Supporting Information

Rapid Access to Azetidines via Allylation of Azabicyclo[1.1.0]butanes by Dual Copper/Photoredox Catalysis

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1 General information

Unless otherwise noted, all reactions of substrates preparation were conducted in flame – dried glassware under a nitrogen atmosphere using anhydrous solvent passed through an activated alumina column (Innovative Technology). Commercially available reagents were used without further purification. Thin layer chromatography (TLC) was performed using Huanghai TLC silica gel plates HSG F254 and visualized using UV light, anisaldehyde or potassium permanganate. The photocatalytic reactions were performed on WATTCAS Parallel Light Reactor (WP – TEC – 1020L) with 10W LED. ¹H and ¹³C NMR spectra were recorded in CDCl₃ on a Bruker 400M spectrometer. Chemical shifts in ¹H NMR spectra were reported in parts per million (ppm) on the δ scale from an internal standard of residual CDCl₃ (7.26 ppm). Data for ¹H NMR were reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad), coupling constant in Hertz (Hz) and integration. Data for ¹³C NMR spectra were reported in terms of chemical shift in ppm from the central peak of CDCl₃ (77.00 ppm). HP 8453 spectrometer was used as the light source for the UV-Vis data. The fluorescence emission spectra were collected on an Edinburgh FLS1000.

2 Picture of reaction set up

The photocatalytic reactions were performed on WATTCAS Parallel Light Reactor (WP – TEC - 1020L).



Figure 1 Picture of the photoreactor

Emission spectra of the 10 W blue LED lamp (maximum emission at $\lambda = 450$ nm). Distance between light source and quartz tube was approximately 0.5 cm and no filter was used for the reaction.

3 Preparation of 1-azabicyclo[1.1.0]butane



Table S1 Preparation of 1-azabicyclo[1.1.0]butane

Step 1. According to a literature procedure¹, an oven-dried Schlenk tube (100 mL) equipped with a magnetic stir bar was cooled to 0 °C under N₂ protection, and add EtOH (25 mL). The mixture was subsequently stirred for 15 minutes at same temperature. Next, Br₂ (10.0 mL, 196 mmol, 2.2 equiv.) was added slowly dropwise to a vigorously stirring ethanol. After the addition was completed, allylamine **S1** (6.7 mL, 90 mmol, 1.0 equiv.) was then added slowly dropwise into the reaction mixture. The ice bath was removed following the addition, and the mixture was stirred at room temperature for 16 h. The resulting precipitate was collected via suction filtration and washed with Et₂O. The crude residue was subsequently dissolved in the methanol (10 mL) followed by a small amount of Et₂O (50 mL) was added until a white precipitate formed. After the complete precipitation, the desired ammonium salt **S2** (21 g, 79%) was collected as a white solid via suction filtration and thoroughly dried under high vacuum.

Step 2. An oven-dried Schlenk tube (50 mL) equipped with a magnetic stir bar was charged with the ammonium salt S2 (1.3 equiv.) and add dry THF (23 mL) under N₂ protection. n-BuLi (2.5 M in Hexane, 4.5 equiv.) was added slowly dropwise (at a rate of 3 mL/h) to a suspension of ammonium salt solution at -50 °C. After the addition was completed, the resulting solution was stirred for 2 h at -50 °C. Then, the Weinreb amide (2.3 mmol, 1.0 equiv.), in dry THF (5 mL), was added slowly dropwise (at a rate of 5.0 mL).

mL/h, syringe pump) into the mixture. After the addition was completed, the reaction flask was removed from cooling bath, and the resulting solution was stirred at room temperature for 2 h. The reaction was quenched with water (15 mL) and then extracted with ethyl acetate (25.0 mL x 3). The combined organic phase was washed with brine, dried over Na₂SO₄, filtered, and concentrated under reduced pressure. The crude residue was purified by silica gel column chromatography (PE:EA = 10:1 to 2:1) to obtain the desired products **1**.

The characterization data for 1-azabicyclo[1.1.0]butanes 1a, 1b, 1c, 1d, 1e, 1k, 1l, 1m, 1q and 1r were consistent with respective reported literature.¹



¹**H NMR** (400 MHz, CDCl₃) δ 7.91 (s, 1H), 7.83 (dt, J = 7.7, 1.3 Hz, 1H), 7.55 (ddd, J = 8.0, 2.2, 1.1 Hz, 1H), 7.41 (t, J = 7.9 Hz, 1H), 3.05 (s, 2H), 1.76 (s, 2H). ¹³**C NMR** (101 MHz, CDCl₃) δ 196.0, 137.8, 134.8, 133.3, 129.9, 128.6, 126.8, 56.7, 28.5. **HRMS**: calculated for C₁₀H₉ClNO [M+H]⁺ 194.0367; found 194.0369.



¹**H** NMR (400 MHz, CDCl₃) δ 7.65 (dd, J = 7.7, 1.7 Hz, 1H), 7.38 (td, J = 7.5, 1.5 Hz, 1H), 7.25 (d, J = 7.7 Hz, 2H), 2.95 (s, 2H), 2.46 (s, 3H), 1.71 (s, 2H). ¹³**C** NMR (101 MHz, CDCl₃) δ 201.0, 137.7, 136.2, 131.5, 131.4, 129.0, 125.3, 56.6, 30.1, 20.2. **HRMS**: calculated for C₁₁H₁₂NO [M+H]⁺ 174.0913; found



174.0916.



¹**H NMR** (400 MHz, CDCl₃) δ 7.68 – 7.63 (m, 1H), 7.60 – 7.47 (m, 1H), 7.24 – 7.20 (m, 1H), 7.18 – 7.09 (m, 1H), 3.02 (s, 2H), 1.77 (s, 2H). ¹³**C NMR** (101 MHz, CDCl₃) δ 196.9 (d, J = 2.6 Hz), 160.9 (d, J = 254.4 Hz), 134.5 (d, J = 8.7 Hz), 130.2 (d, J = 2.3 Hz), 125.3 (d, J = 13.8 Hz), 124.4 (d, J = 3.6 Hz), 116.4 (d, J = 21.9 Hz), 56.7 (d, J = 2.8 Hz), 30.4, 30.4. ¹⁹**F NMR** (377 MHz, CDCl₃) δ -110.8. **HRMS**: calculated for C₁₀H₉FNO [M+H]⁺ 178.0663; found 178.0665.



1i

¹**H NMR** (400 MHz, CDCl₃) δ 7.47 (dd, J = 8.5, 6.0 Hz, 1H), 7.36 (dd, J = 8.2, 2.1 Hz, 1H), 7.09 (td, J = 8.3, 2.2 Hz, 1H), 2.92 (s, 2H), 1.78 (s, 2H). ¹³**C NMR** (101 MHz, CDCl₃) δ 199.6, 163.5 (d, J = 256.4

Hz), 131.2, 131.1, 120.8 (d, J = 24.6 Hz), 120.8, 114.8 (d, J = 21.3 Hz), 57.1, 30.2. ¹⁹F NMR (377 MHz, CDCl₃) δ -106.0. HRMS: calculated for C₁₀H₈BrFNO [M+H]⁺ 255.9768; found 255.9772.



¹**H NMR** (400 MHz, CDCl₃) δ 7.59 (s, 2H), 7.39 – 7.14 (s, 1H), 3.05 (s, 2H), 2.38 (s, 6H), 1.74 (s, 2H). ¹³**C NMR** (101 MHz, CDCl₃) δ 197.3, 138.2, 136.5, 135.1, 126.4, 56.6, 28.6, 21.1. **HRMS**: calculated for C₁₂H₁₄NO [M+H]⁺ 188.1070; found 188.1073.



1n

¹**H** NMR (400 MHz, CDCl₃) δ 8.08 (s, 1H), 7.44 (d, J = 1.6 Hz, 1H), 6.78 (d, J = 1.8 Hz, 1H), 3.03 (s, 2H), 1.63 (s, 2H). ¹³**C** NMR (101 MHz, CDCl₃) δ 190.3, 148.0, 144.2, 126.5, 108.6, 55.6, 29.5. **HRMS**: calculated for C₈H₈NO₂ [M+H]⁺ 150.0550; found 150.0551.



