Oxyenamides as Versatile Building Blocks for a Highly Stereoselective One-Pot Synthesis of the 1,3-Diamino-2-ol-Scaffold Containing Three Continuous Stereocenters

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1 General Information

**Experimental methods.** Unless otherwise mentioned, all reactions were carried out under nitrogen atmosphere in flame dried glassware applying standard Schlenk techniques. All yields refer to isolated yields of compounds estimated to be >95% pure as determined by $^1$H-NMR.

**Chromatography.** Flash column chromatography was performed using a puriflash XS 420+ Flash purifier machine from Interchim with prepacked flash columns (Puriflash_SilicaHP_30μm_F0012, Puriflash_SilicaHP_30μm_F0025 or Puriflash_SilicaHP_30μm_F0040) and the respectively specified solvent mixture. All yields refer to isolated yields of compounds estimated to be >95% pure as determined by $^1$H NMR. Thin layer chromatography was performed on aluminum sheets coated with SiO$_2$ (TLC silica gel 60 F254). The spots were visualized by ultraviolet light, iodine, cerium ammonium molybdate (CAM) or vanillin.

**Solvents.** Solvents for reactions and column chromatography were obtained from different commercial suppliers in >97% purity and used as received. Solvents for column chromatography were technical standard.

**Materials.** All starting materials obtained from commercial sources were used without further purification. Anhydrous BF$_3$·OEt$_2$ was obtained from different providers and used directly. Prolonged storage times were avoided.

*N*-Acylimine precursors were synthesized from the corresponding amides and aldehydes using the previously reported protocol of Halli *et al.*[1]

**Analytical Data and Instrumentation**

NMR spectroscopy Proton nuclear magnetic resonance spectra ($^1$H NMR) and carbon spectra ($^{13}$C NMR) were recorded at 400 or 600 MHz ($^1$H) and 101 MHz ($^{13}$C), respectively. Chemical shifts are reported as $\delta$ - values relative to the residual CDCl$_3$ ($\delta = 7.26$ ppm for $^1$H and $\delta = 77.16$ ppm for $^{13}$C), DMSO-d$_6$ ($\delta = 2.50$ ppm for 1H and $\delta = 39.51$ ppm for $^{13}$C). Coupling constants ($J$) are given in Hz and multiplicities of the signals are abbreviated as follows: s = singlet; d = doublet; t = triplet; q = quartet; sp = septet; m = multiplet; dd = doublet of doublets and dt = doublet of triplets dqd = doublet of quartets of doublets.

**Melting points.** Melting points are reported uncorrected.
Mass spectrometry. Mass spectra (MS) were measured using electrospray ionization (ESI) techniques. High resolution mass spectra (HRMS) were measured using electron ionization mass spectroscopy (EI-MS-TOF).

Infrared spectroscopy. Infrared spectra (IR) of neat substances were recorded on a FT-IR (Fourier transform infrared spectroscopy) spectrometer equipped with a diamond universal ATR sampling technique (attenuated total reflectance). The absorption bands are reported in wave numbers (cm\(^{-1}\)).

Elemental analysis. Elemental analyses (CHN) were performed with a vario Micro cube.

Diastereomeric ratio. The diastereomeric ratios (dr) were determined via \(^1\)H-NMR analysis both for the crude product after aqueous workup and after isolation via column chromatography. A diastereomeric ratio of \(dr > 98:2\) indicates that no other isomer was observed by \(^1\)H NMR. Yields refer to isolated yields of the analytically pure 1,2-syn-2,3-anti-1,3-diamin-2-ol (\(dr > 98:2\)). If other diastereomers could be isolated, a combined yield is given in addition. Minor diastereomers were not fully characterized. In some cases no minor isomers could be isolated after column chromatography, although their formation was observed via NMR analysis of the crude reaction mixture. Presumably, small amounts of the side products were lost during column chromatography.

Crystal structure determinations.

Data for 1c, 5b and 5c (CCDC 2087484, 2087485, 2087486) were collected on a STOE IPDS II two-circle diffractometer with a Genix Microfocus tube with mirror optics using MoK\(\alpha\) radiation (\(\lambda = 0.71073\) Å). The data were scaled using the frame scaling procedure in the X-AREA program system (Stoe & Cie, 2002)[2]. The structures were solved using the software programs SHELXS-2018/3, and the positions of all non-hydrogen atoms were refined with SHELXL-2018/3.[3]

Data for 6a, 7a, 7c, 7g, 7h and 7i (CCDC 2097900, 2097895, 2097896, 2097898, 2097897, 2097899) were collected at 150.0(1) K on a Gemini S Ultra by Rigaku Oxford Diffraction, equipped with a molybdenum (\(\lambda = 0.71073\) Å) and a copper (\(\lambda = 1.54184\) Å) radiation source and a low-temperature control device. Due to the positioning of the two sources in the device, data collection is somewhat limited to smaller angles, which may result in alerts in some checkcif files. Absorption correction was done with CrysAlis Pro 1.171.38.41 and 1.171.40.67a, respectively. All structures were solved using the software programs SHELXS-2018/3, and the positions of all non-hydrogen atoms were refined with SHELXL-2018/3.[3]
2 Preparation and analytical data

2.1 Preparation of the N-protected aminoalcohols

**Typical procedure 1 (TP1)**

![Chemical structure diagram](image)

To a solution of ethanolamine (1.0 equiv) and Et$_3$N (1.0 equiv) in dichlormethane (3 mL/mmol) was added dropwise the corresponding acyl chloride or acid anhydride (1.1 equiv) at 0 °C. After stirring for 3 h at room temperature, the reaction was quenched with saturated aqueous NH$_4$Cl (100 mL) and the mixture was extracted with CH$_2$Cl$_2$ (3x 100 mL). The combined organic layers were dried over Na$_2$SO$_4$, filtered and the solvents were evaporated under reduced pressure. Purification of the crude residue by flash column chromatography (n-hexane/EtOAc) afforded the analytically pure product.[4]

2.1.1 N-(2-hydroxyethyl)benzamide S1a

Prepared according to TP1 from ethanolamine (3.1 mL, 50 mmol, 1.0 equiv), Et$_3$N (9.0 mL, 55 mmol, 1.1 equiv) and benzoyl chloride (5.8 mL, 50.0 mmol, 1.0 equiv) in a total of 200 mL dichlormethane. Purification of the crude residue by flash column chromatography (n-hexane/EtOAc = 1:1 → 1:9) afforded the analytically pure product as a colorless solid (5.26 g, 64%). Analytical data are in accordance with the literature.[4]

**Analytical data:**

- **R$_f$** (n-hexane:EtOAc = 1:1) 0.07
- **m.p.** 62-64 °C
- **$^1$H NMR** (400 MHz, Chloroform-d) δ = 7.82 – 7.67 (m, 2H), 7.48 – 7.41 (m, 1H), 7.39 – 7.31 (m, 2H), 7.14 (d, J=6.2, 1H), 3.82 – 3.68 (m, 3H), 3.55 (q, J=5.2, 2H).
- **$^{13}$C-NMR** (101 MHz, Chloroform-d) δ = 168.9, 134.1, 131.8, 128.6, 127.1, 62.0, 42.9.
- **IR (ATR, v in cm$^{-1}$):** 3336 (m), 3272 (w), 2946 (w), 2775 (w), 1632 (s), 1576 (m), 1542 (s), 1488 (m), 1417 (m), 1311 (m), 1229 (m), 1185 (w), 1056 (s), 933 (w) 899 (w), 804 (w), 695 (s).
- **MS (ESI) m/z** calcd for C$_9$H$_{12}$NO$_2$Na 188.1 [M+Na]$^+$, found 188.1 [M+Na]$^+$.

2.1.2 tert-butyl (2-hydroxyethyl)carbamate S1b

Prepared according to TP1 from ethanolamine (3.1 mL, 50 mmol, 1.0 equiv), Et$_3$N (9.0 mL, 55 mmol, 1.1 equiv) and tert-butyl chloroformate (5.8 mL, 50.0 mmol, 1.0 equiv) in a total of 200 mL dichlormethane. Purification of the crude residue by flash column chromatography (n-hexane/EtOAc = 1:1 → 1:9) afforded the analytically pure product as a colorless solid (9.16 g, 94%). Analytical data are in accordance with the literature.[4]
Prepared according to TP1 from ethanolamine (1.2 mL, 20 mmol, 1.0 equiv), Et₃N (2.8 mL, 20 mmol, 1.0 equiv) and di-tert-butyl dicarbonate (4.2 mL, 22.0 mmol, 1.1 equiv) in a total of 60 mL dichloromethane. Purification of the crude residue by flash column chromatography (n-hexane/EtOAc = 1:1) afforded the analytically pure product as a colorless liquid (2.20 g, 68%). Analytical data are in accordance with the literature.⁵

Rᵣ (n-hexane:EtOAc = 1:1) 0.27.

¹H NMR (400 MHz, Chloroform-d) δ = 3.68 (dd, J=5.6, 4.6, 2H), 3.27 (t, J=5.1, 2H), 1.44 (s, 9H).

¹³C-NMR (101 MHz, Chloroform-d) δ = 156.9, 79.9, 62.5, 43.4, 28.5.

IR (ATR, v in cm⁻¹): 3352 (w), 2977 (w), 2877 (w), 1687 (s), 1519 (s), 1454 (w), 1392 (m), 1366 (s), 1274 (s), 1249 (s), 1161 (s), 1064 (m), 865 (w).

MS (ESI) m/z calcd for C₇H₁₅NO₃Na 184.1 [M+Na]⁺, found 184.1 [M+Na]⁺.

2.1.3 benzyl (2-hydroxyethyl)carbamate S1c

Prepared according to TP1 from ethanolamine (1.2 mL, 20 mmol, 1.0 equiv), Et₃N (2.8 mL, 20 mmol, 1.0 equiv) and benzyl chloroformate (3.8 mL, 22.0 mmol, 1.1 equiv) in a total of 60 mL dichloromethane. Purification of the crude residue by flash column chromatography (n-hexane/EtOAc = 1:1) afforded the analytically pure product as a colorless solid (2.60 g, 67%). Analytical data are in accordance with the literature.⁵

Rᵣ (n-hexane:EtOAc = 1:1) 0.19.

m.p. 63–65 °C

¹H NMR (400 MHz, Chloroform-d) δ = 7.44 – 7.28 (m, 5H), 5.30 (bs, 1H), 5.10 (s, 2H), 3.69 (t, J=5.1, 2H), 3.34 (d, J=5.3, 2H), 2.51 (s, 1H).

¹³C-NMR (101 MHz, Chloroform-d) δ = 157.3, 136.4, 128.6, 128.3, 128.2, 67.0, 62.2, 43.6.

IR (ATR, v in cm⁻¹): 3319 (m), 3061 (w), 2940 (w), 1690 (s), 1539 (s), 1449 (m), 1323 (w), 1262 (s), 1213 (m), 1148 (m), 1113 (w), 1058 (w), 1031 (m), 989 (m), 774 (m).

MS (ESI) m/z calcd C₁₀H₁₃NO₃Na 218.1 [M+Na]⁺, found 218.1 [M+Na]⁺.
Preparation and analytical data

2.2 Preparation of the aldehydes

Typical procedure 2 (TP2)

\[ \text{R}^1 \text{R}^2 \text{N} \text{H} \text{C} = \text{O} \]

To a solution of N-protected aminoalcohol \( S1 \) (1.0 equiv) in ethylacetate (5 mL/mmol) was added 2-iodoxybenzoic acid (2.0 equiv) in one portion. The resulting suspension was refluxed for 3 h. After TLC analysis showed complete consumption of the starting material the reaction mixture was filtered through a short plug of Celite and the residue washed with ethylacetate. The solvents were removed under reduced pressure and the crude product was dried for 2-3 h under oil pump vacuum (10\(^{-2}\) mbar) to afford the desired aldehyde. All aldehydes of type 2 are not stable and rapidly decompose upon prolonged storage. Therefore, all aldehydes were used directly without further purification.\(^{[7]}\)

2.2.1 \( N\)-(2-oxoethyl)benzamide \( 2a \)

Prepared according to TP2 from \( N\)-(2-hydroxyethyl)benzamide \( S1a \) (1.01 g, 6.10 mmol, 1.0 equiv), 2-iodoxybenzoic acid (3.42 g, 12.2 mmol, 2.0 equiv) in a total of 30 mL ethylacetate. Removal of the solvents afforded the crude aldehyde as a colorless liquid (990 mg, 99%). Analytical data are in accordance with the literature.\(^{[4]}\)

\( R_f \) (n-hexane:EtOAc = 3:7) 0.27.

\( ^1H \) NMR (400 MHz, Chloroform-\( d \)) \( \delta = 9.75 \) (s, 1H), 7.90 – 7.73 (m, 2H), 7.56 – 7.49 (m, 1H), 7.48 – 7.41 (m, 2H), 7.03 (s, 1H), 4.39 (d, \( J=4.8 \), 2H).

2.2.2 tert-butyl (2-oxoethyl)carbamate \( 2b \)

Prepared according to TP2 from tert-butyl (2-hydroxyethyl)carbamate \( S1b \) (708 mg, 4.39 mmol, 1.0 equiv), 2-iodoxybenzoic acid (2.46 g, 8.78 mmol, 2.0 equiv) in a total of 23 mL ethylacetate. Removal of the solvents afforded the crude aldehyde as a colorless liquid (640 mg, 92%). Analytical data are in accordance with the literature.\(^{[8]}\)

\( R_f \) (n-hexane:EtOAc = 1:1) 0.43.

\( ^1H \) NMR (400 MHz, Chloroform-\( d \)) \( \delta = 9.65 \) (s, 1H), 5.18 (s, 1H), 4.08 (d, \( J=5.1 \), 2H), 1.45 (s, 9H).
Preparation and analytical data

2.2.3 benzyl (2-oxoethyl)carbamate 2c

Prepared according to TP2 from benzyl (2-hydroxyethyl)carbamate S1c (1.01 g, 5.15 mmol, 1.0 equiv), 2-iodoxybenzoic acid (2.88 g, 10.3 mmol, 2.0 equiv) in a total of 25 mL ethylacetate. Removal of the solvents afforded the crude aldehyde as a colorless liquid (994 mg, 95%). Analytical data are in accordance with the literature.[9]

Rf (n-hexane:EtOAc = 1:1) 0.42.

^1H NMR (400 MHz, Chloroform-d) δ = 9.67 (s, 1H), 7.42 – 7.27 (m, 5H), 5.42 (s, 1H), 5.13 (s, 2H), 4.17 (d, J=5.0, 2H).

2.3 Preparation of the (Z)-Oxyenamides/(Z)-Oxyencarbamates

Typical procedure 3 (TP3)

To a stirred solution of triethylamine (1.7 equiv) and the corresponding acyl chloride (1.3 equiv) in dichloromethane (2 mL/mmol) was added dropwise a solution of the aldehyde 2a-c (1.0 equiv) in dichloromethane (2 mL/mmol) over 5 min. The reaction mixture was stirred for 1 h at room temperature. After TLC analysis showed complete consumption of the aldehyde, saturated NaHCO₃ solution was added (20 mL). The organic layers were separated and the aqueous phase was extracted with dichlormethane (2x 30 mL). The combined organic layers were dried over Na₂SO₄, filtered and the solvents were evaporated under reduced pressure. Purification by flash chromatography afforded the desired (Z)-oxyenamide/(Z)-oxyencarbamate 1a-e as analytically pure product. All oxyenamides of type 1 tend to decompose upon contact to any type of acid. Therefore, column chromatography was performed with 0.2 vol% NEt₃ as additive. CDCl₃ for NMR spectroscopy was passed through short plug of basic alumina before use.

2.3.1 (Z)-2-benzamidovinyl benzoate 1a

Prepared according to TP3 from N-(2-oxoethyl)benzamide 2a (774 mg, 4.74 mmol, 1.0 equiv), triethylamine (1.1 mL, 8.06 mmol, 1.7 equiv) and benzoyl chloride (0.72 mL, 6.16 mmol, 1.3 equiv).
Preparation and analytical data

a total of 20 mL dichlormethane. Purification by flash chromatography (n-hexane:EtOAc + 0.2 vol% NEt$_3$ = 19:1 → 9:1) afforded (Z)-2-benzamidovinyl benzoate 1a (927 mg, 73%) as colorless solid. 

R$_f$ (n-hexane:EtOAc = 4:1) 0.38.

m.p. 172-175 °C.

$^1$H NMR (400 MHz, Chloroform-d) $\delta$ = 8.17 – 8.06 (m, 2H), 7.97 (d, J=10.2, 1H), 7.91 – 7.81 (m, 2H), 7.68 – 7.62 (m, 1H), 7.61 – 7.56 (m, 1H), 7.55 – 7.48 (m, 4H), 7.11 (d, J=5.1, 1H), 6.86 (dd, J=10.7, 5.1, 1H).

$^{13}$C NMR (101 MHz, Chloroform-d) $\delta$ = 164.0, 162.7, 134.0, 133.4, 132.4, 130.0, 129.0, 128.9, 128.8, 127.3, 121.9, 109.5.

IR (ATR, $\nu$ in cm$^{-1}$): 3275 (w), 3110 (w), 3032 (w), 1723 (m), 1686 (w), 1643 (m), 1601 (w), 1580 (w), 1519 (s), 1484 (s), 1451 (w), 1249 (s), 1146 (m), 1113 (s), 1093 (s), 1068 (s), 798 (w), 687 (s).

MS (ESI) m/z calcd for C$_{16}$H$_{13}$NO$_3$Na 290.1 [M+Na]$^+$, found 290.2 [M+Na]$^+$.

HRMS (EI) m/z calcd for C$_{16}$H$_{13}$NO$_3$ 267.0895 [M]$^+$, found 267.0901 [M]$^+$.

2.3.2 (Z)-2-benzamidovinyl pivalate 1b

Prepared according to TP3 from N-(2-oxoethyl)benzamide 2a (721 mg, 4.42 mmol, 1.0 equiv), triethylamine (1.04 mL, 7.51 mmol, 1.7 equiv) and pivaloyl chloride (0.71 mL, 5.75 mmol, 1.3 equiv) in a total of 20 mL dichlormethane. Purification by flash chromatography (n-hexane:EtOAc + 0.2 vol% NEt$_3$ = 19:1 → 9:1) afforded (Z)-2-benzamidovinyl pivalate 1b (609 mg, 56%) as colorless solid.

R$_f$ (n-hexane:EtOAc = 4:1) 0.45.

m.p. 92-94 °C.

$^1$H NMR (400 MHz, Chloroform-d) $\delta$ = 7.94 – 7.70 (m, 3H), 7.61 – 7.54 (m, 1H), 7.53 – 7.42 (m, 2H), 6.90 (d, J=5.0, 1H), 6.75 (dd, J=10.6, 5.0, 1H), 1.32 (s, 9H).

$^{13}$C NMR (101 MHz, Chloroform-d) $\delta$ = 174.1, 163.6, 133.4, 132.4, 129.1, 127.1, 127.2, 122.0, 108.9, 39.2, 27.3.

IR (ATR, $\nu$ in cm$^{-1}$): 3345 (w), 2984 (w), 1687 (w), 1478 (s), 1395 (w), 1364 (w), 1272 (s), 1124 (s), 1026 (w), 885 (m), 751 (m), 717 (m), 694 (m).

MS (ESI) m/z calcd for C$_{14}$H$_{17}$NO$_3$Na 270.1 [M+Na]$^+$, found 270.1 [M+Na]$^+$.

HRMS (EI) m/z calcd for C$_{14}$H$_{17}$NO$_3$ 247.1208 [M]$^+$, found 247.1206 [M]$^+$.

2.3.3 (Z)-2-benzamidovinyl acetate 1c

Prepared according to TP3 from N-(2-oxoethyl)benzamide 2a (721 mg, 4.42 mmol, 1.0 equiv), triethylamine (1.04 mL, 7.51 mmol, 1.7 equiv) and pivaloyl chloride (0.71 mL, 5.75 mmol, 1.3 equiv) in a total of 20 mL dichlormethane. Purification by flash chromatography (n-hexane:EtOAc + 0.2 vol% NEt$_3$ = 19:1 → 9:1) afforded (Z)-2-benzamidovinyl pivalate 1b (609 mg, 56%) as colorless solid.

