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Supplementary Information

For

A Novel Electrochemical Hofmann-Type Rearrangement Enables

Facile Access to α-Oxoisocyanate for N-Carbamoylacetamides

Synthesis

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1. General informations

All the reagents and solvents were purchased from commercial suppliers and used without purification unless otherwise noted. All the electrochemical reactions were performed in a Schlenk tube and monitored by TLC. Flash column chromatography was performed with silica gel (200–300 mesh). Cyclic voltammograms were recorded on a CHI 760E potentiostat (Shanghai Chenhua, China) in a three-electrode cell configuration with a glassy carbon working electrode (3 mm diameter) and a platinum wire counter electrode versus an Ag/AgCl reference electrode. The Bet surface area was studied on a Micromeritics 3Flex2038. NMR spectra were recorded on a Bruker AV-400 instrument. Data were reported as chemical shifts in ppm relative to TMS (0.00 ppm) for ¹H and CDCl₃ (77.2 ppm) or d⁶-DMSO (40.0 pmm) for ¹³C. The abbreviations used for explaining the multiplicities were as follows: s = singlet, d = doublet, t = triplet, q = quartet, p = pentet, m = multiplet. High-resolution mass spectra (HRMS) were recorded on a Bruker Esquire LC 6000 ion trap mass spectrometer using electrospray ionization.

2. Procedures for electrolysis

General Procedure A for the synthesis of *N*-carbamoylacetamides. To a magnetic stir barcontained, 10 mL dry Schlenk tube was added α -oxoamides (0.2 mmol), amine nucleophiles (0.4 mmol, 2.0 equiv), TBAI (0.04 mmol, 20 mol%) and a mixed solvent of MeCN/THF (v/v =1:1, 5.0 mL). The tube was equipped with a graphite felt (GF) anode (0.3 cm x 1.0 cm x 1.5 cm, BET surface area: 1.9435 m²/g) and a platinum cathode (Pt) (0.1 cm x 1.0 cm x 1.0 cm). The solution then electrolyzed at a constant current (20 mA) at room temperature and monitored by TLC until the completion ($j_{anode} = 0.015$ mA cm⁻²). The reaction mixture was concentrated under reduced pressure and the resulting residue was chromatographed through silica gel eluting with petroleum ether/ethyl acetate to give the pure products.

General Procedure B for the synthesis of *N*-acetylcarbamates. To a magnetic stir barcontained,10 mL dry Schlenk tube was added α -oxoamides (0.2 mmol), alcohols (5.0 equiv), TBAI (0.04 mmol, 20 mol%) and MeCN (5.0 mL). The tube was equipped with a graphite felt (GF) anode (0.3 cm x 1.0 cm x 1.5 cm, BET surface area: 1.9435 m²/g) and a platinum cathode (Pt) (0.1 cm x 1.0 cm x 1.0 cm). The solution was then electrolyzed at a constant current (10 mA) at room temperature and monitored by TLC until the completion ($j_{anode} = 0.007$ mA cm⁻²). The reaction mixture was concentrated under reduced pressure and the resulting residue was purified by chromatography through silica gel eluting with petroleum ether/ethyl acetate to give the pure products.

Gram-scale synthesis of 1. To a dry 5.0 L beaker was added α -oxobenzeneamine (10 mmol, 1.49 g), cyclohexylamine (20 mmol, 2.3 mL), TBAI (20 mol%, 0.74 g), MeCN (150 mL), THF (150 mL). Then the beaker was equipped with three parallel electrodes that consist of two GF anodes (0.3 cm x 3.0 cm x 5.0 cm, BET surface area: 1.9435 m²/g) and a sandwiched Pt cathode (0.1 cm x 2.0 cm x 2.0 cm). The solution was electrolyzed at a constant current of 200 mA for 2.75 h at room temperature ($j_{anode} = 0.015$ mA cm⁻², 2.1 F mol ⁻¹). The reaction mixture was concentrated under reduced pressure the resulting residue was purified by column chromatography on silica gel eluting with petroleum ether/ethyl acetate (7/1) to give 1.85 g of pure *N*-(cyclohexylcarbamoyl)benzamide **1** (Yield = 75%).



Figure S1. Reaction setup for electrolysis.

3. Characterization data for products



N-(cyclohexylcarbamoyl)benzamide (1). The title product was prepared following general Procedure A and purified by column chromatography eluting with petroleum ether/ethyl acetate (7/1) in 79 % yield (38.8 mg). White solid. Electricity = 4.4 F mol^{-1} .

¹H NMR (400 MHz, Chloroform-*d*) δ 9.72 (s, 1H), 8.69 (d, *J* = 7.6 Hz, 1H), 7.94 (d, *J* = 7.7 Hz, 2H), 7.51 (t, *J* = 7.4 Hz, 1H), 7.40 (t, *J* = 7.7 Hz, 2H), 3.71 (qd, *J* = 9.7, 4.3 Hz, 1H), 1.92 (dd, *J* = 9.0, 4.4 Hz, 2H), 1.75 – 1.63 (m, 2H), 1.55 (dt, *J* = 13.1, 4.0 Hz, 1H), 1.41 – 1.16 (m, 5H); ¹³C NMR (101 MHz, CDCl₃) δ 168.46, 153.85, 133.10, 132.70, 128.82, 128.06, 49.14, 32.98, 25.73, 24.88.

ESI HRMS *m*/*z* (M+H)⁺ calcd 247.1441, obsd 247.1442.



N-(cyclohexylcarbamoyl)-4-methylbenzamide (2). The title product was prepared following General Procedure A and purified by column chromatography eluting with petroleum ether/ethyl acetate (7/1) in 70% yield (36.4 mg). White solid. Electricity = 4.4 F mol^{-1} .

¹H NMR (400 MHz, Chloroform-*d*) δ 9.78 (s, 1H), 8.73 (d, J = 7.7 Hz, 1H), 7.84 (d, J = 8.1 Hz, 2H), 7.19 (d, J = 8.1 Hz, 2H), 3.71 (tdt, J = 11.0, 7.8, 3.9 Hz, 1H), 2.35 (s, 3H), 1.91 (dt, J = 8.4, 3.5 Hz, 2H), 1.69 (dt, J = 13.0, 3.8 Hz, 2H), 1.55 (dq, J = 12.9, 4.1 Hz, 1H), 1.41 – 1.15 (m, 5H); ¹³C NMR (101 MHz, CDCl₃) δ 168.43, 154.01, 143.81, 129.85, 129.48, 128.12, 49.06, 32.97, 25.73, 24.86, 21.77.

ESI HRMS *m*/*z* (M+H)⁺ calcd 261.1598, obsd 261.1597.



N-(cyclohexylcarbamoyl)-3-methylbenzamide (3). The title product was prepared following General Procedure A and purified by column chromatography eluting with petroleum ether/ethyl acetate (7/1) in 60% yield (31.2 mg). White solid. Electricity = 4.4 F mol^{-1} .

¹H NMR (400 MHz, Chloroform-*d*) δ 9.81 (s, 1H), 8.74 (d, *J* = 7.8 Hz, 1H), 7.77 (s, 1H), 7.73 (d, *J* = 7.4 Hz, 1H), 7.36 – 7.23 (m, 2H), 3.82 – 3.62 (m, 1H), 2.36 (s, 3H), 1.90 (dt, *J* = 12.1, 3.7 Hz, 2H), 1.68 (dt, *J* = 13.2, 3.7 Hz, 2H), 1.54 (dt, *J* = 14.3, 3.8 Hz, 1H), 1.40 – 1.12 (m, 5H); ¹³C NMR (101 MHz, CDCl₃) δ 168.73, 153.91, 138.65, 133.81, 132.64, 128.66, 128.63, 125.24, 48.92, 33.01, 25.70, 24.83, 21.52.

ESI HRMS *m*/*z* (M+H)⁺ calcd 261.1598, obsd 261.1598.



N-(cyclohexylcarbamoyl)-2,3-dihydrobenzo[b][1,4]dioxine-6-carboxamide (4)¹. The title product was prepared following General Procedure A and purified by column chromatography eluting with petroleum ether/ethyl acetate (5/2) in 70% yield (42.6 mg). White solid. Electricity = 4.4 F mol^{-1} .

¹H NMR (400 MHz, Chloroform-*d*) δ 9.94 – 9.60 (m, 1H), 8.72 (d, *J* = 7.7 Hz, 1H), 7.63 – 7.55 (m, 1H), 7.48 (dd, *J* = 8.4, 2.6 Hz, 1H), 6.83 (d, *J* = 8.5 Hz, 1H), 4.36 – 4.10 (m, 4H), 3.74 (tdt, *J* = 11.0, 7.8, 3.8 Hz, 1H), 1.93 (dt, *J* = 11.8, 3.9 Hz, 2H), 1.69 (dq, *J* = 13.1, 3.8 Hz, 2H), 1.55 (dt, *J* = 13.1, 4.1 Hz, 1H), 1.41 – 1.14 (m, 5H); ¹³C NMR (101 MHz, CDCl₃) δ 167.65, 154.07, 147.90, 143.62, 125.77, 121.92, 117.74, 117.49, 64.78, 64.25, 49.03, 33.07, 25.75, 24.96. ESI HRMS *m*/*z* (M+H)⁺ calcd 305.1496, obsd 305.1498.



N-(cyclohexylcarbamoyl)-[1,1'-biphenyl]-4-carboxamide (5). The title product was prepared following General Procedure A and purified by column chromatography eluting with petroleum ether/ethyl acetate (7/1) in 63% yield (40.6 mg). White solid. Electricity = 4.4 F mol^{-1} .

¹H NMR (400 MHz, Chloroform-*d*) δ 9.67 (s, 1H), 8.72 (d, J = 7.7 Hz, 1H), 8.01 (d, J = 8.0 Hz, 2H), 7.59 (dd, J = 26.9, 7.7 Hz, 4H), 7.48 – 7.28 (m, 3H), 3.88 – 3.48 (m, 1H), 2.06 – 1.83 (m, 2H), 1.79 – 1.63 (m, 2H), 1.59 – 1.48 (m, 1H), 1.43 – 1.05 (m, 5H); ¹³C NMR (101 MHz, CDCl₃) δ 168.13, 153.83, 145.89, 139.87, 131.29, 129.17, 128.60, 128.46, 127.49, 127.41, 49.14, 33.00, 25.74, 24.86.

ESI HRMS *m*/*z* (M+H)⁺ calcd 323.1754, obsd 323.1757.



3-chloro-*N***-(cyclohexylcarbamoyl)benzamide (6).** The title product was prepared following General Procedure A and purified by column chromatography eluting with petroleum ether/ethyl acetate (7/1) in 55% yield (30.8 mg). White solid. Electricity = 4.4 F mol^{-1} .

¹H NMR (400 MHz, Chloroform-*d*) δ 10.45 (s, 1H), 8.72 (d, *J* = 7.9 Hz, 1H), 8.21 (s, 1H), 7.92 (d, *J* = 7.9 Hz, 1H), 7.63 (d, *J* = 7.9 Hz, 1H), 7.27 (t, *J* = 7.9 Hz, 1H), 3.82 (dp, *J* = 14.2, 4.4 Hz, 1H), 2.05 – 1.81 (m, 2H), 1.67 (dd, *J* = 9.3, 4.3 Hz, 2H), 1.60 – 1.49 (m, 2H), 1.44 – 1.15 (m, 5H); ¹³C NMR (101 MHz, CDCl₃) δ 167.29, 153.97, 135.96, 134.70, 131.31, 130.26, 127.02, 122.94, 48.90, 33.03, 25.70, 24.83.

