Supplementary Information

Chemoenzymatic formal total synthesis of pancratistatin from narciclasine type compounds via Myers transposition: Model study for a short conversion of narciclasine to pancratistatin

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Experimental

Materials and Methods. All solvents were dried and distilled before usage. Reactions were done in inert atmosphere (Ar or N₂). All reagents were obtained from commercial sources. Before using, all glassware was oven or flame dried. NMR analysis was carried out on 300, 400, and 600 Brüker spectrometers running Topspin 2.1 and 3.5 software. Probes were equipped with gradients and VT (variable temperature) accessories. Chemical shifts are given in δ, and coupling constants J are given in Hz. Melting points were determined using a capillary melting point apparatus. Mass spectra (HRMS) measurements were recorded using an LTQ Orbitrap XL or double focusing sector (DFS) mass spectrometer, and the molecular mass-associated ion was determined by electrospray ionization, fast atom bombardment, or electron ionization. Infrared spectra were recorded on an FT-IR spectrophotometer as CHCl₃ solutions or neat and are reported in wave numbers (cm⁻¹). Flash grade 60 silica gel was used for column chromatography unless otherwise noted. TLC was performed on silica gel 60 F₂₅₄-coated aluminum sheets, stained with UV and cerium ammonium molybdate (CAM, Hanessian’s Stain) or KMnO₄ solutions.
5-Bromo-2-hydroxy-3-methoxybenzaldehyde (11)\(^1\)

\[
\text{OHC} \begin{array}{c}
\text{Br} \\
\text{HO} \\
\text{OMe}
\end{array}
\]

\[\text{o-Vanillin (25 g, 0.16 mol) and sodium acetate (20.34 g, 0.25 mol) were dissolved in glacial acetic acid (500 mL). A solution of bromine (8.46 mL, 0.165 mol) in glacial acetic acid (60 mL) was added dropwise to the reaction mixture over a period of 45 min. The solution deepened in colour throughout the addition, and was left to stir at room temperature for 16 h. The reaction mixture was concentrated under reduced pressure, and when the volume of the residual reaction mixture was reduced to approximately 100 mL it was quenched with saturated solution of Na}_2\text{S}_2\text{O}_3 (50 mL). The resulting solution was adjusted to pH 5 by the addition of Na}_2\text{CO}_3 and Na}_2\text{HCO}_3 solutions, and the organic phase was extracted with DCM (5 x 200 mL). The combined organic phase was washed with H}_2\text{O (100 mL), dried over Na}_2\text{SO}_4, filtered and concentrated under reduced pressure. The residual mixture was redissolved in a DCM (50 mL) and the resulting solution was passed through a plug of silica (1" thick) followed by 250 mL of DCM. The filtrate was concentrated under reduced pressure, yielding yellow flakes product (34.55 g, 91% crude). This crude product was found to be of sufficient purity for use in subsequent reactions.}\]

11: \(R_f = 0.6 \) [hexanes:EtOAc (4:1)]; mp = 119-122 °C (DCM); \(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta 11.01\) (s, 1H), 9.86 (s, 1H), 7.32 (d, J = 2.1 Hz, 1H), 7.18 (d, J = 2.1 Hz, 1H), 3.92 (s, 3H); \(^{13}\)C NMR (75 MHz, CDCl\(_3\)) \(\delta 195.7, 151.3, 149.7, 126.5, 121.7, 121.3, 111.4, 56.9.\)

5-Bromo-3-methoxybenzene-1,2-diol (12)\(^1\)

Bromide 11 (18.0 g, 77.9 mmol) was dissolved in a 2% aqueos NaOH (330 mL). A solution of 35% H\(_2\)O\(_2\) (44.3 mL, 513 mmol) in H\(_2\)O (350 mL) was added dropwise to the reaction mixture over 1 h. The reaction mixture became deep red-purple throughout the addition, and some white precipitate was observed. The mixture was allowed to stir at room temperature until full consumption of starting material (6 h). Reaction mixture was acidified with 3 M HCl (100 mL). The product was extracted with DCM (6 x 150 mL). The combined organic layers were washed with saturated Na\(_2\)SO\(_3\) solution (300 mL). The organic phase was dried over Na\(_2\)SO\(_4\), filtered and concentrated
under reduce pressure. 5-Bromo-3-methoxybenzene-1,2-diol (12) was purified by column chromatography [hexanes:EtOAc (6:1)] resulting in light-grey crystals (10.38 g, 61%).

12: \( R_f = 0.3 \) [hexanes:EtOAc (4:1)]; mp = 75 °C (EtOAc) [lit. mp = 76 °C]; IR (CHCl₃) 3410, 1613, 1502 cm⁻¹; \(^1 H\) NMR (300 MHz, CDCl₃) \( \delta 6.77 (d, J = 2.1 \text{ Hz}, 1H), 6.61 (d, J = 2.1 \text{ Hz}, 1H), 5.31 \) (m, 2H), 3.87 (s, 3H); \(^13 C\) NMR (75 MHz, CDCl₃) 147.5, 144.8, 131.8, 112.4, 111.9, 107.0, 56.5.

6-Bromo-4-methoxybenzo[d][1,3]dioxole (13)

Diiodomethane (9.89 mL, 122 mmol) was added to a suspension of catechol (17.92 g, 81.81 mmol) and oven-dried, ground K₂CO₃ (22.61 g, 163.6 mmol) in DMF (170 mL). The reaction mixture was stirred at 100 °C for 2 h. After starting material was fully consumed, the reaction mixture was diluted with H₂O (900 mL). The solution was passed through a plug of Celite®, and the resulting filtrate was extracted DCM (5 x 200 mL). The combined organic layers were dried over Na₂SO₄, filtered and concentrated under reduced pressure. The resulting mixture was purified by column chromatography [hexanes:EtOAc (9:1)] and yielded compound 13 as a white crystalline solid (14.60 g, 77%).

13: \( R_f = 0.8 \) [hexanes:EtOAc (4:1)]; mp = 79-80 °C (EtOAc) [lit. 80-82 °C]; \(^1 H\) NMR (300 MHz, CDCl₃) \( \delta 6.68 \) (m, 2H), 5.97 (s, 2H), 3.88 (s, 3H); \(^13 C\) NMR (75 MHz, CDCl₃) \( \delta 149.8, 144.5, 135.2, 113.6, 111.3, 106.5, 102.2, 57.1 \); anal. calcd for C₈H₇BrO₃: C, 41.59; H, 3.05; found: C, 41.65; H, 2.99.

