Direct Connective Synthesis of 5,5-Disubstituted Hydantoin by Tandem α-Amination and α-Arylation of Silyl Enol Ethers

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1 Experimental

1.1 General Directions: Reactions requiring anhydrous conditions (where specified) were executed under dry nitrogen or argon atmospheres in glassware that was dried using either a combination of vacuum and heat-gun, oven, or flame drying. Reaction mixtures were stirred magnetically. Air- and moisture-sensitive liquids and solutions were transferred via syringe into the reaction vessels through rubber septa. Reactions run in a microwave oven were completed on a Biotage Initiator+. All reagents were purchased (unless specified) at highest commercial quality and used as received. Non-anhydrous solvents were purchased (unless specified) at the highest commercial quality and used as received. Anhydrous CH$_2$Cl$_2$ and THF were obtained from the University of Bristol’s dry solvent system and were purified by filtration over a column of activated alumina. All temperatures described below −10 °C were achieved using a Julabo cryostat

1.2 Analytical Directions

Rf: TLC was performed on aluminium backed silica plates (0.2 mm, 60 F254) which were developed using standard visualising agents: UV fluorescence (254 & 366 nm), phosphomolybdic acid / Δ, vanillin / Δ, potassium permanganate / Δ and Seebach / Δ. Chromatography: Flash chromatography was performed on an automated Biotage Isolera TM Spectra Four using gradient elution on pre-packed silica gel Biotage® SNAP Ultra columns.

MP: Melting points were measured on a Kofler hotstage melting point apparatus and are uncorrected.

IR: IR spectra were recorded on neat compounds using a Perkin Elmer (Spectrum One) FT-IR spectrometer (ATR sampling accessory). Only strong and selected absorbance’s (νmax expressed in cm$^{-1}$) are reported.

$^1$H NMR: Spectra were recorded on Jeol ECS (400 MHz) or Bruker NMR (400 MHz or 500 MHz) instruments. Chemical shifts (δ H) are quoted in parts per million (ppm) was
used. Spin-spin coupling constants (J) are reported in Hertz (Hz). 2D NMR experiments HSQC and HMBC where necessary. Spin-spin coupling constants (J) are reported in Hertz (Hz).

13C NMR: Spectra were recorded on Jeol ECS (101 MHz) or Bruker NMR (101 MHz or 125 MHz) instruments. Chemical shifts (δ C) are quoted in parts per million (ppm) and referenced to the appropriate solvent peak(s). Spin-spin coupling constants (J) are reported in Hertz (Hz).

HRMS: High resolution mass spectra were recorded on a Bruker Daltronics MicrOTOF 2 mass spectrometer (ESI).

1.3 Literature Known Starting Materials

Starting materials carbamoyl chlorides were prepared according to the procedures reported. Spectroscopic data for the materials prepared as described above were consistent with those reported in the literature.

1.4 General scheme for Starting materials preparation

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1.5 General Procedure 1: Carbamoyl Chloride Synthesis from the secondary Amines

A flame-dried two-necked round bottom flask was allowed to cool to RT under vacuum. Triphosgene (0.46 equiv) was then added and the reaction vessel subsequently nitrogen/vacuum cycled three times. Anhydrous CH₂Cl₂ (0.7 M) was then added under an atmosphere of nitrogen and the reaction was cooled to 0 °C. Pyridine (1 equiv) was then added dropwise and the reaction allowed to stir for 5 min at 0 °C. Aniline (1 equiv) was then added to the reaction mixture dropwise and allowed to stir for 5 min. The reaction mixture was then allowed to warm to RT until consumption of the aniline was observed by TLC. The reaction mixture was quenched with HCl (1 M, 3 × 20 mL) and extracted with CH₂Cl₂ (3 x 20 mL). The combined organic phases were washed with sat. NaHCO₃ (20 mL), dried over MgSO₄, filtered and the subsequent filtrate concentrated under vacuum to yield the crude carbamoyl chloride. Purification through a pad of silica eluting with 10% EtOAc/Petrol (200 mL) gave the desired carbamoyl chloride, which could be used directly in the next step or stored in the freezer at −20 °C until required. (N.B. prior to purification the carbamoyl chlorides often have vibrant colours. Some of the carbamoyl chlorides solidify on standing at −20 °C).

\[
\begin{align*}
\text{NMe} & \quad \text{O} \\
\text{CF}_3 & \quad \text{Cl}
\end{align*}
\]

\(v_{\text{max}}/\text{cm}^{-1}\) (neat): 2987, 1732, 1322, 1120, 698

**Methyl(3-(trifluoromethyl)phenyl)carbamic chloride (S1f)**

**¹H NMR** (400 MHz; CDCl₃) \(\delta\) 7.67–7.57 (m, 3H), 7.51–7.49 (m, 1H), 3.45 (s, 3H); **¹³C NMR** (101 MHz; CDCl₃) \(\delta\) 148.8, 143.5, 132.3 (q, \(J_{C-F} = 33.0\) Hz), 131.0 (br), 130.3, 125.3 (br), 124.6 (br), 123.4 (q, \(J_{C-F} = 272.6\) Hz), 40.3; **HRMS** (ESI) calcd for \(\text{[C}_9\text{H}_7\text{ClF}_3\text{NONa]}\) requires \(\text{[M + Na]}^+\) 260.0066, found 260.0059
\( V_{\text{max}} / \text{cm}^{-1} \text{(neat)}: \) 2976, 1728, 1401, 1233, 773

**Methyl(naphthalen-1-yl)carbamic chloride (S5i)** (colourless Semi-solid) \(^1\text{H} \text{ NMR} \) (400 MHz; CDCl\(_3 \) \( \delta \) 7.92 (dd, \( J = 7.9, 4.0 \) Hz, 2H), 7.85 (d, \( J = 8.7 \) Hz, 1H), 7.64 – 7.47 (m, 3H), 7.38 (d, \( J = 7.3 \) Hz, 1H), 4.17 (dq, \( J = 14.2, 7.2 \) Hz, 1H), 3.59 (dt, \( J = 13.6, 6.9 \) Hz, 1H), 1.26 (t, \( J = 7.2 \) Hz, 3H); \(^{13}\text{C} \text{ NMR} \) (101 MHz; CDCl\(_3 \) \( \delta \) 149.8, 137.8, 134.7, 130.2, 129.4, 128.7, 127.6, 126.8, 125.5, 122.3, 48.07, 13.2; \text{HRMS} \) (ESI) calcd for [C\(_{13}\)H\(_{12}\)ClNONa] requires [M + Na\(^+\)] 256.0505, found 256.0494

\( V_{\text{max}} / \text{cm}^{-1} \text{(neat)}: \) 2945, 1735, 1481, 1351, 1267, 1059,

**(2-Chlorophenyl)(methyl)carbamic chloride (S5j), \(^1\text{H} \text{ NMR} \) (400 MHz; CDCl\(_3 \) \( \delta \) 7.51 – 7.46 (m, 1H), 7.36 – 7.29 (m, 3H), 3.30 (s, 3H). \(^{13}\text{C} \text{ NMR} \) (101 MHz; CDCl\(_3 \) \( \delta \) 149.3, 140.4, 133.0, 130.6, 130.3, 129.8, 128.2, 38.9. \text{HRMS} \) (ESI) calcd for [C\(_8\)H\(_7\)Cl\(_2\)NONa] requires [M + Na\(^+\)] 225.9802, found 225.9797

1.6 General Procedure 2: Synthesis of Symmetrical arylhydrazine-1,2-dicarboxamide:

A solution of arylcarbamic chloride (1.0 equiv) in MeCN (1.5 M) was added dropwise to a solution of hydrazine monohydrate (1 equiv) in EtOH (1.5 M) at 0 \(^\circ\)C. After 10 minutes a solution of arylcarbamic chloride (1.0 equiv) in MeCN (1.5 M) and a solution of Na\(_2\)CO\(_3\) (1 equiv) in H\(_2\)O (0.75 M) were added to the reaction flask simultaneously. The resulting solution was stirred at room temperature for 20 h, giving a precipitate. The reaction was concentrated under reduced pressure, re-dissolved in DCM, filtered and concentrated under reduced pressure to give a crude residue. Purification by flash silica chromatography afforded the title compound.
General Procedure 3: Synthesis of Symmetrical α, β unsaturated azocarbonamides

A solution of N-bromosuccinimide (1.2-1.5 equiv) in DCM (0.15 M) was added dropwise to a solution of pyridine (2 equiv) and arylhydrazine-1,2-dicarboxamide S1 in DCM (11 mL, 0.30 M) at 0 °C. The reaction was stirred at RT for 3 h, before being quenched with sat. aq. NaHCO₃ (40 mL) and the aqueous layer was extracted with DCM (3 × 20 mL). The combined organics were washed with brine (1 × 20 mL), dried over MgSO₄ and concentrated under reduced pressure to give a crude residue. Purification by flash silica chromatography afforded the title compound as an orange solid.

N¹,N²-dimethyl-N¹,N²-diphenylhydrazine-1,2-dicarboxamide (S1a). A solution of methyl(phenyl)carbamic chloride (750 mg, 4.4 mmol) in MeCN (2.9 mL, 1.5 M) was added dropwise to a solution of hydrazine monohydrate (142 mg, 4.4 mmol, 1 equiv) in EtOH (2.9 mL, 1.5 M) at 0 °C. After 10 minutes a solution of methyl(phenyl)carbamic chloride (750 mg, 4.4 mmol) in MeCN (2.9 mL, 1.5 M) and a solution of Na₂CO₃ (465 mg 4.4 mmol) in H₂O (5.8 mL, 0.75 M) were added to the reaction flask simultaneously. The resulting solution was stirred at room temperature for 20 h, giving a precipitate. The reaction was concentrated under reduced pressure, re-dissolved in DCM, filtered and concentrated under reduced pressure to give a crude residue. Purification by flash silica chromatography (5% MeOH/DCM) afforded the title compound (1013 mg, 75%) as a white solid.

**MP:** 145-147 °C

**ν<sub>max</sub>/cm<sup>-1</sup>(neat):** 3287, 2922, 1662, 1512, 1376, 1335, 1138, 824

**¹H NMR** (400 MHz; CDCl₃) δ 7.42 (d, J = 8.3 Hz, 2H), 7.40 – 7.35 (m, 6H), 7.29 (tt, J = 6.1, 1.6 Hz, 2H), 6.06 (s, 2H), 3.27 (s, 6H); **¹³C NMR** (101 MHz; CDCl₃) δ ¹³C NMR (101 MHz,
CDCl\textsubscript{3} \(\delta\) 159.2, 142.3, 130.0, 127.6, 127.2, 37.4; HRMS m/z (ESI\textsuperscript{+}) \([C_{16}H_{18}N_{4}O_{2}Na]\) requires \([M + Na]^+\): 321.1327; found: 321.1320

\((E)-N_1^1,N_2^2\text{-dimethyl-}N_1^1,N_2^2\text{-diphenyldiazene-1,2-dicarboxamide (1a)}\). A solution of \(N\)-bromosuccinimide (356 mg, 2.23 mmol, 1.2 eq.) in DCM (11 mL, 0.15 M) was added dropwise to a solution of pyridine (0.30 mL, 3.3 mmol, 2 eq.) and \(N_1^1,N_2^2\text{-dimethyl-}N_1^1,N_2^2\text{-diphenyldiazine-1,2-dicarboxamide S1a (500 mg, 1.67 mmol) in DCM (5.5 mL, 0.30 M) at 0 \^\circ\text{C}. The reaction was stirred at RT for 3 h, before being quenched with sat. aq. NaHCO\textsubscript{3} (40 mL) and the aqueous layer was extracted with DCM (3 \(\times\) 20 mL). The combined organics were washed with brine (1 \(\times\) 20 mL), dried over MgSO\textsubscript{4} and concentrated under reduced pressure to give a crude residue. Purification by flash silica chromatography (10% EtOAc/Hexane) afforded the title compound (372 mg, 75%) as an orange solid.

MP: 171-173 \^\circ\text{C}

\(\nu_{\text{max}} /\text{cm}^{-1}\) (neat): 2921, 1710, 1705, 1574, 1362,

\(^1\text{H} NMR\) (400 MHz, CDCl\textsubscript{3}) \(\delta\) 7.39 – 7.24 (m, 10H), 3.39 (s, 6H); \(^{13}\text{C} NMR\) (100 MHz, CDCl\textsubscript{3}) \(\delta\) \(^{13}\text{C} NMR\) (101 MHz, CHLOROFORM-\(D\)) \(\delta\) 160.9, 140.6, 129.4, 128.0, 127.1, 38.5; HRMS (ESI) calcd for \([C_{16}H_{16}N_{4}O_{2}Na]\) requires \([M + Na]^+\) 319.1171, found 319.1164

\(N_1^1, N_2^2\text{-dimethyl-}N_1^1, N_2^2\text{-di-p-tolylhydrazine-1,2-dicarboxamide (S1b)}\). A solution of \(N\)-methyl(p-tolyl)carbamic chloride (750 mg, 4.09 mmol) in MeCN (2.73 mL, 1.5 M) was added dropwise to a solution of hydrazine monohydrate (131 mg, 4.09 mmol, 1 equiv) in EtOH (2.73 mL, 1.5 M) at 0 \^\circ\text{C. After 10 minutes a solution of} \(N\)-methyl(p-tolyl)carbamic chloride (750 mg, 4.09 mmol) in MeCN (2.73 mL, 1.5 M) and a solution of Na\textsubscript{2}CO\textsubscript{3} (430 mg 4.09 mmol) in H\textsubscript{2}O (5.46 mL, 0.75 M) were added to the reaction flask simultaneously. The resulting solution
was stirred at room temperature for 20 h, giving a precipitate. The reaction was concentrated under reduced pressure, re-dissolved in DCM, filtered and concentrated under reduced pressure to give a crude residue. Purification by flash silica chromatography (5% MeOH/DCM) afforded the title compound (1023 mg, 76%) as a white solid.

**MP:** 150-152 °C

**\( \nu_{\text{max}} / \text{cm}^{-1} \ (\text{neat}) \):** 3287, 2922, 1662, 1512, 1476, 1335, 1138, 824

**\( ^1H \text{ NMR} \) (400 MHz; CDCl\(_3\)) \( \delta \):** 7.25 – 7.22 (m, 4H), 7.20 – 7.17 (m, 4H), 6.04 (br, s, 2H), 3.23 (s, 6H), 2.23 (s, 6H); **\( ^{13}C \text{ NMR} \) (101 MHz; CDCl\(_3\)) \( \delta \):** 158.0, 139.6, 137.9, 130.8, 127.1, 37.7, 21.2; **HRMS m/z (ESI) \([\text{M} + \text{Na}]^+ \):** calcd for [C\(_{18}\)H\(_{22}\)N\(_4\)O\(_2\)Na] requires [M + Na]\(^+\): 349.1640; found: 349.1644

\( (E)\)-N\(_1\),N\(_2\)-dimethyl-N\(_1\),N\(_2\)-di-p-tolylidazene-1,2-dicarboxamide (1b); A solution of \( N\)-bromosuccinimide (651 mg, 3.68 mmol, 1.2 equiv) in DCM (20 mL, 0.15 M) was added dropwise to a solution of pyridine (0.557 mL, 6.12 mmol, 2 equiv) and N\(_1\),N\(_2\)-dimethyl-N\(_1\),N\(_2\)-di-p-tolylhydrazine-1,2-dicarboxamide S1b (1g, 3.06 mmol) in DCM (10 mL, 0.30 M) at 0 °C. The reaction was stirred at RT for 3 h, before being quenched with sat. aq. NaHCO\(_3\) (40 mL) and the aqueous layer was extracted with DCM (3 \( \times \) 20 mL). The combined organicns were washed with brine (1 \( \times \) 20 mL), dried over MgSO\(_4\) and concentrated under reduced pressure to give a crude residue. Purification by flash silica chromatography (30% EtOAc/Hexane) afforded the title compound (876 mg, 88%) as orange needles.

**MP:** 181-183 °C

**\( \nu_{\text{max}} / \text{cm}^{-1} \ (\text{neat}) \):** 2922, 1709, 1572, 1365, 1125, 820, 555

\( ^1H \text{ NMR} \) (400 MHz, CDCl\(_3\)) \( \delta \): 7.12 (d, \( J = 8.0 \) Hz, 4H), 6.86 (d, \( J = 8.0 \) Hz, 4H), 3.37 (s, 6H) 2.34 (s, 6H); **\( ^{13}C \text{ NMR} \) (100 MHz, CDCl\(_3\)) \( \delta \):** 161.1, 138.1, 137.9, 130.0, 126.9, 38.6, 21.2; **HRMS (ESI) calcd for [C\(_{18}\)H\(_{20}\)N\(_4\)O\(_2\)Na] requires [M + Na]\(^+\):** 347.1484, found 347.1477
N₁,N₂-bis(4-cyanophenyl)-N¹,N²-dimethylhydrazine-1,2-dicarboxamide (S¹c). A solution of (4-cyanophenyl)(methyl)carbamic chloride (400 mg, 2.06 mmol) in MeCN (1.37 mL, 1.5 M) was added dropwise to a solution of hydrazine monohydrate (65 mg, 2.03 mmol, 1 equiv) in EtOH (1.37 mL, 1.5 M) at 0 °C. After 10 minutes a solution of (4-cyanophenyl)(methyl)carbamic chloride (400 mg, 2.06 mmol) in MeCN (1.37 mL, 1.5 M) and a solution of Na₂CO₃ (259 mg 2.47 mmol) in H₂O (2.74 mL, 0.75 M) were added to the reaction flask simultaneously. The resulting solution was stirred at room temperature for 20 h, giving a precipitate. The reaction was concentrated under reduced pressure, re-dissolved in DCM, filtered and concentrated under reduced pressure to give a crude residue. Purification by flash silica chromatography (5% MeOH/DCM) afforded the title compound (509 mg, 71%) as a white solid.

**MP**: 200-202 °C

**Vₘₐₓ /cm⁻¹ (neat)**: 3320, 2970, 2227, 1665, 1603, 1505, 1333, 1110, 754

¹H NMR (400 MHz; CDCl₃) δ 7.76 – 7.73 (m, 4H), 7.59 – 7.56 (m, 4H), 6.33 (br, s, 2H), 3.36 (s, 6H); ¹³C NMR (101 MHz; CDCl₃) δ 156.9, 146.5, 133.9, 127.0, 118.0, 110.8, 37.4; **HRMS** m/z (ESI⁺) [C₁₈H₁₆N₆O₂Na] requires [M + Na]⁺: 371.1232; found: 371.1243

(E)-N¹,N²-bis(4-cyanophenyl)-N¹,N²-dimethylidiazene-1,2-dicarboxamide (1c); A solution of N-bromosuccinimide (305 mg, 1.7 mmol, 1.2 equiv) in DCM (9.4 mL, 0.15 M) was added dropwise to a solution of pyridine (0.260 mL, 2.8 mmol, 2 equiv) and N¹,N²-bis(4-cyanophenyl)-N¹,N²-dimethylhydrazine-1,2-dicarboxamide S¹c (500, 1.4 mmol) in DCM (4.7 mL, 0.30 M) at 0 °C. The reaction was stirred at RT for 3 h, before being quenched with sat.
aq. NaHCO₃ (40 mL) and the aqueous layer was extracted with DCM (3 × 20 mL). The combined organics were washed with brine (1 × 20 mL), dried over MgSO₄ and concentrated under reduced pressure to give a crude residue. Purification by flash silica chromatography (30% EtOAc/Hexane) afforded the title compound (420 mg, 84%) as orange needles.

**MP:** 204-206 °C

**ν<sub>max</sub>/cm<sup>-1</sup>(neat):** 3398, 2312, 1720, 1658, 1023, 995

**¹H NMR** (500 MHz, CDCl₃) δ 7.66 (d, J = 8.6 Hz, 4H), 7.25 – 7.15 (m, 4H), 3.46 (s, 6H);

**¹³C NMR** (126 MHz, CDCl₃) 160.0, 144.3, 133.3, 127.4, 117.7, 111.8, 29.7; **HRMS** (ESI) calcd for [C₁₈H₁₄N₆O₂Na] requires [M + Na]+ 369.1076, found 369.1070

N¹,N²-bis(4-fluorophenyl)-N¹,N²-dimethylhydrazine-1,2-dicarboxamide (S1d); A solution of (4-fluorophenyl)(methyl)carbamic chloride (500 mg, 2.67 mmol) in MeCN (1.78 mL, 1.5 M) was added dropwise to a solution of hydrazine monohydrate (85 mg, 2.65 mmol, 1 equiv) in EtOH (1.78 mL, 1.5 M) at 0 °C. After 10 minutes a solution of (4-fluorophenyl)(methyl)carbamic chloride (500 mg, 2.67 mmol) in MeCN (1.5 mL, 1.5 M) and a solution of Na₂CO₃ (245 mg 2.3 mmol) in H₂O (3.5 mL, 0.75 M) were added to the reaction flask simultaneously. The resulting solution was stirred at room temperature for 20 h, giving a precipitate. The reaction was concentrated under reduced pressure, re-dissolved in DCM, filtered and concentrated under reduced pressure to give a crude residue. Purification by flash silica chromatography (05% MeOH/DCM) afforded the title compound (630 mg, 70%) as a white solid.

**MP:** 100-102 °C

**ν<sub>max</sub>/cm<sup>-1</sup>(neat):** 3286, 2967, 1786, 1660, 1505, 1338, 1220, 1140, 842, 752
\[^1\text{H} \text{NMR}\] (400 MHz; CDCl\textsubscript{3}) $\delta$ 7.36 – 7.33 (m, 4H), 7.11 – 7.07 (m, 4H), 6.00 (br, s, 2H), 3.23 (s, 6H); \[^{13}\text{C} \text{NMR}\] (101 MHz; CDCl\textsubscript{3}) $\delta$ 161.0 (d, $J_{\text{C-F}} = 249.0$ Hz), 157.9, 138.1, 129.2 (d, $J_{\text{C-F}} = 8.0$ Hz), 117.2 (d, $J_{\text{C-F}} = 23.2$ Hz), 37.9; HRMS m/z (ESI\textsuperscript{+}) $[\text{C}_{16}\text{H}_{16}\text{F}_{2}\text{N}_{4}\text{O}_{2}\text{Na}]$ requires $[\text{M+Na}]^+$ 357.1139; found: 357.1136

\[(E)-N^1,N^2\text{-bis}(4\text{-fluorophenyl})\text{-N}^1,N^2\text{-dimethyldiazene-1,2-dicarboxamide \ (1d)}; \text{ A solution}\]
\[\text{of } N\text{-bromosuccinimide (381 mg, 2.15 mmol, 1.2 equiv) in DCM (11.9 mL, 0.15 M) was added}\]
\[\text{dropwise to a solution of pyridine (0.32 mL, 3.5 mmol, 2 equiv) and } N^1,N^2\text{-bis(4-}\]
\[\text{fluorophenyl)-N}^1,N^2\text{-dimethylhydrazine-1,2-dicarboxamide S1d (250 mg, 0.89 mmol) in}\]
\[\text{DCM (5.56 mL, 0.30 M) at 0 °C. The reaction was stirred at RT for 5 h, before being quenched}\]
\[\text{with sat. aq. NaHCO}_3 (20 mL) and the aqueous layer was extracted with DCM (3 × 20 mL).}\]
\[\text{The combined organics were washed with brine (1 × 20 mL), dried over MgSO}_4 \text{ and}\]
\[\text{concentrated under reduced pressure to give a crude residue. Purification by flash silica}\]
\[\text{chromatography (30% EtOAc/Hexane) afforded the title compound (550 mg, 92%) as orange}\]
\[\text{needles.}\]

\textbf{MP:} 161-163 °C

$V_{\text{max}} \text{/cm}^{-1} \text{(neat):}$ 2986, 1713, 1507, 1370, 1222, 842

\[^1\text{H} \text{NMR}\] (400 MHz, CDCl\textsubscript{3}) $\delta$ 7.07-6.99 (m, 8H), 3.41 (s, 6H); \[^{13}\text{C} \text{NMR}\] (100 MHz, CDCl\textsubscript{3}) $\delta$ 161.2 (d, $J_{\text{C-F}} = 219.0$ Hz), 160.5, 136.5, 128.9 (d, $J_{\text{C-F}} = 9.0$ Hz), 116.4 (d, $J_{\text{C-F}} = 23.2$ Hz), 38.9; HRMS (ESI) calcld for [C\textsubscript{16}H\textsubscript{14}F\textsubscript{2}N\textsubscript{4}O\textsubscript{2}\textsubscript{Na}] requires [M + Na]$^+$ 355.0983, found 355.0985
**N<sup>1</sup>,N<sup>2</sup>-bis(3-chlorophenyl)-N<sup>1</sup>,N<sup>2</sup>-dimethylhydrazine-1,2-dicarboxamide (S1e)**: A solution of (3-chlorophenyl)(methyl)carbamic chloride (400 mg, 1.98 mmol) in MeCN (1.3 mL, 1.5 M) was added dropwise to a solution of hydrazine monohydrate (63 mg, 1.98 mmol, 1 equiv) in EtOH (1.3 mL, 1.5 M) at 0 °C. After 10 minutes a solution of (4-fluorophenyl)(methyl)carbamic chloride (500 mg, 2.67 mmol) in MeCN (1.3 mL, 1.5 M) and a solution of Na<sub>2</sub>CO<sub>3</sub> (207 mg 1.98 mmol) in H<sub>2</sub>O (3.0 mL, 0.75 M) were added to the reaction flask simultaneously. The resulting solution was stirred at room temperature for 20 h, giving a precipitate. The reaction was concentrated under reduced pressure, re-dissolved in DCM, filtered and concentrated under reduced pressure to give a crude residue. Purification by flash silica chromatography (05% MeOH/DCM) afforded the title compound (600 mg, 82%) as white needles.

**MP:** 164-166 °C

**V<sub>max</sub> /cm<sup>-1</sup>(neat):** 3280, 2969, 1660 1591, 1479, 1351

**1H NMR** (400 MHz; CDCl<sub>3</sub>) δ 7.35 (dd, 4.9, 2.9 Hz, 3H), 7.32 – 7.30 (m, 2H), 7.28 (dt, 3.6, 1.8 Hz, 2H), 7.27 – 7.24 (m, 1H), 6.13 (s, 2H), 3.25 (s, 6H); **13C NMR** (101 MHz; CDCl<sub>3</sub>) δ 157.41, 143.47, 135.53, 131.15, 128.11, 127.47, 125.41, 37.74; **HRMS m/z (ESI<sup>+</sup>)** [C<sub>16</sub>H<sub>16</sub>Cl<sub>2</sub>N<sub>4</sub>O<sub>2</sub>Na] requires [M+Na]<sup>+</sup> 389.0548; found: 389.0548

**[E]-N<sup>1</sup>,N<sup>2</sup>-bis(3-chlorophenyl)-N<sup>1</sup>,N<sup>2</sup>-dimethylidazene-1,2-dicarboxamide (1e)**: A solution of N-bromosuccinimide (402 mg, 2.2 mmol, 1.2 equiv) in DCM (12.6 mL, 0.15 M) was added dropwise to a solution of pyridine (0.34 mL, 3.7 mmol, 2 equiv) and N<sup>1</sup>,N<sup>2</sup>-bis(3-chlorophenyl)-N<sup>1</sup>,N<sup>2</sup>-dimethylhydrazine-1,2-dicarboxamide S1e (690 mg, 1.89 mmol) in DCM (6.3 mL, 0.30 M) at 0 °C. The reaction was stirred at RT for 5 h, before being quenched with sat. aq. NaHCO<sub>3</sub> (20 mL) and the aqueous layer was extracted with DCM (3 × 20 mL). The combined organics were washed with brine (1 × 20 mL), dried over MgSO<sub>4</sub> and
concentrated under reduced pressure to give a crude residue. Purification by flash silica chromatography (10% EtOAc/Hexane) afforded the title compound (620 mg, 90%) as orange needles.