R$_f$ (n-hexane:EtOAc = 4:1) 0.45.

m.p. 92-94 °C.

$^1$H NMR (400 MHz, Chloroform-d) $\delta$ = 7.94 – 7.70 (m, 3H), 7.61 – 7.54 (m, 1H), 7.53 – 7.42 (m, 2H), 6.90 (d, J=5.0, 1H), 6.75 (dd, J=10.6, 5.0, 1H), 1.32 (s, 9H).

$^{13}$C NMR (101 MHz, Chloroform-d) $\delta$ = 174.1, 163.6, 133.4, 132.4, 129.1, 127.1, 127.2, 122.0, 108.9, 39.2, 27.3.

IR (ATR, $\nu$ in cm$^{-1}$): 3345 (w), 2984 (w), 1687 (w), 1478 (s), 1395 (w), 1364 (w), 1272 (s), 1124 (s), 1026 (w), 885 (m), 751 (m), 717 (m), 694 (m).

MS (ESI) m/z calcd for C$_{14}$H$_{17}$NO$_3$Na 270.1 [M+Na]$^+$, found 270.1 [M+Na]$^+$.

HRMS (EI) m/z calcd for C$_{14}$H$_{17}$NO$_3$ 247.1208 [M]$^+$, found 247.1206 [M]$^+$.
To a stirred solution of triethylamine (1.17 mL, 8.43 mmol, 1.7 equiv), 4-dimethylaminopyridine (122 mg, 0.992 mmol, 0.2 equiv) and acetic anhydride (0.58 mL, 7.44 mmol, 1.3 equiv) in dichloromethane (10 mL) was added dropwise a solution of the aldehyde 1a (810 mg, 4.96 mmol, 1.0 equiv) in dichloromethane (10 mL). The reaction mixture was stirred for 3 h at room temperature. After TLC analysis showed complete consumption of the aldehyde, saturated NaHCO₃ solution was added (20 mL). The organic layers were separated and the aqueous phase was extracted with dichloromethane (2 x 30 mL). The combined organic layers were dried over Na₂SO₄, filtered and the solvents were evaporated under reduced pressure. Purification by flash chromatography (n-hexane:EtOAc + 0.2 vol% NEt₃ = 9:1 → 4:1) afforded (Z)-2-benzamidovinyl acetate 1c (572 mg, 56%) as colorless solid.

Rᵣ (n-hexane:EtOAc = 4:1) 0.22.

dept=80-82 °C.

_1H NMR (400 MHz, Chloroform-d) δ = 7.97 – 7.78 (m, 3H), 7.60 – 7.51 (m, 1H), 7.52 – 7.43 (m, 2H), 6.90 (d, J=5.2, 1H), 6.71 (dd, J=10.7, 5.1, 1H), 2.22 (s, 3H).

_13C NMR (101 MHz, Chloroform-d) δ = 166.7, 164.0, 133.4, 132.4, 128.9, 127.3, 121.5, 108.6, 20.8.

IR (ATR, ν in cm⁻¹): 3255 (w), 3206 (w), 3221 (w), 1750 (m), 1702 (w), 1640 (s), 1603 (w), 1579 (w), 1514 (s), 1484 (s), 1362 (m), 1294 (m), 1207 (s), 1147 (s), 1116 (s), 1040 (m), 1028 (m), 878 (m), 756 (m), 682 (m).

MS (ESI) m/z calcld for C₁₁H₁₁NO₃Na 228.1 [M+Na]+, found 228.1 [M+Na]+.

HRMS (EI) m/z calcld for C₁₁H₁₁NO₃ 205.0739 [M]+, found 205.0740 [M]+.

2.3.4 (Z)-2-(((tert-butoxycarbonyl)amino)vinyl)benzoate 1d

Prepared according to TP3 from tert-butyl (2-oxoethyl)carbamate 2b (637 mg, 4.0 mmol, 1.0 equiv), triethylamine (0.95 mL, 6.80 mmol, 1.7 equiv) and benzoyl chloride (0.60 mL, 5.20 mmol, 1.3 equiv) in a total of 16 mL dichloromethane. Purification by flash chromatography (n-hexane:EtOAc + 0.2 vol% NEt₃ = 19:1 → 9:1) afforded (Z)-2-(((tert-butoxycarbonyl)amino)vinyl)benzoate 1d (567 mg, 54%) as colorless solid.

Rᵣ (n-hexane:EtOAc = 9:1) 0.43.

dept=143-144 °C.

_1H NMR (400 MHz, Chloroform-d) δ = 8.09 (dd, J=8.1, 1.5, 2H), 7.71 – 7.57 (m, 1H), 7.49 (dd, J=8.4, 7.1, 2H), 6.88 (d, J=5.0, 1H), 6.47 (d, J=11.2, 1H), 6.33 (dd, J=11.5, 4.8, 1H), 1.51 (s, 9H).

_13C NMR (101 MHz, Chloroform-d) δ = 162.9, 152.2, 133.8, 130.0, 129.0, 128.8, 119.2, 110.8, 81.3, 28.4.

IR (ATR, ν in cm⁻¹): 3295 (w), 3124 (w), 2982 (w), 1702 (s), 1700 (m), 1686 (s), 1602 (w), 1502 (s), 1494 (s), 1454 (m), 1369 (m), 1259 (s), 1240 (s), 1148 (s), 1094 (s), 1073 (s), 1027 (m), 886 (m), 704 (s).
MS (ESI) m/z calcd for C_{14}H_{17}NO_4Na 286.1 [M+Na]^+, found 286.2 [M+Na]^+.

HRMS (EI) m/z calcd for C_{14}H_{17}NO_3 263.1158 [M+H]^+, found 263.1159 [M+H]^+.

2.3.5 (Z)-2-(((benzoyloxy)carbonyl)amino)vinyl benzoate 1e

Prepared according to TP3 from benzyl (2-oxoethyl)carbamate 2c (945 mg, 4.89 mmol, 1.0 equiv), triethylamine (1.16 mL, 8.31 mmol, 1.7 equiv) and benzoyl chloride (0.74 mL, 6.36 mmol, 1.3 equiv) in a total of 20 mL dichloromethane. Purification by flash chromatography (n-hexane:EtOAc + 0.2 vol% NEt₃ = 19:1 → 9:1) afforded (Z)-2-(((benzoyloxy)carbonyl)amino)vinyl benzoate 1e (870 mg, 60%) as colorless solid. 

Rₐ (n-hexane:EtOAc = 9:1) 0.24.

m.p. 69-71 °C.

^1H NMR (400 MHz, Chloroform-d) δ = 8.20 – 7.98 (m, 2H), 7.68 – 7.54 (m, 1H), 7.48 (t, J=7.8, 2H), 7.44 – 7.27 (m, 5H), 7.01 – 6.80 (m, 1H), 6.71 (d, J=11.0, 1H), 6.38 (dd, J=11.0, 5.1, 1H), 5.20 (s, 2H).

^13C NMR (101 MHz, Chloroform-d) δ = 162.8, 153.1, 135.7, 133.9, 130.0, 128.8, 128.8, 128.7, 128.7, 119.9, 110.5, 67.9.

IR (ATR, ν in cm⁻¹): 3270 (w), 3128 (w), 3030 (w), 1729 (s), 1689 (s), 1601 (w), 1518 (s), 1450 (m), 1360 (w), 1228 (s), 1159 (m), 1100 (s), 1074 (s), 1026 (m), 906 (w), 741 (m), 696 (s).

MS (ESI) m/z calcd for C_{17}H_{25}NO_3 297.0997 [M]^+, found 297.0997 [M]^+.

2.4 Preparation of N,O-Acetals

Typical procedure 4 (TP4)

A flame dried and nitrogen flushed Schlenk tube, equipped with a septum and a magnetic stirrer, was charged with (Z)-oxenamide-/encarbamate 1a-e (1.0 equiv), N-acylimine precursor 3a (1.1 equiv) and dichloromethane (10 mL/mmol). The solution was cooled to -55 °C and SiCl₄ (2.0 equiv) was added dropwise. The resulting mixture was warmed to -10 °C within 2.5 h to 4 h. After TLC analysis of an aliquot showed complete consumption of the (Z)-oxenamide-/encarbamate, methanol (3 mL/mmol) was added at -10 °C. The resulting solution was warmed to room temperature and stirred for 10 min.
Saturated aqueous NH₄Cl (20 mL) was added and the organic layer was separated. The aqueous phase was extracted with dichloromethane (2x 25 mL). The combined organic layers were dried over Na₂SO₄ and the solvents were evaporated under reduced pressure. Purification by flash chromatography afforded the N,O-acetal as analytically pure product. All N,O-acteals 4a-e were only briefly characterized via ¹H-NMR and used directly as mixture of diastereomers in the subsequent transformations.

2.4.1 N,O-Acetal 4a

Prepared according to TP4 from (Z)-2-benzamidovinyl benzoate 1a (1.34 g, 5.0 mmol, 1.0 equiv), N-acylimine precursor 3a (1.33 g, 5.5 mmol, 1.1 equiv), SiCl₄ (1.15 mL, 10.0 mmol, 2.0 equiv) and methanol (15 mL) in a total of 50 mL dichloromethane. Purification by flash chromatography via puriflash XS 420+ machine, HP_15μm_F0040 flash column (n-hexane:EtOAc = 95:5 → 50:50) afforded the desired N,O-acetal 4a as a colorless foam (2.28 g, 90%, isolated dr = 70:30).

¹H NMR (400 MHz, Chloroform-d) δ = 8.09 – 8.01 (m, 1.4H), 8.00 – 7.93 (m, 0.6H), 7.80 – 7.78 (m, 0.6H), 7.73 – 7.63 (m, 3.4H), 7.61 – 7.29 (m, 14H), 7.10 (t, J=9.6, 1.3H), 6.81 (d, J=9.8, 0.3H), 5.88 – 5.77 (m, 1H), 5.71 – 5.65 (m, 1H), 5.55 (dd, J=9.9, 6.3, 0.3H), 5.48 (dd, J=9.5, 3.1, 0.7H), 3.45 (s, 0.9H), 3.39 (s, 2.1H). (peaks not assigned to single stereoisomers)

2.4.2 N,O-Acetal 4b

Prepared according to TP4 from (Z)-2-benzamidovinyl pivalate 1b (742 mg, 3.0 mmol, 1.0 equiv), N-acylimine precursor 3a (796 mg, 3.3 mmol, 1.1 equiv), SiCl₄ (0.69 mL, 6.0 mmol, 2.0 equiv) and methanol (9 mL) in a total of 30 mL dichloromethane. Purification by flash chromatography via puriflash XS 420+ machine, HP_15μm_F0040 flash column (n-hexane:EtOAc = 93:7 → 30:70) afforded the desired N,O-acetal 4b as a colorless foam (1.24 g, 85%, isolated dr = 83:17).

¹H NMR (400 MHz, Chloroform-d) δ = 7.87 – 7.81 (m, 0.4H), 7.80 – 7.71 (m, 2H), 7.70 – 7.62 (m, 1.6H), 7.58 – 7.29 (m, 11H), 7.15 (d, J=9.3, 0.2H), 7.08 (d, J=8.7, 1.8H), 6.85 (d, J=9.6, 0.8H), 6.66 (d, J=8.8, 0.2H), 5.77 (dd, J=9.2, 3.4, 0.2H), 5.70 (dd, J=8.7, 6.4, 0.8H), 5.45 – 5.33 (m, 2H), 3.43 (s, 0.5H), 3.36 (s, 1.5H), 1.17 (s, 7.5H), 1.05 (s, 1.5H). (peaks not assigned to single stereoisomers)
2.4.3  *N,O*-Acetal 4c

Prepared according to TP4 from (Z)-2-benzamidovinyl acetate 1c (616 mg, 3.0 mmol, 1.0 equiv), *N*-acylimine precursor 3a (796 mg, 3.3 mmol, 1.1 equiv), SiCl₄ (0.69 mL, 6.0 mmol, 2.0 equiv) and methanol (9 mL) in a total of 30 mL dichloromethane. Purification by flash chromatography via puriflash XS 420+ machine, HP_15μm_F0040 flash column (n-hexane:EtOAc = 95:5 → 50:50) afforded the desired *N,O*-acetal 4c as a colorless foam (1.18 g, 88%, isolated dr = 67:33).

**¹H NMR** (400 MHz, Chloroform-d) δ = 7.92 – 7.67 (m, 4H), 7.63 – 7.29 (m, 11H), 7.03 (dd, ě=12.9, 9.0, 1H), 6.92 (d, ě=9.5, 0.5H), 6.76 (d, ě=9.0, 0.5iH), 5.71 (ddd, ě=19.3, 9.0, 5.3, 1H), 5.49 – 5.36 (m, 2H), 3.41 (s, 1.6H), 3.37 (s, 1.4H), 2.13 (s, 1.4H), 2.03 (s, 1.6H). *(peaks not assigned to single stereoisomers)*

2.4.4  *N,O*-Acetal 4d

Prepared according to TP4 from (Z)-2-((tert-butoxycarbonyl)amino)vinyl benzoate 1d (132 mg, 0.5 mmol, 1.0 equiv), *N*-acylimine precursor 3a (133 mg, 0.55 mmol, 1.1 equiv), SiCl₄ (0.12 mL, 1.0 mmol, 2.0 equiv) and methanol (3.5 mL) in a total of 5 mL dichloromethane. Purification by flash chromatography via puriflash XS 420+ machine, HP_15μm_F0025 flash column (n-hexane:EtOAc = 95:5 → 60:40) afforded the desired *N,O*-acetal 4d as a colorless foam (214 mg, 85%, isolated dr = 60:40).

**¹H NMR** (400 MHz, Chloroform-d) δ = 8.09 (d, ě=7.5, 0.8H), 8.01 (d, ě=7.5, 1.2H), 7.87 – 7.72 (m, 1H), 7.64 (d, ě=7.6, 0.8H), 7.60 – 7.52 (m, 1H), 7.52 – 7.27 (m, 1H), 7.09 (d, ě=8.5, 0.2H), 5.75 – 5.62 (m, 1H), 5.58 (t, ě=5.8, 1H), 5.18 – 5.10 (m, 1H), 4.89 (dd, ě=10.6, 5.9, 0.6H), 4.79 (dd, ě=10.4, 2.7, 0.4H), 3.35 (s, 1.5H), 3.30 (s, 1.5H), 1.38 (s, 3H), 1.34 (s, 6H). *(peaks not assigned to single stereoisomers)*

2.4.5  *N,O*-Acetal 4e

Prepared according to TP4 from (Z)-2-(((benzyloxy)carbonyl)amino)vinyl benzoate 1e (297 mg, 1.0 mmol, 1.0 equiv), *N*-acylimine precursor 3a (265 mg, 1.1 mmol, 1.1 equiv), SiCl₄ (0.23 mL, 2.0 mmol, 2.0 equiv) and methanol (7 mL) in a total of 10 mL dichloromethane. Purification by flash...
chromatography via puriflash XS 420+ machine, HP_15μm_F0025 flash column (n-hexane:EtOAc = 95:5 → 60:40) afforded the desired N,O-acetal 4e as a colorless foam (432 mg, 80%, isolated dr = 52:48).

$^1$H NMR (400 MHz, Chloroform-d) δ = 8.05 (d, J=7.6, 1H), 7.99 (d, J=7.7, 1H), 7.75 (d, J=7.6, 0.8H), 7.64 – 7.55 (m, 2.2H), 7.52 – 7.27 (m, 14H), 7.24 – 7.19 (m, 1.2H), 7.05 (d, J=8.5, 0.8H), 5.78 – 5.64 (m, 1H), 5.61 – 5.57 (m, 1H), 5.46 (d, J=10.3, 1H), 5.13 – 4.94 (m, 2.5H), 4.86 (dd, J=10.2, 2.8, 0.5H), 3.36 (s, 1.2H), 3.31 (s, 1.8H). (peaks not assigned to single stereoisomers)

2.5 Reductions

**Typical procedure 5 (TP5) – Reduction of the N,O-acetals**

A flame dried and nitrogen flushed Schlenk tube, equipped with a septum and a magnetic stirrer, was charged with N,O-acetal 4a-e (1.0 equiv) and dichloromethane (10 mL/mmol) and cooled to -50 °C. After addition of BF$_3$·OEt$_2$ (2.0 equiv) the reaction mixture was stirred for 30 min at -50 °C. Triethylsilane (6.0 equiv) was added at -50 °C. The solution was allowed to slowly warm to room temperature and stirred for additionally 24 h at room temperature. After TLC analysis of an aliquot showed complete consumption of the starting material, the reaction was quenched with saturated aqueous NH$_4$Cl (3 mL) and diluted with dichloromethane. The organic layer was separated and the aqueous phase was extracted with dichloromethane (2x 5 mL). The combined organic layers were dried over Na$_2$SO$_4$ and the solvents were evaporated under reduced pressure. Purification by flash chromatography afforded the desired 1,2-syn-1,3-diamin-2-ol 5a-e as analytically pure product.

Typical procedure 6 (TP6) – One-Pot-Reduction

A flame dried and nitrogen flushed Schlenk tube, equipped with a septum and a magnetic stirrer, was charged with (Z)-oxenamide/-encarbamate 1a-e (1.0 equiv), N-acylimine precursor 3a (1.1 equiv) and dichloromethane (10 mL/mmol). The solution was cooled to -65 °C and SiCl$_4$ or BF$_3$·OEt$_2$ (2.0 equiv) was added. The reaction was allowed to warm to -10 °C within 4 h. After TLC showed complete consumption of (Z)-oxenamide/-encarbamate the reaction mixture was again cooled to -65 °C and K-selectride (4.0 equiv with SiCl$_4$ as Lewis acid) or L-selectride (4.0 equiv with BF$_3$·OEt$_2$ as Lewis acid) was added. The mixture was allowed to slowly warm to room temperature overnight and then quenched
Preparation and analytical data

with saturated aqueous NH₄Cl (3 mL). The organic layer was separated and the aqueous phase was extracted with dichloromethane (2x 5 mL). The combined organic layers were dried over Na₂SO₄ and the solvents were evaporated under reduced pressure. Purification by flash chromatography (n-hexane:EtOAc) afforded the desired 1,2-syn-1,3-diamin-2-ol 5a-e as analytically pure product.

2.5.1 1,3-Diamino-2-ol 5a

\[
\begin{align*}
\text{Bz} & \quad \text{NH} & \quad \text{HN} & \quad \text{Bz} \\
\text{H} & \quad \text{O} & \quad \text{Ph} & \quad \text{Bz}
\end{align*}
\]

\(5a\)

a) From the reduction of the \(N,O\)-acetal
Prepared according to TP5 from \(N,O\)-acetal 4a (131 mg, 0.25 mmol, 1.0 equiv), BF₃·OEt₂ (0.13 mL, 0.5 mmol, 2.0 equiv) and triethylsilane (0.25 mL, 1.5 mmol, 6.0 equiv) in a total of 2.5 mL dichloromethane. Purification by flash chromatography via puriflash XS 420+ machine, HP_15\(\mu\)m F0012 flash column (n-hexane:EtOAc = 95:5 → 50:50) afforded the desired 1,3-diamino-2-ol 5a as a colorless foam (96.7 mg, 79%, isolated \(\text{dr}>98:2\); \(\text{dr}\) of the crude mixture >98:2, as determined by \(^1\)H NMR analysis of the crude product after aqueous workup).

b) Via the One-Pot-Reduction
Prepared according to TP6 from (Z)-2-benzamidovinyl benzoate 1a (66.8 mg, 0.25 mmol, 1.0 equiv), \(N\)-acylimine precursor 3a (66.4 mg, 0.275 mmol, 1.1 equiv), SiCl₄ (58 mL, 0.5 mmol, 2.0 equiv) and \(K\)-selectride (1.0 mL, 1 mmol, 4.0 equiv, 1 M solution in THF) in a total of 2.5 mL dichloromethane. Purification by flash chromatography via puriflash XS 420+ machine, HP_15\(\mu\)m F0012 flash column (n-hexane:EtOAc = 95:5 → 50:50) afforded the desired 1,3-diamino-2-ol 5a as colorless solid (87.3 mg, 73%, isolated \(\text{dr}>98:2\) \(\text{dr}\) of the crude mixture >98:2 as determined by \(^1\)H NMR analysis of the crude product after aqueous workup).