ESI HRMS *m*/*z* (M+H)⁺ calcd 281.1051, obsd 281.1052.



3-bromo-*N***-(cyclohexylcarbamoyl)benzamide (7).** The title product was prepared following General Procedure A and purified by column chromatography eluting with petroleum ether/ethyl acetate (7/1) in 57% yield (36.9 mg). White solid. Electricity = 4.4 F mol^{-1} .

¹H NMR (400 MHz, Chloroform-*d*) δ 10.76 – 10.22 (m, 1H), 8.72 (s, 1H), 8.08 (s, 1H), 7.88 (d, J = 7.0 Hz, 1H), 7.48 (d, J = 8.0 Hz, 1H), 7.34 (t, J = 7.9 Hz, 1H), 4.02 – 3.53 (m, 1H), 2.02 – 1.85 (m, 2H), 1.68 (dt, J = 13.1, 3.9 Hz, 2H), 1.55 (dt, J = 13.2, 4.0 Hz, 1H), 1.41 – 1.11 (m, 5H);¹³C NMR (101 MHz, CDCl₃) δ 167.41, 154.07, 134.98, 134.48, 133.02, 130.00, 128.46, 126.61, 48.98, 33.02, 25.70, 24.84.

ESI HRMS *m*/*z* (M+H)⁺ calcd 325.0546, obsd 325.0549.



4-bromo-*N***-(cyclohexylcarbamoyl)benzamide (8).** The title product was prepared following General Procedure A and purified by column chromatography eluting with petroleum ether/ethyl acetate (7/1) in 83% yield (53.8 mg). White solid. Electricity = 4.4 F mol^{-1} .

¹H NMR (400 MHz, Chloroform-*d*) δ 10.39 (s, 1H), 8.71 (d, *J* = 7.6 Hz, 1H), 7.88 (d, *J* = 8.3 Hz, 2H), 7.52 (d, *J* = 8.3 Hz, 2H), 3.68 (dtq, *J* = 10.8, 7.8, 3.9 Hz, 1H), 1.89 (dt, *J* = 12.2, 3.8 Hz, 2H), 1.76 – 1.65 (m, 2H), 1.57 (dt, *J* = 13.2, 4.0 Hz, 1H), 1.42 – 1.16 (m, 5H); ¹³C NMR (101 MHz, CDCl₃) δ 167.80, 154.16, 131.98, 131.55, 129.92, 128.11, 49.24, 32.87, 25.70, 24.82.

ESI HRMS *m*/*z* (M+H)⁺ calcd 325.0546, obsd 325.0544.



N-(cyclohexylcarbamoyl)-4-iodobenzamide (9). The title product was prepared following General Procedure A and purified by column chromatography eluting with petroleum ether/ethyl acetate (7/1) in 75% yield (55.8 mg). White solid. Electricity = 4.4 F mol⁻¹. ¹H NMR (400 MHz, Chloroform-*d*) δ 10.17 (s, 1H), 8.67 (d, *J* = 7.7 Hz, 1H), 7.91 – 7.62 (m, 4H), 3.67 (tdt, *J* = 11.3, 7.9, 3.9 Hz, 1H), 1.97 – 1.83 (m, 2H), 1.70 (dt, *J* = 13.5, 4.0 Hz, 2H), 1.57 (dt, *J* = 13.1, 4.0 Hz, 1H), 1.41 – 1.14 (m, 5H); ¹³C NMR (101 MHz, CDCl₃) δ 167.96, 153.98, 138.04, 132.14, 129.73, 100.77, 49.23, 32.90, 25.71, 24.83. ESI HRMS *m/z* (M+H)⁺ calcd 373.0407, obsd 373.0405.



N-(cyclohexylcarbamoyl)-4-(trifluoromethyl)benzamide (10). The title product was prepared following General Procedure A and purified by column chromatography eluting with petroleum ether/ethyl acetate (7/1) in 50% yield (31.4 mg). White solid. Electricity = 4.4 F mol^{-1} .

¹H NMR (400 MHz, Chloroform-*d*) δ 10.50 (s, 1H), 8.67 (d, J = 7.6 Hz, 1H), 8.11 (d, J = 8.1

Hz, 2H), 7.65 (d, J = 8.1 Hz, 2H), 3.97 - 3.21 (m, 1H), 1.90 (dt, J = 11.9, 3.6 Hz, 2H), 1.70 (dt, J = 13.2, 3.8 Hz, 2H), 1.58 (dt, J = 13.1, 4.0 Hz, 1H), 1.42 - 1.09 (m, 5H); 13 C NMR (101 MHz, CDCl₃) δ 167.52, 154.05, 136.01, 134.51 (q, J = 33.0 Hz), 128.83, 125.70 (q, J = 3.8 Hz), 123.71 (q, J = 272.8 Hz), 49.40, 32.88, 25.70, 24.80.

ESI HRMS *m*/*z* (M+H)⁺ calcd 315.1315, obsd 315.1314.



N-(cyclohexylcarbamoyl)-4-nitrobenzamide (11). The title product was prepared following General Procedure A and purified by column chromatography eluting with petroleum ether/ethyl acetate (6/1) in 45% yield (26.2 mg). White solid. Electricity = 4.4 F mol^{-1} .

¹H NMR (400 MHz, Chloroform-*d*) δ 10.72 (s, 1H), 8.66 (d, *J* = 7.5 Hz, 1H), 8.22 (q, *J* = 8.5 Hz, 4H), 3.68 (dq, *J* = 14.6, 5.4 Hz, 1H), 2.05 – 1.85 (m, 2H), 1.76 – 1.66 (m, 2H), 1.65 – 1.56 (m, 1H), 1.45 – 1.12 (m, 5H); ¹³C NMR (101 MHz, CDCl₃) δ 166.81, 153.98, 150.49, 138.18, 129.68, 123.79, 49.46, 32.82, 25.66, 24.75.

ESI HRMS *m*/*z* (M+H)⁺ calcd 292.1292, obsd 292.1293.



Methyl 4-((cyclohexylcarbamoyl)carbamoyl)benzoate (12). The title product was prepared following General Procedure A and purified by column chromatography eluting with petroleum ether/ethyl acetate (7/1) in 57% yield (34.7 mg). White solid. Electricity = 4.4 F mol^{-1} .

¹H NMR (400 MHz, Chloroform-*d*) δ 10.44 (s, 1H), 8.70 (d, *J* = 7.6 Hz, 1H), 8.05 (s, 4H), 3.88 (s, 3H), 3.69 (dt, *J* = 10.5, 4.7 Hz, 1H), 2.00 – 1.85 (m, 2H), 1.75 – 1.64 (m, 2H), 1.62 – 1.50 (m, 1H), 1.43 – 1.04 (m, 5H); ¹³C NMR (101 MHz, CDCl₃) δ 167.86, 166.29, 154.02, 136.51, 133.92, 129.83, 128.33, 52.65, 49.23, 32.85, 25.70, 24.73.

ESI HRMS *m*/*z* (M+H)⁺ calcd 305.1496, obsd 305.1496.

N-(cyclohexylcarbamoyl)-2-hydroxybenzamide (13). The title product was prepared following General Procedure A and purified by column chromatography eluting with petroleum ether/ethyl acetate (6/1) in 79% yield (41.4 mg). Brown oil. Electricity = 4.4 F mol^{-1} .

¹H NMR (400 MHz, Chloroform-*d*) δ 14.27 (s, 1H), 7.21 (d, *J* = 7.9 Hz, 2H), 6.84 (d, *J* = 8.3 Hz, 1H), 6.75 (t, *J* = 7.5 Hz, 1H), 6.49 (s, 1H), 6.26 (s, 1H), 3.44 (tt, *J* = 9.2, 3.8 Hz, 1H), 1.81 – 1.64 (m, 4H), 1.64 – 1.51 (m, 1H), 1.45 (q, *J* = 10.2, 9.5 Hz, 2H), 1.27 (h, *J* = 11.0 Hz, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 165.56, 165.40, 162.45, 132.96, 129.57, 118.62, 118.08, 115.80,

61.81, 34.12, 25.47, 24.13. ESI HRMS *m/z* (M+H)⁺ calcd 263.1390, obsd 263.1394.



N-(cyclohexylcarbamoyl)-1-naphthamide (14). The title product was prepared following General Procedure A and purified by column chromatography eluting with petroleum ether/ethyl acetate (7/1) in 62% yield (36.7 mg). White solid. Electricity = 4.4 F mol⁻¹. ¹H NMR (400 MHz, Chloroform-*d*) δ 9.54 (s, 1H), 8.55 (d, *J* = 7.7 Hz, 1H), 8.30 (d, *J* = 8.3 Hz, 1H), 7.90 (d, *J* = 8.2 Hz, 1H), 7.80 (d, *J* = 7.9 Hz, 1H), 7.71 (d, *J* = 7.1 Hz, 1H), 7.48 (dt, *J* = 18.3, 7.1 Hz, 2H), 7.39 (t, *J* = 7.7 Hz, 1H), 3.54 (qd, *J* = 10.3, 9.9, 4.3 Hz, 1H), 1.83 (dd, *J* = 11.1, 5.3 Hz, 2H), 1.73 – 1.61 (m, 2H), 1.52 (dd, *J* = 10.8, 6.3 Hz, 1H), 1.36 – 1.05 (m, 5H); ¹³C NMR (101 MHz, CDCl₃) δ 170.46, 153.49, 133.85, 132.38, 131.66, 130.20, 128.63, 127.70, 126.71, 125.22, 124.53, 49.04, 32.92, 25.67, 24.84.

ESI HRMS *m*/*z* (M+H)⁺ calcd 297.1598, obsd 297.1599.



N-(cyclohexylcarbamoyl)-9H-fluorene-2-carboxamide (15). The title product was prepared following General Procedure A and purified by column chromatography eluting with petroleum ether/ethyl acetate (7/1) in 51% yield (34.0 mg). White solid. Electricity = 4.4 F mol⁻¹.

¹H NMR (400 MHz, Chloroform-*d*) δ 9.51 (s, 1H), 8.75 (d, J = 7.7 Hz, 1H), 8.11 (s, 1H), 7.94 (d, J = 8.0 Hz, 1H), 7.77 (d, J = 7.7 Hz, 2H), 7.51 (d, J = 7.1 Hz, 1H), 7.33 (p, J = 7.4 Hz, 2H), 3.89 (s, 2H), 3.82 – 3.70 (m, 1H), 2.06 – 1.85 (m, 2H), 1.76 – 1.65 (m, 2H), 1.60 – 1.50 (m, 1H), 1.41 – 1.24 (m, 5H); ¹³C NMR (101 MHz, CDCl₃) δ 168.60, 153.83, 146.59, 144.46, 143.67, 140.54, 130.77, 128.30, 127.30, 127.15, 125.44, 124.73, 121.02, 120.02, 49.02, 37.07, 33.07, 25.76, 24.86.

ESI HRMS *m*/*z* (M+H)⁺ calcd 335.1754, obsd 335.1753.

