Electronic Supplementary Information (ESI)

Effect of a *cis*-4-Aminopiperidine-3-carboxylic Acid (*cis*-APiC) Residue on Mixed-helical Folding of Unnatural Peptides

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Synthesis and Characterization Data

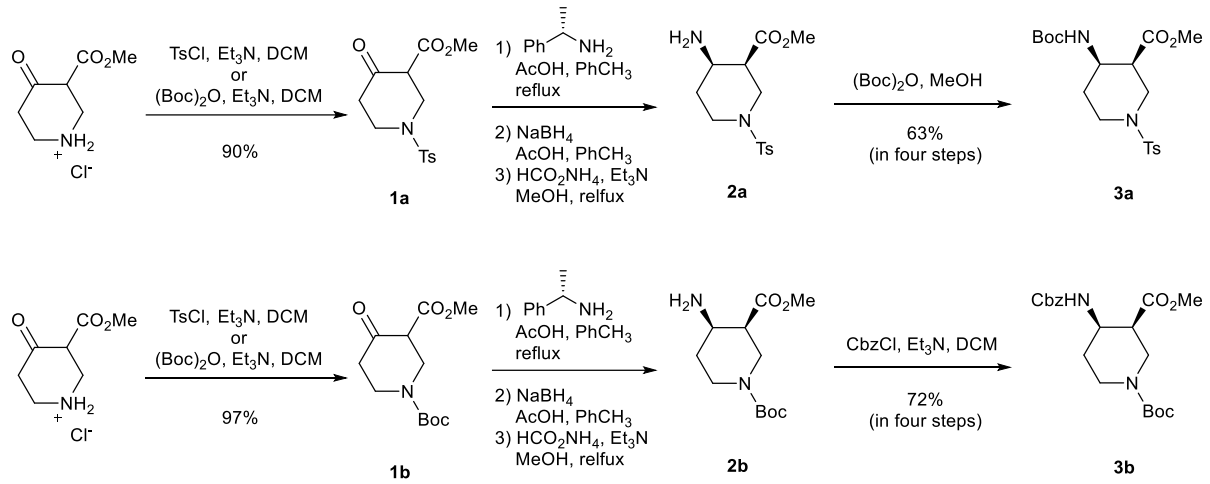
General

α-Amino acids and 1-ethyl-3-(3-dimethylaminopropyl)-carbodiimide (EDCI) were purchased from Chem-Impex International. Other reagents were purchased from Sigma-Aldrich, Alfa Aesar, Samchun Chemical, and TCI. Yields were not optimized.

Synthesis of APiC monomers

Two APiC monomers, **3a** and **3b** were prepared by a method slightly modified from the known procedure (Scheme 1; *Eur. J. Org. Chem.*, 2003, **2003**, 721).

Scheme S1. Synthesis of APiC monomers.



(3*S*, 4*R*)-Methyl-4-*tert*-butoxycarbonyl-1-tosylaminopiperidine-3-carboxylate (3a)

To a solution of methyl 4-oxopiperidine-3-carboxylate hydrochloride (1.00 g, 5.16 mmol) in DCM (40 mL), TEA (0.87 mL, 6.2 mmol) and *p*-TsCl (1.5 g, 7.7 mmol) were added at rt and was stirred for 2 d. The reaction mixture was extracted with EtOAc, washed with brine, dried over anhydrous $MgSO_4$ and then filtered through Celite pad. The organic layer was concentrated under reduced pressure to give a crude product, which was purified by flash column chromatography (hexane : EtOAc = 15:1) to afford product **1a** as a yellow oil (1.45 g, 4.67 mmol, 90%), R_f = 0.3 (hexane : EtOAc = 7:1).