\(R_f\) (n-hexane:EtOAc = 6:4) 0.37.

\(\text{m.p.}\) 196-199 °C.

\(^1\)H NMR (400 MHz, Chloroform-\(d\)) \(\delta = 8.07 - 7.93\) (m, 2H), 7.80 (dd, \(J=7.3, 1.8, 4H\)), 7.59 – 7.53 (m, 1H), 7.52 – 7.46 (m, 4H), 7.45 – 7.27 (m, 9H), 7.24 (d, \(J=9.0, 1H\)), 7.11 (t, \(J=6.1, 1H\)), 5.78 – 7.53 (m, 1H), 5.68 (dd, \(J=8.8, 5.8, 1H\)), 3.96 (dt, \(J=13.7, 5.8, 1H\)), 3.60 (dt, \(J=14.2, 5.3, 1H\)).

\(^{13}\)C NMR (101 MHz, Chloroform-\(d\)) \(\delta = 167.7, 166.8, 138.0, 134.1, 133.9, 133.6, 132.0, 131.8, 129.9, 129.4, 129.2, 128.8, 128.7, 128.7, 128.5, 127.3, 127.2, 127.2, 75.1, 54.9, 41.1.

\(\text{IR (ATR, \(v\) in cm}^{-1}\)): 3237 (w), 3066 (w), 2933 (w), 1711 (m), 1636 (s), 1602 (w), 1536 (s), 1489 (m), 1451 (w), 1297 (m), 1269 (s), 1106 (m), 1071 (w), 1041 (w), 800 (w), 690 (s).

\(\text{MS (ESI)}\ m/z\) calcd for \(C_{30}H_{26}N_2NaO_4\) 501.2 [M+Na]⁺, found 501.4 [M+Na]⁺.
HRMS (EI) m/z calcd for C_{28}H_{31}N_{2}O_{4} 459.2278 [M+H]^{+}, found 459.2284 [M+H]^{+}.

2.5.2 1,3-Diamino-2-ol 5b

\[
\text{BzNH} \quad \text{HN} \quad \text{Bz} \\
\text{H} \quad \text{O} \quad \text{Piv} \\
\text{Ph}
\]

\text{5b}

\text{a) From the reduction of the N,O-acetal}

Prepared according to TP5 from N,O-acetal 4b (122 mg, 0.25 mmol, 1.0 equiv), BF\textsubscript{3}-OEt\textsubscript{2} (0.13 mL, 0.5 mmol, 2.0 equiv) and triethylsilane (0.25 mL, 1.5 mmol, 6.0 equiv) in a total of 2.5 mL dichloromethane. Purification by flash chromatography via puriflash XS 420+ machine, HP\_15μm\_F0012 flash column (n-hexane:EtOAc = 95:5 → 50:50) afforded the desired 1,3-diamino-2-ol 5b as a colorless foam (28.3 mg, 27%, isolated dr >98:2; dr of the crude mixture >98:2, as determined by \textsuperscript{1}H NMR analysis of the crude product after aqueous workup).

\text{b) Via the One-Pot-Reduction}

Prepared according to TP6 from (Z)-2-benzamidovinyl pivalate 1b (61.8 mg, 0.25 mmol, 1.0 equiv), N-acylimine precursor 3a (66.4 mg, 0.275 mmol, 1.1 equiv), BF\textsubscript{3}-OEt\textsubscript{2} (0.13 mL, 0.5 mmol, 2.0 equiv) and L-selectride (1.0 mL, 1 mmol, 4.0 equiv, 1 M solution in THF) in a total of 2.5 mL dichloromethane. Purification by flash chromatography via puriflash XS 420+ machine, HP\_15μm\_F0012 flash column (n-hexane:EtOAc = 95:5 → 50:50) afforded the desired 1,3-diamino-2-ol 5b as colorless solid (73.4 mg, 64%, isolated dr >98:2; dr of the crude mixture >98:2, as determined by \textsuperscript{1}H NMR analysis of the crude product after aqueous workup).

\text{Rf} (n-hexane:EtOAc = 6:4) 0.35.

\text{m.p.} 102-106 °C.

\text{\textsuperscript{1}H NMR} (400 MHz, Chloroform-d) \text{δ} = 7.87 – 7.80 (m, 2H), 7.82 – 7.74 (m, 2H), 7.58 – 7.38 (m, 8H), 7.39 – 7.27 (m, 3H), 7.07 (d, J=9.0, 1H), 6.85 (t, J=6.1, 1H), 5.58 (dd, J=9.0, 5.8, 1H), 5.50 (dt, J=6.8, 5.5, 1H), 3.86 (dt, J=14.2, 7.0, 1H), 3.46 (dt, J=14.2, 5.2, 1H), 1.11 (s, 9H).

\text{\textsuperscript{13}C NMR} (101 MHz, Chloroform-d) \text{δ} = 178.8, 167.5, 167.2, 138.1, 134.0, 133.8, 132.0, 131.8, 129.1, 128.8, 128.7, 128.3, 127.2, 127.1, 127.1, 127.1, 74.1, 54.9, 41.0, 39.1, 27.2.

\text{IR (ATR, ν in cm}^{-1})\): 3305 (w), 2970 (w), 1710 (m), 1641 (s), 1603 (w), 1579 (w), 1527 (s), 1484 (s), 1397 (w), 1281 (s), 1151 (s), 1032 (m), 800 (w), 694 (s).

\text{MS (ESI) m}/\text{z calcd for C}_{28}\text{H}_{31}\text{N}_{2}\text{NaO}_{4} 481.2 [M+Na]^{+}, found 481.4 [M+Na]^{+}.

\text{HRMS (EI) m}/\text{z calcd for C}_{28}\text{H}_{31}\text{N}_{2}\text{O}_{4} 459.2278 [M+H]^{+}, found 459.2284 [M+H]^{+}. 
2.5.3 1,3-Diamino-2-ol 5c

\[ \text{Bz} \quad \text{NH} \quad \text{HN} \quad \text{Bz} \\
\text{H} \quad \text{O} \quad \text{Ph} \]

a) From the reduction of the \( N,O \)-acetal

Prepared according to TP5 from \( N,O \)-acetal 4c (112 mg, 0.25 mmol, 1.0 equiv), \( \text{BF}_3 \cdot \text{OEt}_2 \) (0.13 mL, 0.5 mmol, 2.0 equiv) and triethylsilane (0.25 mL, 1.5 mmol, 6.0 equiv) in a total of 2.5 mL dichloromethane. Purification by flash chromatography via puriflash XS 420+ machine, HP\(_{15}\)µm_F0012 flash column (n-hexane:EtOAc = 90:10 → 30:70) afforded the desired 1,3-diamino-2-ol 5c as a colorless foam (79.4 mg, 74%, isolated \( d_r > 98:2 \); \( d_r \) of the crude mixture >98:2, as determined by \(^1\)H NMR analysis of the crude product after aqueous workup).

b) Via the One-Pot-Reduction

Prepared according to TP6 from (Z)-2-benzamidovinyl acetate 1c (61.8 mg, 0.25 mmol, 1.0 equiv), \( N \)-acylimine precursor 3a (66.4 mg, 0.275 mmol, 1.1 equiv), \( \text{SiCl}_4 \) (58 mL, 0.5 mmol, 2.0 equiv) and K-selectride (1.0 mL, 1 mmol, 4.0 equiv, 1 M solution in THF) in a total of 2.5 mL dichloromethane. Purification by flash chromatography via puriflash XS 420+ machine, HP\(_{15}\)µm_F0012 flash column (n-hexane:EtOAc = 90:10 → 30:70) afforded the desired 1,3-diamino-2-ol 5c as colorless solid (70.2 mg, 67%, isolated \( d_r > 98:2 \); \( d_r \) of the crude mixture >98:2, as determined by \(^1\)H NMR analysis of the crude product after aqueous workup).

\( R_f \) (n-hexane:EtOAc = 6:4) 0.14.

\( \text{m.p.} \geq 200^\circ \text{C} \).

\(^1\)H NMR (400 MHz, Chloroform-\( d \)) \( \delta = 7.89 – 7.78 \) (m, 4H), 7.60 – 7.28 (m, 11H), 7.10 (t, J=6.0, 1H), 7.01 (d, J=9.0, 1H), 5.59 (dd, J=9.1, 4.8, 1H), 5.56 – 5.48 (m, 1H), 4.03 – 3.87 (m, 1H), 3.50 – 3.31 (m, 1H), 2.04 (s, 3H).

\(^{13}\)C NMR (101 MHz, Chloroform-\( d \)) \( \delta = 170.8, 167.8, 167.5, 138.0, 134.0, 133.8, 132.2, 131.8, 129.2, 128.9, 128.7, 128.4, 127.2, 127.2, 127.0, 74.1, 54.2, 40.7, 21.1.

IR (ATR, \( \nu \) in cm\(^{-1}\)): 3268 (w), 3071 (w), 1730 (s), 1632 (s), 1604 (w), 1538 (s), 1490 (m), 1424 (w), 1369 (m), 1316 (m), 1232 (s), 1113 (w), 1043 (m), 943 (w), 803 (w), 693 (s).

MS (ESI) m/z calcld for \( \text{C}_{25}\text{H}_{24}\text{N}_{2}\text{O}_{4} \) 439.2 [M+Na]\(^+\), found 439.3 [M+Na]\(^+\).

HRMS (El) m/z calcld for \( \text{C}_{25}\text{H}_{25}\text{N}_{2}\text{O}_{4} \) 417.1809 [M+H]\(^+\), found 417.1812 [M+H]\(^+\).
2.5.4 1,3-Diamino-2-ol 5d

\[ \begin{align*}
\text{Boc} & \text{H} \quad \text{NH} \quad \text{NH} \quad \text{Bz} \\
\text{H} & \quad \text{O} \quad \text{Ph} \quad \text{Bz}
\end{align*} \]

5d

**a) From the reduction of the N,O-acetal**

Prepared according to TP5 from N,O-acetal 4d (126 mg, 0.25 mmol, 1.0 equiv), BF₃·OEt₂ (0.13 mL, 0.5 mmol, 2.0 equiv) and triethylsilane (0.25 mL, 1.5 mmol, 6.0 equiv) in a total of 2.5 mL dichloromethane. Purification by flash chromatography via puriflash XS 420+ machine, HP_15μm_F0012 flash column (n-hexane:EtOAc = 95:5 → 50:50) afforded the desired 1,3-diamino-2-ol 5d as a colorless foam (16.9 mg, 15%, isolated dr >98: 2; dr of the crude mixture >98:2, as determined by ¹H NMR analysis of the crude product after aqueous workup).

**b) Via the One-Pot-Reduction**

Prepared according to TP6 from (Z)-2-[(tert-butoxycarbonyl)amino]vinyl benzoate 1d (65.8 mg, 0.25 mmol, 1.0 equiv), N-acylimine precursor 3a (66.4 mg, 0.275 mmol, 1.1 equiv), BF₃·OEt₂ (0.13 mL, 0.5 mmol, 2.0 equiv) and L-selectride (1.0 mL, 1 mmol, 4.0 equiv, 1 M solution in THF) in a total of 2.5 mL dichloromethane. Purification by flash chromatography via puriflash XS 420+ machine, HP_15μm_F0012 flash column (n-hexane:EtOAc = 95:5 → 50:50) afforded the desired 1,3-diamino-2-ol 5d as colorless solid (59.8 mg, 50%, isolated dr >98:2; dr of the crude mixture >98:2, as determined by ¹H NMR analysis of the crude product after aqueous workup).

**Rf** (n-hexane:EtOAc = 7:3) 0.38.

**m.p.** 169-171 °C.

**¹H NMR** (400 MHz, Chloroform-d) δ = 8.03 (d, J=7.4, 2H), 7.73 (d, J=7.6, 2H), 7.55 (d, J=7.4, 1H), 7.49 – 7.27 (m, 10H), 7.21 (d, J=8.4, 1H), 5.70 – 5.58 (m, 1H), 5.54 (t, J=7.8, 1H), 4.98 (s, 1H), 3.53 – 3.29 (m, 2H), 1.39 (s, 9H).

**¹³C NMR** (101 MHz, Chloroform-d) δ = 167.1, 155.9, 138.3, 134.1, 133.6, 131.8, 130.0, 129.5, 129.2, 128.7, 128.6, 128.4, 127.3, 127.1, 79.9, 75.5, 55.2, 41.7, 28.4.

**IR (ATR, v in cm⁻¹):** 3406 (w), 3273 (w), 2974 (w), 1717 (m), 1698 (s), 1631 (s), 1511 (m), 1452 (w), 1365 (m), 1268 (s), 1241 (s), 1164 (m), 1108 (s), 1067 (m), 1026 (m), 855 (w), 708 (s), 690 (s).

**MS (ESI) m/z calcd for C₂₈H₃₀N₂NaO₅ 497.2 [M+Na]^+**, found 497.4 [M+Na]^+.

**HRMS (EI) m/z calcd for C₂₈H₃₁N₂O₅ 475.2227 [M+H]^+, found 475.2225 [M+H]^+.
2.5.5 1,3-Diamino-2-ol 5e

\[ \text{Cbz} \cdot \text{NH} \cdot \text{HN} \cdot \text{Bz} \]

5e

\[ \text{H} \cdot \text{O} \cdot \text{Ph} \cdot \text{Bz} \]

a) From the reduction of the N,N-acetal
Prepared according to TP5 from N,N-acetal 4e (135 mg, 0.25 mmol, 1.0 equiv), BF₃·OEt₂ (0.13 mL, 0.5 mmol, 2.0 equiv) and triethylsilane (0.25 mL, 1.5 mmol, 6.0 equiv) in a total of 2.5 mL dichloromethane. Purification by flash chromatography via puriflash XS 420+ machine, HP_15µm_F0012 flash column (n-hexane:EtOAc = 95:5 \rightarrow 50:50) afforded the desired 1,3-diamino-2-ol 5e as a colorless foam (62. mg, 27%, isolated \( \text{dr} > 98:2 \); \( \text{dr} \) of the crude mixture >98:2, as determined by \(^1\text{H} \) NMR analysis of the crude product after aqueous workup).

b) Via the One-Pot-Reduction
Prepared according to TP6 from (Z)-2-(((benzyloxy)carbonyl)amino)vinyl benzoate 1e (61.8 mg, 0.25 mmol, 1.0 equiv), \( N \)-acylimine precursor 3a (66.4 mg, 0.275 mmol, 1.1 equiv), BF₃·OEt₂ (0.13 mL, 0.5 mmol, 2.0 equiv) and L-selectride (1.0 mL, 1 mmol, 4.0 equiv, 1 M solution in THF) in a total of 2.5 mL dichloromethane. Purification by flash chromatography via puriflash XS 420+ machine, HP_15µm_F0012 flash column (n-hexane:EtOAc = 95:5 \rightarrow 50:50) afforded the desired 1,3-diamino-2-ol 5e as colorless solid (61.7 mg, 50%, isolated \( \text{dr} > 98:2 \); \( \text{dr} \) of the crude mixture >98:2, as determined by \(^1\text{H} \) NMR analysis of the crude product after aqueous workup).

\( R_f \) (n-hexane:EtOAc = 7:3) 0.20.

\text{m.p.} \ 185-187 ^\circ \text{C}.

\(^1\text{H} \text{ NMR} \) (400 MHz, Chloroform-\( \text{d} \)) \( \delta = 8.01 \) (d, \( J=8.2, 1.4, 2 \text{H} \)), 7.71 (d, \( J=7.6, 2 \text{H} \)), 7.62 – 7.52 (m, 1H), 7.50 – 7.27 (m, 15H), 7.06 (d, \( J=8.7, 1 \text{H} \)), 5.66 (td, \( J=7.0, 4.5, 1 \text{H} \)), 5.55 (t, \( J=7.9, 1 \text{H} \)), 5.29 – 5.19 (m, 1H), 5.06 (s, 2H), 3.67 – 3.50 (m, 1H), 3.49 – 3.34 (m, 1H).

\(^{13}\text{C} \text{ NMR} \) (101 MHz, Chloroform-\( \text{d} \)) \( \delta = 167.2, 167.1, 156.5, 138.2, 136.4, 134.0, 133.7, 131.8, 130.0, 129.4, 129.3, 128.7, 128.7, 128.6, 128.5, 128.3, 128.3, 127.3, 127.1, 75.2, 67.1, 55.1, 42.2.

\text{IR (ATR, } \nu \text{ in cm}^{-1}\text{):} 3378 \text{ (w),} 3340 \text{ (w),} 3029 \text{ (w),} 1730 \text{ (m),} 1702 \text{ (s),} 1632 \text{ (m),} 1062 \text{ (w),} 1525 \text{ (s),} 1489 \text{ (w),} 1451 \text{ (w),} 1341 \text{ (w),} 1275 \text{ (s),} 1245 \text{ (s),} 1169 \text{ (w),} 1115 \text{ (m),} 1027 \text{ (w),} 899 \text{ (w),} 718 \text{ (s),} 694 \text{ (s).}

\text{MS (ESI) } m/z \text{ calcd for C}_{31}H_{29}N_2NaO_5 531.2 [M+Na]^+, \text{ found 531.4 [M+Na]^+}.  
\text{HRMS (EI) } m/z \text{ calcd for C}_{31}H_{29}N_2O_5 509.2071 [M+H]^+, \text{ found 509.2083 [M+H]^+}.  

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S18
2.6 1,3-Diamino-2-ols from different (Z)-Oxyenamides/(Z)-Oxyencarbamates

Typical procedure 7 (TP7)

A flame dried and nitrogen flushed Schlenk tube, equipped with a septum and a magnetic stirrer, was charged with (Z)-oxyenamide/encarbamate 1a-e (1.0 equiv), N-acylimine precursor 3a (1.1 equiv) and dichloromethane (10 mL/mmol). The solution was cooled to -65 °C and SiCl₄ (2.0 equiv) was added. The reaction was allowed to warm to -10 °C within 4 h. After TLC analysis showed complete consumption of the (Z)-oxyenamide/encarbamate, the mixture was again cooled to -65 °C and 1,3,5-trimethoxybenzene (4.0 equiv) was added in one portion. The reaction was allowed to warm to 15°C overnight and then quenched with saturated aqueous NH₄Cl (3 mL). The organic layer was separated and the aqueous phase was extracted with dichloromethane (2x 5 mL). The combined organic layers were dried over Na₂SO₄ and the solvent was evaporated under reduced pressure. Purification by flash chromatography afforded the desired 1,2-syn-2,3-anti-1,3-diamino-2-ol 6a-e as analytically pure product.

2.6.1 1,3-Diamino-2-ol 6a

Prepared according to TP7 from (Z)-2-benzamidovinyl benzoate 1a (66.8 mg, 0.25 mmol, 1.0 equiv), N-acylimine precursor 3a (66.4 mg, 0.275 mmol, 1.1 equiv), SiCl₄ (58 µL, 0.5 mmol, 2.0 equiv) and 1,3,5-trimethoxybenzene (172 mg, 1.0 mmol, 4.0 equiv) in a total of 2.5 mL dichloromethane. Purification by flash chromatography via puriflash XS 420+ machine, HP_15µm_F0012 flash column (n-hexane:EtOAc = 92:8 → 40:60) afforded the desired 1,3-diamino-2-ol 6a as a colorless foam (145 mg, 90%, isolated dr >98:2; dr of the crude mixture >98:2, as determined by ¹H NMR analysis of the crude product after aqueous workup).

Rₛ (n-hexane:EtOAc = 6:4) 0.25.

m.p. 110-115 °C.

