overset{\text{EDCI/HOBT/DIEA/DMF}}{\rightarrow} \text{R}_2 \text{N} \overset{\text{OH}}{\rightarrow} \text{R}_1 \text{H} \overset{\text{N}}{\rightarrow} \text{R}_2 \text{N} \overset{\text{OH}}{\rightarrow} \text{R}_1 \text{H}
\]

Scheme S2. Preparation of dipeptides through solution-phase peptide synthesis.

H-Trp-OMe·HCl (254 mg, 1 mmol), R₂-AA-OH (1 mmol), EDCI (290 mg, 1.5 mmol) and HOBT (202 mg, 1.5 mmol) were dissolved in 10 mL DMF, then DIEA (390 mg, 3 mmol) was added, stirred in room temperature overnight. Upon completion, 30 mL EtOAc and 30 mL H₂O were added, the organic layer was separated and washed with 30 mL 1N HCl, 30 mL saturated sodium bicarbonate, 30 mL saturated sodium chloride and dried with anhydrous sodium sulfate, filtered, concentrated in vacuum to get dipeptides R₂-AA-Trp-OMe without further purified for the next step.

C. General procedure for the substrates which modification with acryloyl chloride

\[
\text{XH} + \overset{\text{Et}_3\text{N, THF}}{\rightarrow} \overset{0 \text{ °C} - \text{r.t}}{\rightarrow} \overset{\text{X} = \text{NH, O}}{\rightarrow} \text{6a-6h}
\]

Scheme S3. Preparation of acrylic modification substrates.

Typically, the biomolecule compound (1 mmol) were dissolved in 5mL THF, Et₃N (150 mg, 1.5 mmol) was added, then cooled to 0 °C. Acryloyl chloride (108 mg, 1.2 mmol) dissolved in 2mL THF was dropwised to the reaction mixture, then removed to room temperature overnight. The reaction mixture was diluted with 5 mL EtOAc and 5 mL H₂O. The organic layer was washed with 5 mL 1N HCl, 5 mL saturated sodium bicarbonate, 5 mL saturated sodium chloride and dried with anhydrous sodium sulfate, filtered, concentrated in vacuum to get the crude product further purified by flash column to get 6a-6h.

D. General procedure for Pd-catalyzed olefination of Trp containing amino acids, dipeptides and tripeptides

Typically, the Trp containing amino acid and peptide substrate (0.2 mmol), Pd(OAc)₂ (9 mg, 0.02 mmol) were suspended in 2 mL dioxane/AcOH=3:1, then alkene (0.4 mmol) and 1,4-Benzoxquinone (43.2 mg, 0.4 mmol) were added. The tube was fitted with a septum and the mixture was heated to 80 °C for 24 h. The reaction mixture was diluted with 5 mL EtOAc and 5 mL H₂O. The organic layer was washed with 5 mL 1N HCl, 5 mL saturated sodium bicarbonate, 5 mL saturated sodium chloride and dried with anhydrous sodium sulfate, filtered, concentrated in vacuum to get the crude product further purified by flash column or PTLC.
E. General procedure of stapled peptide precursor

The CTC Resin (300 mg, 0.3 mmol) was suspended in 5mL DCM, then Fmoc-AA-OH (0.9 mmol) and DIEA (154.8 mg, 1.2 mmol) were added, reacted in the shaker, after 2 h, 300 μl MeOH was added for 10 min, then the Fmoc-AA-CTC Resin washed with DMF for three times. Fmoc-AA-CTC Resin deprotect the Fmoc with 20% piperidine/DMF for 30 min. After reaction, the H-AA-CTC Resin washed with DMF for four times. Subsequent amino acids coupling using standard solution-phase peptide synthesis (SPPS). The peptides were cut from CTC Resin using 25% HFIP/DCM for 1 h, filtered, the resins were washed DCM for three times, combined the filtrate and concentrated in vacuum to get peptides. Finally the linear peptides (0.2 mmol) 1A (44 mg, 0.2 mmol) which was prepared according to literature report,1 EDCI (60 mg, 0.3 mmol) and HOBT (40 mg, 0.3 mmol) were dissolved in 3 mL DMF, then DIEA (78 mg, 0.6 mmol) was added, stirred in room temperature for 12 h. Upon completion, 10 mL EtOAc and 10 mL H₂O were added, the organic layer was separated and washed with 10 mL 1N HCl, 10 mL saturated sodium bicarbonate, 10 mL saturated sodium chloride and dried with anhydrous sodium sulfate, filtered, concentrated in vacuum to get the linear peptides 8a-8i without purified for the next step.

Scheme S3a. Procedure for stapled peptide precursor 8a-8i
Scheme S3b. Procedure for stapled peptide precursor 8j

The CTC Resin (300 mg, 0.3 mmol) was suspended in 5mL DCM, then Fmoc-Gly-OH (267 mg, 0.9 mmol) and DIEA (154.8 mg, 1.2 mmol) were added, reacted in the shaker, after 2 h, 300 μl MeOH was added for 10 min, then the Fmoc-Gly-CTC Resin washed with DMF for three times. Fmoc-Gly-CTC Resin deprotect the Fmoc with 20% piperidine/DMF for 30 min. After reaction, the H-Gly-CTC Resin washed with DMF for four times. Subsequent amino acids coupling using standard solution-phase peptide synthesis (SPPS) until all the amino acid was incorporated. The peptides were cut from CTC Resin using 25% HFIP/DCM for 1 h, filtered, the resins were washed DCM for three times, combined the filtrate and concentrated in vacuum to get peptide. Finally the linear peptide (88.6 mg, 0.2 mmol) H-Trp-OMe.HCl (66.2 mg, 0.2 mmol), EDCI (58 mg, 0.3 mmol) and HOBT (40 mg, 0.3 mmol) were dissolved in 3 mL DMF, then DIEA (78 mg, 0.6 mmol) was added, stirred in room temperature for 12 h. Upon completion, 10 mL EtOAc and 10 mL H2O were added, the organic layer was separated and washed with 10 mL 1N HCl, 10 mL saturated sodium bicarbonate, 10 mL saturated sodium chloride and dried with anhydrous sodium sulfate, filtered, concentrated in vacuum to get the linear peptide 8j without purified for the next step.

Scheme S3c. Procedure for stapled peptide precursor 8k

The CTC Resin (300 mg, 0.3 mmol) was suspended in 5mL DCM, then Fmoc-Trp-OH (383 mg, 0.9 mmol) and DIEA (204.8 mg, 1.2 mmol) were added, reacted in the shaker, after 2 h, 300 μl MeOH was added for 10 min, then the Fmoc-Trp-CTC Resin washed with DMF for three times. Fmoc-Trp-CTC Resin deprotect the Fmoc with 20% piperidine/DMF for 30 min. After reaction, the H-Trp-CTC Resin washed with DMF for four times. Subsequent amino acids coupling using standard solution-phase peptide synthesis (SPPS) until all the amino acid was incorporated. The peptides were cut from CTC Resin using 25% HFIP/DCM for 1 h, filtered, the resins were washed DCM for three times, combined the filtrate and concentrated in vacuum to get peptide. Finally the linear peptide (88.8 mg, 0.2 mmol) H-Trp-OMe.HCl (66.2 mg, 0.2 mmol), EDCI (58 mg, 0.3 mmol) and HOBT (40 mg, 0.3 mmol) were dissolved in 3 mL DMF, then DIEA (78 mg, 0.6 mmol) was added, stirred in room temperature for 12 h. Upon completion, 10 mL EtOAc and 10 mL H2O were added, the organic layer was separated and washed with 10 mL 1N HCl, 10 mL saturated sodium bicarbonate, 10 mL saturated sodium chloride and dried with anhydrous sodium sulfate, filtered, concentrated in vacuum to get the linear peptide 8k without purified for the next step.
mmol) and DIEA (154.8 mg, 1.2 mmol) were added, reacted in the shaker, after 2 h, 300 μl MeOH was added for 10 min, then the Fmoc-Trp-CTC Resin washed with DMF for three times. Fmoc-Trp-CTC Resin deprotect the Fmoc with 20% piperidine/DMF for 30 min. After reaction, the H-Trp-CTC Resin washed with DMF for four times. Subsequent amino acids coupling using standard solution-phase peptide synthesis (SPPS) until all the amino acid was incorporated. The peptide were cut from CTC Resin using 25% HFIP/DCM for 1 h, filtered, the resins were washed DCM for three times, combined the filtrate and concentrated in vacuum to get peptide 8k without purified for the next step.

F. General procedure of Pd-catalyzed olefination stapled peptides

Typically, the Trp containing stapled peptide precursor (0.2 mmol), Pd(OAc)$_2$ (9 mg, 0.02 mmol) were suspened in 10 mL dioxane/AcOH=3:1, then 1,4-Benzoquinone (43.2 mg, 0.4 mmol) were added. The tube was fitted with a septum and the mixture was heated to 80 °C for 24 h. The reaction mixture was diluted with EtOAc (40 mL) and H$_2$O (30 mL). The organic layer was washed with 20 mL 1N HCl, 20 mL saturated sodium bicarbonate, 20 mL saturated sodium chloride and dried with anhydrous sodium sulfate, filtered, concentrated in vacuum to get the crude product further purified by flash column or PTLC.

G. General procedure of remove the peptides protecting groups.

A: According to the previous experience, the stapled peptide 9g (100 mg, 0.1 mmol) was added to 2 mL 95% TFA/H$_2$O (v/v) under 0 °C, then removed to room temperature for 1h. The ice ether 10 mL was added, a lot of solid form, filtered, washed with ether for three times, dried in vacuum to get 68 mg white solid 10a in 85% yield.

B: According to the previous experience, the stapled peptide 9k (60 mg, 0.1 mmol) was added to 2 mL 4M HCl/dioxane solution under 0 °C, then removed to room temperature for 1h. The ice ether 10 mL was added, a lot of solid form, filtered, washed with ether for three times, dried in vacuum to get 51 mg white solid 10b in 95% yield.

H. General procedure of construction stapled peptide with solid phase peptide synthesis (SPPS).
The Fmoc-Trp-Wang resin (0.2 mmol) soak in DMF for 0.5 h, then deprotect the Fmoc with 20% piperidine/DMF for 30 min. After reaction, the H-Trp-Wang Resin washed with DMF for four times. Subsequent amino acids coupling using standard solution-phase peptide synthesis (SPPS) until all the amino acid was incorporated. The peptide resin was suspended in 10 mL dioxane/MeOH=3:1, Pd(OAc)$_2$ (9 mg, 0.02 mmol) and 1,4-Benzoquinone (43.2 mg, 0.4 mmol) were added. The tube was fitted with a septum and the mixture was heated to 80 °C for 24 h. After reaction, the mixture was washed with DMF three times, H$_2$O two times and MeOH three times then dried in vacuum. After dried, the resin was added to 5 mL 95% TFA/H$_2$O (v/v) under 0 °C, then shook in room temperature for 1h. filtered, washed with TFA for two times. Combined the filtrate and 20 mL ice ether was added , a lot of solid form, filtered, the solid washed with ether for three times, dried in vacuum to get crude 10c. The crude 10c was further purified by reverse preparative chromatography and freeze-drying to get 51 mg white solid 10c in 40% yield.
### Table S1 Optimization of reaction conditions.\(^{[a]}\)

<table>
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<th>Entry</th>
<th>Oxidant</th>
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<th>Solvent</th>
<th>(T) ((^{\circ})C)</th>
<th>(Y) (%)(^{[b]})</th>
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\(^{[a]}\)Reaction conditions: \(1\)a (0.2 mmol), \(2\)a (0.4 mmol), oxidant (0.2 mmol), Pd(OAc)\(_2\) (0.02 mmol), additive (0.2 mmol), solvent (2 mL), 24 h. \(^{[b]}\)Isolated yields. \(^{[c]}\)\(O_2\) 1 atm. \(^{[d]}\)AcOH (1.2 mmol).
Table S2 Optimization of reaction conditions.[a]

<table>
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<th>Entry</th>
<th>Pd catalyst</th>
<th>Oxidant</th>
<th>Olefination reagent 2a</th>
<th>T (℃)</th>
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[a] Reaction conditions: 1a (0.2 mmol), dioxane/CH₃OH=3:1 (2 mL), 24 h. [b] Isolated yields. [c] 12 h. [d] 48 h

**Fig S1.** TLC show the result of the reaction between 1a and 2a under 254nm
Fig S2. Determination of the configuration of double bond in product 3a by $^1$H-NMR (600 MHz, DMSO). The coupling constant was $J_{ab}=16.2$ Hz, and therefore the double bond is in $E$-configuration.
**Fig S3.** HPLC spectra of a) racemate and b) 3a. Chromatographic column: Daicel Chiralpak AD-H 5μm, solvent: n-hexane/PrOH, wavelength: 254.
Fig S4. Determination of the configuration of double bond in product 9b by $^1$H-NMR (600 MHz, DMSO). The coupling constant was $J_{ab}=15.6$ Hz, and therefore the double bond is in $E$-configuration.