¹**H** NMR (400 MHz, CDCl₃) δ 9.27 – 9.14 (m, 1H), 8.79 – 8.69 (m, 1H), 8.60 (dd, *J* = 4.5, 2.2 Hz, 1H), 3.41 (s, 2H), 1.76 (s, 2H). ¹³**C** NMR (101 MHz, CDCl₃) δ 196.7, 147.9, 147.6, 144.2, 143.1, 57.6, 29.0. **HRMS**: calculated for C₈H₇N₃NaO [M+Na]⁺ 184.0481; found 184.0481.

1p

¹**H NMR** (500 MHz, CDCl₃) δ 3.44 (t, J = 8.5 Hz, 1H), 2.86 (s, 2H), 2.44 – 2.27 (m, 2H), 2.21 – 2.09 (m, 2H), 1.99 (dp, J = 10.4, 8.4 Hz, 1H), 1.87 (tq, J = 10.0, 5.1, 4.6 Hz, 1H), 1.50 (s, 2H). ¹³**C NMR** (126 MHz, CDCl₃) δ 207.1, 55.0, 42.5, 24.3, 17.9. **HRMS**: calculated for C₈H₁₂NO [M+H]⁺ 138.0913; found 138.0915.



¹**H** NMR (400 MHz, CDCl₃) δ 2.87 (t, J = 1.2 Hz, 2H), 1.62 (s, 1H), 1.46 (t, J = 1.2 Hz, 2H), 1.21 (s, 6H), 1.20 (s, 6H). ¹³**C** NMR (101 MHz, CDCl₃) δ 203.8, 55.0, 41.2, 35.8, 32.0, 23.7, 16.3. **HRMS**: calculated for C₁₁H₁₈NO [M+H]⁺ 180.1383; found 180.1386.



¹**H NMR** (400 MHz, CDCl₃) δ 2.90 (s, 2H), 2.18 – 1.99 (m, 3H), 1.90 (d, *J* = 3.0 Hz, 6H), 1.71 (qd, *J* = 15.3, 13.6, 3.3 Hz, 6H), 1.45 (s, 2H). ¹³**C NMR** (101 MHz, CDCl₃) δ 209.0, 55.8, 47.5, 37.8, 36.3, 27.6. **HRMS**: calculated for C₁₄H₂₀NO [M+H]⁺ 218.1539; found 218.1543.





¹**H** NMR (400 MHz, CDCl₃) δ 7.31 – 7.26 (m, 2H), 7.23 – 7.15 (m, 3H), 2.97 – 2.92 (m, 4H), 2.88 – 2.84 (m, 2H), 1.54 (s, 2H). ¹³**C** NMR (101 MHz, CDCl₃) δ 205.3, 140.5, 128.5, 128.2, 126.2, 55.3, 40.8, 29.8, 29.2. **HRMS**: calculated for C₁₂H₁₄NO [M+H]⁺ 188.1070; found 188.1071.



¹**H NMR** (400 MHz, CDCl₃) δ 7.12 (dd, J = 8.5, 5.5 Hz, 2H), 6.98 – 6.93 (m, 2H), 2.92 – 2.88 (m, 4H), 2.86 – 2.79 (m, 2H), 1.54 (s, 2H). ¹³**C NMR** (101 MHz, CDCl₃) δ 205.1, 161.3 (d, J = 244.1 Hz), 136.1 (d, J = 3.3 Hz), 129.6 (d, J = 8.0 Hz), 115.2 (d, J = 21.5 Hz), 55.3, 40.7, 29.7, 28.3. ¹⁹**F NMR** (377 MHz, CDCl₃) δ -117.0. **HRMS**: calculated for C₁₂H₁₃FNO [M+H]⁺ 206.0976; found 206.0981.



¹**H NMR** (400 MHz, CDCl₃) δ 6.78 (d, J = 8.2 Hz, 1H), 6.70 (d, J = 6.5 Hz, 2H), 3.85 (s, 3H), 3.84 (s, 3H), 2.93 (s, 2H), 2.85 (dp, J = 10.4, 5.3, 4.3 Hz, 4H), 1.54 (s, 2H). ¹³**C NMR** (101 MHz, CDCl₃) δ 205.4, 148.8, 147.3, 133.1, 120.0, 111.5, 111.2, 55.8, 55.7, 55.3, 41.0, 29.8, 28.8. **HRMS**: calculated for C₁₄H₁₈NO₃ [M+H]⁺ 248.1281; found 248.1284.



¹**H NMR** (400 MHz, CDCl₃) δ 7.32 (td, J = 8.0, 7.6, 3.1 Hz, 2H), 7.29 – 7.22 (m, 1H), 7.21 – 7.15 (m, 2H), 3.70 (td, J = 7.4, 2.0 Hz, 1H), 2.85 (s, 2H), 2.06 (ddd, J = 17.3, 8.5, 5.5 Hz, 1H), 1.80 – 1.63 (m, 1H), 1.40 (s, 2H), 0.81 (td, J = 7.4, 3.3 Hz, 3H). ¹³**C NMR** (101 MHz, CDCl₃) δ 205.7, 138.0, 128.9, 128.4, 127.3, 56.9, 55.7, 55.4, 29.9, 25.7, 11.8. **HRMS**: calculated for C₁₃H₁₆NO [M+H]⁺ 202.1226; found 202.1229.



¹**H NMR** (400 MHz, CDCl₃) δ 7.19 (dd, J = 9.0, 0.9 Hz, 2H), 6.77 (d, J = 8.8 Hz, 2H), 3.12 (d, J = 1.4 Hz, 2H), 1.53 (s, 6H), 1.48 (d, J = 1.4 Hz, 2H). ¹³**C NMR** (101 MHz, CDCl₃) δ 209.3, 153.6, 129.3, 127.5, 120.1, 84.7, 56.1, 27.3, 24.5. **HRMS**: calculated for C₁₃H₁₅ClNO₂ [M+H]⁺ 252.0786; found 252.0790.



¹**H NMR** (400 MHz, CDCl₃) δ 8.02 (d, J = 8.2 Hz, 2H), 7.87 (d, J = 8.0 Hz, 2H), 3.09 – 3.04 (m, 6H), 1.78 (s, 2H), 1.51 (dt, J = 14.8, 7.4 Hz, 4H), 0.81 (dt, J = 16.4, 8.0 Hz, 6H). ¹³**C NMR** (101 MHz, CDCl₃) δ 196.5, 144.3, 139.0, 129.1, 127.0, 127.0, 56.7, 56.7, 49.8, 28.6, 21.8, 21.8, 11.0, 11.0. **HRMS**: calculated for C₁₇H₂₄NO₃S [M+H]⁺ 322.1471; found 322.1476.



1aa

¹**H NMR** (400 MHz, CDCl₃) δ 7.66 – 7.60 (m, 2H), 7.59 – 7.53 (m, 2H), 7.42 – 7.27 (m, 6H), 3.17 (s, 4H), 3.01 (s, 2H), 1.59 (s, 2H). ¹³**C NMR** (101 MHz, CDCl₃) δ 204.1, 161.7, 145.3, 135.0, 132.3, 128.8, 128.5, 128.4, 128.3, 127.9, 127.8, 126.3, 55.4, 35.7, 29.7, 21.7. **HRMS**: calculated for C₂₁H₁₉N₂O₂ [M+H]⁺ 331.1441; found 331.1445.



¹**H NMR** (500 MHz, CDCl₃) δ 7.83 – 7.64 (m, 4H), 7.49 – 7.41 (m, 2H), 6.93 – 6.83 (m, 2H), 3.09 (s, 2H), 1.62 (s, 6H), 1.46 (s, 2H). ¹³**C NMR** (126 MHz, CDCl₃) δ 209.1, 194.0, 159.2, 138.4, 136.1, 132.1, 131.1, 130.9, 128.5, 117.4, 85.0, 56.0, 27.3, 24.7. **HRMS**: calculated for C₂₀H₁₉ClNO₃ [M+H]⁺ 356.1048; found 356.1052.





¹**H NMR** (400 MHz, CDCl₃) δ 7.09 (s, 4H), 3.93 (q, *J* = 6.9 Hz, 1H), 2.97 – 2.77 (m, 2H), 2.44 (d, *J* = 7.2 Hz, 2H), 1.84 (dt, *J* = 13.5, 6.8 Hz, 1H), 1.48 – 1.31 (m, 5H), 0.89 (s, 3H), 0.87 (s, 3H). ¹³**C NMR** (101 MHz, CDCl₃) δ 206.2, 140.7, 136.9, 129.7, 127.5, 55.8, 55.3, 49.2, 44.9, 30.0, 29.5, 22.3, 18.2. **HRMS**: calculated for C₁₆H₂₂NO [M+H]⁺ 244.1696; found 244.1699.

