Supporting Information

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1. General methods

Unless otherwise specified, all reactions were conducted under an inert atmosphere and anhydrous conditions. All the solvents were purified according to the standard procedures. All chemicals which are commercially available were employed without further purification. Thin-layer chromatography (TLC) was performed on silica gel plates (60F-254) using UV-light (254 nm). Flash chromatography was conducted on silica gel (200-300 mesh). ¹H and ¹³C NMR spectra were recorded at ambient temperature in CDCl₃ or DMSO on a 400 MHz NMR spectrometer. Chemical shifts were reported in parts per million (ppm). The data are reported as follows: for ¹H NMR, chemical shift in ppm from tetramethylsilane with the solvent as internal standard (CDCl₃ δ 7.26 ppm), (DMSO δ 2.50 ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet or overlap of non-equivalent resonances), integration; for ¹³C NMR, chemical shift in ppm from tetramethylsilane with the solvent as internal indicator (CDCl₃ δ 77.1 ppm), (DMSO δ 39.5 ppm), multiplicity with respect to protons. All high-resolution mass spectra were obtained on a Q-TOF Micro LC/MS System ESI spectrometer to be given in m/z. Enantiomeric excesses values were determined with HPLC (chiral column; mobile phase n-hexane/i-PrOH). ACAs 2 are synthesized according to modified literature-reported procedures^[1]; cyclic ketones are either commercially available or prepared according to the literature^[2].

2. Representative procedures

Optimization of the reaction conditions

Table S1 Effect of catalysts.



^aReaction conditions: **1a** (0.1 mmol), **2a** (0.15 mmol), and **Cat.** (10 mol%) in a specified solvent (1 mL) at room temperature (r.t.) for 120 h.

^bIsolated yields.

^cdr values were determined by ¹H NMR.

^dee values were determined by HPLC analysis on a chiral stationary phase.

Table S2 Effect of solvents.

0 	+ Boc ^{∕N} ≷N	O N H Za	CPA-2 (10 mol% solvent, r.t		CI N N HN-Boc 3a
Entry ^a	Cat.	Solvent	Yield (%) ^b	dr ^c	<i>ee</i> (%) ^d
1	CPA2	toluene	85	> 20:1	95
2	CPA2	CH_2Cl_2	52	> 20:1	97
3	CPA2	CH ₃ CN	n.r.	-	-
4	CPA2	THF	n.r.	-	-
5	CPA2	PhCl	44	> 20:1	95
6	CPA2	PhBr	31	> 20:1	94

^aReaction conditions: **1a** (0.1 mmol), **2a** (0.15 mmol), and **CPA-2** (10 mol%) in solvent specified (1 mL) at r.t. for 120 h.

^bIsolated yields.

^cdr values were determined by ¹H NMR.

dee values were determined by HPLC analysis on a chiral stationary phase.

Table S3 Effect of additives.



^aReaction conditions: **1a** (0.1 mmol), **2a** (0.15 mmol), and **CPA-2** (10 mol%) in toluene (1 mL) at specific temperature. for 120 h.

^bIsolated yields.

^cdr values were determined by ¹H NMR.

dee values were determined by HPLC analysis on a chiral stationary phase.

Optimization of the reaction conditions

Table S4 Effect of catalysts.

0 U	+ Boc ^{_N} ≷N	D N H H	Cat. (10 mol%) toluene, r.t.		OH N OH N HN-Boc
1x		2d			3x
Entry ^a	Cat.	Solvent	Yield (%) ^b	dr ^c	<i>ee</i> (%) ^d
1	CPA1	toluene	82	> 20:1	71
2	CPA2	toluene	73	> 20:1	67
3	CPA3	toluene	n.r.	-	-
4	CPA4	toluene	68	> 20:1	19

^aReaction conditions: **1a** (0.1 mmol), **2a** (0.15 mmol), and **Cat.** (10 mol%) in toluene specified (1 mL) at r.t. for 120 h.

^bIsolated yields.

4

5

6

7

^cdr values were determined by ¹H NMR.

dee values were determined by HPLC analysis on a chiral stationary phase.

Table S5 Effect of solvents.

CPA1

CPA1

CPA1

CPA1



n.r.

63

67

76

-

> 20:1

> 20:1

> 20:1

-

83

80

90

THF

PhCl

PhBr

PhCF₃

^aReaction conditions: 1a (0.1 mmol), 2a (0.15 mmol), and CPA-1 (10 mol%) in solvent specified (1 mL) at r.t. for 120 h.
^bIsolated yields.
^cdr values were determined by ¹H NMR.
^dee values were determined by HPLC analysis on a chiral stationary phase.

Experimental procedures for the transformation of the products



To the solution of compound 3q (90.2 mg, 0.2 mmol) in CH₂Cl₂ (2 mL) was add boron trifluoride ether (50 µL, 0.4 mmol), the reaction mixture was stirred at room temperature for 2 h. After the completion of the reaction which was indicated by TLC, the reaction mixture was treated with H₂O and extracted with dichloromethane and washed with brine. The combined organic layers were dried with anhydrous Na₂SO₄ and the solvent was removed under reduced pressure. The residue was purified through preparative thin layer chromatography on silica gel (petroleum ether/ethyl acetate = 2:1) to afford pure product **5**.



To the solution of compound **3n** (70.6 mg, 0.2 mmol) in CH₃CN (2 mL) was add ethyl 2-bromoacetate (44 μ L, 0.4 mmol). Then, Cs₂CO₃ (130 mg, 0.4 mmol) was added to the reaction mixture, which was stirred at 50 °C for 2 h. After the completion of the reaction which was indicated by TLC, the reaction mixture was treated with H₂O and extracted with ethyl acetate and washed with brine. The combined organic layers were dried with anhydrous Na₂SO₄ and the solvent was removed under reduced pressure. The residue was purified through preparative thin layer chromatography on silica gel (petroleum ether/ethyl acetate = 3:1) to afford pure product **6**.



To the solution of compound **6** (82.2mg, 0.2 mmol) in CH₃CN (2 mL) was add Cs₂CO₃ (97.6 mg, 0.3 mmol), the reaction mixture was stirred at 80 °C for 6 h. After the completion of the reaction which was indicated by TLC, the reaction mixture was treated with H₂O and extracted with ethyl acetate and washed with brine. The combined organic layers were dried with anhydrous Na₂SO₄ and the solvent was removed under reduced pressure. The residue was purified through preparative thin layer chromatography on silica gel (petroleum ether/ethyl acetate = 1:2) to afford pure product **7**.



To the solution of compound **4b** (90.2 mg, 0.2 mmol) in DCM (1 mL) was add TFA (77 μ L, 1 mmol), the reaction mixture was stirred at room temperature for 2 h. After the completion of the reaction which was indicated by TLC, the reaction mixture was treated with saturated NaHCO₃ aqueous solution and extracted with dichloromethane and washed with brine. The combined organic layers were dried with anhydrous Na₂SO₄ and the solvent was removed under reduced pressure. The residue was purified through preparative thin layer chromatography on silica gel (petroleum ether/ethyl acetate = 4:1) to afford pure product **8**.



To the solution of compound **4b** (90.2 mg, 0.2 mmol) in MeOH (2 mL) was add sodium borohydride (11.4 mg, 0.3 mmol). the reaction mixture was stirred at room temperature for 5 h. After the completion of the reaction which was indicated by TLC, the reaction mixture was treated with H₂O and extracted with ethyl acetate and washed with brine. The combined organic layers were dried with anhydrous Na₂SO₄ and the solvent was removed under reduced pressure. The residue was purified through preparative thin layer chromatography on silica gel (petroleum ether/ethyl acetate = 4:1) to afford pure product **9**.

3. Characterization of products

tert-Butyl ((3aS,6aS)-3-(4-chlorophenyl)-3a-hydroxy-6a-methyl-2-oxohexahydro cyclopenta[d]imidazol-1(2H)-yl)carbamate (3a):

A white solid; 64.8 mg; isolated yield = 85%; m.p. 142.4 - 142.9 °C; dr > 20:1. $[\alpha]^{21.0}_{D} = +165.00$ (c 0.10, EA); HPLC (IG-3 column, *i*propanol/*n*-hexane = 10/90, flow rate 1.0 mL/min, $\lambda = 254$ nm), product: $t_1 = 5.72 \text{ min (minor)}, t_2 = 6.77 \text{ min (major)}, ee = 95\%; {}^{1}\text{H}$ NMR (400 MHz, DMSO) δ 9.01 – 8.60 (m, 1H), 7.55 (d, J = 8.8 Hz, N-Boc 2H), 7.41 (d, J = 8.8 Hz, 2H), 6.50 (s, 1H), 2.03 – 1.97 (m, 1H), 1.93 - 1.85 (m, 1H), 1.73 - 1.61 (m, 1H), 1.49 - 1.34 (m, 12H), 1.20 (s,

3H). ¹³C NMR (100 MHz, DMSO) δ 155.7, 154.3, 136.4, 129.0, 128.5, 126.4, 96.1, 79.6, 69.1, 37.0, 28.1, 20.8, 19.9. HRMS (ESI) m/z calcd for C₁₈H₂₄ClN₃O₄Na⁺ [M + $Na^+ = 404.1347$, found = 404.1343.

tert-Butyl ((3aS,6aS)-3a-hydroxy-6a-methyl-2-oxo-3-phenylhexahydrocyclopenta [d]imidazol-1(2H)-yl)carbamate (3b):



OH

Н

A white solid; 52.1 mg; isolated yield = 75%; m.p. 129.4 - 129.9 °C; dr > 20:1. $[\alpha]^{21.0}_{D} = -79.01$ (c 0.10, EA); HPLC (IH-3 column, *i*propanol/*n*-hexane = 10/90, flow rate 1.0 mL/min, λ = 254 nm), product: $t_1 = 6.55 \text{ min (major)}, t_2 = 14.59 \text{ min (minor)}, ee = 92\%$; ¹H NMR (400 MHz, DMSO) δ 8.95 – 8.56 (m, 1H), 7.56 – 7.44 (m, 2H), 7.41 - 7.31 (m, 2H), 7.24 - 7.16 (m, 1H), 6.41 (s, 1H), 2.09 - 1.98

(m, 1H), 1.91 – 1.83 (m, 1H), 1.72 – 1.57 (m, 1H), 1.50 – 1.40 (m, 12H), 1.22 (s, 3H). ¹³C NMR (100 MHz, DMSO) δ 156.2, 155.0, 137.7, 128.9, 126.1, 125.6, 96.4, 79.9, 69.4, 37.4, 37.4, 28.5, 21.2, 20.4. HRMS (ESI) m/z calcd for C₁₈H₂₅N₃O₄Na⁺ [M + Na]⁺ = 370.1737, found = 370.1737.

tert-Butyl ((3aS,6aS)-3-(4-fluorophenyl)-3a-hydroxy-6a-methyl-2-oxohexahydroc yclopenta[d]imidazol-1(2H)-yl)carbamate (3c):



A white solid; 51.8 mg; isolated yield = 71%; m.p. 121.4 - 121.9 °C; dr > 20:1. $[\alpha]^{21.0}$ = -90.00 (c 0.10, EA); HPLC (IG-3 column, *i*propanol/*n*-hexane = 10/90, flow rate 1.0 mL/min, λ = 254 nm), product: $t_1 = 5.71 \text{ min (minor)}, t_2 = 6.20 \text{ min (major)}, ee = 94\%$; ¹HNMR (400 MHz, DMSO) δ 9.05 – 8.48 (m, 1H), 7.59 – 7.38 (m, 2H), 7.31 - 7.09 (m, 2H), 6.42 (s, 1H), 2.11 - 1.93 (m, 1H), 1.88 -