N-Tosyl compound **1a** (1.45 g, 4.67 mmol), (R)-(+)-*α*-methylbenzylanmine (0.86 mL, 6.64 mmol), gracial acetic acid (0.40 mL, 6.64 mmol) and toluene (125 mL) were mixed in a three-necked round-bottomed flask. The reaction mixture was stirred for 10 min at rt, and stirred under reflux for 6 h with azeotropic removal of water. The reaction mixture was cooled to room temperature. The fitted Dean-stark apparatus was replaced with a distillation apparatus. The mixture was heated at 130 °C to distill off toluene. The mixture was cooled to room temperature and distillation apparatus was removed. The mixture was diluted with glacial acetic acid, cooled to 0 °C in an ice bath. Sodium borohydride (0.53 g, 14 mmol) was slowly added in four portions over 2 h period to the cold mixture with vigorous stirring, maintaining the internal temperature below 50 °C. The ice bath was removed and the mixture was stirred for additional 2 h at rt. The mixture was cooled in an ice bath, followed by a slow addition of water with vigorous stirring, maintaining the internal temperature below 50 °C. The pH of the mixture was adjusted to 9.0 by the addition of aqueous 10 M sodium hydroxide solution, maintaining the internal temperature below 30 °C. And then reaction mixture was extracted with EtOAc and successively washed with 10% citric acid, brine, saturated $NaHCO_3$ and brine. The organic fraction was dried over anhydrous $MgSO_4$, filtered, and concentrated under reduced pressure. The residue was purified by flash column chromatography (hexane:EtOAc = 4:1) to afford the *N*-(1-phenylethyl)-protected APiC derivative as yellow oil in quantitative yield (~ 2 g, 4.67 mmol from **1a**), R_f = 0.3 (hexane : EtOAc = 4:1).

Pd/C (4.9 g) is suspended in a mixture of methanol (200 mL) and acetic acid (1.4 mL, 25 mmol) under nitrogen purging. HCO_2NH_4 (1.6 g, 25 mmol) and the APiC derivative (~ 2 g, 4.67 mmol from **1a**) was added and then the mixture was refluxed for 9 h. The resulting mixture was filtered through Celite pad and washed with methanol. The filtrate was concentrated under reduced pressure to give **2a**, which was directly used for the next step without purification.

To a stirred a solution of **2a** (4.67 mmol from **1a**) in methanol (100 mL), di-*tert*-butyl dicarbonate (1.61 g, 7.38 mmol) were added. The reaction mixture was stirred overnignt at rt and then concentrated under reduced pressure to remove methanol. The resulting mixture was extracted two times with EtOAc and washed with brine. The organic fraction was dried over anhydrous $MgSO_4$, filtered, and concentrated under reduced pressure. The resulting oil was purified by flash column chromatography (hexane:EtOAc = 10:1) to afford **3a** as a colorless solid (1.22 g, 2.96 mmol, 63% in four steps from **1a**), R_f = 0.45 (hexane: EtOAc = 2:1): ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.63 (d, 2H, *J* = 8.2 Hz), 7.34 (d, 2H, *J* = 8.0 Hz), 5.45 (d, 1H, *J* = 7.2 Hz), 3.91 (d, 1H, *J* = 7.9 Hz), 3.80-3.67 (m, 2H), 3.74 (s, 1H), 3.5 (s, 1H), 2.86 (q, 1H), 2.70 (d, 1H, *J* = 10 Hz), 2.59 (t, 1H), 2.45 (s, 3H), 2.08-2.03 (m, 1H), 1.82-1.77 (m, 1H), 1.45 (s, 1H), 1.40 (s, 9H); ^{13}C ($CDCl_3$, 100 MHz) δ 171.8, 155.1, 143.9, 132.9, 129.8 (2C), 127.6 (2C), 79.7, 52.2, 47.4, 47.3, 45.2, 43.9, 26.8, 28.3 (3C), 21.6.

(3*S*, 4*R*)-Methyl-4-benzyloxycarbonyl-1-*tert*-butoxycarbonylaminopiperidine-3-carboxylate (3b)

To a solution of methyl 4-oxopiperidine-3-carboxylate hydrochloride (736 mg, 3.80 mmol) in DCM (23 mL), TEA (0.58 mL, 4.20 mmol) and di-*tert*-butyl dicarbonate (912 mg, 4.20 mmol) were added at rt and was stirred for 12 h. The reaction mixture was extracted with EtOAc, washed with brine, dried over anhydrous $MgSO_4$ and then filtered through Celite pad. The organic layer was concentrated under reduced pressure to give a crude product, which was purified by flash column chromatography (hexane : EtOAc = 5:1) to afford product **1b** as a yellow oil (950 mg, 3.68 mmol, 97%), R_f = 0.67 (hexane : EtOAc = 4:1).