4 Optimization of reaction conditions

4.1 The effect of copper salts

| O N | + / + | TMSCN | [Cu] (10 mol%) 4CzIPN (2 mol%) Boc ₂ O (2.5 equiv) LiBr (2 equiv) 450 nm LEDs | NC O | | |
|--------------------|-------|-------|--|------|--|--|
| 1a | 2 | 3 | CH ₃ CN (0.1 M), RT, 28 h | 4a | | |
| Entry ^a | | [Cu] | | | | |
| 1 | | 74 | | | | |
| 2 | | CuCN | | | | |
| 3 | | 84 | | | | |

[a] Reaction conditions: **1a** (0.2 mmol, 1 equiv.), **2** (2 equiv.), **3** (1.5 equiv.), 28 h. [b] Yields were determined by ¹H NMR analysis with 1,3,5-trimethoxybenzene as the internal standard.

4.2 The effect of additives

| O N | + // + | TMSCN | Cu(CH ₃ CN) ₄ PF ₆ (10 mol%) 4CzIPN (2 mol%) Boc ₂ O (2.5 equiv) [Additives] (2 equiv) | NC | |
|--------------------|--------|-------------|---|----|--|
| 1a | 2 | 3 | 450 nm LEDs CH ₃ CN (0.1 M), RT, 28 h | 4a | |
| Entry ^a | | [additives] | | | |
| 1 | | 71 | | | |
| 2 | | 38 | | | |
| 3 | | 84 | | | |

[a] Reaction conditions: **1a** (0.2 mmol, 1 equiv.), **2** (2 equiv.), **3** (1.5 equiv.), 28 h. [b] Yields were determined by ¹H NMR analysis with 1,3,5-trimethoxybenzene as the internal standard.

4.3 The effect of solvents



[a] Reaction conditions: **1a** (0.2 mmol, 1 equiv.), **2** (2 equiv.), **3** (1.5 equiv.), 28 h. [b] Yields were determined by ¹H NMR analysis with 1,3,5-trimethoxybenzene as the internal standard.

4.4 The effect of photocatalysts



[a] Reaction conditions: **1a** (0.2 mmol, 1 equiv.), **2** (2 equiv.), **3** (1.5 equiv.), 28 h. [b] Yields were determined by ¹H NMR analysis with 1,3,5-trimethoxybenzene as the internal standard.

| 1a O N N 1a | + + + | TMSCN 3 | Cu(CH ₃ CN) ₄ PF ₆ (10 mol%) 4CzIPN (2 mol%) Boc ₂ O (2.5 equiv) LiBr (2 equiv) 450 nm LEDs CH ₃ CN (0.1 M), RT, 28 h | NC 4a | |
|-------------------------|--------|--|---|----------|--|
| Entry ^a | [varia | Yield of $4a (\%)^b$ | | | |
| 1 | | none | | | |
| 2 | | no Cu(CH ₃ CN) ₄ PF ₆ | | | |
| 3 | | no LiBr | | | |
| 4 | | no 4CzIPN | | | |
| 5 | | no light | | | |

4.5 Control Experiments

[a] Reaction conditions: **1a** (0.2 mmol, 1 equiv.), **2** (2 equiv.), **3** (1.5 equiv.), 28 h. [b] Yields were determined by ¹H NMR analysis with 1,3,5-trimethoxybenzene as the internal standard. [c] Isolated yield.

5 Stern-Volmer luminescence quenching analysis

Emission intensities were recorded using Edinburgh FLS1000 Fluorescense Spectrophotometer for all experiments. All samples used in the luminescence quenching-based screening studies were prepared under oxygen-free conditions. The quenchers were weighed into vials and placed inside a glovebox under a positive pressure of argon. CH_3CN was degassed by argon sparging for one hour and also placed inside along with micropipettes and their tips, cuvettes, empty vials, waste containers and parafilm. The solutions were irradiated at 374 nm and the emission intensity was collected at 450-700 nm. The excited state lifetime of the 4CzIPN is $5.1\mu s.^2$



Figure S2 4CzIPN emission quenching by Cu(CH₃CN)₄PF₆.



Figure S3 4CzIPN emission quenching by 1a+Boc₂O adduct.



Figure S4 4CzIPN emission quenching by 3-brominated azetidine 9.

6 Mechanistic Studies



6.1 Radical trapping experiments

Scheme S1 Radical trapping experiments

In a flame-dried 10 mL reaction tube equipped with a magnetic stirrer bar was added with $Cu(CH_3CN)_4PF_6$ (0.1 equiv.), 4CzIPN (0.02 equiv.), Boc_2O (2.5 equiv.), LiBr (2 equiv.) and **1a** (0.2 mmol, 1.0 equiv.). The reaction tube was transferred to an argon-filled glovebox and followed by the addition of CH₃CN (0.1 M), 1,3-butadiene **2** (2 M in THF, 2 equiv.), TMSCN **3** (1.5 equiv.) and TEMPO (0.4 mmol, 2 equiv.). The resulting mixture was removed out the glovebox. Then, the reaction mixture was stirred at room temperature with irradiation of 10 W 450 nm LED for 28 h. The reaction solution was detected by ¹H NMR analysis and the **4a** was not found. However, when ABB **1a** reacted without 1,3-butadiene and TMSCN, the radical-trapping adduct **8** was derived in 87% yield.

6.2 The evidence for the presence 3-brominated azetidine



Scheme S2 The evidence for the presence 3-brominated azetidine

To a solution of **1a** (0.5 mmol, 1 equiv.) in dry CH₃CN (0.1 M) was added Boc₂O (2.5 equiv.) and LiBr (2 equiv.) under N₂ protection. Then, the reaction mixture was stirred at room temperature for 12 h. The solvent was evaporated in vacuo and the crude material was purified by flash column chromatography to furnish the product **9**. Then, in a flame-dried 10 mL reaction tube equipped with a magnetic stirrer bar was added with Cu(CH₃CN)₄PF₆ (0.1 equiv.), 4CzIPN (0.02 equiv.), Na₂CO₃ (1 equiv.) and **1a** (0.2 mmol, 1.0 equiv.). The reaction tube was transferred to an argon-filled glovebox and followed by the addition of CH₃CN (0.1 M), 1,3-butadiene **2** (2 M in THF, 2 equiv.) and TMSCN **3** (1.5 equiv.). Then, the resulting mixture was removed out the glovebox and stirred at room temperature with irradiation of 10 W 450 nm LED for 28 h. The product **4a** was derived in 73% yield

7 General procedure and characterization data



In a flame-dried 10 mL reaction tube equipped with a magnetic stirrer bar was added with $Cu(CH_3CN)_4PF_6$ (0.1 equiv.), 4CzIPN (0.02 equiv.), Boc_2O (2.5 equiv.), LiBr (2 equiv.) and **1a** (0.2 mmol, 1.0 equiv.). The reaction tube was transferred to an argon-filled glovebox and followed by the addition of CH₃CN (0.1 M), 1,3-butadiene **2** (2 M in THF, 2 equiv.) and TMSCN **3** (1.5 equiv.). Then, the reaction mixture was stirred at room temperature with irradiation of 10 W 450 nm LED for 28 h. After the reaction completed, the solvent was evaporated in vacuo and the crude material was purified by flash column chromatography to furnish the desired azetidine products.



