

Iron(III)-Templated Macrolactonization of Trihydroxamate Siderophores

Supporting Information

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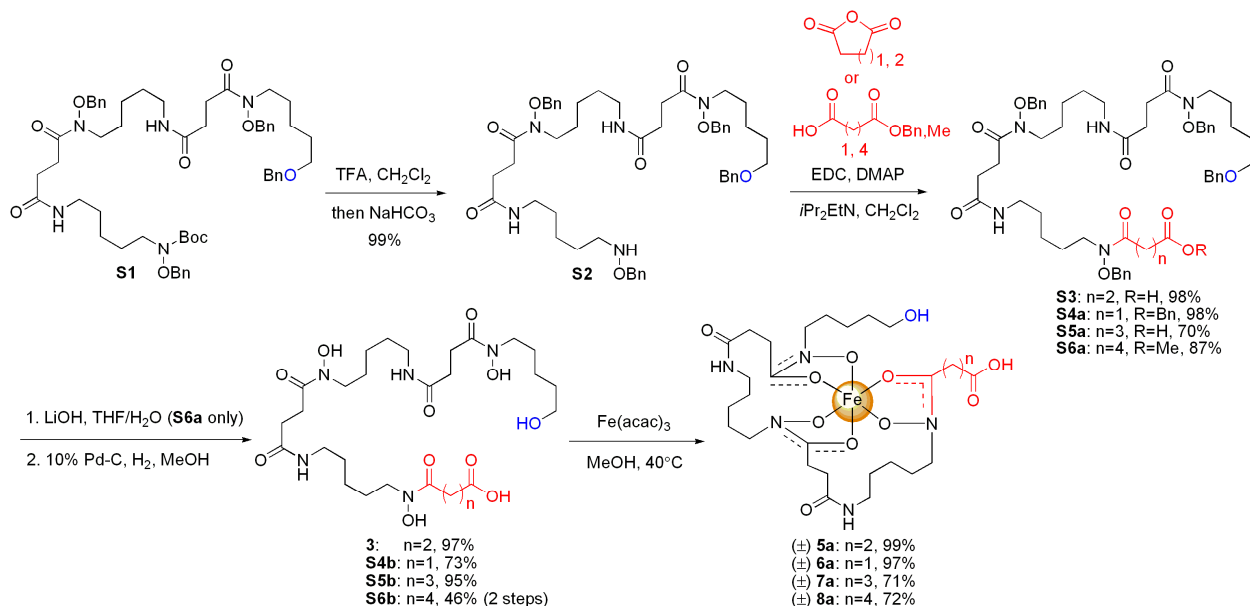
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Table of Contents

I.	Synthesis of Siderophore Hydroxy Acid Substrates	Scheme S1; S2.
II.	Synthesis of Siderophore Methyl Esters	Scheme S2; S2.
III.	Experimental Procedures and Compound Characterization Data	S3-S11.
IV.	HPLC Chromatograms of Reactions from Table 1	Figures S1-S8; S12-S15.
V.	Graph of % Lactone vs Time for Reactions in Table 1	Figure S9; Table S1; S16-S18.
VI.	Graph of % Products vs Time for Reaction in Table 1, Entry 3	Figure S10; S19.
VII.	HPLC Chromatograms from Synthesis and Purification of 5b	Figure S11; S20.
VIII.	HPLC Chromatograms of Siderophore Me Ester Hydrolyses ..	Figure S12-S15; S21-S23.
IX.	1 st Order Rate Plots for Methyl Ester Hydrolyses	Figures S16-S19; S24-S25.
X.	¹ H-NMR and ¹³ C-NMR Spectra of Pure Compounds	S26-S42.
XI.	HPLC Chromatograms of Siderophore-Fe(III) Complexes ...	Figures S20-S21; S43-S44.
XII.	X-ray Diffraction Data for Macrolactone 5b	Tables S2-S8; Figure S22; S45-S55.
XIII.	Acknowledgments.....	S55.
XIV.	References	S55.

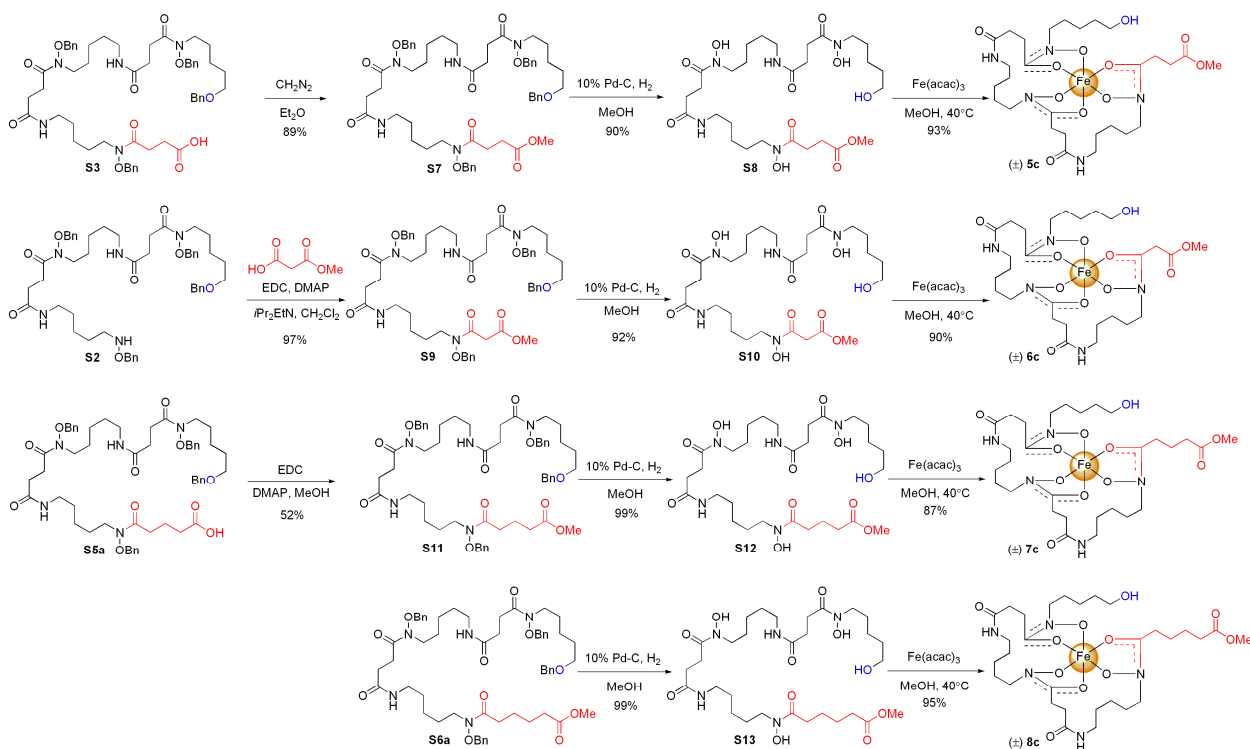
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I. Synthesis of Siderophore Hydroxy Acid Substrates 5a-8a



Scheme S1. Synthesis of siderophore-Fe(III) complex hydroxy acid substrates (**5a-8a**) for use in the Fe(III)-templated Yamaguchi macrolactonization reactions.

II. Synthesis of Siderophore Methyl Esters 5c-8c



Scheme S1. Synthesis of siderophore-Fe(III) methyl ester complexes (**5c-8c**) for use in kinetic hydrolysis studies.

III. Experimental Procedures and Compound Characterization

General Materials and Methods

All reactions were performed under a dry argon atmosphere, unless otherwise stated. All solvents and reagents were obtained from commercial sources and used without further purification unless otherwise stated. *N*-Boc-*O*-Benzyl-protected siderophore **S1** was synthesized as described previously by Roosenberg and Miller.¹ Dichloromethane (CH₂Cl₂) was distilled from calcium hydride. Tetrahydrofuran (THF) was distilled from Na/benzophenone. Dimethylformamide (DMF), diisopropylethylamine (*i*Pr₂EtN), and acetonitrile (CH₃CN) were used from Acros Seal anhydrous bottles. Silica gel column chromatography was performed using Sorbent Technologies silica gel 60 (32-63 μm). ¹H-NMR and ¹³C-NMR spectra were obtained on a 300 MHz, 500 MHz, or 600 MHz Varian DirectDrive spectrometer and FIDs were processed using ACD/ChemSketch version 10.04. Chemical shifts (δ) are given in parts per million (ppm) and are referenced to non-deuterated residual solvent. Coupling constants (*J*) are reported in hertz (Hz). High resolution, accurate mass measurements were obtained on a Finnigan MAT 8430 spectrometer using fast atom bombardment (FAB) ionization or with a Bruker micrOTOF II electrospray ionization time-of-flight mass spectrometer in positive ion mode. Sample was introduced via flow injection at a rate of 4 μL/min, and mass spectra were accumulated from 50-3000 *m/z* for two minutes. Crystallographic data were collected at Beamline 11.3.1 at the Advanced Light Source (ALS), Lawrence Berkeley National Laboratory. Analytical high-performance liquid chromatography (HPLC) was performed on a Waters 1525 Binary HPLC Pump instrument with a Waters 2487 Dual λ Absorbance Detector set at 427 nm operated by Breeze version 3.30 software. HPLC-MS was performed on a Waters ZQ instrument consisting of a chromatography module Alliance HT, photodiode array detector 2996, and mass spectrometer Micromass ZQ with an MS electrospray source operate at capillary voltage 3.5 kV and a desolvation temperature of 300 °C. Both HPLC and HPLC-MS instruments used a YMC Pro C18 reverse phase column (3.0 x 50 mm) fit with precolumn frit (0.5 μm) and YMC Pro C18 guard column (2.0 x 10 mm) for all analyses. Mobile phases used were 10 mM ammonium acetate in HPLC grade water (A) and HPLC grade acetonitrile (B). A gradient was formed from 5%–80% of B in 10 min, then 80%–95% of B in 2 min, and then 95%–5% of B in 3 min at a flow rate of 0.7 mL/min (total run time of 15 min). Semi-preparative HPLC purifications were performed on a Waters semi-preparative binary pump system at a flow rate of 15 mL/min with detection by UV detection at 427 nm with separation facilitated by a YMC-Pack Pro C18 column, 150 x 20 mm (I.D.), particle size 5 μm fit with a guard column. Thin layer chromatography (TLC) was performed with aluminum-backed Merck 60-F₂₅₄ silica gel plates or aluminum-backed Merck RP-C18 F₂₅₆ silica gel plates using a 254 nm lamp or aq. FeCl₃ for visualization. Melting points were determined in capillary tubes using a Thomas Hoover melting point apparatus and are uncorrected.

General Procedure A: Hydrogenolysis of benzyl protected siderophores.

Fully benzyl protected siderophore (**S3**, **S4a-S6a**, **S7**, **S9**, **S11**) was dissolved in MeOH (~0.01 M) in an HCl-washed, oven-dried round bottom flask fitted with a magnetic stir bar. The flask was flushed with argon, charged with 10% Pd-C (~10% w/w), and flushed with H₂ gas (balloon) several times using intermediate vacuum evacuations. The mixture was then left stirring under an H₂ atmosphere (~1 atm; balloon) and periodically monitored by RP-C18 TLC (1.5:1 CH₃CN:H₂O; FeCl₃ Stain). Once complete, the mixture was flushed with argon, vacuum

filtered through celite, and concentrated under reduced pressure. The crude product was dissolved in a minimal amount of MeOH and precipitated by addition of Et₂O. The siderophore (**3**, **S4b-S6b**, **S8**, **S10**, **S12**, **S13**) was isolated as a white or off-white solid after trituration with Et₂O and drying under vacuum.

General Procedure B: Complexation of siderophores to Fe(III).

The siderophore (**3**, **S4b-S6b**, **S8**, **S10**, **S12**, **S13**) was dissolved or suspended in MeOH (0.002 M) and the solution was heated to 40 °C (oil bath temp.). Fe(acac)₃ (1.1 equiv) was added and the clear, orange solution was stirred for 2 h. The MeOH was removed under reduced pressure giving the siderophore-Fe(III) complex as an orange film. The complex was then dissolved in a minimal amount of MeOH and precipitated by addition of Et₂O. The siderophore-Fe(III) complex (**5a,c-8a,c**) was isolated as an orange powder after trituration with Et₂O and drying under vacuum.

Hydroxylamine S2. The *N*-Boc protecting group of compound **S1** (5.01 g, 0.0051 mol) was removed by treatment with anhydrous TFA in CH₂Cl₂ followed by free basing with sat. aq. NaHCO₃ to give the corresponding hydroxylamine (**S2**) in 99% yield as an amorphous solid (4.49 g, 0.0051 mol). ¹H-NMR (500 MHz, CDCl₃) δ 7.40–7.26 (m, 20 H), 6.33 (br s, 2 H), 4.85 (s, 2 H), 4.84 (s, 2 H), 4.70 (s, 2 H), 4.47 (s, 2 H), 3.69–3.56 (m, 4 H), 3.44 (t, *J* = 6.6 Hz, 2 H), 3.21 (t, *J* = 6.3 Hz, 2 H), 3.17 (t, *J* = 6.0 Hz, 2 H), 2.91 (t, *J* = 7.2 Hz, 2 H), 2.86–2.74 (m, 4 H), 2.52–2.44 (m, 4 H), 1.70–1.22 (m, 18 H).

tetra-O-Benzyl danoxamine (S3). This compound was prepared by a modified literature procedure.¹ Hydroxylamine **S2** (4.49 g, 0.0051 mol), succinic anhydride (1.02 g, 0.010 mol), and catalytic DMAP (32.6 mg, 0.27 mmol) were dissolved in freshly distilled CH₂Cl₂ (100 mL). After 26.5 h at rt, TLC (9% MeOH in DCM; FeCl₃ stain) showed no remaining hydroxylamine (**S2**). The mixture was diluted with CH₂Cl₂ (50 mL) and 1 N HCl (35 mL) was added, respectively. The organic layer was separated and washed with brine (35 mL), dried over anhydrous MgSO₄, filtered through celite, and concentrated under reduced pressure. The crude product was purified by silica gel column chromatography (5%–9.5% MeOH in CH₂Cl₂ as eluent) to give the desired product (**S3**) in 98% yield as a white solid (recrystallized from hexanes/EtOAc at -20 °C; 4.90 g, 0.005 mol). All characterization data matched that previously reported in the literature.¹ Lit. Mp = 63–64.5 °C, found 64–66 °C; ¹H-NMR (500 MHz, CDCl₃) δ 7.37–7.31 (m, 20 H), 6.82 (s, 1 H), 6.51 (s, 1 H), 4.84 (s, 2 H), 4.83 (s, 2 H), 4.81 (s, 2 H), 4.47 (s, 2 H), 3.72–3.70 (m, 2 H), 3.63–3.61 (m, 4 H), 3.43 (t, *J* = 10.0 Hz, 2 H), 3.22–3.16 (m, 4 H), 2.80–2.79 (m, 4 H), 2.67–2.65 (m, 4 H), 2.53–2.47 (m, 4 H), 1.66–1.58 (m, 9 H), 1.49–1.44 (m, 4 H), 1.38–1.22 (m, 6 H); ¹³C-NMR (125 MHz, CDCl₃) δ 175.0, 174.3, 172.4, 172.3, 138.5, 134.4, 134.1, 129.2, 129.2, 129.1, 128.9, 128.8, 128.7, 128.6, 128.3, 127.5, 127.4, 77.2, 76.3, 76.3, 76.0, 72.8, 70.0, 39.3, 39.2, 30.6, 29.3, 28.6, 28.3, 28.3, 28.0, 27.9, 26.8, 26.6, 26.5, 26.2, 23.6, 23.5, 23.3; HRMS-FAB (*m/z*): [M+H]⁺ calcd. for C₅₅H₇₄N₅O₁₁: 980.5385, found 980.5384.

Desferridanoxamine (3). *tetra-O-Benzyl danoxamine (S3*; 340.0 mg, 0.35 mmol) was dissolved in 35 mL of MeOH in an HCl-washed round bottom flask sealed under argon. The flask was charged with 10% Pd-C (50.0 mg) and exposed to a balloon of hydrogen gas (~1 atm). Reaction progress was monitored by RP-C18 TLC (1.5:1 CH₃CN:H₂O; FeCl₃ stain) and after 11 h no

starting material (**S3**) remained. The flask was flushed with argon and the mixture was diluted with warm MeOH, vacuum filtered through a pad of celite using a fine glass frit, and concentrated under reduced pressure. The resulting solid was dissolved in a minimal amount of MeOH and precipitated by addition of cold Et₂O. After trituration with Et₂O, the siderophore desferridanoxamine (**3**) was obtained in 97% yield as a white solid (208.0 mg, 0.34 mmol). Mp 134–140 °C; ¹H-NMR (600 MHz, DMSO-*d*₆) δ 11.87 (br s, COOH, 1 H), 9.62 (br s, N-OH, 3 H), 7.78 (t, *J* = 5.3 Hz, 2 H), 4.35 (br s, 1 H), 3.47–3.42 (m, 6 H), 3.39–3.36 (m, 2 H), 3.02–2.97 (m, 4 H), 2.57 (t, *J* = 6.6 Hz, 6 H), 2.39 (t, *J* = 6.6 Hz, 2 H), 2.26 (t, *J* = 6.9 Hz, 4 H), 1.49 (dt, *J* = 14.2, 7.1 Hz, 6 H), 1.43–1.34 (m, 6 H), 1.27–1.17 (m, 6 H); ¹³C-NMR (150 MHz, DMSO-*d*₆) δ 174.1, 172.0, 171.9, 171.6, 171.3, 60.6, 47.2, 47.1, 38.4, 32.2, 29.9, 28.8, 28.7, 27.6, 27.5, 27.1, 26.2, 26.0, 23.5, 23.4, 22.7; HRMS-ESI (*m/z*): [M+H]⁺ calcd. for C₂₇H₅₀N₅O₁₁: 620.3501, found 620.3506; HPLC retention time 3.22 min.

(±) **Danoxamine 5a**. Desferridanoxamine (**3**; 154.0 mg, 0.25 mmol) was dissolved in 10 mL of MeOH at 40 °C (oil bath temperature). Fe(acac)₃ (97.0 mg, 0.28 mmol) was added and the clear, orange solution was stirred for 2 h. The solution was cooled to rt and the MeOH was evaporated under reduced pressure. The resulting orange residue was dissolved in a minimal amount of MeOH and precipitated by addition of cold Et₂O. After trituration with Et₂O, the Fe(III)-complexed siderophore danoxamine (**5a**) was isolated in 99% yield as an orange powder (165.2 mg, 0.25 mmol). Mp 151–154 °C (dec.); HRMS-ESI (*m/z*): [M+H]⁺ calcd. for C₂₇H₄₇FeN₅O₁₁: 673.2616, found 673.2647; HPLC retention time 2.68 min.

Benzyl protected siderophore S4a. Hydroxylamine **S2** (98.0 mg, 0.11 mmol), *i*Pr₂EtN (19.16 μL, 0.11 mmol), monobenzylmalonate (27.0 mg, 0.14 mmol), catalytic DMAP (3.5 mg, 0.03 mmol), and EDC-HCl (43.0 mg, 0.22 mmol) were dissolved in 2.0 mL of CH₂Cl₂. After 60 h, TLC (6% MeOH in CH₂Cl₂; FeCl₃ stain) showed no remaining hydroxylamine **S2**. After 90 h, the mixture was diluted with 15 mL of CH₂Cl₂ and washed with 10% aq. citric acid (2 x 10 mL), brine (10 mL), 10% aq. NaHCO₃ (2 x 10 mL), and brine (10 mL), dried over anhydrous MgSO₄, filtered, and concentrated under reduced pressure. This gave 115.3 mg of a clear, colorless oil that was purified by silica gel column chromatography (1 x 4 in silica gel; 3%–6% MeOH in CH₂Cl₂) to give the desired product (**S4a**) in 98% yield as a viscous oil (113.8 mg, 0.11 mmol). ¹H-NMR (600 MHz, CDCl₃) δ 7.40–7.28 (m, 25 H), 6.30 (br s, 2 H), 5.13 (s, 2 H), 4.86 (s, 2 H), 4.85 (s, 2 H), 4.78 (s, 2 H), 4.48 (s, 2 H), 3.65 (t, *J* = 6.7 Hz, 2 H), 3.45 (s, 2 H), 3.44 (t, *J* = 6.6 Hz, 2 H), 3.21–3.17 (m, 4 H), 2.83–2.76 (m, 4 H), 2.48 (t, *J* = 6.5 Hz, 4 H), 1.66–1.59 (m, 8 H), 1.52–1.43 (m, 4 H), 1.38–1.25 (m, 6 H); ¹³C-NMR (150 MHz, CDCl₃) δ 174.0, 173.8, 172.2, 172.1, 167.4, 167.3, 138.5, 135.3, 134.3, 133.9, 129.2, 129.1, 129.0, 128.9, 128.8, 128.7, 128.7, 128.6, 128.5, 128.4, 128.3, 128.3, 127.5, 127.4, 76.3, 76.3, 76.3, 76.2, 72.8, 70.1, 67.0, 45.5, 44.9, 44.8, 40.7, 39.3, 39.2, 30.7, 30.5, 29.7, 29.3, 28.9, 28.5, 28.1, 28.0, 26.7, 26.4, 26.1, 23.7, 23.6, 23.4; HRMS-ESI (*m/z*): [M+H]⁺ calcd. for C₆₁H₇₈N₅O₁₁: 1056.5692, found 1056.5687.

Siderophore hydroxy acid S4b. Benzyl protected siderophore **S4a** (43.0 mg, 0.041 mmol) was deprotected according to general procedure **A** to give the pure siderophore (**S4b**) in 73% as an off-white powder (18 mg, 0.030 mmol). Mp 139–141 °C (dec.); ¹H-NMR (600 MHz, CD₃OD) δ 3.63 (t, *J* = 6.7 Hz, 2 H), 3.59 (t, *J* = 7.0 Hz, 4 H), 3.55 (t, *J* = 6.6 Hz, 2 H), 3.18–3.15 (m, 4 H), 2.78–2.75 (m, 4 H), 2.46 (t, *J* = 7.3 Hz, 2 H), 2.45 (t, *J* = 7.3 Hz, 2 H), 1.69–1.61 (m, 6 H), 1.58–1.50 (m, 6 H), 1.40–1.31 (m, 6 H); ¹³C-NMR (150 MHz, CD₃OD) δ 175.1, 175.1, 174.6, 174.6,

173.3, 169.8, 62.9, 48.7, 40.4, 33.4, 31.7, 31.7, 30.1, 30.0, 29.2, 29.1, 27.7, 27.5, 27.4, 25.0, 24.9, 24.1; HRMS-ESI (m/z): [M+Na]⁺ calcd. for C₂₆H₄₇N₅NaO₁₁: 628.3164, found 628.3172.

(±) **Siderophore-Fe(III) complex hydroxy acid 6a**. Siderophore **S4b** (8.0 mg, 0.013 mmol) was complexed to Fe(III) according to general procedure **B** to give the siderophore-Fe(III) complex (**6a**) in 97% yield as an orange powder (8.4 mg, 0.013 mmol). Mp 189–191 °C (dec.); HRMS-ESI (m/z): [M+H]⁺ calcd. for C₂₆H₄₅FeN₅O₁₁: 659.2460, found 659.2465; HPLC retention time 2.32 min.

Benzyl protected siderophore hydroxy acid S5a. Hydroxylamine **S2** (196.0 mg, 0.22 mmol), *i*Pr₂EtN (38.3 μL, 0.22 mmol), glutaric anhydride (50.2 mg, 0.44 mmol), and catalytic DMAP (7.0 mg, 0.057 mmol) were dissolved in 3.0 mL of CH₂Cl₂, respectively, giving a clear, colorless solution. After 60 h, TLC (6% MeOH in CH₂Cl₂; FeCl₃ stain) showed no remaining starting material (**S2**). After 89 h, the mixture was diluted with CH₂Cl₂ (15 mL) and washed with 10% aq. citric acid (2 x 10 mL) and brine (1 x 10 mL), dried over anhydrous MgSO₄, filtered, and concentrated under reduced pressure. This gave 207.6 mg of a clear, colorless oil that was purified by silica gel column chromatography (1.25 x 4 in silica gel; 3%–6% MeOH in CH₂Cl₂). Pure product (**S5a**) was obtained in 70% yield as a clear, colorless, viscous oil (154.0 mg, 0.155 mmol). ¹H-NMR (600 MHz, CDCl₃) δ 7.41–7.29 (m, 20 H), 6.57 (br s, 1 H), 6.50 (br s, 1 H), 4.85 (s, 4 H), 4.79 (br s, 2 H), 4.48 (s, 2 H), 3.71–3.59 (m, 6 H), 3.44 (t, *J* = 6.6 Hz, 2 H), 3.24–3.16 (m, 4 H), 2.85–2.78 (m, 4 H), 2.54–2.45 (m, 6 H), 2.43–2.37 (m, 2 H), 1.99–1.92 (m, 2 H), 1.67–1.58 (m, 8 H), 1.52–1.45 (m, 4 H), 1.40–1.33 (m, 2 H), 1.33–1.23 (m, 4 H); ¹³C-NMR (150 MHz, CDCl₃) δ 175.3, 174.2, 173.9, 172.4, 138.5, 134.3, 134.2, 129.2, 129.2, 129.2, 129.0, 128.9, 128.7, 128.7, 128.3, 127.6, 127.5, 76.3, 76.2, 72.8, 70.1, 45.5, 44.7, 44.4, 39.3, 39.2, 33.1, 33.0, 30.9, 30.7, 29.3, 28.8, 28.4, 28.1, 28.0, 26.7, 26.3, 23.6, 23.5, 23.4, 19.9, 19.7; HRMS-ESI (m/z): [M+Na]⁺ calcd. for C₅₆H₇₅N₅NaO₁₁: 1016.5355, found 1016.5357.

Siderophore hydroxy acid S5b. Benzyl protected siderophore **S5a** (29.7 mg, 0.03 mmol) was deprotected according to general procedure **A** to give the pure siderophore (**S5b**) in 95% yield as an off-white powder (18.0 mg, 0.028 mmol). Mp 131–134 °C; ¹H-NMR (600 MHz, CD₃OD) δ 3.61–3.57 (m, 6 H), 3.55 (t, *J* = 6.6 Hz, 2 H), 3.18–3.15 (m, 4 H), 2.76 (t, *J* = 7.3 Hz, 4 H), 2.53 (t, *J* = 7.5 Hz, 2 H), 2.45 (t, *J* = 7.2 Hz, 4 H), 2.31 (t, *J* = 7.5 Hz, 2 H), 1.88 (quintet, *J* = 7.4 Hz, 2 H), 1.66–1.61 (m, 6 H), 1.58–1.49 (m, 6 H), 1.39–1.31 (m, 6 H); ¹³C-NMR (150 MHz, CD₃OD) δ 175.8, 175.8, 175.1, 174.6, 174.6, 62.9, 40.4, 33.4, 33.1, 33.0, 31.7, 30.1, 30.1, 29.1, 27.7, 27.5, 27.5, 25.1, 25.0, 24.1, 23.1, 22.9; HRMS-ESI (m/z): [M+Na]⁺ calcd. for C₂₈H₅₁N₅NaO₁₁: 656.3477, found 656.3485.