**MP:** 116-118 °C

\[ \nu_{\text{max}} / \text{cm}^{-1} (\text{neat}): \] 2987, 1713, 1364, 786, 693

**\(^1\)H NMR** (400 MHz, CDCl\(_3\)) \(\delta\) 7.28 (d, \(J = 4.0 \) Hz, 5H), 7.08 (s, 2H), 6.87 (s, 1H), 3.40 (s, 6H); **\(^{13}\)C NMR** (100 MHz, CDCl\(_3\)) \(\delta\) 160.4, 141.7, 135.0, 130.5, 128.4, 127.1, 125.6, 125.2, 38.6; HRMS (ESI) caled for [C\(_{16}\)H\(_{14}\)Cl\(_2\)N\(_4\)O\(_2\)] requires [M + Na]+ 387.0392, found 387.0389

![Structure](image-url)

**N\(^1\),N\(^2\)-dimethyl-N\(^1\),N\(^2\)-bis(3-(trifluoromethyl)phenyl)hydrazine-1,2-dicarboxamide(S1f)**.

A solution of methyl(3-(trifluoromethyl)phenyl)carbamic chloride (400 mg, 1.68 mmol) in MeCN (1.1 mL, 1.5 M) was added dropwise to a solution of hydrazine monohydrate (85 mg, 2.65 mmol, 1 equiv) in EtOH (1.1 mL, 1.5 M) at 0 °C. After 10 minutes a solution of methyl(3-(trifluoromethyl)phenyl)carbamic chloride (400 mg, 1.68 mmol) in MeCN (1.1 mL, 1.5 M) and a solution of Na\(_2\)CO\(_3\) (212 mg 2.0 mmol) in H\(_2\)O (2.2 mL, 0.75 M) were added to the reaction flask simultaneously. The resulting solution was stirred at room temperature for 20 h, giving a precipitate. The reaction was concentrated under reduced pressure, re-dissolved in DCM, filtered and concentrated under reduced pressure to give a crude residue. Purification by flash silica chromatography (5% MeOH/DCM) afforded the title compound (663 mg, 90%) as white needles.

**MP:** 112-114 °C

\[ \nu_{\text{max}} / \text{cm}^{-1} (\text{neat}): \] 3274, 2968, 1658, 1613, 1593, 1492, 1327, 1120, 701
$^1$H NMR (400 MHz; CDCl$_3$) $\delta$ 7.65 – 7.63 (m, 2H), 7.60 – 7.55 (m, 6H), 6.09 (br, s, 1H), 3.31 (s, 6H); $^{13}$C NMR (101 MHz; CDCl$_3$) $\delta$ 157.3, 142.9, 132.8, 132.4, 130.8, 130.6, 126.0 (q, $J_{CF} = 272$ Hz), 124.5 (q, $J_{CF} = 4.0$ Hz, CF$_3$), 123.9 (d, $J_{CF} = 4.0$ Hz, CF$_3$), 37.7; HRMS m/z (ESI$^+$) [C$_{18}$H$_{16}$F$_6$N$_4$O$_2$Na] requires [M + Na]$^+$: 457.1075; found: 457.1057

(E)-N$^1$,N$^2$-dimethyl-N$^1$,N$^2$-bis(3-(trifluoromethyl)phenyl)diazene-1,2-dicarboxamide (1f);

A solution of N-bromosuccinimide (244.7 mg, 1.38 mmol, 1.2 equiv) in DCM (7.6 mL, 0.15 M) was added dropwise to a solution of pyridine (0.20 mL, 2.3 mmol, 2 equiv) and N$^1$,N$^2$-dimethyl-N$^1$,N$^2$-bis(3-(trifluoromethyl)phenyl)hydrazine-1,2-dicarboxamide S1f (500 mg, 1.15 mmol) in DCM 3.8 mL, 0.30 M) at 0 °C. The reaction was stirred at RT for 5 h, before being quenched with sat. aq. NaHCO$_3$ (20 mL) and the aqueous layer was extracted with DCM (3 × 20 mL). The combined organics were washed with brine (1 × 20 mL), dried over MgSO$_4$ and concentrated under reduced pressure to give a crude residue. Purification by flash silica chromatography (30% EtOAc/Hexane) afforded the title compound (420 mg, 84%) as orange needles.

MP: 143-145 °C

$V_{max}$/cm$^{-1}$ (neat): 2936, 1718, 1709 1452, 1328, 1121, 1071, 699

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.57-7.33 (m, 7H), 7.19-7.13 (m, 1H), 3.44 (s, 6H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 160.1, 141.4, 132.2 (d, $J_{CF} = 33.4$ Hz), 130.6, 130.10, 124.9, (d, $J_{CF} = 23.0$ Hz), 123.3 (q, $J_{CF} = 272.7$ Hz), 121.7 (d, $J_{CF} = 22.0$ Hz), 38.6; HRMS (ESI) calcd for [C$_{18}$H$_{16}$F$_6$N$_4$O$_2$Na] requires [M + Na]$^+$ 455.0919, found 455.0903

N$^1$,N$^2$-dimethyl-N$^1$,N$^2$-di(pyridin-2-yl)hydrazine-1,2-dicarboxamide (S1g). A solution of N-methyl(pyridin-2-yl)carbamic chloride (400 mg, 2.35 mmol) in MeCN (1.56 mL, 1.5 M)
was added dropwise to a solution of hydrazine monohydrate (75mg, 2.3 mmol, 1 equiv) in EtOH (1.56 mL, 1.5 M) at 0°C. After 10 minutes a solution of N-methyl(pyridin-2-yl)carbamic chloride (400 mg, 2.35 mmol) in MeCN (1.56 mL, 1.5 M) and a solution of Na₂CO₃ (247 mg 2.3 mmol) in H₂O (3.1 mL, 0.75 M) were added to the reaction flask simultaneously. The resulting solution was stirred at room temperature for 20 h, giving a precipitate. The reaction was concentrated under reduced pressure, re-dissolved in DCM, filtered and concentrated under reduced pressure to give a crude residue. Purification by flash silica chromatography (2% MeOH/DCM) afforded the title compound (560 mg, 79%) as a pale white solid.

**MP**: 160-162 °C

**Vₘₐₓ / cm⁻¹ (neat)**: 3112, 2983, 1666, 1592, 1573, 1469, 1431, 1316, 1133, 774

**¹H NMR** (400 MHz; CDCl₃) δ 12.0 (br s, 2H), 8.31 – 8.29 (m, 2H), 7.71 – 7.67 (m, 2H), 7.00–6.94 (m, 4H), 3.42 (s, 6H); ¹³C NMR (101 MHz; CDCl₃) δ 156.8, 155.4, 146.3, 138.8, 117.5, 111.6, 33.1; HRMS m/z (ESI⁺) [C₁₄H₁₆N₆O₂Na] requires: 323.1232; found: 323.1228.

(E)-N¹,N²-dimethyl-N¹,N²-di(pyridin-2-yl)diazene-1,2-dicarboxamide (1g): A solution of N-bromosuccinimide (396 mg, 2.23 mmol, 1.2 equiv) in DCM (12 mL, 0.15 M) was added dropwise to a solution of pyridine (0.34 mL, 4.2 mmol, 2 equiv) and N¹,N²-dimethyl-N¹,N²-di(pyridin-2-yl)hydrazine-1,2-dicarboxamide S₁g (560 mg, 1.8 mmol) in DCM (6 mL, 0.30 M) at 0 °C. The reaction was stirred at RT for 3 h, before being quenched with sat. aq. NaHCO₃ (40 mL) and the aqueous layer was extracted with DCM (3 × 20 mL). The combined organics were washed with brine (1 × 20 mL), dried over MgSO₄ and concentrated under reduced pressure to give a crude residue. Purification by flash silica chromatography (40% EtOAc/Hexane) afforded the title compound (438 mg, 78%) as orange needles.

**MP**: 134-136 °C

**Vₘₐₓ / cm⁻¹ (neat)**: 2918, 1768, 1717, 1437, 1362, 1113, 785
$^1$H NMR (400 MHz, CDCl$_3$) δ 8.42 (d, $J = 4.0$ Hz, 2H), 7.73–7.69 (m, 2H), 7.26–7.25 (m, 2H), 7.17–7.14 (m, 2H), 3.35 (br s, 6H); $^{13}$C NMR (101 MHz, CDCl$_3$) δ 161.0, 152.9, 148.3, 137.9, 121.8, 119.6, 29.5; HRMS (ESI) calcd for [C$_{14}$H$_{14}$N$_6$O$_2$Na] requires [M + Na]$^+$ 321.1076, found 321.1071

1.8 General Procedure 4: Carbamoyl Chloride and tert-Butyl carbamate coupling

Pyridine (2.0 equiv) was added in one portion to a solution of carbamoyl chloride and tert-butyl carbazate (1.3 equiv) in MeCN (0.5 M) and the resulting solution stirred at RT for 18–40 h. The reaction was quenched with H$_2$O (20 mL) and the aqueous layer was extracted with DCM (3 × 15 mL). The combined organics were washed with brine (1 × 15 mL), dried over MgSO$_4$ and concentrated under reduced pressure to give a crude residue. Purification by flash silica chromatography.

1.9 General Procedure 5: Synthesis of unsymmetrical $\alpha, \beta$ unsaturated azocarbonamides

A solution of N-bromosuccinimide (1.2-1.5 equiv) in DCM (0.15 M) was added dropwise to a solution of pyridine (2 equiv) and arylcarbamoyl)hydrazine-1-carboxylate S5 in DCM (11 mL, 0.30 M) at 0 °C. The reaction was stirred at RT for 3 h, before being quenched with sat. aq. NaHCO$_3$ (40 mL) and the aqueous layer was extracted with DCM (3 × 20 mL). The combined organics were washed with brine (1 × 20 mL), dried over MgSO$_4$ and concentrated under reduced pressure to give a crude residue. Purification by flash silica chromatography afforded the s an orange solid.

tert-Butyl 2-(methyl(p-toly)carbamoyl)hydrazine-1-carboxylate (S5a). Pyridine (0.69 mL, 2 equiv) was added in one portion to a solution of methyl(p-toly)carbamic chloride (700 mg, 3.8 mmol, 1.0 equiv) and tert-butyl carbazate (656 mg, 4.9 mmol, 1.3 equiv) in MeCN (7.6 mL, 0.5 M) and the resulting solution stirred at RT for 18 h. The reaction was quenched with
H$_2$O (20 mL) and the aqueous layer was extracted with DCM (3 × 15 mL). The combined organics were washed with brine (1 × 15 mL), dried over MgSO$_4$ and concentrated under reduced pressure to give a crude residue. Purification by flash silica chromatography (40% EtOAc/Petrol) afforded the title compound (1100 mg, 96%) as white needles.

**M.P.:** 106-108 °C

$V_{\text{max}}$/cm$^{-1}$ (neat): 3279, 2977, 1725, 1672, 1513, 1366, 1161, 1018, 754

$^1$H NMR (400 MHz; CDCl$_3$) $\delta$ 7.19 (d, $J = 6.5$ Hz, 4H), 6.32 (s, 1H), 6.03 (s, 1H), 3.23 (s, 3H), 2.34 (s, 3H), 1.41 (s, 9H); $^{13}$C NMR (101 MHz; CDCl$_3$) $\delta$ 157.2, 156.5, 139.5, 137.9, 130.8, 127.1, 81.2, 37.8, 28.3, 21.1; HRMS m/z (ESI$^+$) [C$_{14}$H$_{21}$N$_3$O$_3$Na]$^+$ requires[M + Na]$^+$: 302.1481; found: 302.1493

**tert-Butyl (E)-2-(methyl(p-tolyl)carbamoyl)diazene-1-carboxylate (5a).** A solution of N-bromosuccinimide (952 mg, 4.5 mmol, 1.5 equiv) in DCM (22 mL, 0.15 M) was added dropwise to a solution of pyridine (0.651 mL, 7.1 mmol, 2 equiv) and tert-butyl 2-(methyl(p-tolyl)carbamoyl)hydrazine-1-carboxylate S4a (1000 mg, 3.5 mmol) in DCM (11 mL, 0.30 M) at 0 °C. The reaction was stirred at RT for 3 h, before being quenched with sat. aq. NaHCO$_3$ (40 mL) and the aqueous layer was extracted with DCM (3 × 20 mL). The combined organics were washed with brine (1 × 20 mL), dried over MgSO$_4$ and concentrated under reduced pressure to give a crude residue. Purification by flash silica chromatography (25% EtOAc/Hexane) afforded the title compound (860 mg, 87%) as an orange solid.

**M.P.:** 83-85 °C

$V_{\text{max}}$/cm$^{-1}$ (neat): 2982, 1762, 1710, 1513, 1371, 1254, 1150, 835

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.13 (d, $J = 8.1$ Hz, 2H), 6.99 (d, $J = 8.1$ Hz, 2H), 3.47 (s, 3H), 2.32 (s, 3H), 1.48 (s, 9H); $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 161.0, 159.8, 138.0, 137.9, 130.0,
tert-Butyl 2-(methyl(phenyl)carbamoyl)hydrazone-1-carboxylate (S5b). Pyridine (1.07 mL, 11.8 mmol, 2.0 equiv) was added in one portion to a solution of N-methyl-N-phenylcarbamoyl chloride (1 g, 5.9 mmol, 1.1 equiv) and tert-butyl carbazate (0.7 mg, 5.36 mmol, 1 equiv) in MeCN (25 mL, 0.21 M) and the resulting solution stirred at RT for 18 h. The reaction was quenched with H₂O (20 mL) and the aqueous layer was extracted with DCM (3 × 15 mL). The combined organics were washed with brine (1 × 15 mL), dried over MgSO₄ and concentrated under reduced pressure to give a crude residue. Purification by flash silica chromatography (40% EtOAc/Petrol) afforded the title compound (1.1 g, 71%) as colourless oil.

\[ V_{\text{max}}/\text{cm}^{-1}(\text{neat}) : 3287, 2977, 1690, 1494, 1157, 699 \]

\[ ^{1}H \text{ NMR} (400 \text{ MHz}; \text{CDCl}_3) \delta 7.47 – 7.40 (m, 2H), 7.38 – 7.29 (m, 3H), 6.42 (br s 1H), 6.11 (br s, 1H), 3.30 (s, 3H), 1.47 (s, 9H); \]

\[ ^{13}C \text{ NMR} (101 \text{ MHz}; \text{CDCl}_3) \delta 156.9, 156.4, 142.8, 130.2, 127.8, 127.2, 81.2, 37.7, 28.2; \]

HRMS (ESI⁺) [C₁₃H₁₉N₃O₃Na]⁺ requires [M+Na]⁺: 288.1324; found: 288.1317

\[ \text{tert-Butyl (E)-2-(methyl(phenyl)carbamoyl)diazene-1-carboxylate (S5b). A solution of } N\text{-bromosuccinimide (540 mg, 3.05 mmol, 1.2 equiv) in DCM (16 mL, 0.15 M) was added} \]

dropwise to a solution of pyridine (0.46 mL, 6.12 mmol, 2 equiv) and tert-butyl (E)-2-(methyl(phenyl)carbamoyl)diazene-1-carboxylate S5b (674 mg, 2.5 mmol) in DCM (8 mL, 0.30 M) at 0 °C. The reaction was stirred at RT for 5 h, before being quenched with sat. aq. NaHCO₃ (40 mL) and the aqueous layer was extracted with DCM (3 × 20 mL). The combined
organics were washed with brine (1 × 20 mL), dried over MgSO₄ and concentrated under reduced pressure to give a crude residue. Purification by flash silica chromatography (30% EtOAc/Hexane) afforded the title compound (357 mg, 53%) as an orange solid.

**MP:** 65-67 °C

**\( V_{\text{max}} / \text{cm}^{-1} \text{(neat)}: \)** 2982, 1762, 1711, 1598, 1371, 1255, 1149, 697

\(^1\text{H NMR}\) (400 MHz, CDCl₃) \( \delta \) 7.40-7.36 (m, 2H), 7.32 (d, \( J = 8.0 \) Hz, 1H), 7.16 (d, \( J = 8.0 \) Hz, 2H), 3.55 (s, 3H), 1.51 (s, 9H); \(^{13}\text{C NMR}\) (100 MHz, CDCl₃) \( \delta \) 160.8, 159.7, 140.5, 129.3, 127.9, 127.3, 86.2, 38.6, 27.7; HRMS (ESI) calcd for [C₁₃H₁₇N₃O₃Na] requires [M + Na]⁺ 286.1168, found 286.1028

![ tert-Butyl 2-((4-cyanophenyl)(methyl)carbamoyl)hydrazine-1-carboxylate (S5c). ]

**tert-Butyl 2-((4-cyanophenyl)(methyl)carbamoyl)hydrazine-1-carboxylate (S5c).** Pyridine (0.65mL, 2 equiv) was added in one portion to a solution of (4-cyanophenyl)(methyl)carbamic chloride (700 g, 3.6 mmol, 1.0 equiv) and tert-butyl carbazate (714 mg, 5.4 mmol, 1.5 equiv) in MeCN (7.2 mL, 0.5 M) and the resulting solution stirred at RT for 18 h. The reaction was quenched with H₂O (20 mL) and the aqueous layer was extracted with DCM (3 × 15 mL). The combined organics were washed with brine (1 × 15 mL), dried over MgSO₄ and concentrated under reduced pressure to give a crude residue. Purification by flash silica chromatography (40% EtOAc/Petrol) afforded the title compound (1g, 95.6%) as a white solid.

**MP:** 161-163 °C

**\( V_{\text{max}} / \text{cm}^{-1} \text{(neat)}: \)** 3300, 2980, 2227, 1722, 1673, 1603, 1479, 1367, 1159, 1111, 847

\(^1\text{H NMR}\) (400 MHz; CDCl₃) \( \delta \) 7.72 – 7.67 (m, 2H), 7.50 (d, \( J = 7.8 \) Hz, 2H), 6.37 (s, 1H), 6.25 (s, 1H), 3.32 (s, 3H), 1.45 (s, 9H); \(^{13}\text{C NMR}\) (101 MHz; CDCl₃) \( \delta \) 156.4, 146.8, 133.9, 126.9, 118.1, 110.5, 81.8, 37.4, 28.2; HRMS m/z (ESI⁺) [C₁₄H₁₈N₄O₃Na]⁺ requires[M + Na]⁺: 313.1277; found: 313.1283
**tert-Butyl (E)-2-((4-cyanophenyl)(methyl)carbamoyl)diazene-1-carboxylate (5c).** A solution of N-bromosuccinimide (952 mg, 4.5 mmol, 1.5 equiv) in DCM (22 mL, 0.15 M) was added dropwise to a solution of pyridine (0.651 mL, 7.1 mmol, 2 equiv) and tert-butyl 2-((4-cyanophenyl)(methyl)carbamoyl)hydrazine-1-carboxylate (1040 mg, 3.5 mmol) in DCM (11 mL, 0.30 M) at 0 °C. The reaction was stirred at RT for 3 h, before being quenched with sat. aq. NaHCO₃ (40 mL) and the aqueous layer was extracted with DCM (3 × 20 mL). The combined organics were washed with brine (1 × 20 mL), dried over MgSO₄ and concentrated under reduced pressure to give a crude residue. Purification by flash silica chromatography (25% EtOAc/Hexane) afforded the title compound (930 mg, 90%) as an orange solid.

**MP:** 92-94 °C

**V<sub>max</sub>/cm<sup>-1</sup> (neat):** 2984, 2230, 1760, 1709, 1603, 1253, 1147, 833

**<sup>1</sup>H NMR** (400 MHz, CDCl₃) δ 7.67 (d, ⁵J = 6.6 Hz, 2H), 7.30 – 7.20 (m, 2H), 3.52 (s, 3H), 1.52 (s, 9H); **<sup>13</sup>C NMR** (126 MHz, CDCl₃) δ 159.6, 144.6, 133.2, 127.8, 117.9, 111.6, 86.9, 38.3, 27.7; HRMS (ESI) calcd for [C₁₄H₁₆N₄O₃Na]⁺ requires [M + Na]⁺ 311.1120, found 311.1118

**tert-Butyl 2-((3-chlorophenyl)(methyl)carbamoyl)hydrazine-1-carboxylate (S5d).** Pyridine (0.65mL, 2 equiv) was added in one portion to a solution of (3-chlorophenyl)(methyl)carbamic chloride (730 g, 3.6 mmol, 1.0 equiv) and tert-butyl carbazate (715 mg, 5.4 mmol, 1.5 equiv) in MeCN (7.2 mL, 0.5 M) and the resulting solution stirred at RT for 18 h. The reaction was quenched with H₂O (20 mL) and the aqueous layer was extracted with DCM (3 × 15 mL). The combined organics were washed with brine (1 × 15 mL), dried over MgSO₄ and concentrated under reduced pressure to give a crude residue. Purification by flash silica chromatography (40% EtOAc/Petrol) afforded the title compound (1000 mg, 90%) as white needles.

**MP:** 87-91 °C
**$V_{\text{max}} / \text{cm}^{-1} (\text{neat})$:** 3285, 2979, 1680, 1476, 1366, 1237, 1157, 696

**$^1\text{H NMR}$ (400 MHz; CDCl$_3$) $\delta$ 7.36 – 7.30 (m, 2H), 7.25 (s, 2H), 6.47 (s, 1H), 6.15 (s, 1H), 3.24 (s, 3H), 1.43 (s, 9H); **$^{13}\text{C NMR}$ (126 MHz; CDCl$_3$) $\delta$ 156.7, 156.4, 143.5, 135.5, 131.1, 128.0, 127.5, 125.4, 123.8, 81.5, 37.7, 28.4; HRMS m/z (ESI$^+$) [C$_{13}$H$_{18}$ClN$_3$O$_3$Na]$^+$ requires [M + Na]$^+$: 322.0934; found: 322.0919

**tert-Butyl (E)-2-((3-chlorophenyl)(methyl)carbamoyl)diazene-1-carboxylate (5d).** A solution of $N$-bromosuccinimide (799 mg, 4.5 mmol, 1.5 equiv) in DCM (20 mL, 0.15 M) was added dropwise to a solution of pyridine (0.546 mL, 6.0 mmol, 2 equiv) and tert-butyl 2-((3-chlorophenyl)(methyl)carbamoyl)hydrazine-1-carboxylate S5d (900 mg, 3.01 mmol) in DCM (10 mL, 0.30 M) at 0°C. The reaction was stirred at RT for 3 h, before being quenched with sat. aq. NaHCO$_3$ (40 mL) and the aqueous layer was extracted with DCM (3 $\times$ 20 mL). The combined organics were washed with brine (1 $\times$ 20 mL), dried over MgSO$_4$ and concentrated under reduced pressure to give a crude residue. Purification by flash silica chromatography (15% EtOAc/Hexane) afforded the title compound (750 mg, 83%) as an orange semi-solid.

**$V_{\text{max}} / \text{cm}^{-1} (\text{neat})$:** 2983, 1761, 1709, 1591, 1370, 1251, 1147, 694

**$^1\text{H NMR}$ (400 MHz, CDCl$_3$) $\delta$ 7.28 (d, $J = 5.5$ Hz, 2H), 7.15 (s, 1H), 7.02 (d, $J = 6.1$ Hz, 1H), 3.50 (s, 3H), 1.50 (s, 9H); **$^{13}\text{C NMR}$ (101 MHz, CDCl$_3$) $\delta$ 160.5, 159.7, 141.7, 134.9, 130.3, 128.3, 127.6, 125.7, 86.6, 38.5, 27.8; HRMS (ESI) calcd for [C$_{13}$H$_{16}$ClN$_3$O$_3$Na]$^+$ requires [M + Na]$^+$ 320.0778, found 320.0777

**tert-Butyl 2-(methyl(3-(trifluoromethyl)phenyl)carbamoyl)hydrazine-1-carboxylate (S5e).** Pyridine (0.64 mL, 7.0 mmol, 2 equiv) was added in one portion to a solution of $N$-methyl(3-(trifluoromethyl)phenyl)carbamic chloride (840 g, 3.5 mmol, 1.0 equiv) and tert-
butyl carbazate (608 mg, 4.6 mmol, 1.3 equiv) in MeCN (7.0 mL, 0.5 M) and the resulting solution stirred at RT for 18 h. The reaction was quenched with H₂O (20 mL) and the aqueous layer was extracted with DCM (3 × 15 mL). The combined organics were washed with brine (1 × 15 mL), dried over MgSO₄ and concentrated under reduced pressure to give a crude residue. Purification by flash silica chromatography (20% to 40% EtOAc/Petrol) afforded the title compound (1.1 g, 93%) as a white needle.

**MP:** 151-153 °C

**ν<sub>max</sub>/cm<sup>-1</sup>(neat):** 3286, 2980, 1716, 1493, 1331, 1163, 1126, 1070

**¹H NMR** (400 MHz; CDCl₃) δ 7.47 – 7.40 (m, 4H), 6.29 (br s 1H), 6.03 (br s, 1H), 3.31 (s, 3H), 1.45 (s, 9H). **¹³C NMR** (126 MHz; CDCl₃) δ 156.6, 156.3, 142.9, 142.6 (q, J<sub>C-F</sub>=32.9 Hz), 130.8, 130.6, 124.4 (q, J<sub>C-F</sub>=3.6 Hz), 123.9 (q, J<sub>C-F</sub>=3.7 Hz), 123.7 (q, J<sub>C-F</sub>=272.2 Hz), 81.6, 37.8, 28.2; HRMS m/z (ESI⁺) [C₁₄H₁₈F₃N₅O₃Na]<sup>+</sup> requires[M + Na]<sup>+</sup>: 356.1198; found: 356.1199

**tert-Butyl (E)-2-(methyl(3-(trifluoromethyl)phenyl)carbamoyl)diazene-1-carboxylate (5e).** A solution of N-bromosuccinimide (877 mg, 4.95 mmol, 1.5 equiv) in DCM (22 mL, 0.15 M) was added dropwise to a solution of pyridine (0.599 mL, 6.59 mmol, 2 equiv) and tert-butyl 2-(methyl(3-(trifluoromethyl)phenyl)carbamoyl)hydrazine-1-carboxylate S5e (1.1g, 3.3 mmol) in DCM (11 mL, 0.30 M) at 0 °C. The reaction was stirred at RT for 3 h, before being quenched with sat. aq. NaHCO₃ (40 mL) and the aqueous layer was extracted with DCM (3 × 20 mL). The combined organics were washed with brine (1 × 20 mL), dried over MgSO₄ and concentrated under reduced pressure to give a crude residue. Purification by flash silica chromatography (20% EtOAc/Hexane) afforded the title compound (874 mg, 80%) as an orange Semi-solid.