7-Methoxybenzo[d][1,3]dioxol-5-ylboronic acid (14)

1.4 M solution of tert-butyllithium in pentane (7.0 mL) was added dropwise to –78 °C solution of compound 13 (1.13 g, 4.89 mmol) in THF (20 mL). During the addition, the reaction mixture turned dark red. After 1 h at –78 °C, trimethyl borate (1.7 mL, 14.67 mmol) was added dropwise. The dark red colour vanished 5 min after the addition of reagent was complete. After 1 h at –78 °C, the temperature of reaction mixture was slowly raised to 0 °C. The reaction was quenched with water (1.0 mL) and stirred for 30 min at room temperature. The volatiles were removed by rotary
evaporator and resulting crude residue can be used in the next reaction. Compound 14 was purified by column chromatography [10 wt% deactivated silica gel, hexanes:EtOAc (1:1)] to obtain the boronic acid 14 (0.651 g, 68%) as a pale yellow solid.

14: $R_f = 0.2$ [hexanes:EtOAc (1:1)]; mp > 200 °C (ethanol/pentane) [lit. mp > 200 °C]; $^1$H NMR (300 MHz, DMSO-$d_6$) $\delta$ 8.80 (s, 1 H), 7.12 (s, 1 H), 7.02 (s, 1 H), 5.98 (d, $J = 2.1$ Hz, 2 H), 3.88 (s, 3 H); $^{13}$C NMR (75 MHz, DMSO-$d_6$) $\delta$ 148.2, 143.1, 136.3, 132.6, 112.8, 106.5, 100.8, 56.1.

3,5-Dibromo-(1$S$,2$S$)-3,5-cyclohexadiene-1,2-diol (16a)$^2$

![3,5-Dibromo-(1$S$,2$S$)-3,5-cyclohexadiene-1,2-diol (16a)](image)

*Escherichia coli* JM109 (pDTG601A) was grown overnight at 35 °C with continuous shaking (150 rpm) in an enriched medium (9.6 g of K$_2$HPO$_4$, 8.4 g of KH$_2$PO$_4$, 3.0 g of (NH$_4$)$_2$SO$_4$, 9.0 g of yeast extract, 60 mg of ampicillin, dissolved in 600 mL of distilled water). The preculture was then transferred to a 12 L fermenter containing 8 L of medium adjusted to pH 7.0 (60.0 g of KH$_2$PO$_4$, 16.0 g of citric acid, 40.0 g of MgSO$_4$, 9.6 mL of concentrated H$_2$SO$_4$, 9.6 mL of a 270.0 g/L solution of ferric ammonium citrate, 16.0 mL of a trace metal solution, 0.7 mL of antifoam, 2.69 g of thiamine hydrochloride, and 800 mg of ampicillin), and the cells were grown for approximately 26 h to an OD = 70 ($\lambda$ = 660 nm). 1,3-Dibromobenzene (15 g, 0.32 mol) was added in portions to the culture, and the diol production was checked every 20 min by measuring a characteristic absorbance peak in the UV region ($\lambda$ = 282 nm). After all metabolic activity ceased (or no more diol formation was observed by UV), the fermentation was stopped, and the pH was adjusted to 7.5 with NH$_4$OH. The cells were separated from the broth by centrifugation at 7000 rpm for 20 min, and the resulting clear solution was saturated with sodium chloride and extracted with EtOAc. The organic layer was dried over anhydrous MgSO$_4$, and the solvent was removed under reduced pressure. The crude product was purified by recrystallization (methylene chloride/pentane) to yield diol 16a as a yellowish solid (6.3 g or 0.79 g/L). Because of its limited stability this material was used quickly following its isolation.

16a: $R_f = 0.4$ [hexanes:EtOAc (1:1)]; mp = 80-81 °C (DCM, pentanes) [lit. mp = 80-81 °C]; $[\alpha]_D^{20}$ +21.0 (c 1.0, acetone); IR (CHCl$_3$) 3255, 1588 cm$^{-1}$; $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 6.43 (dd, $J = 1.5$, 0.9 Hz, 1H), 6.25 (dd, $J = 4.2$, 1.5 Hz, 1H), 4.41 (dd, $J = 6.3$, 4.2 Hz, 1H), 4.29 (dd, $J = 6.3$, 0.9, 1H), 2.80 (bs, 2H); $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 131.7, 130.3, 129.9, 114.9, 72.1, 71.0.
1,8-Dibromo-11-carbomethoxy-4,4-dimethyl-(1R,2S,6S,7S)-3,5,10,11-
trioazatricyclo[5.2.2.02,6]-8-undecene (17a)

The solution of diol 16a (6.3 g, 23.5 mmol) and p-toluensulfonic acid (cat., tip of a spatula) in 2,2-
dimethoxypropane (63 mL) was mixed at room temperature until the full consumption of diol (5 h,
vide TLC). The reaction mixture was cooled to 0 °C and was followed by the addition of water (15
mL) NaIO₄ (5.01 g, 23.5 mmol). The solution of methyl hydroxycarbamate (MocNHOH, 2.35 g,
25.85 mmol) in methanol (30 mL) was added dropwise. The reaction mixture was left to warm up
to room temperature and stir for 12 h at room temperature, then it was quenched with saturated
Na₂S₂O₃ solution (25 mL) and volume of the mixture was reduced under vacuum. The aqueous
layer was extracted with DCM (3x250 mL), the organic layer was dried with MgSO₄, filtered, and
the product was concentrated, dissolved in DCM (50 mL) and passed through a plug of silica. The
crude product was purified by column chromatography (gradient EtOAc:Hex (9:1) to (4:1)) and
17a was obtained as white crystals (6.4 g, 68 %)

17a: Rₓ = 0.6 [hexanes:EtOAc (4:1)]; mp = 148-149 °C (i-PrOH) [lit. 150-152 °C (EtOAc)]; ¹H
NMR (300 MHz, CDCl₃) δ 6.73-6.67 (m, 1H), 5.17 (dd, J = 4.3, 2.2 Hz, 1H), 4.70 (dd, J = 6.8, 4.3
Hz, 1H), 4.59 (dd, J = 6.9, 0.7 Hz, 1H), 3.84 (s, 3H), 1.42 (s, 3H), 1.35 (s, 3H); ¹³C NMR (75 MHz,
CDCl₃) δ 156.0, 132.7, 120.9, 112.3, 87.2, 81.3, 61.4, 54.5, 25.8, 25.6.