¹H NMR (400 MHz, Chloroform-d) δ = 7.83 (d, J=9.8, 1H), 7.73 – 7.64 (m, 4H), 7.61 – 7.52 (m, 2H), 7.47 – 7.33 (m, 5H), 7.33 – 7.24 (m, 6H), 7.22 – 7.16 (m, 3H), 7.15 – 7.04 (m, 1H), 6.45 (dd, J=9.8, 7.1, 1H), 5.95 – 5.87 (m, 3H), 5.66 (dd, J=8.5, 4.1, 1H), 3.65 (s, 6H), 3.60 (s, 3H).
**Preparation and analytical data**

\[ ^{13}C \text{NMR (101 MHz, Chloroform-}d) \delta = 166.7, 166.5, 165.3, 161.1, 159.1, 139.6, 134.8, 134.7, 133.1, 131.4, 131.4, 129.9, 128.6, 128.5, 128.3, 127.5, 127.3, 127.2, 127.1, 106.4, 91.0, 77.1, 56.0, 55.4, 54.7, 46.2. \]

**IR (ATR, \(v\) in cm\(^{-1}\))**: 3441 (w), 4004 (w), 2970 (w), 1743 (s), 1662 (m), 1600 (m), 1511 (m), 1482 (m), 1452 (m), 1367 (m), 1225 (s), 1204 (s), 1120 (s), 1068 (m), 1028 (m), 950 (w), 814 (w) 705 (s).

**MS (ESI) m/z calcd for \(C_{28}H_{36}N_2NaO_7\) 667.2 [M+Na]\(^+\), found 667.6 [M+Na]\(^+\).

**HRMS (EI) m/z calcd for \(C_{28}H_{36}N_2O_7\) 644.2507 [M+H]\(^+\), found 644.2507 [M+H]\(^+\).

2.6.2 1,3-Diamino-2-ol \(6b\)

Prepared according to TP7 from (Z)-2-benzamidovinyl pivalate \(1b\) (mg, 0.25 mmol, 1.0 equiv), \(N\)-acylimine precursor \(3a\) (66.4 mg, 0.275 mmol, 1.1 equiv), \(SiCl_4\) (58 µL, 0.5 mmol, 2.0 equiv), 1,3,5-trimethoxybenzene (172 mg, 1.0 mmol, 4 equiv) in a total of 2.5 mL dichloromethane. The reaction was allowed to warm to rt overnight. Purification by flash chromatography via puriflash XS 420+ machine, HP_15μm_F0012 flash column \((n\)-hexane:EtOAc = 92:8 \(\rightarrow\) 40:60) afforded the desired 1,3-diamino-2-ol \(6b\) as a colorless foam (98.4 mg, 63%, isolated \(d_r>98:2\); \(d_r\) of the crude mixture \(>98:2\), as determined by \(^1H\) NMR analysis of the crude product after aqueous workup).

Rf \((n\)-hexane:EtOAc = 6:4) 0.28.

m.p. 104-109 °C.

\(^1H\ NMR (400 MHz, CDCl_3) \delta 7.88 – 7.84 (m, 2H), 7.69 (d, J = 10.0 Hz, 1H), 7.64 – 7.59 (m, 2H), 7.53 – 7.47 (m, 1H), 7.45 – 7.40 (m, 3H), 7.36 – 7.32 (m, 4H), 7.27 – 7.23 (m, 2H), 7.17 -7.12 (m, 2H), 6.53 – 6.39 (m, 1H), 6.10 (s, 2H), 5.75 (dd, J = 8.8, 3.4 Hz, 1H), 5.60 (dd, J = 8.3, 3.4 Hz, 1H), 3.85 (s, 6H), 3.77 (s, 3H), 0.85 (s, 9H).

\(^{13}C\ NMR (151 MHz, CDCl_3) \delta 176.5, 166.7, 166.3, 161.1, 159.3, 139.6, 134.9, 134.7, 131.5, 131.4, 128.7, 128.5, 128.5, 127.4, 127.3, 127.1, 126.8, 107.0, 91.2, 75.4, 56.2, 55.5, 54.4, 45.3, 38.8, 27.0.

**IR (ATR, v in cm\(^{-1}\))**: 3447 (w), 2970 (w), 1740 (s), 1664 (m), 1607 (m), 1512 (m), 1482 (m), 1455 (m) 1367 (m) 1223 (m), 1204 (s), 1146 (s), 1122 (s), 1033 (m), 950 (w), 815 (w), 695 (m).

**MS (ESI) m/z calcd for \(C_{37}H_{48}N_2NaO_7\) 647.3 [M+Na]\(^+\), found 647.6 [M+Na]\(^+\).

**HRMS (EI) m/z calcd for \(C_{37}H_{48}N_2O_7\) 624.2836 [M+H]\(^+\), found 624.2824 [M+H]\(^+\).
2.6.3 1,3-Diamino-2-ol 6c

Prepared according to TP7 from (Z)-2-benzamidovinyl acetate 1c (51.3 mg, 0.25 mmol, 1.0 equiv), N-acylimine precursor 3a (66.4 mg, 0.275 mmol, 1.1 equiv), SiCl₄ (58 µL, 0.5 mmol, 2.0 equiv), 1,3,5-trimethoxybenzene (172 mg, 1.0 mmol, 4.0 equiv) in a total of 2.5 mL dichloromethane. The reaction was allowed to warm to rt overnight. Purification by flash chromatography via puriflash XS 420+ machine, HP_15μm_F0012 flash column (n-hexane:EtOAc = 75:25 → 10:90) afforded the desired 1,3-diamino-2-ol 6c as a colorless foam (111 mg, 76%, isolated dr = 98:2; dr of the crude mixture >98:2, as determined by ¹H NMR analysis of the crude product after aqueous workup).

Rᶠ (n-hexane:EtOAc = 6:4) 0.17.

m.p. 98-102 °C.

¹H NMR (400 MHz, CDCl₃) δ 7.90 (d, J=9.9, 1H), 7.81 – 7.76 (m, 2H), 7.69 – 7.63 (m, 2H), 7.52 – 7.25 (m, 10H), 7.22 – 7.16 (m, 1H), 7.11 (d, J=8.2, 1H), 6.42 – 6.33 (m, 1H), 6.11 (s, 2H), 5.65 (dd, J=7.3, 2.9, 1H), 5.57 (dd, J=8.2, 2.8, 1H), 3.84 (s, 6H), 3.77 (s, 3H), 1.79 (s, 3H).

¹³C NMR (151 MHz, CDCl₃) δ 169.4, 166.8, 166.4, 161.2, 159.3, 140.0, 134.9, 134.8, 131.5, 131.4, 128.6, 128.6, 127.5, 127.3, 127.1, 126.7, 106.3, 91.1, 76.7, 56.2, 55.4, 54.2, 46.1, 20.6.

IR (ATR, ν in cm⁻¹): 3440 w), 2970 (w), 2943 (w), 1742 (s), 1662 (m), 1605 (m), 1512 (m), 1482 (m) 1420 (w), 1386 (m), 1221 (s), 1204 (s), 1149 (w), 1122 (m), 1032 (w), 949 (w), 815 (w), 695 (m).

MS (ESI) m/z calcd for C₃₄H₃₄N₂O₇ 605.2 [M+Na]^+, found 605.5 [M+Na]^+.

HRMS (EI) m/z calcd for C₃₄H₃₄N₂O₇ 582.2366 [M]^+, found 582.2372 [M]^+.

2.6.4 1,3-Diamino-2-ol 6e

Prepared according to TP7 from (Z)-2-(((benzyloxy)carbonyl)amino)vinyl benzoate 1e (74.3 mg, 0.25 mmol, 1.0 equiv), N-acylimine precursor 3a (66.4 mg, 0.275 mmol, 1.1 equiv), SiCl₄ (58 µL, 0.5 mmol, 2.0 equiv), 1,3,5-trimethoxybenzene (172 mg, 1.0 mmol, 4.0 equiv) in a total of 2.5 mL dichloromethane. The reaction was allowed to warm to rt overnight. Purification by flash chromatography via puriflash XS 420+ machine, HP_15μm_F0012 flash column (n-hexane:EtOAc = 75:25 → 45:55) afforded the desired 1,3-diamin-2-ol 6e as a colorless foam (92.2 mg, 58%, crude dr = 71:29
as determined by $^1$H NMR analysis (400 MHz) of the crude product after aqueous workup; overall isolated yield for all diastereomers 117 mg, 74%; $dr = 79:21$, as calculated from the isolated products. 

**Rf** (n-hexane:EtOAc = 6:4) 0.33.

**m.p.** 84-89 °C.

**$^1$H NMR** (400 MHz, Chloroform-$d$) $\delta = 7.85$ (d, $J=7.5$, 2H), 7.71 (d, $J=7.7$, 2H), 7.55 – 7.39 (m, 4H), 7.34 (p, $J=7.3$, 6.1, 8H), 7.27 – 7.04 (m, 5H), 6.27 (d, $J=10.3$, 1H), 6.06 (dd, $J=10.2$, 8.3, 1H), 5.96 (s, 2H), 5.89 (dd, $J=8.4$, 3.3, 1H), 5.83 – 5.68 (m, 1H), 5.15 – 4.88 (m, 2H), 3.73 (s, 6H), 3.67 (s, 3H).

**$^{13}$C NMR** (101 MHz, Chloroform-$d$) $\delta = 166.9$, 164.9, 161.1, 159.0, 156.0, 139.7, 136.6, 135.2, 133.0, 131.4, 129.8, 129.4, 128.7, 128.6, 128.3, 128.2, 127.5, 127.3, 126.9, 106.7, 90.9, 67.1, 56.0, 55.4, 54.3, 47.4.

**IR (ATR, ν in cm$^{-1}$):** 3438 (w), 2940 (w), 1715 (m), 1664 (m), 1595 (m), 1500 (m), 1452 (m) 1419 (w), 1260 (m), 1204 (m), 1150 (m), 1067 (m), 1026 (m), 950 (w), 814 (w), 696 (s).

**MS (ESI) m/z calcd for C$_{40}$H$_{38}$N$_2$NaO$_8$ 697.2 [M+Na]$^+$, found 697.6 [M+Na]$^+$.

**HRMS (EI) m/z calcd for C$_{28}$H$_{36}$N$_2$O$_7$ 674.2628 [M+H]$^+$, found 674.2617 [M+H]$^+$.

### 2.7 1,3-Diamino-2-ols from different Nucleophiles

**Typical procedure 8 (TP8)**

A flame dried and nitrogen flushed Schlenk tube, equipped with a septum and a magnetic stirrer, was charged with (Z)-oxenamde 1a (1.0 equiv), N-acylimine precursor 3a (1.1 equiv) and dichloromethane (10 mL/mmol). The solution was cooled to -65 °C and SiCl$_4$ (2.0 equiv) was added. The reaction was allowed to warm to -10 °C within 4 h. After TLC analysis showed complete consumption of the (Z)-oxenamde, the mixture was again cooled to -65 °C and the corresponding nucleophile (4.0 equiv) was added in one portion. The reaction was allowed to warm to 15°C overnight and then quenched with saturated aqueous NH$_4$Cl (3 mL). The organic layer was separated and the aqueous phase was extracted with dichloromethane (2x 5 mL). The combined organic layers were dried over Na$_2$SO$_4$ and the solvent was evaporated under reduced pressure. Purification by flash chromatography afforded the desired 1,2-syn-2,3-anti-1,3-diamino-2-ol 7a-k as analytically pure product.
2.7.1 1,3-Diamino-2-ol 7a

Prepared according to TP8 from (Z)-2-benzamidovinyl benzoate 1a (66.8 mg, 0.25 mmol, 1.0 equiv), N-acylimine precursor 3a 66.4 mg, 0.275 mmol, 1.1 equiv), SiCl4 (58 µL, 0.5 mmol, 2.0 equiv), 1,3-dimethoxybenzene (134 µg, 1 mmol, 4.0 equiv) in a total of 2.5 mL dichloromethane. Purification by flash chromatography via puriflash XS 420+ machine, HP_15µm_F0012 flash column (n-hexane:EtOAc = 92:8 → 40:60) afforded the desired 1,3-diamin-2-ol 7a as a colorless foam (123 mg, 80%, isolated dr >98:2; dr of the crude mixture >98:2, as determined by 1H NMR analysis of the crude product after aqueous workup).

RF (n-hexane:EtOAc = 6:4) 0.28.

m.p. 111-117 °C.

1H NMR (400 MHz, Chloroform-d) δ = 7.94 (d, J=8.4, 1H), 7.88 – 7.73 (m, 4H), 7.66 – 7.58 (m, 2H), 7.49 (tdd, J=7.7, 4.8, 1.3, 2H), 7.45 – 7.21 (m, 12H), 7.18 (d, J=8.4, 1H), 6.95 (d, J=8.6, 1H), 6.41 (dd, J=8.4, 2.4, 1H), 6.28 (d, J=2.4, 1H), 6.15 (dd, J=6.1, 5.2, 1H), 5.79 (dd, J=8.4, 5.2, 1H), 5.56 (dd, J=8.6, 6.1, 1H), 3.74 (s, 3H), 3.63 (s, 3H).

13C NMR (151 MHz, Chloroform-d) δ = 167.0, 166.8, 166.4, 160.9, 158.4, 139.1, 134.4, 134.1, 133.3, 131.6, 131.5, 130.2, 129.7, 129.6, 128.9, 128.6, 128.5, 128.5, 128.0, 127.7, 127.3, 127.1, 117.4, 104.5, 99.1, 76.5, 55.5, 55.5, 54.7, 52.6.

IR (ATR, ν in cm⁻¹): 330 (w), 3061 (w), 2937 (w), 1715 (m), 1646 (m), 1608 (m), 1582 (m), 1507 (s), 1482 (s), 1452 (m), 1262 (s), 1207 (m), 1110 (m), 1207 (m), 931 (w), 833 (w), 705 (s), 695 (s).

MS (ESI) m/z calcd for C38H34N2O6Na 637.2 [M+Na]⁺, found 637.5 [M+Na]⁺.

HRMS (El) m/z calcd for C38H34N2O6 614.2417 [M]⁺, found 614.2429 [M]⁺.

2.7.2 1,3-Diamino-2-ol 7b

Prepared according to TP8 from (Z)-2-benzamidovinyl benzoate 1a (66.8 mg, 0.25 mmol, 1.0 equiv), N-acylimine precursor 3a 66.4 mg, 0.275 mmol, 1.1 equiv), SiCl4 (58 µL, 0.5 mmol, 2.0 equiv), indole (118 mg, 1.0 mmol, 4.0 equiv) in a total of 2.5 mL dichloromethane. Purification by flash chromatography via puriflash XS 420+ machine, HP_15µm_F0012 flash column (n-hexane:EtOAc = 92:8 → 40:60) afforded the desired 1,3-diamin-2-ol 7b as a colorless foam (129 mg, 87%, isolated dr >98:2;
Preparation and analytical data

Prepared according to TP8 from (Z)-2-benzamidovinyl benzoate 1a (66.8 mg, 0.25 mmol, 1.0 equiv), N-acylimine precursor 3a 66.8 mg, 0.275 mmol, 1.1 equiv), SiCl4 (58 µL, 0.5 mmol, 2.0 equiv), 5-bromoindole (196 mg, 1.0 mmol, 4.0 equiv) in a total of 2.5 mL dichloromethane. Purification by flash chromatography via puriflash XS 420+ machine, HP_15µm_F0012 flash column (n-hexane:EtOAc = 92:8 → 30:70) afforded the desired 1,3-diamino-2-ol 7c as a colorless foam (138 mg, 82%, isolated dr >98:2; dr of the crude mixture >98:2, as determined by 1H NMR analysis of the crude product after aqueous workup).

**Rf (n-hexane:EtOAc = 6:4) 0.17.**

**m.p.** >200 °C.

1H NMR (400 MHz, DMSO-d6) δ = 11.16 (d, J=2.7, 1H), 9.23 (d, J=9.3, 1H), 9.01 (d, J=8.7, 1H), 7.98 – 7.88 (m, 2H), 7.81 – 7.74 (m, 2H), 7.73 – 7.65 (m, 3H), 7.58 – 7.52 (m, 1H), 7.51 – 7.34 (m, 11H), 7.28 – 7.15 (m, 4H), 7.08 (dd, J=8.6, 2.0, 1H), 6.18 (dd, J=7.7, 5.7, 1H), 5.85 – 5.73 (m, 2H).

13C NMR (101 MHz, DMSO-d6) δ = 167.5, 165.9, 164.7, 139.7, 135.6, 135.0, 134.3, 132.9, 131.0, 130.7, 129.6, 129.5, 128.4, 128.3, 128.1, 128.0, 128.0, 127.6, 127.6, 127.5, 127.2, 125.5, 123.4, 121.4, 113.3, 112.4, 111.3, 76.7, 53.7, 45.8.
Preparation and analytical data

IR (ATR, $\nu$ in cm$^{-1}$): 3421 (w), 3247 (w), 3060 (w), 2361 (w), 1717 (w), 1637 (m), 1579 (w), 1509 (m), 1481 (m), 1451 (w), 1314 (w), 1264 (s), 1177 (w), 1106 (m), 1026 (m), 883 (m), 796 (m), 760 (m), 698 (s)

MS (ESI) $m/z$ calcd for $C_{38}H_{30}BrN_{3}O_{4}$ 694.1 [M+Na]$^+$, found 694.0 [M+Na]$^+$.

HRMS (EI) $m/z$ calcd for $C_{38}H_{32}BrN_{3}O_{4}$ 672.1420 [M]$^+$, found 672.1400 [M]$^+$.

2.7.4 1,3-Diamino-2-ol 7d

Prepared according to TP8 from (Z)-2-benzamidovinyl benzoate 1a (66.8 mg, 0.25 mmol, 1.0 equiv), N-acylimine precurs or 3a (66.8 mg, 0.275 mmol, 1.1 equiv), SiCl$_4$ (58 µL, 0.5 mmol, 2.0 equiv), 5-iodoindole (248 mg, 1.0 mmol, 4.0 equiv) in a total of 2.5 mL dichloromethane. Purification by flash chromatography via puriflash XS 420+ machine, HP_15µm_F0012 flash column (n-hexane:EtOAc = 92:8 → 40:60) afforded the desired 1,3-diamin-2-ol 7d as a colorless foam (138 mg, 77%, isolated $dr$ >98:2; $dr$ of the crude mixture >98:2, as determined by $^1$H NMR analysis of the crude product after aqueous workup).

$R_f$ (n-hexane:EtOAc = 6:4) 0.16.

m.p. 138-143 °C.

$^1$H NMR (400 MHz, Chloroform-$d$) $\delta$ = 9.57 (d, $J$=2.6, 1H), 8.06 – 7.99 (m, 2H), 7.70 – 7.61 (m, 4H), 7.55 – 7.47 (m, 3H), 7.44 – 7.38 (m, 1H), 7.32 (ddt, $J$=13.9, 9.8, 6.3, 1H), 7.22 (t, $J$=7.7, 2H), 7.06 (d, $J$=9.0, 1H), 6.93 (d, $J$=8.5, 1H), 6.75 (d, $J$=7.1, 1H), 6.48 (dd, $J$=9.3, 3.1, 1H), 5.69 (t, $J$=9.2, 1H), 5.64 (dd, $J$=7.1, 3.1, 1H).

$^{13}$C NMR (101 MHz, Chloroform-$d$) $\delta$ = 167.8, 167.5, 167.2, 137.7, 135.3, 134.0, 133.9, 133.6, 131.8, 131.7, 130.9, 129.9, 129.4, 129.1, 128.9, 128.9, 128.7, 128.6, 127.9, 127.8, 127.1, 126.9, 125.1, 113.7, 109.9, 83.6, 55.4, 47.8.

IR (ATR, $\nu$ in cm$^{-1}$): 3417 (w), 3270 (w), 3060 (w), 1711 (w), 1640 (m), 1602 (w), 1579 (w), 1509 (m), 1482 (m), 1450 (m), 1314 (w), 1264 (s), 1177 (w), 1096 (m), 1069 (m) 1026 (m), 878 (m), 795 (m), 697 (s).

MS (ESI) $m/z$ calcd for $C_{38}H_{29}IN_3O_4$ 718.1 [M-H]$^-$, found 718.3 [M-H]$^-$.