(±) **Siderophore-Fe(III) complex hydroxy acid 7a**. Siderophore **S5b** (8.0 mg, 0.013 mmol) was complexed to Fe(III) according to general procedure **B** to give the siderophore-Fe(III) complex (**7a**) in 71% as an orange powder (8.5 mg, 0.012 mmol). Mp 164–169 °C (dec.); HRMS-ESI (m/z): [M+Na]⁺ calcd. for C₂₈H₄₈FeN₅NaO₁₁: 709.2592, found 709.2582; HPLC retention time 2.2 min.

Benzyl protected siderophore methyl ester S6a. Hydroxylamine **S2** (122.0 mg, 0.14 mmol), adipic acid monomethyl ester (29.0 mg, 0.18 mmol), *i*Pr₂EtN (37.5 mg, 0.29 mmol), catalytic DMAP (4.2 mg, 0.034 mmol), and EDC-HCl (55mg, 0.29 mmol) were dissolved in 5 mL of

CH₂Cl₂, respectively. After 17 h, TLC (6% MeOH in CH₂Cl₂; FeCl₃ stain) showed no remaining starting material (**S2**). The mixture was diluted with CH₂Cl₂ (15 mL) and was washed with 10% aq. citric acid (10 mL) and brine (10 mL), dried over anhydrous MgSO₄, filtered, and concentrated under reduced pressure. This gave 150 mg of a waxy, off-white solid that was purified via silica gel column chromatography (1 x 6 in silica gel; 3%–5% MeOH in CH₂Cl₂). Pure product (**S6a**) was obtained in 87% yield as a waxy, off-white solid (124.2 mg, 0.12 mmol). Mp 71–73 °C; ¹H-NMR (500 MHz, CDCl₃) δ 7.41–7.28 (m, 20 H), 6.32 (br s, 2 H), 4.85 (s, 2 H), 4.84 (s, 2 H), 4.79 (s, 2 H), 4.48 (s, 2 H), 3.65 (s, 3 H), 3.64–3.59 (m, 6 H), 3.44 (t, *J* = 6.5 Hz, 2 H), 3.22–3.17 (m, 4 H), 2.83–2.77 (m, 4 H), 2.50–2.46 (m, 4 H), 2.39 (t, *J* = 6.6 Hz, 2 H), 2.31 (t, *J* = 7.0 Hz, 2 H), 1.66–1.58 (m, 12 H), 1.53–1.47 (m, 4 H), 1.39–1.35 (m, 2 H), 1.33–1.25 (m, 4 H); ¹³C-NMR (125 MHz, CDCl₃) δ 173.9, 172.1, 172.1, 138.5, 134.3, 129.1, 129.1, 128.9, 128.9, 128.9, 128.7, 128.7, 128.6, 128.3, 127.5, 127.4, 77.2, 76.3, 76.3, 76.2, 72.8, 70.1, 51.5, 45.5, 45.0, 44.6, 39.3, 39.3, 33.8, 31.9, 30.7, 30.5, 29.3, 29.1, 28.4, 28.1, 28.0, 26.6, 26.5, 26.4, 24.6, 24.0, 24.0, 23.6, 23.4; HRMS-ESI (*m/z*): [*M*+*H*]⁺ calcd. for C₅₈H₈₀N₅O₁₁: 1022.5849, found 1022.5838.

Siderophore hydroxy acid S6b. Benzyl protected methyl ester siderophore **S6a** (44.0 mg, 0.043 mmol) was dissolved in a 3:1 THF:H₂O mixture (2 mL) and anhydrous LiOH (3.5 mg, 0.15 mmol) was added. After 2.5 h, TLC (6% MeOH in CH₂Cl₂; FeCl₃ stain) showed no remaining starting material (**S6a**). The reaction was quenched with satd. aq. citric acid (5 mL) and the THF was evaporated under reduced pressure. The aq. slurry was extracted with CH₂Cl₂ (2 x 15 mL) and the combined CH₂Cl₂ layers were washed with brine (5 mL), dried over anhydrous MgSO₄, filtered, and concentrated under reduced pressure. This gave 30.0 mg of a clear, colorless oil that was purified by silica gel column chromatography (0.5 x 2.5 silica gel; 5%–9% MeOH in CH₂Cl₂). Pure benzyl protected carboxylic acid siderophore was obtained in 52% yield as a clear, colorless oil (22.3 mg, 0.022 mmol). ¹H-NMR (600 MHz, CDCl₃) δ 7.42–7.30 (m, 20 H), 6.58 (br s, 1 H), 6.49 (br s, 1 H), 4.85 (s, 4 H), 4.79 (s, 2 H), 4.48 (s, 2 H), 3.72–3.59 (m, 6 H), 3.44 (t, *J* = 6.6 Hz, 2 H), 3.22–3.16 (m, 4 H), 2.84–2.77 (m, 4 H), 2.52–2.46 (m, 4 H), 2.44–2.39 (m, 2 H), 2.32 (t, *J* = 6.6 Hz, 2 H), 1.71–1.58 (m, 12 H), 1.53–1.45 (m, 4 H), 1.40–1.34 (m, 2 H), 1.34–1.27 (m, 4 H); ¹³C-NMR (150 MHz, CDCl₃) δ 175.6, 174.6, 174.3, 173.9, 172.4, 172.3, 138.5, 134.4, 134.2, 129.2, 129.2, 129.1, 128.9, 128.9, 128.7, 128.7, 128.7, 128.3, 127.6, 127.5, 76.3, 76.1, 72.8, 70.1, 45.5, 44.8, 44.3, 39.4, 39.3, 33.8, 31.8, 30.7, 30.6, 29.3, 28.7, 28.4, 28.1, 28.0, 26.6, 26.5, 26.3, 24.6, 24.2, 23.8, 23.6, 23.4; HRMS-ESI (*m/z*): [*M*+*Na*]⁺ calcd. for C₅₇H₇₇N₅NaO₁₁: 1030.5512, found 1030.5482. The benzyl protected carboxyl acid siderophore (10.8 mg, 0.011 mmol) was deprotected according to general procedure **A** to give the pure siderophore (**S6b**) in 99% yield as a light tan solid (7.1 mg, 0.011 mmol). Mp 108–111 °C; ¹H-NMR (500 MHz, CD₃OD) δ 3.63–3.57 (m, 6 H), 3.55 (t, *J* = 6.6 Hz, 2 H), 3.16 (t, *J* = 6.8 Hz, 4 H), 2.76 (t, *J* = 7.2 Hz, 4 H), 2.49 (t, *J* = 6.7 Hz, 2 H), 2.45 (t, *J* = 7.0 Hz, 4 H), 2.28 (t, *J* = 6.8 Hz, 2 H), 1.68–1.59 (m, 10 H), 1.58–1.47 (m, 6 H), 1.41–1.30 (m, 6 H); ¹³C-NMR (125 MHz, CD₃OD) δ 175.9, 175.1, 174.6, 174.5, 62.9, 40.4, 36.2, 33.4, 33.1, 31.6, 30.1, 29.1, 27.6, 27.5, 27.5, 26.5, 25.8, 25.1, 25.0, 24.1; HRMS-ESI (*m/z*): [*M*+*Na*]⁺ calcd. for C₂₉H₅₃N₅NaO₁₁: 670.3634, found 670.3638.

(±) **Siderophore-Fe(III) complex hydroxy acid 8a.** Siderophore **S6b** (6.9 mg, 0.011 mmol) was complexed to Fe(III) according to general procedure **B** to give the siderophore-Fe(III)

complex (**8a**) in 72% yield as an orange powder (5.4 mg, 0.008 mmol). HRMS-ESI (m/z): [M+H]⁺ calcd. for C₂₉H₅₁FeN₅O₁₁: 701.2929, found 701.2960; HPLC retention time 2.64 min.

Benzyl protected siderophore methyl ester S7. A solution of Diazald[®] (113.5 mg, 0.53 mmol) in 1.5 mL of Et₂O was added dropwise to a solution of KOH (143.0 mg, 2.55 mmol) in 1.0 mL of 5:4 Ethanol:H₂O at 65 °C (oil bath temperature) using a diazomethane smooth-joint glassware kit. The diazomethane generated *in situ* was immediately condensed as a dilute Et₂O solution using a dry ice/acetone cooled cold finger into a solution of tetra-*O*-benzyl danoxamine **S3** (50.0 mg, 0.051 mmol) in 6 mL of 1:1:1 Et₂O:EtOAc:DCM at 0 °C. Once all of the diazomethane was condensed the reaction was stirred for 30 min, then quenched with 10% acetic acid in Et₂O. The volatiles were removed under reduced pressure giving 54.3 mg of a clear, colorless oil. This material was dissolved in 15 mL of CH₂Cl₂ and washed with satd. aq. NaHCO₃ (10 mL), dried over anhydrous MgSO₄, filtered, and concentrated under reduced pressure. This gave the desired product (**S7**) in 89% yield as a white, waxy solid (45.0 mg, 0.045 mmol) with no need for purification. Mp 78–80 °C; ¹H-NMR (600 MHz, CDCl₃) δ 7.41–7.30 (m, 20 H), 6.34 (br s, 1 H), 6.32 (br s, 1 H), 4.85 (s, 2 H), 4.85 (s, 2 H), 4.85 (s, 2 H), 4.48 (s, 2 H), 3.68 (s, 3 H), 3.67–3.60 (m, 6 H), 3.44 (t, *J* = 6.5 Hz, 2 H), 3.23–3.17 (m, 4 H), 2.84–2.76 (m, 4 H), 2.73 (t, *J* = 5.9 Hz, 2 H), 2.62 (t, *J* = 6.6 Hz, 2 H), 2.51–2.46 (m, 4 H), 1.67–1.58 (m, 8 H), 1.53–1.45 (m, 4 H), 1.40–1.33 (m, 2 H), 1.33–1.25 (m, 4 H); ¹³C-NMR (150 MHz, CDCl₃) δ 174.0, 173.8, 173.5, 173.1, 172.1, 172.1, 138.5, 134.4, 134.3, 129.1, 129.1, 128.9, 128.9, 128.8, 128.7, 128.7, 128.6, 128.3, 127.5, 127.4, 76.3, 76.3, 76.2, 72.8, 70.1, 51.7, 45.5, 45.2, 44.7, 39.3, 30.7, 30.5, 29.3, 29.0, 28.4, 28.4, 28.1, 27.9, 27.3, 26.7, 26.4, 26.3, 23.9, 23.6, 23.4; HRMS-ESI (m/z): [M+Na]⁺ calcd. for C₅₆H₇₅N₅NaO₁₁: 1016.5355, found 1016.5326.

Siderophore methyl ester S8. Benzyl protected siderophore **S7** (34.8 mg, 0.035 mmol) was deprotected according to general procedure **A** to give the siderophore (**S8**) in 92% yield as a white solid (20.0 mg, 0.032 mmol). Mp 132–133 °C; ¹H-NMR (600 MHz, CD₃OD) δ 3.66 (s, 3 H), 3.59 (t, *J* = 6.7 Hz, 6 H), 3.55 (t, *J* = 6.6 Hz, 2 H), 3.18–3.14 (m, 4 H), 2.80–2.75 (m, 6 H), 2.58 (t, *J* = 6.7 Hz, 2 H), 2.48–2.43 (m, 4 H), 1.67–1.60 (m, 4 H), 1.59–1.48 (m, 8 H), 1.40–1.30 (m, 6 H); ¹³C-NMR (150 MHz, CD₃OD) δ 175.2, 174.9, 174.5, 174.5, 174.4, 174.2, 62.8, 52.2, 40.3, 33.3, 32.4, 32.4, 31.5, 31.5, 30.2, 30.0, 30.0, 29.9, 29.4, 28.9, 28.9, 28.3, 27.5, 27.3, 27.3, 25.2, 24.9, 24.9, 24.3, 24.0; HRMS-ESI (m/z): [M+H]⁺ calcd. for C₂₈H₅₂N₅O₁₁: 634.3658, found 634.3649.

(±) **Siderophore-Fe(III) complex methyl ester 5c.** Siderophore **S8** (7.5 mg, 0.012 mmol) was complexed to Fe(III) according to general procedure **B** to give the siderophore-Fe(III) complex (**5c**) in 93% yield as an orange powder (7.5 mg, 0.011 mmol). Mp 95–100 °C (dec.); HRMS-ESI (m/z): [M+Na]⁺ calcd. for C₂₈H₄₈FeN₅NaO₁₁: 709.2592, found 709.2651; HPLC retention time 3.38 min.

Benzyl protected siderophore methyl ester S9. Hydroxylamine **S2** (160.0 mg, 0.18 mmol), monomethylmalonate (42.3 mg, 0.36 mmol), *i*Pr₂EtN (29.3 mg, 0.23 mmol), catalytic DMAP (6.9 mg, 0.06 mmol), and EDC-HCl (88.0 mg, 0.46 mmol) were dissolved in 5 mL of CH₂Cl₂. After 20.5 h, TLC (6% MeOH in CH₂Cl₂; FeCl₃ stain) showed no remaining starting material (**S2**). The mixture was diluted with CH₂Cl₂ (15 mL) and washed with 10% aq. citric acid (10 mL), brine (5 mL), 10% aq. NaHCO₃ (5 mL), and brine (5 mL), dried over anhydrous MgSO₄,

filtered, and concentrated under reduced pressure. This gave 207.1 mg of a clear, colorless oil that was purified by silica gel column chromatography (1 x 4 in silica gel; 3%–6% MeOH in CH₂Cl₂). Pure product (**S9**) was obtained in 97% yield as a clear, colorless, highly viscous oil (172.7 mg, 0.18 mmol). ¹H-NMR (600 MHz, CDCl₃) δ 7.41–7.31 (m, 20 H), 6.32 (br s, 2 H), 4.85 (s, 2 H), 4.85 (s, 2 H), 4.81 (s, 2 H), 4.48 (s, 2 H), 3.68 (s, 3 H), 3.67–3.61 (m, 6 H), 3.44 (t, *J* = 6.5 Hz, 2 H), 3.40 (s, 2 H), 3.23–3.18 (m, 4 H), 2.80 (br s, 4 H), 2.48 (t, *J* = 6.6 Hz, 4 H), 1.69–1.59 (m, 8 H), 1.53–1.47 (m, 4 H), 1.39–1.33 (m, 4 H), 1.31–1.26 (m, 2 H); ¹³C-NMR (150 MHz, CDCl₃) δ 174.0, 173.8, 172.1, 172.1, 167.9, 167.5, 138.5, 134.4, 133.9, 129.2, 129.1, 129.1, 128.9, 128.8, 128.7, 128.7, 128.6, 128.3, 127.5, 127.4, 76.3, 72.8, 70.1, 52.2, 45.5, 44.9, 44.7, 40.4, 39.3, 39.2, 30.7, 30.5, 29.3, 28.9, 28.4, 28.1, 28.0, 26.7, 26.4, 26.1, 23.7, 23.6, 23.4; HRMS-ESI (*m/z*): [M+Na]⁺ calcd. for C₅₅H₇₃N₅NaO₁₁: 1002.5199, found 1002.5214.

Siderophore methyl ester S10. Benzyl protected siderophore **S9** (60.0 mg, 0.061 mmol) was deprotected according to general procedure **A** to give the siderophore (**S10**) in 92% yield as a white solid (35.0 mg, 0.056 mmol). Mp 126.5–129 °C; ¹H-NMR (600 MHz, CD₃OD) δ 3.71 (s, 3 H), 3.62 (t, *J* = 6.9 Hz, 2 H), 3.61–3.57 (m, 4 H), 3.55 (t, *J* = 6.6 Hz, 2 H), 3.51 (s, 2 H), 3.19–3.15 (m, 4 H), 2.76 (t, *J* = 7.2 Hz, 4 H), 2.48–2.43 (m, 4 H), 1.69–1.60 (m, 6 H), 1.59–1.49 (m, 6 H), 1.40–1.30 (m, 6 H); ¹³C-NMR (150 MHz, CD₃OD) δ 175.1, 174.6, 174.6, 170.0, 169.0, 62.9, 52.8, 52.8, 52.8, 49.0, 48.9, 48.9, 41.2, 40.4, 33.4, 31.6, 31.6, 30.1, 30.0, 29.1, 29.1, 27.7, 27.5, 27.3, 25.0, 24.9, 24.1; HRMS-ESI (*m/z*): [M+Na]⁺ calcd. for C₂₇H₄₉N₅NaO₁₁: 642.3321, found 642.3302.

(±) **Siderophore-Fe(III) complex methyl ester 6c.** Siderophore **S10** (15.0 mg, 0.024 mmol) was complexed to Fe(III) according to general procedure **B** to give the siderophore-Fe(III) complex (**6c**) in 90% yield as an orange powder (14.5 mg, 0.022 mmol). Mp 127–130 °C (dec.); HRMS-ESI (*m/z*): [M+H]⁺ calcd. for C₂₇H₄₇FeN₅O₁₁: 673.2616, found 673.2643; HPLC retention time 3.15 min.

Benzyl protected siderophore methyl ester S11. Benzyl protected siderophore **S5a** (67.0 mg, 0.067 mmol), DMAP (0.8 mg, 0.0067 mmol), and EDC-HCl (25.7 mg, 0.134 mmol) were dissolved in 5 mL of MeOH. After 3 h, TLC (3% MeOH in CH₂Cl₂; FeCl₃ stain) showed no remaining starting material (**S5a**). The MeOH was evaporated under reduced pressure to give the desired product (**S11**) in 52% yield as a clear, viscous oil (35.0 mg, 0.035 mmol) with no need for purification. ¹H-NMR (600 MHz, CDCl₃) δ 7.42–7.24 (m, 20 H), 6.34 (br s, 2 H), 4.85 (s, 2 H), 4.85 (s, 2 H), 4.79 (s, 2 H), 4.48 (s, 2 H), 3.64 (s, 3 H), 3.64–3.58 (m, 4 H), 3.44 (t, *J* = 6.5 Hz, 2 H), 3.22–3.17 (m, 4 H), 2.84–2.76 (m, 4 H), 2.51–2.42 (m, 6 H), 2.35 (t, *J* = 7.2 Hz, 2 H), 1.99–1.89 (m, 4 H), 1.68–1.58 (m, 8 H), 1.53–1.45 (m, 4 H), 1.40–1.33 (m, 2 H), 1.33–1.24 (m, 6 H); ¹³C-NMR (150 MHz, CDCl₃) δ 174.0, 173.8, 173.6, 172.2, 172.1, 138.5, 134.3, 129.3, 129.1, 128.9, 128.6, 128.5, 128.5, 128.2, 128.1, 127.8, 127.7, 127.4, 127.3, 76.2, 75.9, 72.8, 70.1, 51.6, 51.4, 45.5, 45.0, 44.7, 39.3, 39.3, 33.2, 31.2, 30.7, 30.5, 29.3, 29.0, 28.1, 26.6, 26.5, 23.9, 23.6, 23.4, 19.8; HRMS-ESI (*m/z*): [M+H]⁺ calcd. for C₅₇H₇₈N₅O₁₁: 1008.5692, found 1008.5705.

Siderophore methyl ester S12. Benzyl protected siderophore **S11** (22.5 mg, 0.022 mmol) was deprotected according to general procedure **A** to give the siderophore (**S12**) in 99% yield as an off-white solid (14.2 mg, 0.022 mmol). Mp 127–129 °C; ¹H-NMR (500 MHz, CD₃OD) δ 3.66

(s, 3 H), 3.60 (t, $J = 6.7$ Hz, 6 H), 3.55 (t, $J = 6.6$ Hz, 2 H), 3.16 (t, $J = 6.6$ Hz, 4 H), 2.76 (t, $J = 7.1$ Hz, 4 H), 2.52 (t, $J = 7.4$ Hz, 2 H), 2.45 (t, $J = 7.0$ Hz, 4 H), 2.38 (t, $J = 7.3$ Hz, 2 H), 1.92–1.84 (m, 2 H), 1.67–1.59 (m, 6 H), 1.59–1.47 (m, 6 H), 1.41–1.25 (m, 6 H); $^{13}\text{C-NMR}$ (125 MHz, CD_3OD) δ 175.5, 175.2, 175.1, 174.6, 174.5, 62.9, 52.2, 40.4, 34.3, 33.4, 32.5, 31.6, 31.6, 30.1, 30.1, 29.1, 29.0, 27.6, 27.5, 25.1, 25.0, 24.1, 21.3; HRMS-ESI (m/z): $[\text{M}+\text{H}]^+$ calcd. for $\text{C}_{29}\text{H}_{54}\text{N}_5\text{O}_{11}$: 648.3814, found 648.3778.

(\pm) **Siderophore-Fe(III) complex methyl ester 7c**. Siderophore **S12** (7.0 mg, 0.011 mmol) was complexed to Fe(III) according to general procedure **B** to give the siderophore-Fe(III) complex (**7c**) in 87% yield as an orange film (6.6 mg, 0.009 mmol). HRMS-ESI (m/z): $[\text{M}+\text{H}]^+$ calcd. for $\text{C}_{29}\text{H}_{51}\text{FeN}_5\text{O}_{11}$: 701.2929, found 701.2932; HPLC retention time 3.50 min.

Siderophore methyl ester S13. Benzyl protected siderophore **S6a** (31.0 mg, 0.030 mmol) was deprotected according to general procedure **A** to give the siderophore (**S13**) in 99% yield as a white solid (20.0 mg, 0.030 mmol). Mp 130–132 °C; $^1\text{H-NMR}$ (600 MHz, CD_3OD) δ 3.65 (s, 3 H), 3.62–3.57 (m, 6 H), 3.54 (t, $J = 6.6$ Hz, 2 H), 3.16 (t, $J = 6.9$ Hz, 4 H), 2.76 (t, $J = 7.2$ Hz, 4 H), 2.48 (t, $J = 7.0$ Hz, 2 H), 2.45 (t, $J = 6.7$ Hz, 4 H), 2.35 (t, $J = 6.9$ Hz, 2 H), 1.72 (br s, 1 H), 1.67–1.60 (m, 10 H), 1.58–1.50 (m, 6 H), 1.39–1.30 (m, 6 H); $^{13}\text{C-NMR}$ (150 MHz, CD_3OD) δ 175.7, 175.5, 174.9, 174.9, 174.4, 174.4, 62.8, 52.0, 48.8, 40.3, 34.5, 33.3, 32.8, 31.5, 31.5, 30.0, 29.9, 28.9, 28.9, 27.5, 27.3, 27.3, 25.7, 25.4, 24.9, 24.9, 24.0; HRMS-ESI (m/z): $[\text{M}+\text{Na}]^+$ calcd. for $\text{C}_{30}\text{H}_{55}\text{N}_5\text{NaO}_{11}$: 684.3790, found 684.3773.

(\pm) **Siderophore-Fe(III) complex methyl ester 8c**. Siderophore **S13** (4.0 mg, 0.006 mmol) was complexed to Fe(III) according to general procedure **B** to give the siderophore-Fe(III) complex (**8c**) in 95% yield as an orange powder (4.1 mg, 0.006 mmol). Mp 114–118 °C (dec.); HRMS-ESI (m/z): $[\text{M}+\text{H}]^+$ calcd. for $\text{C}_{30}\text{H}_{53}\text{FeN}_5\text{O}_{11}$: 715.3086, found 715.3114; HPLC retention time 3.92 min.

Desferridanoxamine macrolactone (4). Danoxamine macrolactone **5b** (9.5 mg, 0.0145 mmol) was dissolved in 5 mL of 0.53 M aq. Na-EDTA (2.65 mmol Na-EDTA). After 15 h, the solution had turned from clear orange to clear and colorless. The desferrisiderophore was extracted into a 1:1 phenol: CHCl_3 mixture (2 x 30 mL). The phenol: CHCl_3 was then diluted with Et_2O (360 mL) and the desferrisiderophore was extracted back into H_2O (3 x 100 mL). The H_2O was evaporated using high vacuum rotary evaporation to give the pure desferridanoxamine macrolactone **4** in 95% yield as a clear, colorless film (8.3 mg, 0.014 mmol). $^1\text{H-NMR}$ (500 MHz, CD_3OD) δ 4.08 (t, $J = 6.1$ Hz, 2 H), 3.61 (t, $J = 6.3$ Hz, 6 H), 3.17 (t, $J = 6.2$ Hz, 4 H), 2.78 (t, $J = 6.3$ Hz, 6 H), 2.57 (t, $J = 6.5$ Hz, 2 H), 2.47 (t, $J = 6.8$ Hz, 4 H), 1.71–1.57 (m, 8 H), 1.56–1.47 (m, 4 H), 1.43–1.26 (m, 6 H); $^{13}\text{C-NMR}$ (125 MHz, CD_3OD) δ 175.1, 174.9, 174.6, 174.6, 174.4, 65.7, 49.4, 48.9, 48.7, 40.3, 40.2, 31.8, 31.7, 30.0, 29.9, 29.8, 29.5, 29.2, 29.1, 28.6, 27.4, 27.3, 27.3, 24.8, 24.6, 24.1; HRMS-ESI (m/z): $[\text{M}+\text{H}]^+$ calcd. for $\text{C}_{27}\text{H}_{48}\text{N}_5\text{O}_{10}$: 602.3396, found 602.3393.

(\pm) **Danoxamine macrolactone (5b)**. Danoxamine (**5a**; 75.0 mg, 0.11 mmol), 2,4,6-trichlorobenzoyl chloride (51.6 μL , 0.33 mmol), $i\text{Pr}_2\text{EtN}$ (115.0 μL , 0.66 mmol), and catalytic DMAP (6.8 mg, 0.056 mmol) were dissolved in 23 mL of anhydrous DMF (0.005 M with respect to **5a**). After 144 h, HPLC (visible detection at 427 nm) showed the desired macrolactone to be the major siderophore-containing reaction component. The reaction was

quenched with H₂O (10 mL) and the DMF/H₂O were removed using high vacuum rotary evaporation. The resulting orange film was partitioned between H₂O (75 mL) and Et₂O (50 mL). The layers were separated and the H₂O was washed with Et₂O (2 x 50 mL) and concentrated to give 72 mg of an orange film. This material was purified by semi-preparative HPLC using 0.1 mM ammonium acetate H₂O (A) and CH₃CN (B) as eluent. A gradient was formed from 95%-20% of A in 10 min, then 20%-5% of A in 2 min, then 5%-95% of A in 3 min (total run time = 15 min). Pure fractions were concentrated to provided danoxamine macrolactone **5b** in 53% yield (39.0 mg, 0.060 mmol). X-ray quality crystals were grown from MeOH/Et₂O at -20 °C. An X-ray structure was obtained by Dr. Allen Oliver (UND) at the Advanced Light Source Beamline at Lawrence Berkeley National Lab as described in section **XII** of this Supporting Information. HRMS-ESI (m/z): [M+Na]⁺ calcd. for C₂₇H₄₄FeN₅NaO₁₀: 677.2330, found 677.2373; HPLC retention time 3.67 min.