**ν<sub>max</sub>/cm<sup>-1</sup>(neat):** 2986, 1764, 1713, 1371, 1329, 1253, 1123, 801, 700
$^1$H NMR (400 MHz, CDCl$_3$) δ 7.55 (d, $J$ = 7.5 Hz, 1H), 7.49 (t, $J$ = 7.8 Hz, 1H), 7.39 (s, 1H), 7.34 (d, $J$ = 7.5 Hz, 1H), 3.54 (s, 3H), 1.47 (s, 9H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 160.2, 159.6, 141.2, 131.9 (q, $J_{C,F}$ = 33.1 Hz), 130.5, 130.0, 125.8 (q, $J_{C,F}$ = 272.6 Hz), 124.7 (q, $J_{C,F}$ = 2.5 Hz), 124.3 (q, $J_{C,F}$ = 2.8 Hz), 122.7 (q, $J_{C,F}$ = 272.3 Hz), 86.6, 38.5, 27.6; HRMS (ESI) calcd for [C$_{14}$H$_{16}$F$_3$N$_3$O$_3$Na]$^+$ requires [M + Na]$^+$ 354.1041, found 354.1035

tert-Butyl 2-(methyl(pyridin-2-yl)carbamoyl)hydrazine-1-carboxylate (S5f). Pyridine (0.60 mL, 2 equiv) was added in one portion to a solution of N-methyl(pyridin-2-yl)carbamic chloride (568 g, 3.3 mmol, 1.0 equiv) and tert-butyl carbazate (573 mg, 4.3 mmol, 1.3 equiv) in MeCN (6.68 mL, 0.5 M) and the resulting solution stirred at RT for 18 h. The reaction was quenched with H$_2$O (20 mL) and the aqueous layer was extracted with DCM (3 × 15 mL). The combined organics were washed with brine (1 × 15 mL), dried over MgSO$_4$ and concentrated under reduced pressure to give a crude residue. Purification by flash silica chromatography (50% EtOAc/Petrol) afforded the title compound (805 mg, 90%) as white needles. MP: 155-157 °C

$V_{\text{max}}$/cm$^{-1}$(neat): 3273, 2977, 1731, 1690, 1477, 1436, 1162, 776

$^1$H NMR (400 MHz; CDCl$_3$) δ 11.58 (d, $J$ = 2.5 Hz, 1H), 8.28–8.26 (m, 1H), 7.70 (dddd, $J$ = 8.0, 7.4, 2.0, 0.6 Hz, 1H), 6.99 (m, 2H), 6.45 (d, $J$ = 2.5 Hz, 1H), 3.40 (s, 3H), 1.47 (s, 9H); $^{13}$C NMR (126 MHz; CDCl$_3$) δ 157.5, 156.2, 155.2, 146.2, 138.9, 117.7, 111.7, 81.3, 33.2, 28.3; HRMS m/z (ESI$^+$) [C$_{12}$H$_{18}$N$_4$O$_3$Na]$^+$ requires[M + Na]$^+$: 289.1277; found: 289.1272.

tert-Butyl (E)-2-(methyl(pyridin-2-yl)carbamoyl)diazene-1-carboxylate (5f). A solution of N-bromosuccinimide (788 mg, 4.46 mmol, 1.5 equiv) in DCM (19 mL, 0.15 M) was added dropwise to a solution of pyridine (0.539 mL, 5.93 mmol, 2 equiv) and tert-butyl 2-(methyl...
(pyridin-2-yl)carbamoyl)hydrazine-1-carboxylate **S5f** (790 mg, 2.96 mmol) in DCM (9.5 mL, 0.30 M) at 0 °C. The reaction was stirred at RT for 3 h, before being quenched with sat. aq. NaHCO₃ (40 mL) and the aqueous layer was extracted with DCM (3 × 20 mL). The combined organics were washed with brine (1 × 20 mL), dried over MgSO₄ and concentrated under reduced pressure to give a crude residue. Purification by flash silica chromatography (20% EtOAc/Hexane) afforded the title compound (588 mg, 75%) as an orange oil.

\[ V_{\text{max}} / \text{cm}^{-1} (\text{neat}): 2982, 1760, 1708, 1587, 1470, 1437, 1369, 1252, 1146, 1110, 784 \]

**H NMR** (400 MHz, CDCl₃) δ 8.47 – 8.43 (m, 1H), 7.71 (t, J = 7.6 Hz, 1H), 7.28 – 7.24 (m, 1H), 7.17 (ddd, J = 7.5, 4.9, 0.9 Hz, 1H), 3.57 (s, 3H), 1.58 (s, 9H); **C NMR** (126 MHz, CDCl₃) δ 160.4, 159.8, 152.9, 148.5, 148.1, 137.8, 121.8, 86.6, 35.8, 27.7; HRMS (ESI) calcd for [C₁₂H₁₆N₄O₃Na]⁺ requires [M + Na]⁺ 287.1120, found 287.1116.

**tert-Butyl 2-((3-methoxyphenyl)(methyl)carbamoyl)hydrazine-1-carboxylate (S5g).**

Pyridine (0.67 mL, 2 equiv) was added in one portion to a solution of (3-methoxyphenyl)(methyl)carbamic chloride (736 g, 3.6 mmol, 1.0 equiv) and **tert**-butyl carbazate (634 mg, 4.8 mmol, 1.3 equiv) in MeCN (7.3 mL, 0.5 M) and the resulting solution stirred at RT for 18 h. The reaction was quenched with H₂O (20 mL) and the aqueous layer was extracted with DCM (3 × 15 mL). The combined organics were washed with brine (1 × 15 mL), dried over MgSO₄ and concentrated under reduced pressure to give a crude residue. Purification by flash silica chromatography (40% EtOAc/Petrol) afforded the title compound (1g, 91%) as a white semi-solid.

\[ V_{\text{max}} / \text{cm}^{-1} (\text{neat}): 3288, 2977, 1690, 1673, 1598, 1487, 1366, 1231, 1157, 1042, 701 \]

**H NMR** (400 MHz; CDCl₃) δ 7.29 (t, J = 8.2 Hz, 1H), 6.91 – 6.81 (m, 3H), 6.45 (s, 1H), 6.17 (s, 1H), 3.78 (s, 3H), 3.24 (s, 3H), 1.42 (s, 9H); **C NMR** (101 MHz; CDCl₃) δ 160.8, 157.0,
tert-butyl (E)-2-((3-methoxyphenyl)(methyl)carbamoyl)diazene-1-carboxylate (5g). A solution of N-bromosuccinimide (621 mg, 3.5 mmol, 1.5 equiv) in DCM (15.5 mL, 0.15 M) was added dropwise to a solution of pyridine (0.424 mL, 4.6 mmol, 2 equiv) and tert-butyl 2-((4-methoxyphenyl)(methyl)carbamoyl)hydrazine-1-carboxylate S5g (690 mg, 2.3 mmol) in DCM (7.75 mL, 0.30 M) at 0 °C. The reaction was stirred at RT for 3 h, before being quenched with sat. aq. NaHCO₃ (20 mL) and the aqueous layer was extracted with DCM (3 × 15 mL). The combined organics were washed with brine (1 × 20 mL), dried over MgSO₄ and concentrated under reduced pressure to give a crude residue. Purification by flash silica chromatography (15% EtOAc/Hexane) afforded the title compound (500 mg, 72%) as orange needles.

**MP:** 97-99 °C

**ν<sub>max</sub>/cm⁻¹ (neat):** 2981, 1759, 1720, 1602, 1371, 1254, 1148, 698

**¹H NMR** (400 MHz, CDCl₃) δ 7.22 (d, J = 8.1 Hz, 1H), 6.81 (dd, J = 8.3, 2.2 Hz, 1H), 6.71 (d, J = 7.8 Hz, 1H), 6.63 (t, J = 2.0 Hz, 1H), 3.77 (s, 3H), 3.50 (s, 3H), 1.49 (s, 9H); **¹³C NMR** (101 MHz, CDCl₃) δ 160.9, 160.2, 159.8, 141.5, 130.0, 119.4, 114.0, 112.9, 86.3, 55.4, 38.5, 27.7; HRMS (ESI) calcd for [C₄H₁₀N₃O₃Na]⁺ requires [M + Na]⁺ 316.1273, found 316.1279.

**tert-Butyl 2-((4-chlorophenyl)(methyl)carbamoyl)hydrazine-1-carboxylate (S5h).** Pyridine (0.62 mL, 2 equiv) was added in one portion to a solution of (4-chlorophenyl)(methyl)carbamic chloride (700 g, 3.4 mmol, 1.0 equiv) and **tert**-butyl carbazate (594 mg, 4.5 mmol, 1.5 equiv) in MeCN (6.9 mL, 0.5 M) and the resulting solution stirred at
RT for 18 h. The reaction was quenched with H₂O (20 mL) and the aqueous layer was extracted with DCM (3 × 15 mL). The combined organics were washed with brine (1 × 15 mL), dried over MgSO₄ and concentrated under reduced pressure to give a crude residue. Purification by flash silica chromatography (40% EtOAc/Petrol) afforded the title compound (995 mg, 96%) as white needles.

**MP**: 84-86 °C

**ν<sub>max</sub>/cm<sup>-1</sup> (neat)**: 3287, 2978, 1716, 1668, 1490, 1366, 1158, 1013

**1H NMR** (400 MHz; CDCl₃) δ 7.39 (d, J = 2.2 Hz, 1H), 7.37 (d, J = 2.1 Hz, 1H), 7.28 (d, J = 8.3 Hz, 2H), 6.37 (s, 1H), 6.05 (s, 1H), 3.24 (s, 3H), 1.43 (s, 9H);

**13C NMR** (101 MHz; CDCl₃) δ 156.8, 156.4, 140.7, 133.6, 130.4, 128.6, 81.5, 37.7, 28.2; HRMS m/z (ESI⁺) [C<sub>13</sub>H<sub>18</sub>ClN<sub>3</sub>O<sub>3</sub>Na]<sup>+</sup> requires [M + Na]<sup>+</sup>: 322.0934; found: 322.0922

**tert-Butyl (E)-2-((4-chlorophenyl)(methyl)carbamoyl)diazene-1-carboxylate (5h).** A solution of N-bromosuccinimide (976 mg, 5.51 mmol, 1.5 equiv) in DCM (24 mL, 0.15 M) was added dropwise to a solution of pyridine (0.668 mL, 7.3 mmol, 2 equiv) and tert-butyl 2-((4-chlorophenyl)(methyl)carbamoyl)hydrazine-1-carboxylate S5h (1100 mg, 3.6 mmol) in DCM (12 mL, 0.30 M) at 0 °C. The reaction was stirred at RT for 3 h, before being quenched with sat. aq. NaHCO₃ (40 mL) and the aqueous layer was extracted with DCM (3 × 20 mL). The combined organics were washed with brine (1 × 20 mL), dried over MgSO₄ and concentrated under reduced pressure to give a crude residue. Purification by flash silica chromatography (20% EtOAc/Hexane) afforded the title compound (896 mg, 82%) as an orange Needles.

**MP**: 80-82 °C

**ν<sub>max</sub>/cm<sup>-1</sup> (neat)**: 2983, 1761, 1708, 1492, 1252, 1148, 834
**1H NMR** (400 MHz, CDCl₃) δ 7.32 (d, J = 8.6 Hz, 2H), 7.07 (d, J = 8.6 Hz, 2H), 3.49 (s, 3H), 1.50 (s, 9H); **13C NMR** (101 MHz, CDCl₃) δ 160.5, 159.7, 139.1, 133.9, 129.6, 128.7, 86.5, 38.6, 27.7; HRMS (ESI) calcd for [C₁₃H₁₆ClN₃O₃Na]⁺ requires [M + Na]⁺ 320.0778, found 320.0772

![Structure](image)

tert-Butyl 2-(ethyl(naphthalen-1-yl)carbamoyl)hydrazine-1-carboxylate (S5i); Pyridine (0.36 mL, 2 equiv) was added in one portion to a solution of ethyl(naphthalen-1-yl)carbamic chloride (470 g, 2.1 mmol, 1.0 equiv) and tert-butyl carbazate (346 mg, 2.6 mmol, 1.3 equiv) in MeCN (4.0 mL, 0.5 M) and the resulting solution stirred at RT for 42 h. The reaction was quenched with H₂O (20 mL) and the aqueous layer was extracted with DCM (3 × 15 mL). The combined organics were washed with brine (1 × 15 mL), dried over MgSO₄ and concentrated under reduced pressure to give a crude residue. Purification by flash silica chromatography (30% EtOAc/Petrol) afforded the title compound (500, 75%) as a white semi-solid.

*V*ₘₐₓ/cm⁻¹ (neat): 3289, 2976, 1720, 1671, 1480, 1366, 1158, 776

**1H NMR** (400 MHz; CDCl₃) δ 7.90 (dt, J = 17.2, 9.0 Hz, 3H), 7.59 – 7.46 (m, 4H), 6.22 (s, 1H), 5.89 (s, 1H), 4.14 (dq, J = 14.2, 7.1 Hz, 1H), 3.49 (dq, J = 14.1, 7.1 Hz, 1H), 1.42 (s, 9H), 1.14 (t, J = 7.1 Hz, 3H); **13C NMR** (101 MHz; CDCl₃) δ 156.3, 136.1, 135.0, 130.8, 129.2, 128.5, 127.5, 127.3, 126.9, 126.0, 122.9, 81.2, 44.7, 28.2, 13.8; HRMS (ESI⁺) [C₁₈H₂₃N₅O₃Na]⁺ requires[M + Na]⁺: 352.1637; found: 352.1628.

![Structure](image)

tert-Butyl (E)-2-(ethyl(naphthalen-1-yl)carbamoyl)diazene-1-carboxylate (S5i); A solution of N-bromosuccinimide (322 mg, 1.8 mmol, 1.5 equiv) in DCM (8.1 mL, 0.15 M) was added dropwise to a solution of pyridine (0.220 mL, 2.4 mmol, 2 equiv) and tert-butyl 2-
(ethyl(naphthalen-1-yl)carbamoyl)hydrazine-1-carboxylate S5i (400 mg, 1.2 mmol) in DCM (4 mL, 0.30 M) at 0 °C. The reaction was stirred at RT for 3 h, before being quenched with sat. aq. NaHCO₃ (20 mL) and the aqueous layer was extracted with DCM (3 × 15 mL). The combined organics were washed with brine (1 × 20 mL), dried over MgSO₄ and concentrated under reduced pressure to give a crude residue. Purification by flash silica chromatography (10% EtOAc/Hexane) afforded the title compound (264 mg, 66%) as an orange semi-solid.

\[ V_{\text{max}}/\text{cm}^{-1}(\text{neat}): 2936, 1761, 1709, 1372, 1268, 1254, 1150, 776 \]

\[ ^1\text{H NMR} \ (400 \text{ MHz, CDCl}_3) \delta \ 7.85 \ (t, J = 9.2 \text{ Hz}, 3\text{H}), 7.60 – 7.50 \ (m, 2\text{H}), 7.46 – 7.41 \ (m, 1\text{H}), 7.31 \ (d, J = 7.3 \text{ Hz}, 1\text{H}), 4.32 \ (dq, J = 14.4, 7.2 \text{ Hz}, 1\text{H}), 3.70 \ (dq, J = 14.3, 7.2 \text{ Hz}, 1\text{H}), 1.30–1.26 \ (m, 12\text{H}); ^{13}\text{C NMR} \ (101 \text{ MHz, CDCl}_3) \delta 161.4, 159.5, 134.6, 134.5, 130.4, 129.4, 128.5, 127.7, 127.5, 126.7, 125.2, 122.7, 85.8, 45.8, 27.5, 13.1; \text{HRMS (ESI) calcd for [C}_{18}\text{H}_{21}\text{N}_{3}\text{O}_{3}\text{Na}]^{+} \text{ requires [M + Na]}^{+} 350.1481, \text{found } 350.1491. \]

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[tert-Butyl 2-((2-chlorophenyl)(methyl)carbamoyl)hydrazine-1-carboxylate (S5j); Pyridine (0.31 mL, 2 equiv) was added in one portion to a solution of (2-chlorophenyl)(methyl)carbamic chloride (352 g, 1.7 mmol, 1.0 equiv) and tert-butyl carbazate (299 mg, 2.2 mmol, 1.3 equiv) in MeCN (3.4 mL, 0.5 M) and the resulting solution stirred at RT for 18 h. The reaction was quenched with H₂O (20 mL) and the aqueous layer was extracted with DCM (3 × 15 mL). The combined organics were washed with brine (1 × 15 mL), dried over MgSO₄ and concentrated under reduced pressure to give a crude residue. Purification by flash silica chromatography (40% EtOAc/Petrol) afforded the title compound (500 mg, 95%) as white needles.

\[ \text{MP: } 107-109 \degree \text{C} \]

\[ V_{\text{max}}/\text{cm}^{-1}(\text{neat}): 3267, 2977, 1719, 1650, 1359, 1150, 770 \]
**1H NMR** (400 MHz; CDCl₃) δ 7.48 (dd, J = 7.5, 2.1 Hz, 1H), 7.43 (d, J = 6.4 Hz, 1H), 7.35 – 7.27 (m, 2H), 6.32 (s, 1H), 5.87 (s, 1H), 3.20 (s, 3H), 1.43 (s, 9H); **13C NMR** (101 MHz; CDCl₃) δ 156.5, 156.3, 138.9, 133.6, 131.1, 130.4, 129.9, 128.7, 81.3, 36.4, 28.2; **HRMS** m/z (ESI⁺) [C₁₃H₁₈ClN₃O₃Na⁺] requires [M + Na]⁺: 322.0934; found: 322.0944

**tert-Butyl (E)-2-((2-chlorophenyl)(methyl)carbamoyl)diazene-1-carboxylate (5j)**: A solution of N-bromosuccinimide (532 mg, 3.0 mmol, 1.5 equiv) in DCM (13 mL, 0.15 M) was added dropwise to a solution of pyridine (0.364 mL, 4.0 mmol, 2 equiv) and tert-butyl 2-((2-chlorophenyl)(methyl)carbamoyl)hydrazine-1-carboxylate S5j (600 mg, 2.0 mmol) in DCM (6.5 mL, 0.30 M) at 0 °C. The reaction was stirred at RT for 3 h, before being quenched with sat. aq. NaHCO₃ (20 mL) and the aqueous layer was extracted with DCM (3 × 15 mL). The combined organics were washed with brine (1 × 15 mL), dried over MgSO₄ and concentrated under reduced pressure to give a crude residue. Purification by flash silica chromatography (10% EtOAc/Hexane) afforded the title compound (410 mg, 68%) as an orange oil.

**νmax/cm⁻¹(neat):** 2983, 1761, 1715, 1481, 1370, 1252, 1480

**1H NMR** (400 MHz, CDCl₃) δ 7.42 (ddt, J = 5.2, 3.0, 1.1 Hz, 1H), 7.30 – 7.25 (m, 3H), 3.42 (s, 3H), 1.45 (s, 9H); **13C NMR** (101 MHz, CDCl₃) δ 160.4, 159.8, 137.9, 132.9, 130.4, 130.1, 130.0, 127.9, 86.3, 37.5, 27.7; **HRMS** (ESI) calcd for [C₁₃H₁₆ClN₃O₃Na⁺] requires [M + Na]⁺: 320.0778, found 320.0779

**1.10 General Procedure 6: Synthesis of Silyl enol ether**

(1-methoxyprop-1-en-1-yl)oxytrimethylsilane, (2a) The compound was prepared according to a reported procedure.² Under nitrogen, a 2.0 M n-BuLi solution in cyclohexane (25 mL, 50

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mmol) in an addition funnel was slowly added to a stirred solution of i-Pr₂NH (7.6 mL, 54.5 mmol) in dry THF (80 mL) at 0 °C over 20 min. The mixture was stirred at 0 °C for 30 minutes and then it was cooled to -78 °C in a cooling bath. A solution of methyl propionate (4g, 45 mmol) and TMSCl (6.9 mL, 54 mmol) in dry THF (40 mL) was added slowly over 1.5 hours from the addition funnel. After stirring at -78 °C for additional 30 minutes, the mixture was slowly warmed up to 25 °C and kept stirred for 18 hours. At the end of the reaction, most of THF was removed by distillation under one atmosphere of argon. The residue was diluted with 80 mL of pentane and the resulting suspension was filtered through a fritted funnel (medium porosity) with pentane washings, to remove LiCl. The filtrate was concentrated, and the crude product was purified by distillation under vacuum which afforded the desired silyl ketene acetal as colorless oil (3.5 g E:Z :: 8:1).

**1H NMR** (400 MHz, CDCl₃) δ 3.66 (q, J = 8.0 Hz, 1H), 3.51 (s, 3H), 1.48 (d, J = 8.0 Hz, 3H), 0.21 (s, 9H)

**13C NMR** (100 MHz, CDCl₃) δ 154.0, 78.8, 54.8, 9.5, 0.18; HRMS (ESI) calcd for [C₇H₁₆O₂SiNa] requires [M + Na]+ 183.0817, found 183.0821

(1-Methoxy-3-phenylprop-1-en-1-yl)oxytrimethylsilane (2b); Under nitrogen, a 2.0 M n-BuLi solution in cyclohexane (25 mL, 50 mmol) in an addition funnel was slowly added to a stirred solution of i-Pr₂NH (7.6 mL, 54.5 mmol) in dry THF (80 mL) at 0 °C over 20 min. The mixture was stirred at 0 °C for 30 minutes and then it was cooled to -78 °C in a cooling bath. A solution of methyl propionate (7.3 g, 45 mmol) and TMSCl (6.9 mL, 54 mmol) in dry THF (40 mL) was added slowly over 1.5 hours from the addition funnel. After stirring at -78 °C for additional 30 minutes, the mixture was slowly warmed up to 25 °C and kept stirred for 18 hours. At the end of the reaction, most of THF was removed by distillation under one atmosphere of argon. The residue was diluted with 80 mL of pentane and the resulting suspension was filtered through a fritted funnel (medium porosity) with pentane washings, to
remove LiCl. The filtrate was concentrated, under reduced pressure to give silyl ketene acetal as colorless oil (10 g E:Z :: 18:1), which was taken on without further purification.

\( V_{\text{max}} /\text{cm}^{-1} (\text{neat}) \): 2952, 1735, 1435, 1159, 750, 698

\(^1\text{H NMR}\) (400 MHz, CDCl\(_3\)) \( \delta \) 7.28–7.22 (m, 4H), 7.19–7.15 (m, 1H), 3.90 (t, \( J = 8.0 \) Hz, 1H), 3.58 (s, 3H), 3.36 (d, \( J = 8.0 \) Hz, 2H), 0.27 (s, 9H); \(^{13}\text{C NMR}\) (100 MHz, CDCl\(_3\)) \( \delta \) 154.3, 143.0, 128.3, 128.2, 125.6, 83.6, 54.7, 30.9, 0.09; HRMS (ESI) calcd for [C\(_{13}\)H\(_{20}\)O\(_2\)SiNa] requires [M + Na]+ 259.1130, found 259.1133.

\((E)-(1\text{-methoxypent-1-en-1-yl} \text{oxy})\text{trimethylsilane (2c)}\): Under nitrogen, a 2.0 M n-BuLi solution in cyclohexane (25 mL, 50 mmol) in an addition funnel was slowly added to a stirred solution of \(\text{i-Pr}_2\text{NH}\) (7.6 mL, 54.5 mmol) in dry THF (80 mL) at 0 °C over 20 min. The mixture was stirred at 0 °C for 30 minutes and then it was cooled to -78 °C in a cooling bath. A solution of methyl pentanoate (5.2 g, 45 mmol) and TMSCl (7.3 mL, 54 mmol) in dry THF (40 mL) was added slowly over 1.5 hours from the addition funnel. After stirring at -78 °C for additional 30 minutes, the mixture was slowly warmed up to 25 °C and kept stirred for 18 hours. At the end of the reaction, most of THF was removed by distillation under one atmosphere of argon. The residue was diluted with 80 mL of pentane and the resulting suspension was filtered through a fritted funnel (medium porosity) with pentane washings, to remove LiCl. The filtrate was concentrated, under reduced pressure to give silyl ketene acetal as colorless oil (7.4 g, E:Z :: 19:1 ), which was taken on without further purification.

\( V_{\text{max}} /\text{cm}^{-1} (\text{neat}) \): 2958, 1709, 1549, 1395, 1259, 1057, 772

\(^1\text{H NMR}\) (400 MHz, CDCl\(_3\)) \( \delta \) 3.64 (t, \( J = 7.3 \) Hz, 1H), 3.47 (s, 3H), 1.89 (q, \( J = 7.3 \) Hz, 2H), 1.31 – 1.24 (m, 2H), 0.85 (t, \( J = 7.4 \) Hz, 3H), 0.19 (s, 9H); \(^{13}\text{C NMR}\) (100 MHz, CDCl\(_3\)) \( \delta \) 153.7, 85.1, 54.8, 26.6, 23.8, 13.6, -0.3; HRMS (ESI) calcd for [C\(_9\)H\(_{20}\)O\(_2\)SiNa] requires [M + Na]+ 211.1130, found 211.1135
methyl 4-(benzyloxy)butanoate (S2d); To a solution of 4-(benzyloxy)butanoic acid (5 g, 25.7 mmol) in methanol (0.1M) was added conc. HCl (cat.) and the solution heated at 60 °C for 8h. The solution was allowed to cool and concentrated under reduced pressure. The colourless oil was dissolved in dichloromethane (20 ml) and washed with water and brine solution and the combined organic extracts were dried over magnesium sulphate and concentrated under reduced pressure to provide the methyl 4-(benzyloxy)butanoate (5.89 g) as a colourless oil.

$V_{\text{max}}$/cm$^{-1}$ (neat): 2950, 2857, 1733, 1436, 1169, 1103, 1058, 735.

$^{1}$H NMR (400 MHz, CDCl$_3$) δ 7.27 – 7.20 (m, 4H), 7.20 – 7.15 (m, 1H), 4.39 (s, 2H), 3.55 (s, 3H), 3.41 (t, J = 6.2 Hz, 2H), 2.34 (t, J = 7.4 Hz, 2H), 1.84 (ddd, J = 13.6, 7.4, 6.2 Hz, 2H);

$^{13}$C NMR (101 MHz, CDCl$_3$) δ 173.8, 138.4, 128.3, 127.5, 127.5, 72.8, 69.1, 51.4, 30.8, 25.1;

HRMS (ESI) calcd for [C$_{12}$H$_{16}$O$_3$Na]$^+$ requires [M + Na]$^+$ 231.0997, found 231.0993

(4-(benzyloxy)-1-methoxybut-1-en-1-yl)oxy)trimethylsilane (2d) Under nitrogen, 2.0 M n-BuLi solution in cyclohexane (19 mL, 38 mmol) in an addition funnel was slowly added to a stirred solution of i-Pr$_2$NH (5.7 mL, 40.85 mmol) in dry THF (60 mL) at 0 °C over 20 min. The mixture was stirred at 0 °C for 30 minutes and then it was cooled to -78 o C in a cooling bath. A solution of methyl pentanoate (5.89 g, 28 mmol) and TMSCl (5.12 mL, 37.8 mmol) in dry THF (30 mL) was added slowly over 1.5 hours from the addition funnel. After stirring at -78 °C for additional 30 minutes, the mixture was slowly warmed up to 25 °C and kept stirred for 24 hours. At the end of the reaction, most of THF was removed by distillation under one atmosphere of argon. The residue was diluted with 50 mL of pentane and the resulting suspension was filtered through a fritted funnel (medium porosity) with pentane washings, to remove LiCl. The filtrate was concentrated, under reduced pressure to give silyl ketene acetal as colorless oil (8.1 g, $E:Z$ 10:1), which was taken on without further purification.
$V_{\text{max}} / \text{cm}^4(\text{neat})$: 2955, 2853, 1697, 1252, 1081

$^1H$ NMR (400 MHz, CDCl$_3$) δ 7.37 – 7.32 (m, 4H), 7.29 – 7.24 (m, 1H), 4.52 (s, 2H), 3.72 (t, $J$ = 7.3 Hz, 1H), 3.52 (s, 3H), 3.44 (t, $J$ = 7.0 Hz, 2H), 2.31 (q, $J$ = 7.1 Hz, 2H), 0.25 (s, 9H).