1.76 (m, 1H), 1.69 – 1.55 (m, 1H), 1.54 – 1.35 (m, 12H), 1.22 (s, 3H). ¹³C NMR (100 MHz, DMSO) δ 161.4, 159.0 (*J* = 240 Hz), 156.2, 155.1, 133.8, 133.7, 128.5, 128.4, 115.8, 115.5 (*J* = 22 Hz), 96.3, 79.9, 69.5, 37.4, 37.4, 28.5, 21.2, 20.3. ¹⁹F NMR (376 MHz, DMSO) δ -117.10. HRMS (ESI) m/z calcd for $C_{18}H_{24}FN_{3}O_{4}Na^{+}[M + Na]^{+} = 388.1643$, found = 388.1641.

tert-Butyl ((3aS,6aS)-3-(4-bromophenyl)-3a-hydroxy-6a-methyl-2-oxohexahydro cyclopenta[d]imidazol-1(2H)-yl)carbamate (3d):



A white solid; 61.2 mg; isolated yield = 72%; m.p. 148.3 – 148.8 °C; dr > 20:1. $[\alpha]^{21.0}_{D}$ = +187.01 (*c* 0.10, EA); HPLC (IG-3 column, *i*-propanol/*n*-hexane = 10/90, flow rate 1.0 mL/min, λ = 254 nm), product: t₁ = 6.16 min (minor), t₂ = 7.77 min (major), *ee* = 93%; ¹H NMR (400 MHz, DMSO) δ 9.03 – 8.57 (m, 1H), 7.54 (d, *J* = 9.0 Hz, 2H), 7.50 (d, *J* = 9.0 Hz, 2H), 6.51 (s, 1H), 2.06 – 1.97 (m, 1H), 1.95 – 1.85 (m, 1H), 1.75 – 1.60 (m, 1H), 1.52 – 1.37 (m, 12H), 1.20 (s,

^H 3H). ¹³C NMR (100 MHz, DMSO) δ 156.1, 154.6, 137.2, 131.8, 127.0, 117.5, 96.5, 80.0, 69.5, 37.4, 37.6, 28.5, 21.2, 20.3. HRMS (ESI) m/z calcd for C₁₈H₂₄BrN₃O₄Na⁺ [M + Na]⁺ = 448.0842, found = 448.0841.

tert-Butyl ((3aS,6aS)-3a-hydroxy-3-(4-iodophenyl)-6a-methyl-2-oxohexahydrocy clopenta[d]imidazol-1(2H)-yl)carbamate (3e):

A white solid; 73.8 mg; isolated yield = 78%; m.p. 135.3 – 135.8 °C; dr > 20:1. $[\alpha]^{21.0}_{D}$ = +260.01 (*c* 0.10, EA); HPLC (IG-3 column, *i*-propanol/*n*-hexane = 10/90, flow rate 1.0 mL/min, λ = 254 nm), product: t₁ = 6.87 min (minor), t₂ = 9.26 min (major), *ee* = 95%; ¹H NMR (400 MHz, DMSO) δ 9.01 – 8.61 (m, 1H), 7.70 (d, *J* = 8.6 Hz, 2H), 7.38 (d, *J* = 8.6 Hz, 2H), 6.50 (s, 1H), 2.15 – 1.82 (m, 2H), 1.76 – 1.62 (m, 1H), 1.49 – 1.29 (m, 12H), 1.21 (s, 3H). ¹³C NMR (100 MHz, DMSO) δ 156.1, 154.6, 137.8, 137.6, 127.2, 96.4, 89.8, 80.0,

69.5, 37.4, 37.4, 28.5, 21.2, 20.3. HRMS (ESI) m/z calcd for $C_{18}H_{24}IN_3O_4Na^+$ [M + Na]⁺ = 496.0703, found = 496.0704.

tert-Butyl ((3aS,6aS)-3a-hydroxy-6a-methyl-2-oxo-3-(*p*-tolyl)hexahydrocyclopent <u>a[d]imidazol-1(2*H*)-yl)carbamate (3f)</u>:



A white solid; 55.6 mg; isolated yield = 77%; m.p. 131.1 - 131.6 °C; dr > 20:1. [α]^{21.0}_D = -51.01 (*c* 0.10, EA); HPLC (IG-3 column, *i*propanol/*n*-hexane = 10/90, flow rate 1.0 mL/min, λ = 254 nm), product: t₁ = 7.68 min (major), t₂ = 9.16 min (minor), *ee* = 94%; ¹H NMR (400 MHz, DMSO) δ 8.96 – 8.51 (m, 1H), 7.32 (d, *J* = 8.2 Hz, 2H), 7.15 (d, *J* = 8.2 Hz, 2H), 6.31 (s, 1H), 2.28 (s, 3H), 2.08 – 1.99 (m, 1H), 1.85 – 1.77 (m, 1H), 1.68 – 1.53 (m, 1H), 1.48 – 1.33 (m, 12H), 1.20 (s, 3H). ¹³C NMR (100 MHz, DMSO) δ 156.2, 155.2,

135.0, 134.9, 129.4, 126.5, 96.3, 79.8, 69.3, 37.5, 37.4, 28.5, 21.2, 21.0, 20.4. HRMS (ESI) m/z calcd for $C_{19}H_{27}N_3O_4Na^+$ [M + Na]⁺ = 384.1894, found = 384.1890.

tert-Butyl ((3aS,6aS)-3a-hydroxy-3-(4-methoxyphenyl)-6a-methyl-2-oxohexahyd rocyclopenta[*d*]imidazol-1(2*H*)-yl)carbamate (3g):



A colorless oil; 57.3 mg; isolated yield = 76%; dr > 20:1. $\left[\alpha\right]^{21.0}$ D = +129.01 (c 0.10, EA); HPLC (IG-3 column, *i*-propanol/*n*-hexane = 10/90, flow rate 1.0 mL/min, $\lambda = 254$ nm), product: t₁ = 12.95 min (minor), $t_2 = 13.78$ min (major), ee = 94%; ¹H NMR (400 MHz, DMSO) δ 9.06 – 8.46 (m, 1H), 7.27 (d, J = 8.8 Hz, 2H), 6.93 (d, J = 8.8 Hz, 2H), 6.25 (s, 1H), 3.75 (s, 3H), 2.07 – 1.97 (m, 1H), 1.82 – 1.73 (m, 1H), 1.62 – 1.50 (m, 1H), 1.49 – 1.33 (m, 12H), 1.20 (s, 3H). ¹³C NMR (100 MHz, DMSO) δ 157.8, 156.3, 155.4, 129.9, 129.0,

114.2, 96.2, 80.0, 69.3, 55.7, 40.5, 40.3, 40.1, 39.9, 39.7, 39.5, 39.2, 37.5, 37.3, 28.5, 21.2, 20.4. HRMS (ESI) m/z calcd for $C_{19}H_{27}N_3O_5Na^+$ [M + Na]⁺ = 400.1843, found = 400.1838.

tert-Butyl ((3aS,6aS)-3-([1,1'-biphenyl]-4-yl)-3a-hydroxy-6a-methyl-2-oxohexahy drocyclopenta[d]imidazol-1(2H)-yl)carbamate (3h):

A white solid; 55.0 mg; isolated yield = 65%; m.p. 134.6 - 135.2 °C; dr > 20:1. $[\alpha]^{21.0}_{D}$ = -49.00 (c 0.10, EA); HPLC (IG-3 column, *i*propanol/*n*-hexane = 10/90, flow rate 1.0 mL/min, λ = 254 nm), product: $t_1 = 6.63 \text{ min (major)}, t_2 = 9.10 \text{ min (minor)}, ee = 93\%$; ¹H NMR (400 MHz, DMSO) δ 9.27 – 8.50 (m, 1H), 7.74 – 7.65 (m, 4H), 7.63 - 7.58 (m, 2H), 7.52 - 7.43 (m, 2H), 7.39 - 7.33 (m, 1H), 6.50 (s, 1H), 2.19 - 1.83 (m, 2H), 1.78 - 1.59 (m, 1H), 1.56 - 1.35 (m, 12H), 1.23 (s, 3H). ¹³C NMR (100 MHz, DMSO) δ 156.2, 154.9, -Boc 140.1, 137.2, 137.1, 129.4, 127.7, 127.1, 126.9, 126.0, 96.5, 80.0,

69.5, 37.5, 37.4, 28.5, 21.3, 20.4. HRMS (ESI) m/z calcd for C₂₄H₂₉N₃O₄Na⁺ [M + $Na^+ = 446.2050$, found = 446.2046.

tert-Butyl ((3aS,6aS)-3-(2-chlorophenyl)-3a-hydroxy-6a-methyl-2-oxohexahydro cyclopenta[d]imidazol-1(2H)-yl)carbamate (3i):



OH

O

A white solid; 55.6 mg; isolated yield = 73%; m.p. 135.4 - 135.9 °C; dr > 20:1. $[\alpha]^{21.0}$ _D = +144.01 (*c* 0.10, EA); HPLC (IG-3 column, *i*propanol/*n*-hexane = 30/70, flow rate 1.0 mL/min, $\lambda = 254$ nm), product: $t_1 = 7.38 \text{ min (minor)}, t_2 = 10.60 \text{ min (major)}, ee = 98\%$; ¹H NMR (400 MHz, DMSO) δ 9.00 – 8.51 (m, 1H), 7.61 – 7.52 (m, 2H), 7.45 - 7.26 (m, 2H), 6.29 (s, 1H), 2.09 - 2.02 (m, 1H), 1.97 - 1.79

(m, 1H), 1.78 – 1.70 (m, 1H), 1.64 – 1.52 (m, 2H), 1.49 – 1.34 (m, 10H), 1.24 (s, 3H). ¹³C NMR (100 MHz, DMSO) δ 156.1, 154.2, 134.7, 134.0, 133.7, 130.3, 129.7, 127.7, 96.6, 79.7, 70.6, 38.3, 38.0, 28.5, 21.7, 20.0. HRMS (ESI) m/z calcd for $C_{18}H_{24}ClN_3O_4Na^+[M + Na]^+ = 404.1348$, found = 404.1349.

tert-Butyl ((3aS,6aS)-3-(3-chlorophenyl)-3a-hydroxy-6a-methyl-2-oxohexahydro cyclopenta[d]imidazol-1(2H)-yl)carbamate (3j):



A white solid; 61.7 mg; isolated yield = 81%; m.p. 145.1 – 145.6 °C; dr > 20:1. $[\alpha]^{21.0}{}_{\rm D}$ = -79.00 (*c* 0.10, EA); HPLC (IG-3 column, *i*propanol/*n*-hexane = 10/90, flow rate 1.0 mL/min, λ = 250 nm), product: t₁ = 8.77 min (minor), t₂ = 9.27 min (major), *ee* = 91%; ¹H NMR (400 MHz, DMSO) δ 9.07 – 8.64 (m, 1H), 7.66 (s, 1H), 7.54 (d, *J* = 8.1 Hz, 1H), 7.38 (t, *J* = 8.1 Hz, 1H), 7.22 (d, *J* = 7.9 Hz, 1H),

6.57 (s, 1H), 2.04 – 1.90 (m, 2H), 1.77 – 1.65 (m, 1H), 1.53 – 1.34 (m, 12H), 1.21 (s, 3H). 13 C NMR (100 MHz, DMSO) δ 156.1, 154.5, 139.4, 133.1, 130.5, 124.7, 124.1, 123.0, 96.6, 80.0, 69.6, 37.4, 37.3, 28.5, 21.3, 20.2. HRMS (ESI) m/z calcd for C₁₈H₂₄ClN₃O₄Na⁺ [M + Na]⁺ = 404.1348, found = 404.1346.

tert-Butyl ((3aS,6aS)-3-(3,5-dimethoxyphenyl)-3a-hydroxy-6a-methyl-2-oxohexa hydrocyclopenta[d]imidazol-1(2H)-yl)carbamate (3k):