Optimization of Yamaguchi conditions for the macrolactonization of danoxamine (Table 1; Entries 1-4). All reactions were performed in anhydrous DMF using 5 mg of danoxamine (**5a**) at a concentration of 0.005 M and 0.5 equivalent of DMAP. Varying amounts of the Yamaguchi reagent (2,4,6-trichlorobenzoyl chloride) and *i*Pr₂EtN were included along with varying reaction temperatures, as indicated in Table 1, Entries 1-4. Relative percent compositions were determined after 72 h by quenching the reaction mixture with MeOH. The quenched mixture was analyzed by HPLC and/or LC-MS with visible detection at 427 nm, the λ_{max} for 1:1 trihydroxamate siderophore:Fe(III) complexes, to identify and quantify all reaction components (**5a-5e**) as shown in Table 1.

Scope of Yamaguchi macrolactonization conditions. Syntheses of ferric siderophore macrolactones 5b-8b (Table 1; Entries 5-8). All reactions were performed in anhydrous DMF using 1 mg of siderophore-Fe(III) hydroxy acid (**5a-8a**) at a concentration of 0.005 M with 3.0 equivalents of 2,4,6-trichlorobenzoyl chloride, 6.0 equivalents of *i*Pr₂EtN, and 0.5 equivalent of DMAP added from stock solutions. Relative percent compositions were determined after 72 h by quenching the reaction mixture with MeOH and analyzing by HPLC with visible detection at 427 nm, the λ_{max} for 1:1 trihydroxamate siderophore:Fe(III) complexes. Some reaction mixtures were heated to 50 °C to ensure complete solubilization of the siderophore, as indicated in Table 1. The identity of the siderophore macrolactones (**5b-8b**) was confirmed by HRMS, LC-MS, and analytical HPLC. **6b, n=1.** HRMS-ESI (m/z): [M+H]⁺ calcd. for C₂₆H₄₃FeN₅O₁₀: 641.2354, found 641.2326; HPLC retention time 3.37 min. **5b, n=2.** HRMS-ESI (m/z): [M+Na]⁺ calcd. for C₂₇H₄₄FeN₅NaO₁₀: 677.2330, found 677.2373; HPLC retention time 3.67 min. **7b, n=3.** HRMS-ESI (m/z): [M+H]⁺ calcd. for C₂₈H₄₇FeN₅O₁₀: 669.2667, found 669.2657; HPLC retention time 3.20 min. **8b, n=4.** HRMS-ESI (m/z): [M+H]⁺ calcd. for C₂₉H₄₉FeN₅O₁₀: 683.2823, found 683.2781; HPLC retention time 4.00 min.

Hydrolysis of siderophore-Fe(III) complex methyl esters (5c-8c) to acids (5a-8a). All reactions were performed in H₂O buffered to pH 10 (K₂CO₃, K₃BO₃, KOH; Fisher) at 22 °C with a siderophore-Fe(III) complex methyl ester (**5c-8c**) concentration of 0.5 mM. Reaction half-lives (t_{1/2}) and R² values were derived from linear first order kinetic plots (ln[siderophore-Fe(III) methyl ester] versus time) generated by integrating the siderophore ester and acid peak areas of HPLC chromatograms collected at various time points with visible detection at 427 nm, the λ_{max} for 1:1 trihydroxamate siderophore:Fe(III) complexes.

IV. HPLC Chromatograms of Reactions from Table 1

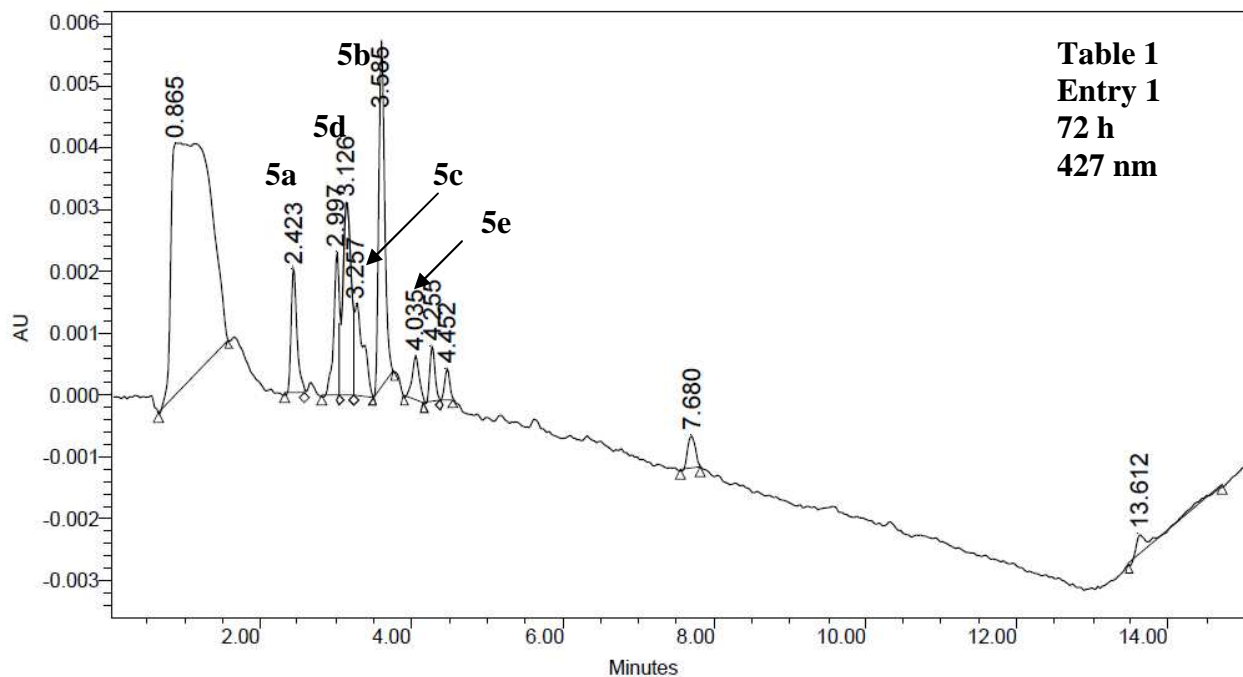


Figure S1. HPLC chromatogram of substrate **5a** macrolactonization reaction mixture at 72 h after MeOH quench using conditions specified in Table 1, Entry 1 of main text.

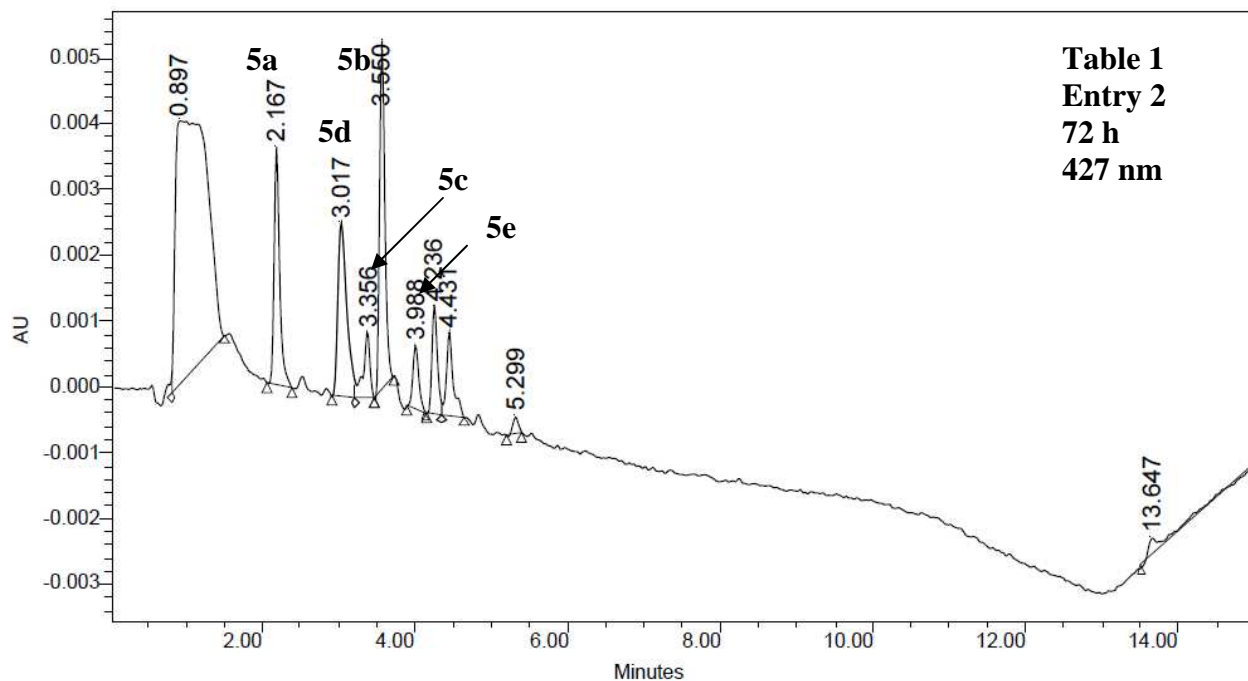


Figure S2. HPLC chromatogram of substrate **5a** macrolactonization reaction mixture at 72 h after MeOH quench using conditions specified in Table 1, Entry 2 of main text.

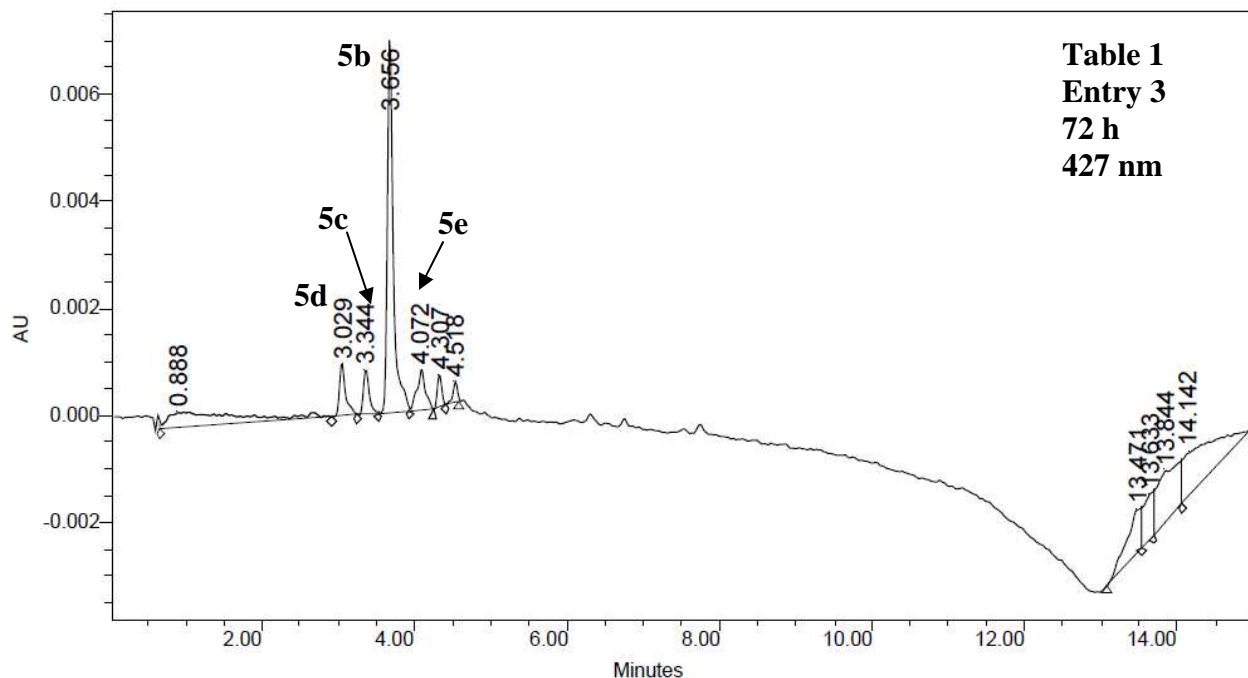


Figure S3. HPLC chromatogram of substrate **5a** macrolactonization reaction mixture at 72 h after MeOH quench using conditions specified in Table 1, Entry 3 of main text.

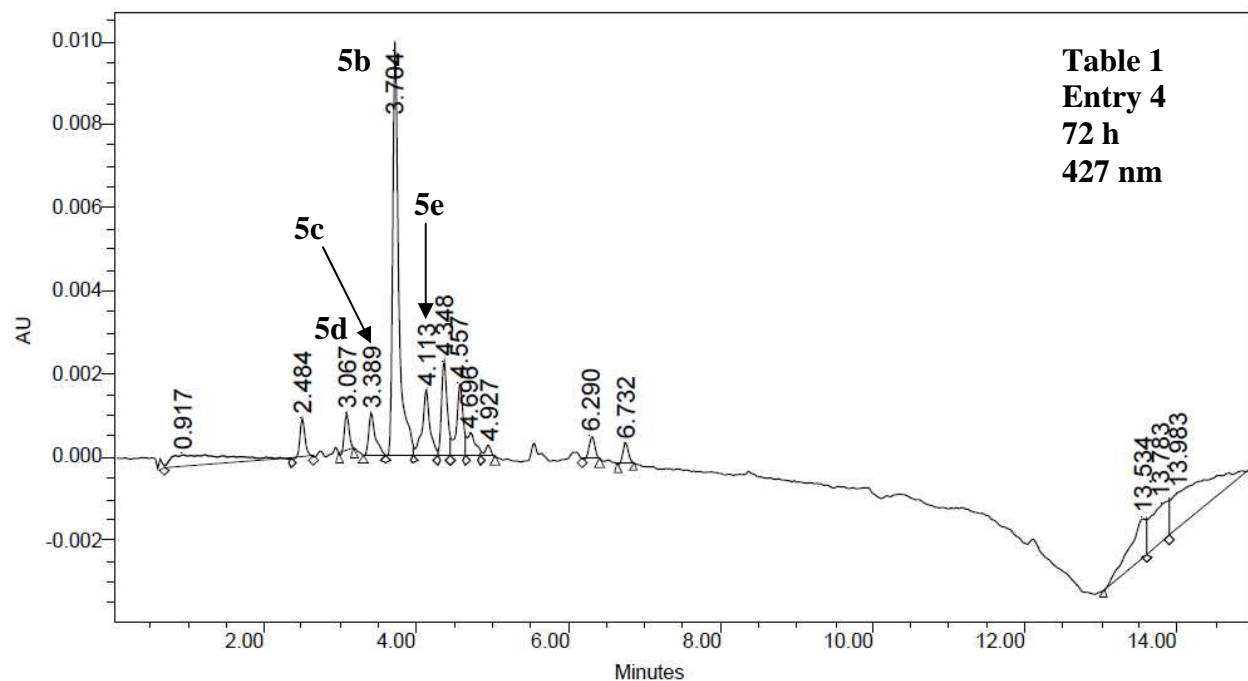


Figure S4. HPLC chromatogram of substrate **5a** macrolactonization reaction mixture at 72 h after MeOH quench using conditions specified in Table 1, Entry 4 of main text.

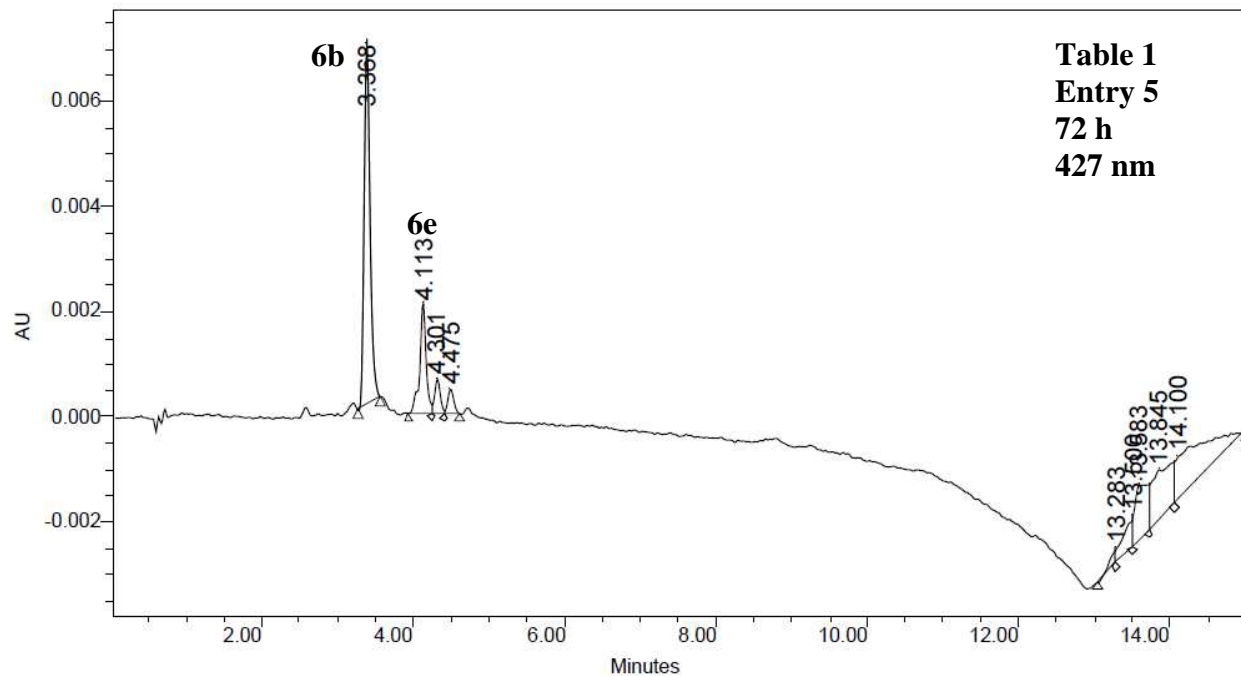


Figure S5. HPLC chromatogram of substrate **6a** macrolactonization reaction mixture at 72 h after MeOH quench using conditions specified in Table 1, Entry 5 of main text.

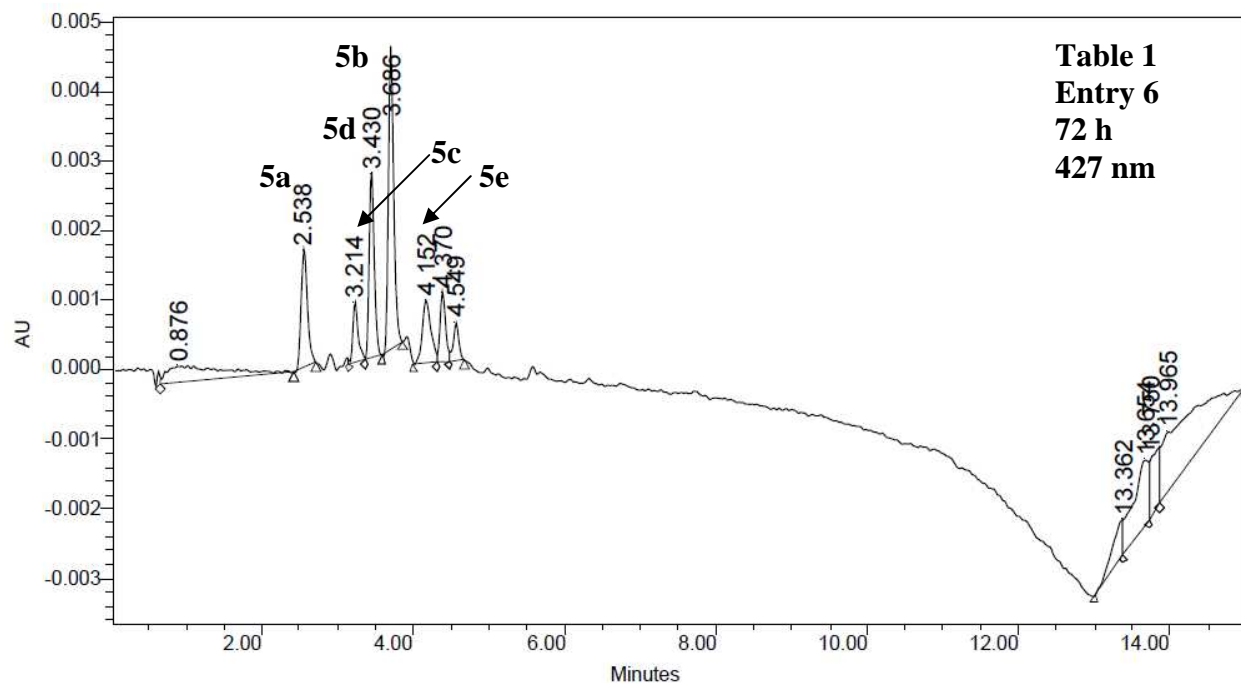


Figure S6. HPLC chromatogram of substrate **5a** macrolactonization reaction mixture at 72 h after MeOH quench using conditions specified in Table 1, Entry 6 of main text.

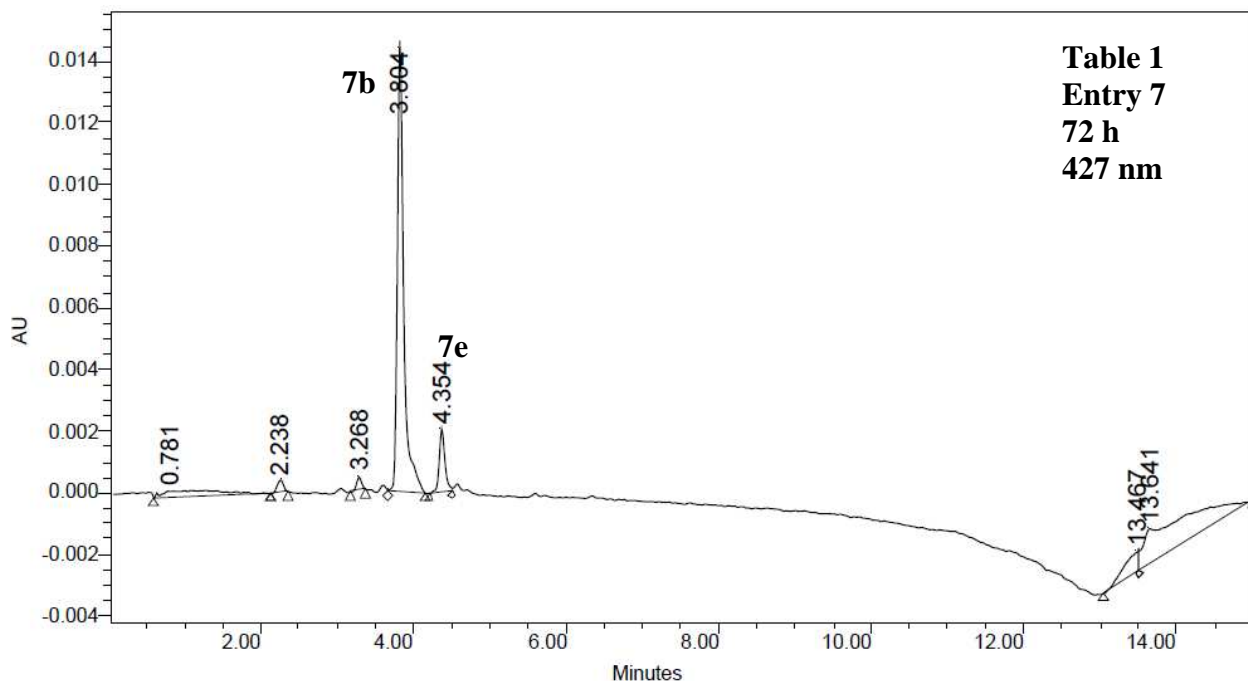


Figure S7. HPLC chromatogram of substrate **7a** macrolactonization reaction mixture at 72 h after MeOH quench using conditions specified in Table 1, Entry 7 of main text.

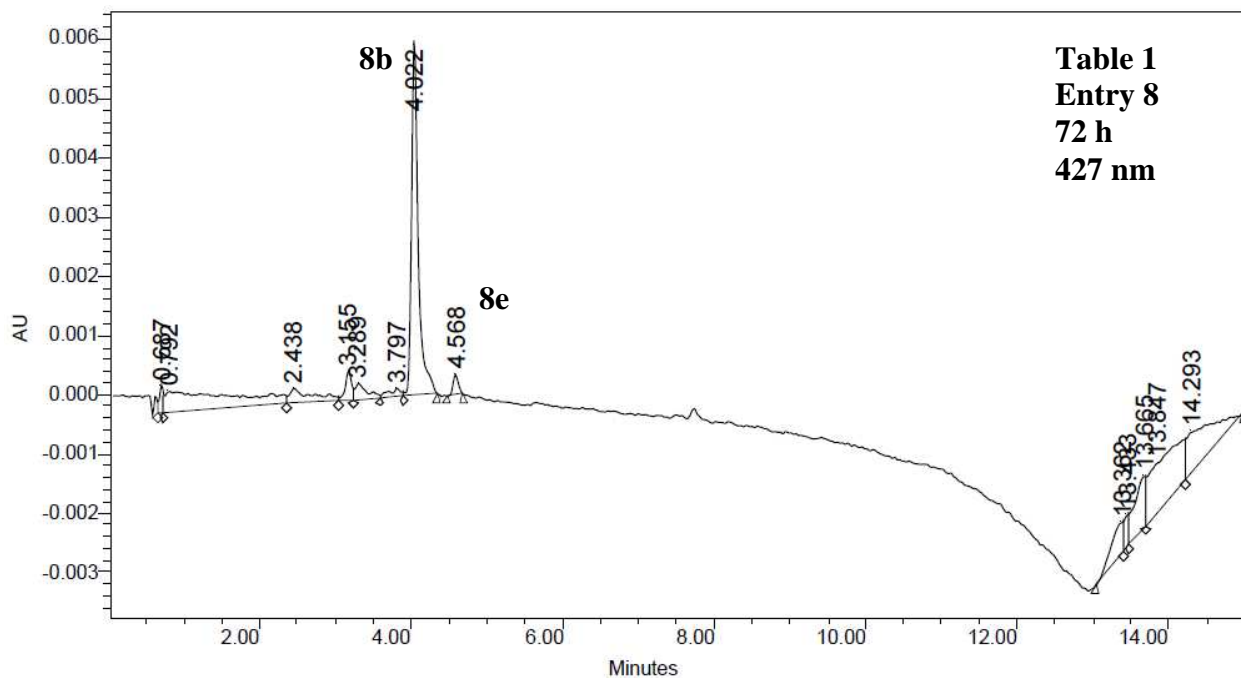


Figure S8. HPLC chromatogram of substrate **8a** macrolactonization reaction mixture at 72 h after MeOH quench using conditions specified in Table 1, Entry 8 of main text.