Methyl (7S,8S)-7,8-bis(acetyloxy)-1,5-dibromo-2-oxa-3-azabicyclo[2.2.2]oct-5-ene-3-
carboxylate (17b)

Diol 16a (0.51 g, 1.89 mmol) was suspended in DCM (5 mL) and cooled to −5 °C. Pyridine (0.30
mL, 3.78 mmol) was added dropwise to the reaction mixture at −5 °C (reaction mixture turns into a
clear brown solution). After 5 min, acetic anhydride (0.35 mL, 3.78 mmol) was added dropwise to
the reaction mixture and temperature was maintained between −5 to 0 °C for 2 h. After full consumption of starting material, the solvent was removed in vacuo (keeping water bath temperature at 25 °C) and resulting residual brown oil was purified by column chromatography [10 wt% deactivated silica gel, hexanes:EtOAc (4:1)] to obtain (1S,6S)-6-(acetyloxy)-3,5-dibromocyclohexa-2,4-dien-1-yl acetate (16c) (0.68 g, 80% yield) as a colourless oil.

This diacetate 16c was immediately dissolved in methanol (10 mL) and the clear solution was cooled to 0 °C. Water (5 mL) was added to the solution, followed by addition of sodium metaperiodate (1.49 g, 6.96 mmol). After 5 min., a solution of methyl hydroxycarbamate (0.63 g, 6.96 mmol) in methanol (10 mL) was added to the reaction mixture at 0 °C (the reaction mixture becomes a thick suspension having a straw yellow colour). The reaction was stirred for 16 h while allowing to slowly warm up to room temperature. After confirmation of complete consumption of starting material (TLC), the reaction mixture was quenched with saturated Na2S2O3 solution (10 mL), and volatiles were removed by rotary evaporation. The product contained in the resulting pale yellow aqueous suspension was extracted with EtOAc (3 × 15 mL). The combined EtOAc extracts were dried over MgSO4, concentrated by rotary evaporation at reduced pressure, and the residue was purified by column chromatography [hexanes:EtOAc (1:1)] to obtain the title compound 17b (0.53 g, 63%) as off white solid.

(1S,6S)-6-(Acetyloxy)-3,5-dibromocyclohexa-2,4-dien-1-yl acetate (16c)

\[
\begin{align*}
\text{Br} & \quad \text{OAc} \\
\text{Br} & \quad \text{OAc}
\end{align*}
\]

This diacetate 16c was immediately dissolved in methanol (10 mL) and the clear solution was cooled to 0 °C. Water (5 mL) was added to the solution, followed by addition of sodium metaperiodate (1.49 g, 6.96 mmol). After 5 min., a solution of methyl hydroxycarbamate (0.63 g, 6.96 mmol) in methanol (10 mL) was added to the reaction mixture at 0 °C (the reaction mixture becomes a thick suspension having a straw yellow colour). The reaction was stirred for 16 h while allowing to slowly warm up to room temperature. After confirmation of complete consumption of starting material (TLC), the reaction mixture was quenched with saturated Na2S2O3 solution (10 mL), and volatiles were removed by rotary evaporation. The product contained in the resulting pale yellow aqueous suspension was extracted with EtOAc (3 × 15 mL). The combined EtOAc extracts were dried over MgSO4, concentrated by rotary evaporation at reduced pressure, and the residue was purified by column chromatography [hexanes:EtOAc (1:1)] to obtain the title compound 17b (0.53 g, 63%) as off white solid.

(1S,6S)-6-(Acetyloxy)-3,5-dibromocyclohexa-2,4-dien-1-yl acetate (16c)

\[
\begin{align*}
\text{Br} & \quad \text{OAc} \\
\text{Br} & \quad \text{OAc}
\end{align*}
\]

\[R_f = 0.5 \text{ [hexanes:EtOAc (4:1)]}; [\alpha]^{19}_D -23.9 \text{ (c 0.8, CHCl}_3\text{)}; \text{IR (CHCl}_3\text{) 1750, 1624, 1578, 1465, 1373, 1239, 1083, 1021, 911 cm}^{-1}; ^1\text{H NMR (300 MHz, DMSO-}d_6\text{)} \delta 6.80 \text{ (t, } J = 1.2 \text{ Hz, 1H), 6.35 (dd, } J = 3.9, 1.5 \text{ Hz, 1H), 5.69 (dd, } J = 6.3, 0.6 \text{ Hz, 1H), 5.63 (dd, } J = 6.3, 3.9 \text{ Hz, 1H), 2.09 (s, 3H), 2.01 (s, 3H); ^13\text{C NMR (75 MHz, DMSO-}d_6\text{)} \delta 169.3, 169.3, 131.9, 125.6, 122.2, 116.6, 68.2, 68.2, 20.4, 20.3; \text{MS (EI) } m/z \text{ (%)} 354 (1), 294 (10), 252 (100), 136 (33), 84 (17), 63 (25); \text{HRMS (EI} c\text{aled for } C_{10}H_{10}Br_2O_4: 351.8946; \text{found 351.8902.; anal. caled for } C_{10}H_{10}Br_2O_4: C, 33.93; H, 2.85; \text{found C, 32.99; H, 2.75 (The discrepancy in the elemental analysis is due to instability of the compound).}
\]

17b: \[R_f = 0.5 \text{ [hexanes:EtOAc (1:1)]; mp = 118-120 °C (ether); [\alpha]^{19}_D +41.2 \text{ (c 1.0, CHCl}_3\text{)}; \text{IR (CHCl}_3\text{) 2927, 1759, 1599, 1441, 1373, 1237, 1207, 1063 cm}^{-1}; ^1\text{H NMR (300 MHz, CDCl}_3\text{)} \delta 6.82 \text{ (d, } J = 2.4 \text{ Hz, 1H), 5.49 (dd, } J = 7.2, 3.6 \text{ Hz, 1H), 5.38 (dd, } J = 7.2, 0.3 \text{ Hz, 1H), 5.11 (dd, } J = 3.9,
2.4 Hz, 1H), 3.83 (s, 3H), 2.1 (s, 3H), 2.06 (s, 3H); $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 169.2, 169.0, 157.6, 133.7, 121.3, 85.8, 72.9, 67.8, 60.4, 54.6, 20.4, 20.3; MS (ESI) $m/z$ (%) 460 [(100), (M+NH$_4^+$)], 381.4 (25), 223 (40), 230 (10); HRMS (EI) calcd for C$_{12}$H$_{13}$Br$_2$NO$_7$: 440.9059; found 440.9048; anal. calcd for C$_{12}$H$_{13}$Br$_2$NO$_7$: C, 32.53; H, 2.96; found C, 32.72; H, 2.80.