A colorless oil; 70.8 mg; isolated yield = 87%; dr > 20:1. $[\alpha]^{21.0}_{D}$ = +123.01 (*c* 0.10, EA); HPLC (IG-3 column, *i*-propanol/*n*hexane = 10/90, flow rate 1.0 mL/min, λ = 254 nm), product: t₁ = 7.68 min (minor), t₂ = 10.35 min (major), *ee* = 98%; ¹H NMR (400 MHz, DMSO) δ 9.02 - 8.60 (m, 1H), 7.06 - 6.87 (m, 2H), 6.61 (s, 1H), 3.79 (s, 6H), 2.11 - 1.93 (m, 2H), 1.86 - 1.63 (m, 1H), 1.57 - 1.37 (m, 12H), 1.21 (s, 3H). ¹³C NMR (100 MHz,

DMSO) δ 156.5, 156.2, 154.7, 138.7, 102.2, 96.7, 96.1, 80.0, 69.6, 56.7, 37.6, 37.5, 28.5, 21.4, 20.2. HRMS (ESI) m/z calcd for C₂₀H₂₉N₃O₆Na⁺ [M + Na]⁺ = 430.1949, found = 430.1955.

tert-Butyl ((3aS,6aS)-3a-hydroxy-6a-methyl-3-(naphthalen-2-yl)-2-oxohexahydro cyclopenta[d]imidazol-1(2H)-yl)carbamate (3l):



A white solid; 50.0 mg; isolated yield = 63%; m.p. 133.3 – 133.8 °C; dr > 20:1. $[\alpha]^{21.0}_{D}$ = -84.00 (*c* 0.10, EA); HPLC (IG-3 column, *i*-propanol/*n*-hexane = 10/90, flow rate 1.0 mL/min, λ = 254 nm), product: t₁ = 5.36 min (major), t₂ = 6.25 min (minor), *ee* = 91%; ¹H NMR (400 MHz, DMSO) δ 9.03 – 8.57 (m, 1H), 8.00 (s, 1H), 7.95 – 7.83 (m, 3H), 7.78 – 7.63 (m, 1H), 7.57 – 7.37 (m, 2H), 6.55 (s, 1H), 2.12 – 2.03 (m, 1H), 1.98 – 1.89 (m, 1H), 1.80 – 1.58 (m, 1H),

$$\begin{split} 1.56-1.36\ (m,\,12H),\, 1.26\ (s,\,3H). \ ^{13}C\ NMR\ (100\ MHz,\, DMSO)\ \delta\ 156.2,\, 155.1,\, 135.5,\\ 133.5,\,\, 131.1,\,\, 128.3,\,\, 128.0,\,\, 127.9,\,\, 126.7,\,\, 125.9,\,\, 125.3,\,\, 123.1,\,\, 96.6,\,\, 79.9,\,\, 69.6,\,\, 37.6,\\ 37.5,\,\, 28.5,\,\, 21.3,\,\, 20.4. \ \ HRMS\ (ESI)\ m/z\ calcd\ for\ C_{22}H_{27}N_3O_4Na^+\ [M\ +\ Na]^+ =\\ 420.1894,\, found = 420.1896. \end{split}$$

<u>Methyl ((3aS,6aS)-3-(4-chlorophenyl)-3a-hydroxy-6a-methyl-2-oxohexahydrocy</u> <u>clopenta[*d*]imidazol-1(2*H*)-yl)carbamate (3m):</u>



A white solid; 44.1 mg; isolated yield = 65%; m.p. 140.3 – 140.8 °C; dr > 20:1. $[\alpha]^{21.0}_{D}$ = +91.00 (*c* 0.10, EA); HPLC (IG-3 column, *i*-propanol/*n*-hexane = 10/90, flow rate 1.0 mL/min, λ = 250 nm), product: t₁ = 11.94 min (minor), t₂ = 15.07 min (major), *ee* = 92%; ¹H NMR (400 MHz, DMSO) & 9.31 (s, 1H), 7.59 – 7.51 (m, 2H), 7.49 – 7.39 (m, 2H), 6.56 (s, 1H), 3.64 (s, 3H), 2.09 – 1.82 (m, 2H), 1.77 – 1.62 (m, 1H), 1.57 – 1.36 (m, 3H),

1.24 (s, 3H). ¹³C NMR (100 MHz, DMSO) δ 157.7, 154.7, 136.6, 129.6, 128.9, 126.9, 96.5, 69.6, 52.6, 37.4, 37.2, 21.2, 20.3. HRMS (ESI) m/z calcd for C₁₅H₁₈ClN₃O₄Na⁺ [M + Na]⁺ = 362.0878, found = 362.0873.

<u>Ethyl ((3aS,6aS)-3-(4-chlorophenyl)-3a-hydroxy-6a-methyl-2-oxohexahydrocycl</u> <u>openta[d]imidazol-1(2H)-yl)carbamate (3n):</u>

A white solid; 47.3 mg; isolated yield = 67%; m.p. 139.4 – 139.9 °C; dr > 20:1. $[\alpha]^{21.0}_{D}$ = +115.01 (*c* 0.10, EA); HPLC (IG-3 column, *i*-propanol/*n*-hexane = 10/90, flow rate 1.0 mL/min, λ = 254 nm), product: t₁ = 10.03 min (minor), t₂ = 12.36 min (major), *ee* = 94%; ¹H NMR (400 MHz, DMSO) δ 9.35 – 8.88 (m, 1H), 7.55 (d, *J* = 8.8 Hz, 2H), 7.43 (d, *J* = 8.8 Hz, 2H), 6.55 (s, 1H), 4.08 (q, *J* = 7.0 Hz, 2H), 2.06 – 1.96 (m, 1H), 1.93 – 1.84 (m, 1H),

1.74 - 1.62 (m, 1H), 1.55 - 1.35 (m, 3H), 1.24 - 1.21 (m, 6H). ¹³C NMR (100 MHz, DMSO) δ 157.2, 154.7, 136.6, 129.5, 128.9, 126.9, 96.5, 69.6, 61.3, 37.4, 37.2, 21.2, 20.3, 14.9. HRMS (ESI) m/z calcd for C₁₆H₂₀ClN₃O₄Na⁺[M + Na]⁺ = 376.1035, found = 376.1037.

Benzyl ((3aS,6aS)-3-(4-chlorophenyl)-3a-hydroxy-6a-methyl-2-oxohexahydrocyc lopenta[d]imidazol-1(2H)-yl)carbamate (3o):



A white solid; 58.9 mg; isolated yield = 71%; m.p. 130.4 – 130.9 °C; dr > 20:1. $[\alpha]^{21.0}_{D}$ = -42.00 (*c* 0.10, EA); HPLC (IG-3 column, *i*-propanol/*n*-hexane = 10/90, flow rate 1.0 mL/min, λ = 254 nm), product: t₁ = 14.78 min (major), t₂ = 18.95 min (minor), *ee* = 93%; ¹H NMR (400 MHz, DMSO) δ 9.54 – 9.07 (m, 1H), 7.60 – 7.48 (m, 2H), 7.46 – 7.26 (m, 7H), 6.57 (s, 1H), 5.22 – 5.03 (m, 2H), 2.09 – 1.97 (m, 1H), 1.95 – 1.85 (m, 1H), 1.77 –

 $1.58 \ (m, 1H), \ 1.55 - 1.35 \ (m, 2H), \ 1.32 - 1.17 \ (m, 4H). \ ^{13}C \ NMR \ (100 \ MHz, \ DMSO) \\ \delta \ 157.2, \ 154.7, \ 139.2, \ 136.9, \ 136.6, \ 129.6, \ 128.9, \ 128.5, \ 128.3, \ 127.0, \ 96.6, \ 69.6, \ 66.6, \\ 37.4, \ 37.2, \ 21.2, \ 20.3. \ \ HRMS \ (ESI) \ m/z \ calcd \ for \ C_{21}H_{22}ClN_3O_4Na^+ \ [M \ + \ Na]^+ = \\ 438.1191, \ found = 438.1187.$

tert-Butyl ((3aS,6aS)-3-(4-bromophenyl)-6a-ethyl-3a-hydroxy-2-oxohexahydrocy clopenta[*d*]imidazol-1(2*H*)-yl)carbamate (3p):



A white solid; 71.1 mg; isolated yield = 81%; m.p. 132.1 – 132.7 °C; dr > 20:1. $[\alpha]^{21.0}_{D}$ = +87.00 (*c* 0.10, EA); HPLC (IG-3 column, *i*-propanol/*n*-hexane = 10/90, flow rate 1.0 mL/min, λ = 254 nm), product: t₁ = 5.89 min (minor), t₂ = 8.91 min (major), *ee* = 94%; ¹H NMR (400 MHz, DMSO) δ 9.07 – 8.46 (m, 1H), 7.54 (d, *J* = 8.7 Hz, 2H), 7.46 (d, *J* = 8.8 Hz, 2H), 6.51 (s, 1H), 1.97 – 1.84 (m, 2H), 1.76 – 1.45 (m, 6H), 1.41 (s, 9H), 0.95 (t, *J* = 7.2 Hz, 3H). ¹³C NMR (100

MHz, DMSO) δ 156.3, 155.0, 137.0, 131.8, 127.6, 117.8, 97.0, 80.0, 71.5, 37.9, 33.6, 28.5, 26.9, 21.2, 9.2. HRMS (ESI) m/z calcd for $C_{19}H_{26}BrN_3O_4Na^+$ [M + Na]⁺ = 462.0999, found = 462.0996.

tert-Butyl ((3aS,6aR)-6a-allyl-3-(4-bromophenyl)-3a-hydroxy-2-oxohexahydrocy clopenta[d]imidazol-1(2H)-yl)carbamate (3q):

OH OH OH N Boc H

A white solid; 70.3 mg; isolated yield = 78%; m.p. 131.6 – 132.4 °C; dr > 20:1. $[\alpha]^{21.0}_{D}$ = +76.00 (*c* 0.10, EA); HPLC (IG-3 column, *i*-propanol/*n*-hexane = 10/90, flow rate 1.0 mL/min, λ = 254 nm), product: t₁ = 5.35 min (minor), t₂ = 7.80 min (major), *ee* = 95%; ¹H NMR (400 MHz, DMSO) δ 9.10 – 8.25 (m, 1H), 7.56 (d, *J* = 8.8 Hz, 2H), 7.48 (d, *J* = 8.9 Hz, 2H), 6.69 (s, 1H), 6.05 – 5.84 (m, 1H), 5.25 – 4.96 (m, 2H), 2.48 – 2.32 (m, 2H), 1.94 – 1.82 (m, 2H), 1.72 – 1.53 (m, 2H), 1.52 – 1.32 (m, 11H). ¹³C NMR (100 MHz, DMSO) δ 156.0,

154.8, 136.9, 135.3, 131.8, 127.4, 118.5, 117.9, 96.9, 80.0, 81.0, 37.5, 33.4, 33.0, 28.5, 21.2. HRMS (ESI) m/z calcd for $C_{20}H_{26}BrN_3O_4Na^+$ [M + Na]⁺ = 474.0999, found = 474.1009.

tert-Butyl ((3aS,6aR)-6a-benzyl-3-(4-bromophenyl)-3a-hydroxy-2-oxohexahydro cyclopenta[d]imidazol-1(2H)-yl)carbamate (3r):



A white solid;77.2 mg; isolated yield = 77%; m.p. 132.8 – 133.4 °C; dr > 20:1. $[\alpha]^{21.0}_{D}$ = +184.01 (*c* 0.10, EA); HPLC (IG-3 column, *i*-propanol/*n*-hexane = 10/90, flow rate 1.0 mL/min, λ = 254 nm), product: t₁ = 5.09 min (minor), t₂ = 7.69 min (major), *ee* = 94%; 1H NMR (400 MHz, DMSO) δ 8.94 – 8.57 (m, 1H), 7.60 – 7.54 (m, 2H), 7.53 – 7.48 (m, 2H), 7.42 – 7.35 (m, 2H), 7.32 – 7.22 (m, 2H), 7.21 – 7.15 (m, 1H), 7.05 (s, 1H), 3.31 – 3.14 (m, 1H), 2.96 – 2.78 (m,