Fig S5. a), b) Two different methods removal of the peptides protecting groups.
Fig S6. a) Construction of stapled peptide with solid phase peptide synthesis (SPPS). b) Gram scale synthesis of 9g.
According to the general procedure D, the crude residue was purified by flash column chromatography on silica gel (ethyl acetate: petroleum ether = 1:4; Rf = 0.4) to yield compound 3a (64.9 mg, 78% yield). 1H NMR (600 MHz, DMSO) δ 11.47 (s, 1H), 7.68 (d, J = 15.8 Hz, 1H), 7.60 (d, J = 8.0 Hz, 1H), 7.34 (d, J = 8.2 Hz, 1H), 7.30 (d, J = 8.0 Hz, 1H), 7.21 (t, J = 7.5 Hz, 1H), 7.03 (t, J = 7.5 Hz, 1H), 6.54 (d, J = 15.8 Hz, 1H), 4.26 – 4.14 (m, 3H), 3.55 (s, 3H), 3.27 (dd, J = 14.4, 6.5 Hz, 1H), 1.31 (s, 6H), 1.28 (t, J = 7.1 Hz, 3H).

13C NMR (151 MHz, DMSO) δ 172.60, 166.87, 155.65, 137.93, 132.50, 131.66, 128.22, 124.82, 119.96, 119.84, 117.13, 115.66, 111.85, 78.81, 60.35, 55.33, 52.25, 28.53, 26.42, 14.72. MS (ESI) m/z (relative intensity) 417.34 (100) [M+H]+, 317.36 (40) [M-Boc+H]+.

HRMS (ESI) m/z calcd for C22H28N2O6Na (M + Na)+ 439.1840, found 439.1844.

According to the general procedure D, the crude residue was purified by flash column chromatography on silica gel (ethyl acetate: petroleum ether = 1:4; Rf = 0.35) to yield compound 3b (64.8 mg, 80% yield). 1H NMR (500 MHz, DMSO) δ 11.45 (s, 1H), 7.67 (d, J = 15.8 Hz, 1H), 7.58 (d, J = 8.0 Hz, 1H), 7.34 (d, J = 8.2 Hz, 1H), 7.27 – 7.18 (m, 2H), 7.03 (dd, J = 11.1, 3.9 Hz, 1H), 6.49 (d, J = 15.8 Hz, 1H), 3.72 (s, 3H), 3.53 (s, 3H), 3.26 (dd, J = 14.3, 6.5 Hz, 1H), 3.20 (dd, J = 14.4, 7.9 Hz, 1H), 1.29 (s, 9H).

13C NMR (126 MHz, DMSO) δ 172.41 (s), 167.20 (s), 155.47 (s), 137.72 (s), 132.46 (s), 131.33 (s), 127.94 (s), 124.75 (s), 119.72 (s), 117.02 (s), 114.91 (s), 111.66 (s), 55.05 (s), 52.08 (s), 51.71 (s), 28.27 (s), 26.17 (s). MS (ESI) m/z (relative intensity) 403.32 (100) [M+H]+.

HRMS (ESI) m/z calcd for C21H26N2O6Na (M + Na)+ 425.1683, found 425.1681.

According to the general procedure D, the crude residue was purified by flash column chromatography on silica gel (ethyl acetate: petroleum ether = 1:4; Rf = 0.38) to yield compound 3c (63.6 mg, 72% yield). 1H NMR (600 MHz, CDCl3) δ 8.72 (d, J = 4.4 Hz, 1H), 7.91 (t, J = 7.6 Hz, 1H), 7.72 (d, J = 16.2 Hz, 1H), 7.67 (d, J = 7.9 Hz, 1H), 7.40 (dd, J = 7.1, 5.2 Hz, 1H), 7.36 (d, J = 8.2 Hz, 1H), 7.31 (d, J = 7.8 Hz, 1H), 7.28 (d, J = 7.7 Hz, 1H), 7.21 (t, J = 7.3 Hz, 1H), 5.63 (d, J = 16.2 Hz, 1H), 5.16 (d, J = 8.0 Hz, 1H), 4.74 (d, J = 6.9 Hz, 1H), 4.14 (t, J = 6.7 Hz, 2H), 3.67 (s, 3H), 3.60 – 3.43 (m, 2H), 1.68 – 1.61 (m, 2H), 1.42 (s, 7H), 1.40 – 1.36 (m, 2H), 0.95 (t, J = 7.4 Hz, 3H).

13C NMR (151 MHz, CDCl3) δ 172.31, 167.15, 155.10, 137.41, 131.55, 131.22, 128.73, 120.24, 119.84, 116.10, 115.21, 111.13, 80.03, 64.53, 54.46, 52.56, 30.79, 28.33, 27.21, 19.18, 13.76. MS (ESI) m/z (relative intensity) 445.83 (100) [M + H]+, 889.35 (60) [2M + H]+.

HRMS (ESI) m/z calcd for C37H51N5O9Na (M + Na)+ 467.2153, found 467.2152.
ether = 1:4; R_f = 0.36) to yield compound 3d (65.7 mg, 74% yield). 1H NMR (600 MHz, CDCl_3) δ 9.07 (s, 1H), 7.60 (d, J = 15.9 Hz, 1H), 7.57 (d, J = 8.0 Hz, 1H), 7.28 (d, J = 8.6 Hz, 1H), 7.22 (t, J = 7.5 Hz, 1H), 7.09 (t, J = 7.4 Hz, 1H), 6.25 (d, J = 15.9 Hz, 1H), 5.17 (d, J = 8.2 Hz, 1H), 4.71 (dt, J = 7.8, 5.3 Hz, 1H), 3.70 (s, 3H), 3.44 (dd, J = 14.6, 5.7 Hz, 1H), 3.39 (dd, J = 14.5, 4.7 Hz, 1H), 1.58 (s, 9H), 1.45 (s, 9H). 13C NMR (151 MHz, CDCl_3) δ 172.22, 166.48, 155.08, 137.37, 131.41, 130.80, 128.80, 124.87, 120.15, 119.86, 117.19, 115.71, 111.14, 80.72, 79.96, 54.49, 53.45, 52.48, 28.34, 28.27, 27.30. MS (ESI) m/z (relative intensity) 445.65 (100) [M+H]^+. HRMS (ESI) m/z calc. for C_{24}H_{35}N_{2}O_{6}Na (M + Na)^+ 467.2153, found 467.2150.

According to the general procedure D, the crude residue was purified by flash column chromatography on silica gel (DCM: MeOH = 20:1; R_f = 0.23) to yield compound 3e (42.3 mg, 65% yield). 1H NMR (600 MHz, CDCl_3) δ 8.92 (s, 1H), 7.75 (d, J = 15.5 Hz, 1H), 7.60 (d, J = 7.2 Hz, 2H), 7.10 – 7.07 (m, 2H), 7.05 – 6.95 (m, 1H), 6.18 (d, J = 15.5 Hz, 1H), 5.40 – 5.25 (m, 1H), 4.50 – 4.70 (m, 1H), 4.25 – 4.15 (q, J = 6.6 Hz, 2H), 3.50 – 3.30 (m, 2H), 1.35 – 1.25 (m, 9H), 1.30 (t, J = 6.6 Hz, 3H). 13C NMR (151 MHz, CDCl_3) δ 175.17, 155.31, 137.51, 132.19, 131.21, 128.46, 125.09, 120.28, 114.80, 111.18, 80.16, 60.96, 54.39, 28.33, 14.21, 11.43. MS (ESI) m/z (relative intensity) 401.34 (100) [M-H]^-. HRMS (ESI) m/z calc. for C_{24}H_{35}N_{2}O_{6}Na (M + Na)^+ 425.1683, found 425.1680.

According to the general procedure D, the crude residue was purified by flash column chromatography on silica gel (DCM: MeOH = 2:1; R_f = 0.26) to yield compound 3f (53.2 mg, 62% yield). 1H NMR (600 MHz, CDCl_3) δ 8.87 (s, 1H), 7.70 (d, J = 15.0 Hz, 1H), 7.60 – 7.57 (m, 1H), 7.24 – 7.10 (m, 2H), 7.06 – 6.98 (m, 1H), 6.15 (d, J = 15 Hz, 1H), 5.28 (s, 1H), 4.65 – 4.45 (m, 1H), 3.45 – 3.32 (m, 2H), 1.51 (s, 9H), 1.45 (s, 9H). 13C NMR (151 MHz, CDCl_3) δ 137.43, 131.19, 128.95, 128.38, 124.82, 120.08, 119.62, 116.90, 116.22, 111.02, 81.18, 79.75, 60.46, 29.70, 28.38, 28.16, 14.19. MS (ESI) m/z (relative intensity) 429.65 (100) [M-H]^-. HRMS (ESI) m/z calc. for C_{24}H_{35}N_{2}O_{6}Na (M + Na)^+ 453.1996, found 453.1999.

According to the general procedure D, the crude residue was purified by flash column chromatography on silica gel (DCM; R_f = 0.52) to yield compound 3g (49.8 mg, 67% yield). 1H NMR (600 MHz, CDCl_3) δ 9.11 (s, 1H), 7.64 (d, J = 15.9 Hz, 1H), 7.55 (d, J = 8.0 Hz, 1H), 7.29 (d, J = 3.9 Hz, 1H), 7.24 (t, J = 7.5 Hz, 1H), 7.09 (t, J = 7.5 Hz, 1H), 6.26 (d, J = 8.0 Hz, 1H), 6.22 (d, J = 15.9 Hz, 1H), 5.07 – 4.99 (m, 1H), 4.31 – 4.24 (m, 3H), 4.23 – 4.19 (m, 1H), 4.11 – 4.03 (m, 1H), 3.48 (dd, J = 14.7, 5.6 Hz, 1H), 3.42 (dd, J = 14.7, 4.8 Hz, 1H), 1.98 (s, 3H), 1.34 (t, J = 7.1 Hz, 3H), 1.27 (t, J = 7.1 Hz, 3H). 13C NMR (151 MHz, CDCl_3) δ 171.58, 170.02, 167.00, 137.42, 131.65, 131.35, 128.76, 125.01, 120.20, 119.69, 116.13, 115.20, 111.32, 61.94, 60.62, 53.16, 26.98, 23.13, 14.34, 13.95. MS (ESI) m/z (relative intensity) 373.25 (100) [M+H]^+. HRMS (ESI) m/z calc. for C_{20}H_{22}N_{2}O_{6}Na (M + Na)^+ 395.1577, found 395.1591.
According to the general procedure D, the crude residue was purified by flash column chromatography on silica gel (ethyl acetate: petroleum ether= 1:3; Rf=0.16) to yield compound 3h (57.6 mg, 64% yield). $^1$H NMR (600 MHz, CDCl$_3$) δ 9.03 (s, 1H), 7.68 (d, $J = 15.9$ Hz, 1H), 7.53 (d, $J = 7.9$ Hz, 1H), 7.47 (t, $J = 7.3$ Hz, 1H), 7.39 – 7.32 (m, 5H), 7.26 (d, $J = 8.1$ Hz, 1H), 7.21 (t, $J = 7.5$ Hz, 1H), 7.05 (t, $J = 7.4$ Hz, 1H), 6.26 (d, $J = 15.9$ Hz, 1H), 5.51 (d, $J = 8.1$ Hz, 1H), 5.14 (q, $J = 12.2$ Hz, 2H), 4.85 – 4.79 (m, 1H), 4.24 (dd, $J = 12.7$, 6.3 Hz, 2H), 3.72 (s, 3H), 3.50 (dd, $J = 14.7$, 5.6 Hz, 1H), 3.44 (dd, $J = 14.7$, 4.6 Hz, 1H), 1.32 (t, $J = 7.1$ Hz, 3H).

$^{13}$C NMR (151 MHz, CDCl$_3$) δ 171.89, 167.13, 155.77, 137.44, 136.25, 133.40, 131.64, 131.37, 130.18, 128.63, 128.58, 128.50, 128.41, 128.14, 128.06, 125.10, 120.34, 119.72, 115.92, 115.21, 111.29, 67.07, 60.66, 54.85, 52.63, 27.18, 14.33. MS (ESI) m/z (relative intensity) 451.65 (100) [M+H]$^+$.

HRMS (ESI) m/z calcd for C$_{25}$H$_{26}$N$_2$O$_6$Na (M + Na)$^+$ 464.1947, found 464.1950.

According to the general procedure D, the crude residue was purified by flash column chromatography on silica gel (ethyl acetate; Rf=0.22) to yield compound 3i (40 mg, 58% yield). $^1$H NMR (600 MHz, DMSO) δ 11.31 (s, 1H), 8.00 (d, $J = 8.5$ Hz, 1H), 7.73 (d, $J = 15.8$ Hz, 1H), 7.70 (d, $J = 8.0$ Hz, 1H), 7.39 (s, 1H), 7.30 (d, $J = 8.2$ Hz, 1H), 7.18 (t, $J = 7.5$ Hz, 1H), 7.04 (s, 1H), 7.00 (t, $J = 7.5$ Hz, 1H), 6.50 (d, $J = 15.8$ Hz, 1H), 4.49 (dd, $J = 14.6$, 7.0 Hz, 1H), 4.20 (q, $J = 7.1$ Hz, 2H), 3.26 (dd, $J = 14.1$, 6.2 Hz, 1H), 3.07 (dd, $J = 14.1$, 7.0 Hz, 1H), 1.77 (s, 3H), 1.28 (t, $J = 7.1$ Hz, 3H). $^{13}$C NMR (151 MHz, DMSO) δ 173.24, 169.37, 166.92, 137.90, 133.10, 131.78, 128.56, 124.60, 120.53, 119.55, 117.73, 115.21, 111.58, 60.22, 53.97, 27.51, 23.01, 14.73. MS (ESI) m/z (relative intensity) 344.34 (100) [M+H]$^+$, 687.23 (50) [2M+H]$^+$. HRMS (ESI) m/z calcd for C$_{18}$H$_{21}$N$_3$O$_4$Na (M + Na)$^+$ 366.1424, found 366.1436.