N-(cyclohexylcarbamoyl)-1H-indole-3-carboxamide (16). The title product was prepared following General Procedure A and purified by column chromatography eluting with petroleum ether/ethyl acetate (5/2) in 79% yield (45.0 mg). White solid. Electricity = 4.4 F mol⁻¹. ¹H NMR (400 MHz, Chloroform-*d*) δ 9.71 (s, 1H), 9.12 (s, 1H), 8.95 (d, *J* = 7.8 Hz, 1H), 8.25 – 8.14 (m, 2H), 7.34 (dd, *J* = 6.1, 3.2 Hz, 1H), 7.25 – 7.13 (m, 2H), 3.74 (dt, *J* = 9.1, 4.7 Hz, 1H), 1.90 (p, *J* = 5.1 Hz, 2H), 1.66 (t, *J* = 4.7 Hz, 2H), 1.55 – 1.44 (m, 1H), 1.29 (p, *J* = 9.4 Hz, 1Hz, 2H), 1.55 – 1.44 (m, 1Hz, 1.29 (p, *J* = 9.4 Hz, 1Hz, 2Hz), 1.55 – 1.44 (m, 1Hz), 1.29 (p, *J* = 9.4 Hz), 1.55 – 1.44 (m, 1Hz), 1.29 (p, *J* = 9.4 Hz), 1.55 – 1.44 (m, 1Hz), 1.29 (p, *J* = 9.4 Hz), 1.55 – 1.44 (m, 1Hz), 1.29 (p, *J* = 9.4 Hz), 1.55 – 1.44 (m, 1Hz), 1.29 (p, *J* = 9.4 Hz), 1.55 – 1.44 (m, 1Hz), 1.29 (p, *J* = 9.4 Hz), 1.55 – 1.44 (m, 1Hz), 1.29 (p, *J* = 9.4 Hz), 1.55 – 1.44 (m, 1Hz), 1.29 (p, *J* = 9.4 Hz), 1.55 – 1.44 (m, 1Hz), 1.29 (p, *J* = 9.4 Hz), 1.55 – 1.44 (m, 1Hz), 1.29 (p, *J* = 9.4 Hz), 1.55 – 1.44 (m, 1Hz), 1.29 (p, *J* = 9.4 Hz), 1.55 – 1.44 (m, 1Hz), 1.29 (p, *J* = 9.4 Hz), 1.55 – 1.44 (m, 1Hz), 1.29 (p, *J* = 9.4 Hz), 1.55 – 1.44 (m, 1Hz), 1.29 (p, *J* = 9.4 Hz), 1.55 – 1.44 (m, 1Hz), 1.55 – 1 4H), 1.18 (td, *J* = 11.3, 5.7 Hz, 1H); ¹³C NMR (101 MHz, CDCl₃) δ 166.08, 154.94, 136.43, 129.68, 126.12, 123.69, 122.50, 121.46, 111.88, 110.40, 49.00, 33.09, 25.69, 24.81. ESI HRMS *m/z* (M+H)⁺ calcd 286.1550, obsd 286.1554.



N-(cyclohexylcarbamoyl)furan-2-carboxamide (17). The title product was prepared following General Procedure A and purified by column chromatography eluting with petroleum ether/ethyl acetate (8/1) in 70% yield (33.0 mg). White solid. Electricity = 4.4 F mol^{-1} .

¹H NMR (400 MHz, Chloroform-*d*) δ 8.56 (s, 1H), 8.29 (d, *J* = 7.9 Hz, 1H), 7.49 (s, 1H), 7.27 (d, *J* = 3.6 Hz, 1H), 6.51 (d, *J* = 3.5 Hz, 1H), 3.71 (qd, *J* = 9.4, 4.4 Hz, 1H), 1.99 – 1.83 (m, 2H), 1.74 – 1.61 (m, 2H), 1.59 – 1.46 (m, 1H), 1.27 (dp, *J* = 39.1, 12.6, 11.6 Hz, 5H); ¹³C NMR (101 MHz, CDCl₃) δ 158.22, 152.42, 146.04, 146.01, 117.57, 113.02, 48.96, 33.01, 25.66, 24.72.

ESI HRMS *m*/*z* (M+H)⁺ calcd 237.1234, obsd 237.1235.



N-(cyclohexylcarbamoyl)thiophene-2-carboxamide (18). The title product was prepared following General Procedure A and purified by column chromatography eluting with petroleum ether/ethyl acetate (8/1) in 68% yield (34.3 mg). White solid. Electricity = 4.4 F mol⁻¹.

¹H NMR (400 MHz, Chloroform-*d*) δ 10.50 (s, 1H), 8.65 (d, *J* = 7.6 Hz, 1H), 8.11 (d, *J* = 3.9 Hz, 1H), 7.56 (d, *J* = 4.9 Hz, 1H), 7.04 (t, *J* = 4.5 Hz, 1H), 3.74 (qd, *J* = 10.1, 9.3, 4.2 Hz, 1H), 2.12 – 1.80 (m, 2H), 1.76 – 1.64 (m, 2H), 1.60 – 1.48 (m, 1H), 1.42 – 1.09 (m, 5H); ¹³C NMR (101 MHz, CDCl₃) δ 163.22, 154.23, 138.02, 133.37, 131.02, 128.24, 49.20, 32.90, 25.70, 24.77.

ESI HRMS *m*/*z* (M+H)⁺ calcd 253.1005, obsd 253.1004.



5-bromo-*N***-(cyclohexylcarbamoyl)thiophene-2-carboxamide (19).** The title product was prepared following General Procedure A and purified by column chromatography eluting with petroleum ether/ethyl acetate (8/1) in 66% yield (43.6 mg). White solid. Electricity = 4.4 F mol^{-1} .

¹H NMR (400 MHz, Chloroform-*d*) δ 10.63 (s, 1H), 8.56 (d, J = 7.6 Hz, 1H), 7.90 (d, J = 4.1 Hz, 1H), 7.00 (d, J = 4.1 Hz, 1H), 3.69 (hept, 1H), 2.04 – 1.79 (m, 2H), 1.75 – 1.64 (m, 2H), 1.59 – 1.50 (m, 1H), 1.43 – 1.09 (m, 5H); ¹³C NMR (101 MHz, CDCl₃) δ 162.15, 154.21,

139.36, 131.52, 131.33, 121.74, 49.36, 32.88, 25.68, 24.81. ESI HRMS *m/z* (M+H)⁺ calcd 331.0110, obsd 331.0113.

N-(butylcarbamoyl)benzamide (20). The title product was prepared following General Procedure A and purified by column chromatography eluting with petroleum ether/ethyl acetate (7/1) in 70% yield (30.8 mg). White solid. Electricity = 4.4 F mol^{-1} .

¹H NMR (400 MHz, Chloroform-*d*) δ 9.95 (s, 1H), 8.76 (t, *J* = 5.8 Hz, 1H), 8.06 – 7.83 (m, 2H), 7.56 – 7.46 (m, 1H), 7.40 (t, *J* = 7.6 Hz, 2H), 3.29 (td, *J* = 7.1, 5.7 Hz, 2H), 1.52 (p, *J* = 7.2 Hz, 2H), 1.34 (h, *J* = 7.3 Hz, 2H), 0.88 (t, *J* = 7.3 Hz, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 168.57, 154.88, 133.09, 132.66, 128.78, 128.14, 39.76, 31.77, 20.27, 13.90. ESI HRMS *m/z* (M+H)⁺ calcd 221.1285, obsd 221.1286.

N-(isopropylcarbamoyl)benzamide (21). The title product was prepared following General Procedure A and purified by column chromatography eluting with petroleum ether/ethyl acetate (7/1) in 53% yield (21.9 mg). White solid. Electricity = 4.4 F mol^{-1} .

¹H NMR (400 MHz, Chloroform-*d*) δ 10.03 (s, 1H), 8.65 (d, *J* = 7.5 Hz, 1H), 7.96 (d, *J* = 7.3 Hz, 2H), 7.50 (t, *J* = 7.4 Hz, 1H), 7.40 (t, *J* = 7.6 Hz, 2H), 4.12 – 3.89 (m, *J* = 6.6 Hz, 1H), 1.20 (d, *J* = 6.6 Hz, 6H); ¹³C NMR (101 MHz, CDCl₃) δ 168.59, 154.11, 133.06, 132.69, 128.78, 128.14, 42.38, 22.85.

ESI HRMS *m*/*z* (M+H)⁺ calcd 207.1128, obsd 207.1129.

N-((4-phenylbutyl)carbamoyl)benzamide (22). The title product was prepared following General Procedure A and purified by column chromatography eluting with petroleum ether/ethyl acetate (7/1) in 55% yield (32.6 mg). White solid. Electricity = 4.4 F mol^{-1} .

¹H NMR (400 MHz, Chloroform-*d*) δ 9.72 (s, 1H), 8.74 (s, 1H), 7.91 (d, *J* = 7.7 Hz, 2H), 7.49 (t, *J* = 7.4 Hz, 1H), 7.39 (t, *J* = 7.6 Hz, 2H), 7.24 – 7.16 (m, 2H), 7.13 – 7.06 (m, 3H), 3.31 (q, *J* = 6.4 Hz, 2H), 2.58 (t, *J* = 7.3 Hz, 2H), 1.84 – 1.48 (m, 4H); ¹³C NMR (101 MHz, CDCl₃) δ 168.48, 154.72, 142.22, 133.14, 132.63, 128.84, 128.57, 128.51, 128.06, 125.98, 39.89, 35.67, 29.37, 28.86.

ESI HRMS *m*/*z* (M+H)⁺ calcd 297.1598, obsd 297.1597.

N-(**benzylcarbamoyl**)**benzamide (23).** The title product was prepared following General Procedure A and purified by column chromatography eluting with petroleum ether/ethyl acetate

(7/1) in 61% yield (30.5 mg). White solid. Electricity = 4.4 F mol⁻¹.

¹H NMR (400 MHz, Chloroform-*d*) δ 9.87 (s, 1H), 9.21 (s, 1H), 8.16 – 7.90 (m, 2H), 7.56 (t, *J* = 7.4 Hz, 1H), 7.43 (t, *J* = 7.7 Hz, 2H), 7.38 – 7.24 (m, 5H), 4.57 (d, *J* = 5.9 Hz, 2H); ¹³C NMR (101 MHz, CDCl₃) δ 168.53, 154.85, 138.26, 133.23, 132.49, 128.89, 128.87, 128.07, 127.68, 127.62, 43.94.

ESI HRMS *m*/*z* (M+H)⁺ calcd 255.1128, obsd 255.1129.

N-((4-methoxybenzyl)carbamoyl)benzamide (24). The title product was prepared following General Procedure A and purified by column chromatography eluting with petroleum ether/ethyl acetate (7/1) in 56% yield (31.8 mg). White solid. Electricity = 4.4 F mol⁻¹.

¹H NMR (400 MHz, Chloroform-*d*) δ 9.97 (s, 1H), 9.09 (s, 1H), 7.93 (d, J = 7.7 Hz, 2H), 7.49 (t, J = 7.4 Hz, 1H), 7.37 (t, J = 7.6 Hz, 2H), 7.20 (d, J = 8.5 Hz, 2H), 6.79 (d, J = 8.3 Hz, 2H), 4.42 (d, J = 5.8 Hz, 2H), 3.72 (s, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 168.56, 159.12, 154.85, 133.17, 132.55, 130.42, 129.10, 128.84, 128.13, 114.21, 55.46, 43.40. ESI HRMS *m/z* (M+H)⁺ calcd 285.1234, obsd 285.1233.



N-((pyridin-2-ylmethyl)carbamoyl)benzamide (25). The title product was prepared following General Procedure A and purified by column chromatography eluting with petroleum ether/ethyl acetate (4/1) in 61% yield (31.1 mg). White solid. Electricity = 4.4 F mol⁻¹.