N-Boc compound **1b** (720 mg, 2.00 mmol) was converted to **2b** by the same method described for the conversion of **1a** to **2a**. To a solution of **2b** (2.00 mmol from **1b**) in DCM (10 mL), benzyl chloroformate (0.31 mL, 2.2 mmol) and TEA (0.31 mL, 2.2 mmol) were added at 0 °C. The mixture was stirred at rt for 12h. The resulting mixture was extracted with EtOAc and then washed with brine. The organic layer was dried over anhydrous $MgSO_4$, filtered, and concentrated under reduced pressure. The residue was purified by flash column chromatography (hexane:EtOAc = 4:1) to afford **3b** as an colorless oil (565 mg, 1.45 mmol, 72% in four steps from **1b**), R_f = 0.3 (hexane:EtOAc = 4:1), ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40-7.30 (m,5H), 5.61 (d, *J* = 8.3 Hz,,1H), 5.09 (d, *J* = 2.7 Hz, 2H), 4.40 (d, *J* = 13.7 Hz, 1H), 3.97 (m, 2H), 3.69 (s, 3H), 3.10 (d, *J* = 13.3Hz, 1H), 3.00-2.87 (m, 2H), 2.83 (m, 1H), 2.08-1.92 (m, 1H), 1.77-1.66 (m, 1H), 1.43 (s, 9H); ^{13}C NMR (100MHz, $CDCl_3$) δ 155.70, 136.37, 128.60, 128.56, 128.49, 128.16, 127.69, 127.01, 126.58, 79.87, 68.82, 65.42, 28.32, 14.57; HRMS m/z $C_{20}H_{28}N_2O_6$, calculated for $[M+Na]^+$ 415.1845, found 415.1806.

General procedures

- Saponification: The amino acid (1 eq) was dissolved in MeOH and THF (v:v = 1:1). LiOH (5 eq) was dissolved in MeOH and H_2O (v:v = 1:1) and added to the solution of the amino acid. The mixture was stirred overnight at 0°C. After reaction, the pH of the mixture was adjusted to pH 1 by the addition of aqueous 1 M HCl and extracted with EtOAc at the 3 times. The organic solution was dried over $MgSO_4$, filtered, and was concentrated in vacuo.

- Boc group deprotection: To a solution of the *N*-Boc compound (1 eq), 4 M HCl in dioxane (1mL/1 mmol of the compound) was slowly added and then the mixture was stirred for 2 h. The mixture was concentrated by blowing N_2 gas stream.

- Cbz group deprotection: Pd/C (10% w/w) was added to MeOH under N_2 gas stream and then the peptide oligomer in MeOH was added. The mixture was charged with H_2 gas in the three overlapping balloons. The mixture stirred for 4 h, filtered through Celite pad, and washed with MeOH. The filtrate was concentrated under reduced pressure.

- Peptide coupling: To a solution of the amine (1 eq) and the carboxylic acid (1 eq) in DCM or DMF, EDCI (1.5

eq), HOBt (1.3 eq) and TEA (1.3 eq) were added. The reaction mixture was stirred for overnight. The mixture was washed successively with aqueous 10% w/w citric acid, aqueous saturated $NaHCO_3$ and brine. The orgarnic layer was dried over $MgSO_4$, filtrated and was concentrated in vacuo. The crude product was purified by silica column chromatography.

Unnatural peptides **4-8** were synthesized by a conventional solution-phase peptide synthesis including the general procedures described above.

Boc-^{L}Ala-ACHC-^{L}Ala-(Ts)APiC-^{L}Ala-OMe (4): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (d, *J* = 9.5Hz, 1H), 7.66 (d, *J* = 9.1 Hz, 2H), 7.61 (m, 2H), 7.32 (d, *J* = 8.4 Hz, 2H,), 7.27 (m, 1H), 5.12 (d, *J* = 5.8 Hz, 1H), 4.55 (quin, *J* = 5.6 Hz, 1H), 4.24 (quin, *J* = 6.6 Hz, 1H), 4.18-4.06 (m, 2H), 3.99 (quin, *J* = 7.5 Hz, 1H), 3.86 (d, *J* = 14.4 Hz, 1H), 3.77 (s, 3H), 3.72 (d, *J* = 10.1 Hz, 1H), 2.84-2.60 (m, 3H), 2.55 (d, *J* = 5.8 Hz, 1H), 2.44 (s, 3H), 2.00-1.76 (m, 4H), 1.76-1.50 (m, 4H), 1.45 (d, *J* = 1.64 Hz, 2H), 1.41 (s, 9H), 1.32 (d, *J* = 7.2 Hz, 3H), 1.29-1.24 (m, 3H); ^{13}C NMR ($CDCl_3$, 100MHz) δ 174.67, 172.69, 170.71, 155.85, 143.79, 133.00, 129.73, 127.63, 80.04, 77.23, 52.64, 50.66, 48.71, 45.93, 42.48, 28.29, 27.83, 21.54, 17.66, 16.89, 16.65; MALDI-TOF m/z 673.369 [M-(Boc)+Na^+], 773.583 [M+Na^+], 789.458[M+K^+].