According to the general procedure D, the crude residue was purified by flash column chromatography on silica gel (ethyl acetate: petroleum ether= 1:3; Rf=0.3) to yield compound 5a (68.9 mg, 65% yield). $^1$H NMR (400 MHz, DMSO) δ 11.37 (s, 1H), 7.94 (d, $J = 8.2$ Hz, 1H), 7.69 (d, $J = 15.8$ Hz, 1H), 7.63 (d, $J = 8.0$ Hz, 1H), 7.32 (d, $J = 8.1$ Hz, 1H), 7.20 (t, $J = 7.5$ Hz, 1H), 7.05 – 7.00 (m, 1H), 6.98 (d, $J = 9.0$ Hz, 1H), 6.51 (d, $J = 15.8$ Hz, 1H), 4.24 (dd, $J = 14.3$, 6.3 Hz, 2H), 3.73 (s, 3H), 3.58 (s, 3H), 3.19 (dd, $J = 14.3$, 5.6 Hz, 1H), 3.06 (dd, $J = 14.2$, 8.4 Hz, 1H), 1.78 – 1.66 (m, 1H), 1.27 (s, 9H), 1.24 – 1.16 (m, 4H), 0.84 – 0.78 (m, 6H). $^{13}$C NMR (101 MHz, DMSO) δ 172.11, 171.80, 167.40, 155.32, 137.95, 133.10, 131.74, 128.41, 124.75, 120.34, 119.61, 117.48, 114.92, 111.68, 78.74, 56.60, 56.11, 52.11, 51.86, 37.15, 29.48, 28.46, 27.54, 25.15, 15.64, 11.55. MS (ESI) m/z (relative intensity) 530.32 (100) [M+H]$^+$, 430.24 (30) [M-Boc+H]$^+$. HRMS (ESI) m/z calcd for C$_{28}$H$_{39}$N$_3$O$_7$Na (M + Na)$^+$ 552.2680, found 552.2681.
According to the general procedure D, the crude residue was purified by flash column chromatography on silica gel (ethyl acetate: petroleum ether= 1:3; Rf =0.3) to yield compound 5b (70.4 mg, 68% yield). \(^1\)H NMR (600 MHz, CDCl\(_3\)) \(\delta 8.13 (s, 1H), 7.75 (d, \(J = 15.7\) Hz, 1H), 7.65 (d, \(J = 7.7\) Hz, 1H), 7.22 (s, 2H), 7.10 – 7.04 (m, 1H), 6.55 (d, \(J = 7.9\) Hz, 1H), 6.29 (d, \(J = 15.9\) Hz, 1H), 5.41 (d, \(J = 5.5\) Hz, 1H), 4.48 (d, \(J = 5.6\) Hz, 1H), 4.41 (dd, \(J = 8.2, 5.1\) Hz, 1H), 4.31 – 4.25 (m, 2H), 3.61 (s, 3H), 3.43 – 3.27 (m, 2H), 2.12 – 1.95 (m, 1H), 1.42 (s, 9H), 1.35 (t, \(J = 7.0\) Hz, 3H), 0.83 (dd, \(J = 10.5, 7.0\) Hz, 6H). \(^{13}\)C NMR (151 MHz, CDCl\(_3\)) \(\delta 171.76, 171.31, 167.21, 155.23, 137.53, 131.79, 131.30, 128.46, 124.84, 120.19, 119.92, 116.74, 115.39, 111.18, 80.00, 60.66, 57.34, 55.80, 52.03, 31.40, 28.28, 18.67, 17.81, 14.32. MS (ESI) \(m/z\) (relative intensity) 516.43 (100) [M+H]+.

HRMS (ESI) \(m/z\) calcd for C\(_{27}H\(_{32}N\(_{2}\)O\(_{7}\)Na (M + Na)+ 538.2524, found 538.2522.

According to the general procedure D, the crude residue was purified by flash column chromatography on silica gel (ethyl acetate: petroleum ether= 1:3; Rf =0.21) to yield compound 5c (60.1 mg, 50% yield). \(^1\)H NMR (600 MHz, CDCl\(_3\)) \(\delta 8.92 (s, 1H), 7.74 (d, \(J = 15.8\) Hz, 1H), 7.68 (d, \(J = 7.2\) Hz, 1H), 7.26 (d, \(J = 7.9\) Hz, 1H), 7.21 (t, \(J = 7.4\) Hz, 1H), 7.07 (t, \(J = 7.4\) Hz, 1H), 6.66 (s, 1H), 6.23 (d, \(J = 15.9\) Hz, 1H), 5.28 (d, \(J = 5.7\) Hz, 1H), 4.57 – 4.41 (m, 2H), 4.32 – 4.23 (m, 2H), 3.68 (d, \(J = 7.4\) Hz, 1H), 3.46 (d, \(J = 7.8\) Hz, 1H), 3.43 – 3.28 (m, 2H), 1.42 (s, 9H), 1.40 (s, 8H), 1.36 (t, \(J = 7.1\) Hz, 4H), 1.07 (s, 9H). \(^{13}\)C NMR (151 MHz, CDCl\(_3\)) \(\delta 170.81, 168.80, 167.00, 162.62, 137.48, 131.83, 131.44, 128.49, 124.97, 120.19, 119.98, 116.75, 115.25, 111.16, 81.82, 72.98, 62.07, 60.51, 55.25, 53.58, 36.50, 31.48, 28.24, 27.98, 27.24, 14.38. MS (ESI) \(m/z\) (relative intensity) 602.49 (100) [M+H]+. HRMS (ESI) \(m/z\) calcd for C\(_{32}H\(_{47}N\(_{3}\)O\(_{8}\)Na (M + Na)+ 624.3255, found 624.3256.

According to the general procedure D, the crude residue was purified by flash column chromatography on silica gel (ethyl acetate: petroleum ether= 1:3; Rf =0.16) to yield compound 5d (68.1 mg, 72% yield). \(^1\)H NMR (600 MHz, CDCl\(_3\)) \(\delta 9.08 (s, 1H), 7.71 (d, \(J = 15.9\) Hz, 1H), 7.63 (d, \(J = 7.9\) Hz, 1H), 7.19 (s, 2H), 7.07 (t, \(J = 7.3\) Hz, 1H), 6.66 (t, \(J = 4.9\) Hz, 1H), 6.27 (d, \(J = 15.9\) Hz, 1H), 5.38 (s, 1H), 4.56 (s, 1H), 4.33 – 4.17 (m, 2H), 4.04 (d, \(J = 17.9\) Hz, 1H), 3.91 (d, \(J = 17.5\) Hz, 1H), 3.70 (s, 3H), 3.38 (s, 2H), 1.42 (s, 9H), 1.34 (t, \(J = 6.8\) Hz, 3H). \(^{13}\)C NMR (151 MHz, CDCl\(_3\)) \(\delta 171.48, 169.92, 167.19, 155.23, 137.44, 131.34, 128.48, 125.00, 120.24, 119.84, 116.51, 115.32, 111.18, 80.07, 60.62, 55.23, 52.34, 41.33, 28.27, 27.92, 14.30. MS (ESI) \(m/z\) (relative intensity) 474.78 (100) [M + H]+. HRMS (ESI) \(m/z\) calcd for C\(_{24}H\(_{31}N\(_{2}\)O\(_{7}\)Na (M + Na)+ 496.2953, found 496.2953.

According to the general procedure D, the crude residue was purified by flash column chromatography on silica gel (ethyl
acetate; petroleum ether = 1:3; Rf = 0.35) to yield compound 5e (67.5 mg, 60% yield). 1H NMR (600 MHz, CDCl3) δ 9.11 (s, 1H), 7.74 (d, J = 15.7 Hz, 1H), 7.65 (d, J = 7.3 Hz, 1H), 7.26 – 7.13 (m, 6H), 7.08 (t, J = 6.9 Hz, 1H), 6.93 (s, 2H), 6.47 (s, 1H), 6.26 (d, J = 15.8 Hz, 1H), 5.32 (s, 1H), 4.73 (s, 1H), 4.47 (s, 1H), 4.35 – 4.19 (m, 2H), 3.60 (s, 3H), 3.43 – 3.25 (m, 2H), 3.00 (qd, J = 13.7, 5.7 Hz, 2H), 1.43 (s, 9H), 1.35 (t, J = 7.1 Hz, 3H). 13C NMR (151 MHz, CDCl3) δ 171.30, 170.91, 167.14, 155.15, 137.51, 135.65, 131.81, 131.35, 129.23, 128.44, 127.02, 125.00, 120.30, 119.90, 116.51, 115.40, 111.22, 80.04, 60.66, 53.54, 52.20, 37.94, 29.70, 28.27, 27.89, 14.34. MS (ESI) m/z (relative intensity) 564.74 (100) [M+H]+. HRMS (ESI) m/z calcd for C13H17N3O4Na (M + Na)+ 586.2524, found 586.2521.

According to the general procedure D, the crude residue was purified by flash column chromatography on silica gel (ethyl acetate; petroleum ether = 1:3; Rf = 0.41) to yield compound 5f (51.5 mg, 52% yield). 1H NMR (600 MHz, CDCl3) δ 8.89 (s, 1H), 7.65 (d, J = 15.9 Hz, 1H), 7.56 (d, J = 8.0 Hz, 1H), 7.29 (d, J = 2.9 Hz, 1H), 7.25 (t, J = 7.5 Hz, 1H), 7.20 (s, 1H), 7.11 (t, J = 7.4 Hz, 1H), 6.20 (d, J = 15.9 Hz, 1H), 5.60 (d, J = 5.2 Hz, 1H), 4.97 (s, 1H), 4.31 – 4.24 (m, 2H), 4.19 (s, 1H), 4.01 (d, J = 9.9 Hz, 1H), 3.69 (s, 3H), 3.69 – 3.59 (m, 2H), 3.47 (t, J = 5.4 Hz, 2H), 1.42 (s, 10H), 1.34 (t, J = 6.9 Hz, 3H). 13C NMR (151 MHz, CDCl3) δ 171.51, 170.08, 167.49, 155.42, 137.38, 131.84, 131.27, 128.55, 125.30, 120.41, 119.70, 116.30, 115.06, 111.38, 62.78, 60.90, 55.41, 53.34, 52.68, 29.69, 28.22, 26.82, 14.29. MS (ESI) m/z (relative intensity) 504.69 (100) [M+H]+. HRMS (ESI) m/z calcd for C23H33N3O7Na (M + Na)+ 526.2160, found 526.2182.

According to the general procedure D, the crude residue was purified by flash column chromatography on silica gel (ethyl acetate; petroleum ether = 1:3; Rf = 0.24) to yield compound 5g (56.8 mg, 60% yield). 1H NMR (600 MHz, CDCl3) δ 9.28 (s, 1H), 7.58 (d, J = 15.9 Hz, 1H), 7.51 (d, J = 8.0 Hz, 1H), 7.28 – 7.25 (m, 1H), 7.21 (t, J = 7.5 Hz, 1H), 7.08 (t, J = 7.5 Hz, 1H), 6.83 (d, J = 7.4 Hz, 1H), 6.19 (d, J = 15.9 Hz, 1H), 5.01 (d, J = 6.0 Hz, 1H), 4.22 (d, J = 6.8 Hz, 2H), 3.83 – 3.75 (m, 2H), 3.71 (s, 3H), 3.47 (dd, J = 14.8, 5.2 Hz, 2H), 3.42 (dd, J = 14.8, 4.8 Hz, 1H), 1.43 (s, 9H), 1.32 (t, J = 7.0 Hz, 3H). 13C NMR (151 MHz, CDCl3) δ 171.52, 169.50, 167.30, 156.08, 137.46, 131.72, 131.37, 128.56, 125.04, 120.25, 119.46, 115.86, 115.07, 111.46, 80.10, 60.72, 53.79, 53.10, 52.63, 28.27, 26.84, 14.29. MS (ESI) m/z (relative intensity) 474.89 (100) [M+H]+. HRMS (ESI) m/z calcd for C23H31N3O7Na (M + Na)+ 496.2054, found 496.2057.

According to the general procedure D, the crude residue was purified by flash column chromatography on silica gel (ethyl acetate; petroleum ether = 1:3; Rf = 0.45) to yield compound 5h (56.5 mg, 58% yield). 1H NMR (600 MHz, CDCl3) δ 9.20 (s, 1H), 7.62 (d, J = 15.9 Hz, 1H), 7.54 (d, J = 7.9 Hz, 1H), 7.30 – 7.27 (m, 1H), 7.22 (t, J = 7.5 Hz, 1H), 7.08 (t, J = 7.5 Hz, 1H), 6.89 (s, 1H), 6.22 (d, J = 15.9 Hz, 1H), 4.99 (d, J = 6.2 Hz, 1H),
4.25 (d, J = 6.8 Hz, 2H), 4.21 (d, J = 5.8 Hz, 1H), 3.69 (s, 3H), 3.46 (qd, J = 14.8, 5.2 Hz, 2H), 1.42 (s, 9H), 1.36 – 1.31 (m, 6H).\textsuperscript{13}C NMR (151 MHz, CDCl\textsubscript{3}) δ 172.58, 171.51, 167.30, 155.46, 137.44, 131.79, 131.30, 128.70, 125.09, 120.25, 119.83, 116.16, 111.06, 111.38, 80.01, 60.71, 53.26, 52.57, 50.13, 28.26, 26.98, 18.08, 14.32. MS (ESI) m/z (relative intensity) 487.98 (100) [M + H]\textsuperscript{+}. HRMS (ESI) m/z calcd for C\textsubscript{25}H\textsubscript{33}N\textsubscript{7}O\textsubscript{2}Na (M + Na\textsuperscript{+}) 510.2211, found 510.2239.