1H), 1.89 – 1.69 (m, 2H), 1.65 – 1.51 (m, 1H), 1.44 – 1.28 (m, 12H) 13C NMR (101 MHz, DMSO) δ 156.3, 154.9, 138.1, 136.8, 131.8, 131.7, 128.3, 127.6, 126.6, 118.0, 97.2, 80.0, 72.5, 72.2, 39.2, 37.3, 32.6, 28.5, 21.1. HRMS (ESI) m/z calcd for C₂₄H₂₈BrN₃O₄Na⁺ [M + Na]⁺ = 524.1155, found = 524.1152.

tert-Butyl ((3aS,6aS)-3-(4-bromophenyl)-6a-heptyl-3a-hydroxy-2-oxohexahydroc yclopenta[d]imidazol-1(2H)-yl)carbamate (3s):



A white solid; 84.5 mg; isolated yield = 83%; m.p. 136.2 – 136.8 °C; dr > 20:1. $[\alpha]^{21.0}_{D}$ = +206.01 (*c* 0.10, EA); HPLC (IG-3 column, *i*-propanol/*n*-hexane = 10/90, flow rate 1.0 mL/min, λ = 254 nm), product: t₁ = 4.44 min (minor), t₂ = 6.89 min (major), *ee* = 96%; ¹H NMR (400 MHz, DMSO) δ 8.94 – 8.49 (m, 1H), 7.58 – 7.51 (m, 2H), 7.49 – 7.45 (m, 2H), 6.49 (s, 1H), 2.00 – 1.83 (m, 2H), 1.74 – 1.52 (m, 4H), 1.48 – 1.40 (m, 12H), 1.25 (s, 9H), 0.85 (t, *J* = 6.5 Hz, 3H). ¹³C NMR (100 MHz, DMSO) δ 156.2, 155.0, 137.1, 131.7, 127.5, 117.8, 97.0, 79.8, 71.3, 37.8, 34.6, 34.0, 31.8, 30.6, 29.1, 28.5, 24.0, 22.6, 21.2, 14.4. HRMS (ESI) m/z calcd for C₂₄H₃₆BrN₃O₄Na⁺ [M + Na]⁺ = 532.1781, found = 532.1788.

tert-Butyl ((3aS,6aR)-3-(4-bromophenyl)-6a-cyclopentyl-3a-hydroxy-2-oxohexah ydrocyclopenta[*d*]imidazol-1(2*H*)-yl)carbamate (3t):



A white solid; 75.7 mg; isolated yield = 79%; m.p. 132.5 – 133.0 °C; dr > 20:1. $[\alpha]^{21.0}_{D}$ = +142.01 (*c* 0.10, EA); HPLC (IG-3 column, *i*-propanol/*n*-hexane = 10/90, flow rate 1.0 mL/min, λ = 254 nm), product: t₁ = 5.83 min (minor), t₂ = 19.10 min (major), *ee* = 93%; ¹H NMR (400 MHz, DMSO) δ 8.90 – 8.35 (m, 1H), 7.61 – 7.52 (m, 2H), 7.48 – 7.41 (m, 2H), 6.71 – 6.25 (m, 1H), 2.39 – 2.17 (m, 1H), 2.08 – 1.75 (m, 4H), 1.71 – 1.47 (m, 6H), 1.44 – 1.26 (m, 13H). ¹³C NMR (100 MHz, DMSO) δ 156.3, 155.0, 137.0, 131.7, 127.9, 127.6, 117.9,

97.5, 80.0, 73.7, 44.78, 38.4, 33.0, 31.0, 28.5, 25.7, 21.4. HRMS (ESI) m/z calcd for $C_{22}H_{30}BrN_3O_4Na^+$ [M + Na]⁺ = 502.1312, found = 502.1309.

<u>Methyl (3aS,6aS)-3-((*tert*-butoxycarbonyl)amino)-1-(4-chlorophenyl)-6a-hydrox</u> <u>y-2-oxohexahydrocyclopenta[*d*]imidazole-3a(1*H*)-carboxylate (3u):</u>



A white solid; 37.4 mg; isolated yield = 44%; m.p. 152.3 – 152.9 °C; dr > 20:1; $[\alpha]^{21.0}_{D}$ = +121.05 (*c* 0.10, EA); HPLC (IF-3 column, *i*-propanol/*n*-hexane = 30/70, flow rate 1.0 mL/min, λ = 254 nm), product: t₁ = 6.93 min (major), t₂ = 15.50 min (minor), *ee* = 91%; ¹H NMR (400 MHz, CDCl₃) δ 8.09 – 7.54 (m, 1H), 7.09 (d, *J* = 8.4 Hz, 2H), 6.96 (d, *J* = 8.4 Hz, 2H), 5.33 (s, 1H), 3.89 (s, 3H), 2.51 – 2.38 (m, 1H), 2.35 – 2.27 (m, 1H), 1.85 – 1.78 (m, 2H), 1.77 – 1.66 (m, 2H), 1.48 (s, 9H); ¹³C NMR (100 MHz, CDCl₃) δ 171.0, 156.2,

(11, 211), 1.48 (3, 511), C HVIR (100 WH2, CDCI3) 0 171.0, 150.2, 155.6, 133.9, 131.4, 128.3, 126.0, 98.5, 81.2, 78.0, 53.2, 35.3, 33.3, 28.2, 22.2. HRMS (ESI) m/z calcd for C₁₈H₂₄ClN₃O₆Na⁺ [M + Na]⁺ = 464.1559, found = 464.1561.

tert-Butyl ((3aS,6aS)-3-(4-bromophenyl)-3a-hydroxy-2-oxohexahydrocyclopenta [*d*]imidazol-1(2*H*)-yl)carbamate (3y):



A white solid; 60.8 mg; isolated yield = 74%; m.p. 129.7 – 130.3 °C; dr > 20:1. $[\alpha]^{21.0}_{D}$ = +42.00 (*c* 0.10, EA); HPLC (IG-3 column, *i*propanol/*n*-hexane = 10/90, flow rate 1.0 mL/min, λ = 254 nm), product: t₁ = 12.30 min (minor), t₂ = 87.70 min (major), *ee* = 75%; ¹H NMR (400 MHz, DMSO) δ 9.23 – 8.56 (m, 1H), 7.73 – 7.36 (m, 4H), 6.81 (s, 1H), 3.78 (s, 1H), 1.92 – 1.84 (m, 1H), 1.82 – 1.60 (m, 4H), 1.60 – 1.47 (m, 1H), 1.42 (s, 9H). ¹³C NMR (100 MHz, DMSO)

δ 155.4, 137.4, 131.8, 126.3, 117.4, 95.8, 80.3, 68.5, 38.0, 30.2, 28.5, 23.5. HRMS (ESI) m/z calcd for C₁₇H₂₂BrN₃O₄Na⁺ [M + Na]⁺ = 434.0686, found = 434.0681.

tert-Butyl ((3aS,8aS)-3-(4-bromophenyl)-3a-hydroxy-8a-methyl-2-oxo-3,3a,8,8a-t etrahydroindeno[1,2-*d*]imidazol-1(2*H*)-yl)carbamate (3w):



A white solid; 57.7 mg; isolated yield = 61%; m.p. 129.6 – 130.4 °C; dr > 20:1. $[\alpha]^{21.0}_{D}$ = -88.00 (*c* 0.10, EA); HPLC (IG-3 column, *i*-propanol/*n*-hexane = 10/90, flow rate 1.0 mL/min, λ = 254 nm), product: t₁ = 5.83 min (major), t₂ = 6.73 min (minor), *ee* = 92%; ¹H NMR (400 MHz, DMSO) δ 9.14 – 8.73 (m, 1H), 7.62 – 7.48 (m, 2H), 7.35 – 7.15 (m, 4H), 7.12 – 7.03 (m, 2H), 6.80 – 6.74 (m, 1H), 3.48 – 3.37 (m, 1H), 2.94 – 2.83 (m, 1H),

1.44 (s, 9H), 1.32 (s, 3H). ¹³C NMR (100MHz, DMSO) δ 156.1 154.8, 141.0, 140.4 136.4, 131.8 129.8, 129.8 126.8, 125.7, 124.9, 119.2, 96.7 80.1 71.3 43.0, 28.5, 19.2. HRMS (ESI) m/z calcd for C₂₂H₂₄BrN₃O₄Na⁺[M + Na]⁺ = 496.0842, found = 496.0840.

tert-Butyl ((3aS,7aS)-3-(4-bromophenyl)-3a-hydroxy-7a-methyl-2-oxooctahydro-1*H*-benzo[*d*]imidazol-1-yl)carbamate (3x):



A white solid; 66.7 mg; isolated yield = 76%; m.p. 133.1 – 133.8 °C; dr > 20:1. $[\alpha]^{21.0}_{D}$ = -76.00 (*c* 0.10, EA); HPLC (IH-3 column, *i*-propanol/*n*-hexane = 10/90, flow rate 1.0 mL/min, λ = 254 nm), product: t₁ = 9.74 min (minor), t₂ = 14.71 min (major), *ee* = 90%; ¹H NMR (400 MHz, DMSO) δ 8.90 – 8.25 (m, 1H), 7.62 – 7.47 (m, 2H), 7.38 – 7.20 (m, 2H), 6.24 (s, 1H), 1.82 – 1.46 (m, 5H), 1.45 – 1.34 (m, 10H), 1.27 – 1.13 (m, 5H). ¹³C NMR (100 MHz, DMSO) δ 156.8, 156.4, 136.3, 131.8, 130.0, 119.3, 88.4, 79.9, 64.8, 34.7, 31.2, 28.5,

21.76, 20.6, 17.7. HRMS (ESI) m/z calcd for $C_{19}H_{26}BrN_3O_4Na^+[M + Na]^+ = 462.0999$, found = 462.0995.

tert-Butyl ((3aS,7aS)-1-(4-bromophenyl)-7a-hydroxy-3a-methyl-2-oxohexahydro pyrano[3,4-d]imidazol-3(2H)-yl)carbamate (3y):



A colorless oil; 68.8 mg; isolated yield = 78%; dr > 20:1. $[\alpha]^{21.0}_{D}$ = +157.00 (*c* 0.10, EA); HPLC (IE-3 column, *i*-propanol/*n*-hexane = 30/70, flow rate 1.0 mL/min, λ = 254 nm), product: t₁ = 4.18 min (minor), t₂ = 4.67 min (major), *ee* = 90%; ¹H NMR (400 MHz, CDCl₃) δ 7.54 – 7.35 (m, 2H), 7.31 – 7.17 (m, 2H), 7.06 (s, 1H), 5.84 (s, 1H), 3.91 – 3.51 (m, 2H), 3.39 – 3.05 (m, 2H), 2.00 – 1.77 (m, 2H), 1.42 (s, 9H), 1.34 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 157.6, 157.2,

134.2, 132.1, 128.5, 120.7, 88.5, 82.8, 74.8, 64.7, 63.2, 29.1, 28.1, 14.2. HRMS (ESI) m/z calcd for $C_{18}H_{24}BrN_3O_5Na^+[M + Na]^+ = 464.0791$, found = 464.0789.

tert-Butyl ((3aS,8aS)-3-(4-bromophenyl)-3a-hydroxy-8a-methyl-2-oxo-3,3a,8,8a-t etrahydroindeno[1,2-*d*]imidazol-1(2*H*)-yl)carbamate (3z):