¹H NMR (400 MHz, Chloroform-*d*) δ 10.32 (s, 1H), 9.54 (t, *J* = 5.5 Hz, 1H), 8.51 (d, *J* = 4.9 Hz, 1H), 7.95 (d, *J* = 7.8 Hz, 2H), 7.59 – 7.51 (m, 1H), 7.46 (t, *J* = 7.4 Hz, 1H), 7.32 (t, *J* = 7.6 Hz, 2H), 7.23 (d, *J* = 7.9 Hz, 1H), 7.10 (t, *J* = 6.2 Hz, 1H), 4.63 (d, *J* = 5.6 Hz, 2H); ¹³C NMR (101 MHz, CDCl₃) δ 168.62, 157.22, 155.24, 149.50, 136.84, 133.06, 132.42, 128.68, 128.21, 122.37, 121.34, 45.41.

ESI HRMS *m*/*z* (M+H)⁺ calcd 256.1081, obsd 256.1080.

N-((cyclohexylmethyl)carbamoyl)benzamide (26). The title product was prepared following General Procedure A and purified by column chromatography eluting with petroleum ether/ethyl acetate (7/1) in 67% yield (34.9 mg). White solid. Electricity = 4.4 F mol^{-1} .

¹H NMR (400 MHz, Chloroform-*d*) δ 9.92 (s, 1H), 8.82 (t, *J* = 5.9 Hz, 1H), 7.96 (dd, *J* = 7.9, 1.6 Hz, 2H), 7.57 – 7.47 (m, 1H), 7.41 (t, *J* = 7.7 Hz, 2H), 3.14 (t, *J* = 6.3 Hz, 2H), 1.76 – 1.64 (m, 4H), 1.63 – 1.57 (m, 1H), 1.50 (ttt, *J* = 10.4, 6.8, 3.4 Hz, 1H), 1.23 – 1.08 (m, 3H), 0.91

(qd, *J* = 11.9, 3.0 Hz, 2H); ¹³C NMR (101 MHz, CDCl₃) δ 168.57, 154.91, 133.11, 132.64, 128.79, 128.14, 46.33, 38.06, 31.01, 26.54, 25.99. ESI HRMS *m/z* (M+H)⁺ calcd 261.1598, obsd 261.1598.



N-((1,2,3,4-tetrahydronaphthalen-1-yl)carbamoyl)benzamide (27). The title product was prepared following General Procedure A and purified by column chromatography eluting with petroleum ether/ethyl acetate (7/1) in 67% yield (39.4 mg). White solid. Electricity = 4.4 F mol^{-1} .

¹H NMR (400 MHz, Chloroform-*d*) δ 10.04 (s, 1H), 9.08 (s, 1H), 8.27 – 7.79 (m, 2H), 7.59 – 7.24 (m, 4H), 7.19 – 6.99 (m, 3H), 5.27 – 5.03 (m, 1H), 2.97 – 2.60 (m, 2H), 2.15 – 1.98 (m, 1H), 1.95 – 1.74 (m, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 168.48, 154.44, 137.49, 136.60, 133.17, 132.58, 129.34, 128.82, 128.14, 127.51, 126.47, 48.46, 30.31, 29.34, 20.16. ESI HRMS *m/z* (M+H)⁺ calcd 295.1441, obsd 295.1440.

Ph H H OME

N-((2-methoxyethyl)carbamoyl)benzamide (28). The title product was prepared following General Procedure A and purified by column chromatography eluting with petroleum ether/ethyl acetate (7/1) in 61% yield (27.1 mg). White solid. Electricity = 4.4 F mol⁻¹. ¹H NMR (400 MHz, Chloroform-*d*) δ 9.76 (s, 1H), 8.92 (s, 1H), 8.03 – 7.84 (m, 2H), 7.54 – 7.47 (m, 1H), 7.40 (t, *J* = 7.7 Hz, 2H), 3.55 – 3.44 (m, 4H), 3.32 (s, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 168.38, 154.89, 133.14, 132.62, 128.83, 128.09, 71.12, 59.06, 39.86. ESI HRMS *m/z* (M+H)⁺ calcd 223.1077, obsd 223.1077.

N-((2-hydroxyethyl)carbamoyl)benzamide (29). The title product was prepared following General Procedure A and purified by column chromatography eluting with petroleum ether/ethyl acetate (5/1) in 79% yield (32.9 mg). White solid. Electricity = 4.4 F mol⁻¹. ¹H NMR (400 MHz, Chloroform-*d*) δ 9.71 (s, 1H), 9.01 (t, *J* = 5.5 Hz, 1H), 7.86 (d, *J* = 7.7 Hz, 2H), 7.50 (t, *J* = 7.4 Hz, 1H), 7.38 (t, *J* = 7.5 Hz, 2H), 3.72 (t, *J* = 5.0 Hz, 2H), 3.45 (q, *J* = 5.4 Hz, 2H), 2.76 (s, 1H); ¹³C NMR (101 MHz, CDCl₃) δ 168.56, 155.73, 133.28, 132.43, 128.91, 128.00, 62.32, 42.91.

ESI HRMS *m*/*z* (M+H)⁺ calcd 209.0921, obsd 209.0921.

N-((1-hydroxy-3-phenylpropan-2-yl)carbamoyl)benzamide (30). The title product was prepared following General Procedure A and purified by column chromatography eluting with petroleum ether/ethyl acetate (5/1) in 72% yield (42.9 mg). White solid. Electricity = 4.4 F mol^{-1} .

¹H NMR (400 MHz, Chloroform-*d*) δ 9.51 (s, 1H), 9.03 (d, *J* = 7.6 Hz, 1H), 7.91 (d, *J* = 7.7 Hz, 2H), 7.57 (t, *J* = 7.4 Hz, 1H), 7.46 (t, *J* = 7.6 Hz, 2H), 7.25 (dp, *J* = 15.3, 7.3 Hz, 5H), 4.19 (ddd, *J* = 12.6, 6.6, 3.5 Hz, 1H), 3.76 (ddd, *J* = 10.0, 5.7, 3.8 Hz, 1H), 3.66 (dt, *J* = 10.9, 5.3 Hz, 1H), 3.07 – 2.88 (m, 2H), 2.59 (t, *J* = 5.5 Hz, 1H); ¹³C NMR (101 MHz, CDCl₃) δ 168.44, 154.91, 137.80, 133.29, 132.50, 129.46, 128.97, 128.77, 127.96, 126.83, 64.45, 54.21, 37.55. ESI HRMS *m/z* (M+H)⁺ calcd 299.1390, obsd 299.1390.



N-((2-hydroxycyclohexyl)carbamoyl)benzamide (31). The title product was prepared following General Procedure A and purified by column chromatography eluting with petroleum ether/ethyl acetate (5/1) in 57% yield (29.9 mg). White solid. Electricity = 4.4 F mol^{-1} .

¹H NMR (400 MHz, Chloroform-*d*) δ 9.59 (s, 1H), 8.79 (d, J = 7.5 Hz, 1H), 7.86 (d, J = 7.7 Hz, 2H), 7.51 (t, J = 7.4 Hz, 1H), 7.41 (t, J = 7.6 Hz, 2H), 3.57 (td, J = 10.6, 7.0 Hz, 1H), 3.41 (td, J = 9.7, 4.2 Hz, 1H), 2.88 (s, 1H), 2.14 – 1.90 (m, 2H), 1.67 (td, J = 7.1, 3.8 Hz, 2H), 1.44 – 1.10 (m, 4H); ¹³C NMR (101 MHz, CDCl₃) δ 168.56, 155.68, 133.30, 132.45, 128.95, 127.99, 74.95, 56.35, 34.38, 31.57, 24.82, 24.15.

ESI HRMS *m*/*z* (M+H)⁺ calcd 263.1390, obsd 263.1394.

N-((2,3-dihydroxypropyl)carbamoyl)benzamide (32). The title product was prepared following General Procedure A and purified by column chromatography eluting with petroleum ether/ethyl acetate (5/1) in 42% yield (20.0 mg). White solid. Electricity = 4.4 F mol⁻¹.

¹H NMR (400 MHz, DMSO- d_6) δ 10.71 (s, 1H), 8.83 (t, J = 5.4 Hz, 1H), 7.95 (d, J = 7.6 Hz, 2H), 7.60 (t, J = 7.4 Hz, 1H), 7.49 (t, J = 7.6 Hz, 2H), 5.00 (d, J = 5.0 Hz, 1H), 4.70 (t, J = 5.6 Hz, 1H), 3.56 (q, J = 5.7 Hz, 1H), 3.49 – 3.41 (m, 1H), 3.38 – 3.33 (m, 1H), 3.27 (dt, J = 11.2, 6.1 Hz, 1H), 3.14 – 3.02 (m, 1H); ¹³C NMR (101 MHz, DMSO) δ 168.67, 154.18, 133.19, 133.10, 128.97, 128.58, 70.41, 64.19, 43.00.

ESI HRMS *m*/*z* (M+H)⁺ calcd 239.1026, obsd 239.1028.



N-((3-(hydroxydimethylsilyl)propyl)carbamoyl)benzamide (33). The title product was

prepared with 3-Aminopropyldimethylethoxysilane (0.4 mmol) following General Procedure A and purified by column chromatography eluting with petroleum ether/ethyl acetate (5/1) in 44% yield (24.6 mg). White solid. Electricity = 4.4 F mol^{-1} .

¹H NMR (400 MHz, Chloroform-*d*) δ 9.29 (s, 1H), 8.81 (d, J = 6.0 Hz, 1H), 7.92 (d, J = 7.7 Hz, 2H), 7.57 (t, J = 7.4 Hz, 1H), 7.45 (t, J = 7.6 Hz, 2H), 3.34 (q, J = 6.8 Hz, 2H), 1.71 (s, 1H), 1.68 – 1.55 (m, 2H), 0.73 – 0.48 (m, 2H), 0.07 (s, 6H); ¹³C NMR (101 MHz, CDCl₃) δ 168.27, 154.28, 133.14, 132.71, 128.95, 127.89, 43.12, 23.80, 15.71, 0.51.

ESI HRMS *m*/*z* (M+H)⁺ calcd 281.1316, obsd 281.1317.



N-((2-(cyclohex-1-en-1-yl)ethyl)carbamoyl)benzamide (34). The title product was prepared following General Procedure A and purified by column chromatography eluting with petroleum ether/ethyl acetate (7/1) in 45% yield (24.5 mg). White solid. Electricity = 4.4 F mol⁻¹. ¹H NMR (400 MHz, Chloroform-*d*) δ 9.59 (s, 1H), 8.74 (t, *J* = 5.4 Hz, 1H), 7.98 (d, *J* = 7.2 Hz, 2H), 7.58 (t, *J* = 7.3 Hz, 1H), 7.48 (t, *J* = 7.6 Hz, 2H), 5.53 (s, 1H), 3.44 (q, *J* = 6.9 Hz, 2H), 2.23 (t, *J* = 7.1 Hz, 2H), 2.09 – 1.92 (m, 4H), 1.68 – 1.43 (m, 4H); ¹³C NMR (101 MHz, CDCl₃) δ 168.28, 154.49, 134.53, 133.09, 132.73, 128.88, 127.99, 123.92, 38.40, 37.86, 28.20, 25.43, 23.03, 22.52.

ESI HRMS *m*/*z* (M+Na)⁺ calcd 295.1417, obsd 295.1416.

N-(phenylcarbamoyl)benzamide (35). The title product was prepared following General Procedure A and purified by column chromatography eluting with petroleum ether/ethyl acetate (7/1) in 70% yield (33.6 mg). White solid. Electricity = 4.4 F mol⁻¹. The 0.5 mmol scale was carried out at 0.1M concentration, delivering **35** in 67% yield (80.4 mg).