$^{13}C$ NMR (100 MHz, CDCl$_3$) δ 154.5, 138.9, 128.3, 127.6, 127.4, 80.4, 72.7, 71.1, 54.6, 25.3, -0.18; HRMS (ESI) calcd for [C$_{15}$H$_{24}$O$_2$SiNa] requires [M + Na]$^+$ 303.1392, found 303.1382

1.11 X-ray crystallography:

X-ray studies of 4b:

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### X-ray studies of 7b:

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1.12 ReactIR studies

**Fig 1.** React IR of azocarbonamides (5c)

**Fig 2.** After 5 min. (Addition of silyl enol ether)

**Fig 3.** Intermediate A

**Fig 4a,** After addition of KHMDS -78°C

**Fig 4b,** After addition of KHMDS -78°C

**Fig 5,** After completion of reaction (D)
1.13 Procedures and Analytical data of hydantoin formation from symmetrical azodicarboxamides

Silyl enol ether 2 (1 equiv.,) was added dropwise to a mixture of symmetric azocarboxamide compound 1 (1 equiv) and AgOTf (10 mol %.) in THF (0.1 M) at -78 °C. The reaction was warmed to RT after 30 minutes and stirred at RT for 3 h. After TLC showed consumption of symmetric azocarboxamide compound 1, the reaction was cooled to -78 °C and KHMDS (1 M in THF, 3 equiv) was added dropwise. After 20 minutes the reaction was warmed to -40 °C and stirred at -40 °C for 4 h. The reaction was quenched with sat. aq. NH₄Cl (15 mL), and the aqueous layer was extracted with EtOAc (3 × 10 mL). The combined organics were washed with brine (1 × 10 mL), dried over MgSO₄ and concentrated under reduced pressure to give a crude residue. Purification by flash silica chromatography desired compound.

\[
\begin{align*}
\text{Methyl } N\text{-}(methyl(phenyl)carbamoyl)-N\text{-}(3\text{-methyl-3-phenylureido)alaninate (3) (Semi-solid), } {^1}\text{H NMR (400 MHz, CDCl}_3) \delta 7.36 - 7.20 (m, 7H), 7.14 (t, J = 7.3 Hz, 1H), 6.91 (d, J = 7.6 Hz, 2H), 5.82 (s, 1H), 4.75 (s, 1H), 3.56 (s, 3H), 3.26 (s, 3H), 3.13 (s, 3H), 1.23 (d, J = 7.3 Hz, 3H);} \\
{^{13}}\text{C NMR (100 MHz, CDCl}_3) \delta 173.1, 160.0, 155.6, 145.4, 142.0, 129.8, 129.6, 127.6, 126.9, 
\end{align*}
\]
125.3, 124.2, 57.5, 52.1, 39.8, 37.5, 14.3; HRMS (ESI) calcd for [C_{20}H_{24}N_{4}O_{4}Na]^+ requires [M + Na]^+ 407.1690, found 407.1690.

![Chemical Structure](image)

3-(3,5-dimethyl-2,4-dioxo-5-phenylimidazolidin-1-yl)-1-methyl-1-phenylurea (4a),

Methoxy-1-trimethylsilyloxypropene (60 mg, 0.37 mmol) was added dropwise to a mixture of (E)-2-benzoyl-N-methyl-N-phenyldiazene-1-carboxamide 1a (101 mg, 0.37 mmol) and AgOTf (8.5 mg, 10 mol %) in THF (3.4 mL, 0.1 M) at -78 °C. The reaction was warmed to RT after 30 minutes and stirred at RT for 3 h. After TLC showed consumption of (E)-2-benzoyl-N-methyl-N-phenyldiazene-1-carboxamide 1a, the reaction was cooled to -78 °C and KHMDS (1 M in THF, 3 equiv) was added dropwise. After 20 minutes the reaction was warmed to -40 °C and stirred at -40 °C for 4 h. The reaction was quenched with sat. aq. NH_{4}Cl (15 mL), and the aqueous layer was extracted with EtOAc (3 × 10 mL). The combined organics were washed with brine (1 × 10 mL), dried over MgSO_{4} and concentrated under reduced pressure to give a crude residue. Purification by flash silica chromatography (60% EtOAC/Hexane) afforded the title compound (91 mg, 75%) as colourless semi-solid.

ν_{max} /cm^{-1}(neat): 3295, 1786, 1721, 1698

^1H NMR (400 MHz, CDCl_{3}) δ 7.42 – 7.35 (m, 2H), 7.35 – 7.27 (m, 6H), 7.27 – 7.23 (m, 2H), 5.99 (s, 1H), 3.30 (s, 3H), 3.10 (s, 3H), 1.91 (s, 3H); ^13C NMR (100 MHz, CDCl_{3}) δ 173.6, 155.7, 141.8, 137.2, 130.3, 129.0, 128.7, 128.2, 127.1, 125.9, 68.7, 38.2, 25.3, 20.1; HRMS (ESI) calcd for [C_{19}H_{20}N_{4}O_{3}Na]^+ requires [M + Na]^+ 375.1428, found 375.1430.
3-(3,5-Dimethyl-2,4-dioxo-5-(p-tolyl)imidazolidin-1-yl)-1-methyl-1-(p-tolyl)urea (4b); 1-Methoxy-1-trimethylsilyloxypropene (74 mg, 0.46 mmol) was added dropwise to a mixture of (E)-N¹,N²-dimethyl-N¹-phenyl-N²-(p-tolyl)diazene-1,2-dicarboxamide 1b (150 mg, 0.46 mmol) and AgOTf (11.6 mg, 10 mol %.) in THF (4.6 mL, 0.1 M) at -78 °C. The reaction was warmed to RT after 30 minutes and stirred at RT for 3 h. After TLC showed consumption of (E)-N¹,N²-dimethyl-N¹-phenyl-N²-(p-tolyl)diazene-1,2-dicarboxamide 1b, the reaction was cooled to -78 °C and KHMDS (1 M in THF, 3 equiv) was added dropwise. After 20 minutes the reaction was warmed to -40 °C and stirred at -40 °C for 4 h. The reaction was quenched with sat. aq. NH₄Cl (15 mL), and the aqueous layer was extracted with EtOAc (3 × 10 mL). The combined organics were washed with brine (1 × 10 mL), dried over MgSO₄ and concentrated under reduced pressure to give a crude residue. Purification by flash silica chromatography (60% EtOAC/Hexane) afforded the title compound (140 mg, 80%) as colourless needles.

**MP:** 166-168°C

**ν<sub>max</sub>/cm⁻¹ (neat):** 3298, 2942, 1783, 1717, 1690, 1513, 1457, 824, 753

**¹H NMR** (400 MHz, CDCl₃) δ 7.15 (s, 4H), 7.11 (s, 4H), 5.98 (br s, 1H) 3.25 (s, 3H), 3.07 (s, 3H), 2.33 (s, 3H), 2.29 (s, 3H), 1.87 (s, 3H); **¹³C NMR** (100 MHz, CDCl₃) δ 173.9, 155.9, 139.2, 138.6, 138.3, 134.3, 130.9, 129.7, 126.9, 125.8, 68.5, 38.2, 25.2, 21.1, 21.0, 20.0; HRMS (ESI) calcd for [C₂₁H₂₄N₄O₃Na] requires [M + Na]+ 403.1746, found 403.1743.
1-(4-Cyanophenyl)-3-(5-(4-cyanophenyl)-3,5-dimethyl-2,4-dioxoimidazolidin-1-yl)-1-methylurea (4c); 1-Methoxy-1-trimethylsilyloxypropene (48 mg, 0.30 mmol,) was added dropwise to a mixture of (E)-N\textsuperscript{1},N\textsuperscript{2}-bis(4-cyanophenyl)-N\textsuperscript{1},N\textsuperscript{2}-dimethyldiazene-1,2-dicarboxamide 1c (104 mg, 0.30 mmol) and AgOTf (7.5 mg, 10 mol %.) in THF (3 mL, 0.1 M) at -78 °C. The reaction was warmed to RT after 30 minutes and stirred at RT for 3 h. After TLC showed consumption of (E)-N\textsuperscript{1},N\textsuperscript{2}-bis(4-cyanophenyl)-N\textsuperscript{1},N\textsuperscript{2}-dimethyldiazene-1,2-dicarboxamide 1c, the reaction was cooled to -78 °C and KHMDS (1 M in THF, 3 equiv) was added dropwise. After 20 minutes the reaction was warmed to -40 °C and stirred at -40 °C for 4 h. The reaction was quenched with sat. aq. NH\textsubscript{4}Cl (10 mL), and the aqueous layer was extracted with EtOAc (3 × 10 mL). The combined organics were washed with brine (1 × 10 mL), dried over MgSO\textsubscript{4} and concentrated under reduced pressure to give a crude residue. Purification by flash silica chromatography (1% to 10% (10% MeOH in DCM)/DCM) afforded the title compound (95 mg, 79%) as a white semi-solid.

$\nu_{\text{max}}/\text{cm}^{-1}\text{(neat)}$: 3299, 3018, 2218, 1786, 1719, 1688, 1505, 1338, 844, 748

$^1$H NMR (400 MHz, CDCl\textsubscript{3}) δ 7.65–7.62 (m, 1H), 7.60–7.57 (m, 3H), 7.56–7.53 (m, 1H), 7.45–7.41 (m, 3H), 6.27 (br s, 1H), 2.94 (s, 3H), 3.04 (s, 3H), 1.83 (s, 3H); $^{13}$C NMR (100 MHz, CDCl\textsubscript{3}) δ 172.1, 155.6, 155.2, 148.8, 145.2, 134.0, 133.6, 132.6, 127.2, 127.0, 126.5, 118.0, 117.7, 112.8, 111.3, 68.4, 38.0, 25.5, 20.3; HRMS (ESI) calcd for [C\textsubscript{21}H\textsubscript{18}N\textsubscript{6}O\textsubscript{3}Na] requires [M + Na]\textsuperscript{+} 425.1338, found 425.1334.
1-(4-Fluorophenyl)-3-(5-(4-fluorophenyl)-3,5-dimethyl-2,4-dioxoimidazolidin-1-yl)-1-methylurea (4d): 1-Methoxy-1-trimethylsilyloxypropene (48 mg, 0.30 mmol,) was added dropwise to a mixture of (E)-N₁,N₂-bis(4-fluorophenyl)-N₁,N₂-dimethylidazene-1,2-dicarboxamide 1d (100 mg, 0.30 mmol) and AgOTf (7.5 mg, 10 mol %.) in THF (3.0 mL, 0.1 M) at -78 °C. The reaction was warmed to RT after 15 minutes, and stirred at RT for 3 h. After TLC showed consumption of (E)-N₁,N₂-bis(4-fluorophenyl)-N₁,N₂-dimethylidazene-1,2-dicarboxamide 1d, the reaction was cooled to -78 °C and KHMDS (1 M in THF, 3 equiv) was added dropwise. After 20 minutes the reaction was warmed to -40 °C and stirred at -40 °C for 4 h. The reaction was quenched with sat. aq. NH₄Cl (10 mL), and the aqueous layer was extracted with EtOAc (3 × 10 mL). The combined organics were washed with brine (1 × 10 mL), dried over MgSO₄ and concentrated under reduced pressure to give a crude residue. Purification by flash silica chromatography (50% to 70% EtOAC + Hexane) afforded the title compound (44 mg, 38%) as colourless needles.

**MP:** 130-132 °C

**Vmax/cm⁻¹ (neat):** 3299, 2988, 1784, 1716, 1683, 1508, 1452, 1222, 840, 751

**¹H NMR (400 MHz, CDCl₃)** δ 7.29–7.22 (m, 4H), 7.09–7.05 (m, 2H), 7.01–6.97 (m, 2H), 5.94 (br s, 1H), 3.24 (s, 3H), 3.07 (s, 3H), 1.84 (s, 3H); **¹³C NMR (100 MHz, CDCl₃)** δ 173.5, 163.5 (d, J_C-F = 249.2 Hz), 162.3 (d, J_C-F = 249.2 Hz), 155.7, 155.6, 137.7 (d, J_C-F = 3.0 Hz), 133.0 (d, J_C-F = 3.0 Hz), 129.2 (d, J_C-F = 9.0 Hz) 128.0 (d, J_C-F = 9.0 Hz), 117.4 (d, J_C-F = 23.2 Hz), 115.9 (d, J_C-F = 23.2 Hz), 68.2, 38.4, 25.3, 20.4; HRMS (ESI) calcd for [C₁₉H₁₈F₂N₄O₃Na] requires [M + Na]+ 411.1245, found 411.1256.
1-(3-Chlorophenyl)-3-(5-(3-chlorophenyl)-3,5-dimethyl-2,4-dioxoimidazolidin-1-yl)-1-methylurea (4e): 1-Methoxy-1-trimethylsilyloxypropene (45 mg, 0.28 mmol) was added dropwise to a mixture of \((E)\)-N\textsubscript{1},N\textsubscript{2}-bis(3-chlorophenyl)-N\textsubscript{1},N\textsubscript{2}-dimethyldiazene-1,2-dicarboxamide 1e (95 mg, 0.26 mmol) and AgOTf (6.5 mg, 10 mol \%). in THF (2.6 mL, 0.1 M) at -78 °C. The reaction was warmed to RT after 30 minutes and stirred at RT for 4 h. After TLC showed consumption of \((E)\)-N\textsubscript{1},N\textsubscript{2}-bis(3-chlorophenyl)-N\textsubscript{1},N\textsubscript{2}-dimethyldiazene-1,2-dicarboxamide 1e, the reaction was cooled to -78 °C and KHMDS (1 M in THF, 3 equiv) was added dropwise. After 20 minutes the reaction was warmed to -40 °C and stirred at -40 °C for 5 h. The reaction was quenched with sat. aq. NH\textsubscript{4}Cl (10 mL), and the aqueous layer was extracted with EtOAc (3 × 10 mL). The combined organics were washed with brine (1 × 10 mL), dried over MgSO\textsubscript{4} and concentrated under reduced pressure to give a crude residue. Purification by flash silica chromatography (60% EtOAC/Hexane) afforded the title compound (97 mg, 89\%) as a pale-yellow oil.

\(\nu_{\text{max}}/\text{cm}^{-1}\text{(neat)}: 3287, 2942, 1785, 1718, 1689, 1591, 1470, 748, 695\)

\(\text{\textsuperscript{1}H NMR}\) (400 MHz, CDCl\textsubscript{3}) \(\delta 7.30–7.29\) (m, 2H), 7.27–7.25 (m, 2H), 7.21–7.19 (m, 2H), 7.16–7.13 (.., 2H), 6.10 (br s, 1H), 3.26 (s, 3H), 3.07 (s, 3H), 1.85 (s, 3H); \(\text{\textsuperscript{13}C NMR}\) (100 MHz, CDCl\textsubscript{3}) \(\delta 173.02, 155.5, 155.4, 145.4, 143.0, 139.2, 135.8, 131.3, 130.3, 129.0, 128.6, 127.5, 126.4, 125.3, 124.3, 68.3, 38.2, 25.4, 20.1; \textbf{HRMS} (ESI) calcd for [C\textsubscript{19}H\textsubscript{18}Cl\textsubscript{2}N\textsubscript{4}O\textsubscript{3}Na] requires [M + Na]+ 443.0654, found 443.0644.
3-(3,5-Dimethyl-2,4-dioxo-5-(3-(trifluoromethyl)phenyl)imidazolidin-1-yl)-1-methyl-1-(3-(trifluoromethyl)phenyl)urea (4f); (1-methoxyprop-1-en-1-yl)oxy) trimethylsilane (33 mg, 0.20 mmol,) was added dropwise to a mixture of (E)-N¹,N²-dimethyl-N¹,N²-bis(3-(trifluoromethyl)phenyl)diazene-1,2-dicarboxamide 1f (100 mg, 0.23 mmol) and AgOTf (5.8 mg, 10 mol %.) in THF (2.3 mL, 0.1 M) at -78 °C. The reaction was warmed to RT after 15 minutes, and stirred at RT for 3 h. After TLC showed consumption of (E)-N¹,N²-dimethyl-N¹,N²-bis(3-(trifluoromethyl)phenyl)diazene-1,2-dicarboxamide 1f the reaction was cooled to -78 °C and KHMDS (1 M in THF, 3 equiv) was added dropwise. After 20 minutes the reaction was warmed to -40 °C and stirred at -40 °C for 3 h. The reaction was quenched with sat. aq. NH₄Cl (10 mL), and the aqueous layer was extracted with EtOAc (3 × 10 mL). The combined organics were washed with brine (1 × 10 mL), dried over MgSO₄ and concentrated under reduced pressure to give a crude residue. Purification by flash silica chromatography (50% to 70% EtOAc + Hexane) afforded the title compound (85 mg, 75%) as a colourless oil.

V<sub>max</sub>/<cm<sup>-1</sup> (neat): 3284, 2987, 1786, 1718, 1449, 1120, 735, 698

<sup>1</sup>H NMR (400 MHz, CDCl₃) δ 7.57–7.50 (m, 7H), 7.48–7.44 (m, 1H), 6.17 (br s, 1H), 3.30 (s 3H), 3.08 (s, 3H), 1.89 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl₃) 172.9, 155.6, 155.4, 142.5, 138.4, 132.9, 132.6, 131.5, 131.2, 130.9, 130.4 (q, J<sub>C-F</sub> = 2.2 Hz), 129.6 (q, J<sub>C-F</sub> = 2.0 Hz), 129.60, 125.7 (q, J<sub>C-F</sub> = 3.8 Hz), 124.8 (q, J<sub>C-F</sub> = 3.7 Hz), 123.9 (q, J<sub>C-F</sub> = 3.8 Hz), 122.8 (q, J<sub>C-F</sub> = 3.9 Hz), 68.3, 25.4, 20.6; HRMS (ESI) calcd for [C<sub>21</sub>H<sub>18</sub>F<sub>6</sub>N<sub>3</sub>O<sub>3</sub>Na] requires [M + Na]<sup>+</sup> 511.1181, found 511.1150.
3-(3,5-Dimethyl-2,4-dioxo-5-(pyridin-2-yl)imidazolidin-1-yl)-1-methyl-1-(pyridin-2-yl)urea (4g): 1-Methoxy-1-trimethylsilyloxypropene (59 mg, 0.36 mmol,) was added dropwise to a mixture of \((E)-N^1,N^2\)-dimethyl-\(N^1,N^2\)-di(pyridin-2-yl)diazene-1,2-dicarboxamide 1g (100 mg, 0.33 mmol) and AgOTf (8.4 mg, 10 mol %) in THF (3.3 mL, 0.1 M) at -78 °C. The reaction was warmed to RT after 30 minutes, and stirred at RT for 4 h. After TLC showed consumption of \((E)-N^1,N^2\)-dimethyl-\(N^1,N^2\)-di(pyridin-2-yl)diazene-1,2-dicarboxamide 1g, the reaction was cooled to -78 °C and KHMDS (1 M in THF, 3 equiv) was added dropwise. After 20 minutes the reaction was warmed to -40 °C and stirred at -40 °C for 4 h. The reaction was quenched with sat. aq. NH₄Cl (10 mL), and the aqueous layer was extracted with EtOAc (3 × 10 mL). The combined organics were washed with brine (1 × 10 mL), dried over MgSO₄ and concentrated under reduced pressure to give a crude residue. Purification by flash silica chromatography (10% MeOH/DCM) afforded the title compound (87 mg, 73%) as white needles.

**MP:** 179-181 °C

**\(ν_{\text{max}} / \text{cm}^{-1} (\text{neat})\):** 3264, 1786, 1716, 1687, 1434, 742

**\(^1H\) NMR (400 MHz, CDCl₃) \(δ\):** 12.09 (br s, 1H), 8.62–8.60 (m, 1H), 8.08–8.06 (m, 1H), 7.74–7.65 (m, 2H), 7.56–7.53 (m, 1H), 7.28–7.34 (m, 1H), 6.97–6.90 (m, 2H), 3.38 (s, 3H), 3.07 (s, 3H), 1.93 (s, 3H); **\(^13C\) NMR (100 MHz, CDCl₃) \(δ\):** 172.8, 156.8, 156.4, 155.8, 155.0, 149.2, 145.8, 139.0, 137.4, 123.5, 121.8, 117.8, 111.8, 70.4, 33.2, 25.3, 19.9; HRMS (ESI) calcd for [\(\text{C}_{17}\text{H}_{18}\text{N}_{6}\text{O}_{3}\text{Na}\)] requires [M + Na]+ 377.1338, found 377.1320.
3-(5-Benzyl-5-(3-chlorophenyl)-2-methyl-2,4-dioxoimidazolidin-1-yl)-1-(3-chlorophenyl) -1-methylure (4h); (1-methoxy-3-phenylprop-1-en-1-yl)oxy)trimethylsilane (58 mg, 0.24 mmol,) was added dropwise to a mixture of (E)-N₁,N₂-bis(3-chlorophenyl)-N₁,N₂- dimethylidiazene-1,2-dicarboxamide 1e (100 mg, 0.27 mmol) and AgOTf (6.9 mg, 10 mol %.) in THF (2.7 mL, 0.1 M) at -78 °C. The reaction was warmed to RT after 15 minutes, and stirred at RT for 3 h. After TLC showed consumption of (E)-N₁,N₂-bis(3-chlorophenyl)-N₁,N₂- dimethylidiazene-1,2-dicarboxamide 1e, the reaction was cooled to -78 °C and KHMDS (1 M in THF, 3 equiv) was added dropwise. After 20 minutes the reaction was warmed to -40 °C and stirred at -40 °C for 3 h. The reaction was quenched with sat. aq. NH₄Cl (10 mL), and the aqueous layer was extracted with EtOAc (3 × 10 mL). The combined organics were washed with brine (1 × 10 mL), dried over MgSO₄ and concentrated under reduced pressure to give a crude residue. Purification by flash silica chromatography (50% to 70% EtOAC + Hexane) afforded the title compound (85 mg, 62%) as a colourless oil.

\( V_{\text{max}} / \text{cm}^{-1} (\text{neat}) \): 3333, 2983, 1788, 1711, 1590, 1452, 733, 698

\(^{1}\text{H NMR} \) (400 MHz, CDCl₃) δ 7.82 (d, \( J = 2.0 \) Hz, 1H), 7.76–7.73 (m, 1H), 7.44–7.43 (m, 2H), 7.36–7.35 (m, 1H), 7.31–7.30 (m, 1H), 7.21–7.16 (m, 3H), 7.07–7.03 (m, 2H) 6.97 (d, \( J = 8.0 \) Hz, 2H), 5.85 (br s, 1H), 3.27 (d, \( J = 12.0 \) Hz, 1H), 3.24 (s, 3H), 3.14 (d, \( J = 12.0 \) Hz, 1H), 3.00 (s, 3H); \(^{13}\text{C NMR} \) (100 MHz, CDCl₃) 172.1, 155.9, 155.4, 143.3, 138.03, 135.9, 134.7, 133.8, 131.5, 130.1, 129.2, 129.1, 128.7, 128.6, 128.2, 128.1, 127.3, 125.9, 125.3, 72.7, 41.3, 38.0, 25.0; HRMS (ESI) calcd for [C₂₅H₂₂Cl₂N₄O₃Na] requires [M + Na]⁺ 519.0967, found 519.0963.
3-(5-Benzyl-3-methyl-2,4-dioxo-5-(3-(trifluoromethyl)phenyl)imidazolidin-1-yl)-1-methyl-1-(3-(trifluoromethyl)phenyl)urea (4i); (1-methoxy-3-phenylprop-1-en-1-yl)oxy)trimethylsilane (49 mg, 0.20 mmol) was added dropwise to a mixture of (E)-N1,N2-dimethyl-N1,N2-bis(3-(trifluoromethyl)phenyl)diazene-1,2-dicarboxamide 1f (100 mg, 0.23 mmol) and AgOTf (5.8 mg, 10 mol %) in THF (2.3 mL, 0.1 M) at -78 °C. The reaction was warmed to RT after 10 minutes, and stirred at RT for 3 h. After TLC showed consumption of (E)-N1,N2-dimethyl-N1,N2-bis(3-(trifluoromethyl)phenyl)diazene-1,2-dicarboxamide 1f, the reaction was cooled to -78 °C and KHMDS (1 M in THF, 3 equiv) was added dropwise. After 20 minutes the reaction was warmed to -40 °C and stirred at -40 °C for 3 h. The reaction was quenched with sat. aq. NH4Cl (10 mL), and the aqueous layer was extracted with EtOAc (3 × 10 mL). The combined organics were washed with brine (1 × 10 mL), dried over MgSO4 and concentrated under reduced pressure to give a crude residue. Purification by flash silica chromatography (50% to 70% EtOAc + Hexane) afforded the title compound (107 mg, 82%) as a colourless oil.

$V_{max}$ /cm$^{-1}$(neat): 3260, 1787, 1720, 1447, 1328, 1126, 748

$^1$H NMR (400 MHz, CDCl3) δ 8.07 (d, J = 8.0 Hz, 2H), 7.72 (d, J = 8.4 Hz, 1H), 7.65–7.61 (m, 2H), 7.58–7.54 (m, 2H), 7.49 (d, J = 8.3 Hz, 1H), 7.17–7.13 (m, 1H), 7.01–6.97 (m, 2H), 6.65 (d, J = 7.2 Hz, 2H), 5.82 (s, 1H), 3.76 (d, J = 14.0 Hz, 1H), 3.26 (s, 3H), 3.16 (d, J = 14.0 Hz, 1H), 2.88 (s, 3H); $^{13}$C NMR (100 MHz, CDCl3) δ 172.0, 155.8, 155.4, 142.8, 137.1, 133.7, 131.2, 131.1 (q, $J_{C,F} = 1.0$ Hz), 130.7 (q, $J_{C,F} = 1.3$ Hz), 129.4, 129.2, 128.5, 128.2, 125.8 (q, $J_{C,F} = 3.8$ Hz), 125.1 (q, $J_{C,F} = 3.7$ Hz), 124.7 (q, $J_{C,F} = 3.7$ Hz), 123.9 (q, $J_{C,F} = 4.0$ Hz), 72.7, 41.5, 38.1, 25.1; HRMS (ESI) calcd for [C$_{27}$H$_{22}$F$_6$N$_4$O$_3$Na] requires [M + Na]$^+$ 587.1494, found 587.1475.
3-(5-Benzyl-3-methyl-2,4-dioxo-5-(pyridin-2-yl)imidazolidin-1-yl)-1-methyl-1-(pyridin-2-yl)urea (4j); (1-methoxy-3-phenylprop-1-en-1-yl)trimethylsilane (71 mg, 0.30 mmol,) was added dropwise to a mixture of (E)-N₁,N₂-dimethyl-N¹,N²-di(pyridin-2-yl)diazene-1,2-dicarboxamide 1g (100 mg, 0.33 mmol) and AgOTf (5.8 mg, 8.4 mol %) in THF (3.3 mL, 0.1 M) at -78 °C. The reaction was warmed to RT after 10 minutes, and stirred at RT for 3 h. After TLC showed consumption of (E)-N₁,N₂-dimethyl-N¹,N²-di(pyridin-2-yl)diazene-1,2-dicarboxamide 1g, the reaction was cooled to -78 °C and KHMDS (1 M in THF, 3 equiv) was added dropwise. After 10 minutes the reaction was warmed to -20 °C and stirred at -40 °C for 3 h. The reaction was quenched with sat. aq. NH₄Cl (10 mL), and the aqueous layer was extracted with EtOAc (3 × 10 mL). The combined organics were washed with brine (1 × 10 mL), dried over MgSO₄ and concentrated under reduced pressure to give a crude residue. Purification by flash silica chromatography (50% to 70% EtOAC + Hexane) afforded the title compound (95 mg, 65%) as a colourless semi-solid.