4a, Rf = 0.25 (PE:EA = 3:1). The crude material was purified by flash column chromatography (using petroleum ether/EtOAc = 3:1) to provide the title compound as a colorless oil in 82% yield (56 mg). ¹H NMR (400 MHz, CDCl₃) δ 7.76 – 7.64 (m, 2H), 7.64 – 7.52 (m, 1H), 7.47 (dd, *J* = 8.3, 7.0 Hz, 2H), 5.75 – 5.57 (m, 1H), 5.39 (dtt, *J* = 15.3, 5.7, 1.3 Hz, 1H), 4.37 (d, *J* = 8.7 Hz, 2H), 3.92 (d, *J* = 8.8 Hz, 2H), 3.03 (dd, *J* = 5.6, 1.6 Hz, 2H), 2.86 (dd, *J* = 7.2, 1.4 Hz, 2H), 1.42 (s, 9H). ¹³C NMR (101 MHz, CDCl₃) δ 199.5, 156.2, 133.5, 133.1, 128.8, 128.8, 128.7, 122.2, 117.0, 79.9, 56.0, 47.0, 40.3, 28.2, 20.3. HRMS: calculated for C₂₀H₂₄N₂NaO₃ [M+Na]⁺ 363.1685; found 363.1685.



4b

4b, Rf = 0.33 (PE:EA = 4:1). The crude material was purified by flash column chromatography (using petroleum ether/EtOAc = 4:1) to provide the title compound as a colorless oil in 75% yield (61 mg). ¹H NMR (400 MHz, CDCl₃) δ 7.81 (d, J = 8.3 Hz, 2H), 7.74 (d, J = 8.3 Hz, 2H), 5.76 – 5.58 (m, 1H), 5.40 (dt, J = 15.3, 5.6 Hz, 1H), 4.37 (d, J = 8.8 Hz, 2H), 3.95 (d, J = 8.8 Hz, 2H), 3.04 (dd, J = 5.6, 1.5 Hz, 2H), 2.93 – 2.78 (m, 2H), 1.42 (s, 9H). ¹³C NMR (101 MHz, CDCl₃) δ 198.5, 156.2, 135.9, 134.7 (q, J = 32.9 Hz), 129.1, 128.4, 125.9 (q, J = 3.8 Hz), 123.2 (q, J = 272.9 Hz), 122.5, 116.9, 80.1, 55.9, 47.1, 40.0, 28.2, 20.3. ¹⁹F NMR (377 MHz, CDCl₃) δ -63.2. HRMS: calculated for C₂₁H₂₃F₃N₂NaO₃ [M+Na]⁺ 431.1558; found 431.1559.



4c, Rf = 0.35 (PE:EA = 2:1). The crude material was purified by flash column chromatography (using petroleum ether/EtOAc = 3:1) to provide the title compound as a colorless oil in 80% yield (59 mg). ¹H NMR (400 MHz, CDCl₃) δ 7.82 – 7.54 (m, 2H), 7.04 – 6.76 (m, 2H), 5.83 – 5.53 (m, 1H), 5.39 (dt, J = 15.2, 5.7 Hz, 1H), 4.34 (d, J = 8.7 Hz, 2H), 3.93 – 3.84 (m, 5H), 3.13 – 2.95 (m, 2H), 2.83 (d, J = 7.3 Hz, 2H), 1.41 (s, 9H). ¹³C NMR (101 MHz, CDCl₃) δ 198.1, 163.6, 156.3, 131.1, 129.1, 126.0, 122.0, 117.0, 113.9, 79.8, 56.2, 55.4, 46.8, 40.5, 28.2, 20.3. HRMS: calculated for C₂₁H₂₆N₂NaO₄ [M+Na]⁺ 393.1790; found 393.1788.



4d

4d, Rf = 0.31 (PE:EA = 3:1). The crude material was purified by flash column chromatography (using petroleum ether/EtOAc = 3:1) to provide the title compound as a colorless oil in 85% yield (67 mg). ¹H NMR (400 MHz, CDCl₃) δ 7.76 – 7.57 (m, 2H), 7.56 – 7.43 (m, 2H), 5.77 – 5.58 (m, 1H), 5.50 – 5.36 (m, 1H), 4.37 (d, *J* = 8.8 Hz, 2H), 3.92 (d, *J* = 8.9 Hz, 2H), 3.04 (dd, *J* = 5.7, 1.5 Hz, 2H), 2.94 – 2.78 (m, 2H), 1.42 (s, 9H), 1.33 (s, 9H). ¹³C NMR (101 MHz, CDCl₃) δ 199.2, 157.4, 156.3, 130.4, 129.1, 128.8, 125.8, 122.1, 117.1, 79.8, 56.1, 47.0, 40.4, 35.1, 30.9, 28.2, 20.3. HRMS: calculated for C₂₄H₃₂N₂NaO₃ [M+Na]⁺ 419.2311; found 419.2311.



4e

4e, Rf = 0.48 (PE:EA = 2:1). The crude material was purified by flash column chromatography (using petroleum ether/EtOAc = 3:1) to provide the title compound as a colorless oil in 82% yield (58 mg). ¹H NMR (400 MHz, CDCl₃) δ 7.54 (s, 1H), 7.47 – 7.31 (m, 3H), 5.82 – 5.55 (m, 1H), 5.40 (dt, *J* = 15.3, 5.7 Hz, 1H), 4.37 (d, *J* = 8.8 Hz, 2H), 3.92 (d, *J* = 8.8 Hz, 2H), 3.03 (dd, *J* = 5.7, 1.5 Hz, 2H), 2.86 (d, *J* = 7.3 Hz, 2H), 2.40 (s, 3H), 1.43 (s, 9H). ¹³C NMR (101 MHz, CDCl₃) δ 199.7, 156.3, 138.8, 134.3, 133.2, 129.3, 129.0, 128.6, 125.9, 122.1, 117.0, 79.9, 56.1, 47.1, 40.4, 28.2, 21.4, 20.3. HRMS: calculated for C₂₁H₂₆N₂NaO₃ [M+Na]⁺ 377.1841; found 377.1838.



4f

4f, Rf = 0.46 (PE:EA = 2:1). The crude material was purified by flash column chromatography (using petroleum ether/EtOAc = 3:1) to provide the title compound as a colorless oil in 87% yield (65 mg). ¹H NMR (400 MHz, CDCl₃) δ 7.70 (t, *J* = 1.9 Hz, 1H), 7.54 (ddt, *J* = 12.4, 7.7, 1.2 Hz, 2H), 7.42 (t, *J* = 7.9 Hz, 1H), 5.85 – 5.54 (m, 1H), 5.40 (dt, *J* = 15.3, 5.6 Hz, 1H), 4.35 (d, *J* = 8.8 Hz, 2H), 3.92 (d, *J* = 8.7 Hz, 2H), 3.04 (dd, *J* = 5.6, 1.5 Hz, 2H), 2.85 (d, *J* = 7.4 Hz, 2H), 1.42 (s, 9H). ¹³C NMR (101 MHz, CDCl₃) δ 198.2, 156.2, 135.2, 134.7, 133.4, 130.1, 128.8, 128.5, 126.7, 122.4, 116.9, 80.0, 56.1, 47.1, 40.1, 28.2, 20.3. HRMS: calculated for C₂₀H₂₃ClN₂NaO₃ [M+Na]⁺ 397.1295; found 397.1295.



4g

4g, Rf = 0.5 (PE:EA = 2:1). The crude material was purified by flash column chromatography (using petroleum ether/EtOAc = 3:1) to provide the title compound as a colorless oil in 77% yield (55 mg). ¹H NMR (400 MHz, CDCl₃) δ 7.39 (td, *J* = 7.5, 1.4 Hz, 1H), 7.30 (d, *J* = 7.6 Hz, 1H), 7.27 – 7.20 (m, 1H), 7.17 (dd, *J* = 7.8, 1.4 Hz, 1H), 5.84 – 5.59 (m, 1H), 5.41 – 5.24 (m, 1H), 4.36 (d, *J* = 8.7 Hz, 2H), 3.85 (d, *J* = 8.6 Hz, 2H), 3.02 (dd, *J* = 5.6, 1.6 Hz, 2H), 2.86 – 2.76 (m, 2H), 2.44 (s, 3H), 1.43 (s, 9H). ¹³C NMR (101 MHz, CDCl₃) δ 203.0, 156.3, 139.4, 134.2, 132.7, 131.6, 129.0, 127.5, 125.3, 121.9, 116.9, 79.9, 56.1, 47.8, 40.2, 28.2, 21.3, 20.3. HRMS: calculated for C₂₁H₂₆N₂NaO₃ [M+Na]⁺ 377.1841; found 377.1840.