Cbz-^{L}Ala-ACHC-^{L}Ala-(Boc)APiC-^{L}Ala-OMe (5): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (m, 1H), 7.63 (d, *J* = 11.6 Hz, 1H), 7.37-7.28 (m, 5H), 7.12 (d, *J* = 5.9 Hz, 1H) 5.69 (m, 1H), 5.34 (m, 1H), 5.14 (d, *J* = 11.8 Hz, 1H) 5.02 (d, *J* = 12.0 Hz, 1H), 4.62 (quin, *J* = 7.6 Hz, 1H), 4.24-4.09 (m, 4H), 3.74 (s, 3H), 3.71-3.52 (m, 2H), 2.86 (m, 1H), 2.77 (m, 1H), 2.66 (m, 1H), 2.50 (m, 1H), 2.24 (t, *J* = 6.6 Hz, 1H), 2.07-1.93 (m, 2H), 1.86-1.71 (m, 3H), 1.69-1.54 (m, 6H), 1.46 (S, 9H), 1.41 (d, *J* = 7.1 Hz, 3H), 1.36 (d, *J* = 8.0 Hz, 3H), 1.32 (d, *J* = 8.5 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 172.73, 156.33, 154.29, 136.29, 130.05, 129.72, 128.52, 128.18, 127.96, 77.22, 67.02, 52.64, 51.29, 48.64, 18.36, 43.69, 42.71, 31.91, 29.70, 29.52, 29.33, 29.16, 28.46, 28.07, 27.22, 26.77, 25.48, 24.67, 22.69, 17.93, 16.80, 16.30, 14.12; UHRMS m/z $C_{36}H_{54}N_6O_{10}$, calculated for [M+Na]$^+$ 753.3799, found 753.3795.

Cbz-^{L}Ala-ACHC-^{L}Ala-APiC-^{L}Ala-OMe (6): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.78 (d, *J* = 3.9 Hz, 1H), 7.65 (d, *J* = 9.2 Hz, 1H), 7.48 (dd, *J* = 5.1 Hz, 2H), 7.38-7.29 (m, 5H), 5.55 (d, *J* = 9.7 Hz, 1H), 5.13 (d, *J* = 12.2 Hz, 1H) 5.03 (d, *J* = 12.6 Hz, 1H), 4.68 (m, 1H), 4.36 (m, 1H), 4.25-4.13 (m, 2H), 3.94 (quin, *J* = 7.8 Hz, 3H), 3.81 (s, 3H), 3.60-3.50 (m, 2H), 3.22-3.09 (m, 2H), 2.79 (m, 1H), 2.68 (m, 1H), 2.57-2.43 (m, 6H), 2.05-1.88 (m, 4H), 1.83-1.74 (m, 2H), 1.66-1.56 (m, 2H), 1.47 (m, 3H), 1.42 (d, *J* = 6.8 Hz, 3H), 1.34 (d, *J* = 6.8 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100MHz) δ 179.15, 176.79, 175.96, 175.22, 171.00, 156.40, 150.33, 135.25, 131.29, 129.24, 128.57, 127.90, 67.91, 67.91, 67.06, 57.84, 53.69, 48.96, 45.32, 43.55, 41.28, 33.58, 31.92, 29.71, 26.63, 24.51, 18.47, 18.26, 14.84; UHRMS m/z $C_{31}H_{46}N_6O_8$, calculated for [M+H]$^+$ 631.3455, found 631.3453.