¹H NMR (400 MHz, Chloroform-*d*) δ 11.05 (s, 1H), 10.16 (s, 1H), 8.13 (d, J = 7.7 Hz, 2H), 7.75 – 7.60 (m, 3H), 7.54 (t, J = 7.6 Hz, 2H), 7.39 (t, J = 7.8 Hz, 2H), 7.19 (t, J = 7.4 Hz, 1H); ¹³C NMR (101 MHz, CDCl₃) δ 168.90, 152.37, 137.43, 133.51, 132.34, 129.18, 129.01, 128.27, 124.61, 120.65.

ESI HRMS *m*/*z* (M+H)⁺ calcd 241.0972, obsd 241.0970.

N-((4-butylphenyl)carbamoyl)benzamide (36). The title product was prepared following General Procedure A and purified by column chromatography eluting with petroleum

ether/ethyl acetate (7/1) in 83% yield (49.2 mg). White solid. Electricity = 4.4 F mol⁻¹. ¹H NMR (400 MHz, DMSO- d_6) δ 11.02 (s, 1H), 10.78 (s, 1H), 8.02 (d, J = 7.7 Hz, 2H), 7.64 (t, J = 7.4 Hz, 1H), 7.53 (t, J = 7.6 Hz, 2H), 7.47 (d, J = 8.1 Hz, 2H), 7.15 (d, J = 8.1 Hz, 2H), 2.53 (t, J = 7.7 Hz, 2H), 1.52 (p, J = 7.4 Hz, 2H), 1.28 (h, J = 7.5 Hz, 2H), 0.88 (t, J = 7.3 Hz, 3H); ¹³C NMR (101 MHz, DMSO) δ 169.15, 151.56, 138.25, 135.69, 133.50, 132.75, 129.19, 129.03, 128.75, 120.33, 34.68, 33.69, 22.18, 14.26.

ESI HRMS *m*/*z* (M+H)⁺ calcd 297.1598, obsd 297.1597.

N-((4-(tert-butyl)phenyl)carbamoyl)benzamide (37). The title product was prepared following General Procedure A and purified by column chromatography eluting with petroleum ether/ethyl acetate (7/1) in 77% yield (45.6 mg). White solid. Electricity = 4.4 F mol^{-1} .

¹H NMR (400 MHz, Chloroform-*d*) δ 10.91 (s, 1H), 10.30 (s, 1H), 8.05 (d, J = 7.5 Hz, 2H), 7.55 (t, J = 7.4 Hz, 1H), 7.47 – 7.38 (m, 4H), 7.29 (d, J = 8.3 Hz, 2H), 1.26 (s, 9H); ¹³C NMR (101 MHz, CDCl₃) δ 168.92, 152.59, 147.56, 134.72, 133.37, 132.36, 128.92, 128.37, 125.93, 120.47, 34.55, 31.56.

ESI HRMS *m*/*z* (M+H)⁺ calcd 297.1598, obsd 297.1597.



N-(mesitylcarbamoyl)benzamide (38). The title product was prepared following General Procedure A and purified by column chromatography eluting with petroleum ether/ethyl acetate (7/1) in 63% yield (35.5 mg). White solid. Electricity = 4.4 F mol^{-1} .

¹H NMR (400 MHz, Chloroform-*d*) δ 10.09 (d, *J* = 7.3 Hz, 2H), 7.94 (d, *J* = 7.6 Hz, 2H), 7.56 – 7.44 (m, 1H), 7.28 (t, *J* = 7.8 Hz, 2H), 6.86 (s, 2H), 2.24 (s, 3H), 2.18 (s, 6H); ¹³C NMR (101 MHz, CDCl₃) δ 168.73, 153.27, 137.04, 135.34, 133.29, 132.11, 130.86, 128.95, 128.84, 128.19, 21.14, 18.61.

ESI HRMS *m*/*z* (M+H)⁺ calcd 283.1441, obsd 283.1442.



N-((2,6-diisopropylphenyl)carbamoyl)benzamide (39). The title product was prepared following General Procedure A and purified by column chromatography eluting with petroleum ether/ethyl acetate (7/1) in 68% yield (44.1 mg). White solid. Electricity = 4.4 F mol⁻¹.

¹H NMR (400 MHz, Chloroform-*d*) δ 10.04 (s, 1H), 9.50 (s, 1H), 8.04 – 7.83 (m, 2H), 7.56 – 7.42 (m, 1H), 7.28 (t, *J* = 7.7 Hz, 3H), 7.15 (d, *J* = 7.7 Hz, 2H), 3.11 (h, *J* = 6.9 Hz, 2H), 1.15

(s, 6H), 1.13 (s, 6H); ¹³C NMR (101 MHz, CDCl₃) δ 168.55, 153.61, 146.41, 133.40, 132.05, 130.65, 128.99, 128.49, 128.02, 123.58, 29.03, 24.14. ESI HRMS *m/z* (M+H)⁺ calcd 325.1911, obsd 325.1910.



N-((((1R,4aS,10aR)-7-isopropyl-1,4a-dimethyl-1,2,3,4,4a,9,10,10a-

octahydrophenanthren-1-yl)methyl)carbamoyl)benzamide (40). The title product was prepared following General Procedure A and purified by column chromatography eluting with petroleum ether/ethyl acetate (7/1) in 52% yield (45.0 mg). White solid. Electricity = 4.4 F mol⁻¹.

¹H NMR (400 MHz, Chloroform-*d*) δ 9.82 (s, 1H), 8.99 (t, *J* = 6.4 Hz, 1H), 7.99 (d, *J* = 7.2 Hz, 2H), 7.57 (t, *J* = 7.3 Hz, 1H), 7.47 (t, *J* = 7.6 Hz, 2H), 7.17 (d, *J* = 8.2 Hz, 1H), 6.99 (dd, *J* = 8.2, 2.0 Hz, 1H), 6.87 (d, *J* = 1.9 Hz, 1H), 3.38 (dd, *J* = 13.5, 6.6 Hz, 1H), 3.18 (dd, *J* = 13.6, 6.3 Hz, 1H), 2.97 – 2.70 (m, 3H), 2.28 (dd, *J* = 12.8, 3.4 Hz, 1H), 1.95 (dt, *J* = 12.3, 4.0 Hz, 1H), 1.86 – 1.62 (m, 4H), 1.52 (ddd, *J* = 12.0, 9.3, 2.6 Hz, 2H), 1.40 (dq, *J* = 12.8, 7.5, 6.6 Hz, 2H), 1.29 – 1.16 (m, 8H), 0.98 (s, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 168.69, 155.02, 147.28, 145.70, 135.00, 133.13, 132.69, 128.82, 128.11, 127.12, 124.47, 124.02, 50.71, 45.47, 38.38, 37.70, 36.40, 33.58, 30.56, 25.69, 24.15, 24.12, 19.30, 18.84, 18.81.

ESI HRMS *m*/*z* (M+H)⁺ calcd 433.2850, obsd 433.2851.

N-(dibutylcarbamoyl)benzamide (41). The title product was prepared following General Procedure A and purified by column chromatography eluting with petroleum ether/ethyl acetate (7/1) in 80% yield (44.2 mg). White solid. Electricity = 4.4 F mol^{-1} .

¹H NMR (400 MHz, Chloroform-*d*) δ 8.83 (s, 1H), 7.80 (d, *J* = 7.7 Hz, 2H), 7.46 (t, *J* = 7.3 Hz, 1H), 7.37 (t, *J* = 7.5 Hz, 2H), 3.26 (t, *J* = 7.4 Hz, 4H), 1.51 (p, *J* = 7.4 Hz, 4H), 1.25 (q, *J* = 7.5 Hz, 4H), 0.84 (t, *J* = 7.3 Hz, 6H); ¹³C NMR (101 MHz, CDCl₃) δ 166.77, 154.49, 133.35, 132.56, 128.65, 128.09, 47.70, 30.16, 20.14, 13.98.

ESI HRMS *m*/*z* (M+H)⁺ calcd 277.1911, obsd 277.1910.



N-benzoylazetidine-1-carboxamide (42). The title product was prepared following General Procedure A and purified by column chromatography eluting with petroleum ether/ethyl acetate (5/1) in 52% yield (21.2 mg). White solid. Electricity = 4.4 F mol^{-1} .

¹H NMR (400 MHz, Chloroform-*d*) δ 9.27 (s, 1H), 7.93 (d, *J* = 7.7 Hz, 2H), 7.55 (t, *J* = 7.4 Hz, 1H), 7.46 (t, *J* = 7.6 Hz, 2H), 4.20 (s, 4H), 2.30 (p, *J* = 7.8 Hz, 2H); ¹³C NMR (101 MHz, CDCl₃) δ 165.09, 154.88, 132.95, 132.80, 128.76, 128.22, 52.76, 49.21, 16.12. ESI HRMS *m/z* (M+H)⁺ calcd 205.0972, obsd 205.0970.

N-benzoylpiperidine-1-carboxamide (43). The title product was prepared following General Procedure A and purified by column chromatography eluting with petroleum ether/ethyl acetate (5/1) in 66% yield (30.6 mg). White solid. Electricity = 4.4 F mol^{-1} .

¹H NMR (400 MHz, Chloroform-*d*) δ 9.01 (s, 1H), 7.84 (d, *J* = 7.4 Hz, 2H), 7.46 (t, *J* = 7.4 Hz, 1H), 7.37 (t, *J* = 7.6 Hz, 2H), 3.56 – 3.23 (m, 4H), 1.65 – 1.45 (m, 6H); ¹³C NMR (101 MHz, CDCl₃) δ 166.25, 153.73, 133.07, 132.66, 128.69, 128.15, 46.57, 25.82, 24.34. ESI HRMS *m/z* (M+H)⁺ calcd 233.1285, obsd 233.1284.



N-benzoyl-4-methylpiperidine-1-carboxamide (44). The title product was prepared following General Procedure A and purified by column chromatography eluting with petroleum ether/ethyl acetate (5/1) in 69% yield (34.0 mg). Brown oil. Electricity = 4.4 F mol⁻¹. ¹H NMR (400 MHz, Chloroform-*d*) δ 8.92 (s, 1H), 7.83 (dd, *J* = 8.4, 1.3 Hz, 2H), 7.52 – 7.44 (m, 1H), 7.38 (t, *J* = 7.7 Hz, 2H), 4.29 – 3.54 (m, 2H), 3.03 – 2.69 (m, 2H), 1.66 – 1.56 (m, 2H), 1.56 – 1.46 (m, 1H), 1.27 – 1.11 (m, 2H), 0.89 (d, *J* = 6.4 Hz, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 166.22, 153.60, 133.07, 132.71, 128.74, 128.12, 46.43, 34.02, 30.90, 21.79. ESI HRMS *m/z* (M+H)⁺ calcd 247.1441, obsd 247.1442.