A colorless oil; 84.3 mg; isolated yield = 71%; dr > 20:1. $[\alpha]^{21.0}_{D}$ = -127.01 (*c* 0.10, EA); HPLC (IF-3 column, *i*-propanol/*n*-hexane = 10/90, flow rate 1.0 mL/min, λ = 254 nm), product: t₁ = 4.44 min (minor), t₂ = 8.27 min (major), *ee* = 92%; ¹H NMR (400 MHz, CDCl₃) δ 7.57 – 7.46 (m, 3H), 7.27 – 7.16 (m, 5H), 7.04 (s, 2H), 3.70 – 2.70 (m, 4H), 2.35 (s, 3H), 2.02 – 1.90 (m, 1H), 1.86 – 1.74 (m, 1H), 1.42 (s, 9H), 1.33 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 156.6, 156.5, 144.0, 133.9, 133.6, 131.8, 130.0, 127.5, 127.2, 120.1,

87.7, 82.6, 65.3, 51.3, 42.0, 28.2, 27.7, 21.6, 15.2. HRMS (ESI) m/z calcd for $C_{25}H_{31}BrN_4O_6SNa^+[M + Na]^+ = 617.1040$, found = 617.1035.

tert-Butyl (3a*S*,7a*S*)-1-(4-bromophenyl)-3-((*tert*-butoxycarbonyl)amino)-7a-hydr oxy-3a-methyl-2-oxooctahydro-5*H*-imidazo[4,5-*c*]pyridine-5-carboxylate (3a'):



A colorless oil; 79.9 mg; isolated yield = 74%; dr > 20:1. $[\alpha]^{21.0}_{D}$ = -158.01 (*c* 0.10, EA); HPLC (ID-3 column, *i*-propanol/*n*-hexane = 10/90, flow rate 1.0 mL/min, λ = 254 nm), product: t₁ = 6.89 min (minor), t₂ = 7.44 min (major), *ee* = 96%; ¹H NMR (400 MHz, CDCl₃) δ 7.51 – 7.28 (m, 3H), 7.21 – 7.14 (m, 1H), 3.92 – 2.69 (m, 4H), 2.02 – 1.75 (m, 2H), 1.47 (s, 18H), 1.30 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 155.8, 154.0, 154.0, 134.7, 131.5, 126.6, 119.4, 87.7, 82.0, 80.7, 77.3, 65.3, 40.0, 39.6, 28.2, 15.7.

HRMS (ESI) m/z calcd for $C_{23}H_{33}BrN_4O_6Na^+[M + Na]^+ = 563.1475$, found = 563.1472.

<u>Benzyl</u> (3aS,7aS)-1-(4-bromophenyl)-3-((*tert*-butoxycarbonyl)amino)-7a-hydrox y-3a-methyl-2-oxooctahydro-5*H*-imidazo[4,5-*c*]pyridine-5-carboxylate (3b'):



A colorless oil; 99.8 mg; isolated yield = 87%; dr > 20:1. $[\alpha]^{21.0}_{D}$ = -188.01 (*c* 0.10, EA); HPLC (IK-3 column, *i*-propanol/*n*-hexane = 10/90, flow rate 1.0 mL/min, λ = 254 nm), product: t₁ = 6.03 min (minor), t₂ = 6.59 min (major), *ee* = 95%; ¹H NMR (400 MHz, CDCl₃) δ 7.62 – 7.29 (m, 6H), 7.20 – 7.04 (m, 3H), 5.32 – 4.96 (m, 2H), 3.90 – 2.74 (m, 4H), 2.06 – 1.76 (m, 2H), 1.49 (s, 9H), 1.33 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 155.2, 155.1, 153.8,

133.2, 130.7, 130.4, 127.6, 127.23, 127.3, 127.1, 125.4, 118.3 86.5, 80.9, 76.3, 76.0, 75.7, 66.6, 64.4, 63.7, 39.2, 38.8, 27.1, 14.7. HRMS (ESI) m/z calcd for $C_{26}H_{31}BrN_4O_6Na^+[M + Na]^+ = 597.1319$, found = 597.1329.

tert-Butyl ((3aR,6aS)-7-(4-chlorophenyl)-2,8-dioxotetrahydro-4H-3a,6a-(epimino methanoimino)cyclopenta[b]furan-9-yl)carbamate (4a):

A white solid; 70.0 mg; isolated yield = 86%; m.p. 120.4 – 120.7 °C; dr > 20:1. $[\alpha]^{21.0}_{D}$ = +434.02 (*c* 0.10, EA); HPLC (IG-3 column, *i*-propanol/*n*-hexane = 30/70, flow rate 1.0 mL/min, λ = 254 nm), product: t₁ = 10.03 min (major), t₂ = 11.08 min (minor), *ee* = 93%; ¹H NMR (400 MHz, CDCl₃) δ 7.57 – 7.43 (m, 2H), 7.33 – 7.28 (m, 2H), 7.20 – 6.92 (m, 1H), 3.43 – 3.16 (m, 1H), 2.78 – 2.60 (m, 1H), 2.49 – 2.26 (m, 1H), 2.24 – 2.04 (m, 2H), 1.99 –

1.87 (m, 2H), 1.87 - 1.78 (m, 1H), 1.46 (s, 9H). ¹³C NMR (100 MHz, CDCl₃) δ 173.7, 155.7, 154.1, 134.2, 131.6, 129.2, 124.7, 105.1, 82.5, 71.4, 39.7, 37.5, 36.6, 28.1, 23.7. HRMS (ESI) m/z calcd for C₁₉H₂₂ClN₃O₅Na⁺[M + Na]⁺ = 430.1140, found = 430.1139.

tert-Butyl ((3aR,6aS)-7-(4-bromophenyl)-2,8-dioxotetrahydro-4H-3a,6a-(epimino methanoimino)cyclopenta[b]furan-9-yl)carbamate (4b):



A white solid; 74.9 mg; isolated yield = 83%; m.p. 114.2 – 114.8 °C; dr > 20:1. $[\alpha]^{21.0}_{D}$ = +466.02 (*c* 0.10, EA); HPLC (IG-3 column, *i*-propanol/*n*-hexane = 30/70, flow rate 1.0 mL/min, λ = 254 nm), product: t₁ = 10.84 min (major), t₂ = 12.65 min (minor), *ee* = 93%; ¹H NMR (400 MHz, DMSO) δ 9.56 – 8.60 (m, 1H), 7.75 – 7.58 (m, 2H), 7.50 – 7.37 (m, 2H), 3.22 – 2.97 (m, 2H), 2.35 – 1.90 (m, 4H), 1.89 – 1.64 (m, 2H), 1.49 – 1.34 (m, 9H). ¹³C

NMR (100 MHz, DMSO) δ 174.5, 156.0, 153.5, 135.7, 132.5, 125.0, 118.2, 104.6, 81.0, 71.7, 39.0, 36.5, 36.1, 28.4, 28.1, 23.8. HRMS (ESI) m/z calcd for C₁₉H₂₂BrN₃O₅Na⁺ [M + Na]⁺ = 474.0635, found = 474.0631.

tert-Butyl ((3aR,6aS)-7-(4-iodophenyl)-2,8-dioxotetrahydro-4H-3a,6a-(epiminom ethanoimino)cyclopenta[b]furan-9-yl)carbamate (4c):



A white solid; 91.8 mg; isolated yield = 92%; m.p. 117.1 – 117.6 °C; dr > 20:1. $[\alpha]^{21.0}_{D}$ = +473.02 (*c* 0.10, EA); HPLC IG-3 column, *i*-propanol/*n*-hexane = 30/70, flow rate 1.0 mL/min, λ = 254 nm), product: t₁ = 14.52 min (major), t₂ = 15.71 min (minor), *ee* = 96%; ¹H NMR (400 MHz, CDCl₃) δ 7.74 – 7.59 (m, 2H), 7.38 – 7.28 (m, 2H), 7.14 – 6.89 (m, 1H), 3.44 – 3.23 (m, 1H), 2.72 – 2.62 (m, 1H), 2.47 – 2.26 (m, 1H), 2.23 – 2.05 (m, 2H), 2.01 –

1.88 (m, 1H), 1.86 – 1.78 (m, 2H), 1.46 (s, 9H). ¹³C NMR (100 MHz, CDCl₃) δ 173.6, 155.7, 153.9, 138.1, 135.5, 125.0, 105.0, 90.3, 82.6, 71.4, 39.7, 37.5, 36.6, 28.1, 23.7. HRMS (ESI) m/z calcd for C₁₉H₂₂IN₃O₅Na⁺ [M + Na]⁺ = 522.0496, found = 522.0497.

tert-Butyl ((3aR,6aS)-7-(4-methoxyphenyl)-2,8-dioxotetrahydro-4H-3a,6a-(epimi nomethanoimino)cyclopenta[b]furan-9-yl)carbamate (4d):

OMe O O N NHBoc

A white solid; 59.6 mg; isolated yield = 74%; m.p. 126.6 – 127.4 °C; dr > 20:1. $[\alpha]^{21.0}_{D}$ = +361.01 (*c* 0.10, EA); HPLC (IG-3 column, *i*-propanol/*n*-hexane = 30/70, flow rate 1.0 mL/min, λ = 254 nm), product: t₁ = 17.41 min (major), t₂ = 18.34 min (minor), *ee* = 94%; ¹H NMR (400 MHz, CDCl₃) δ 7.41 – 7.34 (m, 2H), 7.17 – 6.95 (m, 1H), 6.93 – 6.80 (m, 2H), 3.78 (s, 3H), 3.40 – 3.25 (m, 1H), 2.72 – 2.58 (m, 1H), 2.54 – 2.25 (m, 1H), 2.19 – 2.09 (m,

1H), 2.72 - 2.58 (iii, 111), 2.54 - 2.25 (iii, 111), 2.19 - 2.09 (iii, 111), 2.07 - 1.95 (iii, 111), 1.95 - 1.75 (iii, 3H), 1.46 (s, 9H). ¹³C NMR (100 MHz, CDCl₃) δ 173.9, 158.2, 155.8, 154.8, 128.1, 126.4, 114.4, 105.5, 82.3, 71.2, 55.5, 40.0, 37.6, 36.4, 28.1, 23.6. HRMS (ESI) m/z calcd for C₂₀H₂₅N₃O₆Na⁺ [M + Na]⁺ = 426.1635, found = 426.1634.

<u>Methyl ((3aR,6aS)-7-(4-chlorophenyl)-2,8-dioxotetrahydro-4H-3a,6a-(epiminom</u> ethanoimino)cyclopenta[b]furan-9-yl)carbamate (4e):



A white solid; 51.1 mg; isolated yield = 70%; m.p. 116.6 – 117.3 °C; dr > 20:1. $[\alpha]^{21.0}_{D}$ = +192.01 (*c* 0.10, EA); HPLC (IG-3 column, *i*-propanol/*n*-hexane = 30/70, flow rate 1.0 mL/min, λ = 254 nm), product: t₁ = 19.88 min (major), t₂ = 21.82 min (minor), *ee* = 96%; ¹H NMR (400 MHz, CDCl₃) δ 7.50 – 7.44 (m, 2H), 7.37 – 7.30 (m, 3H), 3.77 (s, 3H), 3.36 – 3.18 (m, 1H), 2.75 – 2.61 (m, 1H), 2.51 – 2.27 (m, 1H), 2.20 – 2.05 (m, 2H), 1.99 – 1.77 (m, 3H). ¹³C NMR (100 MHz,

CDCl₃) δ 173.4, 157.4, 154.2, 134.0, 131.8, 129.3, 124.8, 105.1, 71.5, 53.6, 39.5, 37.3, 36.6, 23.7. HRMS (ESI) m/z calcd for C₁₆H₁₆ClN₃O₅Na⁺[M + Na]⁺ = 388.0671, found = 388.0667.