4h, Rf = 0.35 (PE:EA = 3:1). The crude material was purified by flash column chromatography (using petroleum ether/EtOAc = 3:1) to provide the title compound as a colorless oil in 76% yield (54 mg). **¹H NMR** (400 MHz, CDCl₃) δ 7.81 (td, *J* = 7.6, 1.8 Hz, 1H), 7.56 (tdd, *J* = 7.4, 5.1, 1.8 Hz, 1H), 7.30 – 7.25 (m, 1H), 7.12 (dd, *J* = 11.3, 8.3 Hz, 1H), 5.66 (dt, *J* = 14.8, 7.2 Hz, 1H), 5.33 (dt, *J* = 15.3, 5.6 Hz, 1H), 4.27 (dd, *J* = 9.2, 2.1 Hz, 2H), 3.85 (dd, *J* = 9.2, 2.1 Hz, 2H), 3.16 – 2.97 (m, 2H), 2.73 (d, *J* = 7.2 Hz, 2H), 1.42 (s, 9H). ¹³C NMR (101 MHz, CDCl₃) δ 197.9 (d, *J* = 2.3 Hz), 160.3 (d, *J* = 252.2 Hz), 156.2, 135.1 (d, *J* = 9.0 Hz), 131.7 (d, *J* = 3.4 Hz), 129.0, 123.2 (d, *J* = 14.6 Hz), 122.1, 117.0, 116.4 (d, *J* = 24.0 Hz), 79.7, 55.0, 48.0, 37.6, 28.2, 20.3. ¹⁹F NMR (377 MHz, CDCl₃) δ -108.6. **HRMS**: calculated for C₂₀H₂₃FN₂NaO₃ [M+Na]⁺ 381.1590; found 381.1587.



4i

4i, Rf = 0.35 (PE:EA = 3:1). The crude material was purified by flash column chromatography (using petroleum ether/EtOAc = 4:1) to provide the title compound as a colorless oil in 65% yield (57 mg). ¹H NMR (400 MHz, CDCl₃) δ 7.40 (dd, J = 8.2, 2.4 Hz, 1H), 7.19 (dd, J = 8.6, 5.7 Hz, 1H), 7.11 (td, J = 8.1, 2.4 Hz, 1H), 5.95 – 5.61 (m, 1H), 5.39 (dt, J = 15.3, 5.5 Hz, 1H), 4.29 (d, J = 8.7 Hz, 2H), 3.83 (d, J = 8.7 Hz, 2H), 3.07 (dd, J = 5.4, 1.6 Hz, 2H), 2.79 (d, J = 7.1 Hz, 2H), 1.43 (s, 9H). ¹³C NMR (101 MHz, CDCl₃) δ 202.5, 163.0 (d, J = 256.5 Hz), 156.2, 135.1 (d, J = 3.7 Hz), 129.4 (d, J = 8.8 Hz), 129.0, 122.3, 121.6 (d, J = 24.6 Hz), 120.4 (d, J = 9.5 Hz), 116.9, 114.8 (d, J = 21.5 Hz), 80.2, 56.0, 47.5, 38.7, 28.2, 20.4. ¹⁹F NMR (377 MHz, CDCl₃) δ -106.2. HRMS: calculated for C₂₀H₂₂BrFN₂NaO₃ [M+Na]⁺ 459.0696; found 459.0693.



4j

4j, Rf = 0.4 (PE:EA = 3:1). The crude material was purified by flash column chromatography (using petroleum ether/EtOAc = 4:1) to provide the title compound as a colorless oil in 70% yield (52 mg). **¹H NMR** (400 MHz, CDCl₃) δ 7.27 (s, 2H), 7.21 (s, 1H), 5.83 – 5.56 (m, 1H), 5.40 (dt, *J* = 15.3, 5.7 Hz, 1H), 4.35 (d, *J* = 8.8 Hz, 2H), 3.90 (d, *J* = 8.7 Hz, 2H), 3.03 (dd, *J* = 5.7, 1.5 Hz, 2H), 2.85 (d, *J* = 7.2 Hz, 2H), 2.35 (s, 6H), 1.42 (s, 9H). **¹³C NMR** (101 MHz, CDCl₃) δ 199.9, 156.3, 138.4, 135.1, 133.3, 129.0, 126.4, 122.0, 117.0, 79.8, 56.3, 47.1, 40.4, 28.2, 21.2, 20.3. **HRMS**: calculated for C₂₂H₂₈N₂NaO₃, [M+Na]⁺ 391.1998; found 391.1997.



4k

4k, Rf = 0.28 (PE:EA = 3:1). The crude material was purified by flash column chromatography (using petroleum ether/EtOAc = 3:1) to provide the title compound as a colorless oil in 91% yield (71 mg). ¹H NMR (400 MHz, CDCl₃) δ 8.16 (d, *J* = 1.7 Hz, 1H), 8.07 – 7.83 (m, 3H), 7.79 (dd, *J* = 8.6, 1.7 Hz, 1H), 7.60 (dddd, *J* = 22.3, 8.2, 6.9, 1.3 Hz, 2H), 5.82 – 5.63 (m, 1H), 5.40 (dt, *J* = 15.2, 5.7 Hz, 1H), 4.47 (d, *J* = 8.7 Hz, 2H), 4.02 (d, *J* = 8.7 Hz, 2H), 3.16 – 2.98 (m, 2H), 2.95 (d, *J* = 7.2 Hz, 2H), 1.44 (s, 9H). ¹³C NMR (101 MHz, CDCl₃) δ 199.6, 156.3, 135.5, 132.2, 130.5, 130.5, 129.6, 128.9, 128.8, 127.7, 127.0, 124.1, 122.2, 117.0, 79.9, 56.0, 47.2, 40.6, 28.2, 20.3. HRMS: calculated for C₂₄H₂₆N₂NaO₃, [M+Na]⁺ 413.1841; found 413.1843.



41

4I, Rf = 0.31 (PE:EA = 2:1). The crude material was purified by flash column chromatography (using petroleum ether/EtOAc = 2:1) to provide the title compound as a colorless oil in 65% yield (43 mg). ¹H NMR (400 MHz, CDCl₃) δ 7.57 (d, *J* = 1.7 Hz, 1H), 7.21 (d, *J* = 3.6 Hz, 1H), 6.56 (dd, *J* = 3.6, 1.7 Hz, 1H), 5.81 – 5.59 (m, 1H), 5.42 (dt, *J* = 15.3, 5.7 Hz, 1H), 4.29 (d, *J* = 9.1 Hz, 2H), 3.84 (d, *J* = 9.1 Hz, 2H), 3.03 (dd, *J* = 5.6, 1.5 Hz, 2H), 2.92 – 2.72 (m, 2H), 1.42 (s, 9H). ¹³C NMR (101 MHz, CDCl₃) δ 188.6, 156.3, 150.9, 146.4, 129.1, 122.0, 118.6, 117.0, 112.5, 79.8, 55.2, 46.4, 39.1, 2.2, 20.3. HRMS: calculated for C₁₈H₂₂N₂NaO₄, [M+Na]⁺ 353.1477; found 353.1474.



4m, Rf = 0.33 (PE:EA = 2:1). The crude material was purified by flash column chromatography (using petroleum ether/EtOAc = 2:1) to provide the title compound as a colorless oil in 71% yield (49 mg). ¹H NMR (400 MHz, CDCl₃) δ 7.68 (d, *J* = 4.8 Hz, 1H), 7.43 (d, *J* = 3.7 Hz, 1H), 7.14 (ddd, *J* = 4.9, 3.8, 1.1 Hz, 1H), 5.78 – 5.60 (m, 1H), 5.53 – 5.34 (m, 1H), 4.35 (d, *J* = 8.7 Hz, 2H), 3.89 (d, *J* = 8.7 Hz, 2H), 3.14 – 2.99 (m, 2H), 2.85 (d, *J* = 7.3 Hz, 2H), 1.42 (s, 9H). ¹³C NMR (101 MHz, CDCl₃) δ 192.9, 156.2, 140.3, 134.4, 132.1, 128.9, 128.3, 122.2, 117.0, 79.9, 56.0, 47.2, 40.6, 28.2, 20.3. HRMS: calculated for C₁₈H₂₂N₂NaO₃S, [M+Na]⁺ 369.1249; found 369.1253.