Methyl ((3a$S$,4$R$,7a$S$)-7'-methoxy-2,2-dimethyl-7-oxo-3a,4,7,7a-tetrahydro-[5,5'-bibenzo[d][1,3]dioxol]-4-yl)carbamate (7a)$^2$

Oxazine 17a (555 mg, 1.39 mmol) was dissolved in benzene (13.2 mL), the solution was degassed with the flow of argon for 15 min, and 2 M solution of Na$_2$CO$_3$ (1.4 mL, 2.78 mmol), and Pd(PPh$_3$)$_4$ (80 mg, 0.069 mmol) were added to the reaction mixture. Then a solution of (7-methoxybenzo[d][1,3]dioxol-5-yl)boronic acid (crude mixture, 1.25 eq.) in 16 mL of ethanol was added and the reaction mixture was refluxed for 16 h. It was then diluted with 7 mL of acetonitrile and 7 mL of water and Mo(CO)$_6$ (404 mg, 1.53 mmol) was added. The mixture was refluxed for 2 h, cooled down, and filtered through a plug of Celite and sand. The crude mixture was concentrated and subjected to column chromatography [10 wt% deactivated silica gel, gradient hexanes:EtOAc (4:1) to (1:1)]. The product was obtained as bright yellow foamy oil (326 mg, 60%)

7a: $R_f$ = 0.6 [hexanes:EtOAc (1:1)]; [\(\alpha\)]$_D^{25}$ = -127.3 (c 0.5, CHCl$_3$) [lit. [\(\alpha\)]$_D^{26}$ = -26.8 (c 1.1, CHCl$_3$)]; $^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 6.85 (s, 1H), 6.79 (s, 1H), 6.45 (s, 1H), 6.03 (s, 2H), 5.26 (d, $J$ = 7.5 Hz, 1H), 5.03 (d, $J$ = 6.7 Hz, 1H), 4.67 (dd, $J$ = 5.0, 2.2 Hz, 1H), 4.45 (d, $J$ = 5.0 Hz, 1H), 3.91 (s, 3H), 3.69 (s, 3H), 1.41 (s, 3H), 1.33 (s, 3H); $^{13}$C NMR (150 MHz, CDCl$_3$) $\delta$ 195.6, 171.3, 156.3, 153.2, 149.8, 144.0, 138.2, 130.1, 124.0, 110.6, 107.7, 102.4, 101.1, 77.2, 73.6, 56.9, 52.9, 48.3, 27.6, 26.1.
(1S,2R,6S)-6-(Acetyloxy)-3-(7-methoxy-2H-1,3-benzodioxol-5-yl)-2-[(methoxycarbonyl)amino]-5-oxocyclohex-3-en-1-yl acetate (7b)

Compound 17b (0.27 g, 0.62 mmol) was dissolved in benzene (5 mL), potassium fluoride (0.036 g, 0.62 mmol) was added in one portion to the solution, and water (0.02 mL) was added to the suspension. This suspension was degassed for 30 min with a stream of argon. It was followed by addition of Pd(PPh₃)₄ (0.036 g, 0.031 mmol), boronic acid 14 (0.12 g, 0.62 mmol) and ethanol (1 mL). The reaction mixture was heated to reflux for 14 h. After complete consumption of the starting materials (checked by TLC), the reaction mixture was cooled to room temperature and quenched with saturated NH₄Cl. The product was extracted with EtOAc (3 × 15 mL), and the combined organic phase was washed with 5 % hydrochloric acid (10 mL) and brine (3 × 10 mL) and then dried over MgSO₄ before the solvent was removed in vacuo. The residue was purified by column chromatography [10 wt% deactivated silica gel, hexanes:EtOAc (1:1)] to afford (5S,6S)-methyl-5,6-diacetoxy-4-bromo-7-(7-methoxybenzo[d][1,3]dioxol-5-yl)-3-oxa-2-aza-bicyclo[2.2.2]oct-7-ene-2-carboxylate (17c) (0.211 g, 67%) as an off-white solid.

(5S,6S)-Methyl-5,6-diacetoxy-4-bromo-7-(7-methoxybenzo[d][1,3]dioxol-5-yl)-3-oxa-2-azabicyclo[2.2.2]oct-7-ene-2-carboxylate (17c) (0.257 g, 0.5 mmol) was dissolved in acetonitrile (25 mL). To this solution, molybdenumhexacarbonyl (0.145 g, 0.55 mmol) was added in a lot. The reaction mixture was heated to reflux and maintained for 3 h (the completion of reaction was checked by TLC). The heterogeneous reaction mixture was allowed to cool to room temperature, and was filtered through a pad of Celite®. The pad was washed with acetonitrile (2 × 20 mL). The combined organic phase was concentrated under reduced pressure, and the residue was purified by column chromatography [10 wt% deactivated silica gel, hexanes:EtOAc, (1:1)] to provide enone 7b (0.162 g, 74 %) as a colourless oil.
(5S,6S)-Methyl 5,6-diacetoxy-4-bromo-7-(7-methoxybenzo[d][1,3]dioxol-5-yl)-3-oxa-2-aza-bicyclo[2.2.2]oct-7-ene-2-carboxylate (17c)

\[
R_f = 0.5 \ [\text{hexanes:EtOAc (1:1)}]; \ mp = 78-80 \ ^\circ \text{C} \ (\text{DCM/Et}_2\text{O}); \ [\alpha]_{D}^{18} +76.2 \ (c \ 0.7, \ \text{CHCl}_3); \ IR \ (\text{CHCl}_3) 2959, 1754, 1731, 1632, 1599, 1510, 1441, 1374, 1241, 1207, 1053 \ \text{cm}^{-1}; \ ^1\text{H} \text{NMR (300 MHz, acetone-}d_6) \ \delta \ 6.96 \ (d, \ J = 1.5 \ Hz, 1H), 6.89 \ (d, \ J = 2.1 \ Hz, 1H), 6.87 \ (d, \ J = 1.8 \ Hz, 1H), 5.55-5.47 \ (m, 3H), 3.94 \ (s, 3H), 3.66 \ (s, 3H), 2.03 \ (s, 3H), 1.95 \ (s, 3H); \ ^{13}\text{C} \text{NMR (75 MHz, acetone-}d_6) \ \delta \ 169.8, 169.5, 158.9, 150.5, 144.9, 144.8, 137.6, 129.8, 125.0, 107.2, 102.9, 100.7, 88.1, 73.7, 68.5, 57.1, 55.7, 54.2, 20.3, 20.2; \ MS \ (\text{ESI}) \ m/z \ (\%) \ 538 \ (60), 447 \ (100), 424 \ (53), 381 \ (18), 284 \ (14), 212 \ (24); \ HRMS (\text{EI}) \text{calcd for C}_{20}H_{21}BrNO_{10}: 514.0343. Found 514.0308; Anal. Calcd for C_{20}H_{20}BrNO_{10}: \text{C, 46.71; H, 3.92. Found C, 46.43; H, 4.14.}