V. Graph of % Macrolactone 5b vs Time for Reactions in Table 1, Entries 1-4

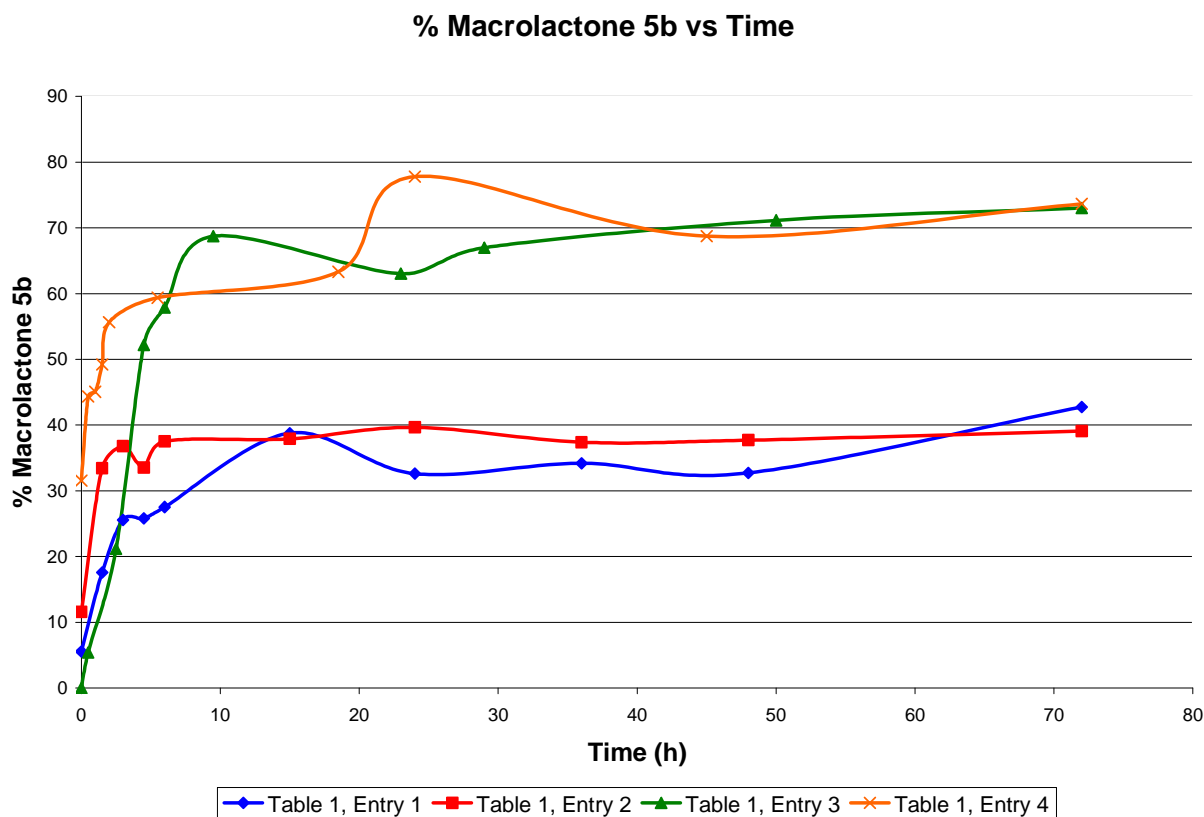


Figure S9. Graph of percent macrolactone **5b** vs time for reactions described in Table 1, Entries 1-4 from the main text. See Table S1 below for raw HPLC data used to calculate relative percent compositions.

Table S1. Peak heights and relative % compositions of 5a-5e for reactions in Table 1, Entries 1-4.					
Table 1, Entry 1 ^a					
Time (h) ^b	5a Height ^c	5b Height	5c Height	5d Height	5e Height
0	14619	1413	4505	4592	293
1.5	4002	1975	1779	3087	390
3	6478	4493	2798	2780	1027
4.5	3719	3285	1501	3544	682
6	3910	4022	1685	4223	770
15	3335	6189	1055	4662	722
24	1890	4087	1816	4116	627
36	1416	4383	2368	3859	792
48	1513	4392	2585	4127	804
72	2041	5562	1515	3179	708
Time (h)	% 5a ^d	% 5b	% 5c	% 5d	% 5e
0	57.5053104	5.558177956	17.72087169	18.06309496	1.15254504
1.5	35.6271699	17.5821241	15.8372652	27.48152764	3.471913113
3	36.8570778	25.56326809	15.91943559	15.81702321	5.843195266
4.5	29.2121593	25.80315765	11.79011861	27.83756186	5.357002592

6	26.7624914	27.52908966	11.53319644	28.90485969	5.270362765
15	20.8920629	38.77090772	6.60903339	29.20503665	4.522959343
24	15.0765795	32.60210593	14.48627951	32.83343969	5.001595405
36	11.0469652	34.19410204	18.47402091	30.1061008	6.178811047
48	11.2733775	32.72483422	19.26085985	30.75031667	5.990611728
72	15.6939639	42.76816609	11.64936563	24.44444444	5.444059977

Table 1, Entry 2

Time (h)	5a Height	5b Height	5c Height	5d Height	5e Height
0	7809	2011	4631	1964	947
1.5	1863	4116	2543	2877	916
3	1707	4054	1917	2515	818
4.5	1583	3471	1973	2517	804
6	2215	4651	2308	2213	1005
15	1782	3936	1984	1938	746
24	1998	4029	1535	1825	774
36	3516	5492	1325	3200	1151
48	3381	5775	1824	3163	1177
72	3550	5237	1004	2650	956

Time (h)	% 5a	% 5b	% 5c	% 5d	% 5e
0	44.9775372	11.58276696	26.67319433	11.31206082	5.454440733
1.5	15.1278928	33.4226553	20.64961429	23.36175396	7.438083638
3	15.5026791	36.81772773	17.40986286	22.84079557	7.428934702
4.5	15.2976421	33.54271357	19.06648628	24.32354078	7.769617317
6	17.8744351	37.53227889	18.6249193	17.85829567	8.110071014
15	17.1577123	37.89716927	19.10263817	18.65973426	7.182746004
24	19.663419	39.65160909	15.10678083	17.96083063	7.617360496
36	23.9444293	37.40125306	9.023426859	21.79242713	7.838463634
48	22.0691906	37.69582245	11.90600522	20.6462141	7.682767624
72	26.4984698	39.09084123	7.494215123	19.78054788	7.135925954

Table 1, Entry 3

Time (h)	5a Height	5b Height	5c Height	5d Height	5e Height
0	7325	0	8686	537	280
0.5	6285	771	5824	859	487
2.5	2890	3213	6144	1628	1301
4.5	1172	7484	2362	1602	1719
6	327	6044	1166	1151	1752
9.5	0	6572	1318	1238	431
23	0	6981	1416	1224	1455
29	0	6117	703	1100	1210
50	0	6964	984	834	1006
72	0	6927	827	979	754

Time (h)	% 5a	% 5b	% 5c	% 5d	% 5e
0	43.5286427	0	51.6163537	3.191110055	1.663893511
0.5	44.179671	5.419654154	40.93912554	6.038239843	3.423309433
2.5	19.0432261	21.17158672	40.48497628	10.72746442	8.572746442
4.5	8.1735128	52.19331892	16.47255736	11.17232722	11.9882837
6	3.13218391	57.89272031	11.16858238	11.02490421	16.7816092
9.5	0	68.7519615	13.78805314	12.95114552	4.508839837
23	0	63.02816901	12.7843987	11.05092091	13.13651138
29	0	66.99890471	7.699890471	12.04819277	13.25301205

50	0	71.14834491	10.05312628	8.520637515	10.2778913
72	0	73.0157057	8.717191947	10.31938442	7.94771793

Table 1, Entry 4

Time (h)	5a Height	5b Height	5c Height	5d Height	5e Height
0	3083	5991	5660	1051	3206
0.5	0	5813	3629	896	2767
1	0	6745	4004	1016	3202
1.5	0	5283	2447	814	2192
2	0	4714	1684	627	1446
5.5	0	5955	2445	589	1041
18.5	0	6879	2198	655	1132
24	0	6588	582	419	879
45	0	6740	1378	639	1047
72	0	9818	1018	918	1575
Time (h)	% 5a	% 5b	% 5c	% 5d	% 5e
0	16.2340056	31.54652204	29.80359117	5.534200411	16.8816808
0.5	0	44.3571156	27.69172072	6.837085082	21.1140786
1	0	45.06581145	26.75218815	6.788267522	21.39373288
1.5	0	49.20827124	22.79247392	7.581967213	20.41728763
2	0	55.64868374	19.87958919	7.401723527	17.07000354
5.5	0	59.37188435	24.37686939	5.872382851	10.37886341
18.5	0	63.31921944	20.23195876	6.029086892	10.4197349
24	0	77.79877185	6.872933396	4.948039679	10.38025508
45	0	68.74745002	14.05548756	6.517747858	10.67931457
72	0	73.65893916	7.637482182	6.887238352	11.81634031

^aAll data values in this table were generated from HPLC chromatograms of macrolactonization reaction mixtures described in Table 1 of the main text. ^bTime points refer to the exact time of quenching the reaction mixture with MeOH. ^cHeight refers to the peak height of the reaction components when monitored at 427 nm. ^dRelative percent compositions were determined for all siderophore components using the peak heights at 427 nm, which is the wavelength of max absorbance for trihydroxamate siderophore-Fe(III) complexes.

Table S1. Peak heights and relative percent compositions determined from HPLC chromatograms monitored at 427 nm for macrolactonization reactions at various time points using conditions indicated in Table 1, Entries 1-4 from the main text.

VI. Graph of Relative % Products vs Time for Reaction in Table 1, Entry 3

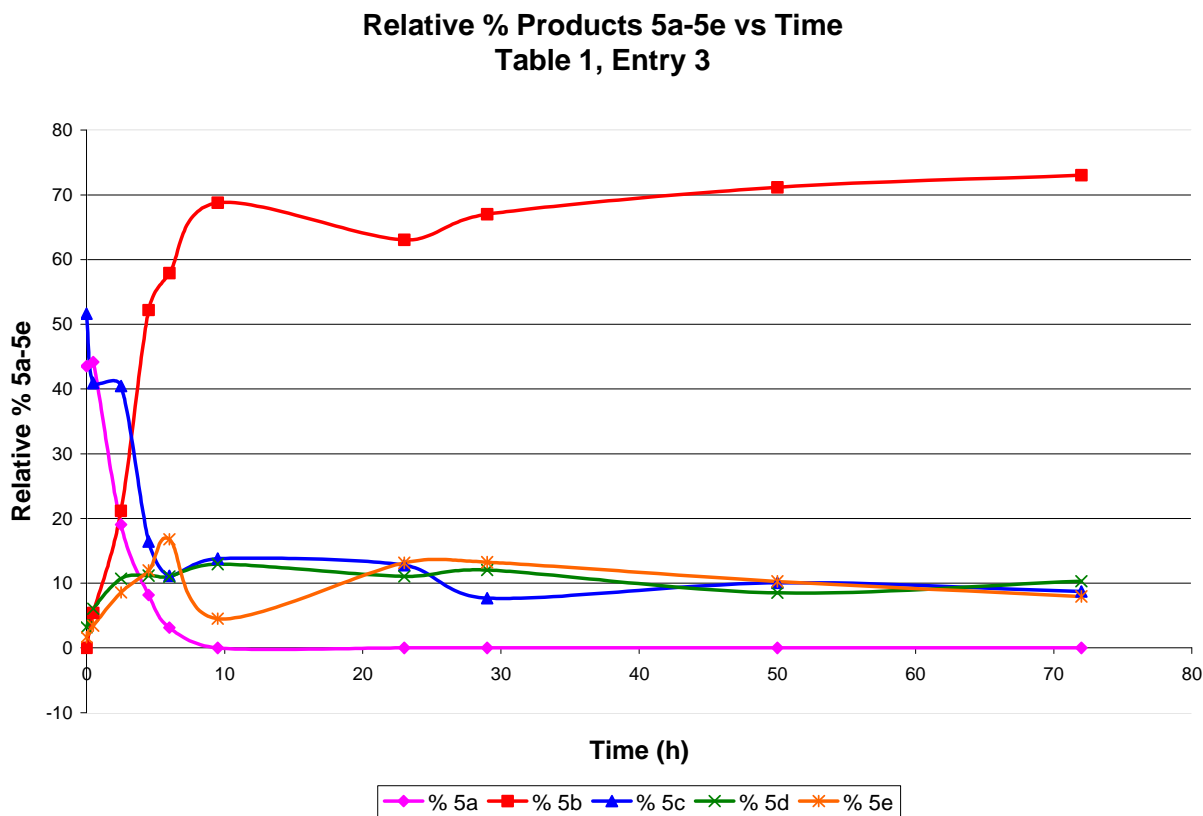


Figure S10. Graph of relative percent products **5a-5e** vs time for the macrolactonization reaction described in Table 1, Entries 3 from the main text. See Table S1 above for raw HPLC data used to calculate relative percent compositions.

VII. HPLC Chromatograms from Synthesis and Purification of **5b**

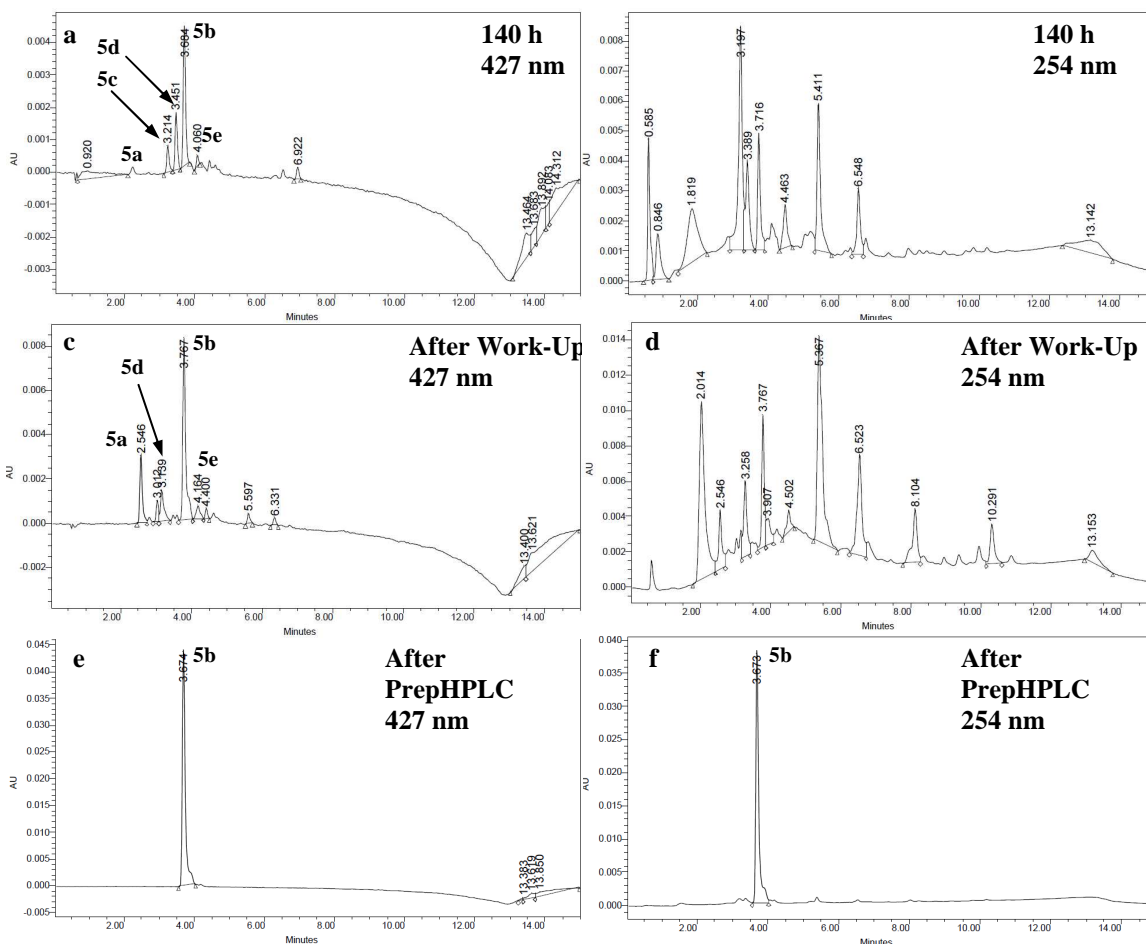


Figure S11. HPLC chromatograms monitored at 427 nm and 254 nm of a scaled-up macrolactonization reaction of siderophore-Fe(III) complex **5b** taken at (a) 140 h after a MeOH quench, (b) after an aqueous work-up and washing with Et₂O, (c) after purification by preparative HPLC. See experimental description in section II for compound **5b** to get exact experimental details for the aqueous work-up and preparative HPLC purification.

VIII. HPLC Chromatograms from Hydrolyses of Siderophore Methyl Esters

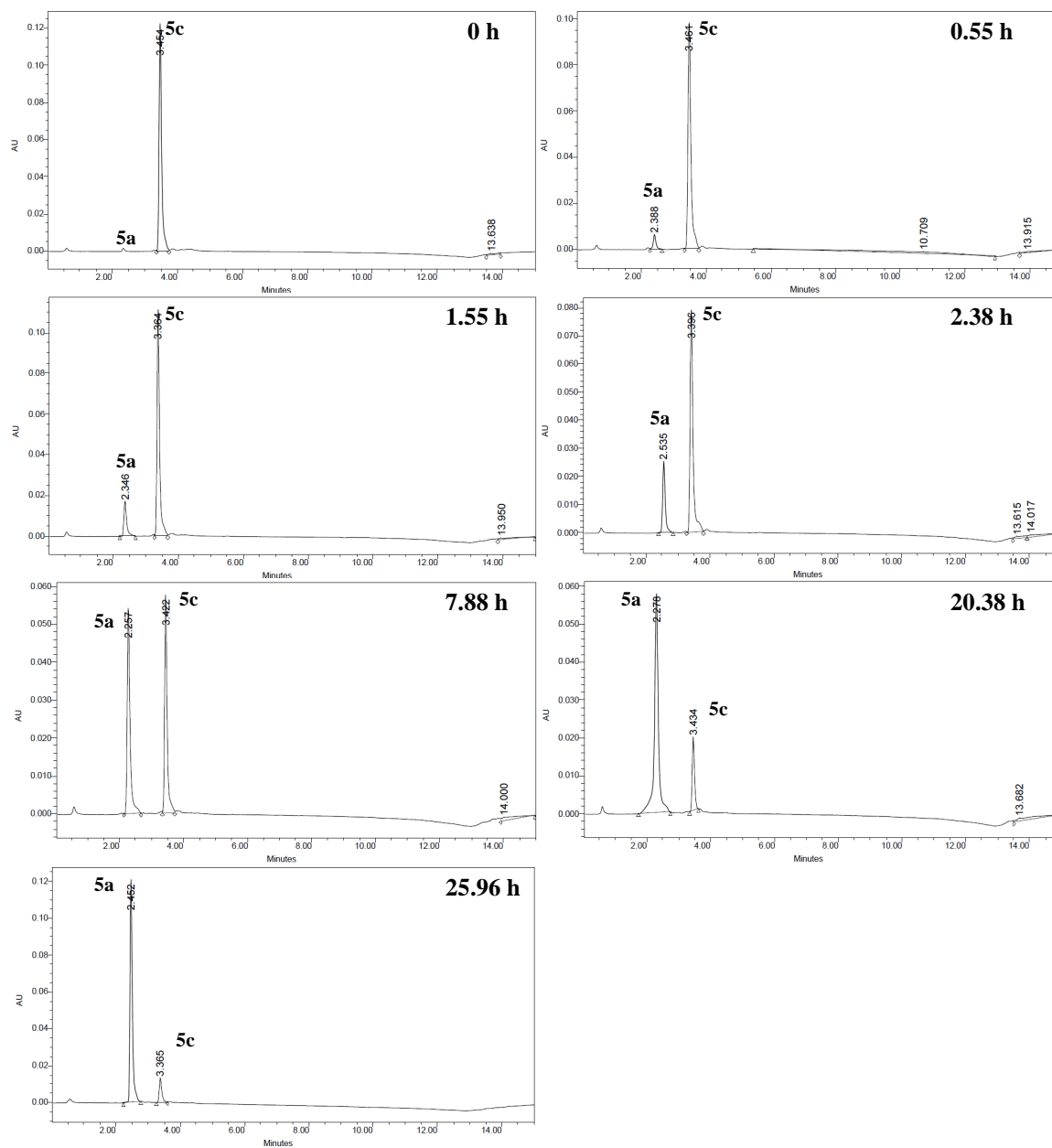


Figure S12. HPLC chromatograms (427 nm; pH 10) for hydrolysis of methyl ester **5c** to acid **5a**.

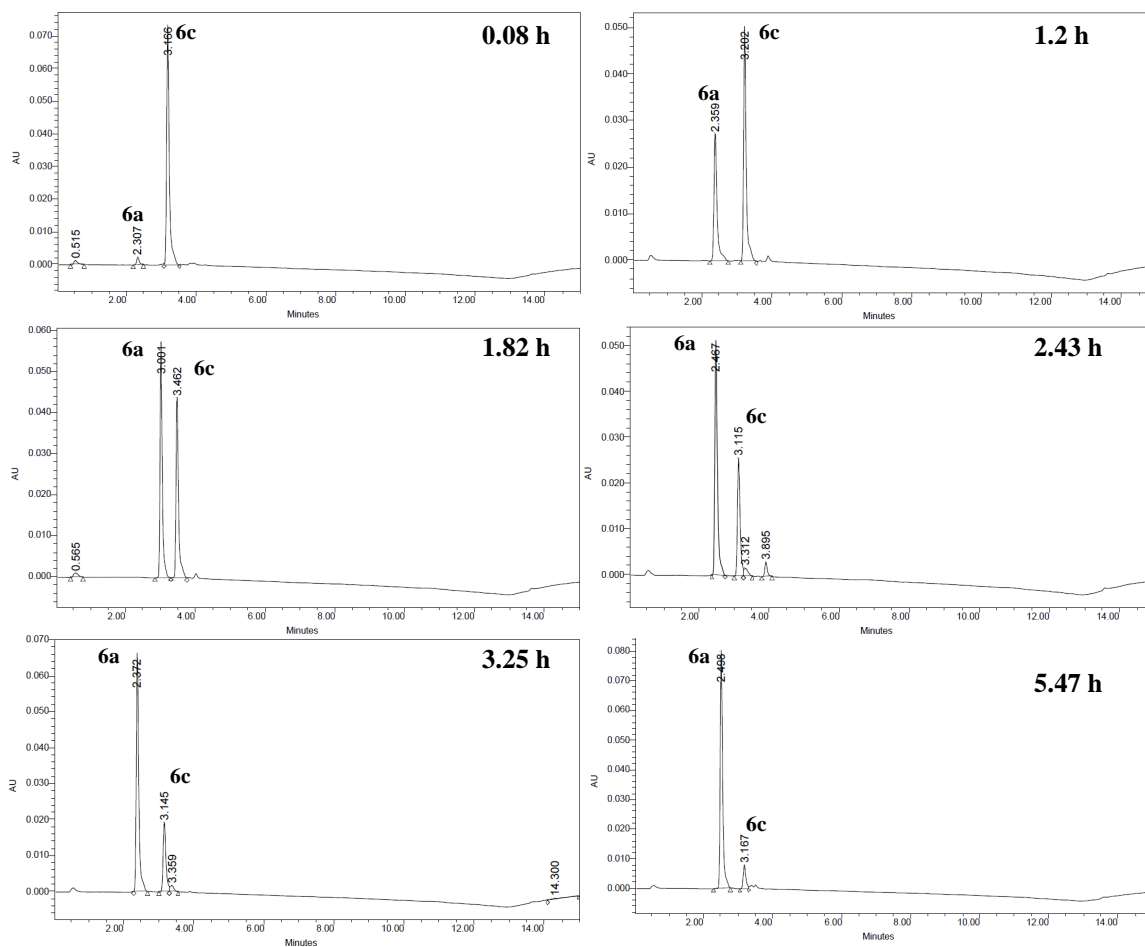


Figure S13. HPLC chromatograms (427 nm; pH 10) for hydrolysis of methyl ester **6c** to acid **6a**.

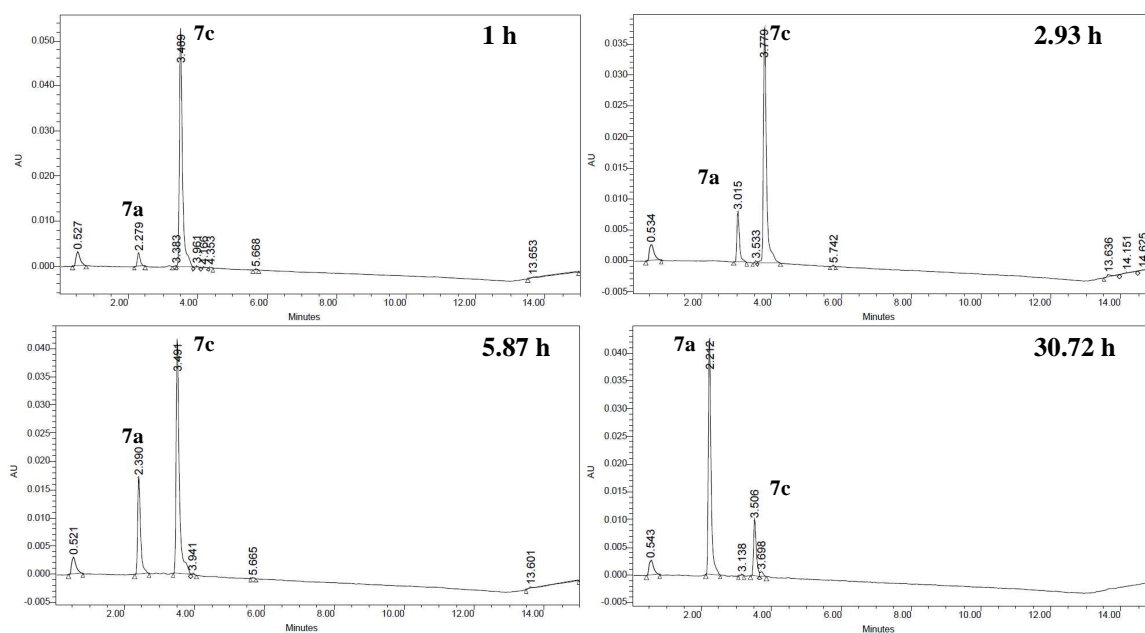


Figure S14. HPLC chromatograms (427 nm; pH 10) for hydrolysis of methyl ester **7c** to acid **7a**.

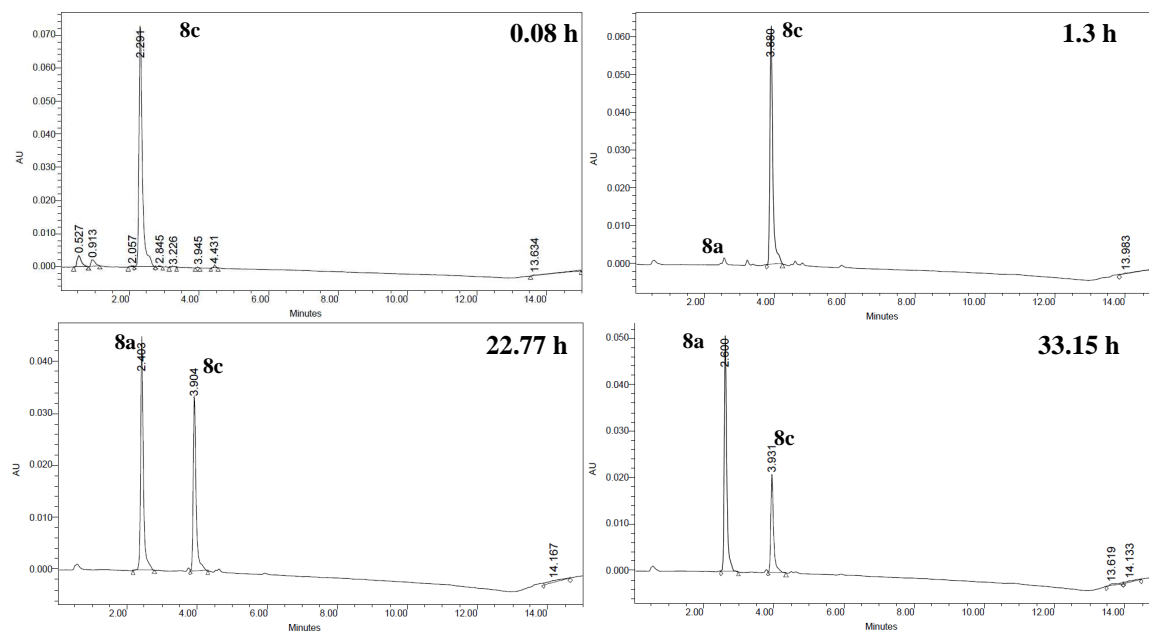


Figure S15. HPLC chromatograms (427 nm; pH 10) for hydrolysis of methyl ester **8c** to acid **8a**.