4n

4n, Rf = 0.31 (PE:EA = 2:1). The crude material was purified by flash column chromatography (using petroleum ether/EtOAc = 2:1) to provide the title compound as a colorless oil in 83% yield (55 mg). ¹**H NMR** (400 MHz, CDCl₃) δ 7.89 (s, 1H), 7.45 (t, *J* = 1.7 Hz, 1H), 6.65 (dd, *J* = 1.9, 0.9 Hz, 1H), 5.78 – 5.58 (m, 1H), 5.53 – 5.32 (m, 1H), 4.28 (d, *J* = 8.8 Hz, 2H), 3.82 (d, *J* = 8.7 Hz, 2H), 3.04 (dd, *J* = 5.5, 1.5 Hz, 2H), 2.82 – 2.69 (m, 2H), 1.41 (s, 9H). ¹³**C NMR** (101 MHz, CDCl₃) δ 194.6, 156.2, 147.1, 144.2, 128.8, 123.4, 122.2, 117.0, 108.8, 80.0, 55.6, 47.4, 39.9, 28.2, 20.3. **HRMS**: calculated for C₁₈H₂₂N₂NaO₄, [M+Na]⁺ 353.1477; found 353.1480.





40, Rf = 0.29 (PE:EA = 1.5:1). The crude material was purified by flash column chromatography (using petroleum ether/EtOAc = 1.5:1) to provide the title compound as a pale yellow oil in 51% yield (35 mg). ¹H NMR (400 MHz, CDCl₃) δ 9.24 (d, *J* = 1.5 Hz, 1H), 8.78 (d, *J* = 2.4 Hz, 1H), 8.60 (dd, *J* = 2.5, 1.5 Hz, 1H), 5.78 – 5.61 (m, 1H), 5.38 (dtt, *J* = 15.3, 5.6, 1.3 Hz, 1H), 4.33 (d, *J* = 9.3 Hz, 2H), 3.94 (d, *J* = 9.3 Hz, 2H), 3.03 (dd, *J* = 5.5, 1.6 Hz, 2H), 3.00 – 2.95 (m, 2H), 1.43 (s, 9H). ¹³C NMR (101 MHz, CDCl₃) δ 199.7, 156.4, 148.1, 145.4, 145.0, 143.0, 129.3, 121.8, 117.0, 79.8, 55.9, 47.4, 39.6, 28.3, 20.3. HRMS: calculated for C₁₈H₂₂N₄NaO₃, [M+Na]⁺ 365.1590; found 365.1589.



4p, Rf = 0.34 (PE:EA = 3:1). The crude material was purified by flash column chromatography (using petroleum ether/EtOAc = 3:1) to provide the title compound as a colorless oil in 54% yield (38 mg). **¹H NMR** (500 MHz, CDCl₃) δ 7.70 (d, J = 8.4 Hz, 2H), 7.62 – 7.55 (m, 1H), 7.48 (t, J = 7.8 Hz, 2H), 5.02 – 4.95 (m, 1H), 4.46 (d, J = 8.7 Hz, 2H), 3.98 (d, J = 8.7 Hz, 2H), 2.96 (s, 2H), 2.93 (d, J = 7.0 Hz, 2H), 1.50 (s, 3H), 1.43 (s, 9H). ¹³C NMR (126 MHz, CDCl₃) δ 199.8, 156.3, 137.6, 133.6, 133.5, 128.9, 128.7, 117.7, 116.3, 80.0, 57.0, 47.8, 47.3, 28.3, 17.0, 16.1. **HRMS**: calculated for $C_{21}H_{26}N_2NaO_3$, [M+Na]⁺ 377.1841; found 377.1834.





5a, Rf = 0.21 (PE:EA = 4:1). The crude material was purified by flash column chromatography (using petroleum ether/EtOAc = 4:1) to provide the title compound as a colorless oil in 70% yield (45 mg). ¹H NMR (400 MHz, CDCl₃) δ 5.59 (dt, *J* = 14.6, 7.0 Hz, 1H), 5.42 (dd, *J* = 13.5, 7.5 Hz, 1H), 4.00 (d, *J* = 8.8 Hz, 2H), 3.62 (d, *J* = 8.9 Hz, 2H), 3.49 – 3.38 (m, 1H), 3.03 (d, *J* = 5.5 Hz, 2H), 2.57 (d, *J* = 6.9 Hz, 2H), 2.29 – 2.17 (m, 2H), 2.11 – 2.02 (m, 2H), 2.01 – 1.93 (m, 1H), 1.88 – 1.78 (m, 1H), 1.39 (s, 9H). ¹³C NMR (101 MHz, CDCl₃) δ 210.2, 156.1, 129.3, 121.7, 116.9, 79.8, 54.7, 47.1, 41.0, 37.8, 28.1, 25.1, 20.3, 17.9. HRMS: calculated for C₁₈H₂₆N₂NaO₃, [M+Na]⁺ 341.1841; found 341.1838.



5b

5b, Rf = 0.28 (PE:EA = 4:1). The crude material was purified by flash column chromatography (using petroleum ether/EtOAc = 4:1) to provide the title compound as a colorless oil in 84% yield (57 mg). ¹H NMR (400 MHz, CDCl₃) δ 5.73 – 5.55 (m, 1H), 5.45 (dt, *J* = 15.3, 5.6 Hz, 1H), 4.08 (d, *J* = 8.8 Hz, 2H), 3.66 (d, *J* = 8.9 Hz, 2H), 3.06 (dd, *J* = 5.5, 1.5 Hz, 2H), 2.75 – 2.48 (m, 3H), 1.93 – 1.72 (m, 2H), 1.67 (d, *J* = 11.5 Hz, 3H), 1.50 – 1.34 (m, 11H), 1.33 – 1.10 (m, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 212.5, 156.2, 129.4, 121.8, 117.0, 79.9, 54.8, 47.8, 46.2, 38.0, 29.3, 28.2, 25.4, 25.4, 20.4. HRMS: calculated for C₂₀H₃₀N₂NaO₃, [M+Na]⁺ 369.2154; found 369.2153.



5c

5c, Rf = 0.22 (PE:EA = 1:1). The crude material was purified by flash column chromatography (using petroleum ether/EtOAc = 1:1) to provide the title compound as a colorless oil in 86% yield (60 mg). ¹H NMR (400 MHz, CDCl₃) δ 5.73 – 5.59 (m, 1H), 5.47 (dt, *J* = 15.3, 5.5 Hz, 1H), 4.10 (d, *J* = 8.7 Hz, 2H), 4.00 (ddd, *J* = 11.7, 4.5, 2.0 Hz, 2H), 3.71 (d, *J* = 8.9 Hz, 2H), 3.42 (td, *J* = 11.9, 2.2 Hz, 2H), 3.16 – 3.02 (m, 2H), 2.87 (tt, *J* = 11.4, 3.8 Hz, 1H), 2.68 (d, *J* = 6.8 Hz, 2H), 1.89 – 1.70 (m, 2H), 1.65 – 1.51 (m, 2H), 1.43 (s, 9H). ¹³C NMR (101 MHz, CDCl₃) δ 210.5, 156.2, 129.2, 122.1, 116.9, 80.2, 66.8, 54.6, 47.8, 43.3, 38.0, 28.9, 28.2, 20.4. HRMS: calculated for C₁₉H₂₈N₂NaO₄, [M+Na]⁺ 371.1947; found 371.1943.



5d

5d, Rf = 0.39 (PE:EA = 3:1). The crude material was purified by flash column chromatography (using petroleum ether/EtOAc = 3:1) to provide the title compound as a colorless oil in 68% yield (49 mg). ¹H NMR (400 MHz, CDCl₃) δ 5.63 (dtt, *J* = 15.5, 7.0, 1.6 Hz, 1H), 5.55 – 5.39 (m, 1H), 4.09 (d, *J* = 8.7 Hz, 2H), 3.65 (d, *J* = 8.7 Hz, 2H), 3.07 (dd, *J* = 5.6, 1.5 Hz, 2H), 2.63 (dd, *J* = 7.0, 1.5 Hz, 2H), 1.43 (s, 9H), 1.35 (s, 1H), 1.23 (s, 6H), 1.22 (s, 6H). ¹³C NMR (101 MHz, CDCl₃) δ 207.6, 156.4, 129.6, 121.5, 117.0, 79.8, 54.7, 48.7, 40.7, 38.8, 35.8, 28.3, 23.7, 20.4, 16.2. HRMS: calculated for C₂₁H₃₂N₂NaO₃, [M+Na]⁺ 383.2311; found 383.2309.