Cbz-(1S,2R)-ACHC-(1R,2S)-ACHC-(3S,4R)-(Boc)APiC-(1R,2S)-ACHC-(1S,2R)-NHMe (7): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (m, 3H), 7.40-7.29 (m, 5H), 5.21(m, 2H), 5.04 (d, *J* = 12.6 Hz, 2H), 4.59 (m, 1H), 4.31 (m, 2H), 4.18 (m, 1H), 4.05 (m, 2H), 3.83 (m, 1H), 2.77 (s, 3H), 2.67 (m, 2H), 2.58 (m, 2H), 2.83 (m, 1H), 2.41 (m, 1H), 2.02-1.29 (m, 32H), 1.43 (s, 9H); ^{13}C NMR ($CDCl_3$, 100MHz) δ 176.13, 175.27, 173.37, 172.57, 171.54, 156.53, 154.49, 136.74, 128.42, 127.91, 127.72, 79.42, 77.30, 66.53, 47.21, 43.35, 31.92, 29.70, 29.15, 28.44, 26.22, 22.70, 21.04, 14.15; HRMS m/z $C_{48}H_{73}N_7O_9$, calculated for [M+H]$^+$ 892.5548, found 892.5538.

Cbz-(1S,2R)-ACHC-(1R,2S)-ACHC-(3S,4R)-APiC-(1R,2S)-ACHC-(1S,2R)-NHMe (8): ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.68 (m, 1H), 8.77 (m, 1H), 8.4 8(d, *J* = 10.0 Hz, 1H), 8.33 (br, 1H), 7.84 (br, 1H), 7.42-7.29 (m, 4H), 7.17 (d, *J* = 13.6 Hz, 1H), 6.90 (m, 1H), 6.13 (m, 1H), 5.22 (d, *J* = 11.2 Hz, 2H), 5.07 (d, *J* = 12.5Hz, 2H), 4.75 (d, *J* = 9.2 Hz, 1H), 4.46 (d, *J* = 8.5 Hz, 1H), 4.40 (m, 1H), 3.87 (m, 2H), 2.91 (d, *J* = 15.4 Hz, 2H), 2.78 (s, 3H), 2.74-2.55 (br m, 3H), 2.47 (d, *J* = 11.3 Hz, 1H), 2.40 (d, *J* = 11.6 Hz, 1H), 2.17 (q, *J* = 10.1 Hz, 2H), 2.06-1.97 (m, 2H), 1.86-1.51 (m, 18H), 1.51-1.31 (m, 8H); ^{13}C NMR ($CDCl_3$, 100MHz) δ 176.29, 173.96, 173.55, 156.23, 136.79, 128.55, 128.20, 66.66, 50.52, 48.31, 47.39, 46.15, 46.01, 43.54, 30.13, 29.73, 29.30, 28.88, 27.63, 26.21, 24.84, 24.70, 24.10, 22.96, 22.71, 21.55, 20.33, 19.40; HRMS m/z $C_{43}H_{65}N_7O_7$, calculated for [M+Na]$^+$ 814.4843, found 814.4826.

Single-crystal X-ray crystallography

Table S1. Crystallization condition and CCDC deposition numbers.

CCDC number	compound	crystallization condition
1923144	**3a**	Solvent diffusion ($CHCl_3$, pentane)
1923145	**4**	Solvent diffusion ($CHCl_3$, pentane)
2120488	**7**	Solvent diffusion ($CHCl_3$, hexane)

Table S2. Backbone torsion angles (˚) for **4**.

	Residue	Φ	Θ	Ψ
N-term	^{L}Ala	-51	-	149
	ACHC	77	66	-82
	^{L}Ala	-70	-	-33
	ACPC(Ts)	158	53	129
C-term	^{L}Ala	-75	-	172

Table S3. Backbone torsion angles (˚) for **7**.

	Residue	Φ	Θ	Ψ
N-term	ACHC	155.46	53.41	-144.22
	ACHC	-88.57	47.73	99.59
	APiC(Boc)	103.6	55.05	-96.76
	ACHC	-98.84	48.86	89.6
C-term	ACHC	123.97	59.14	165.65

Crystal structure report

• Compound **3a**

Data Collection

A colorless crystal with approximate dimensions 0.2 × 0.1 × 0.1 mm^3 was selected under oil under ambient conditions and attached to the tip of a MiTeGen MicroMount©. The crystal was mounted in a stream of cold nitrogen at 220 K and centered in the X-ray beam by using a video camera.

The crystal evaluation and data collection were performed on a Bruker D8 Venture diffractometer with Mo K_α (λ = 0.71073 Å) radiation and the diffractometer to crystal distance of 4.00 cm.