According to the general procedure D, the crude residue was purified by flash column chromatography on silica gel (ethyl acetate: petroleum ether = 1:3; R\textsubscript{f}=0.32) to yield compound 5i (63.1 mg, 48% yield). \textsuperscript{1}H NMR (600 MHz, CDCl\textsubscript{3}) δ 8.96 (s, 1H), 7.61 (d, J = 15.9 Hz, 1H), 7.43 (d, J = 7.9 Hz, 1H), 7.29 (d, J = 7.8 Hz, 1H), 7.24 (t, J = 7.5 Hz, 1H), 7.09 – 7.04 (m, 3H), 6.86 (d, J = 8.1 Hz, 2H), 6.60 (d, J = 7.8 Hz, 1H), 6.20 (d, J = 15.9 Hz, 1H), 5.15 (s, 1H), 4.94 (dd, J = 12.4, 5.3 Hz, 1H), 4.35 (s, 1H), 4.26 (d, J = 6.9 Hz, 2H), 3.66 (s, 3H), 3.46 – 3.35 (m, 3H), 3.10 – 3.04 (m, 1H), 3.00 – 2.86 (m, 1H), 1.36 (s, 9H), 1.34 – 1.31 (m, 12H). \textsuperscript{13}C NMR (151 MHz, CDCl\textsubscript{3}) δ 171.22, 171.17, 167.19, 155.36, 154.07, 137.37, 131.72, 131.64, 131.20, 129.75, 128.63, 125.17, 124.27, 120.38, 119.77, 116.07, 115.08, 111.38, 79.94, 78.43, 78.27, 56.84, 53.10, 52.52, 37.61, 28.83, 28.22, 26.92, 14.33. MS (ESI) m/z (relative intensity) 636.21 (100) [M+H]\textsuperscript{+}. HRMS (ESI) m/z calcd for C\textsubscript{33}H\textsubscript{42}N\textsubscript{7}O\textsubscript{3}Na (M + Na\textsuperscript{+}) 658.3599, found 658.3597.

According to the general procedure D, the crude residue was purified by flash column chromatography on silica gel (ethyl acetate: petroleum ether = 1:3; R\textsubscript{f}=0.27) to yield compound 5j (60.3 mg, 43% yield). \textsuperscript{1}H NMR (500 MHz, CDCl\textsubscript{3}) \textsuperscript{1}H NMR (500 MHz, Chloroform-d) δ 9.22 (s, 1H), 8.11 (t, J = 7.4 Hz, 1H), 7.57 (dd, J = 19.5, 11.9 Hz, 2H), 7.44 (s, 1H), 7.34 (d, J = 7.4 Hz, 1H), 7.31 – 7.26 (m, 1H), 7.20 (ddd, J = 20.6, 14.1, 8.0 Hz, 3H), 6.95 (d, J = 7.8 Hz, 1H), 6.71 (d, J = 7.9 Hz, 1H), 6.21 (d, J = 15.8 Hz, 1H), 5.31 (d, J = 7.9 Hz, 1H), 4.92 (q, J = 5.8 Hz, 1H), 4.45 (dd, J = 15.7, 8.2 Hz, 1H), 4.21 (q, J = 7.2, 6.8 Hz, 2H), 3.62 (s, 3H), 3.37 (tt, J = 14.5, 7.3 Hz, 2H), 3.28 – 3.02 (m, 2H), 1.63 (s, 9H), 1.37 (s, 9H), 1.29 (d, J = 7.3 Hz, 3H). \textsuperscript{13}C NMR (126 MHz, CDCl\textsubscript{3}) δ 171.18, 171.08, 167.24, 149.57, 137.40, 135.47, 131.67, 131.25, 130.40, 128.61, 128.58, 125.05, 124.44, 124.32, 122.57, 120.17, 119.54, 119.10, 118.97, 115.89, 115.76, 115.16, 111.38, 83.51, 79.98, 60.70, 54.65, 53.20, 52.49, 29.67, 28.16, 28.11, 27.00, 14.27. MS (ESI) m/z (relative intensity) 703.56 (100) [M+H]\textsuperscript{+}. HRMS (ESI) m/z calcd for C\textsubscript{35}H\textsubscript{46}N\textsubscript{7}O\textsubscript{4}Na (M + Na\textsuperscript{+}) 725.3157, found 725.3159.

According to the general procedure D, the crude residue was purified by flash column chromatography on silica gel (ethyl acetate: petroleum ether = 1:3; R\textsubscript{f}=0.35) to yield compound 5k (56.5 mg, 45% yield). \textsuperscript{1}H NMR (600 MHz, CDCl\textsubscript{3}) δ 8.66 (s, 1H), 7.66 (d, J = 15.9 Hz, 1H), 7.61 (d, J = 7.9 Hz, 1H), 7.42 – 7.28 (m, 5H), 7.28 (d, J = 6.0 Hz, 1H), 7.23 (t, J = 7.5 Hz, 1H), 7.10 (t, J = 7.5 Hz, 2H), 6.13 (d, J = 15.9 Hz, 1H), 5.99 (d, J = 8.4 Hz, 1H), 5.11 – 5.04 (m, 3H), 4.96 (dd, J = 12.8, 5.6 Hz,
According to the general procedure D, the crude residue was purified by flash column chromatography on silica gel (ethyl acetate: petroleum ether= 2:3; Rf = 0.41) to yield compound 5l (41.3 mg, 42% yield). 1H NMR (600 MHz, CDCl3) δ 8.47 (d, J = 7.4 Hz, 1H), 7.91 (d, J = 8.5 Hz, 1H), 7.63 (d, J = 15.8 Hz, 1H), 7.59 (d, J = 8.1 Hz, 1H), 7.34 (d, J = 8.2 Hz, 1H), 7.24 – 7.19 (m, 1H), 7.03 (t, J = 7.5 Hz, 1H), 6.98 (d, J = 8.5 Hz, 2H), 6.65 – 6.60 (m, 2H), 6.54 (d, J = 15.8 Hz, 1H), 4.49 (dd, J = 14.4, 7.5 Hz, 1H), 4.46 – 4.42 (m, 1H), 4.19 (qd, J = 7.0, 1.2 Hz, 2H), 3.48 (d, J = 8.0 Hz, 3H), 3.29 (dd, J = 14.3, 8.0 Hz, 1H), 3.23 (dd, J = 14.3, 6.5 Hz, 1H), 2.83 (dd, J = 13.9, 4.6 Hz, 1H), 2.57 (dd, J = 13.9, 9.7 Hz, 1H), 1.73 (s, 3H), 1.26 (t, J = 7.1 Hz, 3H). 13C NMR (151 MHz, DMSO) δ 174.24, 174.09, 171.62, 169.08, 158.39, 140.12, 134.47, 133.87, 132.67, 130.54, 130.35, 127.12, 122.19, 118.70, 117.94, 117.48, 114.07, 62.61, 56.62, 56.16, 54.49, 39.50, 31.67, 28.92, 25.13, 16.91. MS (ESI) m/z (relative intensity) 522.45 (100) [M+H]+. HRMS (ESI) m/z calcd for C28H36N2O7Na (M + Na)+ 544.2579, found 544.2581.

According to the general procedure D, the crude residue was purified by flash column chromatography on silica gel (ethyl acetate: petroleum ether= 1:3; Rf = 0.30) to yield compound 5m (65.3 mg, 62% yield). 1H NMR (600 MHz, CDCl3) δ 7.65 (d, J = 15.9 Hz, 1H), 7.60 (d, J = 8.0 Hz, 1H), 7.29 (s, 1H), 7.23 (t, J = 7.5 Hz, 1H), 7.09 (t, J = 7.4 Hz, 1H), 6.19 (d, J = 15.2 Hz, 1H), 5.07 – 4.86 (m, 2H), 4.31 – 4.23 (m, 2H), 3.65 (s, 3H), 3.43 (qd, J = 14.7, 5.7 Hz, 2H), 2.31 – 2.12 (m, 3H), 1.84 – 1.60 (m, 6H), 1.38 (s, 9H), 1.35 (t, J = 7.1 Hz, 3H). 13C NMR (151 MHz, CDCl3) δ 174.57, 171.87, 167.12, 154.96, 137.41, 131.19, 128.65, 125.07, 120.21, 115.01, 111.28, 80.08, 66.98, 60.62, 53.58, 52.41, 28.20, 27.26, 24.18, 14.35. MS (ESI) m/z (relative intensity) 528.88 (100) [M+H]+. HRMS (ESI) m/z calcd for C30H30N2O7Na (M + Na)+ 550.2524, found 550.2521.

According to the general procedure D, the crude residue was purified by flash column chromatography on silica gel (ethyl acetate: petroleum ether= 2:3; Rf = 0.28) to yield compound 5n (85.6 mg, 65% yield). 1H NMR (600 MHz, CDCl3) δ 9.06 (s, 1H), 7.69 (d, J = 15.9 Hz, 1H), 7.58 (d, J = 8.0 Hz, 1H), 7.29 (d, J = 8.7 Hz, 1H), 7.24 (t, J = 7.6 Hz, 1H), 7.12 (t, J = 7.4 Hz, 1H), 6.59 (d, J = 7.9 Hz, 1H), 6.27 (d, J = 15.9 Hz, 1H), 5.22 (d, J = 8.5 Hz, 1H), 4.98 (dd, J = 13.2, 5.7 Hz, 1H), 4.28 (q, J = 7.0 Hz, 2H), 3.95 (d, J = 6.3 Hz, 1H), 3.67 (s, 3H), 3.44 (d, J = 4.6 Hz, 2H), 1.75 – 1.66 (m, 3H), 1.66 – 1.56 (m, 3H), 1.46 (s, 9H), 1.35 (t, J = 7.0 Hz, 3H), 1.33 (t, J = 7.1 Hz, 3H), 1.26 (t, J = 7.1 Hz, 3H).
According to the general procedure D, the crude residue was purified by flash column chromatography on silica gel (ethyl acetate: petroleum ether = 1:3; R$_f$ = 0.21) to yield compound 5o (62.2 mg, 53% yield). $^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 8.97 (s, 1H), 7.69 (d, $J$ = 15.8 Hz, 1H), 7.61 (d, $J$ = 7.6 Hz, 1H), 7.22 – 7.15 (m, 2H), 7.07 – 6.98 (m, 1H), 6.86 (d, $J$ = 7.1 Hz, 1H), 6.41 (s, 1H), 6.20 (d, $J$ = 15.9 Hz, 1H), 5.12 (d, $J$ = 6.3 Hz, 1H), 4.80 (d, $J$ = 6.8 Hz, 1H), 4.37 (dd, $J$ = 8.3, 5.1 Hz, 1H), 4.31 – 4.24 (m, 2H), 4.19 (s, 1H), 3.62 (s, 3H), 3.44 (dd, $J$ = 13.8, 5.2 Hz, 1H), 3.30 (dd, $J$ = 14.4, 7.6 Hz, 1H), 2.03 (dd, $J$ = 12.3, 6.7 Hz, 1H), 1.44 (s, 9H), 1.35 (t, $J$ = 7.1 Hz, 3H), 1.31 – 1.24 (m, 3H), 0.82 – 0.76 (m, 6H). $^{13}$C NMR (151 MHz, CDCl$_3$) $\delta$ 172.16, 171.43, 170.69, 167.15, 155.76, 137.51, 137.43, 131.61, 131.24, 128.44, 125.04, 120.38, 119.87, 116.51, 115.48, 111.24, 80.00, 60.73, 59.83, 57.42, 54.39, 51.99, 31.29, 28.36, 28.32, 27.44, 19.18, 18.64, 17.76, 17.17, 14.36. MS (ESI) $m/z$ (relative intensity) 615.54 (100) [M+H]$^+$. HRMS (ESI) $m/z$ calcd for C$_{32}$H$_{46}$N$_4$O$_8$Na (M + Na)$^+$ 637.3208, found 637.3201.

According to the general procedure D, the crude residue was purified by flash column chromatography on silica gel (ethyl acetate: petroleum ether = 1:3; R$_f$ = 0.24) to yield compound 5p (58.6 mg, 50% yield). $^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 9.17 (s, 1H), 7.74 (d, $J$ = 15.9 Hz, 1H), 7.67 (d, $J$ = 8.0 Hz, 1H), 7.24 – 7.20 (m, 2H), 7.10 – 7.06 (m, 1H), 6.68 (s, 1H), 6.29 (d, $J$ = 15.9 Hz, 1H), 5.12 (d, $J$ = 6.3 Hz, 1H), 4.80 (d, $J$ = 6.8 Hz, 1H), 4.37 (dd, $J$ = 8.3, 5.1 Hz, 1H), 4.31 – 4.24 (m, 2H), 4.19 (s, 1H), 3.62 (s, 3H), 3.44 (dd, $J$ = 13.8, 5.2 Hz, 1H), 3.30 (dd, $J$ = 14.4, 7.6 Hz, 1H), 2.03 (dd, $J$ = 12.3, 6.7 Hz, 1H), 1.44 (s, 9H), 1.35 (t, $J$ = 7.1 Hz, 3H), 0.82 – 0.76 (m, 6H). $^{13}$C NMR (151 MHz, CDCl$_3$) $\delta$ 172.55, 171.54, 170.71, 167.38, 155.36, 137.50, 131.80, 131.24, 128.46, 124.94, 120.20, 116.69, 115.27, 111.30, 80.13, 60.76, 57.53, 54.45, 52.04, 50.27, 31.29, 29.69, 28.28, 18.64, 18.35, 17.81, 14.32. MS (ESI) $m/z$ (relative intensity) 587.43 (100) [M+H]$^+$. HRMS (ESI) $m/z$ calcd for C$_{30}$H$_{42}$N$_4$O$_8$Na (M + Na)$^+$ 609.2895, found 609.2899.