HRMS (EI) $m/z$ calcd for $C_{38}H_{32}IN_3O_4$ 719.1281 [M]$^+$, found 719.1244 [M]$^+$. 

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S25
2.7.5 1,3-Diamino-2-ol 7e

Prepared according to TP8 from (Z)-2-benzamidovinyl benzoate 1a (66.8 mg, 0.25 mmol, 1.0 equiv), N-acylimine precursor 3a 66.8 mg, 0.275 mmol, 1.1 equiv), SiCl₄ (58 µL, 0.5 mmol, 2.0 equiv), 2-methylindole (131 mg, 1.0 mmol, 4.0 equiv) in a total of 2.5 mL dichloromethane. Purification by flash chromatography via puriflash XS 420+ machine, HP_15µm_F0012 flash column (n-hexane:EtOAc = 92:8 → 40:60) afforded the desired 1,3-diamin-2-ol 7e as a colorless foam (105 mg, 69%, crude dr = 80:20, as determined by ¹H NMR analysis (400 MHz) of the crude product after aqueous workup; overall isolated yield for all diastereomers 117 mg, 77%; dr = 90:10, as calculated from the isolated products).

**Rf** (n-hexane:EtOAc = 6:4) 0.14.

m.p. 125-130 °C.

**¹H NMR** (400 MHz, Chloroform-d) δ = 8.11 (s, 1H), 8.02 – 7.96 (m, 2H), 7.74 (d, J=8.0, 1H), 7.71 – 7.65 (m, 2H), 7.59 – 7.51 (m, 1H), 7.48 – 7.27 (m, 13H), 7.14 (t, J=7.5, 2H), 7.01 (t, J=7.5, 1H), 6.63 (d, J=8.8, 1H), 6.55 (dd, J=7.3, 3.7, 1H), 5.83 (dd, J=6.8, 3.7, 1H), 5.53 (dd, J=8.8, 7.2, 1H), 2.06 (s, 3H).

**¹³C NMR** (101 MHz, Chloroform-d) δ = 167.3, 167.2, 166.5, 139.0, 135.9, 134.5, 134.2, 134.0, 133.6, 131.7, 131.5, 130.4, 129.5, 129.2, 128.7, 128.6, 128.5, 128.3, 127.8, 127.1, 126.8, 121.7, 120.1, 119.7, 111.1, 106.8, 55.1, 49.5, 12.1.

**IR (ATR, v in cm⁻¹):** 3303 (w), 3060 (w), 2921 (w), 1721 (m), 1638 (m), 1602 (w), 1579 (w), 1517 (m), 1484 (m), 1453 (m), 1311 (w), 1261 (s), 1094 (m), 1069 (m), 1026 (m), 925 (w), 799 (w), 743 (w), 693 (s).

**MS (ESI) m/z** calcd for C₃₉H₃₃N₃O₄Na 630.2 [M+Na]⁺, found 630.1 [M+Na]⁺.

**HRMS (EI) m/z** calcd for C₃₉H₃₃N₃O₄ 607.2471 [M]⁺, found 607.2483 [M]⁺.

2.7.6 1,3-Diamino-2-ol 7f

Prepared according to TP8 from (Z)-2-benzamidovinyl benzoate 1a (66.8 mg, 0.25 mmol, 1.0 equiv), N-acylimine precursor 3a 87.3 mg, 0.275 mmol, 1.1 equiv), SiCl₄ (58 µL, 0.5 mmol, 2.0 equiv), 3-methylindole (131 mg, 1.0 mmol, 4.0 equiv) in a total of 2.5 mL dichloromethane. Purification by flash chromatography via puriflash XS 420+ machine, HP_15µm_F0012 flash column (n-hexane:EtOAc = 95:5 → 50:50) afforded the desired 1,3-diamin-2-ol 7f as a colorless foam (124 mg, 82%, isolated dr >98:2;
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$dr$ of the crude mixture >98:2, as determined by $^1$H NMR analysis of the crude product after aqueous workup).

Rf ($n$-hexane:EtOAc = 6:4) 0.49.

m.p. $>$200°C.

$^1$H NMR (400 MHz, Chloroform-$d$) δ = 9.52 (s, 1H), 8.01 – 7.95 (m, 2H), 7.69 – 7.64 (m, 2H), 7.62 – 7.59 (m, 2H), 7.58 – 7.51 (m, 2H), 7.49 – 7.40 (m, 5H), 7.39 – 7.28 (m, 9H), 7.25 – 7.20 (m, 1H), 7.16 – 7.10 (m, 1H), 7.01 (d, J=7.5, 1H), 6.84 (d, J=8.9, 1H), 6.42 (dd, J=7.2, 4.5, 1H), 5.70 (dd, J=7.5, 4.4, 1H), 5.63 (dd, J=9.0, 7.1, 1H), 2.10 (s, 3H).

$^{13}$C NMR (101 MHz, Chloroform-$d$) δ = 168.0, 167.1, 166.6, 137.6, 133.8, 133.8, 133.7, 132.0, 131.8, 129.8, 129.5, 129.4, 129.0, 128.8, 128.8, 128.8, 128.6, 128.5, 127.5, 127.1, 127.0, 122.7, 119.5, 119.1, 111.7, 111.6, 76.5, 54.8, 47.5, 8.7.

IR (ATR, v in cm$^{-1}$): 3311 (w), 3059 (w), 3031 (w), 1722 (m), 1636 (s), 1602 (w), 1518 (s), 1485 (s), 1453 (m), 1347 (w), 1267 (s), 1111 (m), 1071 (w), 1027 (w), 921 (w), 811 (w), 798 (w), 707 (s), 685 (w).

MS (ESI) m/z calcd for C$_{39}$H$_{33}$N$_{3}$O$_{4}$Na 630.2 [M+Na]$^+$, found 630.1 [M+Na]$^+$.

HRMS (EI) m/z calcd for C$_{39}$H$_{33}$N$_{3}$O$_{4}$ 607.2471 [M]$^+$, found 607.2462 [M]$^+$.

2.7.7 1,3-Diamino-2-ol 7g

Prepared according to TP8 from (Z)-2-benzamidovinyl benzoate 1a (66.8 mg, 0.25 mmol, 1.0 equiv), N-acylimine precursor 3a (87.3 mg, 0.275 mmol, 1.1 equiv), SiCl$_4$ (58 µL, 0.5 mmol, 2.0 equiv), 2-methoxythiophene (102 µL, 1.0 mmol, 4.0 equiv) in a total of 2.5 mL dichloromethane. Purification by flash chromatography via puriflash XS 420+ machine, HP_15µm_F0012 flash column ($n$-hexane:EtOAc = 92:8 → 40:60) afforded the desired 1,3-diamin-2-ol 7g as a colorless foam (105 mg, 71%, crude $dr$ = 90:10, as determined by $^1$H NMR analysis (400 MHz) of the crude product after aqueous workup; overall isolated yield for all diastereomers 117 mg, 79%; $dr$ = 90:10, as calculated from the isolated products).

Rf ($n$-hexane:EtOAc = 6:4) 0.37.

m.p. 110-115 °C.

$^1$H NMR (400 MHz, CDCl$_3$) δ = 8.19 – 8.11 (m, 2H), 7.65 – 7.60 (m, 2H), 7.59 – 7.51 (m, 3H), 7.48 – 7.28 (m, 12H), 7.24 (s, 1H), 6.89 (d, J=8.7, 1H), 6.67 – 6.64 (m, 2H), 6.21 (dd, J=9.3, 2.8, 1H), 6.06 (d, J=3.9, 1H), 5.49 (t, J=9.0, 1H), 5.41 (dd, J=7.3, 2.8, 1H), 3.89 (s, 3H).
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$^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ = 167.8, 167.2, 166.7, 166.5, 138.0, 134.0, 133.9, 133.9, 131.8, 131.6, 130.2, 129.3, 129.1, 128.8, 128.7, 128.5, 128.0, 127.1, 126.9, 126.8, 123.3, 76.9, 60.2, 55.5, 51.7.

IR (ATR, $v$ in cm$^{-1}$): 3294 (w), 3030 (w), 2970 (w), 1722 (m), 1640 (m), 102 (w), 1579 (w), 1501 (m), 1482 (s), 1429 (w), 1366 (w), 1264 (s), 1206 (s), 1096 (m), 1026 (m), 798 (w), 767 (w), 703 (s).

MS (ESI) m/z calcd for C$_{35}$H$_{30}$N$_2$NaO$_5$S 613.2 [M+Na]$^+$, found 613.5 [M+Na]$^+$.

HRMS (EI) m/z calcd for C$_{28}$H$_{24}$N$_2$O$_3$S$^4$: 468.1576 [M$-$BzH]$^+$, found 468.1576 [M$-$BzH]$^+$. (We were not able to obtain HRMS data for the parent molecule without fragmentation. Therefore an additional CHN analysis was performed.)

CHN calcd for C$_{35}$H$_{30}$N$_2$NaO$_5$S: C 71.17; H 5.12, N 4.74, S 5.43, found: C 71.15, H 5.07, N 4.74, S 5.42.

2.7.8 1,3-Diamino-2-ol 7h

Prepared according to TP8 from (Z)-2-benozamidovinyl benzoate 1a (66.8 mg, 0.25 mmol, 1.0 equiv), N-acylimine precursors 3a (87.3 mg, 0.275 mmol, 1.1 equiv), SiCl$_4$ (58 µL, 0.5 mmol, 2.0 equiv), 2-methylfuran (172 mg, 1.0 mmol, 4.0 equiv) in a total of 2.5 mL dichloromethane. Purification by flash chromatography via puriflash XS 420+ machine, HP_15µm_F0012 flash column (n-hexane:EtOAc = 92:8 → 40:60) afforded the desired 1,3-diamino-2-ol 7h as a colorless foam (106 mg, 74%, crude $dr$ = 88:12, as determined by $^1$H NMR analysis (400 MHz) of the crude product after aqueous workup; overall isolated yield for all diastereomers 118 mg, 84%; $dr$ = 90:10, as calculated from the isolated products).

$R_f$ (n-hexane:EtOAc = 6:4) 0.47.

m.p. 98-105 °C.

$^1$H NMR (400 MHz, Chloroform-$d$) $\delta$ = 8.10 – 8.04 (m, 2H), 7.77 – 7.72 (m, 2H), 7.64 – 7.60 (m, 2H), 7.55 (d, J=7.4, 1H), 7.53 – 7.28 (m, 13H), 7.12 (d, J=7.9, 1H), 7.06 (d, J=8.5, 1H), 6.22 (d, J=3.1, 1H), 6.08 (dd, J=8.2, 3.0, 1H), 5.94 (dd, J=3.1, 1.2, 1H), 5.62 – 5.42 (m, 2H), 2.22 (s, 3H).

$^{13}$C NMR (101 MHz, Chloroform-$d$) $\delta$ = 167.4, 166.9, 166.8, 152.6, 147.3, 138.2, 133.9, 133.9, 133.7, 131.8, 131.6, 130.0, 129.4, 129.2, 128.7, 128.6, 128.6, 127.9, 127.3, 127.0, 110.4, 106.6, 55.3, 49.3, 13.6.

IR (ATR, $v$ in cm$^{-1}$): 3285 (w), 3062 (w), 2922 (w), 1721 (m), 1640 (m), 102 (w), 1579 (w), 1501 (m), 1483 (s), 1450 (m), 1264 (s), 1109 (m), 1070 (m), 1025 (m), 935 (w), 793 (w), 693 (s).

MS (ESI) m/z calcd for C$_{35}$H$_{30}$N$_2$NaO$_5$S 581.2 [M+Na]$^+$, found 581.5 [M+Na]$^+$.

HRMS (EI) m/z calcd for C$_{28}$H$_{24}$N$_2$O$_3$S 436.1787 [M$-$BzH]$^+$, found 436.1799 [M$-$BzH]$^+$. (We were not able to obtain HRMS data for the parent molecule without fragmentation. Therefore an additional CHN analysis was performed.)
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**CHN calcd for C$_{35}$H$_{30}$N$_{2}$O$_{5}$: C 75.25; H 5.41, N 5.01, found: C 75.14, H 5.49, N 4.96.**

2.7.9 1,3-Diamino-2-ol 7i

Prepared according to **TP8** from (Z)-2-benzamidovinyl benzoate 1a (66.8 mg, 0.25 mmol, 1.0 equiv), N-acylimine precursors 3a 87.3 mg, 0.275 mmol, 1.1 equiv), SiCl$_{4}$ (58 µL, 0.5 mmol, 2.0 equiv), pyrazole (69.5 mg, 1.0 mmol, 4.0 equiv) in a total of 2.5 mL dichloromethane. Purification by flash chromatography via puriflash XS 420+ machine, HP_15µm_F0012 flash column (n-hexane:EtOAc = 95:5 → 35:65) afforded the desired 1,3-diamin-2-ol 7i as a colorless foam (96 mg, 67%, crude $d_r = 83:17$, as determined by $^1$H NMR analysis (400 MHz) of the crude product after aqueous workup; overall isolated yield for all diastereomers 110 mg, 81%; $d_r = 87:13$, as calculated from the isolated products).

**m.p.** 194-198 °C.

$^1$H NMR (400 MHz, Chloroform-d) $\delta$ = 7.91 – 7.85 (m, 2H), 7.83 (d, $J$=9.0, 1H), 7.68 – 7.58 (m, 5H), 7.56 – 7.44 (m, 5H), 7.41 – 7.27 (m, 9H), 7.26 – 7.15 (m, 2H), 6.78 (dd, $J$=9.1, 6.5, 1H), 6.31 (t, $J$=6.6, 1H), 6.16 (t, $J$=2.1, 1H), 5.78 (dd, $J$=8.8, 6.6, 1H).

$^{13}$C NMR (101 MHz, Chloroform-d) $\delta$ = 167.0, 166.9, 166.4, 140.9, 138.4, 134.0, 133.8, 132.8, 132.3, 131.8, 130.6, 129.9, 128.8, 128.7, 128.6, 128.5, 127.5, 127.1, 105.8, 75.8, 65.9, 54.6.

IR (ATR, v in cm$^{-1}$): 3377 (w), 3060 (w), 3032 (w), 1719 (w), 1662 (m), 1602 (w), 1580 (w), 1520 (m), 1487 (m), 1449 (w), 1317 (m), 1285 (m), 1257 (s), 1092 (m), 1026 (m), 970 (w), 786 (w), 757 (m), 707 (s), 690 (s).

MS (ESI) m/z calcd for C$_{33}$H$_{28}$N$_{4}$O$_{4}$Na 567.2 [M+Na]$^+$, found 567.4 [M+Na]$^+$.

HRMS (El) m/z calcd for C$_{30}$H$_{24}$N$_{2}$O$_{4}$ 476.1736 [M-C$_{3}$H$_{4}$N$_{2}$]$^+$, found 476.1754 [M-C$_{3}$H$_{4}$N$_{2}$]$^+$. (We were not able to obtain HRMS data for the parent molecule without fragmentation. Therefore an additional CHN analysis was performed.)

**CHN calcd for C$_{33}$H$_{28}$N$_{4}$O$_{4}$: C 72.78; H 5.18, N 10.29, found: C 72.96; H 5.36, N 9.99.**

2.7.10 1,3-Diamino-2-ol 7j

Prepared according to **TP8** from (Z)-2-benzamidovinyl benzoate 1a (66.8 mg, 0.25 mmol, 1.0 equiv), N-acylimine precursors 3a 87.3 mg, 0.275 mmol, 1.1 equiv), SiCl$_{4}$ (58 µL, 0.5 mmol, 2.0 equiv),...
trimethylsilyl azide (132 µL, 1.0 mmol, 4.0 equiv) in a total of 2.5 mL dichloromethane. Purification by flash chromatography via puriflash XS 420+ machine, HP_15µm_F0012 flash column (n-hexane:EtOAc = 92:8 → 40:60) afforded the desired 1,3-diamin-2-ol 7j as a colorless foam (61.2 mg, 43%, crude $dr = 75:25$, as determined by $^1$H NMR analysis (400 MHz) of the crude product after aqueous workup; overall isolated yield for all diastereomers 78.4 mg, 57%; $dr = 87:13$, as calculated from the isolated products).

$R_f$ (n-hexane:EtOAc = 6:4) 0.47.

$m.p.$ 102-109 °C.

$^1$H NMR (600 MHz, Chloroform-d) $\delta = 8.05 – 8.01$ (m, 2H), 7.94 (d, $J$=8.5, 1H), 7.87 – 7.82 (m, 2H), 7.62 – 7.59 (m, 2H), 7.59 – 7.55 (m, 3H), 7.54 – 7.52 (m, 1H), 7.46 – 7.36 (m, 8H), 7.34 – 7.30 (m, 2H), 6.75 (d, $J$=8.6, 1H), 5.88 (dd, $J$=8.5, 3.0, 1H), 5.76 (dd, $J$=8.6, 7.4, 1H), 5.66 (dd, $J$=7.4, 3.1, 1H).

$^{13}$C NMR (151 MHz, Chloroform-d) $\delta = 167.6, 167.4, 138.1, 134.2, 133.7, 132.8, 132.5, 131.9, 130.2, 129.7, 129.0, 128.9, 128.8, 128.7, 127.8, 127.6, 127.0, 76.4, 66.6, 54.8.$

IR (ATR, $\nu$ in cm$^{-1}$): 3282 (w), 3062 (w), 2970 (w), 2109 (s), 1725 (m), 1693 (s), 1602 (w), 1580 (w), 1516 (s), 1484 (s), 1450 (m), 1313 (m), 1248 (s), 1147 (w), 1094 (m), 1069 (m), 1026 (m), 926 (w), 799 (w), 691 (s).

MS (ESI) m/z calcd for $C_{30}H_{25}N_5O_4Na$ 542.2 [M+Na]$^+$, found 542.4 [M+Na]$^+$. HRMS (EI) m/z calcd for $C_{30}H_{24}N_2O_4$: 476.1753 [M-HN$_3$]$^+$, found 476.1736 [M-HN$_3$]$^+$. (We were not able to obtain HRMS data for the parent molecule without fragmentation. Therefore an additional CHN analysis was performed.)

CHN calcd for $C_{30}H_{25}N_5O_4$: C 69.35; H 4.85, N 13.48, found: C 69.06, H 4.86, N 13.28.

2.7.11 1,3-Diamino-2-ol 7k

Prepared according to TP8 from (Z)-2-benzamidovinyl benzoate 1a (66.8 mg, 0.25 mmol, 1.0 equiv), N-acylimine precursor 3a 87.3 mg, 0.275 mmol, 1.1 equiv), SiCl$_4$ (58 µL, 0.5 mmol, 2.0 equiv), ethanethiol (75.6 µL, 1.0 mmol, 4.0 equiv) in a total of 2.5 mL dichloromethane. Purification by flash chromatography via puriflash XS 420+ machine, HP_15µm_F0012 flash column (n-hexane:EtOAc = 95:5 → 70:30) afforded the desired 1,3-diamin-2-ol 7k as a colorless foam (112 mg, 83%, isolated $dr = 90:10$; $dr$ of the crude mixture 83:17 as determined by $^1$H NMR analysis of the crude product after aqueous workup). Separation of diastereomers was not possible for 7k. Analytical data are given for the isolate mixture of two diastereomers ($dr = 90:10$).

$R_f$ (n-hexane:EtOAc = 6:4) 0.47.
m.p. 95-100 °C.