ν<sub>max</sub>/cm<sup>-1</sup>(neat): 3234, 2989, 1787, 1718, 1690, 1593, 1434, 731, 699

<sup>1</sup>H NMR (400 MHz, CDCl₃) δ 12.23 (s, 1H), 8.64 – 8.60 (m, 1H), 8.22 (dd, J = 5.2, 1.5 Hz, 1H), 7.75 – 7.72 (m, 2H), 7.40 (d, J = 7.0 Hz, 2H), 7.29 – 7.24 (m, 5H), 6.99 (dd, J = 7.3, 5.0 Hz, 1H), 6.95 (d, J = 8.6 Hz, 1H), 3.82 (d, J = 14.2 Hz, 1H), 3.70 (d, J = 14.2 Hz, 1H), 3.31 (s, 3H), 2.84 (s, 3H). <sup>13</sup>C NMR (101 MHz, CDCl₃) δ 171.8, 156.4, 155.5, 155.0, 154.8, 149.0, 145.5, 139.2, 138.1, 137.0, 134.5 130.3, 127.5, 128.48, 123.7, 122.8, 117.9, 111.9, 74.6, 38.4, 33.3, 24.9; HRMS (ESI) calcd for [C<sub>23</sub>H₂₂N₆O₃Na] requires [M + Na]<sup>+</sup> 453.1651, found 453.1647.
1.13 General Procedure 7: A general, connective synthesis of protected \( N \)-aminoxydantoin (7):

Silyl enol ether 2 (1 equiv.) was added dropwise to a mixture of azocarboxylate 5 (1 equiv) and AgOTf (10 mol%) in THF (0.1 M) at -78 °C. The reaction was warmed to RT after 10 minutes and stirred at RT for 2-3 h. After TLC showed consumption of azocarboxylate 5, the reaction was cooled to -78 °C and KHMDS (1 M in THF, 3 equiv) was added dropwise. After 10 minutes the reaction was warmed to -20 °C and stirred at -20 °C for 1-4 h. The reaction was quenched with sat. aq. NH\(_4\)Cl (10 mL), and the aqueous layer was extracted with EtOAc (3 \( \times \) 10 mL). The combined organics were washed with brine (1 \( \times \) 10 mL), dried over MgSO\(_4\) and concentrated under reduced pressure to give a crude residue. Purification by flash silica chromatography (EtOAc + Hexane) afforded the title compound.

**tert-Butyl 2-(1-methoxy-1-oxopropan-2-yl)-2-(methyl(p-tolyl)carbamoyl) hydrazinecarboxylate (6)**

\(^1^H\) NMR (400 MHz, CDCl\(_3\)) \( \delta \) 7.17 – 7.02 (m, 4H), 5.93 (br s, 1H), 4.86 (br s, 1H), 3.69 (s, 3H), 3.19 (s, 3H), 2.30 (s, 3H), 1.44 – 1.24 (m, 12H); \(^{13}^C\) NMR (101 MHz, CDCl\(_3\)) \( \delta \) 171.2, 159.9, 154.4, 142.3, 135.7, 130.1, 124.7, 80.6, 66.8, 52.2, 40.1, 28.1, 20.9, 14.1. HRMS (ESI) calcd for [C\(_{18}\)H\(_{27}\)N\(_3\)O\(_5\)Na] requires [M + Na]+ 388.1848, found 388.1845.

1.15 Procedure and Analytical data of aza boc-hydantoins (7)
tert-Butyl (3,5-dimethyl-2,4-dioxo-5-(p-tolyl)imidazolidin-1-yl)carbamate (7a); (1-methoxyprop-1-en-1-yl)oxy)trimethylsilane (66 mg, 0.41 mmol,) was added dropwise to a mixture of tert-butyl (E)-2-(methyl(p-tolyl)carbamoyl)diazene-1-carboxylate 4a (115 mg, 0.41 mmol) and AgOTf (10.4 mg, 10 mol %) in THF (4.1 mL, 0.1 M) at -78 °C. The reaction was warmed to RT after 10 minutes and stirred at RT for 2 h. After TLC showed consumption of 4a, the reaction was cooled to -78 °C and KHMDS (1 M in THF, 3 equiv) was added dropwise. After 10 minutes the reaction was warmed to -20 °C and stirred at -20 °C for 2 h. The reaction was quenched with sat. aq. NH$_4$Cl (10 mL), and the aqueous layer was extracted with EtOAc (3 × 10 mL). The combined organics were washed with brine (1 × 10 mL), dried over MgSO$_4$ and concentrated under reduced pressure to give a crude residue. Purification by flash silica chromatography (20% EtOAc + Hexane) afforded the title compound (100 mg, 72%) as a colourless needle

**MP:** 180-182 °C

$V_{\text{max}}$/cm$^{-1}$(neat): 3289, 2979, 1786, 1710, 1454, 1245, 1157, 1046, 756

$^1$H NMR (400 MHz, CDCl$_3$) δ 7.23 – 7.14 (m, 4H), 6.56 (s, 1H), 3.09 (s, 3H), 2.33 (s, 3H), 1.83 (s, 3H), 1.44 (s, 9H); $^{13}$C NMR (126 MHz, CDCl$_3$) δ 173.6, 155.3, 154.7, 138.8, 133.6, 129.8, 125.9, 82.5, 68.3, 28.0, 25.2, 21.0, 19.9; HRMS (ESI) calcd for [C$_{17}$H$_{23}$N$_3$O$_4$Na]$^+$ requires [M + Na]$^+$ 356.1586, found 356.1587
tert-Butyl (3,5-dimethyl-2,4-dioxo-5-phenylimidazolidin-1-yl)carbamate (7b); 1-Methoxy-1-trimethylsilyloxypropene (71 mg, 0.44 mmol,) was added dropwise to a mixture of tert-butyl (E)-2-(methyl(phenyl)carbamoyl)diazene-1-carboxylate 5b (100 mg, 0.38 mmol) and AgOTf (9.5 mg, 10 mol %.) in THF (3.8 mL, 0.1 M) at -78 °C. The reaction was warmed to RT after 30 minutes and stirred at RT for 2 h. After TLC showed consumption of 5b, the reaction was cooled to -78 °C and KHMDS (1 M in THF, 3 equiv) was added dropwise. After 10 minutes the reaction was warmed to -20 °C and stirred at -20 °C for 2 h. The reaction was quenched with sat. aq. NH₄Cl (10 mL), and the aqueous layer was extracted with EtOAc (3 × 10 mL). The combined organics were washed with brine (1 × 10 mL), dried over MgSO₄ and concentrated under reduced pressure to give a crude residue. Purification by flash silica chromatography (20% EtOAC/Hexane) afforded the title compound (78 mg, 60%) as white needles.

**MP:** 176-178 °C

**ν<sub>max</sub>/cm<sup>-1</sup> (neat):** 3289, 2980, 1787, 1707, 1448, 1155, 751

**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)** δ 7.40–7.31 (m, 5H), 6.33 (br s, 1H), 3.09 (s, 3H), 1.85 (s, 3H), 1.43 (s, 9H); **<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)** δ 173.4, 154.6, 129.1, 128.9, 125.9, 82.6, 68.5, 28.0, 25.2, 19.9; HRMS (ESI) calcd for [C<sub>16</sub>H<sub>21</sub>N<sub>3</sub>O<sub>4</sub>Na] requires [M + Na]<sup>+</sup> 342.1430, found 342.1419.

![Structural diagram](image)

tert-Butyl (5-(4-cyanophenyl)-3,5-dimethyl-2,4-dioxoimidazolidin-1-yl)carbamate (7c); (1-methoxyprop-1-en-1-yloxy)trimethylsilane (77 mg, 0.48 mmol,) was added dropwise to a mixture of tert-butyl (E)-2-((4-cyanophenyl)(methyl)carbamoyl)diazene-1-carboxylate 5c (140 mg, 0.48 mmol) and AgOTf (12.2 mg, 10 mol %) in THF (4.8 mL, 0.1 M) at -78 °C. The
reaction was warmed to RT after 10 minutes and stirred at RT for 3 h. After TLC showed consumption of tert-butyl \((E)-2-((4\text{-cyanophenyl})(methyl)carbamoyldiazene-1\text{-carboxylate 5c, the reaction was cooled to }-78 \degree C\) and KHMDs \((1\text{ M in THF, 3 equiv})\) was added dropwise. After 10 minutes the reaction was warmed to \(-20 \degree C\) and stirred at \(-20 \degree C\) for 2 h. The reaction was quenched with sat. aq. NH\(_4\)Cl \((10\text{ mL})\), and the aqueous layer was extracted with EtOAc \((3 \times 10\text{ mL})\). The combined organics were washed with brine \((1 \times 10\text{ mL})\), dried over MgSO\(_4\) and concentrated under reduced pressure to give a crude residue. Purification by flash silica chromatography \((30\% \text{ EtOAC + Hexane})\) afforded the title compound \((120\text{ mg, 71.8\%})\) as a colourless needle.

\[ \text{MP: 180-182 \degree C} \]

\[ V_{\text{max} /\text{cm}^{-1}(\text{neat})}: 3298, 2981, 2230, 1789, 1712, 1454, 1246, 1156, 1047, 845, 753 \]

\[ ^1\text{H NMR (400 MHz, CDCl}_3 \text{)} \delta 7.68 (d, J = 8.7 \text{ Hz, 2H}), 7.52 (d, J = 8.4 \text{ Hz, 2H}), 6.35 (s, 1\text{H}), 3.10 (s, 3\text{H}), 1.87 (s, 3\text{H}), 1.44 (s, 9\text{H}); ^{13}\text{C NMR (126 MHz, CDCl}_3 \text{)} \delta 172.3, 155.1, 154.6, 142.0, 132.6, 127.0, 118.1, 112.8, 83.0, 68.2, 28.0, 25.4, 20.3; \text{HRMS (ESI) calcd for [C}_{17}\text{H}_{20}\text{NaO}_4\text{Na}^+ \text{ requires [M + Na}^+ 367.1382, \text{ found 367.1388.} \]

\[ \text{tert-Butyl (5-(3-chlorophenyl)-3,5-dimethyl-2,4-dioxoimidazolidin-1-yl)carbamate (7d): (1-methoxyprop-1-en-1-yl)oxy)trimethylsilane (67\text{ mg, 0.41 mmol}) was added dropwise to a mixture of tert-butyl (E)-2-((3-chlorophenyl)(methyl)carbamoyldiazene-1-carboxylate 5d (125\text{ mg, 0.42 mmol}) and AgOTf (10.6 mg, 10 \text{ mol %}) in THF (4.2 mL, 0.1 M) at -78 \degree C. The reaction was warmed to RT after 10 minutes and stirred at RT for 2 h. After TLC showed consumption of tert-butyl (E)-2-((3-chlorophenyl)(methyl)carbamoyldiazene-1-carboxylate 5d, the reaction was cooled to -78 \degree C and KHMDs (1 M in THF, 3 equiv) was added dropwise. After 10 minutes the reaction was warmed to -20 \degree C and stirred at -20 \degree C for 2 h. The reaction} \]

\[ \text{tert-Butyl (5-(3-chlorophenyl)-3,5-dimethyl-2,4-dioxoimidazolidin-1-yl)carbamate (7d): (1-methoxyprop-1-en-1-yl)oxy)trimethylsilane (67\text{ mg, 0.41 mmol}) was added dropwise to a mixture of tert-butyl (E)-2-((3-chlorophenyl)(methyl)carbamoyldiazene-1-carboxylate 5d (125\text{ mg, 0.42 mmol}) and AgOTf (10.6 mg, 10 \text{ mol %}) in THF (4.2 mL, 0.1 M) at -78 \degree C. The reaction was warmed to RT after 10 minutes and stirred at RT for 2 h. After TLC showed consumption of tert-butyl (E)-2-((3-chlorophenyl)(methyl)carbamoyldiazene-1-carboxylate 5d, the reaction was cooled to -78 \degree C and KHMDs (1 M in THF, 3 equiv) was added dropwise. After 10 minutes the reaction was warmed to -20 \degree C and stirred at -20 \degree C for 2 h. The reaction} \]
was quenched with sat. aq. NH₄Cl (10 mL), and the aqueous layer was extracted with EtOAc (3 × 10 mL). The combined organics were washed with brine (1 × 10 mL), dried over MgSO₄ and concentrated under reduced pressure to give a crude residue. Purification by flash silica chromatography (25% EtOAC+Hexane) afforded the title compound (90 mg, 60%) as a colourless needle

**MP:** 169-171 °C

**ν<sub>max</sub>/cm⁻¹ (neat):** 3293, 2979, 1788, 1708, 1453, 1244, 1155, 1046, 753

**¹H NMR** (400 MHz, CDCl₃) δ 7.32 (d, J = 3.0 Hz, 3H), 7.23 (dd, J = 4.2, 2.9 Hz, 1H), 6.37 (s, 1H), 3.10 (s, 3H), 1.84 (s, 3H), 1.44 (s, 9H); **¹³C NMR** (126 MHz, CDCl₃) δ 172.8, 155.0, 154.6, 135.1, 130.3, 129.1, 126.4, 124.3, 82.8, 68.1, 28.0, 25.4, 20.1. HRMS (ESI) calcd for [C₁₆H₂₀ClN₃O₄Na]<sup>+</sup> requires [M + Na]<sup>+</sup> 376.1040, found 376.1041

**tert-Butyl (3,5-dimethyl-2,4-dioxo-5-(3-(trifluoromethyl)phenyl)imidazolidin-1-yl)carbamate (7e):** (1-methoxyprop-1-en-1-yl)oxy)trimethylsilane (48 mg, 0.30 mmol,) was added dropwise to a mixture of tert-butyl (E)-2-(methyl(3-(trifluoromethyl)phenyl)carbamoyl)diazene-1-carboxylate 5e (100 mg, 0.30 mmol) and AgOTf (7.6 mg, 10 mol %) in THF (3.0 mL, 0.1 M) at -78 °C. The reaction was warmed to RT after 10 minutes, and stirred at RT for 3 h. After TLC showed consumption of tert-butyl (E)-2-(methyl(3-(trifluoromethyl)phenyl)carbamoyl)diazene-1-carboxylate 5e, the reaction was cooled to -78 °C and KHMDS (1 M in THF, 3 equiv) was added dropwise. After 10 minutes the reaction was warmed to -20 °C and stirred at -20 °C for 2 h. The reaction was quenched with sat. aq. NH₄Cl (10 mL), and the aqueous layer was extracted with EtOAc (3 × 10 mL). The combined organics were washed with brine (1 × 10 mL), dried over MgSO₄ and concentrated under reduced pressure to give a crude residue. Purification by flash silica
chromatography (30% EtOAC + Hexane) afforded the *title compound* (91 mg, 65%) as colourless needles.

**MP:** 177-179 °C

**$V_{\text{max}}$/cm\(^{-1}\) (neat):** 3292, 2982, 1789, 1709, 1328, 1123, 754, 699

**$^1$H NMR** (400 MHz, CDCl\(_3\)) $\delta$ 7.66 – 7.54 (m, 3H), 7.54 – 7.46 (m, 1H), 6.64 (s, 1H), 3.09 (s, 3H), 1.87 (s, 3H), 1.41 (s, 9H); **$^{13}$C NMR** (100 MHz, CDCl3) $\delta$ 172.8, 155.4, 154.8, 138.1, 131.6, 131.3, 130.9, 127.7 (q, $J_{C,F} = 2.6$ Hz), 129.6, 126.2 (q, $J_{C,F} = 272.2$ Hz), 125.7 (q, $J_{C,F} = 3.6$ Hz), 122.9 (q, $J_{C,F} = 3.5$ Hz), 82.9, 68.3, 28.0, 25.4, 20.5; HRMS (ESI) calcd for [C\(_{17}\)H\(_{20}\)F\(_3\)N\(_3\)O\(_4\)Na]\(^+\) requires [M + Na]\(^+\) 410.1304, found 410.1283

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

tert-Butyl (3,5-dimethyl-2,4-dioxo-5-(pyridin-2-yl)imidazolidin-1-yl)carbamate (7f); (E)-((1-methoxyprop-1-en-1-yl)oxy)trimethylsilane (60 mg, 0.37 mmol,) was added dropwise to a mixture of tert-butyl (E)-2-(methyl(pyridin-2-yl)carbamoyl)diazene-1-carboxylate 5f (100 mg, 0.37 mmol) and AgOTf (9.5 mg, 8.4 mol %) in THF (3.7 mL, 0.1 M) at -78 °C. The reaction was warmed to RT after 10 minutes, and stirred at RT for 3 h. After TLC showed consumption of tert-butyl (E)-2-(methyl(pyridin-2-yl)carbamoyl)diazene-1-carboxylate 5f, the reaction was cooled to -78 °C and KHMDS (1 M in THF, 3 equiv) was added dropwise. After 10 minutes the reaction was warmed to -20 °C and stirred at -40 °C for 2 h. The reaction was quenched with sat. aq. NH\(_4\)Cl (10 mL), and the aqueous layer was extracted with EtOAc (3 $\times$ 10 mL). The combined organics were washed with brine (1 $\times$ 10 mL), dried over MgSO\(_4\) and concentrated under reduced pressure to give a crude residue. Purification by flash silica chromatography (30% EtOAC + Hexane) afforded the *title compound* (60 mg, 50%) as a colourless semi-solid.
$V_{\text{max}} / \text{cm}^{-1} \text{(neat)}$: 3288, 2980, 1789, 1711, 1452, 1154, 748

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.46 (ddd, $J = 4.8, 1.7, 0.8$ Hz, 1H), 7.69 (td, $J = 7.8, 1.8$ Hz, 1H), 7.49 (d, $J = 7.9$ Hz, 1H), 7.23 – 7.18 (m, 1H), 6.83 (s, 1H), 2.99 (s, 3H), 1.83 (s, 3H), 1.40 (s, 9H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 172.3, 154.7, 149.2, 137.5, 123.5, 121.6, 81.9, 69.9, 28.1, 25.2, 19.8; HRMS (ESI) calcd for [C$_{15}$H$_{20}$N$_4$O$_4$Na]$^+$ requires [M + Na]$^+$ 343.1382, found 343.1370

tert-Butyl (5-benzyl-3-methyl-2,4-dioxo-5-(p-tolyl)imidazolidin-1-yl)carbamate (7g): (1-methoxy-3-phenylprop-1-en-1-yl)oxy)trimethylsilane (85 mg, 0.36 mmol,) was added dropwise to a mixture of tert-butyl (E)-2-(methyl(p-tolyl)carbamoyl)diazene-1-carboxylate 5a (100 mg, 0.36 mmol) and AgOTf (9.0 mg, 10 mol %) in THF (3.6 mL, 0.1 M) at -78 °C. The reaction was warmed to RT after 10 minutes and stirred at RT for 2 h. After TLC showed consumption of tert-butyl (E)-2-(methyl(p-tolyl)carbamoyl)diazene-1-carboxylate 5a, the reaction was cooled to -78 °C and KHMDS (1 M in THF, 3 equiv) was added dropwise. After 10 minutes the reaction was warmed to -20 °C and stirred at -20 °C for 2 h. The reaction was quenched with sat. aq. NH$_4$Cl (10 mL), and the aqueous layer was extracted with EtOAc (3 × 10 mL). The combined organics were washed with brine (1 × 10 mL), dried over MgSO$_4$ and concentrated under reduced pressure to give a crude residue. Purification by flash silica chromatography (20% EtOAc + Hexane) afforded the title compound (125 mg, 85%) as a semi-solid.

$V_{\text{max}} / \text{cm}^{-1} \text{(neat)}$: 2978, 1730, 1665, 1513, 1366, 1238, 1153, 749
\textbf{H NMR} (400 MHz, CDCl$_3$) δ 7.26 – 7.17 (m, 4H), 7.09 (bt, J = 12.0, 6.0 Hz, 5H), 3.20 (s, 3H), 3.08 (dd, J = 13.8, 6.0 Hz, 1H), 3.02 – 2.89 (m, 1H), 2.32 (s, 3H), 1.39 (s, 9H); \textbf{C NMR} (101 MHz, CDCl$_3$) δ 171.2, 160.0, 154.4, 142.1, 137.5, 135.6, 130.1, 129.2, 128.2, 126.4, 124.4, 81.0, 61.0, 39.9, 35.3, 28.1, 20.9; HRMS (ESI) calcd for [C$_{23}$H$_{27}$N$_3$O$_4$Na]$^+$ requires [M + Na]$^+$ 432.1899, found 432.1902

\textit{tert-Butyl (5-benzyl-5-(3-methoxyphenyl)-3-methyl-2,4-dioxoimidazolidin-1-yl) carbamate (7h):} (1-methoxy-3-phenylprop-1-en-1-yl)oxytrimethylsilane (80 mg, 0.34 mmol,) was added dropwise to a mixture of tert-butyl (E)-2-((3-methoxyphenyl)(methyl)carbamoyl)diazene-1-carboxylate 5g (100 mg, 0.34 mmol) and AgOTf (8.6 mg, 10 mol %) in THF (3.4 mL, 0.1 M) at -78 °C. The reaction was warmed to RT after 10 minutes and stirred at RT for 3.5 h. After TLC showed consumption of tert-butyl (E)-2-((3-methoxyphenyl)(methyl)carbamoyl)diazene-1-carboxylate 5g, the reaction was cooled to -78 °C and KHMDS (1 M in THF, 3 equiv) was added dropwise. After 10 minutes the reaction was warmed to -20 °C and stirred at -20 °C for 2 h. The reaction was quenched with sat. aq. NH$_4$Cl (10 mL), and the aqueous layer was extracted with EtOAc (3 × 10 mL). The combined organics were washed with brine (1 × 10 mL), dried over MgSO$_4$ and concentrated under reduced pressure to give a crude residue. Purification by flash silica chromatography (25% EtOAC + Hexane) afforded the title compound (75 mg, 51%) as colorless semi-solid

$V_{\text{max}}$ /cm$^{-1}$ (neat): 3282, 2978, 1788, 1709, 1453, 1155, 734, 700

\textbf{H NMR} (400 MHz, CDCl$_3$) δ 7.35 – 7.26 (m, 4H), 7.18 (dd, J = 7.6, 1.7 Hz, 3H), 7.13 (d, J = 7.7 Hz, 1H), 6.91 (dd, J = 8.2, 2.4 Hz, 1H), 6.35 (s, 1H), 3.80 (s, 3H), 3.63 – 3.48 (m, 2H), 2.81 (s, 3H), 1.32 (s, 9H); \textbf{C NMR} (101 MHz, CDCl$_3$) δ 172.2, 159.8, 154.9, 154.5, 136.7,
134.0, 129.8, 129.6, 128.9, 119.5, 82.5, 72.9, 55.4, 40.3, 27.8, 24.8; HRMS (ESI) calcd for [C$_{23}$H$_{27}$N$_3$O$_5$Na]$^+$ requires [M + Na]$^+$ 448.1848, found 448.1844

tert-Butyl (5-benzyl-5-(4-cyanophenyl)-3-methyl-2,4-dioxoimidazolidin-1-yl)carbamate (7i); (E)-((1-methoxy-3-phenylprop-1-en-1-yl)oxy)trimethylsilane (73 mg, 0.30 mmol,) was added dropwise to a mixture of tert-butyl (E)-2-((4-cyanophenyl)(methyl)carbamoyl)diazene-1-carboxylate 5c (100 mg, 034 mmol) and AgOTf (8.7 mg, 10 mol %) in THF (3.4 mL, 0.1 M) at -78 °C. The reaction was warmed to RT after 10 minutes and stirred at RT for 1 h. After TLC showed consumption of tert-butyl (E)-2-((4-cyanophenyl) (methyl)carbamoyl)diazene-1-carboxylate 5c, the reaction was cooled to -78 °C and KHMDS (1 M in THF, 3 equiv) was added dropwise. After 10 minutes the reaction was warmed to -20 °C and stirred at -20 °C for 1 h. The reaction was quenched with sat. aq. NH$_4$Cl (10 mL), and the aqueous layer was extracted with EtOAc (3 × 10 mL). The combined organics were washed with brine (1 × 10 mL), dried over MgSO$_4$ and concentrated under reduced pressure to give a crude residue. Purification by flash silica chromatography (30% EtOAC + Hexane) afforded the title compound (120 mg, 82%) as colourless needles

**MP:** 184-185 °C

**$\nu_{\max} / \text{cm}^{-1} \text{(neat)}$:** 3295, 2980, 2231, 1790, 1712, 1451, 1156, 754

**$^1$H NMR** (500 MHz, CDCl$_3$) $\delta$ 7.82 (d, $J = 7.8$ Hz, 2H), 7.73 (d, $J = 8.7$ Hz, 2H), 7.39 – 7.31 (m, 3H), 7.17 (dd, $J = 7.6$, 1.7 Hz, 2H), 6.24 (s, 1H), 3.67 (d, $J = 12.9$ Hz, 1H), 3.49 (d, $J = 13.9$ Hz, 1H), 2.88 (s, 3H), 1.39 (s, 9H); **$^{13}$C NMR** (126 MHz, CDCl$_3$) $\delta$ 171.4, 154.7, 154.3, 140.4, 133.2, 132.3, 129.3, 129.1, 128.3, 128.2, 118.3, 112.9, 83.1, 72.5, 40.3, 27.8, 24.9;

HRMS (ESI) calcd for [C$_{23}$H$_{24}$Na$_4$O$_4$Na]$^+$ requires [M + Na]$^+$ 443.1695, found 443.1672
tert-Butyl \((5\text{-benzyl}-5\text{-}(4\text{-chlorophenyl})\text{-}3\text{-methyl}-2,4\text{-dioxoimidazolin}-1\text{-yl})\text{carbamate}\) (7j); (1-methoxy-3-phenylprop-1-en-1-yl)oxy)trimethylsilane (79 mg, 0.33 mmol,) was added dropwise to a mixture of tert-butyl \((E)-2\text{-}((4\text{-chlorophenyl})(methyl)carbamoyl)\text{diazone-1-carboxylate}\) 5h (100 mg, 0.33 mmol) and AgOTf (8.4 mg, 10 mol %) in THF (3.3 mL, 0.1 M) at -78 °C. The reaction was warmed to RT after 10 minutes and stirred at RT for 2 h. After TLC showed consumption of tert-butyl \((E)-2\text{-}((4\text{-chlorophenyl})(methyl)carbamoyl)\text{diazone-1-carboxylate}\) 5h, the reaction was cooled to -78 °C and KHMDS (1 M in THF, 3 equiv) was added dropwise. After 10 minutes the reaction was warmed to -20 °C and stirred at -20 °C for 2 h. The reaction was quenched with sat. aq. NH₄Cl (10 mL), and the aqueous layer was extracted with EtOAc (3 × 10 mL). The combined organics were washed with brine (1 × 10 mL), dried over MgSO₄ and concentrated under reduced pressure to give a crude residue. Purification by flash silica chromatography (20% EtOAc + Hexane) afforded the title compound (120 mg, 83%) as a white needles.

\textbf{MP:} 169-171°C

\textbf{\textit{ν}}_{\text{max}} /\text{cm}^{-1}(\text{neat}): 3273, 2979, 1789, 1708, 1453, 1156, 753

\textbf{\textit{^1}}H \text{NMR} (400 MHz, CDCl₃) δ 7.53 (d, \(J = 8.2\) Hz, 2H), 7.37 (d, \(J = 8.7\) Hz, 2H), 7.29 (q, \(J = 5.5\) Hz, 3H), 7.14 (dd, \(J = 7.5, 1.8\) Hz, 2H), 6.25 (s, 1H), 3.61 – 3.42 (m, 2H), 2.82 (s, 3H), 1.33 (s, 9H); \textbf{\textit{^13}}C \text{NMR} (101 MHz, CDCl₃) δ 171.9, 154.6, 154.4, 135.0, 133.7, 133.6, 129.5, 128.9, 128.8, 128.7, 127.9, 82.7, 72.3, 40.2, 27.8, 24.7; HRMS (ESI) calcd for [C₂₂H₂₄ClN₃O₄Na]⁺ requires [M + Na]⁺ 452.1353, found 452.1338
**tert-Butyl (5-benzyl-5-(3-chlorophenyl)-3-methyl-2,4-dioxoimidazolidin-1-yl)carbamate (7k);** (1-methoxy-3-phenylprop-1-en-1-yl)oxytrimethylsilane (76 mg, 0.32 mmol) was added dropwise to a mixture of tert-butyl (E)-2-((3-chlorophenyl)(methyl)carbamoyl)diazene-1-carboxylate 5d (107 mg, 0.36 mmol) and AgOTf (9.07 mg, 10 mol %) in THF (3.6 mL, 0.1 M) at -78 °C. The reaction was warmed to RT after 10 minutes and stirred at RT for 2 h. After TLC showed consumption of tert-butyl (E)-2-((3-chlorophenyl)(methyl)carbamoyl)diazene-1-carboxylate 5d, the reaction was cooled to -78 °C and KHMDS (1 M in THF, 3 equiv) was added dropwise. After 10 minutes the reaction was warmed to -20 °C and stirred at -20 °C for 2 h. The reaction was quenched with sat. aq. NH₄Cl (10 mL), and the aqueous layer was extracted with EtOAc (3 × 10 mL). The combined organics were washed with brine (1 × 10 mL), dried over MgSO₄ and concentrated under reduced pressure to give a crude residue. Purification by flash silica chromatography (20% EtOAC + Hexane) afforded the title compound (113 mg, 78%) as a colourless needle **MP:** 152-154 °C.