<u>Ethyl ((3aR,6aS)-7-(4-chlorophenyl)-2,8-dioxotetrahydro-4H-3a,6a-(epiminomet hanoimino)cyclopenta[b]furan-9-yl)carbamate (4f)</u>:



A white solid; 50.8 mg; isolated yield = 67%; m.p. 115.2 – 115.8 °C; dr > 20:1. $[\alpha]^{21.0}_{D}$ = +318.01 (*c* 0.10, EA); HPLC (IG-3 column, *i*-propanol/*n*-hexane = 30/70, flow rate 1.0 mL/min, λ = 254 nm), product: t₁ = 12.21 min (major), t₂ = 17.04 min (minor), *ee* = 97%; ¹H NMR (400 MHz, CDCl₃) δ 7.50 – 7.45 (m, 2H), 7.35 – 7.29 (m, 2H), 7.27 (s, 1H), 4.26 – 4.17 (m, 2H), 3.40 – 3.19 (m, 1H), 2.75 – 2.59 (m, 1H), 2.51 – 2.30 (m, 1H),

2.24 - 2.03 (m, 2H), 2.00 - 1.76 (m, 3H), 1.27 (t, J = 7.1 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 173.5, 156.9, 154.1, 134.0, 131.7, 129.3, 124.7, 105.1, 71.5, 62.9, 39.6, 37.3, 36.6, 23.7, 14.3. HRMS (ESI) m/z calcd for C₁₇H₁₈ClN₃O₅Na⁺ [M + Na]⁺ = 402.0827, found = 402.0825.

<u>Benzyl ((3aR,6aS)-7-(4-chlorophenyl)-2,8-dioxotetrahydro-4H-3a,6a-(epiminome thanoimino)cyclopenta[b]furan-9-yl)carbamate (4g)</u>:

A white solid;67.9 mg; isolated yield = 77%; m.p. 119.1 – 119.8 °C; dr > 20:1. $[\alpha]^{21.0}_{D}$ = +217.01 (*c* 0.10, EA); HPLC (IG-3 column, *i*-propanol/*n*-hexane = 30/70, flow rate 1.0 mL/min, λ = 254 nm), product: t₁ = 25.76 min (major), t₂ = 35.17 min (minor), *ee* = 94%; ¹H NMR (400 MHz, CDCl₃) δ 7.64 – 7.40 (m, 3H), 7.36 – 7.28 (m, 7H), 5.26 – 5.10 (m, 2H), 3.42 – 3.11 (m, 1H), 2.71 – 2.52 (m, 1H), 2.45 – 2.20 (m, 1H), 2.20 – 2.02

(m, 2H), 1.93 - 1.77 (m, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 173.4, 156.8, 154.1, 135.2, 133.9, 131.8, 129.3, 128.7, 128.6, 128.4, 124.9, 105.1, 71.5, 68.4, 39.6, 37.3, 36.6, 23.6. HRMS (ESI) m/z calcd for C₂₂H₂₀ClN₃O₅Na⁺[M + Na]⁺ = 464.0984, found = 464.0983.

tert-Butyl ((3aR,7aS)-8-(4-iodophenyl)-2,9-dioxohexahydro-3a,7a-(epiminometha noimino)benzofuran-10-yl)carbamate (4h):



A white solid; 86.2 mg; isolated yield = 84%; m.p. 119.3 – 119.7 °C; dr > 20:1. $[\alpha]^{21.0}_{D}$ = +382.02 (*c* 0.10, EA); HPLC (IG-3 column, *i*-propanol/*n*-hexane = 30/70, flow rate 1.0 mL/min, λ = 254 nm), product: t₁ = 18.68 min (major), t₂ = 22.77 min (minor), *ee* = 90%; ¹H NMR (400 MHz, CDCl₃) δ 7.76 – 7.67 (m, 2H), 7.17 – 7.12 (m, 2H), 6.91 (s, 1H), 3.17 – 2.96 (m, 1H), 2.75 – 2.63 (m, 1H), 2.49 – 2.35 (m, 1H), 2.19 – 2.02 (m, 1H), 1.86 – 1.73 (m,

(iii, 111), 2.49 = 2.53 (iii, 111), 2.19 = 2.02 (iii, 111), 1.80 = 1.73 (iii, 111), 1.65 = 1.73 (iii, 111), 1.65

<u>tert-Butyl ((4aR,7aS)-8-(4-bromophenyl)-2,9-dioxotetrahydro-2*H*,5*H*-4a,7a-(epiminomethanoimino)cyclopenta[b]pyran-10-yl)carbamate (4i):</u>



A colorless oil; 39.1 mg; isolated yield = 56%; dr > 20:1. $[\alpha]^{21.0}_{D}$ = +33.30 (*c* 0.10, EA); HPLC (IG-3 column, *i*-propanol/*n*-hexane = 30/70, flow rate 1.0 mL/min, λ = 254 nm), product: t₁ = 7.12 min (minor), t₂ = 9.22 min (major), *ee* = 96%; ¹H NMR (400 MHz, CDCl₃) δ 7.48 – 7.38 (m, 2H), 7.32 – 7.23 (m, 2H), 6.61 (s, 1H), 2.59 – 2.28 (m, 2H), 2.27 – 2.02 (m, 2H), 2.02 – 1.86 (m, 1H), 1.84 – 1.53 (m, 5H), 1.43 (s, 9H). ¹³C NMR (101 MHz, CDCl₃) δ

171.1, 154.9, 134.1, 132.3, 127.7, 120.7, 101.6, 66.6, 37.9, 29.7, 28.1, 27.8, 26.1, 21.8.HRMS (ESI) m/z calcd for $C_{20}H_{24}BrN_3O_5Na^+$ [M + Na]⁺ = 488.0784, found = 488.0792.

(3aR,6aS)-3a-Allyl-3-amino-1-(4-bromophenyl)-6a-hydroxyhexahydrocyclopenta [d]imidazol-2(1H)-one (5):

Br OH T N N NH₂

OH

A colorless oil; 61.1 mg; isolated yield = 87%; dr > 20:1. $[\alpha]^{21.0}_{D}$ = +104.00 (*c* 0.10, EA); HPLC (IG-3 column, *i*-propanol/*n*-hexane = 10/90, flow rate 1.0 mL/min, λ = 254 nm), product: t₁ = 15.76 min (minor), t₂ = 18.11 min (major), *ee* = 92%; ¹H NMR (400 MHz, DMSO) δ 7.51 (s, 4H), 6.54 (s, 1H), 6.18 – 5.85 (m, 1H), 5.17 – 4.99 (m, 2H), 4.27 (s, 2H), 2.48 – 2.41 (m, 1H), 2.01 – 1.86 (m, 2H), 1.78 – 1.42 (m, 3H), 1.36 – 1.15 (m, 2H). ¹³C NMR (100 MHz, DMSO) δ 157.0, 137.5, 136.0, 131.7, 126.6, 118.3, 117.0, 96.5, 38.9, 37.7, 33.1, 21.3. HRMS

(ESI) m/z calcd for $C_{15}H_{18}BrN_3O_2Na^+[M + Na]^+ = 374.0474$, found = 374.0472.

<u>Ethyl N-((3aS,6aS)-3-(4-chlorophenyl)-3a-hydroxy-6a-methyl-2-oxohexahydrocy</u> clopenta[*d*]imidazol-1(2*H*)-yl)-*N*-(ethoxycarbonyl)glycinate (6):

Cl A colorless oil; 69.4 mg; isolated yield = 79%; dr = $1.2:1. [\alpha]^{21.0}_{D}$ = +331.01 (*c* 0.10, EA); HPLC (IF-3 column, *i*-propanol/*n*-hexane = 30/70, flow rate 1.0 mL/min, λ = 254 nm), major product: t₁ = 5.80 min (minor), t₂ = 7.49 min (major), *ee* = 94%; minor product: t₁ = 4.72 min (major), t₂ = 6.83 min (minor), *ee* = 94%; ¹H NMR (400 MHz, CDCl₃) δ 7.55 – 7.38 (m, 2H), 7.30 – 7.15 (m, 2H), 5.34 – 4.33 NCOOEt (m, 2H), 4.31 – 4.09 (m, 4H), 3.97 – 3.43 (m, 1H), 2.71 – 2.29 (m, 1H), 2.08 – 1.94 (m, 1H), 1.89 – 1.41 (m, 5H), 1.39 – 1.26 (m, 6H), 1.24 – 1.22 (m, 2H). ¹³C NMR (100 MHz, CDCl₃) δ 169.0, 157.0,

155.0, 134.78, 131.2, 128.8, 126.3, 98.2, 70.1, 63.8, 61.5, 55.1, 40.3, 34.7, 21.1, 17.6, 14.2. HRMS (ESI) m/z calcd for $C_{20}H_{26}ClN_3O_6Na^+$ [M + Na]⁺ = 462.1402, found = 462.1401.

(3aS,6aS)-1-(4-Chlorophenyl)-6a-hydroxy-3a-methylhexahydrocyclopenta[d]imi dazol-2(1H)-one (7):



Br

HO

// O A white solid; 35.6 mg; isolated yield = 67%; m.p. 126.2 – 126.8 °C; dr > 20:1. $[\alpha]^{21.0}_{D}$ = +88.00 (*c* 0.10, EA); HPLC (IG-3 column, *i*-propanol/*n*-hexane = 30/70, flow rate 1.0 mL/min, λ = 254 nm), product: t₁ = 4.88 min (minor), t₂ = 5.44 min (major), *ee* = 94%; ¹H NMR (400 MHz, DMSO) δ 7.64 – 7.53 (m, 2H), 7.42 – 7.34 (m, 2H), 7.20 (s, 1H), 6.32 (s, 1H), 1.92 – 1.80 (m, 1H), 1.80 – 1.71 (m, 1H), 1.69 – 1.58 (m, 2H), 1.56 – 1.45 (m, 1H), 1.40 – 1.28 (m, 1H), 1.23 (s, 3H). ¹³C NMR

(100 MHz, DMSO) δ 156.9, 137.5, 128.6, 128.4, 126.0, 98.7, 63.7, 41.9, 36.6, 23.2, 21.4. HRMS (ESI) m/z calcd for C₁₃H₁₅ClN₂O₂Na⁺ [M + Na]⁺ = 289.0714, found = 289.0710.

(6aS,9aR)-6-(4-Bromophenyl)-6a-hydroxytetrahydro-1*H*-cyclopenta[4,5]imidazo [1,5-*b*]pyrazole-2,5(3*H*,6*H*)-dione (8):

A white solid; 64.6 mg; isolated yield = 92%; m.p. 129.4 – 129.8 °C; dr > 20:1. $[\alpha]^{21.0}_{D}$ = +120.01 (*c* 0.10, EA); HPLC (IG-3 column, *i*-propanol/*n*-hexane = 30/70, flow rate 1.0 mL/min, λ = 254 nm), product: t₁ = 4.59 min (major), t₂ = 5.22 min (minor), *ee* = 93%; ¹H NMR (400 MHz, DMSO) δ 11.86 (s, 1H), 7.66 (d, *J* = 8.9 Hz, 2H), 7.43 (d, *J* = 8.9 Hz, 2H), 3.21 – 3.07 (m, 2H), 2.35 – 2.01 (m, 4H), 1.94 – 1.70 (m, 2H). ¹³C NMR (100 MHz, DMSO) δ 174.1, 152.6, 135.2, 132.7, 125.5, 118.9, 105.1, 72.2, 38.9, 36.4, 36.0, 23.9. HRMS (ESI) m/z calcd for C₁₄H₁₄BrN₃O₃Na⁺ [M + Na]⁺ = 374.0111, found = 374.0122.

tert-Butyl ((3aS,6aR)-3-(4-bromophenyl)-3a-hydroxy-6a-(2-hydroxyethyl)-2-oxo hexahydrocyclopenta[d]imidazol-1(2H)-yl)carbamate (9):



A white solid; 79.2 mg; isolated yield = 87%; m.p. 141.4 – 141.8 °C; dr > 20:1. $[\alpha]^{21.0}_{D}$ = +134.01 (*c* 0.10, EA); HPLC (IG-3 column, *i*-propanol/*n*-hexane = 30/70, flow rate 1.0 mL/min, λ = 254 nm), product: t₁ = 4.59 min (major), t₂ = 5.22 min (minor), *ee* = 93%; ¹H NMR (400 MHz, DMSO) δ 8.95 – 8.42 (m, 1H), 7.58 – 7.48 (m, 4H), 7.04 (s, 1H), 5.56 (s, 1H), 3.75 – 3.61 (m, 1H), 3.58 – 3.51 (m, 1H), 2.04 – 1.76 (m, 4H), 1.71 – 1.48 (m, 4H), 1.42 (s, 9H) ¹³C NMR (100 MHz, DMSO) δ 156.3, 154.8, 137.2, 131.7, 127.1, 117.6, 96.8, 80.2,

72.0, 57.0, 38.4, 35.5, 35.5, 28.5, 21.7. HRMS (ESI) m/z calcd for $C_{19}H_{26}BrN_3O_5Na^+$ [M + Na]⁺ = 478.0948, found = 478.0945.