7b: \ R_f = 0.4 \ [\text{hexanes:EtOAc (1:1)}]; \ [\alpha]_{D}^{20} -228.0 \ (c \ 0.8, \ \text{CHCl}_3); \ IR \ (\text{CHCl}_3) 3434, 2927, 1750, 1725, 1694, 1633, 1594, 1510, 1450, 1433, 1373, 1230, 1220, 1203, 1046 \ \text{cm}^{-1}; \ ^1\text{H} \text{NMR (300 MHz, methanol-}d_4) \ \delta \ 6.92 \ (d, \ J = 1.5 \ Hz, 1H), 6.88 \ (d, \ J = 1.5 \ Hz, 1H), 6.53 \ (s, 1H), 6.02 \ (s, 2H), 5.92 \ (d, \ J = 3.0 \ Hz, 1H), 5.58 \ (t, \ J = 3.0 \ Hz, 1H), 5.11 \ (d, \ J = 3.0 \ Hz, 1H), 3.90 \ (s, 3H), 3.68 \ (s, 3H), 2.13 \ (s, 3H), 2.05 \ (s, 3H); \ ^{13}\text{C} \text{NMR (75 MHz, methanol-}d_4) \ \delta \ 192.2, 171.5, 171.3, 158.7, 153.9, 151.2, 145.2, 139.4, 130.8, 124.3, 109.3, 103.5, 101.9, 73.6, 72.5, 57.4, 53.1, 51.9, 20.6, 20.4; \ MS (\text{EI}) \ m/z \ (%) \ 435 \ (30), 375 \ (14), 333 \ (100), 305 \ (19), 301 \ (35), 149 \ (35); \ HRMS (\text{EI}) \text{calcd for C}_{20}H_{21}NO_{10}: 435.1165; found 435.1168.; anal. calcd for C_{20}H_{21}NO_{10}: \text{C, 55.17; H, 4.86; found C, 55.09; H, 4.95.}

Methyl ((3aS,4R,7R,7aR)-7-hydroxy-7'-methoxy-2,2-dimethyl-3a,4,7,7a-tetrahydro-[5,5'-bibenzo[d][1,3]dioxol]-4-y)carbamate (8a)^2

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\text{HNMoc}
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The solution of enone 7a (50 mg, 0.13 mmol) in methanol (0.5 mL) was degassed with a stream of argon for 15 min. After addition of cerium (III) chloride heptahydrate (71 mg, 0.19 mmol) the reaction mixture was stirred for 20 min, then cooled to 0 °C and sodium borohydride (6 mg, 0.14 mmol) was added in 2 portions. Reaction mixture was allowed to warm up slowly to room temperature and stirred for 3 h. The reaction mixture was diluted with 5 mL of EtOAc and the grey precipitate was filtered through a plug of Celite. After concentration under reduced pressure the product was purified by preparative TLC [hexanes:EtOAc (1:1)] to furnish 8a as a white foamy oil (48 mg, 96%).

8a: Rf = 0.2 [hexanes:EtOAc (1:1)]; [α]_D^{24} = -61.6 (c 0.8, CHCl_3) [lit. [α]_D^{25} = -14.4 (c = 0.8, CHCl_3)];
1H NMR (600 MHz, CDCl_3) δ 6.57 (m, 2H), 6.08 (s, 1H), 5.96 (s, 2H), 4.67 (dd, J = 10.6, 6.3 Hz, 3H), 4.55 (s, 1H), 4.41 (d, J = 10.2 Hz, 1H), 3.89 (s, 3H), 3.68 (s, 3H), 2.77 (d, J = 10.3 Hz, 1H), 1.34 (s, 3H), 1.30 (s, 3H); 13C NMR (150 MHz, CDCl_3) δ 156.6, 149.3, 143.7, 137.3, 135.4, 133.7, 130.8, 109.4, 105.7, 101.8, 100.1, 75.3, 66.7, 56.8, 52.6, 51.1, 29.8, 26.3, 24.8.

(1S,2R,5R,6R)-6-(Acetyloxy)-5-hydroxy-3-(7-methoxy-2H-1,3-benzodioxol-5-yl)-2-[(methoxycarbonyl)amino]cyclohex-3-en-1-yl acetate (8b)

Cerium chloride heptahydrate (0.266 g, 0.72 mmol) was added to a stirred solution of enone 7b (0.207 g, 0.48 mmol) in methanol (5 mL). After 5 min, the mixture was cooled to 0 °C, and NaBH_4 (0.02 g, 0.52 mmol) was added. The reaction mixture was stirred at 0 °C until the total consumption of starting material (1 h, checked by TLC). The reaction was quenched by addition of 50 % aqueous acetic acid (0.3 mL) to neutral pH. Water (20 mL) and EtOAc (20 mL) were added, and the heterogeneous mixture was extracted with EtOAc (3 × 20 mL). The combined organic layers were washed with water (15 mL), brine (15 mL) and dried over MgSO_4. The solvent was removed under reduced pressure and the resulting residue was purified by column chromatography [10 wt% deactivated silica gel, hexanes:EtOAc (1:1)] to obtain the allylic alcohol 8b (0.163 g, 78%) as a white solid.