According to the general procedure D, the crude residue was purified by flash column chromatography on silica gel (ethyl acetate: petroleum ether = 1:3; R$_f$ = 0.26) to yield compound 5q (73.4 mg, 60% yield). $^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 8.91 (s, 1H), 7.76 (d, $J$ = 15.9 Hz, 1H), 7.68 (s, 1H), 7.30 (s, 1H), 7.26 (t, $J$ = 7.8 Hz, 1H), 7.11 (t, $J$ = 7.3 Hz, 1H), 6.93 (d, $J$ = 7.7 Hz, 1H), 6.72 (s, 1H), 6.25 (d, $J$ = 15.9 Hz, 1H), 4.76 (s, 1H), 4.37 (s, 1H), 4.32 – 4.27 (m, 2H), 4.24 (s, 1H), 3.63 (s, 3H), 3.35 (dd,
$J = 96.5, 25.3 \text{ Hz}, 4 \text{H}$, 2.03 – 1.92 (m, 4H), 1.42 – 1.32 (m, 12H), 0.84 – 0.73 (m, 6H). $^{13}$C NMR (151 MHz, CDCl$_3$) δ 171.58, 166.91, 137.43, 131.27, 125.11, 120.53, 119.78, 115.78, 115.50, 111.21, 82.36, 80.49, 60.72, 51.97, 47.33, 28.21, 18.68, 18.06, 14.36. MS (ESI) $m/z$ (relative intensity) 613.69 (100) [M+H]$^+$. HRMS (ESI) $m/z$ calcd for C$_{32}$H$_{44}$N$_{4}$O$_{8}$Na (M + Na)$^+$ 635.3051, found 635.3046.

According to the general procedure D, the crude residue was purified by flash column chromatography on silica gel (ethyl acetate: petroleum ether = 1:1; $R_f$ = 0.43) to yield compound 5r (59.2 mg, 44% yield). $^1$H NMR (600 MHz, CDCl$_3$) δ 9.24 (s, 1H), 7.71 (d, $J = 15.9$ Hz, 1H), 7.65 (d, $J = 8.0$ Hz, 1H), 7.22 – 7.16 (m, 2H), 7.05 (t, $J = 7.8$ Hz, 1H), 6.88 (d, $J = 6.7$ Hz, 2H), 6.27 (d, $J = 15.9$ Hz, 1H), 5.34 (d, $J = 8.1$ Hz, 1H), 4.88 – 4.81 (m, 1H), 4.41 (dd, $J = 8.4, 5.1$ Hz, 1H), 4.29 – 4.21 (m, 2H), 4.17 – 4.10 (m, 1H), 3.63 (s, 3H), 3.38 (dd, $J = 14.2, 7.8$ Hz, 1H), 2.24 (dd, $J = 17.7, 10.5$ Hz, 2H), 2.13 – 2.02 (m, 2H), 1.83 – 1.73 (m, 1H), 1.45 (s, 9H), 1.43 (s, 9H), 1.34 (t, $J = 7.1$ Hz, 3H), 0.82 (dd, $J = 18.6, 6.9$ Hz, 6H). $^{13}$C NMR (151 MHz, CDCl$_3$) δ 171.94, 171.63, 171.49, 171.03, 167.25, 155.87, 137.54, 131.77, 131.27, 128.49, 124.79, 120.11, 119.80, 116.73, 115.30, 111.33, 82.13, 79.87, 60.64, 57.50, 54.67, 53.56, 52.02, 32.51, 31.32, 29.68, 28.80, 28.33, 28.02, 27.97, 18.73, 17.90, 14.31. MS (ESI) $m/z$ (relative intensity) 701.56 (100) [M+H]$^+$. HRMS (ESI) $m/z$ calcd for C$_{35}$H$_{52}$N$_{4}$O$_{10}$Na (M + Na)$^+$ 623.3576, found 623.3578.

According to the general procedure D, the crude residue was purified by flash column chromatography on silica gel (ethyl acetate: petroleum ether = 1:1; $R_f$ = 0.24) to yield compound 5s (115.2 mg, 48% yield). $^1$H NMR (600 MHz, DMSO) δ 11.45 (s, 1H), 8.45 (d, $J = 7.4$ Hz, 1H), 8.12 (t, $J = 5.5$ Hz, 1H), 7.99 (d, $J = 7.4$ Hz, 1H), 7.88 (d, $J = 7.5$ Hz, 2H), 7.67 (dd, $J = 17.3, 8.9$ Hz, 3H), 7.62 (d, $J = 15.8$ Hz, 1H), 7.57 (d, $J = 8.0$ Hz, 1H), 7.40 (t, $J = 7.5$ Hz, 2H), 7.34 (d, $J = 8.2$ Hz, 1H), 7.30 (t, $J = 7.5$ Hz, 2H), 7.21 (t, $J = 7.6$ Hz, 1H), 7.03 (t, $J = 7.4$ Hz, 1H), 6.54 (d, $J = 15.8$ Hz, 1H), 6.38 (s, 1H), 4.54 (dd, $J = 14.3, 7.3$ Hz, 1H), 4.39 (dd, $J = 8.7, 4.0$ Hz, 1H), 4.32 – 4.17 (m, 6H), 3.79 (dd, $J = 16.8, 5.7$ Hz, 1H), 3.65 (dd, $J = 16.8, 5.5$ Hz, 1H), 3.49 (s, 3H), 3.30 (dd, $J = 14.3, 7.8$ Hz, 1H), 3.22 (dd, $J = 14.3, 6.3$ Hz, 1H), 3.01 (d, $J = 5.6$ Hz, 2H), 2.93 (s, 2H), 2.74 – 2.67 (m, 1H), 2.47 (s, 3H), 2.41 (s, 3H), 1.99 (s, 3H), 1.70 – 1.61 (m, 1H), 1.55 – 1.47 (m, 1H), 1.38 (s, 6H), 1.35 (s, 9H), 1.26 (t, $J = 7.1$ Hz, 3H). $^{13}$C NMR (151 MHz, DMSO) δ 171.92, 171.13, 169.86, 169.06, 166.87, 157.91, 156.22, 144.27, 144.14, 141.16, 137.88, 137.74, 132.22, 131.92, 131.62, 128.21, 128.10, 127.52, 125.68, 124.91, 124.78, 120.55, 119.98, 119.88, 116.38, 115.72, 111.86, 86.73, 80.62, 66.22, 60.42, 53.91, 52.33, 51.89, 47.06, 42.92, 42.04, 37.96, 28.73, 28.12, 26.85, 21.22, 19.39, 18.04, 14.69, 14.54, 12.71. MS (ESI) $m/z$ (relative intensity) 1175.96 (100) [M+H]$^+$. HRMS (ESI) $m/z$ calcd for C$_{36}$H$_{52}$N$_{4}$O$_{10}$SNa (M + Na)$^+$ 1197.4937, found 1197.4935.
acetate: petroleum ether = 1:3; R<sub>f</sub> = 0.18) to yield compound 7a (63.6 mg, 54% yield). <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ 8.78 (s, 1H), 7.69 (d, J = 15.9 Hz, 1H), 7.58 (d, J = 8.0 Hz, 1H), 7.29 (d, J = 7.7 Hz, 1H), 7.25 (t, J = 7.3 Hz, 1H), 7.11 (t, J = 7.2 Hz, 1H), 6.19 (d, J = 15.9 Hz, 1H), 5.62 (s, 1H), 5.17 (d, J = 7.5 Hz, 1H), 4.71 (d, J = 6.9 Hz, 1H), 4.68 – 4.64 (m, 1H), 4.62 (d, J = 11.3 Hz, 1H), 4.48 (d, J = 9.8 Hz, 1H), 3.81 (s, 3H), 3.70 (s, 3H), 3.44 (dd, J = 14.3, 5.4 Hz, 1H), 3.37 (dd, J = 14.5, 4.1 Hz, 1H), 1.48 (s, 9H), 1.44 (s, 9H). <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>) δ 172.10, 170.54, 166.36, 155.34, 155.00, 137.50, 132.83, 130.93, 128.77, 125.42, 120.13, 117.26, 113.52, 111.18, 80.43, 80.00, 64.37, 54.43, 53.15, 52.81, 52.52, 29.69, 28.31, 27.35. MS (ESI) m/z (relative intensity) 590.45 (100) [M+H]<sup>+</sup>, 490.56 (30) [M-Boc+H]<sup>+</sup>. HRMS (ESI) m/z calcd for C<sub>25</sub>H<sub>30</sub>N<sub>2</sub>O<sub>10</sub>Na (M + Na)<sup>+</sup> 612.2528, found 612.2516.

According to the general procedure D, the crude residue was purified by flash column chromatography on silica gel (ethyl acetate: petroleum ether = 1:1; R<sub>f</sub> = 0.33) to yield compound 7b (65.8 mg, 62% yield). <sup>1</sup>H NMR (600 MHz, DMSO) δ 11.43 (s, 1H), 7.71 (d, J = 15.8 Hz, 1H), 7.61 (d, J = 7.9 Hz, 1H), 7.35 (d, J = 8.1 Hz, 1H), 7.26 (d, J = 8.0 Hz, 1H), 7.22 (t, J = 7.6 Hz, 1H), 7.04 (t, J = 7.5 Hz, 1H), 6.98 (t, J = 5.4 Hz, 1H), 6.55 (d, J = 15.8 Hz, 1H), 4.20 (dd, J = 14.9, 7.5 Hz, 1H), 4.15 (t, J = 5.5 Hz, 2H), 3.55 (s, 3H), 3.33 – 3.20 (m, 4H), 1.39 (s, 9H), 1.32 (s, 9H). <sup>13</sup>C NMR (151 MHz, DMSO) δ 172.58, 166.82, 156.13, 155.64, 137.94, 132.70, 131.65, 128.22, 124.84, 119.97, 119.83, 117.20, 115.45, 111.82, 78.79, 78.26, 63.26, 55.36, 55.31, 52.24, 28.67, 28.52, 28.44. MS (ESI) m/z (relative intensity) 532.67 (100) [M+H]<sup>+</sup>. HRMS (ESI) m/z calcd for C<sub>27</sub>H<sub>32</sub>N<sub>2</sub>O<sub>10</sub>Na (M + Na)<sup>+</sup> 531.2581, found 531.2590.

According to the general procedure D, the crude residue was purified by flash column chromatography on silica gel (ethyl acetate: petroleum ether = 1:1; R<sub>f</sub> = 0.22) to yield compound 7c (71.5 mg, 52% yield). <sup>1</sup>H NMR (600 MHz, DMSO) δ 11.48 (s, 1H), 8.49 (d, J = 7.2 Hz, 1H), 7.70 (d, J = 15.7 Hz, 1H), 7.60 (d, J = 7.9 Hz, 1H), 7.33 (d, J = 8.1 Hz, 1H), 7.28 (d, J = 7.9 Hz, 1H), 7.22 (t, J = 7.6 Hz, 1H), 7.03 (t, J = 7.5 Hz, 1H), 6.65 (d, J = 9.0 Hz, 1H), 6.53 (d, J = 15.7 Hz, 1H), 4.71 (dd, J = 11.6, 5.9 Hz, 1H), 4.45 (dd, J = 11.3, 4.4 Hz, 1H), 4.37 (dd, J = 10.9, 6.1 Hz, 1H), 4.18 (dd, J = 14.9, 7.5 Hz, 1H), 3.95 – 3.90 (m, 1H), 3.68 (s, 3H), 3.53 (s, 3H), 3.28 (dd, J = 14.3, 6.5 Hz, 1H), 3.22 (dd, J = 14.3, 8.1 Hz, 1H), 2.03 – 1.90 (m, 1H), 1.37 (s, 10H), 1.31 (s, 9H), 0.89 – 0.82 (m, 6H). <sup>13</sup>C NMR (151 MHz, DMSO) δ 172.59, 172.19, 170.30, 166.60, 155.88, 155.65, 138.03, 133.22, 131.52, 128.22, 124.98, 120.07, 119.87, 117.58, 114.72, 114.22, 81.81, 81.75, 63.44, 59.67, 55.39, 52.65, 52.23, 51.68, 31.08, 28.60, 28.52, 26.40, 19.53, 18.34. MS (ESI) m/z (relative intensity) 688.97 (100) [M+H]<sup>+</sup>. HRMS (ESI) m/z calcd for C<sub>14</sub>H<sub>14</sub>N<sub>4</sub>O<sub>1</sub>Na (M + Na)<sup>+</sup> 711.3212, found 711.3230.

According to the general procedure D, the crude residue was purified by flash column chromatography on silica gel (ethyl acetate: petroleum ether = 1:1; R<sub>f</sub> = 0.21) to yield compound 7d (65.8 mg, 41% yield). <sup>1</sup>H NMR (500 MHz, DMSO) δ 11.43 (s, 1H), 8.50 (d, J = 7.2 Hz, 1H), 8.25 (d, J = 8.0 Hz, 1H), 7.75 (d,
According to the general procedure D, the crude residue was purified by flash column chromatography on silica gel (ethyl acetate: petroleum ether = 1:1; R_f = 0.24) to yield compound 7e (65.8 mg, 39% yield). 