IX. 1st Order Rate Plots for Methyl Ester Hydrolyses

Hydrolysis of Siderophore Methyl Ester 5c to Acid 5a at pH 10						
Time (h)	5c Peak Area	5a Peak Area	% 5c	% 5a	ln[%Ester]	5c Half Life
0	679116	13859	98	1.9999	4.584968	8.1 h
0.55	635431	40271	94.04	5.9599	4.543722	
1.55	606423	105983	85.123	14.877	4.4441	
2.38	506217	140949	78.221	21.779	4.359533	
7.88	319497	340131	48.436	51.564	3.880242	
20.38	101138	505512	16.672	83.328	2.813704	
25.96	76582	617202	11.038	88.962	2.401372	

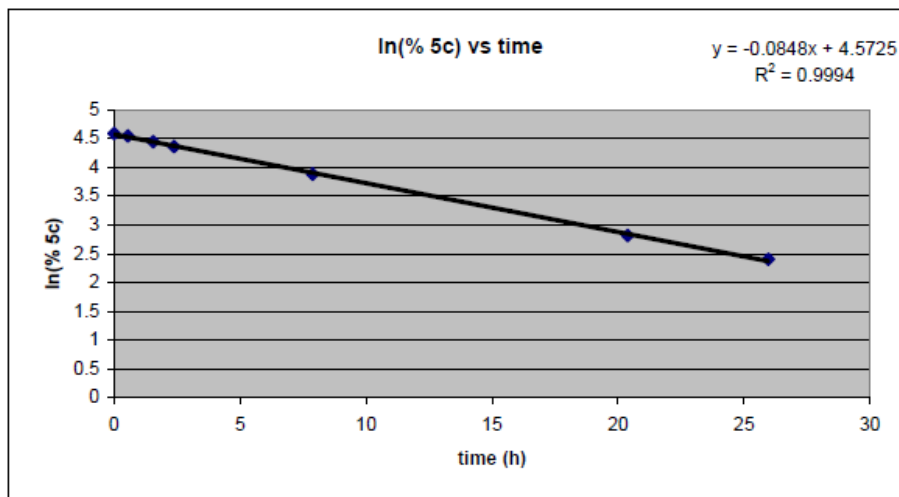


Figure S16. First order kinetic plot for hydrolysis of methyl ester **5c** to acid **5a** at pH 10.

Hydrolysis of Siderophore Methyl Ester 6c to Acid 6a at pH 10						
Time (h)	6c Peak Area	6a Peak Area	% 6c	% 6a	ln[%6c]	6c Half Life
0.08	382913	12112	96.93386	3.066135	4.574029	1.6 h
1.2	258034	169184	60.39867	39.60133	4.100967	
1.82	225297	258521	46.56648	53.43352	3.840881	
2.43	136762	264927	34.04674	65.95326	3.527734	
3.25	108870	333914	24.58761	75.41239	3.202243	
5.47	43643	393772	9.977481	90.02252	2.300331	

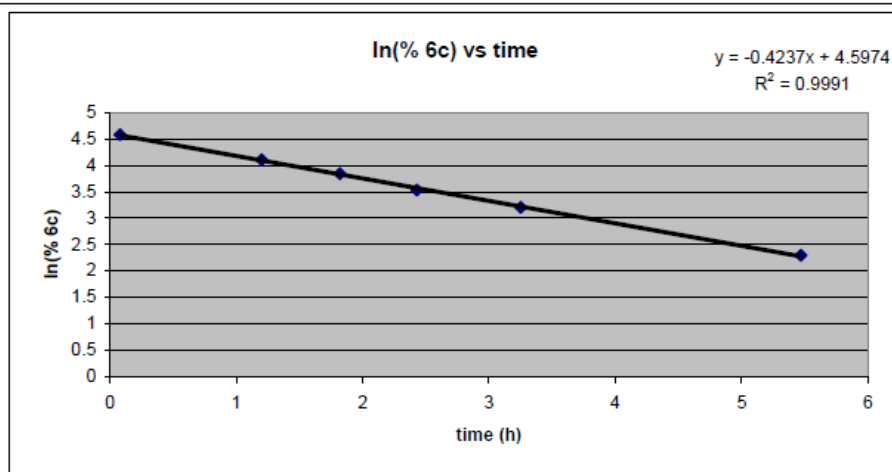


Figure S17. First order kinetic plot for hydrolysis of methyl ester **6c** to acid **6a** at pH 10.

Hydrolysis of Siderophore Methyl Ester 7c to Acid 7a at pH 10						
Time (h)	7c Peak Area	7a Peak Area	% 7c	% 7a	ln[%7c]	7c Half Life
1	322777	17980	94.72351	5.276487	4.550962	13 h
2.93	233448	41956	84.76565	15.23435	4.43989	
5.87	263078	100929	72.27279	27.72721	4.280448	
30.72	55603	233971	19.20165	80.79835	2.954996	

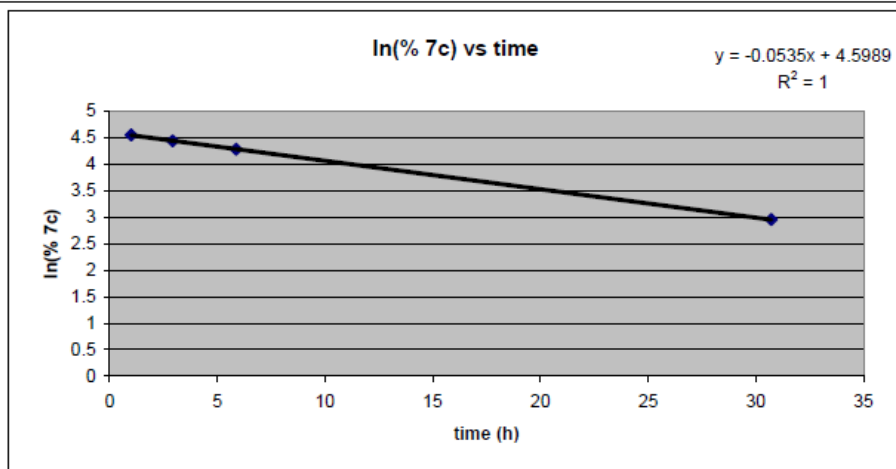


Figure S18. First order kinetic plot for hydrolysis of methyl ester 7c to acid 7a at pH 10.

Hydrolysis of Siderophore Methyl Ester 8c to Acid 8a at pH 10						
Time (h)	8c Peak Area	8a Peak Area	% 8c	% 8a	ln[%Ester] 8c	8c Half Life
0.08	358378	0	100	0	4.60517	19.9 h
1.3	366570	7481	98.00001	1.999995	4.584968	
1.97	324903	24796	92.90933	7.090669	4.531624	
3.33	352045	51342	87.27227	12.72773	4.469033	
5.55	321419	78084	80.45471	19.54529	4.387694	
8.95	280856	115247	70.90479	29.09521	4.261338	
22.77	193760	243483	44.31403	55.68597	3.791301	
33.15	118944	256325	31.69566	68.30434	3.45618	

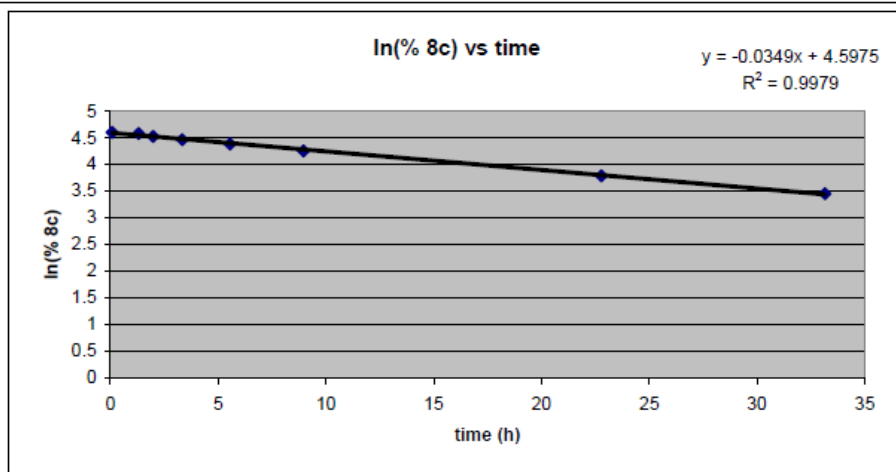
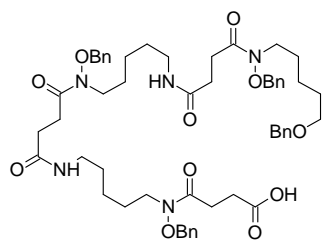
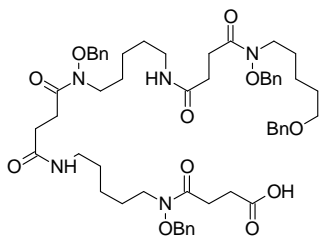
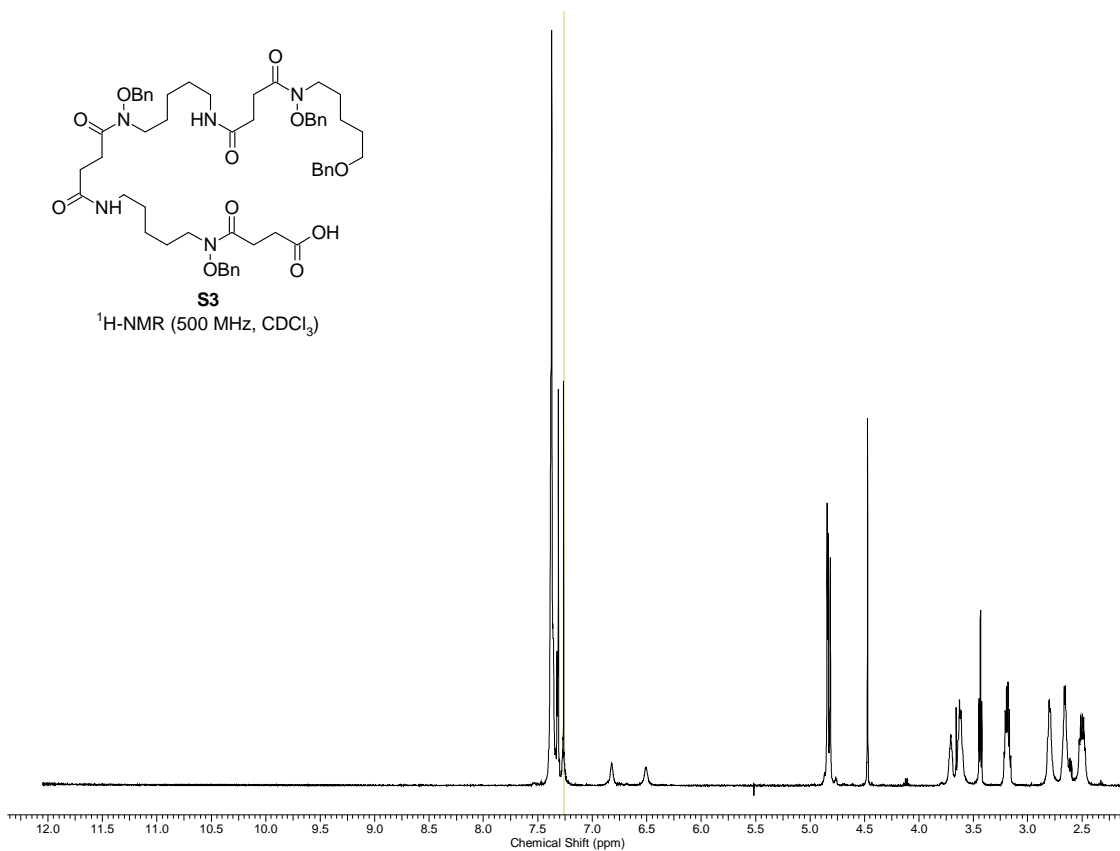


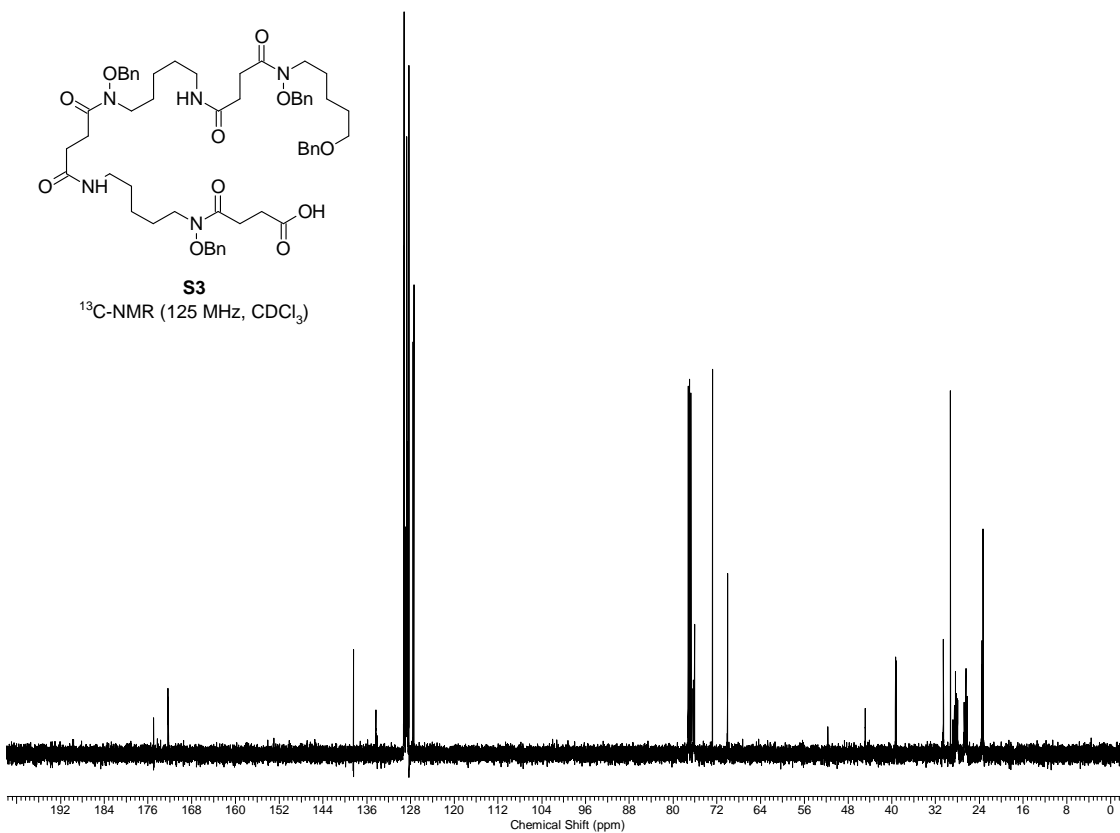
Figure S19. First order kinetic plot for hydrolysis of methyl ester 8c to acid 8a at pH 10.

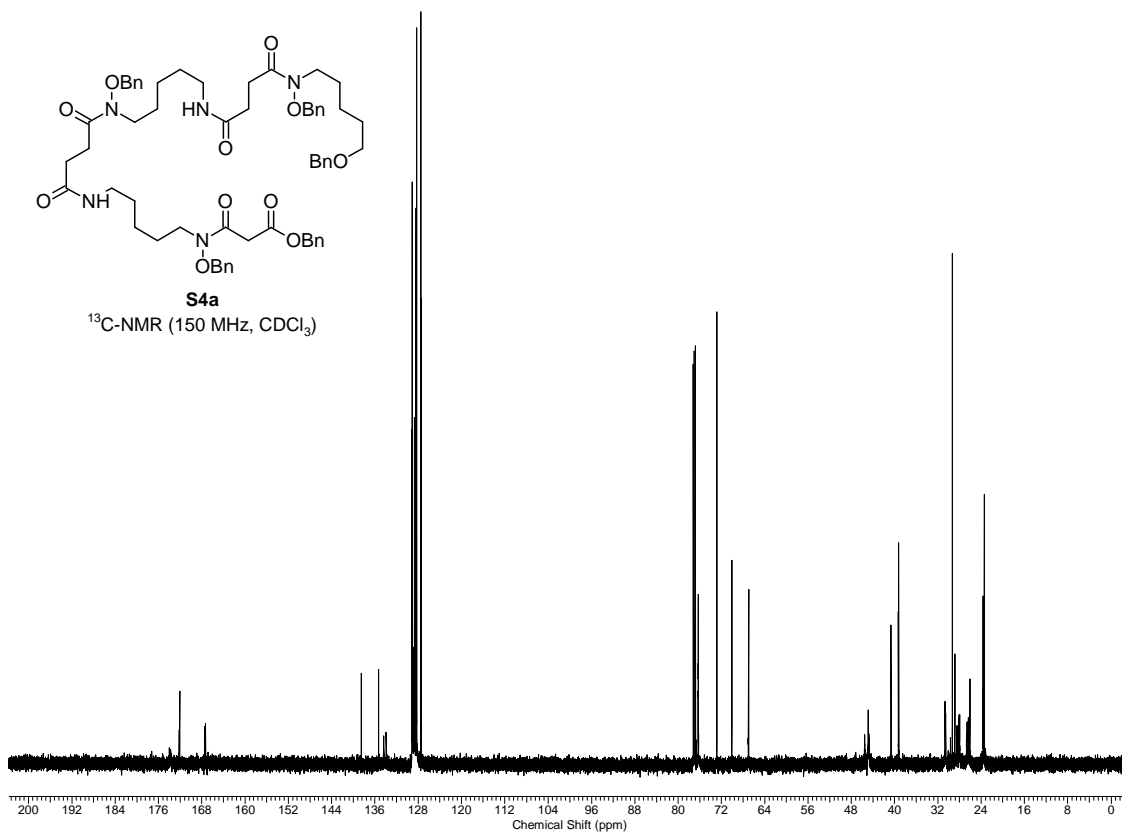
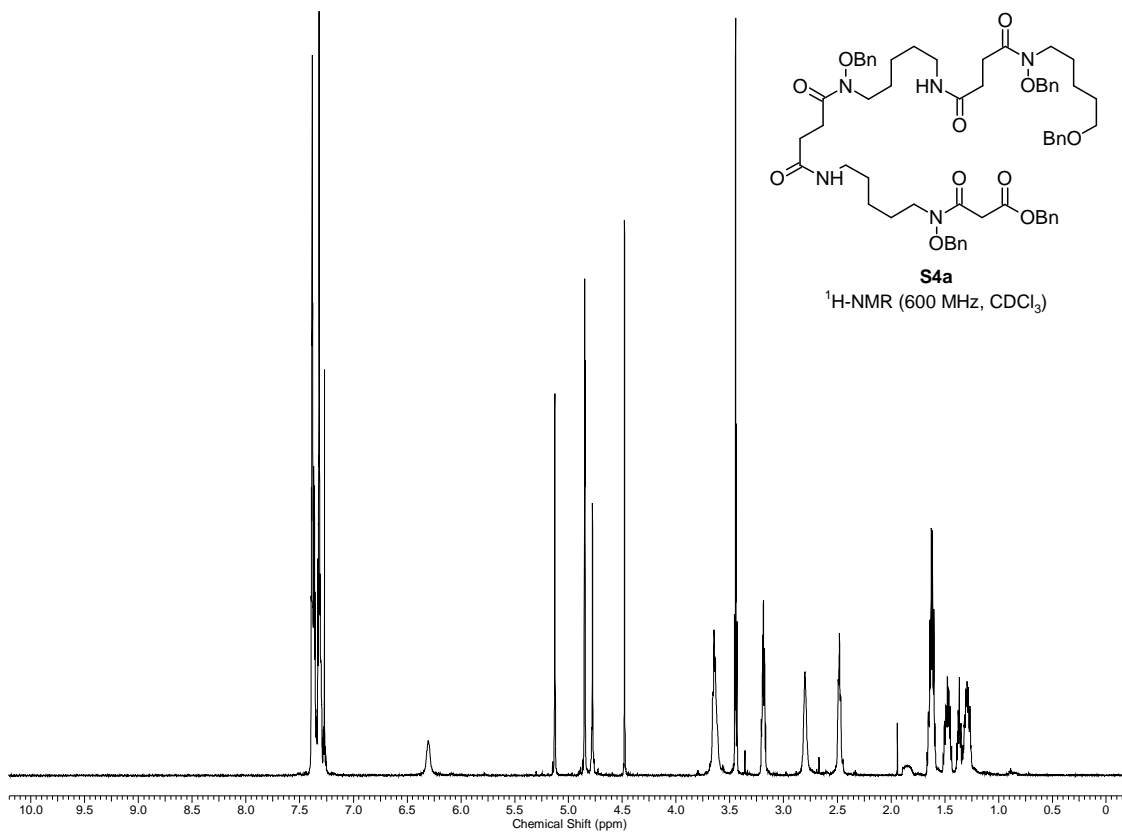


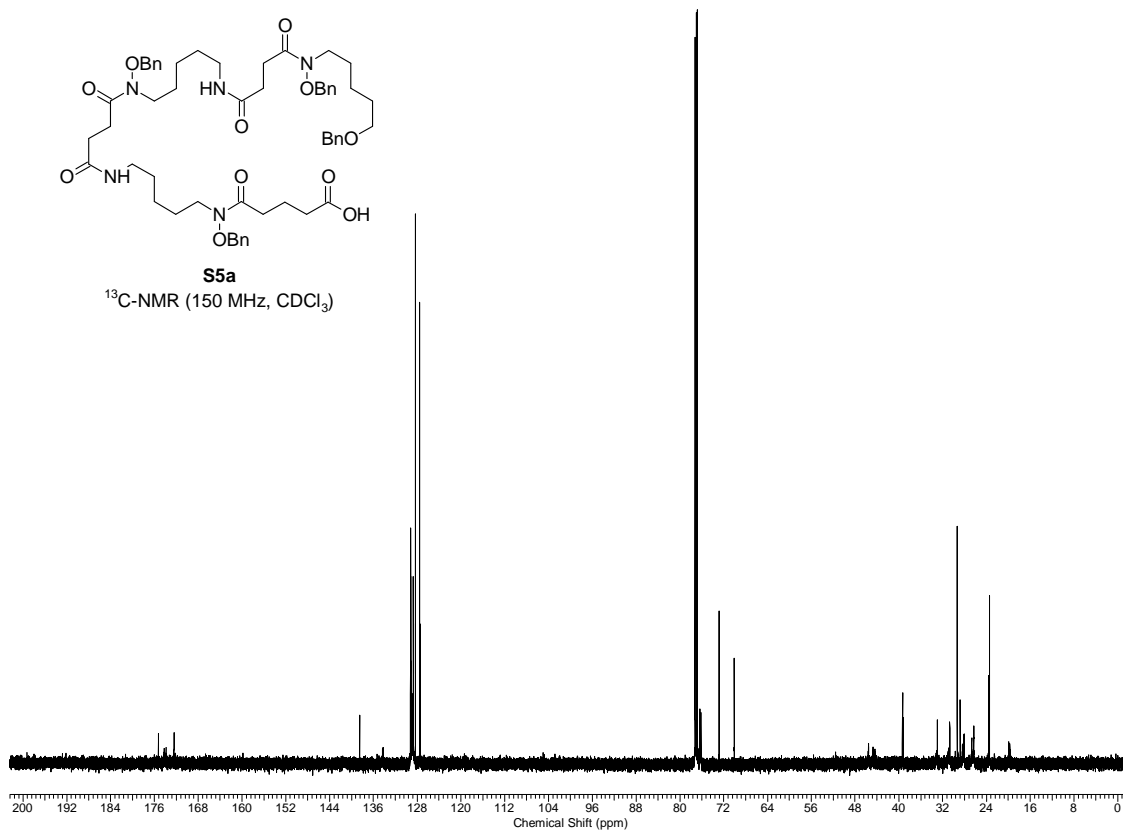
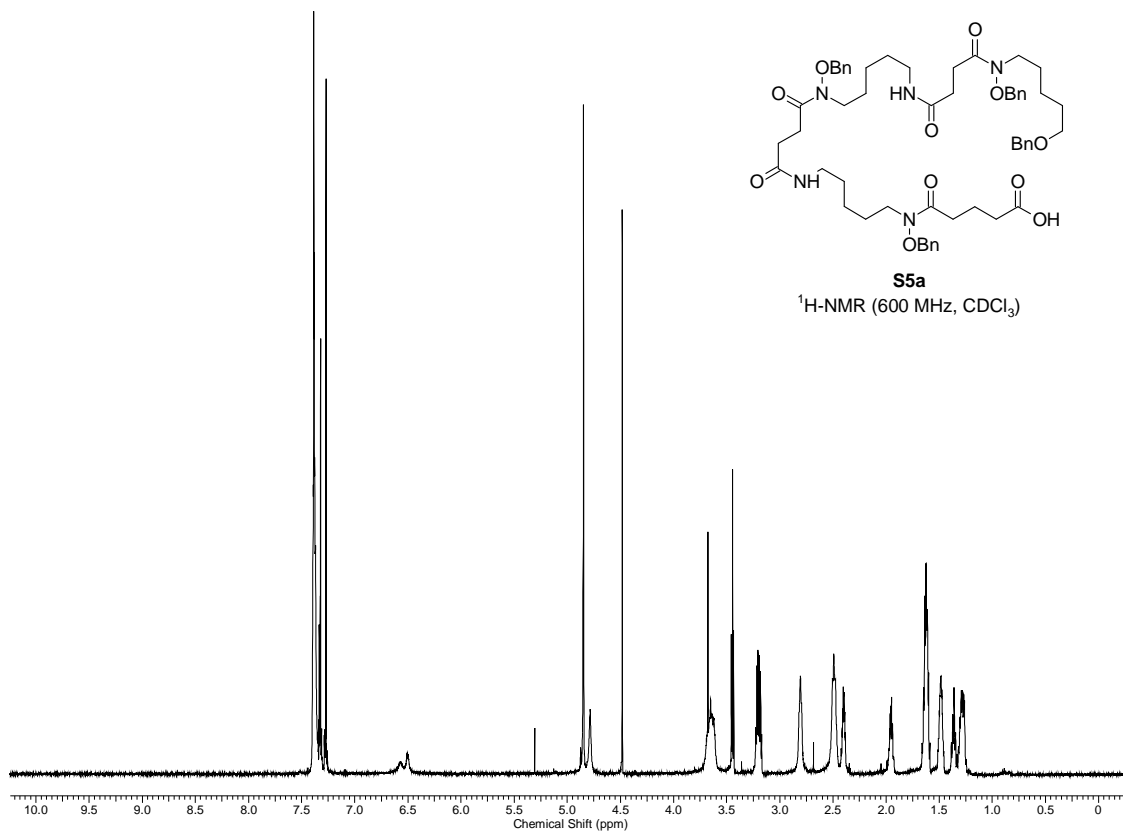
S3
¹H-NMR (500 MHz, CDCl₃)