Ethyl 1-(benzoylcarbamoyl)piperidine-4-carboxylate (45). The title product was prepared following General Procedure A and purified by column chromatography eluting with petroleum ether/ethyl acetate (5/1) in 81% yield (49.3 mg). Colorless oil. Electricity = 4.4 F mol⁻¹. ¹H NMR (400 MHz, Chloroform-*d*) δ 9.07 (s, 1H), 7.84 (d, *J* = 7.4 Hz, 2H), 7.48 (t, *J* = 7.4 Hz, 1H), 7.42 - 7.34 (m, 2H), 4.08 (q, *J* = 7.1 Hz, 2H), 4.00 - 3.79 (m, 2H), 3.04 (t, *J* = 11.6 Hz, 2H), 2.46 (tt, *J* = 10.7, 4.0 Hz, 1H), 1.90 (dq, *J* = 12.2, 3.9 Hz, 2H), 1.74 (ddt, *J* = 13.7, 10.6,

5.5 Hz, 2H), 1.19 (t, *J* = 7.1 Hz, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 174.28, 166.28, 153.80, 132.83, 128.74, 128.15, 60.77, 45.36, 40.82, 27.96, 14.32. ESI HRMS *m/z* (M+H)⁺ calcd 305.1496, obsd 305.1496.



Ethyl 1-((4-bromobenzoyl)carbamoyl)piperidine-4-carboxylate (46). The title product was prepared following General Procedure A and purified by column chromatography eluting with petroleum ether/ethyl acetate (5/1) in 98% yield (74.9 mg). White solid. Electricity = 4.4 F mol^{-1} .

¹H NMR (400 MHz, Chloroform-*d*) δ 9.32 (s, 1H), 7.72 (d, J = 8.3 Hz, 2H), 7.51 (d, J = 8.3 Hz, 2H), 4.08 (q, J = 7.1 Hz, 2H), 3.96 – 3.79 (m, 2H), 3.04 (t, J = 11.3 Hz, 2H), 2.47 (t, J = 10.4 Hz, 1H), 1.90 (dd, J = 13.5, 4.1 Hz, 2H), 1.83 – 1.64 (m, 2H), 1.19 (t, J = 7.1 Hz, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 174.19, 165.55, 153.82, 131.98, 131.71, 129.88, 127.81, 60.82, 45.25, 40.77, 27.97, 14.35.

ESI HRMS *m*/*z* (M+H)⁺ calcd 383.0601, obsd 383.0605.



Ethyl 1-((1H-indole-3-carbonyl)carbamoyl)piperidine-4-carboxylate (47). The title product was prepared following General Procedure A and purified by column chromatography eluting with petroleum ether/ethyl acetate (5/2) in 86%yield (59.0 mg). White solid. Electricity = 4.4 F mol^{-1} .

¹H NMR (400 MHz, Chloroform-*d*) δ 9.98 (s, 1H), 8.85 (s, 1H), 8.11 – 8.04 (m, 1H), 7.95 (s, 1H), 7.37 – 7.27 (m, 1H), 7.12 (p, *J* = 4.9 Hz, 2H), 4.04 (q, *J* = 7.2 Hz, 2H), 4.00 – 3.91 (m, 2H), 2.97 (t, *J* = 12.4 Hz, 2H), 2.39 (dt, *J* = 10.9, 6.3 Hz, 1H), 1.89 – 1.77 (m, 2H), 1.66 (q, *J* = 10.7 Hz, 2H), 1.15 (t, *J* = 7.1 Hz, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 174.50, 164.25, 154.23, 136.61, 130.40, 125.92, 123.34, 122.17, 120.97, 112.28, 110.15, 60.85, 45.08, 40.82, 28.02, 14.32.

ESI HRMS *m*/*z* (M+H)⁺ calcd 344.1605, obsd 344.1608.

N-benzoyl-1,4-dioxa-8-azaspiro[4.5]decane-8-carboxamide (48). The title product was prepared following General Procedure A and purified by column chromatography eluting with petroleum ether/ethyl acetate (5/2) in 64% yield (37.2 mg). White solid. Electricity = 4.4 F mol^{-1} .

¹H NMR (400 MHz, Chloroform-*d*) δ 8.83 (s, 1H), 7.82 (d, *J* = 7.7 Hz, 2H), 7.48 (t, *J* = 7.3 Hz, 1H), 7.38 (t, *J* = 7.5 Hz, 2H), 3.91 (s, 4H), 3.69 – 3.39 (m, 4H), 1.72 (t, *J* = 5.8 Hz, 4H); ¹³C NMR (101 MHz, CDCl₃) δ 166.33, 153.58, 133.00, 132.81, 128.79, 128.11, 106.96, 64.61, 43.87, 34.94.

ESI HRMS *m*/*z* (M+H)⁺ calcd 291.1339, obsd 291.1337.

N-benzoyl-3,4-dihydroisoquinoline-2(1H)-carboxamide (49). The title product was prepared following General Procedure A and purified by column chromatography eluting with petroleum ether/ethyl acetate (7/1) in 76% yield (42.6 mg). White solid. Electricity = 4.4 F mol⁻¹. ¹H NMR (400 MHz, Chloroform-*d*) δ 9.25 (s, 1H), 7.88 (d, *J* = 7.6 Hz, 2H), 7.49 (t, *J* = 7.3 Hz, 1H), 7.39 (t, *J* = 7.6 Hz, 2H), 7.13 – 7.04 (m, 3H), 7.00 (s, 1H), 4.62 (s, 2H), 3.89 – 3.45 (m, 2H), 2.86 (t, *J* = 6.1 Hz, 2H); ¹³C NMR (101 MHz, CDCl₃) δ 166.22, 154.33, 134.56, 132.89, 132.86, 128.91, 128.79, 128.28, 126.86, 126.56, 126.39, 50.39, 43.01, 28.79. ESI HRMS *m/z* (M+H)⁺ calcd 281.1285, obsd 281.1283.



N-benzoylmorpholine-4-carboxamide (50). The title product was prepared following General Procedure A and purified by column chromatography eluting with petroleum ether/ethyl acetate (5/1) in 63% yield (29.5 mg). White solid. Electricity = 4.4 F mol^{-1} .

¹H NMR (400 MHz, Chloroform-*d*) δ 9.37 (s, 1H), 7.83 (d, *J* = 7.7 Hz, 2H), 7.46 (t, *J* = 7.4 Hz, 1H), 7.36 (t, *J* = 7.6 Hz, 2H), 3.64 (t, *J* = 4.7 Hz, 4H), 3.45 (t, *J* = 4.7 Hz, 4H); ¹³C NMR (101 MHz, CDCl₃) δ 166.31, 154.13, 132.84, 132.68, 128.66, 128.18, 66.61, 46.18. ESI HRMS *m/z* (M+H)⁺ calcd 235.1077, obsd 235.1078.



N-benzoyl-2-benzyloctahydro-5H-pyrrolo[3,4-c]pyridine-5-carboxamide (51). The title product was prepared following General Procedure A and purified by column chromatography eluting with petroleum ether/ethyl acetate (5/1) in 40% yield (28.6 mg). Brown oil. Electricity = 4.4 F mol^{-1} .

¹H NMR (400 MHz, Chloroform-*d*) δ 8.88 (s, 1H), 7.89 (d, *J* = 7.6 Hz, 2H), 7.56 (t, *J* = 7.4 Hz, 1H), 7.45 (t, *J* = 7.6 Hz, 2H), 7.38 – 7.31 (m, 4H), 7.30 – 7.23 (m, 1H), 4.80 (d, *J* = 41.2 Hz, 1H), 3.80 (s, 1H), 3.75 – 3.63 (m, 2H), 3.13 (t, *J* = 11.4 Hz, 1H), 2.93 – 2.81 (m, 2H), 2.75 (dd, *J* = 9.3, 5.8 Hz, 1H), 2.59 (dd, *J* = 9.2, 2.2 Hz, 1H), 2.29 (t, *J* = 7.9 Hz, 1H), 1.88 – 1.78 (m,

1H), 1.77 – 1.70 (m, 1H), 1.70 – 1.56 (m, 2H); ¹³C NMR (101 MHz, CDCl₃) δ 166.47, 154.75, 139.22, 133.08, 132.76, 128.76, 128.71, 128.42, 128.10, 127.11, 60.63, 58.80, 54.47, 54.07, 42.61, 35.69, 26.41, 23.28.

ESI HRMS *m*/*z* (M+H)⁺ calcd 364.2020, obsd 364.2021.

Methyl benzoylcarbamate (52). The title product was prepared following General Procedure B with methanol (10.0 eq) and purified by column chromatography eluting with petroleum ether/ethyl acetate (7/1) in 59% yield (21.1 mg). White solid. Electricity = 4.7 F mol^{-1} .

¹H NMR (400 MHz, Chloroform-*d*) δ 8.50 (s, 1H), 7.78 (d, *J* = 7.9 Hz, 2H), 7.55 – 7.45 (m, 1H), 7.38 (t, *J* = 7.5 Hz, 2H), 3.73 (s, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 165.23, 152.09, 133.10, 133.03, 128.91, 127.85, 53.23.

ESI HRMS *m*/*z* (M+H)⁺ calcd 180.0655, obsd 180.0656.

Ethyl benzoylcarbamate (53). The title product was prepared following General Procedure B with ethanol (10.0 eq) and purified by column chromatography eluting with petroleum ether/ethyl acetate (7/1) in 49% yield (19.0 mg). White solid. Electricity = 4.7 F mol⁻¹.

¹H NMR (400 MHz, Chloroform-*d*) δ 8.34 (s, 1H), 7.78 (d, *J* = 7.7 Hz, 2H), 7.50 (t, *J* = 7.3 Hz, 1H), 7.40 (t, *J* = 7.7 Hz, 2H), 4.21 (q, *J* = 7.1 Hz, 2H), 1.24 (t, *J* = 7.1 Hz, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 165.19, 151.36, 133.09, 128.94, 127.79, 62.50, 14.35.

ESI HRMS *m*/*z* (M+H)⁺ calcd 194.0812, obsd 194.0812.

2,2,2-trifluoroethyl benzoylcarbamate (54). The title product was prepared following General Procedure B with trifluoroethanol (10.0 eq) and purified by column chromatography eluting with petroleum ether/ethyl acetate (6/1) in 75% yield (37.1 mg). White solid. Electricity = 4.7 F mol^{-1} .

¹H NMR (400 MHz, Chloroform-*d*) δ 8.74 (s, 1H), 7.90 (d, *J* = 7.7 Hz, 2H), 7.60 (t, *J* = 7.3 Hz, 1H), 7.49 (t, *J* = 7.5 Hz, 2H), 4.57 (q, *J* = 8.3 Hz, 2H); ¹³C NMR (101 MHz, CDCl₃) δ 164.97, 149.42, 133.57, 132.47, 129.10, 128.00, 122.81 (q, *J* = 277.2 Hz), 61.45 (q, *J* = 37.3 Hz); ¹⁹F NMR (376 MHz, CDCl₃) δ -73.90.

ESI HRMS *m*/*z* (M+Na)⁺ calcd 270.0348, obsd 270.0348.



4-methylpentyl benzoylcarbamate (55). The title product was prepared following General Procedure B and purified by column chromatography eluting with petroleum ether/ethyl acetate

(6/1) in 60% yield (29.9 mg). White solid. Electricity = 4.7 F mol^{-1} .

¹H NMR (400 MHz, Chloroform-*d*) δ 8.32 (s, 1H), 7.85 (d, *J* = 7.7 Hz, 2H), 7.58 (t, *J* = 7.4 Hz, 1H), 7.47 (t, *J* = 7.6 Hz, 2H), 4.21 (t, *J* = 6.9 Hz, 2H), 1.75 – 1.64 (m, 2H), 1.57 (dq, *J* = 13.3, 6.7 Hz, 1H), 1.31 – 1.17 (m, 2H), 0.89 (d, *J* = 6.6 Hz, 6H); ¹³C NMR (101 MHz, CDCl₃) δ 165.14, 151.42, 133.19, 133.07, 128.95, 127.80, 66.92, 34.87, 27.83, 26.63, 22.58. ESI HRMS *m/z* (M+Na)⁺ calcd 250.1438, obsd 250.1437.