**NH NHBoc**

**Chemical Formula:** C_{42}H_{61}N_{5}O_{14}

**Exact Mass:** 859.4215

According to the general procedure D, the crude residue was purified by flash column chromatography on silica gel (ethyl acetate: petroleum ether = 1:4; R_f = 0.52) to yield compound 7f (64.1 mg, 61% yield). 

**Chemical Formula:** C_{30}H_{42}N_{2}O_{6}

**Exact Mass:** 526.3043
According to the general procedure D, the crude residue was purified by flash column chromatography on silica gel (ethyl acetate: petroleum ether = 3:2; R<sub>f</sub> = 0.20) to yield compound 3k (48.15 mg, 40% yield). <sup>1</sup>H NMR (600 MHz, DMSO) δ 11.39 (s, 1H), 10.85 (s, 1H), 10.25 (s, 1H), 7.75 (d, J = 8.6 Hz, 2H), 7.68 (d, J = 15.5 Hz, 1H), 7.59 (d, J = 8.2 Hz, 1H), 7.37 (d, J = 8.1 Hz, 1H), 7.27 (d, J = 8.7 Hz, 3H), 7.19 (dd, J = 11.5, 4.2 Hz, 1H), 7.03 (dd, J = 11.3, 4.1 Hz, 1H), 6.66 (d, J = 15.5 Hz, 1H), 4.21 (dd, J = 15.0, 7.5 Hz, 1H), 3.54 (s, 3H), 3.30 (dd, J = 14.3, 6.7 Hz, 1H), 3.23 (dd, J = 14.3, 7.8 Hz, 1H), 2.52 – 2.44 (m, 2H), 2.20 – 2.13 (m, 2H), 1.91 – 1.80 (m, 2H), 1.31 (s, 9H), 0.78 (t, J = 7.4 Hz, 3H). <sup>13</sup>C NMR (151 MHz, DMSO) δ 176.27, 173.26, 172.67, 170.78, 164.45, 155.64, 138.84, 137.83, 134.82, 132.19, 129.06, 128.52, 127.10, 124.23, 120.15, 119.71, 119.67, 115.75, 111.86, 78.80, 60.21, 55.39, 52.22, 50.29, 32.63, 29.61, 28.53, 28.11, 26.58, 26.50, 21.20, 21.14, 14.54, 9.39. MS (ESI) m/z (relative intensity) 603.75 (100) [M+H]<sup>+</sup>. HRMS (ESI) m/z calcd for C<sub>33</sub>H<sub>38</sub>N<sub>2</sub>O<sub>5</sub>Na (M + Na)<sup>+</sup> 625.2633, found 625.2644.

According to the general procedure D, the crude residue was purified by flash column chromatography on silica gel (ethyl acetate: petroleum ether = 1:2; R<sub>f</sub> = 0.28) to yield compound 3k (69.8 mg, 55% yield). <sup>1</sup>H NMR (600 MHz, DMSO) δ 11.45 (s, 1H), 7.74 (d, J = 15.8 Hz, 1H), 7.61 (d, J = 8.0 Hz, 1H), 7.35 (d, J = 8.2 Hz, 1H), 7.29 (d, J = 8.1 Hz, 1H), 7.22 (t, J = 7.6 Hz, 1H), 7.04 (t, J = 7.5 Hz, 1H), 6.56 (d, J = 15.8 Hz, 1H), 4.65 (dd, J = 7.9, 2.5 Hz, 1H), 4.46 (d, J = 11.6 Hz, 1H), 4.37 (d, J = 2.2 Hz, 1H), 4.28 (d, J = 8.2 Hz, 1H), 4.20 – 4.13 (m, 1H), 4.05 (d, J = 11.6 Hz, 1H), 3.79 (d, J = 11.7 Hz, 1H), 3.64 (d, J = 13.0 Hz, 1H), 3.55 (s, 3H), 3.28 (dd, J = 14.4, 6.3 Hz, 1H), 3.21 (dd, J = 14.4, 8.3 Hz, 1H), 1.48 (s, 3H), 1.39 (s, 6H), 1.30 (s, 12H). <sup>13</sup>C NMR (151 MHz, DMSO) δ 172.59, 166.17, 155.65, 137.98, 133.24, 131.48, 128.21, 125.00, 120.09, 119.89, 117.69, 114.79, 111.85, 108.65, 101.57, 78.79, 70.52, 70.42, 69.76, 64.64, 61.02, 55.35, 52.26, 28.53, 28.11, 26.58, 26.50, 21.20, 21.14, 14.54, 9.39. MS (ESI) m/z (relative intensity) 631.65 (100) [M+H]<sup>+</sup>. HRMS (ESI) m/z calcd for C<sub>33</sub>H<sub>38</sub>N<sub>2</sub>O<sub>5</sub>Na (M + Na)<sup>+</sup> 653.2681, found 653.2689.

According to the general procedure F, the crude residue was purified by flash column chromatography on silica gel (ethyl acetate: petroleum ether = 2:1; R<sub>f</sub> = 0.3) to yield compound 3b (80.3 mg, 62% yield). <sup>1</sup>H NMR (600 MHz, DMSO) δ 11.41 (s, 1H), 8.73 (s, 1H), 8.56 (d, J = 9.2 Hz, 1H), 7.50 (d, J = 7.3 Hz, 1H), 7.33 (d, J = 8.2 Hz, 1H), 7.27 (d, J = 15.8 Hz, 1H), 7.21 (t, J = 7.6 Hz, 1H), 6.99 (t, J = 7.5 Hz, 1H), 6.33 (d, J = 15.8 Hz, 1H), 5.10 (s, 1H), 4.45 (dd, J = 21.9, 9.0 Hz, 2H), 4.25 (s, 1H), 4.08 (t, J = 10.6 Hz, 1H), 3.72 (s, 3H), 3.69 – 3.62 (m, 1H), 3.51 (dd, J = 16.2, 3.6 Hz, 1H), 3.43 (dd, J = 14.3, 7.4 Hz, 1H), 3.10 (d, J = 13.4 Hz, 1H), 1.34 (s, 9H). <sup>13</sup>C NMR (151 MHz, DMSO) δ 169.90, 166.09, 137.62, 133.78, 131.99, 124.84, 120.32, 119.82, 114.67, 111.59, 78.89, 74.45, 63.58, 52.84, 52.72, 50.35, 28.54, 27.14. MS (ESI) m/z (relative intensity) 515.81 (100) [M+H]<sup>+</sup>. HRMS (ESI) m/z
According to the general procedure F, the crude residue was purified by flash column chromatography on silica gel (ethyl acetate; Rt=0.23) to yield compound 9c (57.3 mg, 47% yield). 1H NMR (600 MHz, DMSO) δ 11.37 (s, 1H), 8.40 (d, J = 7.6 Hz, 1H), 8.31 (dd, J = 7.4, 4.7 Hz, 1H), 8.12 (d, J = 7.5 Hz, 1H), 7.87 (d, J = 8.0 Hz, 1H), 7.82 (d, J = 15.9 Hz, 1H), 7.31 (d, J = 8.2 Hz, 1H), 7.19 (t, J = 7.6 Hz, 1H), 7.04 – 6.97 (m, 2H), 6.38 (d, J = 15.9 Hz, 1H), 4.65 – 4.56 (m, 1H), 4.51 (dd, J = 11.1, 3.0 Hz, 1H), 4.46 – 4.41 (m, 1H), 4.36 – 4.32 (m, 1H), 4.16 – 4.01 (m, 2H), 3.69 (s, 3H), 3.55 – 3.49 (m, 1H), 3.45 (dd, J = 14.4, 4.1 Hz, 1H), 3.08 (dd, J = 14.4, 8.9 Hz, 1H), 1.22 (s, 9H). 13C NMR (151 MHz, DMSO) δ 172.22, 171.67, 169.94, 169.76, 166.16, 155.63, 137.96, 133.72, 130.97, 129.03, 127.47, 124.66, 120.86, 119.32, 114.26, 110.73, 78.52, 62.62, 57.35, 52.74, 52.25, 48.82, 43.01, 29.46, 28.43, 18.13. MS (ESI) m/z (relative intensity) 586.56 (100) [M+H]+. HRMS (ESI) m/z calculated for C28H35N5O10Na (M + Na)+ 608.2327, found 608.2318.

According to the general procedure F, the crude residue was purified by flash column chromatography on silica gel (ethyl acetate: petroleum ether= 4:1; Rt=0.3) to yield compound 9d (57.7 mg, 43% yield). 1H NMR (600 MHz, DMSO) δ 11.45 (s, 1H), 8.39 (d, J = 5.5 Hz, 1H), 7.99 – 7.95 (m, 1H), 7.79 (d, J = 8.1 Hz, 1H), 7.73 (d, J = 15.9 Hz, 1H), 7.46 (d, J = 5.8 Hz, 1H), 7.44 (d, J = 5.1 Hz, 1H), 7.32 (d, J = 8.2 Hz, 1H), 7.20 (t, J = 7.5 Hz, 1H), 7.02 (t, J = 7.4 Hz, 1H), 6.38 (d, J = 15.8 Hz, 1H), 4.91 – 4.84 (m, 1H), 4.52 (dd, J = 11.2, 4.0 Hz, 1H), 4.33 (td, J = 9.4, 2.7 Hz, 1H), 4.23 (dd, J = 11.2, 2.4 Hz, 1H), 4.14 (dd, J = 8.0, 2.5 Hz, 1H), 4.07 (dd, J = 6.2, 2.7 Hz, 1H), 3.99 (dd, J = 16.2, 7.6 Hz, 1H), 3.76 – 3.71 (m, 1H), 3.70 (s, 3H), 3.34 (dd, J = 14.9, 2.5 Hz, 1H), 3.18 – 3.10 (m, 1H), 1.29 (s, 9H), 1.07 (s, 9H), 1.05 (d, J = 6.2 Hz, 3H). 13C NMR (151 MHz, DMSO) δ 172.41, 170.74, 169.98, 169.42, 166.06, 162.78, 156.17, 137.95, 133.77, 130.51, 129.14, 124.87, 120.92, 120.47, 119.69, 113.80, 111.67, 78.94, 73.96, 67.07, 64.27, 59.43, 57.23, 52.92, 51.72, 43.02, 36.24, 28.60, 28.53, 24.85, 20.94. MS (ESI) m/z (relative intensity) 672.70 (100) [M+H]+. HRMS (ESI) m/z calculated for C33H35N5O10Na (M + Na)+ 694.3059, found 694.3075.
3H), 3.52 (dd, J = 16.8, 4.7 Hz, 1H), 3.10 – 3.03 (m, 2H), 2.63 (dd, J = 13.7, 9.7 Hz, 1H), 1.29 (s, 9H), 1.21 (s, 9H). 13C NMR (151 MHz, DMSO) δ 176.70, 171.12, 170.86, 169.83, 166.22, 155.47, 138.13, 134.09, 132.73, 132.35, 131.03, 128.56, 124.67, 123.62, 120.88, 119.50, 119.23, 78.98, 78.53, 77.89, 63.60, 56.64, 55.27, 52.85, 51.76, 43.41, 36.44, 29.02, 28.55, 26.66. MS (ESI) m/z (relative intensity) 734.49 (100) [M+H]+. HRMS (ESI) m/z calc for C_{36}H_{52}N_{10}O_{12}Na (M + Na)+ 756.3215, found 756.3220.

According to the general procedure F, the crude residue was purified by flash column chromatography on silica gel (ethyl acetate: petroleum ether= 4:1; R_f=0.27) to yield compound 9f (53.5 mg, 39% yield). 1H NMR (600 MHz, DMSO) δ 11.38 (s, 1H), 8.68 (d, J = 8.4 Hz, 1H), 8.35 (dd, J = 7.7, 4.6 Hz, 1H), 8.22 (d, J = 7.3 Hz, 1H), 7.95 (d, J = 3.8 Hz, 1H), 7.88 (d, J = 15.9 Hz, 1H), 7.29 (d, J = 8.2 Hz, 1H), 7.20 – 7.16 (m, 1H), 7.12 (d, J = 9.2 Hz, 1H), 7.00 (t, J = 7.5 Hz, 1H), 6.40 (d, J = 15.8 Hz, 1H), 4.72 (dd, J = 15.1, 6.9 Hz, 1H), 1.36 (s, 9H), 1.13 (s, 9H).

13C NMR (151 MHz, DMSO) δ 171.85, 170.62, 169.98, 169.76, 160.99, 155.56, 153.97, 133.74, 130.82, 129.71, 129.13, 128.92, 127.40, 124.70, 121.49, 119.58, 119.52, 114.48, 111.42, 80.51, 78.37, 62.66, 57.62, 52.63, 52.40, 50.06, 43.16, 38.01, 36.25, 28.36, 28.11. MS (ESI) m/z (relative intensity) 686.59 (100) [M+H]+. HRMS (ESI) m/z calc for C_{33}H_{47}N_{10}O_{11}Na (M + Na)+ 708.2851, found 708.2868.