**ν<sub>max</sub>/cm<sup>-1</sup> (neat):** 3268, 2980, 1789, 1709, 1454, 1155, 753, 701

**<sup>1</sup>H NMR (400 MHz, CDCl₃)** δ 7.78 (d, J = 8.3 Hz, 2H), 7.70 (d, J = 8.4 Hz, 2H), 7.32 (qd, J = 5.9, 2.2 Hz, 3H), 7.13 (dd, J = 7.5, 1.9 Hz, 2H), 6.19 (s, 1H), 3.63 (d, J = 14.3 Hz, 1H), 3.45 (d, J = 13.9 Hz, 1H), 2.84 (s, 3H), 1.35 (s, 9H); **<sup>1</sup>C NMR (101MHz, CDCl₃)** δ 171.7, 155.0, 154.5, 137.2, 134.6, 133.5, 130.0, 129.7, 129.1, 128.8, 128.0, 127.7, 125.7, 82.7, 72.4, 40.2, 27.8, 24.8; HRMS (ESI) calcd for [C₂₂H₂₄ClN₃O₄Na]⁺ requires [M + Na]⁺ 452.1353, found 452.1331
tert-Butyl (5-benzyl-3-methyl-2,4-dioxo-5-(3-(trifluoromethyl)phenyl)imidazolidin-1-yl)carbamate (7l); (1-methoxy-3-phenylprop-1-en-1-yl)oxytrimethylsilane (121.9 mg, 0.51 mmol,) was added dropwise to a mixture of tert-butyl (E)-2-(methyl(3-(trifluoromethyl)phenyl)carbamoyl)diazene-1-carboxylate 5e (190 mg, 0.57 mmol) and AgOTf (15.2 mg, 10 mol %) in THF (6.0 mL, 0.1 M) at -78 °C. The reaction was warmed to RT after 10 minutes, and stirred at RT for 3 h. After TLC showed consumption of tert-butyl (E)-2-(methyl(3-(trifluoromethyl)phenyl)carbamoyl)diazene-1-carboxylate 5e, the reaction was cooled to -78 °C and KHMDS (1 M in THF, 3 equiv) was added dropwise. After 10 minutes the reaction was warmed to -20 °C and stirred at -40 °C for 2 h. The reaction was quenched with sat. aq. NH₄Cl (10 mL), and the aqueous layer was extracted with EtOAc (3 × 10 mL). The combined organics were washed with brine (1 × 10 mL), dried over MgSO₄ and concentrated under reduced pressure to give a crude residue. Purification by flash silica chromatography (30% EtOAc + Hexane) afforded the title compound (155 mg, 70%) as colourless needles.

MP: 141-143 °C

ν_max /cm⁻¹(neat): 3268, 2988, 1790, 1713, 1329, 1129, 748, 699

¹H NMR (400 MHz, CDCl₃) δ 7.78 (s, 1H), 7.65 (d, J = 7.9 Hz, 1H), 7.50 (d, J = 7.7 Hz, 1H), 7.40 (t, J = 7.9 Hz, 1H), 7.16 (d, J = 7.1 Hz, 3H), 7.02 (dd, J = 7.5, 1.9 Hz, 2H), 6.26 (s, 1H), 3.41 (dd, J = 16.9, 13.6 Hz, 2H), 2.69 (s, 3H), 1.16 (s, 9H); ¹³C NMR (100 MHz, CDCl₃) δ 171.6, 154.6, 154.2, 136.4, 133.4, 130.9 (q, J_C-F = 12.4 Hz), 129.4, 129.2, 128.9, 128.1, 125.7 (q, J_C-F = 3.8 Hz), 125.2 (q, J_C-F = 272.5 Hz), 124.0 (q, J_C-F = 3.8 Hz), 82.8, 72.4, 40.6, 27.7, 24.8; HRMS (ESI) calcd for [C₂₃H₂₄F₃N₃O₄Na]⁺ requires [M + Na]⁺ 486.1617, found 486.1615
tert-Butyl \((5\text{-benzyl-3-methyl-2,4-dioxo-5-}\text{-(trifluoromethyl)phenyl})\text{imidazolidin-1-yl})\text{carbamate (7m)}; \((1\text{-methoxy-3-phenylprop-1-en-1-yl)oxy})\text{trimethylsilane (81 mg, 0.34 mmol,})\text{ was added dropwise to a mixture of tert-butyl \((E)-2\text{-}(methyl(pyridin-2-yl)carbamoyl)diazene-1\text{-carboxylate 5f (157 mg, 0.59 mmol) and AgOTf (14.9 mg, 10 mol %) in THF (5.94 mL, 0.1 M) at -78 °C. The reaction was warmed to RT after 10 minutes, and stirred at RT for 2 h. After TLC showed consumption of tert-butyl \((E)-2\text{-}(methyl(pyridin-2-yl)carbamoyl)diazene-1\text{-carboxylate 5f, the reaction was cooled to -78 °C and KHMDS (1 M in THF, 3 equiv) was added dropwise. After 10 minutes the reaction was warmed to -20 °C and stirred at -20 °C for 2 h. The reaction was quenched with sat. aq. NH₄Cl (10 mL), and the aqueous layer was extracted with EtOAc (3 × 10 mL). The combined organics were washed with brine (1 × 10 mL), dried over MgSO₄ and concentrated under reduced pressure to give a crude residue. Purification by flash silica chromatography (30% EtOAC + Hexane) afforded the title compound (163 mg, 85%) as a pale-yellow semi-solid.

\(\nu_{\text{max}}/\text{cm}^{-1}\) (neat): \(2977, 1792, 1706, 1594, 1435, 1136, 748\)

\(^1\text{H}\text{ NMR (400 MHz, CDCl}_3\) \(\delta 11.77 \text{ (s, 1H), 8.26 (d, } J = 3.6 \text{ Hz, 1H), 7.77 – 7.65 (m, 1H), 7.31 (d, } J = 7.1 \text{ Hz, 2H), 7.28 – 7.23 (m, 2H), 7.18 (t, } J = 7.0 \text{ Hz, 1H), 6.99 (d, } J = 8.5 \text{ Hz, 2H), 3.40 (s, 3H), 3.25 (dd, } J = 13.4, 7.9 \text{ Hz, 1H), 3.14 (dd, } J = 14.0, 7.5 \text{ Hz, 1H), 1.37 \text{ (s, 9H); }^{13}\text{C NMR (101 MHz, CDCl}_3\) 171.2, 157.4, 155.3, 146.0, 138.9, 138.0, 137.2, 129.4, 128.5, 128.3, 126.4, 117.6, 111.8, 82.07 74.14, 33.39, 28.08, 14.15; HRMS (ESI) calcd for [C\(_{21}\)H\(_{24}\)Na\(_4\)O\(_4\)Na\] \(^+\) requires [M + Na\] \(^+\) 419.1695, found 419.1675

![Chemical structure](attachment:image)

**tert-Butyl \((5\text{-benzyl-3-methyl-5-(naphthalen-1-yl)-2,4-dioxoimidazolidin-1-yl})\text{carbamate (7n); (1-methoxy-3-phenylprop-1-en-1-yl)oxy})\text{trimethylsilane (81 mg, 0.34 mmol,})\text{ was added**
dropwise to a mixture of tert-butyl (E)-2-(ethyl(naphthalen-1-yl)carbamoyl)diazene-1-carboxylate \textit{5i} (100 mg, 0.34 mmol) and AgOTf (8.7 mg, 10 mol %) in THF (3.4 mL, 0.1 M) at -78 °C. The reaction was warmed to RT after 10 minutes and stirred at RT for 2.5 h. After TLC showed consumption of tert-butyl (E)-2-(ethyl(naphthalen-1-yl)carbamoyl)diazene-1-carboxylate \textit{5i}, the reaction was cooled to -78 °C and KHMDS (1 M in THF, 3 equiv) was added dropwise. After 10 minutes the reaction was warmed to -20 °C and stirred at -20 °C for 4 h. The reaction was quenched with sat. aq. \textit{NH}_{4}Cl (10 mL), and the aqueous layer was extracted with EtOAc (3 \times 10 mL). The combined organics were washed with brine (1 \times 10 mL), dried over MgSO\textsubscript{4} and concentrated under reduced pressure to give a crude residue.

Purification by flash silica chromatography (20% EtOAC + Hexane) afforded the title compound (90 mg, 56%) as colorless oil.

\textit{V}_{\text{max}}/\text{cm}^{-1} (\text{neat}): 3264, 2978, 1785, 1712, 1495, 1392, 1158, 775

\textit{^1}H NMR (400 MHz, CDCl\textsubscript{3}) \delta 7.88 – 7.78 (m, 3H), 7.53 – 7.42 (m, 3H), 7.39 – 7.30 (m, 3H), 7.28 – 7.21 (m, 3H), 6.21 (s, 1H), 4.00 (d, \textit{J} = 13.0 Hz, 1H), 3.54 (d, \textit{J} = 12.9 Hz, 1H), 3.25 (q, \textit{J} = 7.2 Hz, 2H), 0.94 (s, 9H), 0.78 (t, \textit{J} = 7.2 Hz, 3H); \textit{^13}C NMR (101MHz, CDCl\textsubscript{3}) \delta 172.3, 155.4, 154.8, 134.5, 133.5, 131.6, 131.0, 130.8, 129.8, 128.7, 127.9, 127.1, 125.8, 124.9, 123.3, 82.3, 71.9, 40.7, 33.8, 27.6, 12.3; HRMS (ESI) calcd for [C\textsubscript{27}H\textsubscript{29}N\textsubscript{3}O\textsubscript{4}Na]\textsuperscript{+} requires [M + Li]\textsuperscript{+} 482.2056, found 482.2058.

\textit{tert-Butyl (5-(3-methoxyphenyl)-3-methyl-2,4-dioxo-5-propylimidazolidin-1-yl)carbamate (7o)}; (1-methoxypent-1-en-1-yl)oxytrimethylsilane (64 mg, 0.34 mmol,) was added dropwise to a mixture of tert-butyl (\textit{E})-2-((3-methoxyphenyl)(methyl)carbamoyl)diazene-1-carboxylate \textit{5g} (100 mg, 0.34 mmol) and
AgOTf (8.6 mg, 10 mol %) in THF (3.4 mL, 0.1 M) at -78 °C. The reaction was warmed to RT after 10 minutes and stirred at RT for 3 h. After TLC showed consumption of tert-butyl (E)-2-((3-methoxyphenyl)(methyl)carbamoyl)diazene-1-carboxylate 5g, the reaction was cooled to -78 °C and KHMDS (1 M in THF, 3 equiv) was added dropwise. After 10 minutes the reaction was warmed to -20 °C and stirred at -20 °C for 4 h. The reaction was quenched with sat. aq. NH₄Cl (10 mL), and the aqueous layer was extracted with EtOAc (3 × 10 mL). The combined organics were washed with brine (1 × 10 mL), dried over MgSO₄ and concentrated under reduced pressure to give a crude residue. Purification by flash silica chromatography (20% EtOAC + Hexane) afforded the title compound (53 mg, 42%) as a colorless Semi-solid.

$V_{\text{max}}/\text{cm}^{-1}\text{(neat):}$ 3284, 2966, 1786, 1710, 1454, 1245, 1154

$^1\text{H NMR}$ (400 MHz, CDCl₃) $\delta$ 7.28 (t, $J = 8.1$ Hz, 1H), 6.92 – 6.83 (m, 3H), 6.17 (s, 1H), 3.78 (s, 3H), 3.09 (s, 3H), 2.28 (td, $J = 13.6$, 4.6 Hz, 1H), 2.06 (td, $J = 13.7$, 3.6 Hz, 1H), 1.40 (s, 9H), 1.26 – 1.17 (m, 2H), 0.94 (t, $J = 7.3$ Hz, 3H); $^{13}\text{C NMR}$ (101MHz, CDCl₃) $\delta$ 172.6, 160.1, 155.5, 154.4, 141.8, 137.2, 130.1, 118.6, 113.7, 82.4, 71.7, 55.4, 28.0, 25.0, 16.8, 14.1; HRMS (ESI) calcd for [C₁₉H₂₇N₃O₅Na]$^+$ requires [M + Na]$^+$ 400.1848, found 400.1854

**tert-Butyl** (5-(2-chlorophenyl)-3-methyl-2,4-dioxo-5-propylimidazolidin-1-yl)carbamate (7p); (1-methoxypent-1-en-1-yl)oxy)trimethylsilane (70 mg, 0.37 mmol,) was added dropwise to a mixture of tert-butyl (E)-2-((2-chlorophenyl)(methyl)carbamoyl)diazene-1-carboxylate 5j (112 mg, 0.37 mmol) and AgOTf (9.5 mg, 10 mol %) in THF (3.7 mL, 0.1 M) at -78 °C. The reaction was warmed to RT after 10 minutes and stirred at RT for 3 h. After TLC showed consumption of tert-butyl (E)-2-((2-chlorophenyl)(methyl)carbamoyl)diazene-1-carboxylate 5j, the reaction was cooled to -78 °C and KHMDS (1 M in THF, 3 equiv) was added dropwise.
After 10 minutes the reaction was warmed to -20 °C and stirred at -20 °C for 4 h. The reaction was quenched with sat. aq. NH₄Cl (10 mL), and the aqueous layer was extracted with EtOAc (3 × 10 mL). The combined organics were washed with brine (1 × 10 mL), dried over MgSO₄ and concentrated under reduced pressure to give a crude residue. Purification by flash silica chromatography (15% EtOAC + Hexane) afforded the title compound (70 mg, 48%) as a colorless solid.

**MP :** 208-210 °C

**ν max/cm⁻¹ (neat):** 3277, 2960, 1781, 1690, 1453, 1150

**¹H NMR (400 MHz, CDCl₃) δ** 7.58 – 7.54 (m, 1H), 7.38 – 7.35 (m, 1H), 7.33 – 7.28 (m, 2H), 6.01 (s, 1H), 3.10 (s, 3H), 2.24 (pd, J = 12.9, 3.8 Hz, 2H), 1.36 (s, 9H), 1.25 – 1.14 (m, 2H), 1.00 (t, J = 7.2 Hz, 3H); **¹³C NMR (101 MHz, CDCl₃) δ** 172.5, 156.1, 154.8, 132.2, 131.5, 130.7, 130.5, 127.2, 82.3, 70.0, 36.2, 27.9, 25.0, 16.2, 14.1; **HRMS (ESI) calcd for** [C₁₈H₂₄ClN₃O₄Na]⁺ requires [M + Na]⁺ 404.1353, found 404.1355

**tert-Butyl** (5-(3-chlorophenyl)-3-methyl-2,4-dioxo-5-propylimidazolidin-1-yl)carbamate (7q); (1-methoxypent-1-en-1-yl)oxy)trimethylsilane (65 mg, 0.35 mmol,) was added dropwise to a mixture of tert-butyl (E)-2-((3-chlorophenyl)(methyl)carbamoyl)diazene-1-carboxylate 5d (104 mg, 0.34 mmol) and AgOTf (8.7 mg, 10 mol %) in THF (3.5 mL, 0.1 M) at -78 °C. The reaction was warmed to RT after 10 minutes and stirred at RT for 3 h. After TLC showed consumption of tert-butyl (E)-2-((3-chlorophenyl)(methyl)carbamoyl)diazene-1-carboxylate 5d, the reaction was cooled to -78 °C and KHMDS (1 M in THF, 3 equiv) was added dropwise. After 10 minutes the reaction was warmed to -20 °C and stirred at -20 °C for 2 h. The reaction was quenched with sat. aq. NH₄Cl (10 mL), and the aqueous layer was extracted with EtOAc
(3 × 10 mL). The combined organics were washed with brine (1 × 10 mL), dried over MgSO₄ and concentrated under reduced pressure to give a crude residue. Purification by flash silica chromatography (20% EtOAC + Hexane) afforded the title compound (123 mg, 92%) as a colorless semi-solid.

\[ V_{\text{max}} / \text{cm}^{-1} (\text{neat}) : \] 3283, 2969, 1781, 1709, 1454, 1245, 1155, 750

\[ ^1H \text{ NMR} \] (400 MHz, CDCl₃) \( \delta \) 7.35 (s, 1H), 7.32 – 7.28 (m, 2H), 7.26 (dd, \( J = 7.0, 1.3 \) Hz, 1H), 6.41 (s, 1H), 3.10 (s, 3H), 2.24 (td, \( J = 13.7, 4.5 \) Hz, 1H), 2.09 (td, \( J = 14.0, 13.4, 3.9 \) Hz, 1H), 1.38 (s, 9H), 1.25 – 1.18 (m, 2H), 0.94 (t, \( J = 7.3 \) Hz, 3H); \( ^{13}C \) NMR (101MHz, CDCl3) \( \delta \) 172.2, 155.3, 154.4, 137.8, 134.9, 130.2, 129.0, 126.9, 124.9, 82.7, 71.3, 35.5, 27.9, 25.1, 16.8, 14.0.; HRMS (ESI) calcd for [C₁₈H₂₄ClN₃O₄Na]^+ requires [M + Na]^+ 404.1353, found 404.1348

\[ \text{tert-Butyl} \quad (3\text{-methyl-2,4-dioxo-5-propyl-5-(3-(trifluoromethyl)phenyl)imidazolidin-1-yl})\text{carbamate} \ (7r) ; \] (1-methoxypent-1-en-1-yl)oxytrimethylsilane (64 mg, 0.34 mmol,) was added dropwise to a mixture of tert-butyl \( (E) \)-2-(methyl(3-(trifluoromethyl)phenyl)carbamoyl)diazene-1-carboxylate \ 5e (113 mg, 0.34 mmol) and AgOTf (8.6 mg, 10 mol %) in THF (3.4 mL, 0.1 M) at -78 °C. The reaction was warmed to RT after 10 minutes and stirred at RT for 3 h. After TLC showed consumption of tert-butyl \( (E) \)-2-(methyl(3-(trifluoromethyl)phenyl)carbamoyl)diazene-1-carboxylate \ 5e, the reaction was cooled to -78 °C and KHMDS (1 M in THF, 3 equiv) was added dropwise. After 10 minutes the reaction was warmed to -20 °C and stirred at -20 °C for 2 h. The reaction was quenched with sat. aq. NH₄Cl (10 mL), and the aqueous layer was extracted with EtOAc (3 × 10 mL). The combined organics were washed with brine (1 × 10 mL), dried over MgSO₄ and
concentrated under reduced pressure to give a crude residue. Purification by flash silica chromatography (20% EtOAC + Hexane) afforded the title compound (80 mg, 56%) as a colorless semi-solid.

$V_{\text{max}}/\text{cm}^{-1}\text{(neat)}$: 3282, 2968, 1784, 1454, 1329, 1163, 1127, 752

$^1$H NMR (400 MHz, CDCl$_3$) δ 7.68 (s, 1H), 7.63 – 7.56 (m, 2H), 7.53 – 7.47 (m, 1H), 6.33 (s, 1H), 3.11 (s, 3H), 2.34 – 2.09 (m, 2H), 1.37 (s, 9H), 1.21 – 1.17 (m, 2H), 0.96 (t, $J = 7.3$ Hz, 3H); $^{13}$C NMR (101MHz, CDCl$_3$) δ 172.2, 155.3, 154.4, 137.0, 131.4 (q, $J_{C,F} = 32.3$ Hz), 130.3, 126.6 (q, $J_{C,F} = 272.4$ Hz), 125.73 (q, $J_{C,F} = 3.2$ Hz), 123.54 (q, $J_{C,F} = 3.5$ Hz), 82.8, 71.3, 35.9, 27.9, 25.2, 16.9, 14.0; HRMS (ESI) calcd for [C$_{19}$H$_{24}$F$_3$N$_3$O$_4$Na]$^+$ requires [M + Na]$^+$ 438.1617, found 438.1611

tert-Butyl (5-(4-cyanophenyl)-3-methyl-2,4-dioxo-5-propylimidazolidin-1-yl)carbamate (7s); (1-methoxypent-1-en-1-yl)oxy)trimethylsilane (67 mg, 0.35 mmol,) was added dropwise to a mixture of tert-butyl (E)-2-((4-cyanophenyl)(methyl)carbamoyl)diazene-1-carboxylate 5c (103 mg, 0.35 mmol) and AgOTf (9.0 mg, 10 mol %) in THF (3.5 mL, 0.1 M) at -78 °C. The reaction was warmed to RT after 10 minutes and stirred at RT for 2.5 h. After TLC showed consumption of tert-butyl (E)-2-((4-cyanophenyl)(methyl)carbamoyl)diazene-1-carboxylate 5c, the reaction was cooled to -78 °C and KHMDS (1 M in THF, 3 equiv) was added dropwise. After 10 minutes the reaction was warmed to -20 °C and stirred at -20 °C for 2 h. The reaction was quenched with sat. aq. NH$_4$Cl (10 mL), and the aqueous layer was extracted with EtOAc (3 × 10 mL). The combined organics were washed with brine (1 × 10 mL), dried over MgSO$_4$ and concentrated under reduced pressure to give a crude residue. Purification by flash silica
chromatography (20% EtOAC + Hexane) afforded the title compound (80 mg, 60%) as a colorless semi-solid.

$V_{\text{max}}/\text{cm}^{-1} (\text{neat})$: 3293, 2923, 2230, 1788, 1711, 1454, 1246, 1156, 843, 752

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.65 (d, $J = 8.3$ Hz, 2H), 7.56 (d, $J = 8.3$ Hz, 2H), 6.44 (s, 1H), 3.09 (s, 3H), 2.19 (dtd, $J = 55.3$, 14.1, 4.2 Hz, 2H), 1.38 (s, 9H), 1.25-121 (m, 2H), 0.94 (t, $J = 7.3$ Hz, 3H); $^{13}$C NMR (101MHz, CDCl$_3$) $\delta$ 171.8, 155.4, 154.5, 141.0, 132.5, 127.7, 118.2, 112.8, 82.9, 71.3, 35.9, 27.9, 25.2, 16.9, 14.0; HRMS (ESI) calcd for [C$_{19}$H$_{24}$N$_4$O$_4$Na]$^+$ requires [M + Na]$^+$ 395.1695, found 395.1699

tert-Butyl (3-ethyl-5-(naphthalen-1-yl)-2,4-dioxo-5-propylimidazolidin-1-yl)carbamate (7t); (1-methoxypent-1-en-1-yl)oxy)trimethylsilane (78 mg, 0.41 mmol,) was added dropwise to a mixture of tert-butyl (E)-2-(ethyl(naphthalen-1-yl)carbamoyl)diazene-1-carboxylate Si (136 mg, 0.41 mmol) and AgOTf (10.4 mg, 10 mol %) in THF (4.1 mL, 0.1 M) at -78 °C. The reaction was warmed to RT after 10 minutes and stirred at RT for 3 h. After TLC showed consumption of tert-butyl (E)-2-(ethyl(naphthalen-1-yl)carbamoyl)diazene-1-carboxylate Si, the reaction was cooled to -78 °C and KHMDS (1 M in THF, 3 equiv) was added dropwise. After 10 minutes the reaction was warmed to -20 °C and stirred at -20 °C for 3 h. The reaction was quenched with sat. aq. NH$_4$Cl (10 mL), and the aqueous layer was extracted with EtOAc (3 × 10 mL). The combined organics were washed with brine (1 × 10 mL), dried over MgSO$_4$ and concentrated under reduced pressure to give a crude residue. Purification by flash silica chromatography (15% EtOAC + Hexane) afforded the title compound (107 mg, 62%) as colourless needles.
MP: 170-172 °C

$V_{\text{max}}$ / cm$^{-1}$ (neat): 3274, 2972, 1783, 1708, 1449, 1351, 1159, 731

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.82 (d, $J$ = 7.8 Hz, 2H), 7.66 (d, $J$ = 7.3 Hz, 1H), 7.49 (d, $J$ = 8.0 Hz, 1H), 7.44 – 7.34 (m, 3H), 5.76 (q, $J$ = 7.2 Hz, 2H), 2.44 (td, $J$ = 12.9, 4.2 Hz, 1H), 2.32 (dt, $J$ = 12.5, 8.1 Hz, 1H), 1.49 – 1.05 (m, 14H), 0.98 (t, $J$ = 7.2 Hz, 3H); $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 172.9, 155.1, 154.4, 134.5, 131.2, 130.7, 130.0, 129.8, 128.0, 127.1, 125.7, 124.9, 122.3, 82.2, 70.7, 37.2, 34.3, 27.7, 16.4, 14.2, 13.1.; HRMS (ESI) calcd for [C$_{23}$H$_{29}$N$_3$O$_4$Na]$^+$ requires [M + Na]$^+$ 434.2056, found 434.2058

**tert-Butyl (5-(2-(benzyloxy)ethyl)-5-(3-chlorophenyl)-3-methyl-2,4-dioxoimidazolidin-1-yl)carbamate (7u)**; (4-(benzyloxy)-1-methoxybut-1-en-1-yl)oxy)trimethylsilane (145 mg, 0.51 mmol,) was added dropwise to a mixture of (E)-tert-butyl 2-((3-chlorophenyl)(methyl)carbamoyl)diazene-carboxylate 5d (154 mg, 0.51 mmol) and AgOTf (13.0 mg, 10 mol %) in THF (5.1 mL, 0.1 M) at -78 °C. The reaction was warmed to RT after 10 minutes and stirred at RT for 2 h. After TLC showed consumption of (E)-tert-butyl 2-((3-chlorophenyl)(methyl)carbamoyl)diazene-carboxylate 5d, the reaction was cooled to -78 °C and KHMDS (1 M in THF, 3 equiv) was added dropwise. After 10 minutes the reaction was warmed to -20 °C and stirred at -20 °C for 1.5 h. The reaction was quenched with sat. aq. NH$_4$Cl (10 mL), and the aqueous layer was extracted with EtOAc (3 × 10 mL). The combined organics were washed with brine (1 × 10 mL), dried over MgSO$_4$ and concentrated under reduced pressure to give a crude residue. Purification by flash silica chromatography (15% EtOAc + Hexane) afforded the title compound (215 mg, 87%) as a colorless oil.