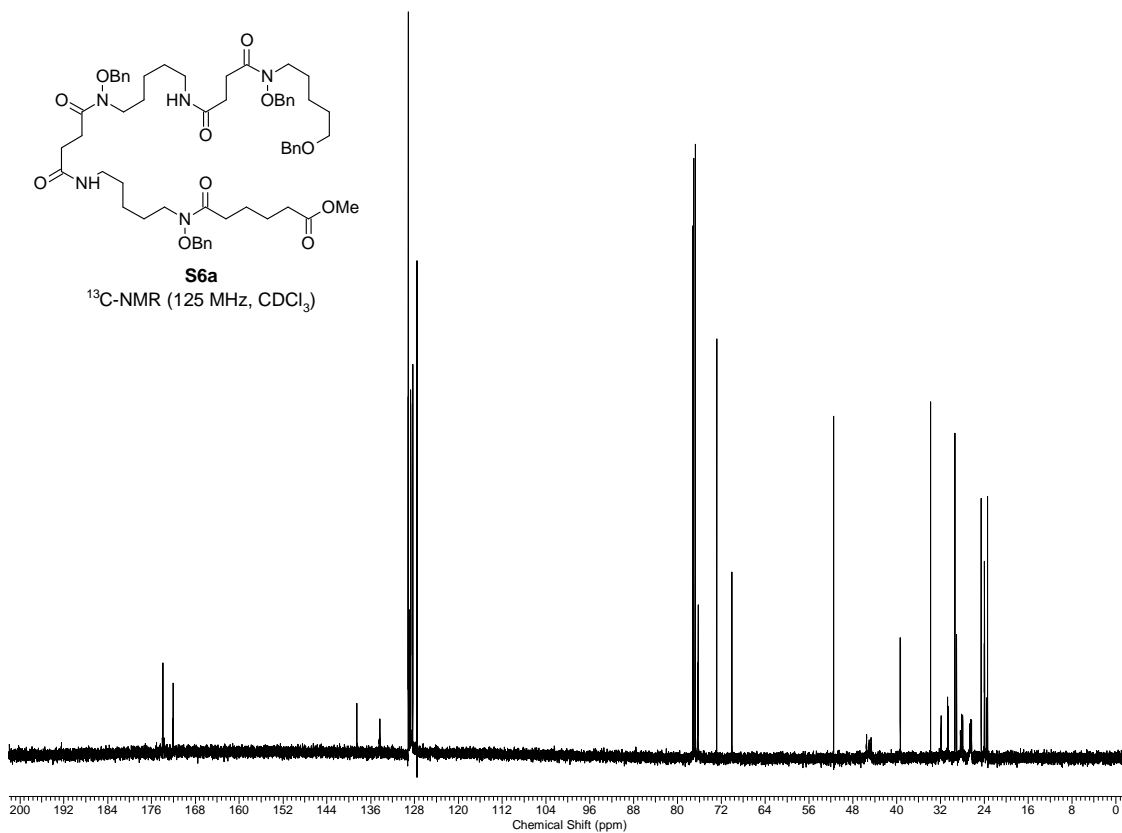
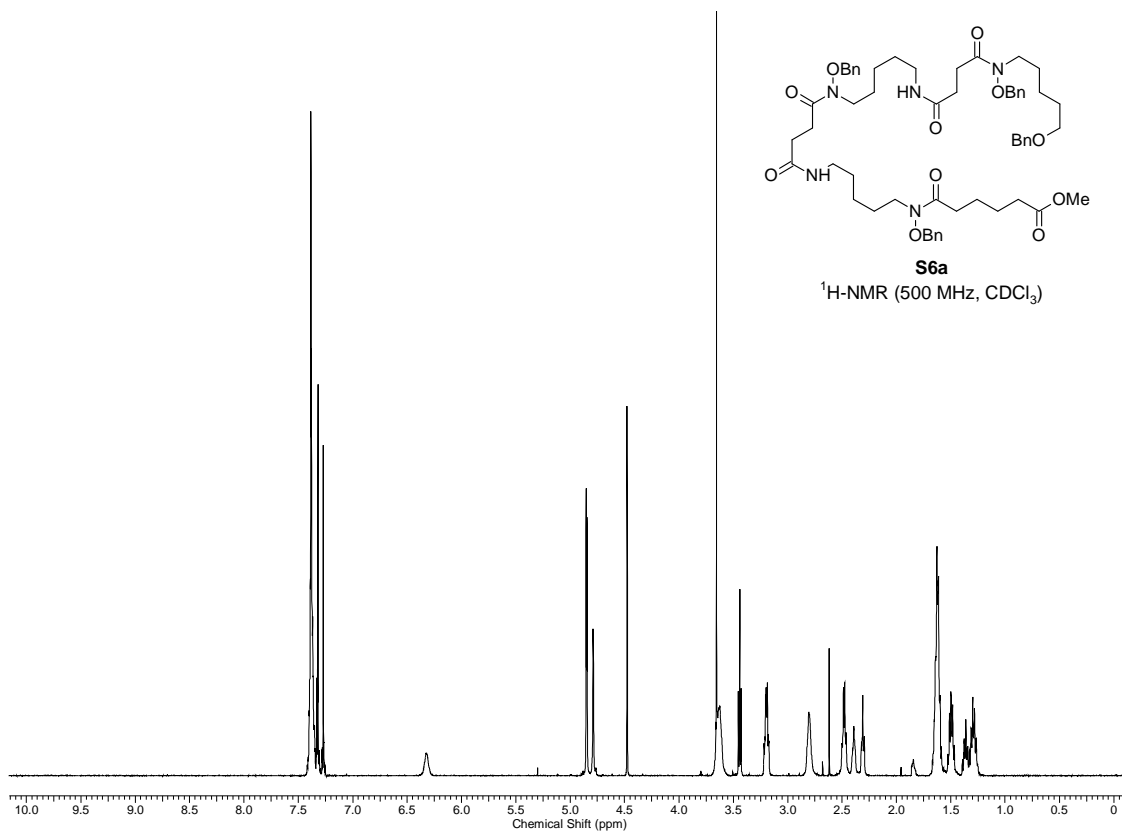


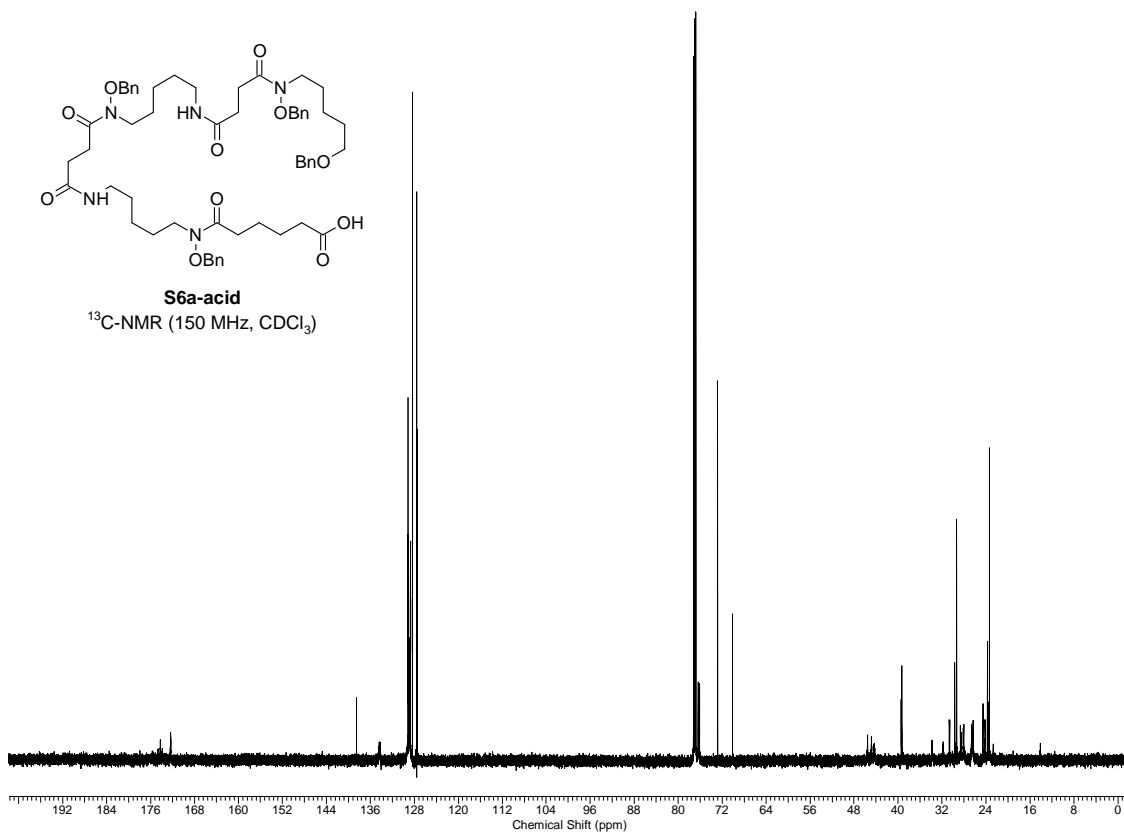
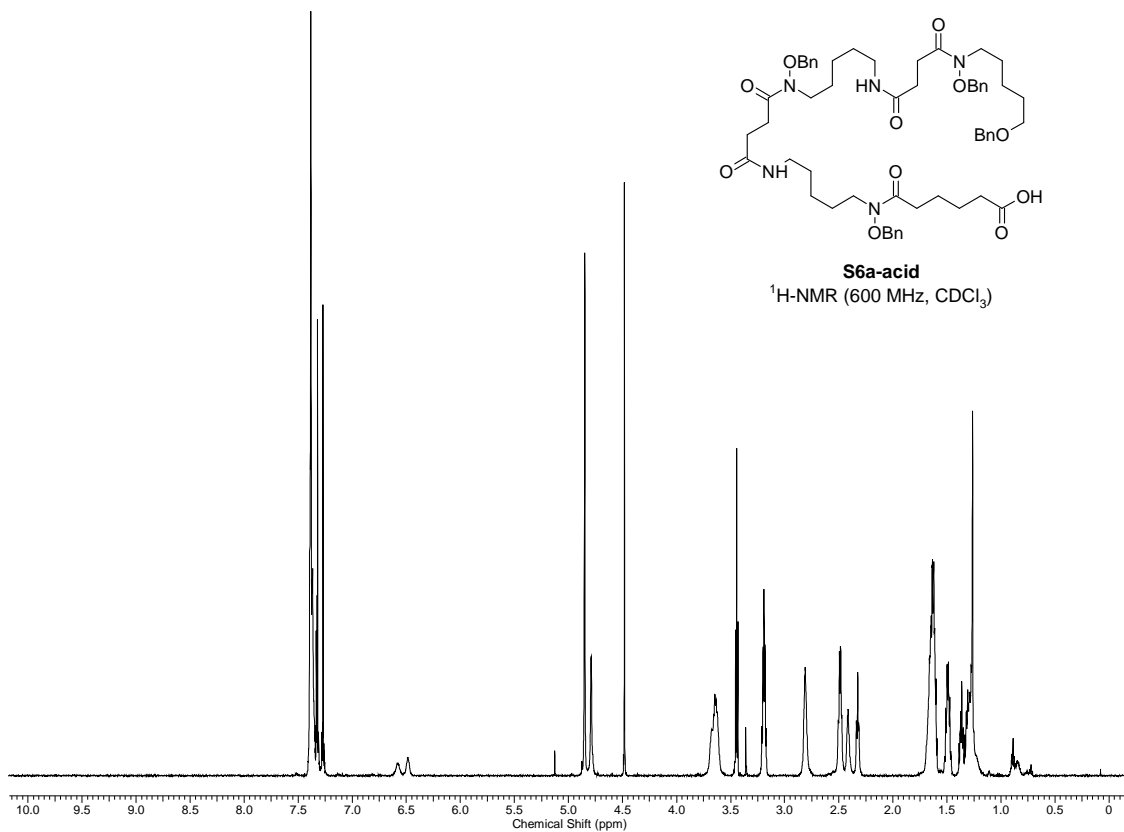
S3
¹³C-NMR (125 MHz, CDCl₃)

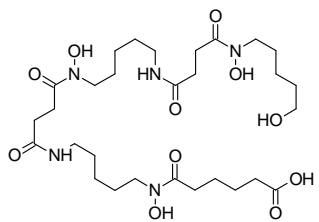






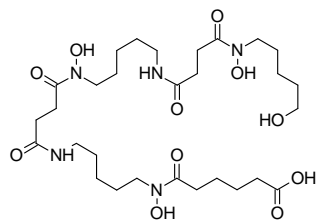
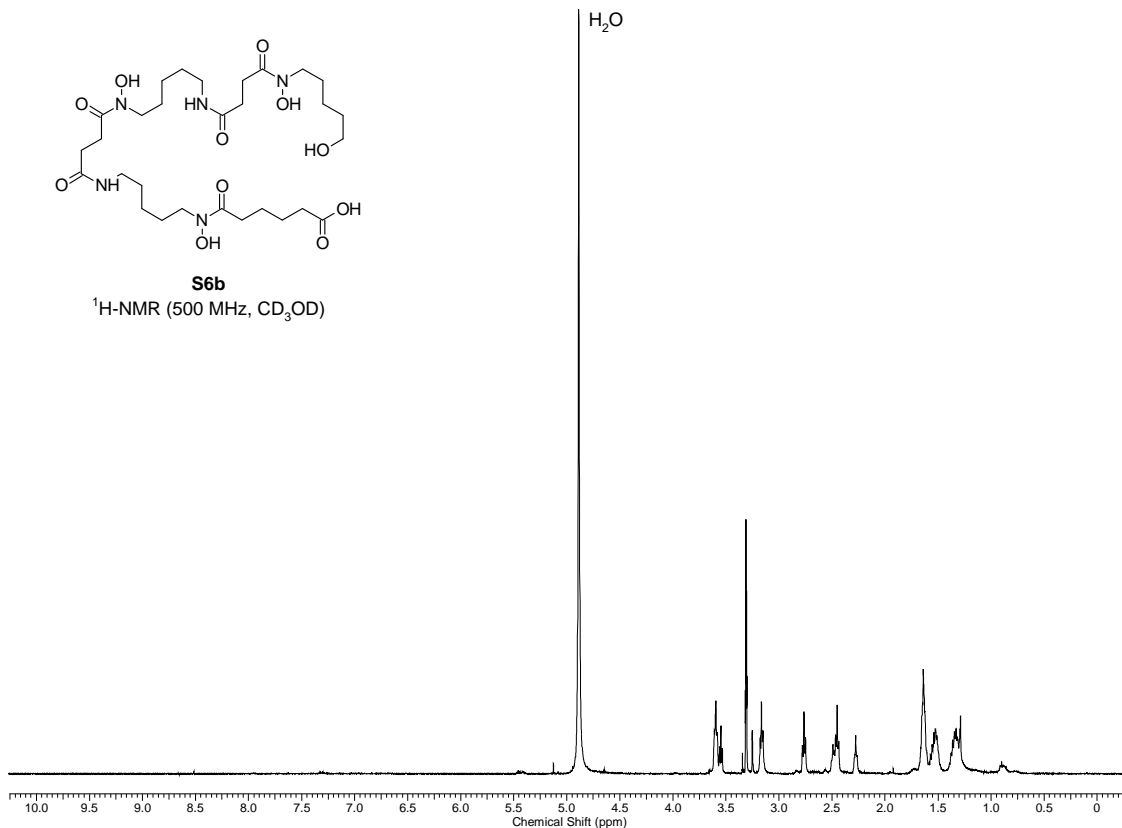






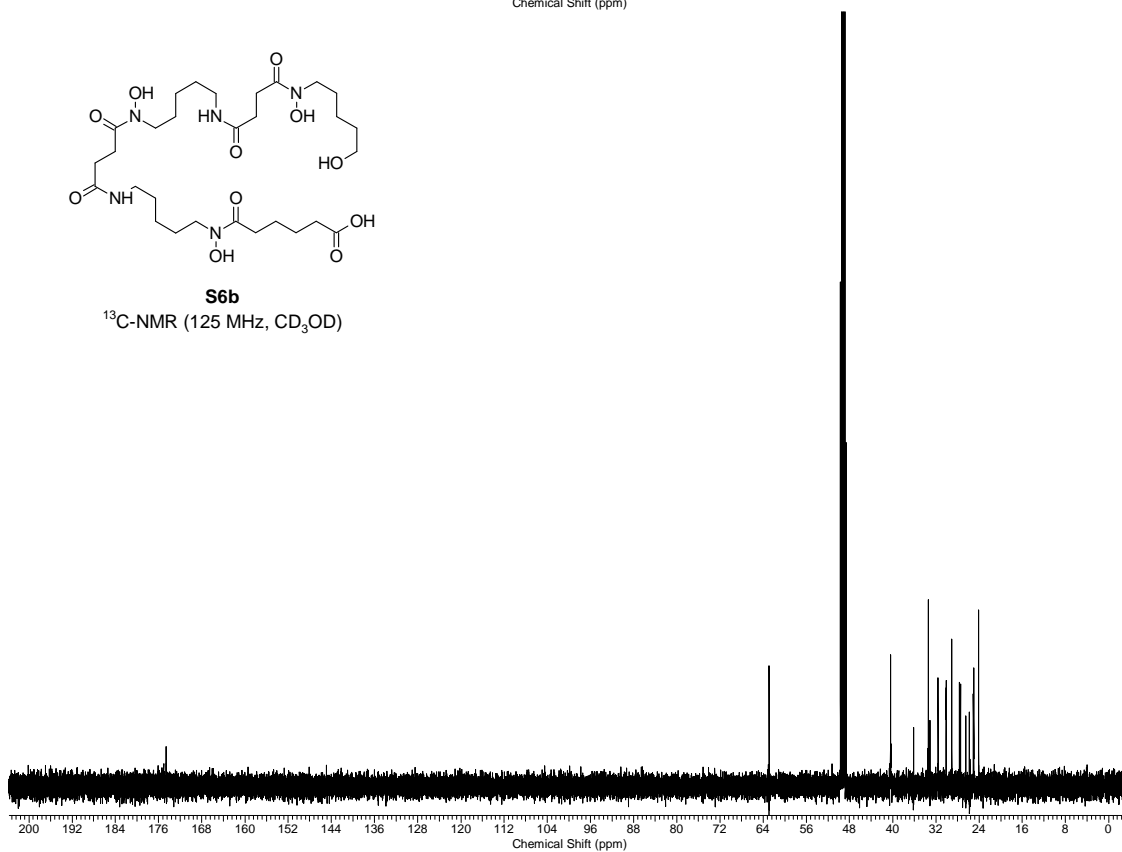
S6b

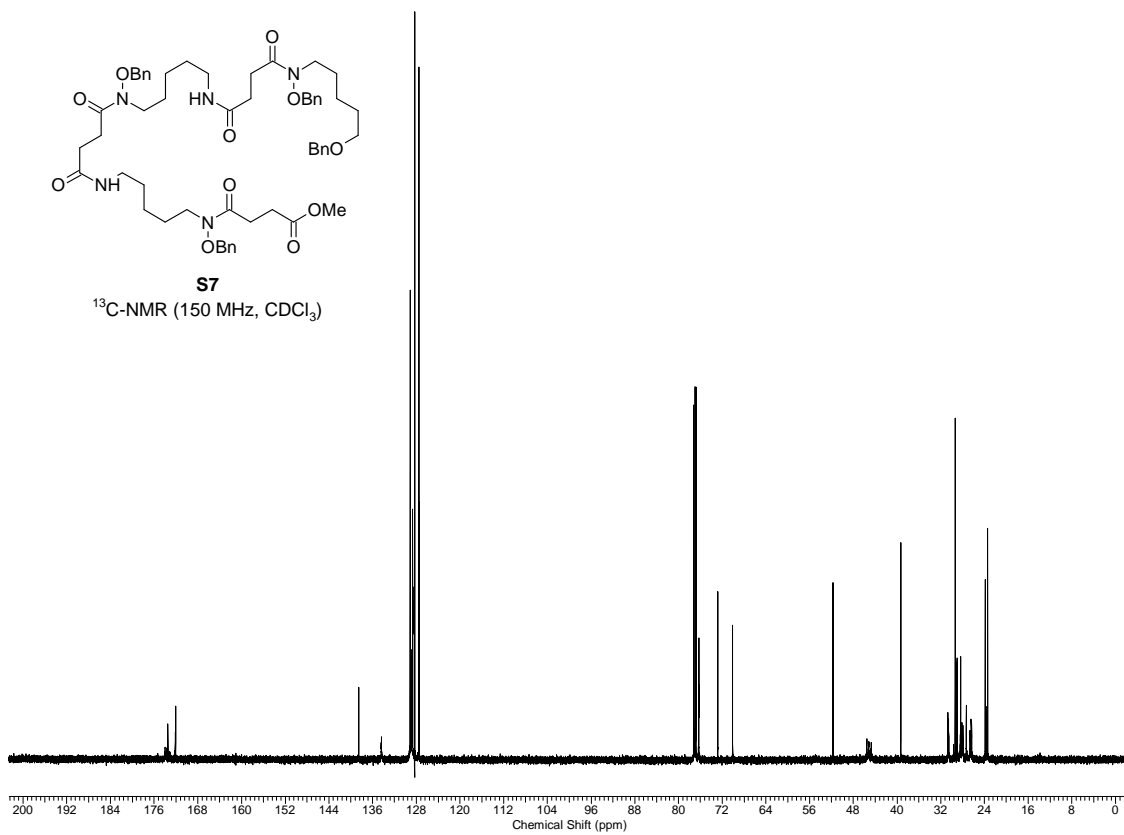
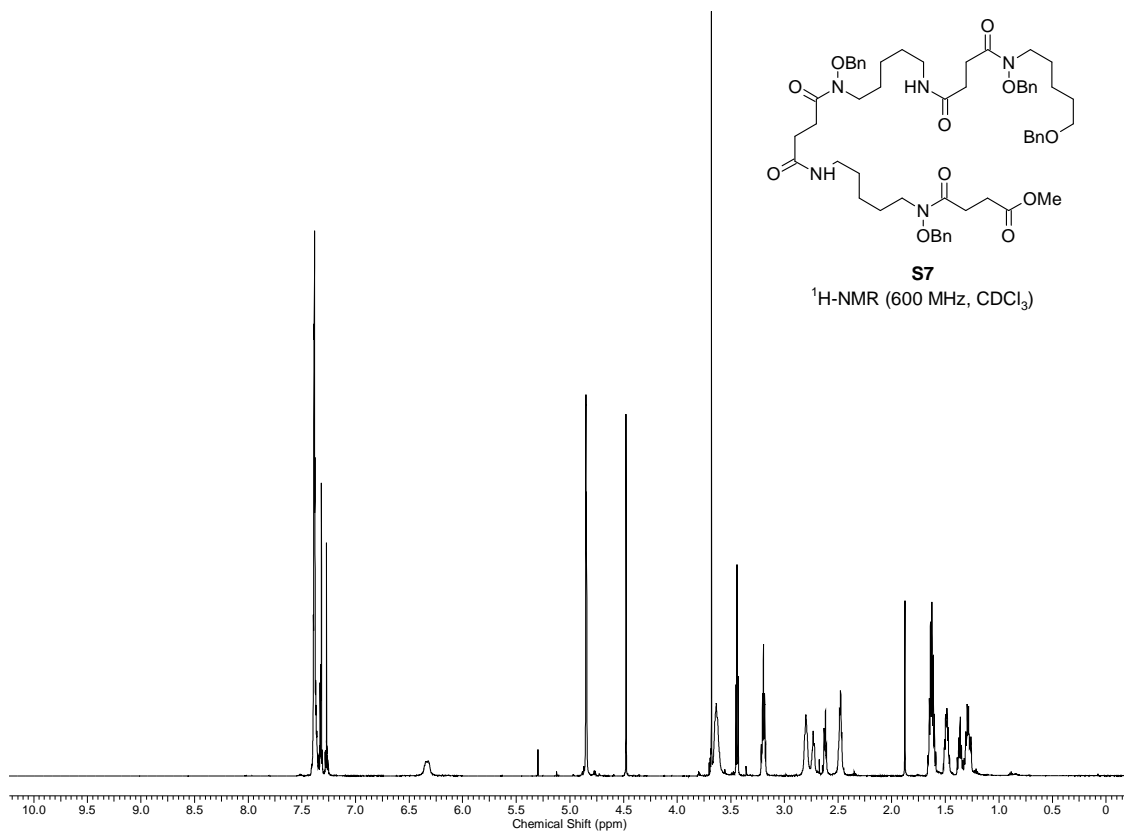
¹H-NMR (500 MHz, CD₃OD)