According to the general procedure F, the crude residue was purified by flash column chromatography on silica gel (ethyl acetate; R_f=0.2) to yield compound 9g (80.7 mg, 40% yield). 1H NMR (600 MHz, DMSO) δ 11.43 (s, 1H), 8.20 (s, 1H), 8.15 (d, J = 8.9 Hz, 1H), 7.94 (s, 1H), 7.89 (d, J = 7.2 Hz, 1H), 7.63 (d, J = 15.9 Hz, 1H), 7.53 (d, J = 8.0 Hz, 1H), 7.34 (d, J = 8.2 Hz, 1H), 7.22 (t, J = 7.5 Hz, 1H), 7.04 (t, J = 7.6 Hz, 1H), 6.82 (d, J = 9.0 Hz, 1H), 6.70 (d, J = 15.4 Hz, 1H), 6.40 (d, J = 15.9 Hz, 1H), 6.34 (dd, J = 17.3, 1.4 Hz, 1H), 4.78 – 4.68 (m, 2H), 4.55 (d, J = 8.3 Hz, 1H), 4.47 – 4.42 (m, 1H), 4.32 (dd, J = 13.6, 7.5 Hz, 1H), 3.79 (s, 1H), 3.69 (s, 3H), 3.65 (d, J = 6.0 Hz, 1H), 3.63 (s, 1H), 3.29 – 3.19 (m, 2H), 2.96 (s, 3H), 2.84 (dd, J = 15.3, 5.7 Hz, 1H), 2.46 (s, 3H), 2.41 (s, 3H), 1.41 (s, 8H), 1.39 (s, 8H), 1.38 (s, 7H). 13C NMR (151 MHz, DMSO) δ 172.53, 171.08, 169.79, 169.73, 169.02, 166.15, 157.93, 156.49, 155.24, 138.10, 137.24, 133.10, 131.89, 129.21, 124.78, 120.88, 120.53, 119.16, 116.75, 114.61, 86.77, 80.51, 79.00, 62.70, 60.22, 56.24, 52.89, 49.88, 42.94, 37.77, 28.76, 28.61, 28.06, 27.12, 21.22, 19.39, 18.04, 14.55, 12.73. MS (ESI) m/z (relative intensity) 1094.81 (100) [M+H]+. HRMS (ESI) m/z calc for C_{52}H_{71}N_{9}O_{15}S 1116.4683, found 1116.4691.
According to the general procedure F, the crude residue was purified by flash column chromatography on silica gel (ethyl acetate: petroleum ether = 1:1; R<sub>f</sub>=0.43) to yield compound 9i (44.4 mg, 34% yield). ¹H NMR (600 MHz, DMSO) δ 11.38 (s, 1H), 8.26 (dd, J = 7.1, 5.4 Hz, 1H), 8.15 (d, J = 7.6 Hz, 1H), 8.05 (d, J = 8.0 Hz, 1H), 8.02 (d, J = 8.3 Hz, 1H), 7.84 (d, J = 8.0 Hz, 1H), 7.73 (d, J = 15.8 Hz, 1H), 7.30 (d, J = 8.2 Hz, 1H), 7.18 (t, J = 7.6 Hz, 1H), 6.99 (t, J = 7.5 Hz, 1H), 6.87 (d, J = 8.7 Hz, 1H), 6.37 (d, J = 15.8 Hz, 1H), 4.77 – 4.70 (m, 1H), 4.60 – 4.50 (m, 2H), 4.44 (dd, J = 11.3, 3.3 Hz, 1H), 4.41 – 4.33 (m, 1H), 4.06 – 3.99 (m, 1H), 3.91 (td, J = 9.9, 4.7 Hz, 1H), 3.70 (s, 3H), 3.59 (dd, J = 16.8, 4.9 Hz, 1H), 3.49 – 3.43 (m, 2H), 3.09 (dd, J = 14.4, 7.3 Hz, 1H), 1.47 – 1.40 (m, 1H), 1.38 (s, 9H), 1.32 – 1.23 (m, 2H), 1.04 (s, 9H), 0.76 (dd, J = 28.9, 6.6 Hz, 6H). ¹³C NMR (151 MHz, DMSO) δ 192.43, 172.63, 171.33, 169.82, 169.72, 166.31, 155.49, 137.95, 133.83, 131.15, 128.93, 128.22, 124.78, 121.12, 119.75, 118.89, 114.19, 111.48, 78.56, 73.22, 62.51, 61.87, 55.08, 53.98, 53.63, 52.81, 52.12, 43.00, 41.40, 40.50, 28.62, 27.62, 27.58, 26.49, 24.65, 23.39, 21.83. MS (ESI) m/z (relative intensity) 770.90 (100) [M+H]<sup>+</sup>. HRMS (ESI) m/z calculated for C<sub>33</sub>H<sub>44</sub>N<sub>10</sub>O<sub>11</sub>Na (M + Na)<sup>+</sup> 793.3743, found 793.3744.

According to the general procedure F, the crude residue was purified by flash column chromatography on silica gel (ethyl acetate: petroleum ether = 1:1; R<sub>f</sub>=0.23) to yield compound 9j (42.1 mg, 36% yield). ¹H NMR (600 MHz, DMSO) δ 11.34 (s, 1H), 8.25 (d, J = 5.7 Hz, 1H), 7.95 (d, J = 4.7 Hz, 1H), 7.68 (d, J = 8.7 Hz, 1H), 7.62 – 7.56 (m, 2H), 7.34 (d, J = 8.2 Hz, 1H), 7.22 (t, J = 7.6 Hz, 1H), 7.05 (t, J = 7.5 Hz, 1H), 6.90 (d, J = 8.0 Hz, 1H), 6.36 (d, J = 15.8 Hz, 1H), 4.62 (dd, J = 13.7, 5.5 Hz, 1H), 4.47 – 4.33 (m, 2H), 4.28 (dd, J = 13.1, 6.4 Hz, 1H), 4.19 (dd, J = 10.7, 6.5 Hz, 1H), 3.74 (s, 3H), 3.62 (dd, J = 17.1, 6.9 Hz, 1H), 3.38 (s, 1H), 3.33 – 3.16 (m, 2H), 1.40 (s, 9H), 1.22 (d, J = 7.1 Hz, 3H). ¹³C NMR (151 MHz, DMSO) δ 172.50, 171.97, 169.41, 169.13, 166.21, 138.08, 133.24, 132.35, 127.75, 124.79, 119.87, 119.48, 117.17, 115.03, 111.92, 78.98, 64.45, 61.52, 52.70, 52.55, 49.37, 42.40, 28.63, 26.32,
According to the general procedure F, the crude residue was purified by flash column chromatography on silica gel (DCM: MeOH: AcOH= 15:1:0.5; Rf = 0.13) to yield compound 9k (92 mg, 33% yield). $^1$H NMR (600 MHz, MeOD) $\delta$ 7.75 (d, $J = 7.7$ Hz, 1H), 7.71 (d, $J = 15.9$ Hz, 1H), 7.31 (d, $J = 8.2$ Hz, 1H), 7.23 – 7.18 (m, 1H), 7.06 (t, $J = 7.3$ Hz, 1H), 6.25 (d, $J = 15.8$ Hz, 1H), 4.70 – 4.58 (m, 2H), 4.26 (dd, $J = 10.6, 4.3$ Hz, 1H), 4.10 (dd, $J = 32.7, 12.0$ Hz, 2H), 3.65 (d, $J = 12.9$ Hz, 1H), 3.35 (s, 1H), 3.31 – 3.24 (m, 1H), 2.07 (dd, $J = 13.3, 6.6$ Hz, 1H), 1.49 (s, 8H), 1.45 (d, $J = 2.5$ Hz, 1H), 1.01 (dd, $J = 26.2, 6.7$ Hz, 6H). $^{13}$C NMR (151 MHz, MeOD) $\delta$ 166.86, 138.35, 133.43, 131.37, 127.82, 124.34, 119.26, 119.08, 111.79, 113.12, 79.56, 64.51, 60.26, 52.66, 41.72, 29.95, 27.29, 25.80, 18.20, 17.66. MS (ESI) m/z (relative intensity) 598.72 (100) [M-H]+. HRMS (ESI) m/z calcld for C$_{29}$H$_{30}$N$_{4}$O$_{9}$Na (M + Na)$^+$ 622.2483, found 622.2478.

According to the general procedure G(A) to yield compound 10a (68 mg, 85% yield). $^1$H NMR (600 MHz, DMSO) $\delta$ 11.39 (s, 1H), 8.48 (d, $J = 7.1$ Hz, 1H), 8.39 (s, 3H), 8.28 (d, $J = 8.5$ Hz, 1H), 7.98 (d, $J = 8.3$ Hz, 1H), 7.66 (d, $J = 8.0$ Hz, 1H), 7.62 (d, $J = 6.0$ Hz, 1H), 7.49 (t, $J = 4.5$ Hz, 1H), 7.41 (d, $J = 15.7$ Hz, 1H), 7.28 (d, $J = 8.2$ Hz, 1H), 7.17 (t, $J = 7.6$ Hz, 1H), 7.02 (d, $J = 7.6$ Hz, 1H), 6.35 (d, $J = 15.7$ Hz, 1H), 4.68 (ddd, $J = 10.2, 8.6, 3.7$ Hz, 1H), 4.45 (dd, $J = 14.2, 7.1$ Hz, 1H), 4.38 (dd, $J = 14.4, 7.5$ Hz, 1H), 4.31 (t, $J = 10.8$ Hz, 1H), 4.25 (dd, $J = 11.0, 3.3$ Hz, 1H), 3.69 (d, $J = 4.6$ Hz, 1H), 3.62 (s, 3H), 3.57 (s, 1H), 3.20 (d, $J = 7.5$ Hz, 1H), 3.03 (dd, $J = 7.2, 2.5$ Hz, 1H), 2.99 – 2.95 (m, 2H), 2.75 (dd, $J = 16.7, 7.0$ Hz, 1H), 2.47 (t, $J = 8.4$ Hz, 1H), 1.51 – 1.47 (m, 1H), 1.41 – 1.37 (m, 1H), 1.33 – 1.26 (m, 2H). $^{13}$C NMR (151 MHz, DMSO) $\delta$ 172.07, 170.79, 170.60, 169.87, 168.84, 168.08, 166.40, 157.24, 138.19, 132.28, 128.02, 120.18, 119.83, 114.93, 114.13, 112.03, 63.21, 52.81, 51.74, 51.46, 50.16, 46.14, 42.33, 40.72, 35.00, 29.37, 26.79, 25.06, 9.02. MS (ESI) m/z (relative intensity) 686.64 (100) [M+H]$^+$. HRMS (ESI) m/z calcld for C$_{30}$H$_{30}$N$_{4}$O$_{10}$Na (M + Na)$^+$ 708.2712, found 708.2717.

According to the general procedure G(B) to yield compound 10b (51 mg, 95% yield). $^1$H NMR (600 MHz, DMSO) $\delta$ 11.48 (s, 1H), 9.41 (d, $J = 4.5$ Hz, 1H), 8.68 (s, 3H), 7.78 (d, $J = 15.9$ Hz, 1H), 7.61 (d, $J = 7.9$ Hz, 1H), 7.36 (d, $J = 8.1$ Hz, 1H), 7.24 (t, $J = 7.5$ Hz, 1H), 7.07 (dd, $J = 13.1, 6.3$ Hz, 2H), 6.56 (d, $J = 6.7$ Hz, 1H), 6.36 (d, $J = 15.9$ Hz, 1H), 4.85 (d, $J = 10.1$ Hz, 1H), 4.63 (d, $J = 10.1$ Hz, 1H), 4.54 – 4.49 (m, 1H), 4.47 (s, 1H), 4.15 (d, $J = 3.0$ Hz, 1H), 3.92 – 3.87 (m, 1H), 3.78 (dd, $J = 11.3, 5.8$ Hz, 1H), 3.74 – 3.69 (m, 2H), 3.44 – 3.41 (m, 2H), 3.13 (dd, $J = 14.1, 11.3$ Hz, 1H), 1.39 – 1.35 (m, 1H), 1.22 – 1.14 (m, 2H), 0.75 (d, $J = 6.5$ Hz, 3H), 0.67 (d, $J = 6.5$ Hz, 3H). $^{13}$C NMR (151 MHz, DMSO) $\delta$ 172.66, 171.12, 169.57, 168.24, 165.58, 138.40, 135.78, 131.76, 127.74, 119.95, 119.60, 118.61, 113.33, 112.02, 66.83, 65.38, 61.17, 58.50, 52.56, 51.94, 24.57, 23.22, 21.60,
According to the general procedure H to yield compound 10c (51 mg, 40% yield). $^1$H NMR (600 MHz, MeOD) δ 7.83 (d, $J = 15.9$ Hz, 1H), 7.73 (d, $J = 7.7$ Hz, 1H), 7.33 (d, $J = 8.2$ Hz, 1H), 7.24 (t, $J = 7.6$ Hz, 1H), 7.09 (t, $J = 7.4$ Hz, 1H), 6.28 (d, $J = 15.9$ Hz, 1H), 4.74 (s, 2H), 4.62 (d, $J = 9.8$ Hz, 1H), 4.55 (d, $J = 10.8$ Hz, 1H), 4.42 (s, 1H), 4.20 – 4.15 (m, 1H), 4.04 (d, $J = 10.1$ Hz, 1H), 3.89 (d, $J = 10.7$ Hz, 1H), 3.66 – 3.58 (m, 1H), 3.27 – 3.18 (m, 1H), 1.33 – 1.29 (m, 1H), 0.82 (dd, $J = 39.4, 6.6$ Hz, 6H).