8b: Rf = 0.2 [hexanes:EtOAc (1:1)]; mp > 200 (ether), [α]_D^{22} = -30.2 (c 0.7, CHCl_3); IR (CHCl_3) 3582, 3436, 2927, 2855, 1730, 1629, 1514, 1464, 1375, 1243, 1211, 1045 cm⁻¹; 1H NMR (300 MHz,
acetone-d$_6$) $\delta$ 6.66 (d, $J = 0.9$ Hz, 1H), 6.58 (d, $J = 1.5$ Hz, 1H), 6.30 (d, $J = 9.6$ Hz, 1H), 5.96 (d, $J = 9.6$ Hz, 2H), 5.87 (d, $J = 1.5$ Hz, 1H), 5.56 (quint, $J = 1.8$ Hz, 1H), 5.18 (dd, $J = 8.7, 2.1$ Hz, 1H), 5.02-4.96 (m, 1H), 4.64-4.58 (m, 1H), 4.19 (d, $J = 8.4$ Hz, 1H), 3.86 (s, 3H), 3.50 (s, 3H), 2.09 (s, 3H), 1.97 (s, 3H); $^{13}$C NMR (75 MHz, acetone-d$_6$) $\delta$ 171.1, 170.7, 157.8, 149.7, 144.3, 138.7, 135.8, 134.3, 129.6, 107.5, 102.3, 101.7, 73.9, 72.3, 67.2, 52.0, 50.8, 20.9, 20.8; MS (EI) $m/z$ (%) 437 (10), 344 (15), 317 (14), 302 (60), 260 (100), 232 (33), 218 (21); HRMS (EI) calcd for C$_{20}$H$_{23}$NO$_{10}$: 437.1316; found 437.1316.; anal. calcd for C$_{20}$H$_{23}$NO$_{10}$: C, 54.92; H, 5.30; found C, 54.91; H, 5.40.

Methyl ((3a$S$,4$R$,5$R$,7$aR$)-7'-methoxy-2,2-dimethyl-3a,4,5,7a-tetrahydro-[5,5'-bibenzo[d][1,3]dioxol]-4-yl)carbamate (9a)$^3$

![Structure of 9a](image)

Allylic alcohol 8a (629 mg, 1.60 mmol), triphenylphosphine (839 mg, 3.20 mmol), 2-nitro-N'-(propan-2-ylidene)benzenesulfonohydrazide (IP-NBSH, 823 mg, 3.20 mmol) was charged into Schlenk flask and kept under high vacuum for 1 h, then dissolved in tetrahydrofuran (6 mL). Reaction mixture was cooled down to 0 °C and di-tert-butyl azadicarboxylate (DBAD, 737 mg, 3.20 mmol) solution in 3 mL of tetrahydrofuran was added dropwise. The reaction mixture was allowed to warm up slowly to room temperature and stirred for 8 h. Reaction mixture was cooled down to 0 °C and the mixture of 2,2,2-trifluoroethanol (3 mL) and water (3 mL) was added dropwise and stirred for 16 h whereupon it was evaporated and submitted to two consecutive chromatographical columns [10 wt% deactivated silica gel, hexanes:EtOAc (1:1), then DCM:MeOH 100:1]. Product was obtained as a white foamy glassy oil (345 mg, 64 %).

9a: $R_f$ = 0.1 [hexanes:EtOAc (1:1)]; $[\alpha]_D^{24}$ +14.3 (c 0.9, CHCl$_3$); IR (neat) 3331, 2984, 2936, 1705, 1607, 1524, 1475, 1071, 1048 cm$^{-1}$, $^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 6.36 (s, 1H), 6.34 (s, 1H), 6.01-5.90 (m, 4H), 4.68 (m, 1H), 4.62 (m, 1H), 4.42 (m, 1H), 3.87 (s, 3H), 3.56 (s, 3H), 3.38 (s, 1H), 1.54 (s, 3H), 1.41 (s, 3H); $^{13}$C NMR (150 MHz, CDCl$_3$) $\delta$ 156.6, 149.0, 143.7, 136.3, 135.6, 134.3, 123.7, 109.8, 107.5, 102.3, 101.6, 72.6, 57.3, 56.7, 52.1, 28.4, 26.1.
Methyl ((3aS,4R,5R,6S,7S,7aR)-6,7-dihydroxy-7’-methoxy-2,2-dimethyl-3a,4,5,6,7,7a-hexahydro-[5,5′-bibenzo[d][1,3]dioxol]-4-yl)carbamate (18a)

Olefin 9a (1.35 g, 3.579 mmol) was dissolved in 20 mL of acetone and 5 mL of water. Then OsO₄ (250 mg, 0.9834 mmol) and N-methylmorpholine-N-oxide (NMO, 419 mg, 3.579 mmol) were added. The reaction mixture was stirred at room temperature for 4 days, then quenched with NaHSO₃ saturated solution (20 mL). The reaction mixture was filtered through a plug of celite, absorbed on deactivated silica and subjected to purification by column chromatography (hexanes:EtOAc (1:2)). Diol 18a was isolated as a white foamy oil (785 mg, 53 %)

18a: Rₓ = 0.1 [hexanes:EtOAc (1:2)], [α]D₊₂⁵ = -55.4 (c 0.5, CHCl₃); ¹H NMR (600 MHz, CDCl₃) δ 6.44 (s, 2H), 5.96 (s, 2H), 4.60 (s, 1H), 4.45-4.26 (m, 2H), 4.19 (s, 1H), 4.04-3.81 (m, 5H), 3.54 (s, 3H), 2.92 (s, 1H), 2.65 (s, 1H), 1.82 (s, 1H), 1.60 (s, 3H), 0.79 (s, 3H); ¹³C NMR (150 MHz, CDCl₃) δ 156.7, 149.4, 144.0, 144.0, 134.8, 132.1, 109.4, 101.7, 77.6, 76.6, 72.7, 69.5, 56.7, 56.7, 55.1, 52.3, 48.3, 29.9, 28.1, 26.0; anal. calcd for C₁₉H₂₅NO₉: C, 55.47; H, 6.13; found C, 54.80; H, 6.44.

Methyl ((3aS,4R,5R,5aS,8aS,8bR)-4-(7-methoxybenzo[d][1,3]dioxol-5-yl)-7,7-dimethyl-2,2-dioxidohexahydro-[1,3]dioxolo[4',5':3,4]benzo[1,2-d][1,3,2]dioxathiol-5-yl)carbamate (19a)

A suspension of sodium hydride (28 mg, 1.17 mmol) was added to a solution of diol 18a (150 mg, 0.37 mmol) in 10 mL of THF at 0 °C. The reaction mixture was stirred for 30 min, then slowly allowed to warm up to room temperature. After 30 min the reaction mixture was cooled down to 0 °C, 1,1′-sulfonyimidazole (144 mg, 0.73 mmol) was added, and reaction was allowed to slowly warm up to room temperature and stir for 5 h. Then reaction mixture was quenched with 5 mL of
water and absorbed on deactivated silica for column chromatography [hexanes:EtOAc (2:1)]. The cyclic sulfate \( 19\text{a} \) was isolated as white glassy foam (116 mg, 67 %)