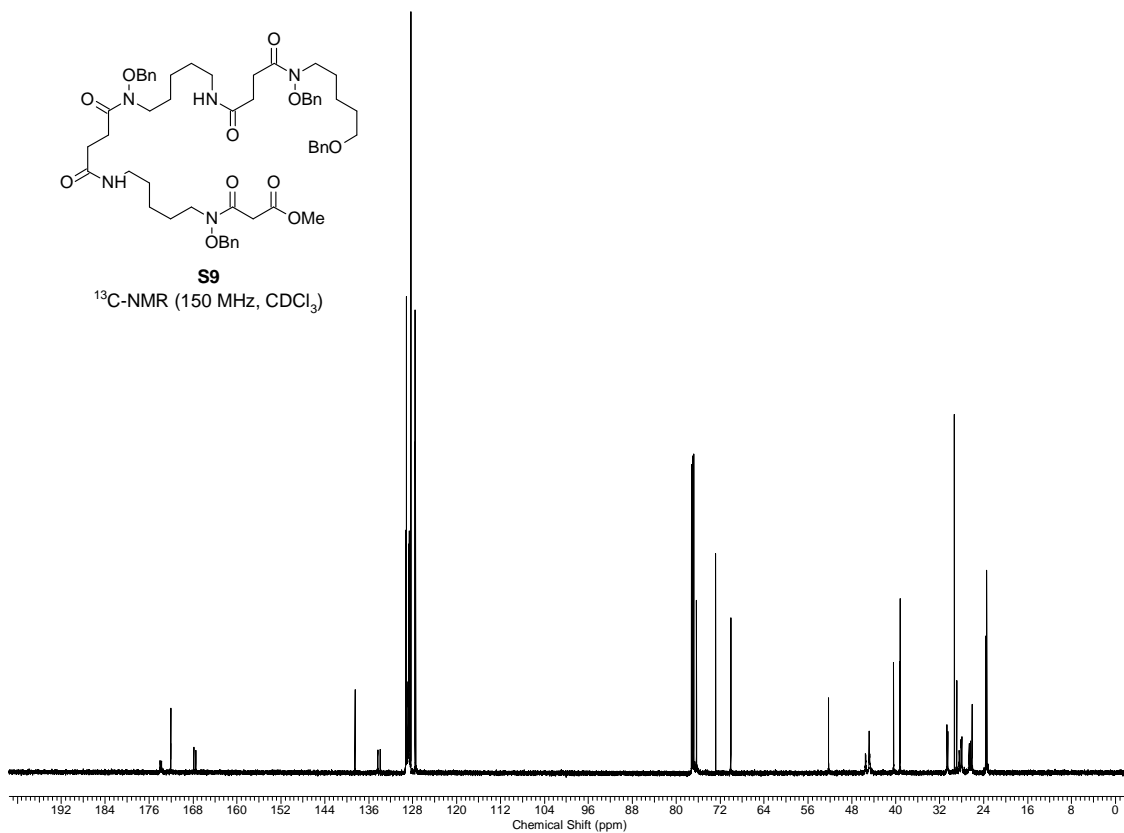
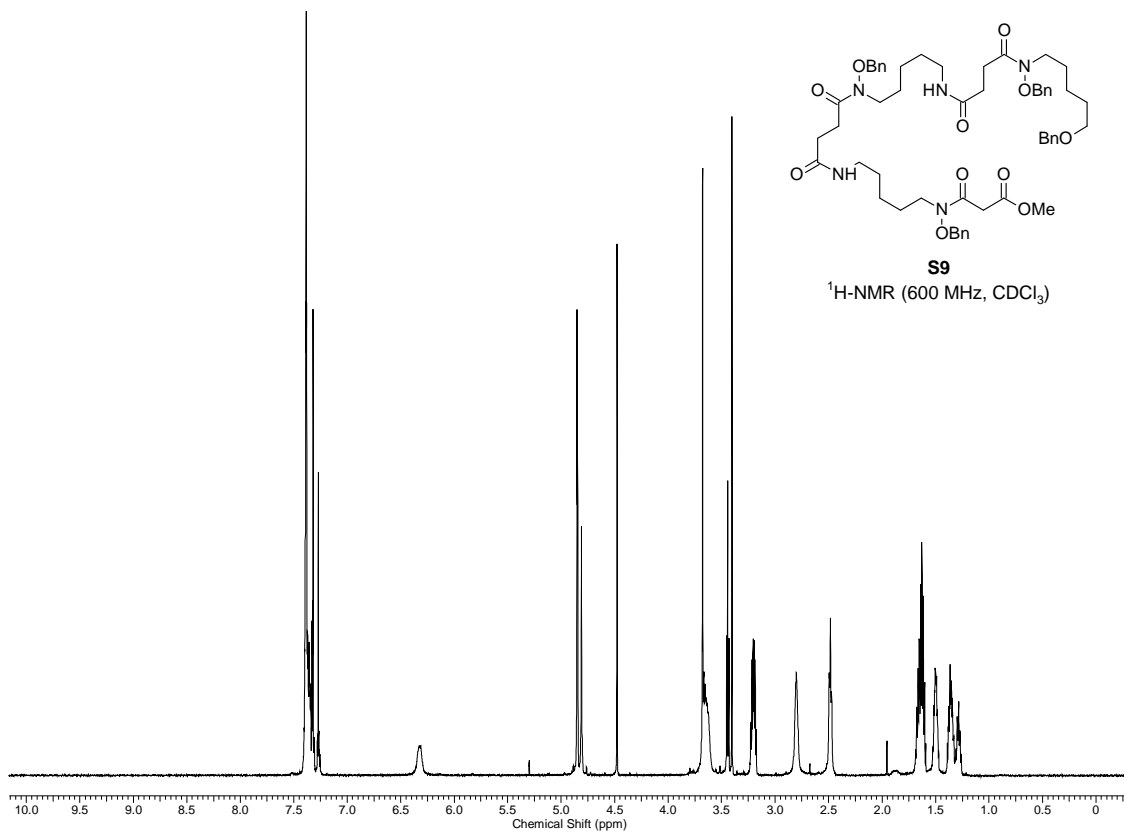


S6b

¹³C-NMR (125 MHz, CD₃OD)







XI. HPLC Chromatograms of Pure Siderophore-Fe(III) Complexes

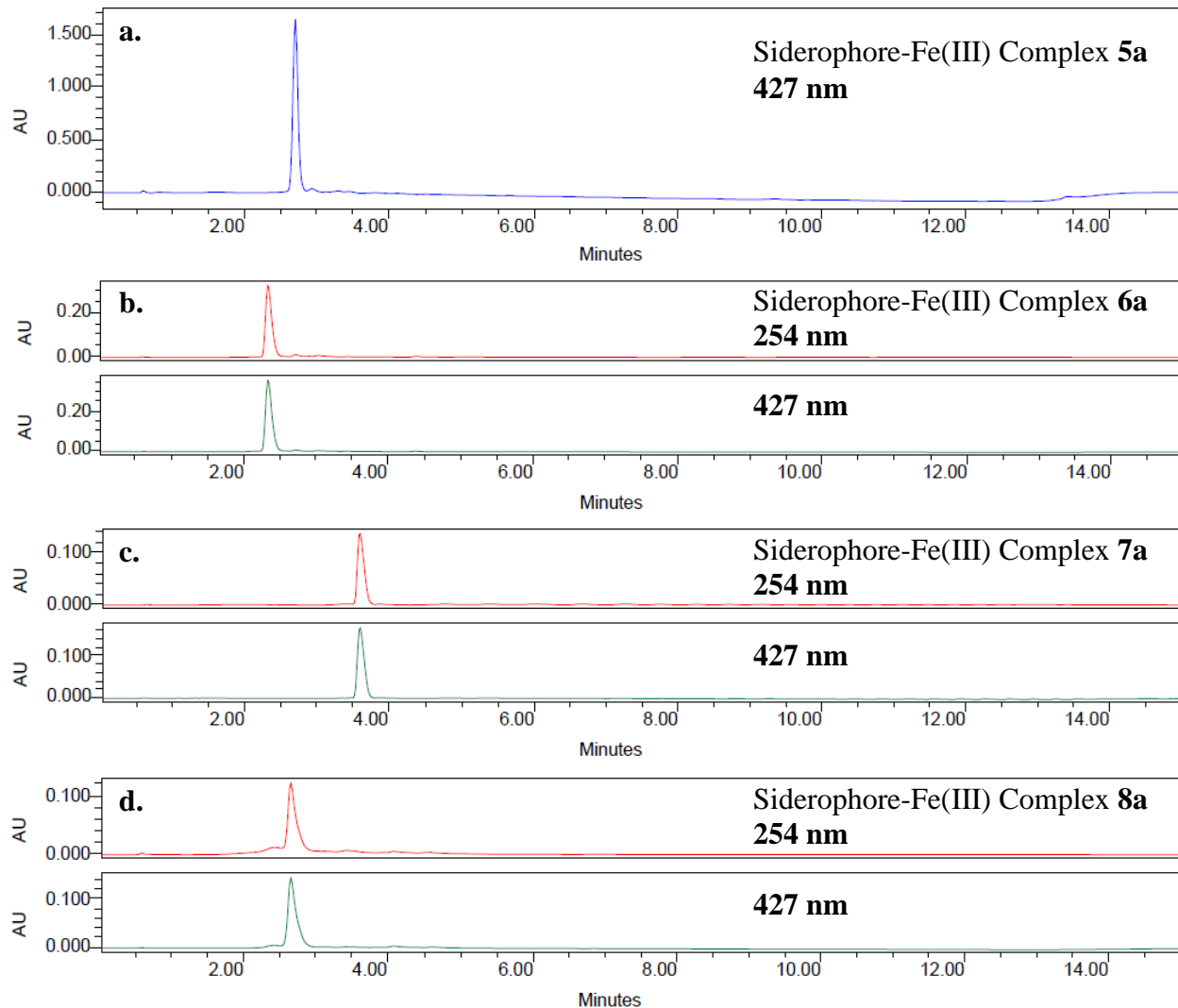


Figure S20. HPLC chromatograms of purified siderophore-Fe(III) complex hydroxy acid substrates for the Yamaguchi macrolactonization reactions. (a) Siderophore-Fe(III) complex hydroxy acid **5a**. (b) Siderophore-Fe(III) complex hydroxy acid **6a**. (c) Siderophore-Fe(III) complex hydroxy acid **7a** (Note: Retention time in this chromatogram is not accurate due to an HPLC injection malfunction, but chromatogram still shows the high compound purity. Actual retention time is 2.2 min as shown in Figure S14). (d) Siderophore-Fe(III) complex hydroxy acid **8a**.

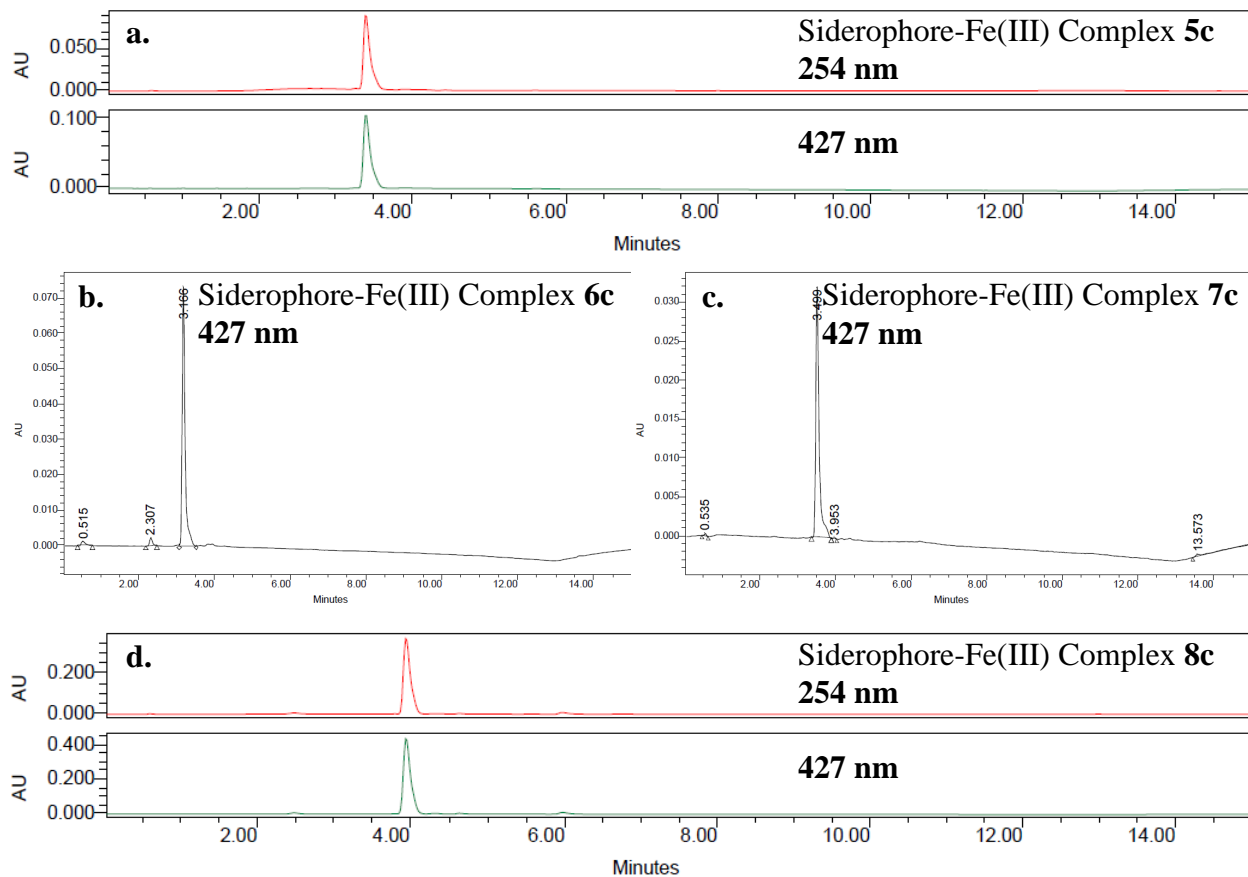


Figure S21. HPLC chromatograms of purified siderophore-Fe(III) complex methyl ester substrates for kinetic hydrolysis studies. (a) Siderophore-Fe(III) complex methyl ester **5c**. (b) Siderophore-Fe(III) complex methyl ester **6c**. (c) Siderophore-Fe(III) complex methyl ester **7c**. (d) Siderophore-Fe(III) complex methyl ester **8c**.

XII. X-ray Diffraction Data for **5b**

Discussion

The complex **5b** crystallizes as red, blade-like crystals. There are two molecules of the complex, a racemic mixture of Λ/Δ -cis coordination isomers, and associated water molecules of crystallization in the unit cell of the primitive, centrosymmetric, triclinic space group P-1.

The structure of the complex is as expected (see Figure 3 in main text). The iron adopts an octahedral coordination geometry and is coordinated by six oxygens of the siderophore macrocycle. Though the data resolution was not as high as often desired, location of the hydrogens on the macrocycle and water molecules was possible. This allowed identification of the lactone oxygen since the amide hydrogens were observed. The amides and water molecule all form hydrogen bonds to nearby H-bond acceptor atoms (see Table S8 of Hydrogen-bonds for details). The molecules form 2D H-bonded sheets within the lattice. The H-bond from N3 to the neighboring oxime oxygen, O1, propagates chains along the *a*-axis. The H-bond from N5 to the carbonyl O7 of a molecule related by translation along the *b*-axis, propagates the sheet along that axis. The water molecule forms a bifurcated hydrogen-bond to the carbonyl oxygens O2 and O9 (which also coordinate the Fe center) and an H-bond to the same carbonyl, O7, contacted by N5.

The data quality is not as high as usually desired, however, the connectivity and identity of the molecules are unequivocal. The bond distances and angles are within reasonable, expected values, though they do have somewhat larger than normal standard uncertainties.

Limited examples of ferrioxamine siderophore x-ray structures have been solved and presented in the literature. These structures include ferrioxamine B,²⁻³ ferrioxamine D₁,⁴ ferrioxamine E,⁵ and a retro-hydroxamate isomeric structure of ferrioxamine E.⁶ A comparative analysis of these structures has been reported and the structural parameters of danoxamine macrolactone presented here are in good agreement.²

The propeller-like structures and conformational features of danoxamine macrolactone (**5b**) and ferrioxamine E, both macrocyclic ferrioxamine siderophores with a preformed cavity for binding Fe(III),^{2,5} compare very well with each other as shown in figure S22 A and B, respectively. One interesting structural difference is observed when viewing space filling models of the two faces of the siderophore structures. Both structures present three carbonyl groups on one face, but on the opposing face ferrioxamine E presents three amide NH groups (H-bond donors) while danoxamine macrolactone presents two amide NH groups (H-bond donors) and one ester oxygen (H-Bond acceptor). This subtle structural difference could influence biological activity of the siderophores since recognition and transport by membrane-associated siderophore receptor/transport proteins is highly dependent on the presented structural features surrounding the Fe(III)-octahedron of the siderophore.²

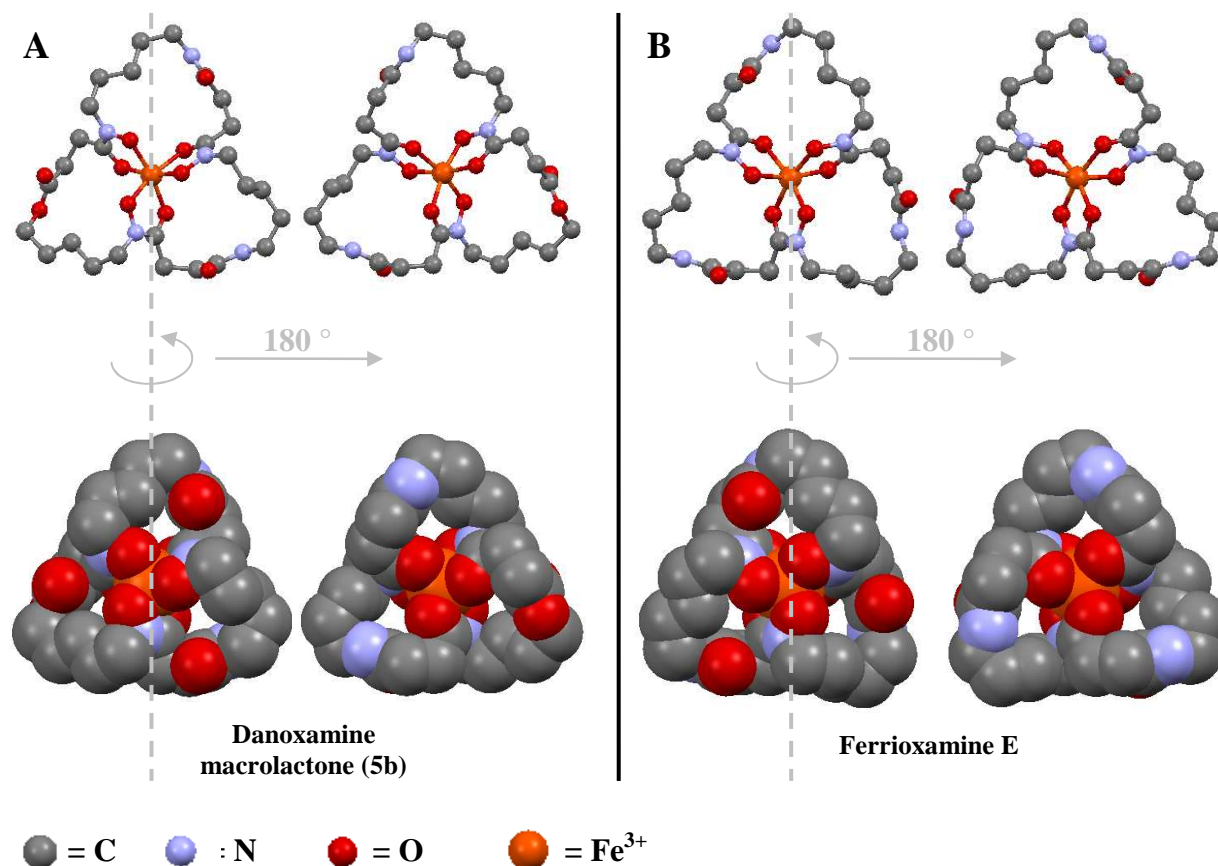


Figure S22. Comparison of danoxamine macrolactone (**5b**; **A**) and ferrioxamine E (**B**) X-ray structures viewed through the pseudo C_3 axis using ball and stick and space filling models generated by Mercury version 2.4 (cif file for ferrioxamine E (FEROXE10)⁵ was obtained from the Cambridge Structural Database).

Crystal Summary

Crystal data for $C_{27}H_{45}FeN_5O_{11}$; $M_r = 671.53$; Triclinic; space group P-1; $a = 7.9412(10)$ Å; $b = 10.3832(14)$ Å; $c = 19.910(3)$ Å; $\alpha = 97.593(10)^\circ$; $\beta = 92.835(9)^\circ$; $\gamma = 106.253(9)^\circ$; $V = 1555.8(4)$ Å³; $Z = 2$; $T = 150(2)$ K; $\lambda(\text{synchrotron}) = 0.77490$ Å; $\mu(\text{synchrotron}) = 0.646$ mm⁻¹; $d_{\text{calc}} = 1.434$ g.cm⁻³; 20051 reflections collected; 4479 unique ($R_{\text{int}} = 0.1468$); giving $R_1 = 0.1000$, $wR_2 = 0.2398$ for 2441 data with $[I > 2\sigma(I)]$ and $R_1 = 0.1754$, $wR_2 = 0.2783$ for all 4479 data. Residual electron density ($e^- \cdot \text{\AA}^{-3}$) max/min: 0.884/-0.896.

An arbitrary sphere of data were collected on a red blade-like crystal, having approximate dimensions of $0.06 \times 0.05 \times 0.015$ mm, on a Bruker APEX-II diffractometer using a combination of ω - and ϕ -scans of 0.3° .⁷ Data were corrected for absorption and polarization effects and analyzed for space group determination. The structure was solved by direct methods and expanded routinely. The model was refined by full-matrix least-squares analysis of F^2 against all reflections. All non-hydrogen atoms were refined with anisotropic thermal displacement parameters. Unless otherwise noted, hydrogen atoms were included in calculated positions. Thermal parameters for the hydrogens were tied to the isotropic thermal parameter of the atom to which they are bonded ($1.5 \times$ for methyl, $1.2 \times$ for all others).⁸⁻¹⁰

Table S2. Crystal data and structure refinement for **5b**.

Identification code	nd65a
Empirical formula	C ₂₇ H ₄₅ FeN ₅ O ₁₁
Formula weight	671.53
Temperature	150(2) K
Wavelength	0.77490 Å
Crystal system	Triclinic
Space group	P-1
Unit cell dimensions	$a = 7.9412(10)$ Å $\alpha = 97.593(10)^\circ$ $b = 10.3832(14)$ Å $\beta = 92.835(9)^\circ$ $c = 19.910(3)$ Å $\gamma = 106.253(9)^\circ$
Volume	1555.8(4) Å ³
Z	2
Density (calculated)	1.434 g.cm ⁻³
Absorption coefficient (μ)	0.646 mm ⁻¹
F(000)	712
Crystal size	0.06 × 0.05 × 0.015 mm ³
θ range for data collection	2.25 to 25.50°
Index ranges	-8 ≤ h ≤ 8, -11 ≤ k ≤ 11, -22 ≤ l ≤ 22
Reflections collected	20051
Independent reflections	4479 [R _{int} = 0.1468]
Completeness to $\theta = 25.50^\circ$	100.0 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7458 and 0.5520
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	4479 / 3 / 403
Goodness-of-fit on F ²	1.039
Final R indices [I > 2σ(I)]	R ₁ = 0.1000, wR ₂ = 0.2398
R indices (all data)	R ₁ = 0.1754, wR ₂ = 0.2783
Largest diff. peak and hole	0.884 and -0.896 e ⁻ .Å ⁻³

Table S3. Atomic coordinates and equivalent isotropic displacement parameters (Å²) for **5b**. U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U(eq)
Fe(1)	0.10065(16)	0.16502(13)	0.23336(8)	0.043(1)
O(1)	0.3196(7)	0.1169(6)	0.2521(3)	0.043(2)
O(2)	0.0956(8)	0.0290(6)	0.1488(3)	0.046(2)
O(3)	0.2568(9)	0.1098(7)	-0.0446(4)	0.062(2)
O(4)	0.4541(8)	0.1312(6)	0.0437(4)	0.047(2)
O(5)	0.2148(7)	0.3290(6)	0.1957(3)	0.044(2)
O(6)	-0.1126(7)	0.2116(6)	0.1936(3)	0.041(2)
O(7)	-0.2076(11)	0.5433(8)	0.2699(4)	0.075(2)
O(8)	0.1183(8)	0.2671(6)	0.3247(4)	0.048(2)

O(9)	-0.0517(7)	0.0176(6)	0.2822(4)	0.043(2)
O(10)	0.1641(10)	-0.0790(8)	0.4331(4)	0.069(2)
N(1)	0.3521(9)	0.0323(7)	0.1988(4)	0.041(2)
N(2)	0.0981(9)	0.3915(7)	0.1723(4)	0.040(2)
N(3)	-0.4232(10)	0.3785(8)	0.3021(5)	0.046(2)
N(4)	0.0359(10)	0.1848(9)	0.3700(5)	0.047(2)
N(5)	0.0912(10)	-0.2912(8)	0.3753(4)	0.046(2)
C(1)	0.2362(12)	-0.0109(9)	0.1463(6)	0.045(3)
C(2)	0.2586(13)	-0.1077(9)	0.0880(6)	0.049(3)
C(3)	0.2058(11)	-0.0689(9)	0.0207(6)	0.051(3)
C(4)	0.3188(12)	0.0669(10)	0.0083(6)	0.043(3)
C(5)	0.3435(13)	0.2422(9)	-0.0622(6)	0.050(3)
C(6)	0.2568(12)	0.3486(10)	-0.0348(6)	0.050(3)
C(7)	0.2616(12)	0.3753(10)	0.0405(5)	0.043(2)
C(8)	0.1734(12)	0.4819(9)	0.0666(5)	0.045(3)
C(9)	0.1741(11)	0.5097(8)	0.1415(5)	0.041(3)
C(10)	-0.0693(11)	0.3237(9)	0.1711(5)	0.038(2)
C(11)	-0.2108(10)	0.3788(9)	0.1427(5)	0.037(2)
C(12)	-0.3707(11)	0.3607(10)	0.1848(5)	0.042(2)
C(13)	-0.3290(13)	0.4337(10)	0.2554(6)	0.043(2)
C(14)	-0.4143(14)	0.4356(11)	0.3713(6)	0.056(3)
C(15)	-0.4286(18)	0.3321(13)	0.4192(7)	0.080(4)
C(16)	-0.2924(16)	0.2502(12)	0.4152(7)	0.076(4)
C(17)	-0.1082(13)	0.3413(11)	0.4337(7)	0.069(4)
C(18)	0.0366(14)	0.2605(11)	0.4359(6)	0.062(3)
C(19)	-0.0502(11)	0.0577(10)	0.3454(6)	0.039(2)
C(20)	-0.1523(13)	-0.0329(9)	0.3911(5)	0.049(3)
C(21)	-0.1271(12)	-0.1740(10)	0.3791(6)	0.048(3)
C(22)	0.0587(15)	-0.1753(12)	0.3977(6)	0.054(3)
C(23)	0.2614(15)	-0.3112(13)	0.3835(6)	0.068(3)
C(24)	0.3574(13)	-0.2946(11)	0.3204(6)	0.057(3)
C(25)	0.3850(12)	-0.1549(10)	0.2972(5)	0.051(3)
C(26)	0.4821(11)	-0.1427(9)	0.2346(5)	0.044(3)
C(27)	0.5170(11)	-0.0078(9)	0.2105(6)	0.047(3)
O(1W)	-0.0543(10)	-0.2530(7)	0.1943(4)	0.063(2)
H(3C)	-0.4994	0.2981	0.2892	0.055
H(5C)	0.0037	-0.3590	0.3542	0.055
H(2A)	0.1852	-0.2003	0.0917	0.059
H(2B)	0.3832	-0.1082	0.0893	0.059
H(3A)	0.2134	-0.1392	-0.0168	0.061
H(3B)	0.0817	-0.0674	0.0200	0.061
H(5A)	0.3405	0.2356	-0.1123	0.060
H(5B)	0.4684	0.2707	-0.0436	0.060
H(6A)	0.3154	0.4347	-0.0511	0.060
H(6B)	0.1322	0.3195	-0.0539	0.060
H(12B)	-0.4227	0.2628	0.1863	0.051

H(14A)	-0.5108	0.4781	0.3775	0.067
H(14B)	-0.3013	0.5078	0.3833	0.067
H(15A)	-0.5168	0.3180	0.4503	0.096
H(16A)	-0.3196	0.1822	0.4466	0.091
H(16B)	-0.3015	0.2010	0.3685	0.091
H(17A)	-0.1028	0.3959	0.4788	0.083
H(17B)	-0.0791	0.4047	0.4001	0.083
H(18A)	0.1546	0.3254	0.4496	0.074
H(18B)	0.0102	0.1978	0.4699	0.074
H(20A)	-0.2790	-0.0406	0.3830	0.058
H(20B)	-0.1136	0.0082	0.4391	0.058
H(21A)	-0.2078	-0.2332	0.4062	0.058
H(21B)	-0.1602	-0.2126	0.3305	0.058
H(23A)	0.2484	-0.4036	0.3946	0.082
H(23B)	0.3321	-0.2451	0.4221	0.082
H(24A)	0.2905	-0.3657	0.2829	0.068
H(24B)	0.4740	-0.3094	0.3289	0.068
H(25A)	0.2688	-0.1400	0.2879	0.061
H(25B)	0.4518	-0.0832	0.3344	0.061
H(26A)	0.5963	-0.1610	0.2438	0.053
H(26B)	0.4134	-0.2138	0.1975	0.053
H(27A)	0.5743	-0.0116	0.1675	0.056
H(27B)	0.5995	0.0622	0.2447	0.056
H(1WA)	-0.029(15)	-0.167(3)	0.215(4)	0.075
H(1WB)	-0.102(14)	-0.311(6)	0.223(3)	0.075

Table S4. Anisotropic displacement parameters (\AA^2) for **5b**.