$^{13}$C NMR (151 MHz, MeOD) δ 166.50, 156.18, 138.54, 134.75, 131.08, 127.77, 124.72, 119.90, 119.45, 119.05, 118.90, 112.50, 110.99, 79.69, 65.39, 60.68, 57.41, 53.13, 52.36, 39.51, 27.29, 24.52, 22.00, 20.09. MS (ESI) m/z (relative intensity) 530.81 (100) [M+H]$^+$. HRMS (ESI) m/z calcd for C$_{25}$H$_{32}$N$_5$O$_8$Na (M + Na)$^+$ 552.2065, found 552.2066.

According to the general procedure D, the crude residue was purified by flash column chromatography on silica gel (ethyl acetate: petroleum ether= 1:4; $R_f = 0.4$) to yield compound 3a (63.5mg, 76% yield). $^1$H NMR (500 MHz, CDCl$_3$) δ 9.16 (s, 1H), 7.64 (d, $J = 15.9$ Hz, 1H), 7.55 (d, $J = 7.9$ Hz, 1H), 7.19 (dt, $J = 14.8, 8.0$ Hz, 2H), 7.07 (ddd, $J = 8.0, 6.7, 1.2$ Hz, 1H), 6.27 (d, $J = 15.9$ Hz, 1H), 5.20 (d, $J = 8.4$ Hz, 1H), 4.79 – 4.68 (m, 1H), 4.33 – 4.16 (m, 2H), 3.72 (s, 3H), 3.42 (qd, $J = 14.6, 5.3$ Hz, 2H), 1.45 (s, 9H), 1.33 (t, $J = 7.1$ Hz, 3H). $^{13}$C NMR (126 MHz, CDCl$_3$) δ 172.27, 167.09, 155.11, 137.45, 132.31, 129.99, 128.69, 125.03, 125.01, 120.18, 119.89, 116.04, 115.19, 111.18, 80.03, 60.57, 54.46, 52.51, 29.67, 28.31, 27.23, 14.32. HRMS (ESI) m/z calcd for C$_{22}$H$_{28}$N$_2$O$_6$Na (M + Na)$^+$ 439.1840, found 439.1841.

According to the general procedure D, the crude residue was purified by flash column chromatography on silica gel (ethyl acetate: petroleum ether= 1:8; $R_f = 0.45$) to yield compound 3a (23.7mg, 55% yield). $^1$H NMR (500 MHz, CDCl$_3$) δ 8.42 (s, 1H), 7.85 (d, $J = 16.0$ Hz, 1H), 7.60 (dq, $J = 7.9, 0.8$ Hz, 1H), 7.33 (dt, $J = 8.2, 1.0$ Hz, 1H), 7.28 (ddd, $J = 8.1, 6.9, 1.1$ Hz, 1H), 7.13 (ddd, $J = 8.0, 6.9, 1.1$ Hz, 1H), 6.19 (d, $J = 16.0$ Hz, 1H), 4.32 (q, $J = 7.1$ Hz, 2H), 2.44 (s, 3H), 1.38 (t, $J = 7.1$ Hz, 3H). $^{13}$C NMR (126 MHz, CDCl$_3$) δ 167.38, 137.45, 132.31, 129.99, 129.08, 125.03, 119.89, 118.71, 113.83, 110.97, 60.56, 29.70, 14.38, 8.91. HRMS (ESI) m/z calcd for C$_{13}$H$_{13}$NO$_2$Na (M + Na)$^+$ 238.0838, found 238.0840.
L. $^1$H NMR and $^{13}$C NMR of products

$^1$H NMR (600 MHz, DMSO) spectrum of 3a

$^{13}$C NMR (151 MHz, DMSO) spectrum of 3a
$^1$H NMR (500 MHz, DMSO) spectrum of 3b

$^1$C NMR (126 MHz, DMSO) spectrum of 3b
$^1$H NMR (600 MHz, DMSO) spectrum of 3c

$^1$C NMR (151 MHz, DMSO) spectrum of 3c
$^1$H NMR (600 MHz, CDCl$_3$) spectrum of 3d

Chemical Formula: $C_{24}H_{35}N_2O_6$
Exact Mass: 444.2260

$^1$C NMR (151 MHz, CDCl$_3$) spectrum of 3d

Chemical Formula: $C_{24}H_{35}N_2O_6$
Exact Mass: 444.2260
\textsuperscript{1}H NMR (600 MHz, CDCl$_3$) spectrum of 3e

\textsuperscript{13}C NMR (151 MHz, CDCl$_3$) spectrum of 3e
$^1$H NMR (600 MHz, CDCl$_3$) spectrum of 3f

$^1$C NMR (151 MHz, CDCl$_3$) spectrum of 3f
**S37**

**H NMR (600 MHz, CDCl\_3) spectrum of 3g**

Chemical Formula: C\textsubscript{20}H\textsubscript{14}N\textsubscript{2}O\textsubscript{5}

Exact Mass: 372.1685

**C NMR (151MHz, CDCl\_3) spectrum of 3g**

Chemical Formula: C\textsubscript{20}H\textsubscript{14}N\textsubscript{2}O\textsubscript{5}

Exact Mass: 372.1685

**1^H NMR (600 MHz, CDCl\_3) spectrum of 3g**

**1^C NMR (151MHz, CDCl\_3) spectrum of 3g**
$^1$H NMR (600 MHz, CDCl$_3$) spectrum of 3h

$^1$C NMR (151 MHz, CDCl$_3$) spectrum of 3h
H NMR (600 MHz, DMSO) spectrum of \(3i\)

\[^1^H\text{NMR (600 MHz, DMSO)}\) spectrum of \(3i\)

\(^1^C\text{NMR (151 MHz, DMSO)}\) spectrum of \(3i\)

Chemical Formula: \(C_{10}H_{12}N_2O_4\)

Exact Mass: 343.1532
$^1$H NMR (400 MHz, DMSO) spectrum of $5a$

$^1$C NMR (101 MHz, DMSO) spectrum of $5a$
$^1$H NMR (600 MHz, CDCl$_3$) spectrum of 5b

$^1$C NMR (151 MHz, CDCl$_3$) spectrum of 5b
H NMR (600 MHz, CDCl₃) spectrum of 5c

$^{13}$C NMR (151 MHz, CDCl₃) spectrum of 5c
$^1$H NMR (600 MHz, CDCl$_3$) spectrum of 5d

$^1$C NMR (151 MHz, CDCl$_3$) spectrum of 5d
\(^1\)H NMR (600 MHz, CDCl\(_3\)) spectrum of 5e

\(^{13}\)C NMR (151 MHz, CDCl\(_3\)) spectrum of 5e
$^1$H NMR (600 MHz, CDCl$_3$) spectrum of 5f

$^1$C NMR (151 MHz, CDCl$_3$) spectrum of 5f
$^1$H NMR (600 MHz, CDCl$_3$) spectrum of 5g

$^1$C NMR (151 MHz, CDCl$_3$) spectrum of 5g
$^1$H NMR (600 MHz, CDCl$_3$) spectrum of 5h

$^1$C NMR (151 MHz, CDCl$_3$) spectrum of 5h
$^1$H NMR (600 MHz, CDCl$_3$) spectrum of 5i

$^1$C NMR (151 MHz, CDCl$_3$) spectrum of 5i
$^1$H NMR (500 MHz, CDCl$_3$) spectrum of 5j

$^1$C NMR (126 MHz, CDCl$_3$) spectrum of 5j
$^{1}$H NMR (600 MHz, CDCl$_3$) spectrum of 5k

$^{13}$C NMR (151 MHz, CDCl$_3$) spectrum of 5k
$^{1}$H NMR (600 MHz, DMSO) spectrum of 51

$^{13}$C NMR (151 MHz, DMSO) spectrum of 51
$^1$H NMR (600 MHz, CDCl$_3$) spectrum of 5m

$^1$C NMR (151 MHz, CDCl$_3$) spectrum of 5m
$^1$H NMR (600 MHz, CDCl$_3$) spectrum of 5n

Chemical Formula: C$_{10}$H$_{14}$N$_3$O$_7$

Exact Mass: 555.2945

$^1$C NMR (151 MHz, CDCl$_3$) spectrum of 5n

Chemical Formula: C$_{10}$H$_{14}$N$_3$O$_7$

Exact Mass: 555.2945
$^1$H NMR (600 MHz, CDCl$_3$) spectrum of 5o

Chemical Formula: C$_{12}$H$_{18}$N$_2$O$_6$

Exact Mass: 614.3316

$^1$C NMR (151 MHz, CDCl$_3$) spectrum of 5o

Chemical Formula: C$_{12}$H$_{18}$N$_2$O$_6$

Exact Mass: 614.3316
$^{1}$H NMR (600 MHz, CDCl$_3$) spectrum of 5p

Chemical Formula: C$_{30}$H$_{42}$N$_{2}$O$_{8}$
Exact Mass: 586.3003
$^1$H NMR (600 MHz, CDCl$_3$) spectrum of 5q

$^1$C NMR (151 MHz, CDCl$_3$) spectrum of 5q
$^1$H NMR (600 MHz, CDCl$_3$) spectrum of 5r

Chemical Formula: C$_{26}$H$_{32}$N$_2$O$_{10}$
Exact Mass: 700.3683

$^1$C NMR (151 MHz, CDCl$_3$) spectrum of 5r

Chemical Formula: C$_{26}$H$_{32}$N$_2$O$_{10}$
Exact Mass: 700.3683
$^1$H NMR (600 MHz, DMSO) spectrum of $5s$

$^1$C NMR (151 MHz, DMSO) spectrum of $5s$
$^{1}H$ NMR (600 MHz, CDCl$_3$) spectrum of 7a

Chemical Formula: C$_{29}$H$_{33}$N$_{5}$O$_{10}$
Exact Mass: 589.2635

$^{13}$C NMR (151 MHz, CDCl$_3$) spectrum of 7a

Chemical Formula: C$_{29}$H$_{33}$N$_{5}$O$_{10}$
Exact Mass: 589.2635
$^1$H NMR (600 MHz, CDCl$_3$) spectrum of 7b

$^1$C NMR (151 MHz, CDCl$_3$) spectrum of 7b
$^1$H NMR (600 MHz, DMSO) spectrum of 7c

$^1$C NMR (151 MHz, DMSO) spectrum of 7c
$\text{H NMR (600 MHz, DMSO) spectrum of 7d}$

$\text{C NMR (151 MHz, DMSO) spectrum of 7d}$
$^1$H NMR (600 MHz, DMSO) spectrum of $7e$

$^1$C NMR (151 MHz, DMSO) spectrum of $7e$
$^1$H NMR (600 MHz, DMSO) spectrum of 7f

$^1$C NMR (151 MHz, DMSO) spectrum of 7f
\[ ^1H \text{NMR (600 MHz, DMSO)} \text{ spectrum of 7g} \]

\[ ^1C \text{NMR (151 MHz, DMSO)} \text{ spectrum of 7g} \]
$^1$H NMR (600 MHz, DMSO) spectrum of 7h

$^1$C NMR (151 MHz, DMSO) spectrum of 7h
\[ ^1H \text{ NMR (600 MHz, DMSO) spectrum of 9b} \]

\[ ^1C \text{ NMR (151 MHz, DMSO) spectrum of 9b} \]
$^{1}$H NMR (600 MHz, DMSO) spectrum of 9c

$^{13}$C NMR (151 MHz, DMSO) spectrum of 9c
$^{1}H$ NMR (600 MHz, DMSO) spectrum of 9d

$^{13}C$ NMR (151 MHz, DMSO) spectrum of 9d
$^1$H NMR (600 MHz, DMSO) spectrum of 9e

$^1$C NMR (151 MHz, DMSO) spectrum of 9e
$^1$H NMR (600 MHz, DMSO) spectrum of 9f

$^1$C NMR (151 MHz, DMSO) spectrum of 9f
$^1$H NMR (600 MHz, DMSO) spectrum of 9g

$^{13}$C NMR (600 MHz, DMSO) spectrum of 9g
$^1$H NMR (600 MHz, DMSO) spectrum of 9h

$^1$C NMR (151 MHz, DMSO) spectrum of 9h
$^1$H NMR (600 MHz, DMSO) spectrum of 9i

$^1$C NMR (151 MHz, DMSO) spectrum of 9i
$^1$H NMR (600 MHz, DMSO) spectrum of $9j$

$^1$C NMR (151 MHz, DMSO) spectrum of $9j$
$^1$H NMR (600 MHz, DMSO) spectrum of 9k

$^1$C NMR (151 MHz, DMSO) spectrum of 9k
\(^1\)H NMR (600 MHz, DMSO) spectrum of 10a

\(^1\)C NMR (151 MHz, DMSO) spectrum of 10a
$^{1}$H NMR (600 MHz, DMSO) spectrum of 10b

$^{13}$C NMR (151 MHz, DMSO) spectrum of 10b
H NMR (600 MHz, CD$_3$OD) spectrum of 10c

Chemical Formula: C$_{20}$H$_{14}$N$_{4}$O$_{8}$$^+$
Exact Mass: 530.2245

C NMR (151 MHz, CD$_3$OD) spectrum of 10c

Chemical Formula: C$_{20}$H$_{14}$N$_{4}$O$_{8}$$^+$
Exact Mass: 530.2245

579
$^1$H NMR (500 MHz, CDCl$_3$) spectrum of rac-3a

$^1$C NMR (126 MHz, CDCl$_3$) spectrum of rac-3a
$^1$H NMR (500 MHz, CDCl$_3$) spectrum of olifination derivative of 3-methyl indole

$^1$C NMR (126 MHz, CDCl$_3$) spectrum of olifination derivative of 3-methyl indole