\( \text{19a:} \ R_f = 0.7 \ [\text{hexanes:EtOAc (1:1)}]; \ [\alpha]_D^{24} = -98.8 (c \ 0.4, \ CHCl_3) \); IR (neat) 3333, 2988, 2942, 2851, 1708, 1636, 1533, 1514, 1453, 1438, 1387, 1253, 1208, 1145, 1088, 1048 cm\(^{-1}\); \(^1\)H NMR (600 MHz, CDCl\(_3\)) \( \delta \) 6.40 (s, 1H), 5.98 (s, 1H), 5.27 (d, \( J = 3.1 \) Hz, 1H), 5.01 (dd, \( J = 10.4, 5.6 \) Hz, 1H), 4.70-4.60 (m, 1H), 4.51 (s, 1H), 4.44 (d, \( J = 92.7 \) Hz, 1H), 4.36 (s, 1H), 4.12 (q, \( J = 7.1 \) Hz, 1H), 3.89 (s, 2H), 3.57 (s, 2H), 3.25 (s, 1H), 1.60 (s, 3H), 1.41 (s, 3); \(^{13}\)C NMR (150 MHz, CDCl\(_3\)) \( \delta \) 149.1, 144.0, 135.3, 129.1, 110.6, 102.9, 101.9, 95.1, 85.5, 80.9, 73.4, 60.5, 56.9, 52.5, 52.0, 46.9, 27.7, 25.8; HRMS (FAB MS ESI+) calcd for \([\text{C}_{19}\text{H}_{23}\text{NO}_{11}\text{S}+\text{H}]^+\): 474.1065, found: 474.1033; anal. calcd for \( \text{C}_{19}\text{H}_{23}\text{NO}_{11}\text{S} \): C 48.20, H 4.90, found C 48.27, H 5.08.

\[ \text{(1R,2R,3S,4S,5R,6R)-2,3,4-Trihydroxy-6-(7-methoxybenzo[d][1,3]dioxol-5-yl)-5-((methoxycarbonyl)amino)cyclohexyl benzoate (21)} \]

Cyclic sulfate \( \text{19a} \) (50 mg, 0.11 mmol) and ammonium benzoate (35.3 mg, 0.26 mmol) were dissolved in 1 mL of DMF and heated for 6 h at 70 °C. DMF removed in high vacuum at 70 °C. Residual mixture dissolved in 1 mL of THF, and added 2 drops of H\(_2\)O and 2 drops of concentrated H\(_2\)SO\(_4\). The mixture was stirred overnight at room temperature whereupon it was quenched with 5 mL of sat. solution of NaHCO\(_3\) and extracted with EtOAc (5 × 5 mL). Organic phases were dried over Na\(_2\)SO\(_4\), filtered and concentrated under reduced pressure. Benzoate \( \text{21} \) was isolated by preparative TLC as a colourless glassy oil (29 mg, 57.8 %)

\[ \text{20:} \ R_f = 0.4 \ [\text{EA}]; \ [\alpha]_D^{25} = +5.1 (c \ 1.0, \ CHCl_3); \ (^1\)H NMR (600 MHz, CDCl\(_3\)) \( \delta \) 8.14-8.04 (m, 2H), 7.58 (t, \( J = 7.4 \) Hz, 1H), 7.44 (t, \( J = 7.8 \) Hz, 2H), 6.50 (s, 1H), 6.44 (s, 1H), 5.13 (dd, \( J = 9.8, 2.7 \) Hz, 1H), 4.63 (d, \( J = 7.5 \) Hz, 1H), 4.42 (s, \( J = 22.3, 12.1 \) Hz, 1H), 4.38 (t, \( J = 10.2 \) Hz, 1H), 4.18-4.00
(m, 2H), 3.96-3.75 (m, 4H), 3.57 (s, J = 24.5 Hz, 3H), 3.00 (s, 1H), 2.59 (t, J = 11.1 Hz, 1H), 1.91 (s, 1H); $^{13}$C NMR (150 MHz, CDCl$_3$) $\delta$ 166.4, 158.6, 149.7, 144.0, 135.0, 133.5, 131.7, 130.1, 129.8, 128.6, 101.8, 76.0, 74.6, 71.1, 70.9, 56.8, 54.6, 52.8, 52.1, 29.9; HRMS (EI MS ESI+) calcd for [C$_{23}$H$_{25}$NO$_{10}$+H]$^+$: 475.1473, found: 475.1486.

21: $R_f = 0.4$ [EA]; $[\alpha]_D^{24}$ +89.3 (c 1.0, CHCl$_3$); $^1$H NMR (400 MHz, acetone-$d_6$) $\delta$ 8.09 (d, J = 7.4 Hz, 2H), 7.63 (t, J = 7.4 Hz, 1H), 7.51 (t, J = 7.7 Hz, 2H), 6.63 (s, 1H), 6.46 (s, 1H), 6.05 (d, J = 9.6 Hz, 1H), 5.83 (d, J = 2.6 Hz, 1H), 5.40-5.31 (m, 1H), 5.20 (s, 1H), 4.79 (d, J = 4.0 Hz, 1H), 4.72 (dd, J = 21.9, 10.3 Hz, 1H), 4.25-4.09 (m, 1H), 4.07-3.93 (m, 1H), 3.74 (d, J = 7.7 Hz, 1H), 3.59 (s, 2H), 3.52 (d, J = 12.1 Hz, 1H), 3.46 (s, 1H); $^{13}$C NMR (100 MHz, acetone-$d_6$) $\delta$ 164.5, 148.2, 143.0, 133.1, 132.7, 130.5, 129.4, 128.3, 108.1, 102.8, 100.7, 76.5, 73.3, 71.6, 55.0, 50.5, 49.8, 45.9; HRMS (EI MS ESI+) calcd for [C$_{23}$H$_{25}$NO$_{10}$+H]$^+$: 475.1473, found: 475.1458.