The anisotropic displacement factor exponent takes the form:

$$-2\pi^2[h^2a^{*2}U_{11} + \dots + 2hka^*b^*U_{12}]$$

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Fe(1)	0.0195(7)	0.0427(9)	0.0729(12)	0.0166(7)	0.0074(6)	0.0142(6)
O(1)	0.028(3)	0.040(4)	0.063(5)	0.006(3)	0.009(3)	0.013(3)
O(2)	0.027(3)	0.045(4)	0.074(5)	0.015(3)	0.007(3)	0.019(3)
O(3)	0.029(4)	0.065(5)	0.090(6)	0.007(4)	0.002(4)	0.015(3)
O(4)	0.021(4)	0.052(4)	0.069(5)	0.014(4)	-0.003(3)	0.009(3)
O(5)	0.022(3)	0.043(4)	0.076(5)	0.021(3)	0.004(3)	0.020(3)
O(6)	0.015(3)	0.038(4)	0.074(5)	0.016(3)	0.006(3)	0.010(3)
O(7)	0.064(5)	0.059(5)	0.087(6)	0.006(4)	0.020(5)	-0.007(4)
O(8)	0.026(3)	0.048(4)	0.076(5)	0.023(4)	0.010(3)	0.011(3)
O(9)	0.026(3)	0.040(4)	0.065(5)	0.015(4)	0.007(3)	0.010(3)
O(10)	0.051(5)	0.078(6)	0.077(6)	-0.003(5)	-0.009(4)	0.028(4)
N(1)	0.021(4)	0.037(4)	0.071(6)	0.017(4)	0.008(4)	0.015(4)
N(2)	0.022(4)	0.037(4)	0.062(6)	0.013(4)	0.001(4)	0.011(3)

N(3)	0.034(5)	0.050(5)	0.057(6)	0.019(5)	0.010(4)	0.012(4)
N(4)	0.035(5)	0.058(6)	0.061(6)	0.016(5)	0.014(4)	0.028(4)
N(5)	0.038(5)	0.039(5)	0.067(6)	0.011(4)	0.004(4)	0.022(4)
C(1)	0.028(5)	0.035(5)	0.076(8)	0.020(5)	0.007(6)	0.012(4)
C(2)	0.033(5)	0.038(6)	0.084(8)	0.018(6)	0.013(5)	0.018(5)
C(3)	0.018(5)	0.040(6)	0.094(9)	0.001(6)	0.009(5)	0.010(4)
C(4)	0.020(5)	0.054(6)	0.064(7)	0.012(6)	0.011(5)	0.021(5)
C(5)	0.037(6)	0.050(6)	0.066(7)	0.010(5)	0.014(5)	0.014(5)
C(6)	0.022(5)	0.068(7)	0.072(8)	0.027(6)	0.007(5)	0.026(5)
C(7)	0.024(5)	0.053(6)	0.058(7)	0.018(5)	-0.003(5)	0.016(4)
C(8)	0.025(5)	0.043(6)	0.071(8)	0.023(5)	0.007(5)	0.010(4)
C(9)	0.021(5)	0.027(5)	0.078(8)	0.015(5)	0.001(5)	0.008(4)
C(10)	0.026(5)	0.039(6)	0.056(7)	0.015(5)	0.009(4)	0.018(4)
C(11)	0.019(4)	0.038(5)	0.057(7)	0.002(5)	-0.003(4)	0.015(4)
C(12)	0.025(5)	0.049(6)	0.056(7)	0.010(5)	-0.006(5)	0.016(4)
C(13)	0.038(6)	0.034(6)	0.060(8)	0.009(5)	0.010(5)	0.014(5)
C(14)	0.044(6)	0.062(7)	0.069(9)	0.012(6)	0.011(6)	0.025(5)
C(15)	0.080(9)	0.105(10)	0.081(9)	0.039(8)	0.019(7)	0.058(8)
C(16)	0.069(9)	0.075(8)	0.095(10)	0.029(7)	0.012(7)	0.029(7)
C(17)	0.040(7)	0.065(7)	0.090(10)	-0.029(7)	0.022(6)	0.009(6)
C(18)	0.048(7)	0.070(8)	0.063(8)	0.013(7)	-0.002(6)	0.012(6)
C(19)	0.022(5)	0.045(6)	0.058(8)	0.020(6)	0.001(5)	0.016(4)
C(20)	0.039(6)	0.047(6)	0.066(7)	0.016(5)	0.007(5)	0.019(5)
C(21)	0.030(5)	0.056(6)	0.059(7)	0.017(5)	-0.005(5)	0.010(5)
C(22)	0.057(7)	0.058(7)	0.055(7)	0.019(6)	0.010(6)	0.023(6)
C(23)	0.051(7)	0.085(8)	0.089(9)	0.044(7)	0.017(7)	0.037(6)
C(24)	0.038(6)	0.065(7)	0.077(8)	0.033(6)	0.001(6)	0.022(5)
C(25)	0.023(5)	0.064(7)	0.064(7)	0.015(6)	-0.001(5)	0.009(5)
C(26)	0.016(5)	0.053(6)	0.064(7)	0.013(5)	-0.002(5)	0.008(4)
C(27)	0.015(5)	0.049(6)	0.079(8)	0.010(5)	0.004(5)	0.013(4)
O(1W)	0.057(5)	0.052(4)	0.081(6)	0.012(4)	0.017(4)	0.016(4)

Table S5. Bond lengths [Å] for **5b**.

atom-atom	distance	atom-atom	distance
Fe(1)-O(5)	1.956(6)	Fe(1)-O(8)	1.957(7)
Fe(1)-O(1)	1.970(6)	Fe(1)-O(6)	2.038(6)
Fe(1)-O(2)	2.040(7)	Fe(1)-O(9)	2.055(6)
O(1)-N(1)	1.368(9)	O(2)-C(1)	1.296(10)
O(3)-C(4)	1.322(12)	O(3)-C(5)	1.452(11)
O(4)-C(4)	1.223(11)	O(5)-N(2)	1.368(9)
O(6)-C(10)	1.266(10)	O(7)-C(13)	1.257(11)
O(8)-N(4)	1.386(9)	O(9)-C(19)	1.271(11)
O(10)-C(22)	1.218(13)	N(1)-C(1)	1.301(12)
N(1)-C(27)	1.498(10)	N(2)-C(10)	1.316(11)

N(2)-C(9)	1.437(10)	N(3)-C(13)	1.313(12)
N(3)-C(14)	1.416(12)	N(4)-C(19)	1.319(12)
N(4)-C(18)	1.436(13)	N(5)-C(22)	1.326(13)
N(5)-C(23)	1.429(12)	C(1)-C(2)	1.484(14)
C(2)-C(3)	1.521(14)	C(3)-C(4)	1.503(13)
C(5)-C(6)	1.516(13)	C(6)-C(7)	1.484(14)
C(7)-C(8)	1.517(13)	C(8)-C(9)	1.480(13)
C(10)-C(11)	1.515(11)	C(11)-C(12)	1.538(12)
C(12)-C(13)	1.479(14)	C(14)-C(15)	1.514(15)
C(15)-C(16)	1.550(16)	C(16)-C(17)	1.500(16)
C(17)-C(18)	1.604(15)	C(19)-C(20)	1.498(13)
C(20)-C(21)	1.523(13)	C(21)-C(22)	1.508(14)
C(23)-C(24)	1.506(15)	C(24)-C(25)	1.541(13)
C(25)-C(26)	1.498(14)	C(26)-C(27)	1.498(12)
N(3)-H(3C)	0.8800	N(5)-H(5C)	0.8800
C(2)-H(2A)	0.9900	C(2)-H(2B)	0.9900
C(3)-H(3A)	0.9900	C(3)-H(3B)	0.9900
C(5)-H(5A)	0.9900	C(5)-H(5B)	0.9900
C(6)-H(6A)	0.9900	C(6)-H(6B)	0.9900
C(7)-H(7A)	0.9900	C(7)-H(7B)	0.9900
C(8)-H(8A)	0.9900	C(8)-H(8B)	0.9900
C(9)-H(9A)	0.9900	C(9)-H(9B)	0.9900
C(11)-H(11A)	0.9900	C(11)-H(11B)	0.9900
C(12)-H(12A)	0.9900	C(12)-H(12B)	0.9900
C(14)-H(14A)	0.9900	C(14)-H(14B)	0.9900
C(15)-H(15A)	0.9500	C(16)-H(16A)	0.9900
C(16)-H(16B)	0.9900	C(17)-H(17A)	0.9900
C(17)-H(17B)	0.9900	C(18)-H(18A)	0.9900
C(18)-H(18B)	0.9900	C(20)-H(20A)	0.9900
C(20)-H(20B)	0.9900	C(21)-H(21A)	0.9900
C(21)-H(21B)	0.9900	C(23)-H(23A)	0.9900
C(23)-H(23B)	0.9900	C(24)-H(24A)	0.9900
C(24)-H(24B)	0.9900	C(25)-H(25A)	0.9900
C(25)-H(25B)	0.9900	C(26)-H(26A)	0.9900
C(26)-H(26B)	0.9900	C(27)-H(27A)	0.9900
C(27)-H(27B)	0.9900	O(1W)-H(1WA)	0.899(10)
O(1W)-H(1WB)	0.900(10)		

Symmetry transformations used to generate equivalent atoms:

Table S6. Bond angles [°] for **5b**.

atom-atom-atom	angle	atom-atom-atom	angle
O(5)-Fe(1)-O(8)	92.2(3)	O(5)-Fe(1)-O(1)	95.1(2)
O(8)-Fe(1)-O(1)	92.9(3)	O(5)-Fe(1)-O(6)	78.9(2)

O(8)-Fe(1)-O(6)	97.6(3)	O(1)-Fe(1)-O(6)	168.1(3)
O(5)-Fe(1)-O(2)	97.0(3)	O(8)-Fe(1)-O(2)	167.9(3)
O(1)-Fe(1)-O(2)	78.6(3)	O(6)-Fe(1)-O(2)	91.8(3)
O(5)-Fe(1)-O(9)	167.6(2)	O(8)-Fe(1)-O(9)	79.6(3)
O(1)-Fe(1)-O(9)	94.6(2)	O(6)-Fe(1)-O(9)	92.9(2)
O(2)-Fe(1)-O(9)	92.4(3)	N(1)-O(1)-Fe(1)	112.1(5)
C(1)-O(2)-Fe(1)	113.5(6)	C(4)-O(3)-C(5)	120.9(8)
N(2)-O(5)-Fe(1)	113.0(5)	C(10)-O(6)-Fe(1)	112.0(5)
N(4)-O(8)-Fe(1)	111.7(5)	C(19)-O(9)-Fe(1)	112.3(6)
C(1)-N(1)-O(1)	118.6(7)	C(1)-N(1)-C(27)	126.9(9)
O(1)-N(1)-C(27)	114.3(8)	C(10)-N(2)-O(5)	115.4(7)
C(10)-N(2)-C(9)	128.2(7)	O(5)-N(2)-C(9)	115.4(6)
C(13)-N(3)-C(14)	126.4(9)	C(19)-N(4)-O(8)	117.5(9)
C(19)-N(4)-C(18)	129.6(9)	O(8)-N(4)-C(18)	112.1(8)
C(22)-N(5)-C(23)	123.2(10)	O(2)-C(1)-N(1)	116.8(9)
O(2)-C(1)-C(2)	121.4(9)	N(1)-C(1)-C(2)	121.7(8)
C(1)-C(2)-C(3)	111.0(8)	C(4)-C(3)-C(2)	113.3(9)
O(4)-C(4)-O(3)	123.5(9)	O(4)-C(4)-C(3)	123.4(9)
O(3)-C(4)-C(3)	113.1(9)	O(3)-C(5)-C(6)	112.1(8)
C(7)-C(6)-C(5)	115.0(8)	C(6)-C(7)-C(8)	113.9(8)
C(9)-C(8)-C(7)	115.3(8)	N(2)-C(9)-C(8)	114.1(8)
O(6)-C(10)-N(2)	120.0(8)	O(6)-C(10)-C(11)	119.7(8)
N(2)-C(10)-C(11)	120.3(8)	C(10)-C(11)-C(12)	113.3(8)
C(13)-C(12)-C(11)	114.1(8)	O(7)-C(13)-N(3)	121.5(10)
O(7)-C(13)-C(12)	121.3(9)	N(3)-C(13)-C(12)	117.2(9)
N(3)-C(14)-C(15)	112.9(9)	C(14)-C(15)-C(16)	116.8(10)
C(17)-C(16)-C(15)	111.4(10)	N(4)-C(18)-C(17)	109.8(9)
O(9)-C(19)-N(4)	118.6(9)	O(9)-C(19)-C(20)	121.6(9)
N(4)-C(19)-C(20)	119.7(10)	C(19)-C(20)-C(21)	111.8(8)
C(22)-C(21)-C(20)	113.5(8)	O(10)-C(22)-N(5)	124.4(10)
O(10)-C(22)-C(21)	121.5(10)	N(5)-C(22)-C(21)	114.1(10)
N(5)-C(23)-C(24)	112.0(9)	C(23)-C(24)-C(25)	114.5(9)
C(26)-C(25)-C(24)	112.6(9)	C(27)-C(26)-C(25)	115.1(8)
C(26)-C(27)-N(1)	112.4(7)	C(13)-N(3)-H(3C)	116.8
C(14)-N(3)-H(3C)	116.8	C(22)-N(5)-H(5C)	118.4
C(23)-N(5)-H(5C)	118.4	C(1)-C(2)-H(2A)	109.4
C(3)-C(2)-H(2A)	109.4	C(1)-C(2)-H(2B)	109.4
C(3)-C(2)-H(2B)	109.4	H(2A)-C(2)-H(2B)	108.0
C(4)-C(3)-H(3A)	108.9	C(2)-C(3)-H(3A)	108.9
C(4)-C(3)-H(3B)	108.9	C(2)-C(3)-H(3B)	108.9
H(3A)-C(3)-H(3B)	107.7	O(3)-C(5)-H(5A)	109.2
C(6)-C(5)-H(5A)	109.2	O(3)-C(5)-H(5B)	109.2
C(6)-C(5)-H(5B)	109.2	H(5A)-C(5)-H(5B)	107.9
C(7)-C(6)-H(6A)	108.5	C(5)-C(6)-H(6A)	108.5
C(7)-C(6)-H(6B)	108.5	C(5)-C(6)-H(6B)	108.5
H(6A)-C(6)-H(6B)	107.5	C(6)-C(7)-H(7A)	108.8

C(8)-C(7)-H(7A)	108.8	C(6)-C(7)-H(7B)	108.8
C(8)-C(7)-H(7B)	108.8	H(7A)-C(7)-H(7B)	107.7
C(9)-C(8)-H(8A)	108.5	C(7)-C(8)-H(8A)	108.5
C(9)-C(8)-H(8B)	108.5	C(7)-C(8)-H(8B)	108.5
H(8A)-C(8)-H(8B)	107.5	N(2)-C(9)-H(9A)	108.7
C(8)-C(9)-H(9A)	108.7	N(2)-C(9)-H(9B)	108.7
C(8)-C(9)-H(9B)	108.7	H(9A)-C(9)-H(9B)	107.6
C(10)-C(11)-H(11A)	108.9	C(12)-C(11)-H(11A)	108.9
C(10)-C(11)-H(11B)	108.9	C(12)-C(11)-H(11B)	108.9
H(11A)-C(11)-H(11B)	107.7	C(13)-C(12)-H(12A)	108.7
C(11)-C(12)-H(12A)	108.7	C(13)-C(12)-H(12B)	108.7
C(11)-C(12)-H(12B)	108.7	H(12A)-C(12)-H(12B)	107.6
N(3)-C(14)-H(14A)	109.0	C(15)-C(14)-H(14A)	109.0
N(3)-C(14)-H(14B)	109.0	C(15)-C(14)-H(14B)	109.0
H(14A)-C(14)-H(14B)	107.8	C(14)-C(15)-H(15A)	121.6
C(16)-C(15)-H(15A)	121.6	C(17)-C(16)-H(16A)	109.3
C(15)-C(16)-H(16A)	109.3	C(17)-C(16)-H(16B)	109.3
C(15)-C(16)-H(16B)	109.3	H(16A)-C(16)-H(16B)	108.0
C(16)-C(17)-C(18)	113.4(9)	C(16)-C(17)-H(17A)	108.9
C(18)-C(17)-H(17A)	108.9	C(16)-C(17)-H(17B)	108.9
C(18)-C(17)-H(17B)	108.9	H(17A)-C(17)-H(17B)	107.7
N(4)-C(18)-H(18A)	109.7	C(17)-C(18)-H(18A)	109.7
N(4)-C(18)-H(18B)	109.7	C(17)-C(18)-H(18B)	109.7
H(18A)-C(18)-H(18B)	108.2	C(19)-C(20)-H(20A)	109.3
C(21)-C(20)-H(20A)	109.3	C(19)-C(20)-H(20B)	109.3
C(21)-C(20)-H(20B)	109.3	H(20A)-C(20)-H(20B)	107.9
C(22)-C(21)-H(21A)	108.9	C(20)-C(21)-H(21A)	108.9
C(22)-C(21)-H(21B)	108.9	C(20)-C(21)-H(21B)	108.9
H(21A)-C(21)-H(21B)	107.7	N(5)-C(23)-H(23A)	109.2
C(24)-C(23)-H(23A)	109.2	N(5)-C(23)-H(23B)	109.2
C(24)-C(23)-H(23B)	109.2	H(23A)-C(23)-H(23B)	107.9
C(23)-C(24)-H(24A)	108.6	C(25)-C(24)-H(24A)	108.6
C(23)-C(24)-H(24B)	108.6	C(25)-C(24)-H(24B)	108.6
H(24A)-C(24)-H(24B)	107.6	C(26)-C(25)-H(25A)	109.1
C(24)-C(25)-H(25A)	109.1	C(26)-C(25)-H(25B)	109.1
C(24)-C(25)-H(25B)	109.1	H(25A)-C(25)-H(25B)	107.8
C(27)-C(26)-H(26A)	108.5	C(25)-C(26)-H(26A)	108.5
C(27)-C(26)-H(26B)	108.5	C(25)-C(26)-H(26B)	108.5
H(26A)-C(26)-H(26B)	107.5	C(26)-C(27)-H(27A)	109.1
N(1)-C(27)-H(27A)	109.1	C(26)-C(27)-H(27B)	109.1
N(1)-C(27)-H(27B)	109.1	H(27A)-C(27)-H(27B)	107.9
H(1WA)-O(1W)-H(1WB)	110(3)		

Symmetry transformations used to generate equivalent atoms:

Table S7. Torsion angles [°] for **5b**.

atom-atom-atom-atom	angle	atom-atom-atom-atom	angle
O(5)-Fe(1)-O(1)-N(1)	-91.6(5)	O(8)-Fe(1)-O(1)-N(1)	176.0(5)
O(6)-Fe(1)-O(1)-N(1)	-32.2(15)	O(2)-Fe(1)-O(1)-N(1)	4.6(5)
O(9)-Fe(1)-O(1)-N(1)	96.2(5)	O(5)-Fe(1)-O(2)-C(1)	88.6(6)
O(8)-Fe(1)-O(2)-C(1)	-51.2(14)	O(1)-Fe(1)-O(2)-C(1)	-5.2(6)
O(6)-Fe(1)-O(2)-C(1)	167.7(6)	O(9)-Fe(1)-O(2)-C(1)	-99.4(6)
O(8)-Fe(1)-O(5)-N(2)	-90.1(6)	O(1)-Fe(1)-O(5)-N(2)	176.9(6)
O(6)-Fe(1)-O(5)-N(2)	7.3(5)	O(2)-Fe(1)-O(5)-N(2)	97.7(5)
O(9)-Fe(1)-O(5)-N(2)	-42.0(16)	O(5)-Fe(1)-O(6)-C(10)	-5.8(6)
O(8)-Fe(1)-O(6)-C(10)	85.0(6)	O(1)-Fe(1)-O(6)-C(10)	-66.5(14)
O(2)-Fe(1)-O(6)-C(10)	-102.6(6)	O(9)-Fe(1)-O(6)-C(10)	164.9(6)
O(5)-Fe(1)-O(8)-N(4)	175.6(5)	O(1)-Fe(1)-O(8)-N(4)	-89.1(5)
O(6)-Fe(1)-O(8)-N(4)	96.5(5)	O(2)-Fe(1)-O(8)-N(4)	-44.2(14)
O(9)-Fe(1)-O(8)-N(4)	5.0(5)	O(5)-Fe(1)-O(9)-C(19)	-54.0(15)
O(8)-Fe(1)-O(9)-C(19)	-4.9(5)	O(1)-Fe(1)-O(9)-C(19)	87.2(6)
O(6)-Fe(1)-O(9)-C(19)	-102.1(6)	O(2)-Fe(1)-O(9)-C(19)	166.0(5)
Fe(1)-O(1)-N(1)-C(1)	-3.8(9)	Fe(1)-O(1)-N(1)-C(27)	-179.9(5)
Fe(1)-O(5)-N(2)-C(10)	-8.0(10)	Fe(1)-O(5)-N(2)-C(9)	-177.6(6)
Fe(1)-O(8)-N(4)-C(19)	-4.8(8)	Fe(1)-O(8)-N(4)-C(18)	-175.6(6)
Fe(1)-O(2)-C(1)-N(1)	4.8(10)	Fe(1)-O(2)-C(1)-C(2)	-178.7(7)
O(1)-N(1)-C(1)-O(2)	-0.7(11)	C(27)-N(1)-C(1)-O(2)	174.8(7)
O(1)-N(1)-C(1)-C(2)	-177.2(7)	C(27)-N(1)-C(1)-C(2)	-1.7(14)
O(2)-C(1)-C(2)-C(3)	45.1(12)	N(1)-C(1)-C(2)-C(3)	-138.6(9)
C(1)-C(2)-C(3)-C(4)	63.0(10)	C(5)-O(3)-C(4)-O(4)	-3.2(14)
C(5)-O(3)-C(4)-C(3)	176.7(7)	C(2)-C(3)-C(4)-O(4)	9.6(13)
C(2)-C(3)-C(4)-O(3)	-170.2(8)	C(4)-O(3)-C(5)-C(6)	-97.4(10)
O(3)-C(5)-C(6)-C(7)	62.4(11)	C(5)-C(6)-C(7)-C(8)	-179.8(8)
C(6)-C(7)-C(8)-C(9)	179.3(8)	C(10)-N(2)-C(9)-C(8)	-73.7(12)
O(5)-N(2)-C(9)-C(8)	94.3(9)	C(7)-C(8)-C(9)-N(2)	-55.5(10)
Fe(1)-O(6)-C(10)-N(2)	3.2(11)	Fe(1)-O(6)-C(10)-C(11)	-177.1(7)
O(5)-N(2)-C(10)-O(6)	3.1(13)	C(9)-N(2)-C(10)-O(6)	171.1(8)
O(5)-N(2)-C(10)-C(11)	-176.6(8)	C(9)-N(2)-C(10)-C(11)	-8.7(15)
O(6)-C(10)-C(11)-C(12)	41.5(12)	N(2)-C(10)-C(11)-C(12)	-138.8(9)
C(10)-C(11)-C(12)-C(13)	62.3(10)	C(14)-N(3)-C(13)-O(7)	5.5(15)
C(14)-N(3)-C(13)-C(12)	-175.0(8)	C(11)-C(12)-C(13)-O(7)	31.1(13)
C(11)-C(12)-C(13)-N(3)	-148.3(8)	C(13)-N(3)-C(14)-C(15)	-140.2(10)
N(3)-C(14)-C(15)-C(16)	56.5(14)	C(14)-C(15)-C(16)-C(17)	62.6(15)
C(15)-C(16)-C(17)-C(18)	175.6(10)	C(19)-N(4)-C(18)-C(17)	-93.3(11)
O(8)-N(4)-C(18)-C(17)	76.1(10)	C(16)-C(17)-C(18)-N(4)	61.0(13)
Fe(1)-O(9)-C(19)-N(4)	3.7(9)	Fe(1)-O(9)-C(19)-C(20)	179.9(6)
O(8)-N(4)-C(19)-O(9)	0.6(11)	C(18)-N(4)-C(19)-O(9)	169.5(8)
O(8)-N(4)-C(19)-C(20)	-175.6(7)	C(18)-N(4)-C(19)-C(20)	-6.7(14)
O(9)-C(19)-C(20)-C(21)	46.2(11)	N(4)-C(19)-C(20)-C(21)	-137.7(9)

C(19)-C(20)-C(21)-C(22)	65.4(11)	C(23)-N(5)-C(22)-O(10)	-7.4(17)
C(23)-N(5)-C(22)-C(21)	176.0(9)	C(20)-C(21)-C(22)-O(10)	16.1(15)
C(20)-C(21)-C(22)-N(5)	-167.2(9)	C(22)-N(5)-C(23)-C(24)	-98.5(13)
N(5)-C(23)-C(24)-C(25)	58.3(13)	C(23)-C(24)-C(25)-C(26)	179.5(9)
C(24)-C(25)-C(26)-C(27)	-178.6(8)	C(25)-C(26)-C(27)-N(1)	-55.1(11)
C(1)-N(1)-C(27)-C(26)	-79.1(12)	O(1)-N(1)-C(27)-C(26)	96.6(9)

Symmetry transformations used to generate equivalent atoms:

Table S8. Hydrogen bonds for **5b** [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
N(3)-H(3C)...O(1)#1	0.88	2.04	2.919(10)	175.4
N(5)-H(5C)...O(7)#2	0.88	2.23	3.043(12)	153.1
O(1W)-H(1WA)...O(9)	0.899(10)	2.24(4)	3.101(10)	161(9)
O(1W)-H(1WA)...O(2)	0.899(10)	2.57(7)	3.109(9)	119(6)
O(1W)-H(1WB)...O(7)#2	0.900(10)	1.902(18)	2.793(10)	170(7)

Symmetry transformations used to generate equivalent atoms:

#1 x-, y, z #2 x, y-1, z

XIII. Acknowledgements

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XIV. References

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