Benzyl benzoylcarbamate (56). The title product was prepared following General Procedure B and purified by column chromatography eluting with petroleum ether/ethyl acetate (6/1) in 51% yield (26.0 mg). White solid. Electricity = 4.7 F mol^{-1} .

¹H NMR (400 MHz, Chloroform-*d*) δ 8.21 (s, 1H), 7.95 – 7.72 (m, 2H), 7.57 (td, *J* = 7.2, 1.3 Hz, 1H), 7.46 (td, *J* = 7.8, 7.3, 1.6 Hz, 2H), 7.42 – 7.33 (m, 5H), 5.24 (s, 2H); ¹³C NMR (101 MHz, CDCl₃) δ 164.98, 151.00, 135.14, 133.20, 133.09, 129.04, 128.86, 128.84, 127.79, 68.14. ESI HRMS *m/z* (M+H)⁺ calcd 256.0968, obsd 256.0967.

 $Ph \xrightarrow{O}_{H} \xrightarrow{O}_{O} \xrightarrow{OEt}$

2-ethoxyethyl benzoylcarbamate (57). The title product was prepared following General Procedure B and purified by column chromatography eluting with petroleum ether/ethyl acetate (6/1) in 61% yield (28.9 mg). White solid. Electricity = 4.7 F mol⁻¹.

¹H NMR (400 MHz, Chloroform-*d*) δ 8.40 (s, 1H), 7.84 (dt, *J* = 7.0, 1.3 Hz, 2H), 7.64 – 7.55 (m, 1H), 7.52 – 7.44 (m, 2H), 4.46 – 4.30 (m, 2H), 3.76 – 3.65 (m, 2H), 3.55 (q, *J* = 7.0 Hz, 2H), 1.22 (t, *J* = 7.0 Hz, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 165.06, 150.88, 133.13, 133.03, 128.96, 127.76, 68.28, 66.79, 65.30, 15.19.

ESI HRMS m/z (M+H)⁺ calcd 238.1074, obsd 238.1079.

(trimethylsilyl)methyl benzoylcarbamate (58). The title product was prepared following General Procedure B and purified by column chromatography eluting with petroleum ether/ethyl acetate (6/1) in 34% yield (17.1 mg). Colorless oil. Electricity = 4.7 F mol⁻¹. ¹H NMR (400 MHz, Chloroform-*d*) δ 8.17 (s, 1H), 7.88 – 7.73 (m, 2H), 7.60 – 7.51 (m, 1H), 7.44 (t, *J* = 7.6 Hz, 2H), 3.89 (s, 2H), 0.08 (s, 9H); ¹³C NMR (101 MHz, CDCl₃) δ 165.07, 152.46, 133.31, 133.04, 128.97, 127.79, 60.04, -2.98. ESI HRMS *m/z* (M+H)⁺ calcd 252.1050, obsd 252.1051.



tert-butyl 4-(((benzoylcarbamoyl)oxy)methyl)piperidine-1-carboxylate (59). The title product was prepared following General Procedure B and purified by column chromatography eluting with petroleum ether/ethyl acetate (5/2) in 55% yield (39.8 mg). Colorless oil. Electricity = 4.7 F mol⁻¹.

¹H NMR (400 MHz, Chloroform-*d*) δ 8.46 (s, 1H), 7.85 (d, *J* = 7.4 Hz, 2H), 7.58 (t, *J* = 7.1 Hz, 1H), 7.48 (t, *J* = 7.1 Hz, 2H), 4.25 – 3.99 (m, 4H), 2.67 (d, *J* = 13.3 Hz, 2H), 1.89 (s, 1H), 1.72 (d, *J* = 12.5 Hz, 2H), 1.45 (s, 9H), 1.33 – 1.11 (m, 2H); ¹³C NMR (101 MHz, CDCl₃) δ 165.13, 154.91, 151.50, 133.14, 133.09, 128.96, 127.83, 79.65, 70.29, 43.36, 35.66, 28.63, 28.55. ESI HRMS *m/z* (M+H)⁺ calcd 363.1914, obsd 363.1912.

Ph N O CO_2Me

Methyl 2-((benzoylcarbamoyl)oxy)acetate (60). The title product was prepared following General Procedure B and purified by column chromatography eluting with petroleum ether/ethyl acetate (6/1) in 57% yield (27.0 mg). White solid. Electricity = 4.7 F mol⁻¹. ¹H NMR (400 MHz, Chloroform-*d*) δ 8.48 (s, 1H), 7.97 – 7.76 (m, 2H), 7.66 – 7.56 (m, 1H), 7.49 (dd, *J* = 8.3, 7.0 Hz, 2H), 4.75 (s, 2H), 3.78 (s, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 168.07, 164.90, 150.42, 133.36, 132.80, 129.06, 127.92, 61.74, 52.62. ESI HRMS *m/z* (M+H)⁺ calcd 238.0710, obsd 238.0714.



((3r,5r,7r)-adamantan-1-yl)methyl benzoylcarbamate (61). The title product was prepared following General Procedure B and purified by column chromatography eluting with petroleum ether/ethyl acetate (6/1) in 48% yield (30.1 mg). White solid. Electricity = 4.7 F mol⁻¹. ¹H NMR (400 MHz, Chloroform-*d*) δ 8.11 (s, 1H), 7.90 – 7.79 (m, 2H), 7.65 – 7.55 (m, 1H), 7.48 (dd, *J* = 8.4, 6.9 Hz, 2H), 3.85 (s, 2H), 2.00 (p, *J* = 3.1 Hz, 3H), 1.77 – 1.70 (m, 3H), 1.70 – 1.63 (m, 3H), 1.58 (d, *J* = 2.9 Hz, 6H); ¹³C NMR (101 MHz, CDCl₃) δ 165.11, 151.68, 133.37, 133.10, 129.03, 127.81, 76.10, 39.27, 37.05, 33.49, 28.13. ESI HRMS *m/z* (M+H)⁺ calcd 314.1751, obsd 314.1748.

Ph H O Ph

Cinnamyl benzoylcarbamate (62). The title product was prepared following General Procedure B and purified by column chromatography eluting with petroleum ether/ethyl acetate (7/1) in 52% yield (29.2 mg). White solid. Electricity = 4.7 F mol⁻¹.

¹H NMR (400 MHz, Chloroform-*d*) δ 8.61 (s, 1H), 7.85 (d, J = 7.7 Hz, 2H), 7.54 (t, J = 7.4 Hz, 1H), 7.43 (t, J = 7.6 Hz, 2H), 7.38 – 7.22 (m, 5H), 6.66 (d, J = 15.8 Hz, 1H), 6.27 (dt, J = 15.8,

6.5 Hz, 1H), 4.83 (d, *J* = 6.7 Hz, 2H); ¹³C NMR (101 MHz, CDCl₃) δ 165.25, 151.23, 135.97, 135.41, 133.09, 132.99, 128.90, 128.74, 128.39, 127.85, 126.79, 122.24, 66.82. ESI HRMS *m/z* (M+H)⁺ calcd 282.1125, obsd 282.1127.

2,2,2-trifluoroethyl (2-(2,2,2-trifluoroethoxy)benzoyl)carbamate (63). The title product was prepared following General Procedure B with isatin and purified by column chromatography eluting with petroleum ether/ethyl acetate (7/1) in 54% yield (38.0 mg). White solid. Electricity = 4.7 F mol^{-1} .

¹H NMR (400 MHz, Chloroform-*d*) δ 10.41 (s, 1H), 8.42 (d, *J* = 8.5 Hz, 1H), 8.08 (dd, *J* = 8.1, 1.6 Hz, 1H), 7.69 – 7.46 (m, 1H), 7.13 (t, *J* = 7.7 Hz, 1H), 4.71 (q, *J* = 8.2 Hz, 2H), 4.58 (q, *J* = 8.4 Hz, 2H); ¹³C NMR (101 MHz, CDCl₃) δ 166.43, 151.62, 141.49, 135.97, 131.44, 123.13 (q, *J* = 277.4 Hz), 123.07 (q, *J* = 277.3 Hz), 122.85, 119.30, 113.60, 61.18 (q, *J* = 36.9 Hz), 61.11 (q, *J* = 37.0 Hz); ¹⁹F NMR (376 MHz, CDCl₃) δ -73.62, -74.11.

ESI HRMS m/z (M+H)⁺ calcd 346.0509, obsd 346.0519.

4. Synthesis of substrates

The α -oxobenzeneacetamide and all the amine and alcohol nucleophiles were purchased from commercial company and used without purification. Other α -oxoamides were synthesized from aryl methyl ketones according to a previously reported procedure.²

$$Ar \xrightarrow{0} + H_2N \xrightarrow{0} S^{\dagger}NH_4 \xrightarrow{1_2} Ar \xrightarrow{0} NH_2$$

General procedure for the synthesis of α -oxoamides. To a round-bottom flask was added aryl methyl ketones (3.0 mmol), ammonium carbamodithioate (6.0 mmol), I₂ (6.0 mmol), DMSO (15 mL). The reaction was stirred at 90 °C for 4 h then poured into a separatory funnel. Then added water, extracted with EtOAc three times (3×20 mL), dried with anhydrous Na₂SO₄ overnight, followed by concentration under reduced pressure. The residue was purified by column chromatography on silica gel to afford the solid α -oxoamides.

Characterization of Selected α-oxoamides.

2-(naphthalen-1-yl)-2-oxoacetamide.² ¹H NMR (400 MHz, DMSO-*d*₆) δ 8.82 (d, *J* = 8.6 Hz, 1H), 8.45 (s, 1H), 8.28 (d, *J* = 8.2 Hz, 1H), 8.13 – 8.05 (m, 3H), 7.82 – 7.56 (m, 3H); ¹³C NMR (101 MHz, DMSO) δ 194.22, 168.09, 135.25, 134.00, 133.77, 130.75, 129.41, 129.23, 127.29, 125.41, 125.36.

2-(4-bromothiophen-2-yl)-2-oxoacetamide. ¹H NMR (400 MHz, DMSO-*d*₆) δ 8.40 (s, 1H), 8.12 (s, 1H), 7.92 (d, *J* = 4.2 Hz, 1H), 7.43 (d, *J* = 4.2 Hz, 1H); ¹³C NMR (101 MHz, DMSO) δ 178.68, 163.83, 137.73, 137.53, 132.17, 126.97.



2-(2,3-dihydrobenzo[b][1,4]dioxin-6-yl)-2-oxoacetamide.³ ¹H NMR (400 MHz, DMSO-*d*₆) δ 8.26 (s, 1H), 7.92 (s, 1H), 7.53 (dd, *J* = 8.5, 2.1 Hz, 1H), 7.47 (d, *J* = 2.1 Hz, 1H), 7.04 (d, *J* = 8.5 Hz, 1H), 4.36 (dd, *J* = 5.9, 2.7 Hz, 2H), 4.31 (dd, *J* = 5.6, 2.8 Hz, 2H); ¹³C NMR (101 MHz, DMSO) δ 189.63, 167.80, 149.62, 143.86, 126.69, 124.61, 118.84, 118.04, 65.23, 64.44.