$V_{\text{max}}$ / cm$^{-1}$ (neat): 3310, 2978, 2933, 1791, 1714, 1453, 1157
$^1$H NMR (400 MHz, CDCl$_3$) δ 7.69–7.57 (m, 2H), 7.38 – 7.28 (m, 7H), 6.82 (s, 1H), 4.53 – 4.34 (m, 2H), 3.62–3.39 (m, 2H), 2.96 (s, 3H), 2.54 (br s, 2H), 1.41 (s, 9H); $^{13}$C NMR (101 MHz, CDCl$_3$) δ $^{13}$C NMR (101 MHz, CDCl$_3$) δ 172.0, 156.1, 154.7, 138.4, 136.6, 130.0, 128.9, 128.6, 128.3, 126.9, 124.9, 81.9, 74.2, 70.4, 66.0, 34.4, 28.0, 25.1; HRMS (ESI) calcd for [C$_{24}$H$_{28}$ClN$_3$O$_5$Na]$^+$ requires [M + Na]$^+$ 496.1615, found 496.1625

tert-Butyl (5-(2-(benzyloxy)ethyl)-5-(4-chlorophenyl)-3-methyl-2,4-dioxoimidazolidin-1-yl)carbamate (7v); (4-(benzyloxy)-1-methoxybut-1-en-1-yloxy)trimethylsilane (142 mg, 0.47 mmol,) was added dropwise to a mixture of tert-butyl (E)-2-((4-chlorophenyl)(methyl)carbamoyl)diazene-1-carboxylate 5h (152 mg, 0.47 mmol) and AgOTf (12.8 mg, 10 mol %) in THF (5.0 mL, 0.1 M) at -78 °C. The reaction was warmed to RT after 10 minutes and stirred at RT for 1.5 h. After TLC showed consumption of tert-butyl (E)-2-((4-chlorophenyl)(methyl)carbamoyl)diazene-1-carboxylate 5h, the reaction was cooled to -78 °C and KHMDS (1 M in THF, 3 equiv) was added dropwise. After 10 minutes the reaction was warmed to -20 °C and stirred at -20 °C for 1.5 h. The reaction was quenched with sat. aq. NH$_4$Cl (10 mL), and the aqueous layer was extracted with EtOAc (3 × 10 mL). The combined organics were washed with brine (1 × 10 mL), dried over MgSO$_4$ and concentrated under reduced pressure to give a crude residue. Purification by flash silica chromatography (15% EtOAC + Hexane) afforded the title compound (183 mg, 76%) as a colorless oil.

$\nu_{\text{max}}$/cm$^{-1}$(neat): 3310, 2979, 2932, 1790, 1714, 1453, 1156, 1094, 731.

$^1$H NMR (400 MHz, CDCl$_3$) δ 7.63 (br s, 2H), 7.32 (q, $J = 5.8, 5.2$ Hz, 7H), 6.84 (br s, 1H), 4.52 – 4.33 (m, 2H), 3.64–3.35 (m, 2H), 2.96 (br s, 3H), 2.53 (br s, 2H), 1.41 (s, 9H); $^{13}$C NMR (101 MHz, CDCl$_3$) δ 172.2, 156.3, 154.8, 136.6, 134.8, 128.8, 128.7, 128.6, 128.3,
128.1, 81.9, 74.3, 70.5, 66.0, 34.4, 28.1, 25.0; HRMS (ESI) calcd for [C_{24}H_{28}Cl_{3}N_{3}O_{5}Na]^{+} requires [M + Na]^{+} 496.1615, found 496.1623

**tert-Butyl (5-(2-(benzyloxy)ethyl)-3-methyl-2,4-dioxo-5-(3-(trifluoromethyl)phenyl)imidazolidin-1-yl)carbamate (7w);** 4-(benzyloxy)-1-methoxybut-1-en-1-yl)oxy)trimethyl silane (126 mg, 0.45 mmol) was added dropwise to a mixture of tert-butyl (E)-2-(methyl(3-(trifluoromethyl)phenyl)carbamoyl)diazene-1-carboxylate 5e (150 mg, 0.45 mmol) and AgOTf (11.0 mg, 10 mol %) in THF (4.5 mL, 0.1 M) at -78 °C. The reaction was warmed to RT after 10 minutes and stirred at RT for 2 h. After TLC showed consumption of tert-butyl (E)-2-(methyl(3-(trifluoromethyl)phenyl)carbamoyl)diazene-1-carboxylate 5e, the reaction was cooled to -78 °C and KHMDS (1 M in THF, 3 equiv) was added dropwise. After 10 minutes the reaction was warmed to -20 °C and stirred at -20 °C for 1.5 h. The reaction was quenched with sat. aq. NH_{4}Cl (10 mL), and the aqueous layer was extracted with EtOAc (3 × 10 mL). The combined organics were washed with brine (1 × 10 mL), dried over MgSO_{4} and concentrated under reduced pressure to give a crude residue. Purification by flash silica chromatography (15% EtOAC + Hexane) afforded the title compound (160 mg, 69%) as a colorless oil.

**ν_{max}/cm^{-1}(neat):** 3314, 2979, 2869, 1792, 1716, 1328, 1159, 1124.

**^{1}H NMR** (400 MHz, CDCl_{3}) δ 8.00 (d, J = 61.1 Hz, 2H), 7.58 (d, J = 7.6 Hz, 1H), 7.48 (t, J = 7.9 Hz, 1H), 7.34 (dt, J = 14.6, 7.2 Hz, 5H), 6.91 (s, 1H), 4.52 - 4.36 (m, 2H), 3.61 – 3.41 (m, 2H), 2.96 (s, 3H), 2.57 (br s, 2H), 1.41 (s, 9H); **^{13}C NMR** (101MHz, CDCl_{3}) δ 171.9, 156.2, 154.8, 137.6, 136.5, 131.1 (q, J = 32.5 Hz), 130.6, 130.2, 129.2, 128.7, 128.6, 128.3, 125.5,
124.03 (d, J = 272.6 Hz) 123.6, 82.0, 74.3, 70.6, 66.0, 34.9, 28.0, 25.1; HRMS (ESI) calcd for [C_{25}H_{28}F_{3}N_{3}O_{5}Na]⁺ requires [M + Na]⁺ 530.1879, found 530.1868

tert-Butyl (5-(2-(benzyloxy)ethyl)-5-(4-cyanophenyl)-3-methyl-2,4-dioxoimidazolidin-1-yl)carbamate (7x); (4-(benzyloxy)-1-methoxybut-1-en-1-yl)oxy)trimethylsilane (89 mg, 0.31 mmol,) was added dropwise to a mixture of (E)-tert-butyl 2-((4-cyanophenyl)(methyl)carbamoyl)diazene-carboxylate 5c (92 mg, 0.31 mmol) and AgOTf (8.05 mg, 10 mol %) in THF (3.1 mL, 0.1 M) at -78 °C. The reaction was warmed to RT after 10 minutes and stirred at RT for 2 h. After TLC showed consumption of (E)-tert-butyl 2-((4-cyanophenyl)(methyl)carbamoyl)diazene-carboxylate 5c, the reaction was cooled to -78 °C and KHMDS (1 M in THF, 3 equiv) was added dropwise. After 10 minutes the reaction was warmed to -20 °C and stirred at -20 °C for 1.5 h. The reaction was quenched with sat. aq. NH₄Cl (10 mL), and the aqueous layer was extracted with EtOAc (3 × 10 mL). The combined organics were washed with brine (1 × 10 mL), dried over MgSO₄ and concentrated under reduced pressure to give a crude residue. Purification by flash silica chromatography (15% EtOAC + Hexane) afforded the title compound (120 mg, 81%) as a colorless oil.

V_{max} /cm⁻¹(neat): 3309, 2978, 2932, 2230, 1791, 175, 1453, 1158, 733.

¹H NMR (400 MHz, CDCl₃) δ 7.90 (d, J = 4.4 Hz, 2H), 7.65 (d, J = 8.8 Hz, 2H), 7.39 – 7.27 (m, 5H), 6.90 (s, 1H), 4.53 – 4.31 (m, 2H), 3.69 – 3.31 (m, 2H), 2.95 (s, 3H), 2.54 (s, 2H), 1.42 (s, 9H); ¹³C NMR (101MHz, CDCl₃) δ ¹³C NMR (101 MHz, CDCl₃) δ 171.5, 156.3, 154.9, 141.5, 136.3, 132.4, 128.8, 128.7, 128.4, 127.6, 118.4, 112.6, 82.1, 74.4, 70.8, 65.9, 34.6, 28.1, 25.2; HRMS (ESI) calcd for [C_{25}H_{28}N_{4}O_{5}Na]⁺ requires [M + Na]⁺ 487.1957, found 487.1967

1.16 General procedure 8: benzyl deprotection
tert-Butyl (5-(3-chlorophenyl)-5-(2-hydroxyethyl)-3-methyl-2,4-dioxoimidazolidin-1-yl)carbamate (7y); To a solution of 7u (130 g, 0.27 mol) in .2M MeOH was added 10% Pd(OH)$_2$/C and the suspension was hydrogenated at atmospheric pressure and ambient temperature for 48 h. Filtration of the catalyst and concentration in vacuo afforded of the desired alcohol 7y, A sample was purified by flash chromatography (hexanes/AcOEt 1:1) to afford pure alcohol 7y as a clear colorless oil (70 mg 66%)

$\nu_{\text{max}}$/cm$^{-1}$(neat): 3475, 3298, 2979, 2934, 1787, 1706, 1156

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.56 – 7.39 (m, 2H), 7.39 – 7.28 (m, 3H), 6.94 (s, 1H), 3.93 – 3.79 (m, 1H), 3.75 – 3.53 (m, 1H), 3.08 (s, 4H), 2.52–2.47 (m, 2H), 1.42 (s, 9H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 172.2, 156.2, 155.3, 134.9, 130.1, 129.0, 126.8, 124.8, 82.7, 70.5, 58.4, 35.1, 28.0, 25.3 ; HRMS (ESI) calcd for [C$_{17}$H$_{22}$ClN$_3$O$_5$Na] requires [M + Na]$^+$ 406.1146, found 406.1159.

1.17 General Procedure 8: Boc-group deprotection:

Trifluoroacetic acid (20% by volume) was added dropwise to a solution of 7 in DCM (0.1 M) at 0 °C. The reaction was the stirred at RT for 4 h and concentrated under reduced pressure to give a crude residue. Reaction mixture was diluted in 3 ml DCM and neutralized with Et$_3$N and again concentrated under reduced pressure. Purification by flash silica chromatography.
4-(3-Amino-4-benzyl-1-methyl-2,5-dioxoimidazolidin-4-yl)benzonitrile \( (8a) \);

Trifluoroacetic acid (0.42 mL, 20% by volume) was added dropwise to a solution of tert-butyl (5-benzyl-5-(4-cyanophenyl)-3-methyl-2,4-dioxoimidazolidin-1-yl)carbamate \( 7i \) (86 mg, 0.20 mmol, 1 equiv) in DCM (2.1 mL, 0.1 M) at 0 \(^\circ\)C. The reaction was stirred at RT for 4 h and concentrated under reduced pressure to give a crude residue. Reaction mixture was diluted in 3 ml DCM and neutralized with Et\(_3\)N and again concentrated under reduced pressure. Purification by flash silica chromatography (30% EtOAC + Hexane) afforded the \textit{title compound} (60 mg, 92%) as colourless needles.

\textbf{MP:} 188-190 \(^\circ\)C

\textbf{\( V_{\text{max}} /\text{cm}^{-1} \)(neat):} 3339, 3270, 2925, 1774, 1710, 1608, 1490, 1454, 1058, 757

\( ^1\text{H NMR} \) (400 MHz; CDCl\(_3\)) \( \delta \) 7.73 (d, \( J = 8.7 \) Hz, 2H), 7.63 (d, \( J = 8.8 \) Hz, 2H), 7.31 – 7.26 (m, 3H), 7.17 (dd, \( J = 7.2 \), 2.3 Hz, 2H), 3.95 (s, 2H), 3.66 (d, \( J = 13.6 \) Hz, 1H), 3.49 (d, \( J = 13.5 \) Hz, 1H), 2.77 (s, 3H); \( ^{13}\text{C NMR} \) (101 MHz, CDCl\(_3\)) \( \delta \) 171.7, 157.0, 141.9, 141.9, 132.8, 132.75, 129.4, 128.9, 128.1, 127.3, 118.2, 112.8, 72.8, 40.3, 24.9; \textbf{HRMS} (ESI) calcd for [C\(_{18}\)H\(_{16}\)N\(_4\)O\(_2\)Na]\(^+\) requires [M + Na]\(^+\) 343.1171, found 343.1177

1-Amino-5-benzyl-5-(4-chlorophenyl)-3-methylimidazolidine-2,4-dione \( (8b) \);

Trifluoroacetic acid (0.25mL, 20% by volume) was added dropwise to a solution of tert-butyl (5-benzyl-5-(4-chlorophenyl)-3-methyl-2,4-dioxoimidazolidin-1-yl)carbamate \( 7j \) (54 mg, 0.12 mmol, 1 equiv) in DCM (1.25 mL, 0.1 M) at 0 \(^\circ\)C. The reaction was stirred at RT for 4 h
and concentrated under reduced pressure to give a crude residue. Reaction mixture was diluted in 3 ml DCM and neutralized with Et₃N and again concentrated under reduced pressure. Purification by flash silica chromatography (30% EtOAC + Hexane) afforded the title compound (32 mg, 78%) as colourless needles.

**MP:** 219-221 °C

**\( \nu_{\text{max}} / \text{cm}^{-1} \text{(neat):} \)** 3276, 3240, 2987, 1771, 1710, 1494, 1454, 1057, 769

\(^1\text{H NMR} \ (400 \text{ MHz, CDCl}_3) \ \delta \ 7.40 – 7.39 \ (m, 3H), 7.29 – 7.24 \ (m, 4H), 7.16 \ (dd, J = 7.3, 2.1 Hz, 2H), 3.92 \ (s, 2H), 3.64 \ (d, J = 13.5 Hz, 1H), 3.47 \ (d, J = 13.5 Hz, 1H), 2.75 \ (s, 3H); \ ^{13}\text{C NMR} \ (100 \text{ MHz, CDCl}_3) \ \delta \ 172.3, 157.0, 135.1, 134.9, 134.2, 129.4, 129.2, 128.8, 127.9, 127.7, 72.6, 39.9, 24.7; HRMS (ESI) calcd for [C\(_{17}\)H\(_{16}\)ClN\(_3\)O\(_2\)Na] requires [M + Na]\(^+\) 352.0829, found 352.0832.

1.18 General Procedure 9: Synthesis of bioactive compound analogues:

Carbaldehyde (1.0 equiv) was added to a solution of 1-amino- Hydantoins 6 (1 equiv) and MgSO\(_4\) (1.5 equiv) in DCM (0.1 M). The resulting suspension was stirred at RT for 6 h, after which the reaction was concentrated under reduced pressure to give a crude residue. Purification by flash silica chromatography.
(E)-4-(4-Benzyl-1-methyl-3-(((5-(4-nitrophenyl)furan-2-yl)methylene)amino)-2,5-
dioxoimidazolidin-4-yl)benzonitrile (9a); 5-(4-Nitrophenyl)furfural (38 mg, 0.17 mmol, 1
equiv) was added to a solution of 4-(3-amino-4-benzyl-1-methyl-2,5-dioxoimidazolidin-4-
yl)benzonitrile 8a (57 mg, 0.17 mmol, 1 equiv) and MgSO4 (32 mg 1.5 equiv) in DCM (1.7
mL, 0.1 M). The resulting suspension was stirred at RT for 6 h, after which the reaction was
concentrated under reduced pressure to give a crude residue. Purification by flash silica
chromatography (30% to 100% EtOAc/Petrol) afforded the title compound (60 mg, 65%) as
yellow needles.

**MP:** 95-97 °C

**ν<sub>max</sub> / cm<sup>-1</sup> (neat):** 2921, 1770, 1712, 1599, 1514, 1330, 851, 750

**<sup>1</sup>H NMR** (400 MHz; CDCl<sub>3</sub>) δ 9.36 (s, 1H), 8.26 (d, J = 9.0 Hz, 2H), 7.85 (d, J = 9.0 Hz, 2H),
7.73 (d, J = 3.0 Hz, 3H), 7.26 – 7.22 (m, 4H), 7.21 – 7.17 (m, 2H), 7.00 (d, J = 3.7 Hz, 1H),
6.96 (d, J = 3.7 Hz, 1H), 3.80 – 3.68 (m, 2H), 2.73 (s, 3H).

**<sup>13</sup>C NMR** (101 MHz; CDCl<sub>3</sub>)

<table>
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<th>δ (ppm)</th>
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<td>170.3, 153.6, 152.9, 151.1, 147.1, 141.8, 141.3, 135.4, 133.1, 132.6, 130.1, 128.6, 128.1, 127.6, 125.8, 124.6, 124.5, 118.3, 115.8, 112.7, 111.1, 110.7, 73.2, 41.5, 24.5</td>
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</tbody>
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**HRMS (ESI) calcd for [C<sub>29</sub>H<sub>21</sub>N<sub>5</sub>O<sub>5</sub>Na] requires [M + Na]<sup>+</sup> 542.1440, found
542.1438.**

![Structure of (E)-5-Benzyl-5-(4-chlorophenyl)-3-methyl-1-(((5-nitrofuran-2-yl)methylene)amino)
imidazolidine-2,4-dione (9b)](image)

**imidazolidine-2,4-dione (9b);** 5-nitrofuran-2-carbaldehyde (12 mg, 0.085 mmol, 1 equiv) was
added to a solution of 1-amino-5-benzyl-5-(4-chlorophenyl)-3-methylimidazolidine-2,4-dione
8b (30 mg, 0.09 mmol, 1 equiv) and MgSO4 (1.5 equiv) in DCM (0.9 mL, 0.1 M). The resulting
suspension was stirred at RT for 6 h, after which the reaction was concentrated under reduced
pressure to give a crude residue. Purification by flash silica chromatography (30% to 100% EtOAc/Petrol) afforded the *title compound* (20 mg, 48%) as a yellow semi-solid.

$V_{\text{max}}/\text{cm}^{-1}$ (neat): 2921, 1772, 1707, 1452, 1347, 1041, 812

$^1$H NMR (400 MHz; CDCl$_3$) $\delta$ 9.76 (s, 1H), 7.44 (d, $J = 8.8$ Hz, 1H), 7.34-7.33 (m, 4H), 7.27 (d, $J = 3.8$ Hz, 1H), 7.22 (dd, $J = 5.1$, 1.8 Hz, 3H), 7.11 (dd, $J = 7.4$, 2.0 Hz, 2H), 3.58 (d, $J = 13.5$ Hz, 1H), 3.42 (d, $J = 13.4$ Hz, 1H), 2.70 (s, 3H).$^{13}$C NMR (101 MHz; CDCl$_3$) $\delta$ 178.4, 172.3, 157.0, 151.0, 135.2, 134.9, 134.2, 129.4, 129.2, 128.8, 127.9, 127.7, 118.7, 111.7, 72.6, 39.9, 24.7; HRMS (ESI) calcd for [C$_{22}$H$_{17}$ClN$_4$O$_5$Na] requires [M + Na]$^+$ 475.0785, found 475.0765.
1.19 General Procedure 10: N-N bond cleavage:

![Chemical Reaction Diagram]

Aminohydantoin (1.0 equiv.) was dissolved in a 3:1 solution of AcOH and 1 M HCl, followed by addition of NaNO₂ dissolved in water. The reaction mixture was refluxed at 110 °C for 3 h, and then cooled to room temperature. The reaction mixture was concentrated under reduced pressure and the dry residue was exposed to sat. NaHCO₃ (4 mL). The aqueous phase was extracted with EtOAc (3 x 3 mL), the organic extracts were combined and concentrated under reduced pressure to give crude product. The crude material was purified by column chromatography (0% to 100% Et₂O in n-pentane) to afford desired product.

3,5-dimethyl-5-(p-tolyl)imidazolidine-2,4-dione (10a);

tert-butyl (3,5-dimethyl-2,4-dioxo-5-(p-tolyl)imidazolidin-1-yl)carbamate 7a (13.9 mg, 0.042 mmol, 1 equiv.) was dissolved in AcOH (1.5 mL), 1 M HCl (0.5 mL) was then added followed by sodium nitrite (9 mg, 0.13 mmol, 3 equiv.) dissolved in water (0.25 mL). The reaction mixture was refluxed at 110 °C for 3 h, and then cooled to room temperature. The reaction mixture was concentrated under reduced pressure and the dry residue was exposed to sat. NaHCO₃ (4 mL). The aqueous phase was extracted with EtOAc (3 x 3 mL), the organic extracts were combined and concentrated under reduced pressure to give crude product. The crude material was purified by column chromatography (0% to 100% Et₂O in n-pentane) to afford the title compound (6.1 mg, 67%) as a fine white powder.

$V_{max}/\text{cm}^{-1}$ (film): 3292, 2924, 1778, 1778, 1461; $^1$H NMR (400 MHz; CDCl₃) δ 7.38 (d, J = 8.2 Hz, 2H), 7.19 (d, J = 8.2 Hz, 2H), 6.00 (s, 1H), 3.02 (s, 3H), 2.34 (s, 3H), 1.81 (s, 3H); $^{13}$C NMR (101 MHz, CDCl₃) δ 175.4, 156.7, 138.5, 135.6, 129.6, 125.1, 63.6, 25.4, 24.9, 21.0; HRMS (ESI) calcd for [C$_{12}$H$_{15}$N$_2$O$_2$] requires [M + H]$^+$ 219.1128, found 219.1129.
3,5-dimethyl-5-phenylimidazolidine-2,4-dione (10b);

 tert-butyl (3,5-dimethyl-2,4-dioxo-5-phenylimidazolidin-1-yl)carbamate 7b (16.0 mg, 0.05 mmol, 1 equiv.) was dissolved in AcOH (1.5 mL), 1 M HCl (0.5 mL) was then added followed by sodium nitrite (10.4 mg, 0.15 mmol, 3 equiv.) dissolved in water (0.25 mL). The reaction mixture was refluxed at 110 °C for 3 h, and then cooled to room temperature. The reaction mixture was concentrated under reduced pressure and the dry residue was exposed to sat. NaHCO₃ (4 mL). The aqueous phase was extracted with EtOAc (3 x 3 mL), the organic extracts were combined and concentrated under reduced pressure to give crude product. The crude material was purified by column chromatography (0% to 100% Et₂O in n-pentane) to afford the title compound (8.5 mg, 83%) as a fine white powder.

$V_{\text{max}}$ /cm⁻¹(film): 3268, 1781, 1710, 1459, 1040; $^1$H NMR (400 MHz; CDCl₃) $\delta$ 7.51 (d, J = 7.5 Hz, 2H), 7.39 (t, J = 7.5 Hz, 2H), 7.36-7.31 (m, 1H), 6.20 (s, 1H), 3.03 (s, 3H); $^{13}$C NMR (101 MHz, CDCl₃) $\delta$ 175.3, 156.8, 138.6, 128.9, 128.5, 125.2, 63.8, 25.6, 24.9; HRMS (+APCI) calcd for [C₁₁H₁₂N₂O₂] requires [M + H]⁺ 205.0972, found 205.0979.
3,5-dimethyl-5-(3-(trifluoromethyl)phenyl)imidazolidine-2,4-dione (10c);

**tert-butyl** (3,5-dimethyl-2,4-dioxo-5-(3-(trifluoromethyl)phenyl)imidazolidin-1-yl)carbamate 7e (23.5 mg, 0.06 mmol, 1 equiv.) was dissolved in AcOH (1.5 mL), 1 M HCl (0.5 mL) was then added followed by sodium nitrite (10.4 mg, 0.15 mmol, 2.5 equiv) dissolved in water (0.25 mL). The reaction mixture was refluxed at 110 °C for 3 h, and then cooled to room temperature. The reaction mixture was concentrated under reduced pressure and the dry residue was exposed to sat. NaHCO₃ (4 mL). The aqueous phase was extracted with EtOAc (3 x 3 mL), the organic extracts were combined and concentrated under reduced pressure to give crude product. The crude material was purified by column chromatography (0% to 100% Et₂O in n-pentane) to afford the **title compound** (12.6 mg, 76%) as a fine white powder.