5e

5e, Rf = 0.41 (PE:EA = 3:1). The crude material was purified by flash column chromatography (using petroleum ether/EtOAc = 4:1) to provide the title compound as a white solid in 75% yield (60 mg). ¹H NMR (400 MHz, CDCl₃) δ 5.59 (dt, *J* = 15.3, 6.7 Hz, 1H), 5.49 (dt, *J* = 15.3, 5.4 Hz, 1H), 4.22 (d, *J* = 8.9 Hz, 2H), 3.64 (d, *J* = 8.8 Hz, 2H), 3.11 – 2.98 (m, 2H), 2.74 (d, *J* = 6.8 Hz, 2H), 2.07 – 1.97 (m, 3H), 1.86 (d, *J* = 3.0 Hz, 6H), 1.81 – 1.60 (m, 6H), 1.42 (s, 9H). ¹³C NMR (101 MHz, CDCl₃) δ 213.5, 156.5, 129.5, 122.0, 117.1, 79.9, 55.9, 48.5, 47.1, 39.1, 38.9, 36.3, 28.2, 27.8, 20.4. HRMS: calculated for C₂₄H₃₄N₂NaO₃, [M+Na]⁺ 421.2467; found 421.2469.



5f

5f, Rf = 0.32 (PE:EA = 3:1). The crude material was purified by flash column chromatography (using petroleum ether/EtOAc = 3:1) to provide the title compound as a pale colorless oil in 80% yield (60 mg). ¹H NMR (400 MHz, CDCl₃) δ 7.33 – 7.24 (m, 2H), 7.23 – 7.11 (m, 3H), 5.51 (dtt, *J* = 15.5, 6.9, 1.6 Hz, 1H), 5.42 – 5.23 (m, 1H), 4.00 (d, *J* = 8.8 Hz, 2H), 3.64 (d, *J* = 8.8 Hz, 2H), 2.98 (dd, *J* = 5.6, 1.6 Hz, 2H), 2.93 (t, *J* = 7.2 Hz, 2H), 2.77 (t, *J* = 7.1 Hz, 2H), 2.66 – 2.46 (m, 2H), 1.42 (s, 9H). ¹³C NMR (101 MHz, CDCl₃) δ 208.2, 156.1, 140.6, 129.0, 128.5, 128.4, 126.3, 121.8, 117.0, 80.0, 54.7, 47.7, 39.3, 38.0, 29.5, 28.2, 20.3. HRMS: calculated for C₂₂H₂₈N₂NaO₃, [M+Na]⁺ 391.1998; found 391.1998.





5g, Rf = 0.22 (PE:EA = 3:1). The crude material was purified by flash column chromatography (using petroleum ether/EtOAc = 3:1) to provide the title compound as a colorless oil in 83% yield (64 mg). ¹H NMR (400 MHz, CDCl₃) δ 7.21 – 7.06 (m, 2H), 7.04 – 6.89 (m, 2H), 5.70 – 5.46 (m, 1H), 5.46 – 5.29 (m, 1H), 3.98 (d, J = 8.8 Hz, 2H), 3.63 (d, J = 8.9 Hz, 2H), 3.00 (dd, J = 5.4, 1.5 Hz, 2H), 2.89 (t, J = 7.2 Hz, 2H), 2.74 (t, J = 7.2 Hz, 2H), 2.64 – 2.44 (m, 2H), 1.41 (s, 9H). ¹³C NMR (101 MHz, CDCl₃) δ 208.1, 161.3 (d, J = 244.2 Hz), 156.1, 136.2 (d, J = 3.1 Hz), 129.8 (d, J = 8.0 Hz), 128.9, 121.8, 116.9, 115.2 (d, J = 21.4 Hz), 80.0, 54.7, 47.7, 39.4, 37.9, 28.6, 28.2, 20.3. ¹⁹F NMR (377 MHz, CDCl₃) δ - 116.6. HRMS: calculated for C₂₂H₂₇FN₂NaO₃, [M+Na]⁺ 409.1903; found 409.1902.



5h

5h, Rf = 0.22 (PE:EA = 1.5:1). The crude material was purified by flash column chromatography (using petroleum ether/EtOAc = 1.5:1) to provide the title compound as a colorless oil in 78% yield (57 mg). ¹H NMR (400 MHz, CDCl₃) δ 6.77 (d, *J* = 8.7 Hz, 1H), 6.70 (dd, *J* = 6.3, 2.1 Hz, 2H), 5.64 – 5.47 (m, 1H), 5.35 (dt, *J* = 15.3, 5.4 Hz, 1H), 4.00 (d, *J* = 8.9 Hz, 2H), 3.85 (s, 3H), 3.83 (s, 3H), 3.63 (d, *J* = 8.9 Hz, 2H), 2.99 (dd, *J* = 5.5, 1.5 Hz, 2H), 2.86 (t, *J* = 7.2 Hz, 2H), 2.74 (t, *J* = 7.0 Hz, 2H), 2.63 – 2.52 (m, 2H), 1.41 (s, 9H). ¹³C NMR (101 MHz, CDCl₃) δ 208.3, 156.1, 148.7, 147.4, 133.1, 128.9, 121.8, 120.1, 116.9, 111.7, 111.2, 79.9, 55.8, 54.7, 47.7, 39.6, 38.0, 29.1, 28.1, 20.2. HRMS: calculated for C₂₄H₃₂N₂NaO₅, [M+Na]⁺ 451.2209; found 451.2209.



5i

5i, Rf = 0.25 (PE:EA = 4:1). The crude material was purified by flash column chromatography (using petroleum ether/EtOAc = 4:1) to provide the title compound as a colorless oil in 85% yield (65 mg). ¹H NMR (400 MHz, CDCl₃) δ 7.32 – 7.29 (m, 2H), 7.28 – 7.16 (m, 3H), 5.35 (s, 1H), 5.21 – 4.85 (m, 1H), 4.10 (d, *J* = 8.9 Hz, 1H), 4.00 (s, 1H), 3.74 (t, *J* = 7.4 Hz, 1H), 3.63 (d, *J* = 8.9 Hz, 1H), 3.54 (d, *J* = 8.9 Hz, 1H), 3.02 – 2.78 (m, 2H), 2.58 (d, *J* = 6.7 Hz, 1H), 2.50 (dd, *J* = 14.7, 7.2 Hz, 1H), 1.98 (dt, *J* = 14.2, 7.1 Hz, 1H), 1.76 (dt, *J* = 13.9, 7.4 Hz, 1H), 1.41 (s, 9H), 0.80 (t, *J* = 7.3 Hz, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 208.8, 156.1, 137.8, 128.8, 128.2, 127.4, 121.5, 116.9, 79.9, 55.7, 54.8, 48.7, 38.2, 28.2, 27.8, 20.3, 12.1. HRMS: calculated for C₂₃H₃₀N₂NaO₃, [M+Na]⁺ 405.2154; found 405.2157.



5j, Rf = 0.27 (PE:EA = 4:1). The crude material was purified by flash column chromatography (using petroleum ether/EtOAc = 4:1) to provide the title compound as a colorless oil in 81% yield (70 mg). ¹H NMR (400 MHz, CDCl₃) δ 7.43 – 7.18 (m, 2H), 6.90 (d, *J* = 8.5 Hz, 2H), 5.68 (dt, *J* = 14.5, 7.0 Hz, 1H), 5.53 (dt, J = 15.4, 5.7 Hz, 1H), 4.30 (d, J = 9.2 Hz, 2H), 3.75 (d, J = 9.2 Hz, 2H), 3.08 (d, J = 5.6 Hz, 2H), 2.95 (d, J = 6.9 Hz, 2H), 1.42 (s, 15H). ¹³C NMR (101 MHz, CDCl₃) δ 211.7, 156.3, 151.5, 129.7, 129.6, 129.3, 124.6, 121.9, 117.0, 87.5, 79.7, 55.6, 48.2, 38.5, 28.2, 25.4, 20.4. HRMS: calculated for C₂₃H₂₉ClN₂NaO₄, [M+Na]⁺ 455.1714; found 455.1717.