5. Synthesis of bioactive molecules



A. De novo synthesis of panuramine

Step 1: To a round-bottom flask was added 2-(bromomethyl)naphthalene (0.66 g, 3.0 mmol) tert-butyl piperidin-4-ylcarbamate (0.6 g, 3.0 mmol), Et_3N (0.6 g, 0.83 mL, 6.0 mmol) and DCM (10.0 mL). The solution was stirred at room temperature for 4.0 hours (monitored by TLC). Then the reaction system was cooled to 0 °C and slowly added trifluoroacetic acid (1.37 g, 0.9 mL, 12.0 mmol). The mixture was warmed to room temperature and stirred for 5.0 hours (monitored by TLC), then quenched with saturated aqueous sodium bicarbonate and extracted with dichloromethane, dried with anhydrous Na₂SO₄ overnight, concentrated under reduced pressure and the residue was purified by column chromatography on silica gel to give 1-(naphthalen-2-ylmethyl)piperidin-4-amine in 90% yield.

Step 2: To a 10 mL Schlenk tube was added α-oxobenzeneacetamide (29.8 mg, 0.2 mmol), 1-(naphthalen-2-ylmethyl)piperidin-4-amine (96.0 mg, 0.4 mmol), tBuOK (44.0 mg, 0.4 mmol), TBAI (14.7 mg, 0.04 mmol, 20 mol%) and a mixed solvent of MeCN/THF (1:1, 5.0 mL). The solution was then electrolyzed at a constant current (20 mA) at room temperature for 1.2 hours (Electricity = 4.4 F mol^{-1}). The reaction mixture was concentrated under reduced pressure and the resulting residue was chromatographed through silica gel eluting with petroleum ether/ethyl acetate (2/1) to give the panuramine in 55% yield (42.6 mg).

Panuramine (64). White solid.

¹H NMR (400 MHz, Chloroform-*d*) δ 9.84 (s, 1H), 8.84 (d, J = 7.5 Hz, 1H), 7.99 (d, J = 7.8 Hz, 2H), 7.82 (dd, J = 8.6, 3.7 Hz, 3H), 7.75 (s, 1H), 7.61 – 7.40 (m, 6H), 3.93 – 3.76 (m, 1H), 3.69 (s, 2H), 2.86 (d, J = 11.4 Hz, 2H), 2.26 (t, J = 11.0 Hz, 2H), 2.01 (dt, J = 13.3, 3.9 Hz, 2H), 1.79 – 1.58 (m, 2H); ¹³C NMR (101 MHz, CDCl₃) δ 168.48, 154.02, 136.11, 133.45, 133.15, 132.92, 132.60, 128.81, 128.08, 128.05, 127.86, 127.81, 127.75, 127.53, 126.14, 125.78, 63.35, 52.26, 47.38, 32.03.

ESI HRMS *m*/*z* (M+H)⁺ calcd 388.2020, obsd 388.2021.

B. Synthesis of insecticides



Diflubenzuron (65).⁴ The title product was prepared following the electrochemical procedure described for the synthesis of **64** and purified by column chromatography eluting with petroleum ether/ dichloromethane (1/1) in 48% yield (29.8 mg). White solid. Electricity = 4.4 F mol⁻¹.

¹H NMR (400 MHz, DMSO-*d*₆) δ 11.47 (s, 1H), 10.23 (s, 1H), 7.72 – 7.55 (m, 3H), 7.41 (d, *J* = 8.4 Hz, 2H), 7.26 (t, *J* = 8.4 Hz, 2H); ¹³C NMR (101 MHz, DMSO) δ 162.59, 159.17 (dd, *J* = 250.3, 7.1 Hz), 150.48, 136.85, 133.78, 133.75, 129.30, 128.22, 122.28, 112.66 (d, *J* = 22.6 Hz); ¹⁹F NMR (376 MHz, DMSO) δ -113.43.

ESI HRMS *m*/*z* (M+H)⁺ calcd 311.0393, obsd 311.0397.



Dichlorbenzuron (66).⁴ The title product was prepared following the electrochemical procedure described for the synthesis of **64** and purified by column chromatography eluting with petroleum ether/ dichloromethane (1/1) in 57% yield (35.1 mg). White solid. Electricity = 4.4 F mol^{-1} .

¹H NMR (400 MHz, DMSO-*d*₆) δ 11.27 (s, 1H), 10.47 (s, 1H), 7.62 (dd, *J* = 8.0, 5.6 Hz, 3H), 7.59 - 7.51 (m, 2H), 7.46 (t, *J* = 7.3 Hz, 1H), 7.41 (d, *J* = 8.5 Hz, 2H); ¹³C NMR (101 MHz,

DMSO) & 169.04, 150.91, 136.98, 135.09, 132.52, 130.28, 130.22, 129.58, 129.34, 128.04, 127.72, 122.04.

ESI HRMS *m*/*z* (M+H)⁺ calcd 309.0192, obsd 309.0191.

Triflumuron (67).⁴ The title product was prepared following the electrochemical procedure described for the synthesis of **64** and purified by column chromatography eluting with petroleum ether/ dichloromethane (1/1) in 60% yield (43.0 mg). White solid. Electricity = 4.4 F mol⁻¹.

¹H NMR (400 MHz, DMSO-*d*₆) δ 11.29 (s, 1H), 10.52 (s, 1H), 7.72 (d, *J* = 8.8 Hz, 2H), 7.63 (dd, *J* = 7.5, 1.6 Hz, 1H), 7.60 – 7.52 (m, 2H), 7.47 (td, *J* = 7.3, 1.7 Hz, 1H), 7.36 (d, *J* = 8.6 Hz, 2H); ¹³C NMR (101 MHz, DMSO) δ 169.06, 151.02, 144.57, 137.24, 135.10, 132.54, 130.31, 130.24, 129.61, 127.73, 122.30, 121.96, 120.65 (q, *J* = 255.9 Hz); 19F NMR (376 MHz, DMSO) δ -57.07.

ESI HRMS *m*/*z* (M+H)⁺ calcd 359.0405, obsd 359.0405.

6. Green chemistry metrics analysis



Molecular weight of product: 240; Sum of molecular weight of reagent: 149 + 93

Atom economy = Molecular weight of product/Sum of molecular weight of reagent = 240/242= 99.2%

Total mass in process: 74.5 + 93.0 + 37.0 + 2.5*0.78*1000 + 2.5*0.89*1000 = 4379.5 mg; Mass of product: 80.4 mg

PMI = Total mass in process/Mass of product = 4379.5/80.4 = 54.5

Green chemistry metrics for other protocols were calculated following the above procedures.

7. Mechanistic studies

A. Cyclic Voltammetry Studies

The cyclic voltammograms were recorded on a CHI 760E electrochemical workstation (Shanghai Chenhua, China) at room temperature in MeCN/THF (1:1, 5 mL). A glassy carbon disk (diameter, 1 mm) was used as working electrode, a Pt wire as auxiliary electrode and a SCE as reference electrode. The glass carbon electrode was polished by Al₂O₃ powder (0.05

 $\mu m)$ before cyclic voltammetry. The scan rate was 100 mV/s. The IUPAC convention was used for plotting the CV data.



Figure S2. Cyclic voltammograms. a, Et_4NPF_6 (0.1 M); b, Et_4NPF_6 (0.1 M), α -oxobenzeneamine (10 mM); c, Et_4NPF_6 (0.1 M), cyclohexylmethanamine (10 mM); d, Et_4NPF_6 (0.1 M), TBAI (10 mM).



Figure S3. Cyclic voltammograms. a', Et₄NPF₆ (0.1 M), TBAI (10 mM), α-oxobenzeneamine (10

mM); b', Et₄NPF₆ (0.1 M), TBAI (10 mM), cyclohexylmethanamine (10 mM); c', Et₄NPF₆ (0.1 M), TBAI (10 mM), α-oxobenzeneamine (10 mM), cyclohexylmethanamine (10 mM).

$Ph + NH_2 + NH_2$	NH ₂ GF Pt Radical scavenger MeCN/THF, rt, 1.2 h 1		
Radical scavenger (3	Radical scavenger (3.0 eq)		1
ТЕМРО		15%	
внт		Trace	
1,1-diphenyl ethylene	1,1-diphenyl ethylene		

B. Radical quenching experiments

Three sets of radical quenching experiments were carried out under the standard conditions for the electrosynthesis of **1** by using TEMPO, BHT or 1,1-diphenyl ethylene as the radical scavenger, respectively. After 1.2 h of electrolysis at a constant current of 20 mA, the TEMPO-added system gave **1** in 15% yield and only a trace of **1** was detected with BHT, while the 1,1-diphenyl ethylene did not effectively suppress the reaction. These results could not provide sufficient evidence for a radical pathway cause the low yield of **1** with TEMPO or BHT might be derived from the quenching of the in-situ generated hypervalent iodine species that is crucial for the transformation.

C. Control experiments



A series of control experiments were performed without passing electricity. The reactions produced product **1** when replacing the TBAI with 3.0 equivalent molecular iodine or NIS. Alternatively, according to a relevant method,⁵ benzoyl isocyanate was prepared and then it was used in the reaction with cyclohexanamine in MeCN/THF (1:1, 5.0 mL) without purification, after stirring at room for 8.0 hours, the desired **1** was isolated in 26% yield. These results indicate molecular iodine

or iodine cation might be the promoter for the transformation and α -oxoisocyanate might be in-situ generated as the key intermediate.

8. Reference

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9. NMR spectra

 1 H NMR of 1





 1 H NMR of **2**











 1 H NMR of **4**



¹³C NMR of 4



1 H NMR of **5**










 1 H NMR of 7







 $^{13}\mathrm{C}\ \mathrm{NMR}$ of $\mathbf{8}$





¹³C NMR of **9**













 1 H NMR of **12**



¹³C NMR of **12**





¹³C NMR of **13**



¹H NMR of 14





¹H NMR of 15









¹³C NMR of **16**







¹³C NMR of **17**



 1 H NMR of **18**



















¹³C NMR of **21**

















 1 H NMR of **24**



¹³C NMR of **24**















 1 H NMR of **27**





 1 H NMR of **28**



¹³C NMR of **28**







 1 H NMR of **30**













 1 H NMR of **32**



¹³C NMR of **32**









¹³C NMR of **34**



 1 H NMR of **35**




 1 H NMR of **36**





¹H NMR of **37**



¹³C NMR of **37**





¹³C NMR of **38**



¹H NMR of **39**





 1 H NMR of **40**







¹³C NMR of **41**







 1 H NMR of **43**













¹H NMR of **45**



 13 C NMR of **45**







 1 H NMR of **47**















¹³C NMR of **49**





¹³C NMR of **50**













 1 H NMR of **53**



 13 C NMR of **53**





¹³C NMR of **54**



¹⁹F NMR of **54**













¹H NMR of 57









¹³C NMR of **58**













¹H NMR of 61







¹³C NMR of **62**





¹³C NMR of **63**


¹⁹F NMR of **63**



¹H NMR of 64



¹³C NMR of **64**



 1 H NMR of **65**



¹³C NMR of **65**



¹⁹F NMR of **65**



 1 H NMR of **66**



¹³C NMR of **66**



¹H NMR of 67



¹³C NMR of **67**



¹⁹F NMR of **67**



¹H NMR of 2-(naphthalen-1-yl)-2-oxoacetamide



¹³C NMR of compound 2-(naphthalen-1-yl)-2-oxoacetamide







¹³C NMR of compound 2-(4-bromothiophen-2-yl)-2-oxoacetamide



¹H NMR of 2-(2,3-dihydrobenzo[b][1,4]dioxin-6-yl)-2-oxoacetamide





¹³C NMR of compound 2-(2,3-dihydrobenzo[b][1,4]dioxin-6-yl)-2-oxoacetamide