The initial cell constants were obtained from two series of ω scans at different starting angles. Each series consisted of 12 frames collected at intervals of 0.5º in a 6º range about ω with the exposure time of 2 seconds per frame. The reflections were successfully indexed by an automated indexing routine built in the APEXII program. The final cell constants were calculated from a set of 9910 strong reflections from the actual data collection.

The data were collected by using the half sphere data collection routine to survey the reciprocal space to the extent of a half sphere to a resolution of 0.81 Å. A total of 32324 data were harvested by collecting 2 sets of frames with 0.5º scans in ω and φ with an exposure time 3 sec per frame. These highly redundant datasets were corrected for Lorentz and polarization effects. The absorption correction was based on fitting a function to the empirical transmission surface as sampled by multiple equivalent measurements. [S1]

Structure Solution and Refinement

The systematic absences in the diffraction data were uniquely consistent for the space group $P2_1$ that yielded chemically reasonable and computationally stable results of refinement [S2-3].

A successful solution by the direct methods provided most non-hydrogen atoms from the *E*-map. The remaining non-hydrogen atoms were located in an alternating series of least-squares cycles and difference Fourier maps. All non-hydrogen atoms were refined with anisotropic displacement coefficients. All hydrogen atoms were included in the structure factor calculation at idealized positions and were allowed to ride on the neighboring atoms with relative isotropic displacement coefficients.

The final least-squares refinement of 523 parameters against 8457 data resulted in residuals *R* (based on F^2 for $I \geq 2\sigma$) and *wR* (based on F^2 for all data) of 0.0380 and 0.0796, respectively. The final difference Fourier map was featureless.

Summary

Crystal Data for $C_{38}H_{56}N_4O_{12}S_2$ (M =824.98): monoclinic, space group $P2_1$ (no. 4), a = 11.3198(4) Å, b = 16.1408(4) Å, c = 12.8871(6) Å, β = 112.5962(9)°, V = 2173.87(13) $Å^3$, Z = 2, T = 220.0 K, μ(MoKα) = 0.184 mm^{-1}, *Dcalc* = 1.260 g/mm^3, 32324 reflections measured ($4.644 \leq 2\Theta \leq 52.084$), 8457 unique ($R_{int}$ = 0.0397, R_{sigma} = 0.0378) which were used in all calculations. The final R_1 was 0.0380 ($I > 2\sigma(I)$) and wR_2 was 0.0796 (all data).

Table S4. Crystal data and structure refinement for **3a**.

Empirical formula	$C_{38}H_{56}N_4O_{12}S_2$
Formula weight	824.98
Temperature/K	220.0
Crystal system	monoclinic
Space group	$P2_1$
a/Å	11.3198(4)
b/Å	16.1408(4)
c/Å	12.8871(6)
α/°	90
β/°	112.5962(9)
γ/°	90
Volume/Å^3	2173.87(13)
Z	2
ρ_{calc}mg/mm^3	1.260
m/mm^{-1}	0.184
F(000)	880.0
Crystal size/mm^3	0.2 × 0.1 × 0.1
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection	4.644 to 52.084°
Index ranges	$-13 \leq h \leq 13$, $-19 \leq k \leq 19$, $-15 \leq l \leq 15$
Reflections collected	32324
Independent reflections	8457 [R_{int} = 0.0397, R_{sigma} = 0.0378]
Data/restraints/parameters	8457/1/523
Goodness-of-fit on F^2	1.023
Final R indexes [I>=2σ (I)]	R_1 = 0.0380, wR_2 = 0.0725
Final R indexes [all data]	R_1 = 0.0597, wR_2 = 0.0796
Largest diff. peak/hole / e Å^{-3}	0.20/-0.23
Flack parameter	0.03(2)

Table S5. Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for **3a**. U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{IJ} tensor.