4. Determination of the absolute configuration

X-ray single crystal data for compound 3b to determine the absolute

configuration



CCDC:2408880

Table 1 Crystal data and structure refinement for 202307171_auto.

Identification code	202307171_auto
Empirical formula	$C_{18}H_{27}N_3O_5$
Formula weight	365.42
Temperature/K	293(2)
Crystal system	monoclinic
Space group	P21
a/Å	7.5356(3)
b/Å	11.5149(5)
c/Å	11.9517(5)
$\alpha/^{\circ}$	90
β/°	105.104(4)
$\gamma/^{\circ}$	90
Volume/Å ³	1001.25(8)
Z	2
$\rho_{calc}g/cm^3$	1.212
μ/mm^{-1}	0.734
F(000)	392.0
Crystal size/mm ³	$0.17 \times 0.12 \times 0.08$
Radiation	$CuK\alpha$ ($\lambda = 1.54184$)
2Θrange for data collection/°	7.662 to 141.03
Index ranges	$-9 \le h \le 9, -14 \le k \le 12, -14 \le l \le 14$
Reflections collected	10486
Independent reflections	3515 [$R_{int} = 0.0378$, $R_{sigma} = 0.0416$]
Data/restraints/parameters	3515/1/248
Goodness-of-fit on F ²	1.039
Final R indexes [I>=2 σ (I)]	$R_1 \!=\! 0.0380, wR_2 \!=\! 0.0975$

Final R indexes [all data]	$R_1 = 0.0414, wR_2 = 0.1013$
Largest diff. peak/hole / e Å ⁻³	0.16/-0.14
Flack parameter	0.01(15)

5. NMR spectra





¹H NMR (400 MHz, DMSO-*d*₆)







¹⁹F NMR (376 MHz, DMSO-*d*₆)

















¹³C NMR (100 MHz, DMSO-*d*₆)







¹³C NMR (100 MHz, DMSO-*d*₆)



¹³C NMR (100 MHz, DMSO-*d*₆)








S38











¹³C NMR (100 MHz, DMSO-*d*₆)





S44









¹³C NMR (100 MHz, DMSO-*d*₆)















































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

¹H NMR (400 MHz, DMSO-*d*₆)









6. HPLC spectra





Signal:	VWD1A,W	avelength=254 nm				
RT [min]	Туре	Width [min]	Area	Height	Area%	Name
5.668	MM m	0.80	6856.74	601.47	49.72	
6.737	MM m	0.78	6935.21	560.49	50.28	
		Sum	13791.95			



Signal:	VWD1A,W	avelength=254 nm				
RT [min]	Туре	Width [min]	Area	Height	Area%	Name
5.723	MM m	0.44	59.00	5.76	2.53	
6.774	MM m	1.01	2271.96	185.45	97.47	
		Sum	2330.95			





Signal:	VWD1A,W	avelength=254 nm	254 nm			
RT [min]	Туре	Width [min]	Area	Height	Area%	Name
6.555	MM m	1.72	481.16	13.28	49.56	
14.848	MB m	4.86	489.71	3.94	50.44	
		Sum	970.87			



Signal:	VWD1A,W	avelength=254 nm				
RT [min]	Туре	Width [min]	Area	Height	Area%	Name
6.553	MM m	0.98	140.16	5.55	3.92	
14.592	MM m	5.61	3438.91	34.55	96.08	
		Sum	3579.07			







						-
Name	Area%	Height	Area	Width [min]	Туре	RT [min]
	49.31	20.25	277.92	0.64	MM m	5.670
	50.69	21.50	285.65	0.72	MM m	6.209
			563.56	Sum		



Signal:	VWD1A,W	avelength=254 nm				
RT [min]	Туре	Width [min]	Area	Height	Area%	Name
5.707	MM m	0.45	52.13	4.76	2.88	
6.204	MM m	0.88	1760.03	151.59	97.12	
		Sum	1812.15			





Area Percent Report

Sorted Multip Dilutic Use Mul	By lier on ltiplie	er & D	: : ilution	Signa 1.000 1.000 Factor w	l 0 0 ith ISTDs	
Signal Peak Re	1: VWI)1 A, Type	Waveleng Width	gth=254 n Area	m Height	Area
#	[min]		[min]	mAU *s	[mAU]	
2	6.145 7.762	BB	0.2574 0.2459	4348.564 4375.202	94 258.56021 15 269.90564	49.8473 50.1527



Area Percent Report

Sorted By Multiplier Dilution Use Multiplier & D	: : ilution	Signal 1.0000 1.0000 Factor wit?	h ISTDs	
Signal 1: VWD1 A, Peak RetTime Type # [min]	Wavelen Width [min]	gth=254 nm Area mAU *s	Height [mAU]	Area %
1 6.160 VB 2 7.768 VB	0.2746 0.2447	161.96577 4500.53271	9.03867 277.29105	3.4738 96.5262
Totals :		4662.49849	286.32971	






Signal:	VWD1A,Wavelength=254 nm

-					
RT [min]	Туре	Width [min]	Area	Height	Area%
7.493	MM m	0.90	2978.27	250.81	49.54
8.979	MM m	1.14	3033.66	163.61	50.46
		Sum	6011.93		



Signal:	VWD1A,W	avelength=254 nm				
RT [min]	Туре	Width [min]	Area	Height	Area%	Name
7.681	MM m	0.41	110.39	9.80	2.91	
9.155	MM m	1.22	3685.60	211.57	97.09	
		Sum	3795.99			





Signal:	VWD1A,W	avelength=254 nm				
RT [min]	Туре	Width [min]	Area	Height	Area%	Name
12.258	BM m	1.40	3483.32	121.51	49.38	
13.433	MM m	1.51	3570.85	121.42	50.62	
		Sum	7054.17			



•		5				
RT [min]	Туре	Width [min]	Area	Height	Area%	N
12.949	MM m	0.83	137.02	5.20	2.97	
13.778	MB m	2.30	4475.97	151.29	97.03	
		Sum	4612.99			





Signal:	VWD1A,W	A,Wavelength=254 nm				
RT [min]	Туре	Width [min]	Area	Height	Area%	Name
6.626	MM m	1.02	4290.86	321.72	50.49	
8.613	MM m	2.51	4208.17	87.54	49.51	
		Sum	8499.03			



Signal:	VWD1A,W	velength=254 nm				
RT [min]	Туре	Width [min]	Area	Height	Area%	Name
6.633	MM m	1.10	3413.22	260.14	96.41	
9.104	MM m	1.62	126.98	3.22	3.59	
		Sum	3540.20			





Signal:	VWD1A,W	avelength=254 nm				
RT [min]	Туре	Width [min]	Area	Height	Area%	Name
7.770	MM m	2.12	412.95	29.32	50.18	
10.707	MM m	1.52	409.91	18.82	49.82	
		Sum	822.85			



RT [min]	Туре	Width [min]	Area	Height	Area%	
7.376	MM m	0.57	10.87	0.92	1.14	
10.597	MM m	1.62	944.96	42.42	98.86	
		Sum	955.84			





Signal:	VWD1A,W	avelength=250 nm				
RT [min]	Туре	Width [min]	Area	Height	Area%	Name
8.226	MM m	1.85	362.84	17.26	50.10	
8.781	MM m	2.02	361.38	17.11	49.90	
		Sum	724.22			



Nam	Area%	Height	Area	Width [min]	Туре	RT [min]
	4.46	5.00	79.35	0.49	MM m	8.769
	95.54	92.83	1698.95	1.64	MM m	9.268
			1778.30	Sum		





Signal:	VWD1A,W	avelength=254 nm				
RT [min]	Туре	Width [min]	Area	Height	Area%	Name
7.720	MM m	0.74	1554.41	130.42	50.44	
10.391	MM m	1.35	1527.53	68.00	49.56	
		Sum	3081.94			



Signal:	VWD1A,W	avelength=254 nm				
RT [min]	Туре	Width [min]	Area	Height	Area%	Name
7.684	MM m	0.39	105.31	9.66	1.04	
10.346	MM m	1.51	9980.48	459.31	98.96	
		Sum	10085.79			





Signal:	VWD1A,W					
RT [min]	Туре	Width [min]	Area	Height	Area%	Name
5.562	MM m	0.71	1208.48	131.43	49.58	
6.443	MM m	0.80	1229.10	102.91	50.42	
		Sum	2437.58			



Signal:	VVVD1A,VV	avelength=250 nm				
RT [min]	Туре	Width [min]	Area	Height	Area%	Name
5.363	MM m	0.33	178.55	20.42	4.24	
6.249	MM m	1.02	4028.62	318.85	95.76	
		Sum	4207.17			









Signal:	VWD1A,W	avelength=250 nm				
RT [min]	Туре	Width [min]	Area	Height	Area%	Name
11.943	BM m	0.65	128.48	6.71	3.64	
15.070	BBA	2.33	3405.63	129.23	96.36	
		Sum	3534.11			





Signal:	VWD1A,W	avelength=254 nm				
RT [min]	Туре	Width [min]	Area	Height	Area%	Name
9.164	MM m	1.54	5652.65	241.42	49.32	
11.596	MM m	1.59	5808.45	250.79	50.68	
		Sum	11461.11			







Signal:	VWD1A,W	avelength=250 nm				
RT [min]	Туре	Width [min]	Area	Height	Area%	Name
14.779	BB	2.55	491.98	14.15	50.57	
19.028	BB	3.61	480.83	8.03	49.43	
		Sum	972.81			







Signal:	VWD1A,Wavelength=250 nm						
RT [min]	Туре	Width [min]	Area	Height	Area%	Name	
5.885	MM m	0.84	739.60	61.97	50.60		
8.944	MM m	1.52	722.18	35.91	49.40		
		Sum	1461.78				



Signal:	VWD1A,W	avelength=250 nm					
RT [min]	Туре	Width [min]	Area	Height	Area%	Na	me
5.888	MM m	0.44	103.31	9.76	2.98		
8.913	MM m	2.10	3361.54	164.88	97.02		
		Sum	3464.85				





Signal:	VWD1A,W	avelength=250 nm				
RT [min]	Туре	Width [min]	Area	Height	Area%	Name
5.331	MM m	1.31	459.74	39.89	49.89	
7.807	MM m	1.15	461.84	24.85	50.11	
		Sum	921.58			



Signal:	VWD1A,W	avelength=250 nm				
RT [min]	Туре	Width [min]	Area	Height	Area%	Name
5.348	MM m	0.49	92.02	8.21	2.40	
7.800	MM m	1.70	3740.12	195.76	97.60	
		Sum	3832.14			