$^1$H NMR (400 MHz, Chloroform-d) $\delta$ = 8.11 – 8.03 (m, 1.7H), 7.98 (dd, J=8.4, 1.4, 0.3H), 7.78 (ddd, J=11.7, 8.4, 1.4, 0.5H), 7.74 – 7.64 (m, 3.5H), 7.63 – 7.56 (m, 3H), 7.52 – 7.31 (m, 11H), 7.08 (d, J=6.5, 1H), 6.92 (d, J=8.9, 0.85H), 6.85 (d, J=9.3, 0.15H), 5.94 – 5.81 (m, 1.85H), 5.76 – 5.63 (m, 0.3H), 5.42 (dd, J=8.9, 1.8, 0.85H), 2.78-2.66 (m, 0.2H), 2.58 (qd, J=7.3, 2.3, 1.8H), 1.32 (t, J=7.3, 0.2H), 1.19 (dt, J=14.8, 7.4, 2.8H). (peaks not assigned to single stereoisomers)

$^{13}$C NMR (101 MHz, Chloroform-d) $\delta$ = 167.5, 167.4, 167.2, 167.0, 166.8, 166.6, 138.1, 138.0, 134.3, 134.0, 133.9, 133.8, 133.7, 133.4, 132.1, 132.1, 131.8, 131.7, 130.2, 129.9, 129.3, 129.0, 128.9, 128.8, 128.7, 128.6, 128.6, 127.7, 127.4, 127.2, 127.2, 127.1, 78.5, 77.9, 56.5, 55.9, 54.9, 54.4, 25.9, 25.5, 14.9, 14.9. (peaks not assigned to single stereoisomers)

IR (ATR, $\nu$ in cm$^{-1}$): 3295 (w), 3061 (w) 2967 (w), 1710 (w), 1638 (m), 1602 (w), 1579 (w), 1513 (m), 1482 (s), 1449 (m), 1313 (m), 1259 (s), 1179 (w), 1108 (m), 1070 (m), 1026 (m), 928 (w), 799 (w), 693 (s).

MS (ESI) m/z calcd for $C_{32}H_{30}N_2O_4SNa$ 561.2 [M+Na]$^+$, found 561.4 [M+Na]$^+$. HRMS (EI) m/z calcd for $C_{30}H_{25}N_2O_4$ $^{477.1814}$[M-$C_2H_5S$]$^+$, found $^{477.1823}$[M-$C_2H_5S$]$^+$. (We were not able to obtain HRMS data for the parent molecule without fragmentation. Therefore an additional CHN analysis was performed.)

CHN calcd for $C_{32}H_{30}N_2O_4S$: C 71.35; H 5.61, N 5.20, S 5.95, found: C 71.07, H 5.64, N 5.23, S 6.15.

2.8 1,3-Diamino-2-ols from different N-Acylimine precursors

Typical procedure 9 (TP9)

A flame dried and nitrogen flushed Schlenk tube, equipped with a septum and a magnetic stirrer, was charged with (Z)-oxenamide 1a (1.0 equiv), N-acylimine precursor 3b-j (1.1 equiv) and dichloromethane (10 mL/mmol). The solution was cooled to -65 °C and SiCl$_4$ (2.0 equiv) was added. The reaction was allowed to warm to -10 °C within 4 h. After TLC analysis showed complete consumption of the (Z)-oxenamide, the mixture was again cooled to -65 °C and 1,3,5-trimethoxybenzene (4.0 equiv) was added in one portion. The reaction was allowed to warm to 15°C overnight and then quenched with saturated aqueous NH$_4$Cl (5 mL). The organic layer was separated and the aqueous phase was extracted with dichloromethane (2x). The combined organic layers were dried over Na$_2$SO$_4$ and the solvent was evaporated under reduced pressure. Purification by flash chromatography afforded the desired 1,2-syn-2,3-anti-1,3-diamino-2-ol 8a-i as analytically pure product.
2.8.1 1,3-Diamino-2-ol 8a

Prepared according to TP9 from (Z)-2-benzamidovinyl benzoate 1a (66.8 mg, 0.25 mmol, 1.0 equiv), N-acylimine precursor 3b (75.8 mg, 0.275 mmol, 1.1 equiv), SiCl4 (58 µL, 0.5 mmol, 2.0 equiv), 1,3,5-trimethoxybenzene (172 mg, 1.0 mmol, 4.0 equiv) in a total of 2.5 mL dichloromethane. Purification by flash chromatography via puriflash XS 420+ machine, HP_15µm F0012 flash column (n-hexane:EtOAc = 92:8 → 40:60) afforded the desired 1,3-diamino-2-ol 8a as a colorless foam (142 mg, 84%, isolated dr >98:2; dr of the crude mixture >98:2, as determined by 1H NMR analysis of the crude product after aqueous workup).

Rf (n-hexane:EtOAc = 6:4) 0.26.

m.p. 93-101 °C.

1H NMR (400 MHz, Chloroform-d) δ 7.93 (d, J = 9.7 Hz, 1H), 7.79 – 7.70 (m, 4H), 7.68 – 7.60 (m, 2H), 7.58 – 7.45 (m, 3H), 7.42 – 7.32 (m, 9H), 7.23 (d, J = 8.5 Hz, 2H), 6.48 (dd, J = 9.7, 7.1 Hz, 1H), 5.98 (s, 2H), 5.92 (dd, J = 7.1, 4.0 Hz, 1H), 5.68 (dd, J = 8.3, 3.9 Hz, 1H), 3.71 – 3.67 (m, 9H).

13C NMR (151 MHz, Chloroform-d) δ 166.7, 166.6, 165.2, 161.2, 159.0, 138.2, 134.6, 134.5, 133.3, 133.2, 131.6, 131.5, 129.7, 129.5, 128.8, 128.7, 128.6, 128.6, 128.4, 127.3, 127.1, 106.1, 101.0, 56.0, 55.4, 54.3, 46.1.

IR (ATR, v in cm⁻¹): 3436 (w), 2939 (w), 2839 (w), 1721 (w), 1663 (m), 1596 (m), 1512 (m), 1484 (s), 1452 (m), 1392 (w), 1261 (m), 1203 (w), 1149 (m), 1121 (s), 1092 (s), 1068 (m), 1028 (m), 950 (w), 815 (m), 709 (s).

MS (ESI) m/z calcld for C39H35ClN2O7Na 701.2 [M+Na]+, found 701.6 [M+Na]+.

HRMS (EI) m/z calcld for C39H35ClN2O7 678.2133 [M]+, found 678.2152 [M]+.

2.8.2 1,3-Diamino-2-ol 8b

Prepared according to TP9 from (Z)-2-benzamidovinyl benzoate 1a (66.8 mg, 0.25 mmol, 1.0 equiv), N-acylimine precursor 3c (75.8 mg, 0.275 mmol, 1.1 equiv), SiCl4 (58 µL, 0.5 mmol, 2.0 equiv), 1,3,5-trimethoxybenzene (172 mg, 1.0 mmol, 4.0 equiv) in a total of 2.5 mL dichloromethane. Purification by flash chromatography via puriflash XS 420+ machine, HP_15µm F0012 flash column (n-hexane:EtOAc = 92:8 → 40:60) afforded the desired 1,3-diamino-2-ol 8b as a colorless foam (95.7 mg,
53%, isolated \( dr >98:2 \); \( dr \) of the crude mixture >98:2, as determined by \(^1\)H NMR analysis of the crude product after aqueous workup).

\( R_f \) (n-hexane:EtOAc = 6:4) 0.26.

\[ \text{m.p.} \ 102-111 ^\circ \text{C.} \]

\[ \text{\(^1\)H NMR (400 MHz, Chloroform-}d\text{)} \ \delta = 7.93 \ (d, J=9.8, 1H), 7.74 \ (ddd, J=10.1, 8.2, 1.3, 4H), 7.69 – 7.61 \ (m, 2H), 7.56 – 7.42 \ (m, 3H), 7.42 – 7.28 \ (m, 11H), 6.47 \ (dd, J=9.7, 7.1, 1H), 5.98 \ (s, 2H), 5.91 \ (dd, J=7.1, 4.0, 1H), 5.66 \ (dd, J=8.3, 4.0, 1H), 3.71 \ (s, 6H), 3.67 \ (s, 3H). \]

\[ \text{\(^{13}\)C NMR (151 MHz, Chloroform-}d\text{)} \ \delta = 166.7, 166.6, 165.2, 161.2, 159.0, 138.7, 134.6, 134.5, 133.2, 131.6, 131.6, 131.5, 129.7, 129.5, 129.2, 128.6, 128.4, 127.3, 127.1, 121.6, 106.2, 91.0, 56.0, 55.4, 54.4, 46.1. \]

\[ \text{IR (ATR, } \nu \text{ in cm}^{-1}\text{): 3435 (w), 3062 (w), 2939 (w), 1722 (w), 1663 (m), 1596 (m), 1512 (s), 1483 (s), 1452 (m), 1429 (w), 1310 (w), 1261 (m), 1203 (m), 1149 (m), 1121 (s), 1068 (m), 1008 (m), 950 (w), 815 (m), 708 (s).} \]

\[ \text{MS (ESI) } m/z \ \text{calcd for } C_{39}H_{35}BrN_2O_7Na 745.2 \ [M+Na]^+, \ \text{found 745.5 \ [M+Na]^+.} \]

\[ \text{HRMS (EI) } m/z \ \text{calcd for } C_{39}H_{35}BrN_2O_7 \ 722.1628 \ [M]^+, \ \text{found 722.1638 \ [M]^+.} \]

\[ \text{2.8.3 1,3-Diamino-2-ol 8c} \]

Prepared according to TP9 from (Z)-2-benzamidovinyl benzoate 1a (66.8 mg, 0.25 mmol, 1.0 equiv), \( N\)-acylimine precursor 3d (70.2 mg, 0.275 mmol, 1.1 equiv), SiCl\(_4\) (58 \( \mu \)L, 0.5 mmol, 2.0 equiv), 1,3,5-trimethoxybenzene (172 mg, 1.0 mmol, 4.0 equiv) in a total of 2.5 mL dichloromethane. Purification by flash chromatography via puriflash XS 420+ machine, HP_15 \( \mu \)m_F0012 flash column (n-hexane:EtOAc = 92:8 \( \rightarrow \) 40:60) afforded the desired 1,3-diamino-2-ol 8c as a colorless foam (153 mg, 93%, isolated \( dr >98:2 \); \( dr \) of the crude mixture >98:2, as determined by \(^1\)H NMR analysis of the crude product after aqueous workup).

\[ R_f \) (n-hexane:EtOAc = 6:4) 0.23.

\[ \text{m.p.} \ 98-101 ^\circ \text{C.} \]

\[ \text{\(^1\)H NMR (400 MHz, Chloroform-}d\text{)} \ \delta = 7.86 – 7.74 \ (m, 3H), 7.74 – 7.66 \ (m, 2H), 7.65 – 7.57 \ (m, 2H), 7.52 – 7.42 \ (m, 3H), 7.37 – 7.31 \ (m, 8H), 7.14 \ (d, J = 8.5 Hz, 1H), 7.05 \ (d, J = 7.9 Hz, 2H), 6.50 \ (dd, J = 9.8, 7.2 Hz, 1H), 6.00 – 5.93 \ (m, 3H), 5.68 \ (dd, J = 8.5, 4.5 Hz, 1H), 3.72 \ (s, 6H), 3.68 \ (s, 3H), 2.24 \ (s, 3H). \]

\[ \text{\(^{13}\)C NMR (151 MHz, Chloroform-}d\text{)} \ \delta = 166.6, 166.3, 165.6, 161.0, 159.1, 137.1, 136.8, 134.9, 134.8, 133.1, 131.3, 131.3, 130.0, 129.6, 129.3, 128.5, 128.4, 127.2, 127.2, 127.1, 106.6, 91.0, 56.0, 55.4, 54.6, 46.3, 21.2. \]
Preparation and analytical data

IR (ATR, ν in cm$^{-1}$): 3439 (w), 2939 (w), 2839 (w), 1721 (w), 1663 (m), 1596 (m), 1512 (s), 1483 (s), 1452 (m), 1419 (w), 1311 (w), 1260 (m), 1203 (m), 1149 (m), 1120 (s), 1068 (m), 1028 (m), 949 (w), 814 (m), 708 (s).

MS (ESI) m/z calcd for $C_{40}H_{38}N_2O_7Na$ 681.3 [M+Na]$^+$, found 681.6 [M+Na]$^+$.

HRMS (E I) m/z calcd for $C_{40}H_{38}N_2O_7$ 658.2688 [M]$^+$, found 658.2688 [M]$^+$.

2.8.4 1,3-Diamino-2-ol 8d

Prepared according to TP9 from (Z)-2-benzamidovinyl benzoate 1a (66.8 mg, 0.25 mmol, 1.0 equiv), N-acylimine precursor 3e (74.6 mg, 0.275 mmol, 1.1 equiv), SiCl$_4$ (58 µL, 0.5 mmol, 2.0 equiv), 1,3,5-trimethoxybenzene (172 mg, 1.0 mmol, 4.0 equiv) in a total of 2.5 mL dichloromethane. Purification by flash chromatography via puriflash XS 420+ machine, HP_15µm_F0012 flash column ($n$-hexane:EtOAc = 92:8 → 40:60) afforded the desired 1,3-diamino-2-ol 8d as a colorless foam (160 mg, 95%, isolated dr >98:2; dr of the crude mixture >98:2, as determined by $^1$H NMR analysis of the crude product after aqueous workup).

m.p. 79-85 °C.

$^1$H NMR (400 MHz, Chloroform-$d$) δ 7.87 – 7.80 (m, 1H), 7.79 – 7.75 (m, 2H), 7.73 – 7.69 (m, 2H), 7.64 – 7.60 (m, 2H), 7.52 – 7.48 (m, 1H), 7.46 – 7.42 (m, 2H), 7.39 – 7.33 (m, 8H), 7.16 (d, J=8.4, 1H), 6.78 (d, J=8.7, 2H), 6.49 (dd, J=9.8, 7.1, 1H), 5.98 (s, 2H), 5.95 (dd, J=7.1, 4.7, 1H), 5.66 (dd, J=8.5, 4.6, 1H), 3.72 (s, 6H), 3.71 (s, 3H), 3.68 (s, 3H).

$^{13}$C NMR (151 MHz, Chloroform-$d$) δ 166.6, 166.4, 165.6, 161.1, 159.1, 159.0, 134.9, 134.8, 133.1, 131.9, 131.3, 129.6, 128.5, 128.5, 128.4, 127.5, 127.2, 127.1, 114.0, 106.6, 91.0, 56.0, 55.4, 55.3, 54.2, 46.3.

IR (ATR, ν in cm$^{-1}$): 3438 (w), 2937 (w), 1720 (w), 1656 (m), 1607 (m), 1511 (s), 1484 (m), 1452 (m), 1330 (w), 1247 (s), 1203 (m), 1179 (m), 1149 (m), 1121 (s), 1068 (m), 1028 (m), 950 (w), 815 (m), 709 (s).

MS (ESI) m/z calcd for $C_{40}H_{38}N_2O_7Na$ 697.3 [M+Na]$^+$, found 697.6 [M+Na]$^+$.

HRMS (E I) m/z calcd for $C_{40}H_{38}N_2O_8$ 674.2628 [M]$^+$, found 674.2633 [M]$^+$.
2.8.5 1,3-Diamino-2-ol 8e

Prepared according to TP9 from (Z)-2-benzamidovinyl benzoate 1a (66.8 mg, 0.25 mmol, 1.0 equiv), N-acylimine precursor 3f (79.0 mg, 0.275 mmol, 1.1 equiv), SiCl₄ (58 µL, 0.5 mmol, 2.0 equiv), 1,3,5-trimethoxybenzene (172 mg, 1.0 mmol, 4.0 equiv) in a total of 2.5 mL dichloromethane. Purification by flash chromatography via puriflash XS 420+ machine, HP_15µm_F0012 flash column (n-hexane:EtOAc = 92:8 → 40:60) afforded the desired 1,3-diamino-2-ol 8e as a colorless foam (98.8 mg, 57%, isolated d.r >98:2; d.r of the crude mixture >98:2, as determined by ¹H NMR analysis of the crude product after aqueous workup).

Rf (n-hexane:EtOAc = 6:4) 0.20.

m.p. 119-123 °C.

¹H NMR (400 MHz, Chloroform-d) δ 8.11 (d, J = 8.7 Hz, 2H), 7.97 (d, J = 9.6 Hz, 1H), 7.83 – 7.77 (m, 2H), 7.72 – 7.64 (m, 4H), 7.61 (d, J = 8.7 Hz, 2H), 7.55 – 7.33 (m, 10H), 6.50 (dd, J = 9.6, 7.3 Hz, 1H), 5.99 (s, 2H), 5.94 (dd, J = 7.2, 3.5 Hz, 1H), 5.76 (dd, J = 7.7, 3.4 Hz, 1H), 3.73 (s, 6H), 3.68 (s, 3H).

¹³C NMR (151 MHz, Chloroform-d) δ 167.0, 166.7, 165.0, 161.3, 147.4, 147.3, 134.3, 134.2, 133.4, 131.8, 131.8, 129.5, 129.4, 128.7, 128.3, 127.4, 127.1, 123.8, 105.8, 91.1, 76.6, 56.1, 55.5, 54.8, 46.1.

IR (ATR, v in cm⁻¹): 3431 (w), 2940 (w), 1723 (m), 1663 (m), 1600 (m), 1513 (s), 1483 (s), 1453 (m), 1419 (w), 1344 (s), 1257 (s), 1224 (w), 1204 (m), 1150 (m), 1121 (s), 1068 (m), 1028 (m), 950 (w), 815 (w), 708 (s).

MS (ESI) m/z calcd for C₃₉H₃₅N₃O₉Na 712.2 [M+Na]+, found 712.6 [M+Na]+.

HRMS (EI) m/z calcd for C₃₉H₃₅N₃O₉ 689.2373 [M]+, found 689.2385 [M]+.

2.8.6 1,3-Diamino-2-ol 8f

Prepared according to TP9 from (Z)-2-benzamidovinyl benzoate 1a (66.8 mg, 0.25 mmol, 1.0 equiv), N-acylimine precursor 3g (87.3 mg, 0.275 mmol, 1.1 equiv), SiCl₄ (58 µL, 0.5 mmol, 2.0 equiv), 1,3,5-trimethoxybenzene (172 mg, 1.0 mmol, 4.0 equiv) in a total of 2.5 mL dichloromethane. Purification by flash chromatography via puriflash XS 420+ machine, HP_15µm_F0012 flash column (n-hexane:EtOAc = 92:8 → 40:60) afforded the desired 1,3-diamino-2-ol 8h as a colorless foam (156 mg,
Preparation and analytical data

86%, isolated dr >98:2; dr of the crude mixture >98:2, as determined by $^1$H NMR analysis of the crude product after aqueous workup).

Rf (n-hexane:EtOAc = 6:4) 0.19.

m.p. 115-119 °C.

$^1$H NMR (400 MHz, Chloroform-d) δ 7.89 (d, J = 9.8 Hz, 1H), 7.78 – 7.74 (m, 4H), 7.64 – 7.60 (m, 2H), 7.56 – 7.27 (m, 19H), 6.54 (dd, J = 9.8, 7.2 Hz, 1H), 6.02 (dd, J = 7.2, 4.5 Hz, 1H), 5.98 (s, 2H), 5.80 – 5.72 (m, 1H), 3.72 (s, 6H), 3.68 (s, 3H).

$^{13}$C NMR (151 MHz, Chloroform-d) δ 166.7, 166.5, 165.5, 161.1, 141.0, 140.4, 138.8, 134.8, 134.7, 133.1, 131.4, 129.9, 129.6, 128.8, 128.6, 128.4, 127.8, 127.4, 127.3, 127.2, 127.1, 106.5, 91.0, 56.0, 55.4, 54.6, 46.3.

IR (ATR, ν in cm$^{-1}$): 3439 (w), 2939 (w), 1721 (w), 1663 (m), 1597 (m), 1512 (m), 1483 (s), 1452 (m), 1418 (w), 1311 (w), 1261 (m), 1203 (m), 1149 (m), 1106 (m), 950 (w), 815 (w), 708 (s), 693 (s).

MS (ESI) m/z calcd for C$_{45}$H$_{40}$N$_2$O$_7$Na 743.3 [M+Na]$^+$, found 743.6 [M+Na]$^+$.

HRMS (El) m/z calcd for C$_{45}$H$_{40}$N$_2$O$_7$ 720.2836 [M]$^+$, found 720.2849 [M]$^+$.