Atom	***x***	***y***	***z***	**U(eq)**
S17	18046.5(9)	-827.7(5)	6807.7(8)	46.6(2)
O2	14226(2)	-392.1(16)	6964(2)	59.2(7)
O12	15558(2)	1641.5(12)	10980.3(18)	40.7(5)
O25	14651(3)	951.6(16)	7292(2)	61.9(7)
O26	16457(2)	360.5(13)	11199(2)	45.4(6)
O27	18648(3)	-1546.0(16)	7447(2)	58.9(7)
O28	18770(3)	-330.8(17)	6348(3)	67.3(8)
N6	17488(3)	-208.7(15)	7526(2)	36.2(6)
N10	16299(3)	1187.4(17)	9734(2)	39.4(7)
C1	13088(4)	-187(3)	6005(4)	77.9(14)
C3	14934(3)	244(2)	7545(3)	40.1(8)
C4	16064(3)	-70.3(17)	8542(3)	33.9(7)
C5	16868(3)	-667.9(17)	8170(3)	34.6(7)
C7	18367(3)	450(2)	8185(3)	45.7(9)
C8	17623(3)	1049(2)	8613(3)	44.8(9)
C9	16944(3)	602.8(18)	9264(3)	34.7(7)
C11	16133(3)	1004.1(18)	10680(3)	35.3(7)
C13	15286(3)	1602(2)	12004(3)	39.4(8)
C14	14304(4)	937(3)	11883(4)	68.4(12)
C15	14718(4)	2453(2)	12012(3)	55.6(10)
C16	16513(4)	1490(3)	13024(3)	66.6(12)
C18	16607(4)	-1150(2)	5717(3)	47.0(9)
C19	16305(4)	-1980(2)	5581(3)	57.5(10)
C20	15155(5)	-2217(3)	4729(4)	70.7(13)
C21	14321(5)	-1652(3)	4027(3)	68.2(12)
C22	14676(5)	-834(3)	4171(4)	71.7(12)
C23	15806(4)	-579(3)	5011(4)	64.4(11)
C24	13070(5)	-1932(4)	3139(4)	101.8(19)
S46	9595.5(8)	2295.2(5)	5672.4(7)	39.0(2)
O3	16152(2)	2912.4(13)	9155.3(19)	43.0(6)
O5	11921(2)	3514.9(15)	9159(2)	51.3(6)
O31	11655(2)	2166.5(15)	9389(2)	53.3(6)
O41	16203.8(19)	4133.5(13)	10048.3(19)	42.4(5)
O54	9128(2)	1783.6(16)	6334(2)	53.1(6)
O55	8888(2)	3005.3(16)	5112(2)	54.2(7)
N35	10998(2)	2634.2(15)	6515(2)	33.7(6)
N39	14367(3)	3667.6(18)	8840(2)	42.1(7)
C30	10876(4)	2373(3)	10005(4)	75.1(13)
C32	12100(3)	2809(2)	8980(2)	36.1(7)
C33	12826(3)	2496.4(18)	8290(3)	33.9(7)
C34	11902(3)	2030.6(18)	7259(3)	35.7(7)
C36	11654(3)	3230.0(19)	6053(2)	38.0(7)
C37	12588(3)	3730.1(19)	7019(3)	39.5(8)
C38	13518(3)	3172.1(19)	7910(3)	35.6(7)
C40	15622(3)	3517.1(19)	9332(3)	33.1(7)
C42	17587(3)	4115(2)	10725(3)	40.5(8)
C43	17890(4)	3406(3)	11545(4)	76.1(14)
C44	18328(4)	4085(3)	9977(4)	64.7(11)
C45	17812(4)	4941(2)	11337(4)	61.1(11)

C47	9850(3)	1665(2)	4660(2)	35.5(7)
C48	10041(3)	2030(2)	3765(3)	45.7(9)
C49	10249(4)	1541(2)	2981(3)	56.7(10)
C50	10283(4)	686(2)	3065(3)	52.8(10)
C51	10121(3)	331(2)	3975(3)	48.3(9)
C52	9903(3)	811.1(19)	4780(3)	41.6(8)
C53	10479(5)	153(3)	2185(4)	85.1(15)