Signal:	VWD1A,W	/avelength=250 nm				
RT [min]	Туре	Width [min]	Area	Height	Area%	Name
5.119	MM m	0.58	345.18	40.84	50.12	
7.779	MM m	1.24	343.55	16.38	49.88	
		Sum	688.73			



Signal:	VWD1A,W	avelength=250 nm				
RT [min]	Туре	Width [min]	Area	Height	Area%	Name
5.087	MM m	0.34	80.38	9.94	2.90	
7.693	MM m	1.65	2689.66	117.85	97.10	
		Sum	2770.04			





Signal:	VWD1A,W	avelength=250 nm				
RT [min]	Туре	Width [min]	Area	Height	Area%	Name
4.434	MM m	0.96	74.26	9.69	49.25	
6.915	MM m	1.02	76.52	3.04	50.75	
		Sum	150.78			



Signal:	VWD1A,W	avelength=250 nm				
RT [min]	Туре	Width [min]	Area	Height	Area%	Name
4.441	MM m	0.25	26.54	4.00	2.02	
6.888	6.888 MM m 1	1.96	1289.28	53.62	97.98	
		Sum	1315.82			





Signal:	VWD1A,Wavelength=250 nm							
RT [min]	Туре	Width [min]	Area	Height	Area%	Name		
5.817	MM m	1.31	241.95	18.95	49.96			
19.179	BM m	4.36	242.33	2.32	50.04			
		Sum	484.28					



Name	Area%	Height	Area	Width [min]	Туре	RT [min]
	3.34	2.94	37.76	0.89	MM m	5.834
	96.66	10.66	1094.45	7.58	MM m	19.101
			1132.21	Sum		







Signal 1: VWD1 A, Wavelength=254 nm





Area Percent Report

Sorted By	:	Signal	
Multiplier	:	1.0000	
Dilution	:	1.0000	
Use Multiplier	& Dilution	Factor with	ISTDs

Signal 1: VWD1 A, Wavelength=254 nm

Peak	RetTime	Type	Width	A	rea	Heig	ht	Area
+	[min]		[min]	mAU	*s	[mAU]	8
1	6.927	MM	0.1885	8341	.80273	737.4	6411	95.7837
2	15.501	MM	0.4519	367	.19839	13.5	4283	4.2163





Signal:	VWD1A,W					
RT [min]	Туре	Width [min]	Area	Height	Area%	Name
7.158	MM m	0.67	387.68	32.60	50.69	
10.518	MM m	3.65	377.09	20.75	49.31	
		Sum	764.77			



•					
RT [min]	Туре	Width [min]	Area	Height	Area%
7.167	MM m	0.45	118.41	10.72	12.30
10.538	MM m	1.80	843.95	46.39	87.70
		Sum	962.36		
10.538	MM m	1.80 Sum	843.95 962.36	46.39	87.70





Signal:	VWD1A,Wavelength=250 nm							
RT [min]	Туре	Width [min]	Area	Height	Area%	Name		
5.777	MM m	0.51	39.08	3.84	49.94			
6.686	MM m	0.63	39.18	3.31	50.06			
		Sum	78.26					



Signal:	VWD1A,W	avelength=250 nm				
RT [min]	Туре	Width [min]	Area	Height	Area%	Name
5.831	MM m	1.01	413.90	37.51	95.91	
6.727	MM m	0.36	17.65	1.61	4.09	
		Sum	431.55			





Signal:	VWD1A,W	avelength=250 nm				
RT [min]	Туре	Width [min]	Area	Height	Area%	Name
10.138	MM m	4.07	826.54	7.48	50.55	
15.328	MM m	10.35	808.50	2.90	49.45	
		Sum	1635.04			







Signal:	VWD1A,Wavelength=250 nm							
RT [min]	Туре	Width [min]	Area	Height	Area%	Name		
4.170	MM m	0.58	459.76	48.99	49.77			
4.641	MM m	0.91	463.95	48.30	50.23			
		Sum	923.71					



Signal:	VWD1A,W	avelength=250 nm				
RT [min]	Туре	Width [min]	Area	Height	Area%	Name
4.179	MM m	0.28	212.20	25.84	4.78	
4.661	MM m	1.27	4223.58	445.91	95.22	
		Sum	4435.78			





Signal:	VWD1A,W	avelength=250 nm				
RT [min]	Туре	Width [min]	Area	Height	Area%	Name
4.449	MM m	0.77	326.40	33.71	50.24	
8.545	MM m	1.00	323.34	16.96	49.76	
		Sum	649.74			



4745.49

Sum





Signal:	VWD1A,W					
RT [min]	Туре	Width [min]	Area	Height	Area%	Name
6.581	MM m	1.36	444.67	17.83	50.60	
7.472	MM m	1.17	434.18	13.11	49.40	
		Sum	878.84			



-					
RT [min]	Туре	Width [min]	Area	Height	Area%
6.585	MM m	0.68	103.43	5.53	2.11
7.439	MM m	4.16	4793.03	138.35	97.89
		Sum	4896.46		





Signal: VWD1A,Wavelength=250 nm

						-
Name	Area%	Height	Area	Width [min]	Туре	RT [min]
	50.04	47.95	414.53	0.59	MM m	6.029
	49.96	41.89	413.83	0.97	MM m	6.580
			828.36	Sum		







Signal:	VWD1A,W	avelength=254 nm				
RT [min]	Туре	Width [min]	Area	Height	Area%	Name
10.022	BV	1.00	825.50	51.94	50.27	
11.033	VB	1.69	816.73	33.81	49.73	
		Sum	1642.23			



						•
Name	Area%	Height	Area	Width [min]	Туре	RT [min]
	96.46	260.59	4188.05	1.30	MM m	10.026
	3.54	6.43	153.53	0.92	MM m	11.076
			4341.58	Sum		





Signal:	VWD1A,W	avelength=250 nm				
RT [min]	Туре	Width [min]	Area	Height	Area%	Name
10.843	MM m	1.74	2733.25	138.92	49.74	
12.522	MM m	2.15	2761.42	110.40	50.26	
		Sum	5494.67			



RT [min]	Туре	Width [min]	Area	Height	Area%	Name
10.835	MM m	2.10	40150.59	1944.78	96.51	
12.654	MM m	1.45	1451.79	59.50	3.49	
		Sum	41602.39			





Signal:	VWD1A,W	avelength=250 nm				
RT [min]	Туре	Width [min]	Area	Height	Area%	Name
14.522	MM m	1.92	2869.93	83.76	49.82	
15.706	MM m	2.82	2890.16	93.78	50.18	
		Sum	5760.10			



Signal:	VWD1A,W	avelength=250 nm				
RT [min]	Туре	Width [min]	Area	Height	Area%	Name
14.556	MM m	2.27	6742.03	195.10	98.13	
15.757	MM m	0.83	128.49	4.63	1.87	
		Sum	6870.52			





Signal:	VWD1A,W	avelength=250 nm				
RT [min]	Туре	Width [min]	Area	Height	Area%	Name
16.981	MM m	1.30	2885.21	95.06	49.51	
18.124	MM m	1.53	2942.80	85.36	50.49	
		Sum	5828.00			



Signal:	VWD1A,W	avelength=250 nm				
RT [min]	Туре	Width [min]	Area	Height	Area%	Name
17.414	MM m	2.22	4203.36	129.12	96.92	
18.337	MM m	1.54	133.65	3.34	3.08	
		Sum	4337.00			





Signal:	VWD1A,W	avelength=250 nm				
RT [min]	Туре	Width [min]	Area	Height	Area%	Name
19.511	MM m	2.63	770.94	17.05	49.81	
21.538	MM m	1.89	776.75	19.90	50.19	
		Sum	1547.69			







Signal:	VWD1A,W	avelength=250 nm				
RT [min]	Туре	Width [min]	Area	Height	Area%	Name
12.257	MM m	1.58	1236.29	60.74	49.84	
17.126	MM m	2.07	1244.07	40.04	50.16	
		Sum	2480.36			



Signal:	VWD1A,W	avelength=250 nm				
RT [min]	Туре	Width [min]	Area	Height	Area%	Name
12.211	MM m	3.11	1721.35	85.35	98.53	
17.040	MM m	0.97	25.69	0.91	1.47	
		Sum	1747.04			











Signal:	VWD1A,W					
RT [min]	Туре	Width [min]	Area	Height	Area%	Name
17.916	MM m	3.35	3921.34	110.79	49.30	
21.818	MM m	2.38	4032.16	91.00	50.70	
		Sum	7953.51			



Signal:	VWD1A,W					
RT [min]	Туре	Width [min]	Area	Height	Area%	Name
18.680	MM m	4.18	4089.32	107.23	95.26	
22.772	MM m	1.26	203.68	5.16	4.74	
		Sum	4293.00			

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Signal:	VWD1A,W	avelength=254 nm				
RT [min]	Туре	Width [min]	Area	Height	Area%	Name
7.147	MM m	1.46	4283.27	269.30	49.76	
9.228	MM m	1.31	4325.40	202.62	50.24	
		Sum	8608.67			



Signal:	VWD1A,W	avelength=254 nm				
RT [min]	Туре	Width [min]	Area	Height	Area%	Name
7.123	MM m	0.57	2.00	0.15	1.58	
9.225	MM m	1.33	124.59	5.15	98.42	
		Sum	126.60			





Signal:	VWD1A,W					
RT [min]	Туре	Width [min]	Area	Height	Area%	Name
15.729	MM m	1.59	4420.64	190.74	50.09	
18.181	MM m	1.44	4404.85	166.30	49.91	
		Sum	8825.50			



22010.25

Sum





Signal:	VWD1A Wavelength=250 nm
olgnai.	vvib iA, vavciciigui=200 iiii

						-
Nam	Area%	Height	Area	Width [min]	Туре	RT [min]
	18.96	213.76	2283.58	0.61	MM m	4.794
	31.12	321.06	3747.56	1.21	MM m	5.966
	18.82	123.18	2266.78	0.96	MM m	6.988
	31.09	223.29	3744.49	0.91	MM m	7.762
			12042.42	Sum		



Signal:	VWD1A,W	avelength=250 nm				
RT [min]	Туре	Width [min]	Area	Height	Area%	Name
4.720	MM m	0.87	13657.14	1574.89	45.36	
5.803	MM m	0.92	15630.04	1802.94	51.91	
6.825	MM m	0.50	360.19	28.57	1.20	
7.485	MM m	0.59	462.52	41.41	1.54	
		Sum	30109.88			





Signal:	VWD1A,W					
RT [min]	Туре	Width [min]	Area	Height	Area%	Name
4.860	MM m	0.48	531.54	71.42	49.75	
5.425	MM m	0.57	536.83	63.20	50.25	
		Sum	1068.37			







Signal:	VWD1A,Wavelength=250 nm		
RT [min]	Type	Width [min]	

				•		-
Name	Area%	Height	Area	Width [min]	Туре	RT [min]
	49.82	875.28	9572.76	0.69	MM m	4.528
	50.18	690.09	9641.50	1.29	MM m	5.064
			19214.26	Sum		



Signal:	VWD1A,W	avelength=250 nm				
RT [min]	Туре	Width [min]	Area	Height	Area%	Name
4.591	MM m	0.69	5120.39	478.33	96.58	
5.224	MM m	0.45	181.45	12.18	3.42	
		Sum	5301.84			








•						
RT [min]	Туре	Width [min]	Area	Height	Area%	
4.342	MM m	0.36	798.38	116.50	3.49	
6.913	MM m	2.26	22057.49	1553.86	96.51	
		Sum	22855.87			

7. References

[1] Liu, B.; Li, K. N.; Luo, S. W.; Huang, J. Z.; Pang, K.; Gong, L. Z. J. Am. Chem. Soc. 2013, 135, 3323–3326.
[2] Rama, H.; Samir Z. Z. Org. Biomol. Chem., 2011, 9, 3396.