(1S,2S,3S,4R,5R,6R)-4-(Benzoyloxy)-5-(7-methoxybenzo[d][1,3]dioxol-5-yl)-6-((methoxycarbonyl)amino)cyclohexane-1,2,3-triyl triacetate (22)$^4$

Triethylamine (0.078 mL, 0.55 mmol), 4-dimethylaminopyridine (DMAP, cat. amount, 1 crystal) and acetic anhydride (0.052 mL, 0.55 mmol) was added to a solution of triol 21 (26 mg, 0.055 mmol) in DCM (0.5 mL). After 1 h, the reaction mixture was concentrated under reduced pressure and the crude product was purified on preparative TLC (hexanes:EtOAc (1:1)) to yield triacetate 22 as a colourless oil (27 mg, 80 %)

22: $R_f = 0.1$ [hexanes:EtOAc (1:1)]; $^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 8.10 (d, J = 7.7 Hz, 1H), 7.60 (t, J = 7.3 Hz, 1H), 7.46 (t, J = 7.4 Hz, 1H), 6.50 (s, 1H), 6.44 (s, 1H), 5.88 (s, 1H), 5.43 (s, 1H), 5.3-5.25 (m, 1H), 5.24 (s, 1H), 4.91 (dd, J = 20.3, 10.0 Hz, 1H), 4.43 (d, J = 9.6 Hz, 1H), 3.59 (s, 1H), 3.55 (s, 2H), 3.31 (d, J = 12.1 Hz, 1H), 2.22 (s, J = 10.2 Hz, 2H), 2.04 (s, J = 15.4 Hz, 2H), 1.98 (s, 1H); $^{13}$C NMR (150 MHz, CDCl$_3$) $\delta$ 169.5, 168.4, 164.4, 157.0, 148.9, 143.5, 134.7, 133.8, 130.1, 129.9, 129.5, 128.7, 107.7, 103.3, 101.6, 77.2, 72.5, 71.1, 68.8, 68.3, 56.1, 52.5, 48.4, 48.0, 21.1, 20.9, 20.8. HRMS (EI MS ESI+) calcd for [C$_{29}$H$_{31}$NO$_{13}$]$^+$: 601.1795, found: 601.1770.
(1R,2S,3S,4S,4aR,11bR)-1-(Benzoyloxy)-7-methoxy-6-oxo-1,2,3,4,4a,5,6,11b-octahydro-
[1,3]-dioxolo[4,5-j]phenanthridine-2,3,4-triy1 triacetate (24)³

To the solution of triacetate 22 (25 mg, 0.042 mmol) and DMAP (25.4 mg, 0.21 mmol) in DCM (2 mL) at 0 °C was added trifluoromethanesulfonic anhydride (56 µL, 0.33 mmol). The reaction mixture was stirred at 3 °C for 18 h, then it was poured into saturated solution of NaHCO₃ (5 mL) and extracted with EtOAc(3 × 5 mL). The combined organic layers were washed with 0.5 M HCl solution (4 mL), dried over Na₂SO₄, and concentrated under reduced pressure. This mixture was dissolved in THF (2 mL) containing 2 M HCl (0.2 mL) and stirred at room temperature for 4 h. The reaction mixture was poured into saturated solution of NaHCO₃ (5 mL) and extracted with EtOAc (3 × 10 mL). The combined organic layers were dried over Na₂SO₄ and concentrated under reduced pressure. The crude product was purified by column chromatography [10 wt% deactivated silica gel, gradient hexanes:EtOAc 1:1 to EtOAc]. Phenanthridone 24 was yielded as colourless glassy oil (10 mg, 42 %).

24: Rₓ = 0.1 [hexanes:EtOAc (1:2)]; ¹H NMR (600 MHz, CDCl₃) δ 8.03-7.98 (m, 2H), 7.58 (t, J = 7.4 Hz, 1H), 7.43 (t, J = 7.8 Hz, 1H), 6.42 (s, 1H), 6.07 (s, 1H), 5.94 (s, 1H), 5.80 (s, 1H), 5.49 (t, J = 3.0 Hz, 1H), 5.34 (t, J = 2.9 Hz, 1H), 5.22 (dd, J = 10.8, 3.5 Hz, 1H), 4.37 (dd, J = 12.5, 11.0 Hz, 1H), 4.05 (s, 3H), 3.49 (dd, J = 12.7, 2.0 Hz, 1H), 2.20 (s, 3H), 2.09 (s, 3H), 1.81 (s, 3H); ¹³C NMR (150 MHz, CDCl₃) δ 170.3, 169.4, 168.5, 165.0, 163.6, 152.6, 145.5, 137.7, 134.0, 133.3, 130.1, 130.0, 129.0, 128.6, 115.7, 101.9, 99.2, 77.2, 71.8, 67.9, 66.9, 66.9, 61.0, 48.0, 40.7, 29.8, 21.0, 20.9, 20.6.
NMR spectra for new compounds

(1S,6S)-6-(Acetyloxy)-3,5-dibromocyclohexa-2,4-dien-1-yl acetate (16c) [DMSO-$d_6$]
Methyl (7S,8S)-7,8-bis(acetyloxy)-1,5-dibromo-2-oxa-3-azabicyclo[2.2.2]oct-5-ene-3-carboxylate (17b) [CDCl₃]
(5S,6S)-Methyl 5,6-diacetoxy-4-bromo-7-(7-methoxybenzo[d][1,3]dioxol-5-yl)-3-oxa-2-aza-bicyclo[2.2.2]oct-7-ene-2-carboxylate (17c) [acetone-$d_6$]
(1S,2R,6S)-6-(Acetyloxy)-3-(7-methoxy-2H-1,3-benzodioxol-5-yl)-2-[(methoxycarbonyl)amino]-5-oxocyclohex-3-en-1-yl acetate (7b) [methanol-$d_4$]
(1S,2R,5R,6R)-6-(Acetyloxy)-5-hydroxy-3-(7-methoxy-2H-1,3-benzodioxol-5-yl)-2-[(methoxycarbonyl)amino]cyclohex-3-en-1-yl acetate (8b) [acetone-d$_6$]
Methyl ((3aS,4R,5R,6S,7aR)-6,7-dihydroxy-7'-methoxy-2,2-dimethyl-3a,4,5,6,7,7a-hexahydro-[5,5'-
bibeno[d][1,3]dioxol]-4-yl)carbamate (18a) [CDCl₃]
Methyl ((3aS,4R,5aS,8aS,8bR)-4-(7-methoxybenzo[d][1,3]dioxol-5-yl)-7,7-dimethyl-2,2-
dioxidohexahydro-[1,3]dioxolo[4',5':3,4]benzo[1,2-d][1,3,2]dioxathiol-5-yl)carbamate (19a) [CDCl₃]
(1R,2S,3S,4S,4aR,11bR)-1-(Benzoyloxy)-7-methoxy-6-oxo-1,2,3,4,4a,5,6,11b-octahydro-[1,3]-dioxolo[4,5-j]phenanthridine-2,3,4-triy triacetate (24) [CDCl₃]α
References