2.8.7 1,3-Diamino-2-ol 8g

Prepared according to TP9 from (Z)-2-benzamidovinyl benzoate 1a (66.8 mg, 0.25 mmol, 1.0 equiv), N-acylimine precursor 3h (75.8 mg, 0.275 mmol, 1.1 equiv), SiCl$_4$ (58 µL, 0.5 mmol, 2.0 equiv), 1,3,5-trimethoxybenzene (172 mg, 1.0 mmol, 4.0 equiv) in a total of 2.5 mL dichloromethane. Purification by flash chromatography via puriflash XS 420+ machine, HP_15µm_F0012 flash column (n-hexane:EtOAc = 92:8 → 40:60) afforded the desired 1,3-diamino-2-ol 8f as a colorless foam (93.8 mg, 55%, isolated dr >98:2; dr of the crude mixture >98:2, as determined by $^1$H NMR analysis of the crude product after aqueous workup).

Rf (n-hexane:EtOAc = 6:4) 0.21.

m.p. 103-110 °C.

$^1$H NMR (400 MHz, Chloroform-d) δ 7.89 (d, J = 10.1 Hz, 1H), 7.85 (d, J = 7.2 Hz, 2H), 7.74 – 7.70 (m, 4H), 7.54 – 7.42 (m, 5H), 7.41 – 7.32 (m, 5H), 7.25 – 7.21 (m, 1H), 7.13 – 7.06 (m, 1H), 7.03 – 6.99 (m, 1H), 6.56 (dd, J = 9.8, 8.6 Hz, 1H), 6.13 (dd, J = 8.4, 2.6 Hz, 1H), 6.07 (dd, J = 7.6, 2.5 Hz, 1H), 6.01 (s, 2H), 3.83 (s, 6H), 3.68 (s, 3H).
Preparation and analytical data

\(^{13}\)C NMR (151 MHz, Chloroform-d) \(\delta = 166.8, 166.5, 164.8, 161.1, 137.2, 135.0, 135.0, 133.1, 132.8, 131.5, 131.4, 130.0, 129.8, 129.4, 128.8, 128.7, 128.6, 128.4, 127.7, 127.4, 127.2, 126.9, 106.7, 91.2, 75.2, 56.5, 55.4, 52.2, 45.7.

IR (ATR, \(\nu\) in cm\(^{-1}\)): 3441 (w), 2940 (w), 1725 (m), 1666 (s), 1595 (m), 1509 (s), 1482 (s), 1419 (w), 1329 (w), 1257 (m), 1203 (m), 1149 (m), 1121 (s), 1067 (m), 1030 (m), 950 (w), 815 (w), 706 (s).

MS (ESI) m/z calcd for \(C_{39}H_{35}ClN_2O_7Na\) 701.2 \([M+Na]\)^+, found 701.5 \([M+Na]\)^+.

HRMS (EI) m/z calcd for \(C_{39}H_{35}ClN_2O_7\) 678.2133 \([M]\)^+, found 678.2123 \([M]\)^+.

2.8.8 1,3-Diamino-2-ol 8h

Prepared according to TP9 from (Z)-2-benzamidovinyl benzoate 1a (66.8 mg, 0.25 mmol, 1.0 equiv), N-acylimine precursor 3i (74.6 mg, 0.275 mmol, 1.1 equiv), SiCl\(_4\) (58 \(\mu\)L, 0.5 mmol, 2.0 equiv), 1,3,5-trimethoxybenzene (172 mg, 1.0 mmol, 4.0 equiv) in a total of 2.5 mL dichloromethane. Purification by flash chromatography via puriflash XS 420+ machine, HP_15µm_F0012 flash column (n-hexane:EtOAc = 92:8 → 40:60) afforded the desired 1,3-diamino-2-ol 8i as a colorless foam (64.4 mg, 38%, isolated \(dr >98:2\); \(dr\) of the crude mixture >98:2, as determined by \(^1\)H NMR analysis of the crude product after aqueous workup).

\(R_f\) (n-hexane:EtOAc = 6:4) 0.30.

m.p. 102-107 °C.

\(^1\)H NMR (400 MHz, Chloroform-d) \(\delta = 7.81 (d, J=9.9, 1H), 7.77 (d, J=7.7, 2H), 7.74 – 7.69 (m, 2H), 7.55 – 7.45 (m, 2H), 7.44 – 7.27 (m, 10H), 7.29 – 7.07 (m, 4H), 6.43 (t, \(J=9.0, 1H\)), 5.99 (s, 2H), 5.91 (dd, \(J=7.8, 3.8, 1H\)), 5.80 (d, \(J=9.1, 1H\)), 5.34 (dd, \(J=9.0, 4.1, 1H\)), 5.05 (s, 2H), 3.74 (s, 6H), 3.69 (s, 3H).

\(^{13}\)C NMR (101 MHz, Chloroform-d) \(\delta = 166.4, 165.1, 161.0, 159.2, 155.8, 140.0, 136.6, 135.1, 133.0, 131.3, 129.8, 129.6, 128.6, 128.4, 128.3, 128.1, 127.5, 127.1, 126.9, 106.6, 91.0, 77.0, 67.0, 56.0, 55.8, 55.3, 45.9.

IR (ATR, \(\nu\) in cm\(^{-1}\)): 3438 (w), 2939 (w), 1715 (m), 1664 (m), 1594 (m), 1508 (m), 1484 (m), 1452 (m), 1330 (w), 1259 (m), 1223 (m), 1204 (m), 1149 (m), 1119 (s), 1053 (s), 1027 (m), 949 (w), 815 (w), 698 (s).

MS (ESI) m/z calcd for \(C_{40}H_{38}N_2O_8Na\) 697.3 \([M+Na]\)^+, found 697.6 \([M+Na]\)^+.

HRMS (EI) m/z calcd for \(C_{28}H_{36}N_2O_7\) 674.2628 \([M+H]\)^+, found 674.2646 \([M+H]\)^+. 
2.8.9 1,3-Diamino-2-ol 8i

Prepared according to TP9 from (Z)-2-benzenimidoylbenzofuran 1a (66.8 mg, 0.25 mmol, 1.0 equiv), N-acylimine precursor 3j (80.0 mg, 0.275 mmol, 1.1 equiv), SiCl₄ (58 µL, 0.5 mmol, 2.0 equiv), 1,3,5-trimethoxybenzene (172 mg, 1.0 mmol, 4.0 equiv) in a total of 2.5 mL dichloromethane. Purification by flash chromatography via puriflash XS 420+ machine, HP_15μm_F0012 flash column (n-hexane:EtOAc = 92:8 → 40:60) afforded the desired 1,3-diamino-2-ol 8g as a colorless foam (107 mg, 61%, isolated dr >98:2; dr of the crude mixture >98:2, as determined by 1H NMR analysis of the crude product after aqueous workup).

Rf (n-hexane:EtOAc = 6:4) 0.17.

m.p. 103-110 °C.

1H NMR (400 MHz, Chloroform-d) δ 7.94 (s, 1H), 7.88 (d, J = 9.7 Hz, 1H), 7.81 – 7.69 (m, 7H), 7.59 – 7.55 (m, 3H), 7.51 – 7.28 (m, 12H), 6.57 (dd, J = 9.8, 7.1 Hz, 1H), 6.09 (dd, J = 7.0, 4.5 Hz, 1H), 5.97 (s, 2H), 5.88 (dd, J = 8.5, 4.5 Hz, 1H), 3.67 – 3.66 (m, 9H).

13C NMR (151 MHz, Chloroform-d) δ 166.7, 166.5, 165.6, 161.1, 159.1, 137.1, 134.8, 134.7, 133.5, 133.1, 133.0, 131.4, 129.9, 129.6, 128.6, 128.5, 128.4, 128.3, 128.2, 127.6, 127.3, 127.1, 126.3, 126.0, 125.9, 125.5, 106.5, 91.0, 56.0, 55.4, 54.9, 46.3.

IR (ATR, v in cm⁻¹): 3438 (w), 2939 (w), 1720 (w), 1663 (m), 1597 (m), 1509 (s), 1482 (s), 1452 (m), 1419 (w), 1314 (w), 1262 (m), 1203 (m), 1149 (m), 1119 (s), 1068 (m), 1028 (m), 950 (m), 815 (m), 752 (w), 709 (s).

MS (ESI) m/z calcd for C₄₃H₃₈N₂O₇Na 717.3 [M+Na]⁺, found 717.6 [M+Na]⁺.

HRMS (EI) m/z calcd for C₄₃H₃₈N₂O₇: 694.2679 [M]⁺, found 694.2672 [M]⁺.

2.9 Deprotection

2.9.1 1,3-Diamino-2-ol 9a

To a solution of 1,3-diamin-2-ol 5a (120 mg, 0.25 mmol, 1.0 equiv) in methanol (3.5 mL) was added at room temperature sodium methoxide (21 mg, 0.375 mmol, 1.5 equiv) in one portion. After stirring for 1 h the reaction mixture was quenched with saturated aqueous NH₄Cl (5 mL). The aqueous phase was extracted with dichloromethane (3x 5 mL) and the combined organic layers were dried over Na₂SO₄.
before the solvent was evaporated under reduced pressure. Purification by flash chromatography via puriflash XS 420+ machine, HP_15μm_F0012 flash column (n-hexane:EtOAc = 90:10 → 20:80) afforded the deprotected 1,2-syn-1,3-diamin-2-ol 9a as a colorless solid (80.5 mg, 86%, isolated dr >98:2; dr of the crude mixture >98:2, as determined by 1H NMR analysis of the crude product after aqueous workup).

Rf (n-hexane:EtOAc = 1:1) 0.47.

m.p. 194-199 °C.

1H NMR (400 MHz, DMSO-d6) δ = 8.59 (d, J=8.6, 1H), 8.39 (t, J=5.5, 1H), 7.93 – 7.88 (m, 2H), 7.87 – 7.80 (m, 2H), 7.60 – 7.42 (m, 8H), 7.33 (dd, J=8.3, 6.8, 2H), 7.28 – 7.22 (m, 1H), 5.20 (d, J=6.4, 1H), 5.12 (dd, J=8.6, 5.3, 1H), 4.20 – 4.00 (m, 1H), 3.39 – 3.34 (m, 1H), 3.26 – 3.15 (m, 1H).

13C NMR (101 MHz, DMSO-d6) δ = 166.5, 166.3, 141.4, 134.6, 134.6, 131.3, 131.1, 128.3, 128.1, 127.5, 127.4, 127.2, 126.8, 71.7, 56.3, 43.6.

IR (ATR, v in cm⁻¹): 3316 (m), 3030 (w), 2870 (w), 1635 (s), 1619 (m), 1577 (m), 1525 (s), 1487 (m), 1440 (w), 1357 (w), 1316 (w), 1279 (m), 1147 (w), 1108 (s), 1091 (m), 1029 (w), 923 (w), 802 (w), 693 (s).

MS (ESI) m/z calcd for C23H22N2O3Na 397.2 [M+Na]⁺, found 397.4 [M+Na]⁺.

HRMS (EI) m/z calcd for C23H20N2O2 356.1525 [M−H2O], found 356.1524 [M−H2O].

2.9.2 1,3-Diamino-2-ol 9b

To a solution of 1,3-diamin-2-ol 5a (161 mg, 0.25 mmol, 1.0 equiv) in methanol (3.5 mL) was added at room temperature sodium methoxide (42 mg, 0.75 mmol, 3.0 equiv) in one portion. After stirring for 2.5 h the reaction mixture was quenched with saturated aqueous NH₄Cl (5 mL). The aqueous phase was extracted with dichloromethane (3x 5 mL) and the combined organic layers were dried over Na₂SO₄ before the solvent was evaporated under reduced pressure. Purification by flash chromatography via puriflash XS 420+ machine, HP_15μm_F0012 flash column (n-hexane:EtOAc = 90:10 → 20:80) afforded the deprotected 1,2-syn-2,3-anti-1,3-diamin-2-ol 9b as a colorless foam (123 mg, 91%, isolated dr >98:2; dr of the crude mixture >98:2, as determined by 1H NMR analysis of the crude product after aqueous workup).

Rf (n-hexane:EtOAc = 1:1) 0.27.

m.p. 106-110 °C.

1H NMR (400 MHz, Chloroform-d) δ = 8.47 (d, J=8.6, 1H), 7.71 – 7.66 (m, 2H), 7.65 – 7.60 (m, 2H), 7.52 – 7.27 (m, 8H), 7.26 – 7.14 (m, 4H), 6.24 (dd, J=8.7, 4.7, 1H), 6.19 (s, 2H), 5.30 (d, J=8.0, 1H), 4.31 (dd, J=4.7, 1.4, 1H), 3.88 (s, 6H), 3.81 (s, 3H), 2.71 (bs, 1H).
\(^{13}\text{C NMR}\) (101 MHz, \textit{Chloroform-d}) \(\delta = 168.2, 166.3, 161.2, 159.0, 141.9, 134.5, 134.0, 131.6, 131.2, 128.6, 128.4, 128.4, 127.1, 127.0, 127.0, 126.8, 105.1, 91.2, 77.8, 56.2, 55.4, 54.1, 50.8.

\textit{IR (ATR, \(\nu\) in cm}^{-1}\)): 3423 (w), 2939 (w), 1646 (m), 1605 (m), 1512 (s), 1482 (s), 1453 (m), 1418 (m), 1329 (w), 12247 (w), 1203 (m), 1148 (m), 1121 (s), 1057 (m), 1031 (m), 951 (w), 923 (w), 814 (w), 694 (s).

\textit{MS (ESI)} m/z calcd for C\(_{32}\)H\(_{32}\)N\(_2\)O\(_6\)Na 563.2 [M+Na]\(^+\), found 563.5 [M+Na]\(^+\).

\textit{HRMS (EI)} m/z calcd for C\(_{32}\)H\(_{30}\)N\(_2\)O\(_5\) 522.2155 [M-H\(_2\)O], found 522.2155 [M-H\(_2\)O].
Figure 1: $^1$H (400 MHz) and $^{13}$C (101 MHz) NMR spectra of $S1a$ in CDCl$_3$. 
Figure 2: $^1$H (400 MHz) and $^{13}$C (101 MHz) NMR spectra of S1b in CDCl$_3$. 
Figure 3: $^1$H (400 MHz) and $^{13}$C (101 MHz) NMR spectra of S1c in CDCl$_3$. 
Figure 4: $^1$H (400 MHz) NMR spectra of 2a in CDCl$_3$.

Figure 5: $^1$H (400 MHz) NMR spectra of 2b in CDCl$_3$. 

Figure 6: $^1$H (400 MHz) NMR spectra of 2c in CDCl$_3$. 
Figure 7: $^1$H (400 MHz) and $^{13}$C (101 MHz) NMR spectra of 1a in CDCl$_3$. 

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$^1$H (400 MHz) and $^{13}$C (101 MHz) NMR spectra of 1a in CDCl$_3$. 

$^1$H (400 MHz) and $^{13}$C (101 MHz) NMR spectra of 1a in CDCl$_3$.
Figure 8: $^1$H (400 MHz) and $^{13}$C (101 MHz) NMR spectra of 1b in CDCl$_3$. 
Figure 9: $^1$H (400 MHz) and $^{13}$C (101 MHz) NMR spectra of 1c in CDCl$_3$. 
Figure 10: $^1$H (400 MHz) and $^{13}$C (101 MHz) NMR spectra of 1d in CDCl$_3$. 
Figure 11: $^1$H (400 MHz) and $^{13}$C (101 MHz) NMR spectra of 1e in CDCl$_3$. 
Figure 1: $^1$H (400 MHz) NMR spectra of 4a in CDCl$_3$.

$\text{d.r.} = 70:30$

Figure 13: $^1$H (400 MHz) NMR spectra of 4b in CDCl$_3$.

$\text{d.r.} = 87:13$
Figure 14: $^1$H (400 MHz) NMR spectra of $4c$ in CDCl$_3$.

Figure 15: $^1$H (400 MHz) NMR spectra of $4d$ in CDCl$_3$. 

\[ d.r. = 54:46 \]

\[ d.r. = 56:44 \]
Figure 16: $^1$H (400 MHz) NMR spectra of 4e in CDCl$_3$. 

$d.r. = 52:48$
Figure 17: $^1$H (400 MHz) and $^{13}$C (101 MHz) NMR spectra of 5a in CDCl$_3$. 

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Figure 18: $^1$H (400 MHz) and $^{13}$C (101 MHz) NMR spectra of 5b in CDCl$_3$. 
Figure 19: $^1$H (400 MHz) and $^{13}$C (101 MHz) NMR spectra of 5c in CDCl$_3$. 
Figure 20: $^1$H (400 MHz) and $^{13}$C (101 MHz) NMR spectra of 5d in CDCl$_3$. 
Figure 21: $^1$H (400 MHz) and $^{13}$C (101 MHz) NMR spectra of 5e in CDCl$_3$. 
Figure 22: $^1$H (400 MHz) and $^{13}$C (101 MHz) NMR spectra of 6a in CDCl$_3$. 
Figure 23: $^1$H (400 MHz) and $^{13}$C (101 MHz) NMR spectra of 6b in CDCl$_3$. 
Figure 24: $^1$H (400 MHz) and $^{13}$C (101 MHz) NMR spectra of 6c in CDCl$_3$. 
Figure 25: $^1$H (400 MHz) and $^{13}$C (101 MHz) NMR spectra of 6e in CDCl$_3$. 
Figure 26: $^1$H (400 MHz) and $^{13}$C (101 MHz) NMR spectra of 7a in CDCl$_3$. 
Figure 27: $^1$H (400 MHz) and $^{13}$C (101 MHz) NMR spectra of 7b in CDCl₃.
Figure 28: $^1$H (400 MHz) and $^{13}$C (101 MHz) NMR spectra of 7c in DMSO-$d_6$. 
Figure 29: $^1$H (400 MHz) and $^{13}$C (101 MHz) NMR spectra of 7d in CDCl$_3$. 
Figure 30: $^1$H (400 MHz) and $^{13}$C (101 MHz) NMR spectra of 7e in CDCl$_3$. 
Figure 31: $^1$H (400 MHz) and $^{13}$C (101 MHz) NMR spectra of 7f in CDCl$_3$. 
Figure 32: $^1$H (400 MHz) and $^{13}$C (101 MHz) NMR spectra of 7g in CDCl$_3$. 
Figure 33: $^1$H (400 MHz) and $^{13}$C (101 MHz) NMR spectra of 7h in CDCl$_3$. 
Figure 34: $^1$H (400 MHz) and $^{13}$C (101 MHz) NMR spectra of 7g in CDCl$_3$. 
Figure 35: $^1$H (400 MHz) and $^{13}$C (101 MHz) NMR spectra of 7h in CDCl$_3$. 
Figure 36: $^1$H (400 MHz) and $^{13}$C (101 MHz) NMR spectra of 7i in CDCl$_3$. 

$d.r. = 90:10$
Figure 37: $^1$H (400 MHz) and $^{13}$C (101 MHz) NMR spectra of 8a in CDCl$_3$. 
Figure 38: $^1$H (400 MHz) and $^{13}$C (101 MHz) NMR spectra of 8b in CDCl$_3$. 
Figure 39: $^1$H (400 MHz) and $^{13}$C (101 MHz) NMR spectra of 8c in CDCl$_3$. 
Figure 40: $^1$H (400 MHz) and $^{13}$C (101 MHz) NMR spectra of 8d in CDCl$_3$. 
Figure 41: $^1$H (400 MHz) and $^{13}$C (101 MHz) NMR spectra of 8e in CDCl$_3$. 

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Figure 42: $^1$H (400 MHz) and $^{13}$C (101 MHz) NMR spectra of 8f in CDCl$_3$. 
Figure 43: $^1$H (400 MHz) and $^{13}$C (101 MHz) NMR spectra of 8g in CDCl$_3$. 
Figure 44: $^1$H (400 MHz) and $^{13}$C (101 MHz) NMR spectra of 8h in CDCl$_3$. 
Figure 45: $^1$H (400 MHz) and $^{13}$C (101 MHz) NMR spectra of 8i in CDCl$_3$. 
Figure 46: $^1$H (400 MHz) and $^{13}$C (101 MHz) NMR spectra of 9a in DMSO-$d_6$. 
Figure 47: $^1$H (400 MHz) and $^{13}$C (101 MHz) NMR spectra of 9b in CDCl$_3$. 
4 X-ray Data

Crystal structure determinations.