$V_{\text{max}/\text{cm}^{-1}(\text{film})}$: 3304, 1782, 1714, 1462, 1330, 1169, 1124; $^{1}H$ NMR (400 MHz; CDCl₃) δ 7.81-7.73 (m, 2H), 7.64 (d, $J = 7.6$ Hz, 1H), 7.56 (t, $J = 7.6$ Hz, 1H), 5.99 (s, 1H), 3.07 (s, 3H), 1.89 (s, 3H); $^{13}C$ NMR (101 MHz, CDCl₃) δ 174.8, 157.0, 140.0, 131.4 (q, $J_{C,F} = 32.8$ Hz), 129.6, 129.1, 125.5 (q, $J_{C,F} = 3.9$ Hz), 124.0 (q, $J_{C,F} = 272.5$ Hz), 122.2 (q, $J_{C,F} = 3.8$ Hz), 63.7, 26.3, 25.1; $^{19}F$ NMR (377 MHz, CDCl₃) δ -62.5 (s). HRMS (ESI) calcd for $[C_{12}H_{11}F_{3}N_{2}O_{2}Na]^{+}$ requires $[M + Na]^{+}$ 295.0665, found 295.0675.
$^1$H and $^{13}$C NMR Spectra
$^1$H NMR

N$^1$,N$^2$-dimethyl-N$^1$,N$^2$-diphenylhydrazine-1,2-dicarboxamide (S1a)
$^{13}$C NMR

N$^1,N^2$-dimethyl-N$^1,N^2$-diphenylhydrazone-1,2-dicarboxamide (S1a)
$^1$H NMR

$(E)$-$N^1,N^2$-dimethyl-$N^1,N^2$-diphenyldiazene-1,2-dicarboxamide (1a)
(E)-N₁,N₂-dimethyl-N¹,N²-diphenyldiazene-1,2-dicarboxamide (1a)
$^1$H NMR

N$_1$,N$_2$-dimethyl-N$_1$,N$_2$-di-p-tolylhydrazine-1,2-dicarboxamide (S1b)
$^{13}$C NMR

$N^{1},N^{2}\text{-dimethyl-}N^{1},N^{2}\text{-di-p-tolylhydrazine-1,2-dicarboxamide (S1b)}$
$^{1}$H NMR

N$^{1}$,N$^{2}$-dimethyl-N$^{1}$,N$^{2}$-di-p-tolylidiazene-1,2-dicarboxamide (1b)
N¹,N²-Dimethyl-N¹,N²-di-p-tolyldiazene-1,2-dicarboxamide (1b)
\(^{1}\text{H NMR}\)

\[ \text{N}^1,\text{N}^2\text{-bis(4-cyanophenyl)-N}^1,\text{N}^2\text{-dimethylhydrazine-1,2-dicarboxamide (S1c)} \]
$^{13}$C NMR

N1,N2-bis(4-cyanophenyl)-N1,N2-dimethylhydrazine-1,2-dicarboxamide (S1c)
\(^1\text{H NMR}\)

\((E)\)-N\(^1\),N\(^2\)-bis(4-cyanophenyl)-N\(^1\),N\(^2\)-dimethylidiazene-1,2-dicarboxamide (1c)
$^{13}$C NMR

$\text{(E)}$-$\text{N}^1,\text{N}^2$-$\text{bis(4-cyanophenyl)}$-$\text{N}^1,\text{N}^2$-$\text{dimethylene-1,2-dicarboxamide}$ (1c)
$^{1}H$ NMR

$N^{1},N^{2}$-bis(4-fluorophenyl)-$N^{1},N^{2}$-dimethylhydrazine-1,2-dicarboxamide (S1d)
$^{13}$C NMR

$N^{1},N^{2}$-bis(4-fluorophenyl)-$N^{1},N^{2}$-dimethylhydrazine-1,2-dicarboxamide (S1d)
$^1$H NMR

(E)-N$^1$,N$^2$-bis(4-fluorophenyl)-N$^1$,N$^2$-dimethyldiazene-1,2-dicarboxamide (1d).
$^{13}$C NMR

(E)-N$_1^1$N$_2^2$-bis(4-fluorophenyl)-N$_1^1$N$_2^2$-dimethylidiazene-1,2-dicarboxamide (1d).
$^1$H NMR

N$^1$,N$^2$-bis(3-chlorophenyl)-N$^1$,N$^2$-dimethylhydrazine-1,2-dicarboxamide (S1e)
$^{13}$C NMR

N$^{1,2}$-bis(3-chlorophenyl)-N$^{1,2}$-dimethylhydrazine-1,2-dicarboxamide (S1e)
$\text{H NMR}$

$(E)-N^1,N^2\text{-bis(3-chlorophenyl)}-N^1,N^2\text{-dimethyldiazene-1,2-dicarboxamide (1e)}$
$^{13}$C NMR

$\text{(E)-N}^1,\text{N}^2$-bis(3-chlorophenyl)$-\text{N}^1,\text{N}^2$-dimethyl diazene-1,2-dicarboxamide (1e)
$^1$H NMR

N$^1$,N$^2$-dimethyl-N$^1$,N$^2$-bis(3-(trifluoromethyl)phenyl)hydrazine-1,2-dicarboxamide (S1f)
$^{13}$C NMR

$N^1,N^2$-dimethyl-$N^1,N^2$-bis(3-(trifluoromethyl)phenyl)hydrazine-1,2-dicarboxamide (S1f)
$^1$H NMR

\[(E)-N_1^1,N_2^2\text{-dimethyl-}N_1^1,N_2^2\text{-bis(3-(trifluoromethyl)phenyl)diazene-1,2-dicarboxamide} \]

(1f).
\( ^{13}\text{C} \text{NMR} \)

\( (E)-\text{N}^1,\text{N}^2-\text{dimethyl-}\text{N}^1,\text{N}^2-\text{bis(3-(trifluoromethyl)phenyl)diazene-1,2-dicarboxamide} \)

(1f)
$^1$H NMR

$N^1,N^2$-dimethyl-$N^1,N^2$-di(pyridin-2-yl)hydrazine-1,2-dicarboxamide (S1g)
$^{13}$C NMR

N$^{1},N^{2}$-dimethyl-N$^{1},N^{2}$-di(pyridin-2-yl)hydrazine-1,2-dicarboxamide (S1g)
(E)-N¹,N²-dimethyl-N¹,N²-di(pyridin-2-yl)diazene-1,2-dicarboxamide (1g).
$^{13}$C NMR

$^{(E)}$-N$^{1}$,N$^{2}$-dimethyl-N$^{1}$,N$^{2}$-di(pyridin-2-yl)diazene-1,2-dicarboxamide (1g).
\(^1H\) NMR

(1-Methoxyprop-1-en-1-yl)oxytrimethylsilane (2a)
\( ^{13}\text{C} \text{NMR} \)

\[
\text{OMe} \quad \text{OTMS}
\]

(1-Methoxyprop-1-en-1-yl)oxy)trimethylsilane (2a)
1H NMR

(1-Methoxy-3-phenylprop-1-en-1-yl)oxy)trimethylsilane (2b)
$^{13}$C NMR

(1-Methoxy-3-phenylprop-1-en-1-yl)oxy)trimethylsilane (2b)
1H NMR

(1-Methoxypent-1-en-1-yl)oxy)trimethylsilane (2c)
13C NMR

\[(E)-((1\text{-methoxypent-1-en-1-yl})\text{oxy})\text{trimethylsilane (2c)}\]
Methyl 4-(benzyloxy)butanoate S2d
$^{13}$C NMR

Methyl 4-(benzyloxy)butanoate (S2d)
$^1$H NMR

$\text{Ph-}O\text{--}\text{O-}\text{Me}$

$\text{OTMS}$

$((4\text{-}(\text{Benzyloxy})\text{-}1\text{-methoxybut}-1\text{-en}-1\text{-yl}oxy)\text{trimethylsilane (2d)}}$
$^{13}$C NMR

$\text{Ph} - \text{O} - \text{C} - \text{O}\text{Me}$

$\text{OTMS}$

$\text{((4-(Benzyloxy)-1-methoxybut-1-en-1-yl)oxy)trimethylsilane (2d)}}$
$^1$H NMR

methyl N-(methyl(phenyl)carbamoyl)-N-(3-methyl-3-phenylureido)alaninate (3)
$^{13}$C NMR

methyl N-(methyl(phenyl)carbamoyl)-N-(3-methyl-3-phenylureido)alaninate (3)
$^1$H NMR

3-(3,5-dimethyl-2,4-dioxo-5-phenylimidazolidin-1-yl)-1-methyl-1-phenylurea (4a)
$^{13}$C NMR

3-(3,5-dimethyl-2,4-dioxo-5-phenylimidazolidin-1-yl)-1-methyl-1-phenylurea (4a)
COSY

3-(3,5-dimethyl-2,4-dioxo-5-phenylimidazolidin-1-yl)-1-methyl-1-phenylurea (4a)
3-(3,5-dimethyl-2,4-dioxo-5-phenylimidazolidin-1-yl)-1-methyl-1-phenylurea (4a)
3-(3,5-dimethyl-2,4-dioxo-5-phenylimidazolidin-1-yl)-1-methyl-1-phenylurea (4a)
3-(3,5-Dimethyl-2,4-dioxo-5-(p-tolyl)imidazolidin-1-yl)-1-methyl-1-(p-tolyl)urea (4b)
$^{13}$C NMR

3-(3,5-Dimethyl-2,4-dioxo-5-(p-tolyl)imidazolidin-1-yl)-1-methyl-1-(p-tolyl)urea (4b)
\[ 1\text{H NMR} \]

\[ \text{1-(4-Cyanophenyl)-3-(5-(4-cyanophenyl)-3,5-dimethyl-2,4-dioxoimidazolidin-1-yl)-1-methylurea (4c)} \]
13C NMR

1-(4-Cyanophenyl)-3-(5-(4-cyanophenyl)-3,5-dimethyl-2,4-dioxoimidazolidin-1-yl)-1-methylurea (4c)
$^1$H NMR

1-(4-Fluorophenyl)-3-(5-(4-fluorophenyl)-3,5-dimethyl-2,4-dioxoimidazolidin-1-yl)-1-methylurea (4d)
175

$^{13}$C NMR

1-(4-Fluorophenyl)-3-(5-(4-fluorophenyl)-3,5-dimethyl-2,4-dioxoimidazolidin-1-yl)-1-
methylurea (4d)
$^{1}H$ NMR

1-(3-Chlorophenyl)-3-(5-(3-chlorophenyl)-3,5-dimethyl-2,4-dioxoimidazolidin-1-yl)-1-methylurea (4e)
$^{13}$C NMR

1-(3-Chlorophenyl)-3-(5-(3-chlorophenyl)-3,5-dimethyl-2,4-dioxoimidazolidin-1-yl)-1-
methylurea (4e)
$^1$H NMR

3-(3,5-Dimethyl-2,4-dioxo-5-(3-(trifluoromethyl)phenyl)imidazolidin-1-yl)-1-methyl-1-(3-(trifluoromethyl)phenyl)urea (4f)
$^{13}$C NMR

3-(3,5-Dimethyl-2,4-dioxo-5-(3-(trifluoromethyl)phenyl)imidazolidin-1-yl)-1-methyl-1-(3-(trifluoromethyl)phenyl)urea (4f)
$^1$H NMR

3-(3,5-Dimethyl-2,4-dioxo-5-(pyridin-2-yl)imidazolidin-1-yl)-1-methyl-1-(pyridin-2-yl)urea (4g)
$^{13}$C NMR

3-(3,5-Dimethyl-2,4-dioxo-5-(pyridin-2-yl)imidazolidin-1-yl)-1-methyl-1-(pyridin-2-yl)urea (4g)
$^1$H NMR

3-(5-Benzyl-5-(3-chlorophenyl)-3-methyl-2,4-dioxoimidazolidin-1-yl)-1-(3-chlorophenyl)-1-methylurea (4h)
$^{13}$C NMR

3-(5-Benzyl-5-(3-chlorophenyl)-3-methyl-2,4-dioxoimidazolidin-1-yl)-1-(3-chlorophenyl)-1-methylurea (4h)
$^1$H NMR

3-(5-Benzyl-3-methyl-2,4-dioxo-5-(3-(trifluoromethyl)phenyl)imidazolidin-1-yl)-1-methyl-1-(3-(trifluoromethyl)phenyl)urea (4i)
$^{13}$C NMR

3-(5-Benzyl-3-methyl-2,4-dioxo-5-(3-(trifluoromethyl)phenyl)imidazolidin-1-yl)-1-methyl-1-(3-(trifluoromethyl)phenyl)urea (4i)
$^1$H NMR

3-(5-Benzyl-3-methyl-2,4-dioxo-5-(pyridin-2-yl)imidazolidin-1-yl)-1-methyl-1-(pyridin-2-yl)urea (4j)
3-(5-Benzyl-3-methyl-2,4-dioxo-5-(pyridin-2-yl)imidazolidin-1-yl)-1-methyl-1-(pyridin-2-yl)urea (4j)
$^{1} \text{H NMR}$

tert-Butyl 2-(methyl(p-tolyl)carbamoyl)hydrazine-1-carboxylate (S5a)
$^{13}$C NMR

tert-Butyl 2-(methyl(p-tolyl)carbamoyl)hydrazine-1-carboxylate (S5a)

![13C NMR spectrum of tert-Butyl 2-(methyl(p-tolyl)carbamoyl)hydrazine-1-carboxylate (S5a)]
$^1$H NMR

tert-Butyl (E)-2-(methyl(p-tolyl)carbamoyl)diazene-1-carboxylate (5a)
$^{13}$C NMR

tert-Butyl (E)-2-(methyl(p-tolyl)carbamoyl)diazene-1-carboxylate (5a)
$^1$H NMR

tert-Butyl 2-(methyl(phenyl)carbamoyl)hydrazine-1-carboxylate (S5b)
$^{13}$C NMR

tert-Butyl 2-(methyl(phenyl)carbamoyl)hydrazine-1-carboxylate (S5b)

![C NMR spectrum image]
$^1$H NMR

tert-Butyl (E)-2-(methyl(phenyl)carbamoyl)diazene-1-carboxylate (5b).
$^{13}\text{C NMR}$

$t\text{ert-Butyl (E)-2-(methyl(phenyl)carbamoyl)diazeno-1-carboxylate (5b).}$
$^1\text{H NMR}$

$t$ert-Butyl 2-((4-cyanophenyl)(methyl)carbamoyl)hydrazine-1-carboxylate (S5c)
$^{13}$C NMR

tert-Butyl 2-((4-cyanophenyl)(methyl)carbamoyl)hydrazine-1-carboxylate (S5c)
**$^1$H NMR**

tert-Butyl (E)-2-((4-cyanophenyl)(methyl)carbamoyl)diazene-1-carboxylate (5c).

![NMR spectrum](image)
\^{13}C\text{ NMR}

tert-Butyl (E)-2-((4-cyanophenyl)(methyl)carbamoyl)diazene-1-carboxylate (5c).
$^1$H NMR

tert-Butyl 2-((3-chlorophenyl)(methyl)carbamoyl)hydrazine-1-carboxylate (S5d)
\[ ^{13}\text{C NMR} \]

\[
\text{tert-Butyl 2-((3-chlorophenyl)(methyl)carbamoyl)hydrazine-1-carboxylate (S5d)}
\]
$^1$H NMR

$t$ert-Butyl (E)-2-((3-chlorophenyl)(methyl)carbamoyl)diazene-1-carboxylate (5d).
$^{13}$C NMR

tert-Butyl (E)-2-((3-chlorophenyl)(methyl)carbamoyl)diazene-1-carboxylate (5d).
$^1$H NMR

tert-Butyl 2-(methyl(3-(trifluoromethyl)phenyl)carbamoyl)hydrazine-1-carboxylate

(S5e)
**$^{13}$C NMR**

![Chemical Structure](attachment:image.png)

tert-Butyl 2-(methyl(3-(trifluoromethyl)phenyl)carbamoyl)hydrazine-1-carboxylate

(S5e)


^1H NMR

tert-Butyl (E)-2-(methyl(3-(trifluoromethyl)phenyl)carbamoyl)diazene-1-carboxylate

(5e).
$^{13}$C NMR

**tert-Butyl (E)-2-(methyl(3-(trifluoromethyl)phenyl)carbamoyl)diazene-1-carboxylate**

(5e).
\(^1\)H NMR

tert-Butyl 2-(methyl(pyridin-2-yl)carbamoyl)hydrazine-1-carboxylate (S5f)
\[ ^{13} \text{C NMR} \]

**tert-Butyl 2-(methyl(pyridin-2-yl)carbamoyl)hydrazine-1-carboxylate (S5f)**

![NMR Spectrum](image-url)
$^1$H NMR

tert-Butyl (E)-2-(methyl(pyridin-2-yl)carbamoyl)diazene-1-carboxylate (5f).
$^{13}$C NMR

tert-Butyl (E)-2-(methyl(pyridin-2-yl)carbamoyl)diazene-1-carboxylate (5f).
$^1$H NMR

tert-Butyl 2-((3-methoxyphenyl)(methyl)carbamoyl)hydrazine-1-carboxylate (S5g)
$^{13}$C NMR

tert-Butyl 2-((3-methoxyphenyl)(methyl)carbamoyl)hydrazine-1-carboxylate (S5g)
1H NMR

tert-Butyl (E)-2-((3-methoxyphenyl)(methyl)carbamoyl)diazene-1-carboxylate (5g).
13C NMR

tert-Butyl (E)-2-((3-methoxyphenyl)(methyl)carbamoyl)diazene-1-carboxylate (5g).
$^1$H NMR

tert-Butyl 2-((4-chlorophenyl)(methyl)carbamoyl)hydrazine-1-carboxylate (S5h)
$^{13}$C NMR

$\text{tert-Butyl } 2-((4\text{-chlorophenyl})(\text{methyl})\text{carbamoyl})\text{hydrazine-1-carboxylate (S5h)}$

[Chemical structure image]

[Graph representing NMR spectrum]

$\delta$ (ppm)
\[ ^1\text{H NMR} \]

**tert-Butyl (E)-2-((4-chlorophenyl)(methyl)carbamoyl)diazene-1-carboxylate (5h).**
tert-Butyl (E)-2-((4-chlorophenyl)(methyl)carbamoyl)diazene-1-carboxylate (5h).
$^1$H NMR

Methyl(naphthalen-1-yl)carbamic chloride SS$i$
Methyl(naphthalen-1-yl)carbamic chloride (SS5i)
$^1$H NMR

tert-Butyl 2-(ethyl(naphthalen-1-yl)carbamoyl)hydrazine-1-carboxylate (S5i)
tert-Butyl 2-(ethyl(naphthalen-1-yl)carbamoyl)hydrazine-1-carboxylate (S5i)
$^{1}$H NMR

*tert*-Butyl (E)-2-(ethyl(naphthalen-1-yl)carbamoyl)diazene-1-carboxylate (5i).
tert-Butyl (E)-2-(ethyl(naphthalen-1-yl)carbamoyl)diazene-1-carboxylate (5i).
$^1$H NMR

(2-Chlorophenyl)(methyl)carbamic chloride (SS5j)
$^{13}\text{C NMR}$

(2-Chlorophenyl)(methyl)carbamic chloride (SS5j)
$^1$H NMR

tert-Butyl 2-((2-chlorophenyl)(methyl)carbamoyl)hydrazine-1-carboxylate (S5j)
$^{13}$C NMR

tert-Butyl 2-((2-chlorophenyl)(methyl)carbamoyl)hydrazine-1-carboxylate (S5j)


$^1$H NMR

tert-Butyl (E)-2-((2-chlorophenyl)(methyl)carbamoyl)diazene-1-carboxylate (5j).
$^{13}$C NMR

tert-Butyl (E)-2-((2-chlorophenyl)(methyl)carbamoyl)diazene-1-carboxylate (5j).
$^1$H NMR

tert-Butyl 2-(1-methoxy-1-oxopropan-2-yl)-2-(methyl($\rho$-tolyl)carbamoyl)hydrazinecarboxylate (6)
$^{13}$C NMR

tert-Butyl 2-(1-methoxy-1-oxopropan-2-yl)-2-(methyl(\(\rho\)-tolyl)carbamoyl)hydrazinecarboxylate (6)
$^1$H NMR

tert-Butyl (3,5-dimethyl-2,4-dioxo-5-(p-tolyl)imidazolidin-1-yl)carbamate (7a)
$^{13}\text{C NMR}$

$\text{tert-Butyl (3,5-dimethyl-2,4-dioxo-5-(p-tolyl)imidazolidin-1-yl)carbamate (7a)}$
$^1$H NMR

tert-Butyl (3,5-dimethyl-2,4-dioxo-5-phenylimidazolidin-1-yl)carbamate (7b)
\[ ^{13}\text{C NMR} \]

**tert-Butyl (3,5-dimethyl-2,4-dioxo-5-phenylimidazolidin-1-yl)carbamate (7b)**

![NMR Spectrum Image]
$^{1}$H NMR

tert-Butyl (5-(4-cyanophenyl)-3,5-dimethyl-2,4-dioxoimidazolidin-1-yl)carbamate (7c)
$^{13}$C NMR

tert-Butyl (5-(4-cyanophenyl)-3,5-dimethyl-2,4-dioxoimidazolidin-1-yl)carbamate (7c)
$^1$H NMR

tert-Butyl (5-(3-chlorophenyl)-3,5-dimethyl-2,4-dioxoimidazolidin-1-yl)carbamate (7d)
\[ \text{\[^{13}\text{C}\] NMR} \]

\[ \text{tert-Butyl (5-(3-chlorophenyl)-3,5-dimethyl-2,4-dioxoimidazolidin-1-yl)carbamate (7d)} \]
1H NMR

tert-Butyl (3,5-dimethyl-2,4-dioxo-5-(3-(trifluoromethyl)phenyl)imidazolidin-1-yl)carbamate (7e)
$^{13}$C NMR

tert-Butyl (3,5-dimethyl-2,4-dioxo-5-(3-(trifluoromethyl)phenyl)imidazolidin-1-yl)carbamate (7e)
\(^1\)H NMR

tert-Butyl (3,5-dimethyl-2,4-dioxo-5-(pyridin-2-yl)imidazolidin-1-yl)carbamate (7f)
$\text{\textsuperscript{13}C NMR}$

$\text{\textit{tert}-Butyl (3,5-dimethyl-2,4-dioxo-5-(pyridin-2-yl)imidazolidin-1-yl)carbamate (7f)}$

![Chemical structure and NMR spectrum](image-url)
$^1$H NMR

tert-Butyl (5-benzyl-3-methyl-2,4-dioxo-5-$(p$-tolyl)imidazolidin-1-yl)carbamate (7g)
$^{13}$C NMR

*tert*-Butyl (5-benzyl-3-methyl-2,4-dioxo-5-($p$-tolyl)imidazolidin-1-yl)carbamate (7g)
\textbf{\textsuperscript{1}H NMR}

\begin{center}
\includegraphics[width=0.5\textwidth]{nmr_spectrum}
\end{center}

\textit{tert-Butyl (5-benzyl-5-(3-methoxyphenyl)-3-methyl-2,4-dioxoimidazolidin-1-yl)carbamate (7h)}
tert-Butyl (5-benzyl-5-(3-methoxyphenyl)-3-methyl-2,4-dioxoimidazolidin-1-yl)carbamate (7h)
**$^1$H NMR**

*tert*-Butyl (5-benzyl-5-(4-cyanophenyl)-3-methyl-2,4-dioxoimidazolidin-1-yl)carbamate

(7i)
\[ ^{13}\text{C NMR} \]

tert-Butyl (5-benzyl-5-(4-cyanophenyl)-3-methyl-2,4-dioxoimidazolidin-1-yl)carbamate

(7i)
\textbf{H NMR}

\textit{tert-Butyl (5-benzyl-5-(4-chlorophenyl)-3-methyl-2,4-dioxoimidazolidin-1-yl)carbamate (7j)}
$^{13}$C NMR

tert-Butyl (5-benzyl-5-(4-chlorophenyl)-3-methyl-2,4-dioxoimidazolidin-1-yl)carbamate

(7j)
**1H NMR**

*tert*-Butyl (5-benzyl-5-(3-chlorophenyl)-3-methyl-2,4-dioxoimidazolidin-1-yl)carbamate

(7k)
\textbf{13C NMR}

\begin{center}
\includegraphics[width=0.3\textwidth]{image.png}
\end{center}

\textit{tert-Butyl (5-benzyl-5-(3-chlorophenyl)-3-methyl-2,4-dioxoimidazolidin-1-yl)carbamate (7k)}
$^1$H NMR

tert-Butyl (5-benzyl-3-methyl-2,4-dioxo-5-(3-(trifluoromethyl)phenyl)imidazolidin-1-yl)carbamate (7l)
$^{13}$C NMR

tert-Butyl (5-benzyl-3-methyl-2,4-dioxo-5-(3-(trifluoromethyl)phenyl)imidazolidin-1-yl)carbamate (7l)
\[ ^1H \text{NMR} \]

**tert-Butyl (5-benzyl-3-methyl-2,4-dioxo-5-(3-(trifluoromethyl)phenyl)imidazolidin-1-yl) carbamate (7m)**
$^{13}$C NMR

**tert-Butyl (5-benzyl-3-methyl-2,4-dioxo-5-(3-(trifluoromethyl)phenyl)imidazolidin-1-yl) carbamate (7m)**

---

**Graphical Representation**

Aromatic region: 75-100 ppm
Aliphatic region: 0-20 ppm
Major peaks at 70-80 ppm
Minor peaks at 0-20 ppm

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**Chemical Shifts**

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**Additional Notes**

Single pulse decoupled gated NQE

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$^1$H NMR

tert-Butyl (5-benzyl-3-methyl-5-(naphthalen-1-yl)-2,4-dioxoimidazolidin-1-yl)carbamate

(7n)
\[ ^{13}\text{C NMR} \]

**tert-Butyl (5-benzyl-3-methyl-5-(naphthalen-1-yl)-2,4-dioxoimidazolidin-1-yl)carbamate**

(7n)
$^1$H NMR

**tert-Butyl (5-(3-methoxyphenyl)-3-methyl-2,4-dioxo-5-propylimidazolidin-1-yl)carbamate**

(7o)
tert-Butyl (5-(3-methoxyphenyl)-3-methyl-2,4-dioxo-5-propylimidazolidin-1-yl)carbamate (7o)
tert-Butyl (5-(2-chlorophenyl)-3-methyl-2,4-dioxo-5-propylimidazolidin-1-yl)carbamate (7p)
\textit{tert}-Butyl (5-(2-chlorophenyl)-3-methyl-2,4-dioxo-5-propylimidazolidin-1-yl)carbamate (7p)
**H NMR**

*tert-Butyl (5-(3-chlorophenyl)-3-methyl-2,4-dioxo-5-propylimidazolidin-1-yl)carbamate*  

(7q)
$^{13}$C NMR

**tert-Butyl (5-(3-chlorophenyl)-3-methyl-2,4-dioxo-5-propylimidazolidin-1-yl)carbamate**

(7q)
$^1$H NMR

tert-Butyl (3-methyl-2,4-dioxo-5-propyl-5-(3-(trifluoromethyl)phenyl)imidazolidin-1-yl)carbamate (7r)
$^{13}$C NMR

tert-Butyl (3-methyl-2,4-dioxo-5-propyl-5-(3-(trifluoromethyl)phenyl)imidazolidin-1-yl)carbamate (7r)
tert-Butyl (5-(4-cyanophenyl)-3-methyl-2,4-dioxo-5-propylimidazolidin-1-yl)carbamate

(7s)
$^{13}$C NMR

tert-Butyl (5-(4-cyanophenyl)-3-methyl-2,4-dioxo-5-propylimidazolidin-1-yl)carbamate

$(7s)$
$^1$H NMR

tert-Butyl (3-ethyl-5-(naphthalen-1-yl)-2,4-dioxo-5-propylimidazolidin-1-yl)carbamate (7t)
$^{13}$C NMR

tert-Butyl (3-ethyl-5-(naphthalen-1-yl)-2,4-dioxo-5-propylimidazolidin-1-yl)carbamate

(7t)
$\text{tert-Butyl (5-((2-(benzyloxy)ethyl)-5-(3-chlorophenyl)-3-methyl-2,4-dioxoimidazolidin-1-yl)carbamate (7u)}}$
$^1$CNMR

tert-Butyl (5-(2-(benzyloxy)ethyl)-5-(3-chlorophenyl)-3-methyl-2,4-dioxoimidazolidin-1-yl)carbamate (7u)
$^1$H NMR

tert-Butyl (5-(2-(benzyloxy)ethyl)-5-(4-chlorophenyl)-3-methyl-2,4-dioxoimidazolidin-1-yl)carbamate (7v)
**$^{13}$C NMR**

**tert-Butyl (5-(2-(benzoyloxy)ethyl)-5-(4-chlorophenyl)-3-methyl-2,4-dioxoimidazolidin-1-yl)carbamate (7v)**
$^1$H NMR

tert-Butyl (5-(2-(benzyloxy)ethyl)-3-methyl-2,4-dioxo-5-(3-(trifluoromethyl)phenyl)imidazolidin-1-yl)carbamate (7w)
$^{13}$C NMR

*tert*-Butyl (5-(2-(benzyloxy)ethyl)-3-methyl-2,4-dioxo-5-(3-(trifluoromethyl)phenyl)imidazolidin-1-yl)carbamate (7w)
"H NMR

tert-Butyl (5-(2-(benzyloxy)ethyl)-5-(4-cyanophenyl)-3-methyl-2,4-dioxoimidazolidin-1-yl)carbamate (7x)
tert-Butyl (5-(2-(benzyloxy)ethyl)-5-(4-cyanophenyl)-3-methyl-2,4-dioxoimidazolidin-1-yl)carbamate (7x)
\(^1\)H NMR

tert-Butyl (5-(3-chlorophenyl)-5-(2-hydroxyethyl)-3-methyl-2,4-dioxoimidazolidin-1-yl)carbamate (7y)

[Chemical Structure Image]
$^{13}$C NMR

$\text{tert-Butyl (5-(3-chlorophenyl)-5-(2-hydroxyethyl)-3-methyl-2,4-dioxoimidazolidin-1-yl)carbamate (7y)}$
$^1$H NMR

4-(3-Amino-4-benzyl-1-methyl-2,5-dioxoimidazolidin-4-yl)benzonitrile (8a)
4-(3-Amino-4-benzyl-1-methyl-2,5-dioxoimidazolidin-4-yl)benzonitrile (8a)
$^1$H NMR

1-Amino-5-benzyl-5-(4-chlorophenyl)-3-methylimidazolidine-2,4-dione (8b)
13C NMR

1-Amino-5-benzyl-5-(4-chlorophenyl)-3-methylimidazolidine-2,4-dione (8b)
(E)-4-(4-Benzyl-1-methyl-3-(((5-(4-nitrophenyl)furan-2-yl)methylene)amino)-2,5-dioxoimidazolidin-4-yl)benzonitrile (9a)
(E)-4-(4-Benzyl-1-methyl-3-(((5-(4-nitrophenyl)furan-2-yl)methylene)amino)-2,5-dioxoimidazolidin-4-yl)benzonitrile (9a)
\(^1\)H NMR

(E)-5-Benzyl-5-(4-chlorophenyl)-3-methyl-1-(((5-nitrofuran-2-yl)methylene)amino) imidazolidine-2,4-dione (9b)
\(^{13}\)C NMR

(E)-5-Benzyl-5-(4-chlorophenyl)-3-methyl-1-(((5-nitrofuran-2-yl)methylene)amino) imidazolidine-2,4-dione (9b)
$^1$H NMR of 10b

$^{13}$C NMR of 10b

HSQC of 10b