6a, Rf = 0.38 (PE:EA = 2:1). The crude material was purified by flash column chromatography (using petroleum ether/EtOAc = 3:1) to provide the title compound as a colorless oil in 76% yield (74 mg). ¹H NMR (400 MHz, CDCl₃) δ 7.89 (d, *J* = 7.9 Hz, 2H), 7.80 (d, *J* = 8.2 Hz, 2H), 5.64 (dt, *J* = 14.8, 7.1 Hz, 1H), 5.39 (dt, *J* = 15.4, 5.7 Hz, 1H), 4.35 (d, *J* = 8.7 Hz, 2H), 3.94 (d, *J* = 8.8 Hz, 2H), 3.27 - 2.97 (m, 6H), 2.85 (d, *J* = 7.2 Hz, 2H), 1.54 (q, *J* = 7.6 Hz, 5H), 1.41 (s, 9H), 0.85 (t, *J* = 7.3 Hz, 6H). ¹³C NMR (101 MHz, CDCl₃) δ 198.4, 156.2, 144.5, 135.8, 129.3, 128.3, 127.4, 122.6, 116.8, 80.1, 55.9, 49.9, 47.1, 40.0, 28.2, 21.9, 20.3, 11.0. HRMS: calculated for C₂₇H₃₈N₂NaO₅S, [M+Na]⁺ 525.2399; found 525.2401.



6b, Rf = 0.21 (PE:EA = 2:1). The crude material was purified by flash column chromatography (using petroleum ether/EtOAc = 2:1) to provide the title compound as a yellow oil in 73% yield (75 mg). ¹H NMR (400 MHz, CDCl₃) δ 7.57 (ddt, *J* = 11.0, 6.0, 1.6 Hz, 4H), 7.45 – 7.27 (m, 6H), 5.66 (dtt, *J* = 15.4, 7.0, 1.6 Hz, 1H), 5.53 – 5.38 (m, 1H), 4.25 (d, *J* = 8.8 Hz, 2H), 3.74 (d, *J* = 8.9 Hz, 2H), 3.18 (t, *J* = 6.4 Hz, 2H), 3.08 (t, *J* = 7.0 Hz, 2H), 2.90 (dd, *J* = 5.5, 1.5 Hz, 2H), 2.79 – 2.60 (m, 2H), 1.43 (s, 9H). ¹³C NMR (101 MHz, CDCl₃) δ 207.2, 161.8, 156.2, 145.4, 134.9, 132.3, 129.3, 128.8, 128.6, 128.5, 128.4, 128.0, 127.7, 126.4, 121.9, 117.0, 80.0, 55.0, 47.7, 38.1, 33.7, 28.2, 21.8, 20.2. HRMS: calculated for C₃₁H₃₃N₃NaO₄, [M+Na]⁺ 534.2369; found 534.2370.



6c, Rf = 0.49 (PE:EA = 2:1). The crude material was purified by flash column chromatography (using petroleum ether/EtOAc = 4:1) to provide the title compound as a colorless oil in 58% yield (62 mg). ¹H NMR (400 MHz, CDCl₃) δ 7.91 – 7.75 (m, 2H), 7.73 (d, *J* = 8.5 Hz, 2H), 7.53 – 7.42 (m, 2H), 7.14 – 6.99 (m, 2H), 5.81 – 5.65 (m, 1H), 5.55 (dt, *J* = 15.3, 5.6 Hz, 1H), 4.33 (d, *J* = 9.2 Hz, 2H), 3.80 (d, *J* = 9.2 Hz, 2H), 3.10 (dd, *J* = 5.7, 1.5 Hz, 2H), 2.97 (d, *J* = 6.6 Hz, 2H), 1.55 (s, 6H), 1.44 (s, 9H). ¹³C NMR (101 MHz, CDCl₃) δ 211.4, 194.1, 157.4, 156.3, 138.8, 135.8, 132.7, 131.8, 131.2, 129.5, 128.6, 122.1, 121.9, 117.0, 88.0, 79.9, 55.7, 48.2, 38.6, 28.3, 25.5, 20.5. HRMS: calculated for C₃₀H₃₃ClN₂NaO₅, [M+Na]⁺ 559.1976; found 559.1975.



6d, Rf = 0.34 (PE:EA = 4:1). The crude material was purified by flash column chromatography (using petroleum ether/EtOAc = 4:1) to provide the title compound as a colorless oil in 85% yield (72 mg). ¹H NMR (400 MHz, CDCl₃) δ 7.13 (d, *J* = 7.9 Hz, 2H), 7.08 (d, *J* = 7.9 Hz, 2H), 5.40 (s, 1H), 5.13 (s, 1H), 4.14 (d, *J* = 8.8 Hz, 1H), 3.96 (dt, *J* = 14.3, 7.3 Hz, 2H), 3.62 (d, *J* = 8.8 Hz, 1H), 3.52 (d, *J* = 8.9 Hz, 1H), 2.98 – 2.81 (m, 2H), 2.64 – 2.55 (m, 1H), 2.50 (dd, *J* = 14.7, 7.1 Hz, 1H), 2.42 (d, *J* = 7.2 Hz, 2H), 1.82 (dt, *J* = 13.5, 6.8 Hz, 1H), 1.41 – 1.36 (m, 12H), 0.87 (s, 3H), 0.86 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 209.5, 156.1, 141.0, 136.6, 129.6, 129.1, 127.5, 121.5, 116.9, 79.9, 55.0, 48.5, 47.6, 44.8, 38.4, 30.1, 28.2, 22.2, 22.2, 20.3, 20.1. HRMS: calculated for C₂₆H₃₆N₂NaO₃, [M+Na]⁺ 447.2624; found 447.2628.

8, Rf = 0.36 (PE:EA = 9:1). The crude material was purified by flash column chromatography (using petroleum ether/EtOAc = 15:1) to provide the title compound as a colorless oil in 87% yield (72 mg). ¹H NMR (400 MHz, CDCl₃) δ 8.03 – 7.88 (m, 2H), 7.68 – 7.51 (m, 1H), 7.49 – 7.42 (m, 2H), 4.58 (d, *J* = 9.8 Hz, 2H), 4.29 (s, 2H), 1.47 (s, 5H), 1.43 (s, 9H), 1.35 – 1.23 (m, 1H), 1.06 – 0.93 (m, 6H), 0.90 (s, 6H). ¹³C NMR (101 MHz, CDCl₃) δ 196.4, 156.3, 133.5, 133.1, 129.8, 128.3, 82.8, 79.5, 59.3, 55.1, 54.6, 39.9, 32.6, 28.2, 20.6, 16.8. HRMS: calculated for C₂₄H₃₆N₂NaO₄, [M+Na]⁺ 439.2573; found 439.2573.

BocN Ph

9, Rf = 0.28 (PE:EA = 12:1). The crude material was purified by flash column chromatography (using petroleum ether/EtOAc = 12:1) to provide the title compound as a colorless oil in 99% yield (168 mg). ¹H NMR (400 MHz, CDCl₃) δ 7.92 (dd, *J* = 8.0, 1.5 Hz, 2H), 7.66 – 7.56 (m, 1H), 7.49 (t, *J* = 7.6 Hz, 2H), 4.91 – 4.76 (m, 2H), 4.57 – 4.38 (m, 2H), 1.43 (s, 9H). ¹³C NMR (101 MHz, CDCl₃) δ 191.7, 155.8, 134.1, 131.2, 129.9, 128.8, 80.6, 62.0, 48.8, 28.2. HRMS: calculated for C₁₅H₁₈BrNNaO₃, [M+Na]⁺ 362.0368; found 362.0370.

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9 NMR Spectra

¹H NMR (400 MHz, CDCl₃)





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<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)
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20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -2: f1 (ppm)



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<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)
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<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)
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¹³C NMR (101 MHz, CDCl₃)







¹³C NMR (101 MHz, CDCl₃)





¹³C NMR (101 MHz, CDCl₃)





20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -2: f1 (ppm)



¹³C NMR (101 MHz, CDCl₃)





20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -2: f1 (ppm)



¹³C NMR (101 MHz, CDCl₃)







¹³C NMR (101 MHz, CDCl₃)









































¹³C NMR (101 MHz, CDCl₃)





20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -2: f1 (ppm)

















¹³C NMR (101 MHz, CDCl₃)





210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 f1(ppm)



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<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)
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210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 f1 (ppm)







210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 f1 (ppm)