Data for 1c, 5b and 5c (CCDC 2087484, 2087485, 2087486) were collected on a STOE IPDS II two-circle diffractometer with a Genix Microfocus tube with mirror optics using MoKα radiation (λ = 0.71073 Å). The data were scaled using the frame scaling procedure in the X-Area program system (Stoe & Cie, 2002)[2]. The structures were solved by direct methods using the program SHELXS-2014/6 and refined against $F^2$ with full-matrix least-squares techniques using the program SHELXL-2014/6.[3]

The crystal of 3c was an extremely thin weakly diffracting needle. All H atoms were geometrically positioned and refined using a riding model.

In 6b and in 6c, the H atoms bonded to N were freely refined.

Data for 6a, 7a, 7c, 7g, 7h and 7i (CCDC 2097900, 2097895, 2097896, 2097898, 2097987, 2097899) were collected at 150.0(1) K on a Gemini S Ultra by Rigaku Oxford Diffraction, equipped with a molybdenum (λ = 0.71073 Å) and a copper (λ = 1.54184 Å) radiation source and a low-temperature control device. Due to the positioning of the two sources in the device, data collection is somewhat limited to smaller angles, which may result in alerts in some checkcif files. Absorption correction was done with CrysAlis Pro 1.171.38.41 and 1.171.40.67a, respectively. All structures were solved using the software programs SHELXS-2018/3, and the positions of all non-hydrogen atoms were refined with SHELXL-2018/3.[3]

In 6a, 7a, 7c, 7g, 7h and 7i the hydrogen atoms were calculated and refined using a riding model and isotropic thermal parameters.

In structure 7a chloroform and water were embedded. In structure 7h dichloromethane was embedded. Due to multiple misplacements and an unsatisfying solution a SQUEEZE[10] calculation was performed before refinement with SHELXL-2018/3.
Table 1. Crystal data and structure refinement for **1c**. Displacement ellipsoids are shown at the 50% probability level.

| Identification code | CCDC 2087484 |
|---------------------|---------------|
| Empirical formula   | C\textsubscript{11} H\textsubscript{11} N O\textsubscript{3} |
| Formula weight      | 205.21 |
| Temperature         | 173(2) K |
| Wavelength          | 0.71073 Å |
| Crystal system      | Orthorhombic |
| Space group         | \( P b c a \) |
| Unit cell dimensions| \( a = 9.3400(7) \) Å \( \alpha = 90^\circ \). \( b = 9.8923(10) \) Å \( \beta = 90^\circ \). \( c = 22.655(3) \) Å \( \gamma = 90^\circ \). |
| Volume              | 2093.2(4) Å\(^3\) |
| \( Z \)             | 8 |
| Density (calculated)| 1.302 Mg/m\(^3\) |
| Absorption coefficient | 0.096 mm\(^{-1}\) |
| \( F(000) \)        | 864 |
| Crystal size        | 0.260 x 0.190 x 0.110 mm\(^3\) |
| Theta range for data collection | 2.827 to 25.487°. |
| Index ranges        | -11<=h<=9, -10<=k<=11, -27<=l<=22 |
| Reflections collected | 4914 |
| Independent reflections | 1912 [\( R(int) = 0.0418 \) ] |
| Completeness to theta = 25.000° | 99.6 % |
| Absorption correction | Semi-empirical from equivalents |
| Max. and min. transmission | 1.000 and 0.800 |
| Refinement method   | Full-matrix least-squares on \( F^2 \) |
| Data / restraints / parameters | 1912 / 0 / 141 |
| Goodness-of-fit on \( F^2 \) | 0.985 |
| Final R indices [\( I>2\sigma(I) \)] | \( R1 = 0.0540, wR2 = 0.1310 \) |
| R indices (all data) | \( R1 = 0.0754, wR2 = 0.1412 \) |
| Largest diff. peak and hole | 0.318 and -0.301 e.Å\(^3\) |
Table 2. Crystal data and structure refinement for 5b. Displacement ellipsoids are shown at the 50% probability level.

Identification code: CCDC 2087485
Empirical formula: C\textsubscript{28}H\textsubscript{30}N\textsubscript{2}O\textsubscript{4}
Formula weight: 458.54
Temperature: 173(2) K
Wavelength: 0.71073 Å
Crystal system: Orthorhombic
Space group: \textit{P} \textit{bc} \textit{a}

Unit cell dimensions:
\begin{align*}
a &= 20.4044(7) \text{ Å} & \alpha &= 90^\circ, \\
b &= 19.7803(10) \text{ Å} & \beta &= 90^\circ, \\
c &= 24.9582(9) \text{ Å} & \gamma &= 90^\circ. \\
\end{align*}

Volume: 10073.3(7) Å\textsuperscript{3}
Z: 16
Density (calculated): 1.209 Mg/m\textsuperscript{3}
Absorption coefficient: 0.081 mm\textsuperscript{-1}
F(000): 3904
Crystal size: 0.180 x 0.090 x 0.040 mm\textsuperscript{3}
Theta range for data collection: 2.172 to 25.027°.
Index ranges:
\begin{align*}
-24 &\leq h \leq 24, \\
-21 &\leq k \leq 23, \\
-29 &\leq l \leq 29.
\end{align*}
Reflections collected: 91129
Independent reflections: 8890 \text{ [R(int) = 0.1172]}
Completeness to theta = 25.000°: 99.9 \%
Absorption correction: Semi-empirical from equivalents
Max. and min. transmission: 1.000 and 0.787
Refinement method: Full-matrix least-squares on F\textsuperscript{2}
Data / restraints / parameters: 8890 / 0 / 629
Goodness-of-fit on F\textsuperscript{2}: 0.994
Final R indices [I>2sigma(I)]: R1 = 0.0568, wR2 = 0.0946
R indices (all data): R1 = 0.1052, wR2 = 0.1092
Largest diff. peak and hole: 0.141 and -0.166 e.Å\textsuperscript{3}
Table 3. Crystal data and structure refinement for 5c. Displacement ellipsoids are shown at the 50% probability level.

- **Identification code**: CCDC 2087486
- **Empirical formula**: C_{25}H_{24}N_{2}O_{4}
- **Formula weight**: 416.46
- **Temperature**: 173(2) K
- **Wavelength**: 0.71073 Å
- **Crystal system**: Monoclinic
- **Space group**: P 21/c
- **Unit cell dimensions**:
  - a = 14.266(4) Å \(\alpha=90^\circ\)
  - b = 16.785(4) Å \(\beta=97.40(2)^\circ\)
  - c = 9.785(3) Å \(\gamma=90^\circ\)
- **Volume**: 2323.6(11) Å³
- **Z**: 4
- **Density (calculated)**: 1.191 Mg/m³
- **Absorption coefficient**: 0.081 mm⁻¹
- **F(000)**: 880
- **Crystal size**: 0.130 x 0.020 x 0.010 mm³
- **Theta range for data collection**: 3.209 to 25.025°.
- **Index ranges**: -16<=h<=15, -19<=k<=18, -11<=l<=11
- **Reflections collected**: 15515
- **Independent reflections**: 4096 [R(int) = 0.2581]
- **Completeness to theta = 25.000°**: 99.8 %
- **Absorption correction**: Semi-empirical from equivalents
- **Max. and min. transmission**: 1.000 and 0.511
- **Refinement method**: Full-matrix least-squares on F²
- **Data / restraints / parameters**: 4096 / 0 / 281
- **Goodness-of-fit on F²**: 0.811
- **Final R indices [I>2sigma(I)]**: R1 = 0.0904, wR2 = 0.1108
- **R indices (all data)**: R1 = 0.2971, wR2 = 0.1816
- **Largest diff. peak and hole**: 0.195 and -0.177 e.Å⁻³
Table 4. Crystal data and structure refinement for 6a. Displacement ellipsoids are shown at the 50% probability level.

| Property                                      | Value                           |
|-----------------------------------------------|---------------------------------|
| Identification code                           | CCDC 2097900                    |
| Empirical formula                             | C_{39}H_{36}N_{2}O_{7}          |
| Formula weight                                 | 644.70                          |
| Temperature                                    | 150(2) K                       |
| Wavelength                                    | 1.54184 Å                       |
| Crystal system                                 | Monoclinic                      |
| Space group                                    | P 21/n                          |
| Unit cell dimensions                          |                                 |
| a                                             | 16.4179(2) Å                    |
| α                                             | 90°                             |
| b                                             | 12.60170(10) Å                  |
| β                                             | 112.839(2)°                     |
| c                                             | 17.2107(2) Å                    |
| γ                                             | 90°                             |
| Volume                                        | 3281.61(8) Å^3                  |
| Z                                             | 4                               |
| Density (calculated)                          | 1.305 Mg/m^3                    |
| Absorption coefficient                        | 0.732 mm^-1                     |
| F(000)                                        | 1360                            |
| Crystal size                                  | 0.440 x 0.330 x 0.320 mm^3      |
| Theta range for data collection               | 3.159 to 62.686°                |
| Index ranges                                  | -18<=h<=17, -14<=k<=14, -17<=l<=19 |
| Reflections collected                         | 28318                           |
| Independent reflections                       | 5249 [R(int) = 0.0219]          |
| Completeness to theta = 62.686°               | 99.8 %                          |
| Absorption correction                         | Semi-empirical from equivalents |
| Max. and min. transmission                    | 1.00000 and 0.73913             |
| Refinement method                             | Full-matrix least-squares on F^2 |
| Data / restraints / parameters                 | 5249 / 0 / 443                  |
| Goodness-of-fit on F^2                        | 1.043                           |
| Final R indices [I>2sigma(I)]                 | R1 = 0.0318, wR2 = 0.0826       |
| R indices (all data)                           | R1 = 0.0338, wR2 = 0.0841       |
| Extinction coefficient                         | 0.00205(13)                     |
| Largest diff. peak and hole                    | 0.184 and -0.146 e. Å^3        |
Table 5. Crystal data and structure refinement for 7a. Displacement ellipsoids are shown at the 50% probability level.

| Property                        | Value                                      |
|---------------------------------|--------------------------------------------|
| Identification code             | CCDC 2097895                               |
| Empirical formula               | C<sub>38</sub>H<sub>35</sub>N<sub>2</sub>O<sub>6</sub> |
| Formula weight                  | 734.04                                     |
| Temperature                     | 150(2) K                                   |
| Wavelength                      | 1.54184 Å                                  |
| Crystal system                  | Triclinic                                  |
| Space group                     | P-1                                        |
| Unit cell dimensions            | a = 11.5431(6) Å, b = 13.0136(5) Å, c = 13.9496(8) Å |
|                                | α = 92.986(4)°, β = 110.690(5)°, γ = 112.077(5)° |
| Volume                          | 1774.80(17) Å³                            |
| Z                               | 2                                          |
| Density (calculated)            | 1.374 Mg/m³                                |
| Absorption coefficient          | 2.752 mm<sup>-1</sup>                      |
| F(000)                          | 764                                        |
| Crystal size                    | 0.350 x 0.300 x 0.210 mm³                  |
| Theta range for data collection | 3.467 to 62.694°.                          |
| Index ranges                    | -12≤h≤13, -13≤k≤14, -16≤l≤15               |
| Reflections collected           | 13753                                      |
| Independent reflections         | 5637 [R(int) = 0.0185]                     |
| Completeness to theta = 62.694° | 99.2 %                                     |
| Absorption correction           | Analytical                                 |
| Max. and min. transmission      | 0.613 and 0.450                           |
| Refinement method               | Full-matrix least-squares on F<sup>2</sup> |
| Data / restraints / parameters  | 5637 / 31 / 472                            |
| Goodness-of-fit on F<sup>2</sup>| 1.047                                      |
| Final R indices [l>2sigma(l)]   | R1 = 0.0467, wR2 = 0.1292                  |
| R indices (all data)            | R1 = 0.0490, wR2 = 0.1315                  |
| Extinction coefficient          | n/a                                        |
| Largest diff. peak and hole     | 0.353 and -0.764 e.Å<sup>-3</sup>         |
Table 6. Crystal data and structure refinement for 7c. Displacement ellipsoids are shown at the 50% probability level.

| Identification code | CCDC 2097896 |
|---------------------|---------------|
| Empirical formula   | C₃₈ H₃₀ Br N₃ O₄ |
| Formula weight      | 672.56 |
| Temperature         | 150(2) K |
| Wavelength          | 1.54184 Å |
| Crystal system      | Triclinic |
| Space group         | P -1 |
| Unit cell dimensions| a = 12.3348(7) Å, α = 61.803(6)°. |
|                     | b = 12.8057(8) Å, β = 65.982(5)°. |
|                     | c = 13.5088(6) Å, γ = 63.355(6)°. |
| Volume              | 1628.5(2) Å³ |
| Z                   | 2 |
| Density (calculated)| 1.372 Mg/m³ |
| Absorption coefficient | 2.084 mm⁻¹ |
| F(000)              | 692 |
| Crystal size        | 0.320 x 0.140 x 0.060 mm³ |
| Theta range for data collection | 3.832 to 62.717°. |
| Index ranges        | -14<=h<=14, -14<=k<=14, -15<=l<=15 |
| Reflections collected | 12558 |
| Independent reflections | 5177 \[R(int) = 0.0332\] |
| Completeness to theta = 62.717° | 99.0 % |
| Absorption correction | Analytical |
| Max. and min. transmission | 0.885 and 0.615 |
| Refinement method   | Full-matrix least-squares on F² |
| Data / restraints / parameters | 5177 / 0 / 415 |
| Goodness-of-fit on F² | 1.245 |
| Final R indices [I>2σ(I)] | R₁ = 0.0376, wR₂ = 0.1265 |
| R indices (all data) | R₁ = 0.0448, wR₂ = 0.1301 |
| Extinction coefficient | n/a |
| Largest diff. peak and hole | 0.769 and -0.729 e.Å⁻³ |
Table 7. Crystal data and structure refinement for 7g. Displacement ellipsoids are shown at the 50% probability level.

| Parameter                              | Value                                      |
|----------------------------------------|--------------------------------------------|
| Identification code                    | CCDC 2097898                               |
| Empirical formula                      | C_{35}H_{30}N_{2}O_{5}S                    |
| Formula weight                         | 590.67                                     |
| Temperature                            | 150(2) K                                   |
| Wavelength                             | 1.54184 Å                                  |
| Crystal system                         | Monoclinic                                 |
| Space group                            | P 21/c                                     |
| Unit cell dimensions                   |                                           |
| a                                       | 12.2754(2) Å                               |
| b                                       | 11.0203(2) Å                               |
| c                                       | 22.3353(5) Å                               |
| Volume                                  | 3002.33(10) Å                              |
| Z                                       | 4                                          |
| Density (calculated)                   | 1.307 Mg/m³                                |
| Absorption coefficient                 | 1.333 mm⁻¹                                 |
| F(000)                                  | 1240                                       |
| Crystal size                           | 0.340 x 0.220 x 0.110 mm³                  |
| Theta range for data collection        | 3.624 to 62.722°                           |
| Index ranges                           | -14≤h≤12, -12≤k≤11, -25≤l≤23               |
| Reflections collected                  | 13700                                      |
| Independent reflections                | 4777 [R(int) = 0.0252]                     |
| Completeness to theta = 62.722°        | 99.4 %                                     |
| Absorption correction                  | Semi-empirical from equivalents            |
| Max. and min. transmission             | 1.000000 and 0.30403                       |
| Refinement method                      | Full-matrix least-squares on F²            |
| Data / restraints / parameters          | 4777 / 0 / 389                             |
| Goodness-of-fit on F²                   | 1.028                                      |
| Final R indices [I>2sigma(I)]           | R1 = 0.0374, wR2 = 0.0916                  |
| R indices (all data)                    | R1 = 0.0411, wR2 = 0.0946                  |
| Extinction coefficient                  | n/a                                        |
| Largest diff. peak and hole            | 0.412 and -0.574 e.Å³                      |
Table 8. Crystal data and structure refinement for 7h. Displacement ellipsoids are shown at the 50% probability level.

| Property                                      | Value                  |
|-----------------------------------------------|------------------------|
| Identification code                           | CCDC 2097897           |
| Empirical formula                             | C_{35}H_{30}N_{2}O_{5} |
| Formula weight                                | 558.61                 |
| Temperature                                   | 150(2) K               |
| Wavelength                                    | 1.5418 Å               |
| Crystal system                                | Monoclinic             |
| Space group                                   | P 21/c                 |
| Unit cell dimensions                          | a = 10.2985(3) Å, α = 90°, b = 26.7638(6) Å, β = 111.086(4)°, c = 12.0788(4) Å, γ = 90° |
| Volume                                        | 3106.32(17) Å³        |
| Z                                             | 4                      |
| Density (calculated)                          | 1.194 Mg/m³            |
| Absorption coefficient                        | 0.648 mm⁻¹             |
| F(000)                                        | 1176                   |
| Crystal size                                  | 0.420 x 0.210 x 0.080 mm³ |
| Theta range for data collection               | 3.303 to 62.723°       |
| Index ranges                                  | -11<=h<=11, -30<=k<=30, -12<=l<=13 |
| Reflections collected                         | 13211                  |
| Independent reflections                       | 4961 [R(int) = 0.0249] |
| Completeness to theta                         | 62.723°, 99.7 %        |
| Absorption correction                         | Semi-empirical from equivalents |
| Max. and min. transmission                    | 1.00000 and 0.57116    |
| Refinement method                             | Full-matrix least-squares on F² |
| Data / restraints / parameters                | 4961 / 75 / 436        |
| Goodness-of-fit on F2                         | 1.038                  |
| Final R indices [I>2sigma(I)]                 | R1 = 0.0472, wR2 = 0.1238 |
| R indices (all data)                          | R1 = 0.0529, wR2 = 0.1286 |
| Extinction coefficient                        | 0.00112(14)            |
| Largest diff. peak and hole                   | 0.715 and -0.248 e.Å⁻³ |
Table 9. Crystal data and structure refinement for 7i. Displacement ellipsoids are shown at the 50% probability level.

| Property                          | Value                  |
|-----------------------------------|------------------------|
| Identification code               | CCDC 2097899           |
| Empirical formula                 | C_{33}H_{28}N_{4}O_{4}  |
| Formula weight                    | 544.59                 |
| Temperature                       | 150(2) K               |
| Wavelength                        | 1.54184 Å              |
| Crystal system                    | Monoclinic             |
| Space group                       | P 21/n                 |
| Unit cell dimensions              | a = 10.8901(2) Å       |
|                                  | b = 15.3683(3) Å       |
|                                  | c = 16.9357(4) Å       |
|                                  | α = 90°.               |
|                                  | β = 98.621(2)°.        |
|                                  | γ = 90°.               |
| Volume                            | 2802.37(10) Å³         |
| Z                                 | 4                      |
| Density (calculated)              | 1.291 Mg/m³            |
| Absorption coefficient            | 0.698 mm⁻¹             |
| F(000)                            | 1144                   |
| Crystal size                      | 0.480 x 0.070 x 0.070 mm³|
| Theta range for data collection   | 3.904 to 62.732°       |
| Index ranges                      | -9<=h<=12, -17<=k<=17, -17<=l<=19 |
| Reflections collected             | 11769                  |
| Independent reflections           | 4484 [R(int) = 0.0255] |
| Completeness to theta = 62.732°  | 99.5%                  |
| Absorption correction             | Semi-empirical from equivalents |
| Max. and min. transmission        | 1.00000 and 0.90782    |
| Refinement method                 | Full-matrix least-squares on F² |
| Data / restraints / parameters    | 4484 / 0 / 370         |
| Goodness-of-fit on F²             | 1.049                  |
| Final R indices [I>2sigma(I)]     | R1 = 0.0352, wR2 = 0.0876 |
| R indices (all data)              | R1 = 0.0403, wR2 = 0.0917 |
| Extinction coefficient            | n/a                    |
| Largest diff. peak and hole       | 0.332 and -0.253 e.Å⁻³ |
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