Table S6. Anisotropic Displacement Parameters ($Å^2 \times 10^3$) for **3a**. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	**U_{11}**	**U_{22}**	**U_{33}**	**U_{23}**	**U_{13}**	**U_{12}**
S17	56.2(6)	41.4(5)	59.3(6)	-4.4(4)	41.0(5)	0.7(4)
O2	46.4(15)	57.2(16)	62.7(17)	-20.1(13)	8.6(13)	-5.0(12)
O12	55.1(14)	28.2(11)	45.0(13)	-0.6(10)	26.1(12)	10(1)
O25	54.3(16)	46.8(16)	68.7(18)	7.0(13)	6.0(14)	9.6(12)
O26	59.0(15)	25.6(12)	57.0(15)	6.2(11)	28.1(13)	7.9(10)
O27	65.5(17)	47.2(15)	73.0(17)	-0.7(13)	36.7(14)	19.6(13)
O28	77(2)	65.1(17)	90(2)	-10.2(15)	65.4(18)	-15.3(15)
N6	43.7(16)	27.7(14)	47.6(16)	-1.5(12)	29.1(14)	-1.7(11)
N10	52.5(18)	26.6(15)	43.1(17)	0.3(13)	23.0(14)	8.0(13)
C1	54(3)	103(4)	59(3)	-21(3)	2(2)	2(2)
C3	36.6(18)	43(2)	47(2)	-3.8(16)	22.4(16)	-0.2(15)
C4	38.6(18)	26.7(16)	43.7(19)	-1.2(14)	23.9(16)	0.1(13)
C5	45.6(19)	24.2(17)	41.6(18)	1.4(13)	25.0(16)	2.0(13)
C7	40.8(19)	40(2)	64(2)	-5.1(17)	29.6(19)	-8.1(16)
C8	44(2)	31.4(18)	63(2)	-9.9(16)	24.7(19)	-9.6(15)
C9	35.3(17)	28.7(16)	41.3(19)	-3.5(14)	16.2(15)	4.2(13)
C11	35.4(18)	25.6(17)	45(2)	-6.6(15)	15.2(16)	-2.4(13)
C13	46.2(19)	34.2(18)	40.1(19)	-3.3(15)	19.2(16)	1.9(15)
C14	71(3)	60(3)	90(3)	-12(2)	49(3)	-15(2)
C15	69(3)	50(2)	56(2)	-6.2(18)	35(2)	13.8(19)
C16	65(3)	80(3)	46(2)	-7(2)	12(2)	10(2)
C18	70(3)	42(2)	48(2)	-4.1(16)	43(2)	-2.1(18)
C19	81(3)	50(2)	61(2)	-7.4(19)	49(2)	-9(2)
C20	102(4)	59(3)	73(3)	-23(2)	58(3)	-29(3)
C21	88(3)	84(3)	49(2)	-13(2)	44(2)	-19(3)
C22	87(3)	86(3)	43(2)	9(2)	27(2)	4(3)
C23	82(3)	59(3)	57(3)	2(2)	32(3)	-5(2)
C24	98(4)	148(5)	65(3)	-36(3)	38(3)	-41(4)
S46	34.6(4)	42.6(5)	39.8(4)	-0.9(4)	14.3(4)	0.1(4)
O3	42.2(13)	30.3(13)	55.9(15)	0.7(10)	18.4(12)	4.7(10)
O5	71.6(17)	39.3(14)	53.9(16)	-4.3(12)	36.1(14)	3.8(12)
O31	64.1(16)	50.9(15)	51.8(14)	-4.4(12)	30.0(13)	-17.1(13)
O41	32.2(12)	38.4(12)	50.8(14)	-9.8(11)	9.6(10)	-1.5(10)
O54	48.6(15)	63.7(16)	56.7(15)	-4.9(13)	31.1(13)	-12.5(12)
O55	46.4(15)	52.5(15)	58.0(16)	-0.3(12)	13.8(13)	13.9(12)
N35	39.9(15)	31.8(14)	31.2(15)	0.9(11)	15.5(12)	-1.3(11)
N39	34.5(16)	35.4(17)	54.5(19)	-13.6(14)	15.2(14)	2.6(13)
C30	77(3)	83(3)	85(3)	-11(3)	53(3)	-24(3)
C32	34.0(18)	41(2)	27.8(17)	1.2(14)	6.2(14)	-1.0(15)
C33	34.5(17)	27.2(17)	34.9(17)	-1.4(13)	7.6(14)	2.8(13)
C34	43.8(19)	27.3(16)	35.8(18)	-0.3(13)	14.9(15)	2.6(14)
C36	47.0(19)	39.0(18)	31.8(17)	3.6(14)	19.3(15)	-1.1(15)

C37	48(2)	33.7(17)	41.3(19)	-1.3(14)	21.8(17)	-9.1(15)
C38	36.3(18)	34.9(17)	37.7(18)	-7.5(14)	16.5(15)	-2.1(14)
C40	38.1(19)	23.5(16)	39.8(18)	-0.3(14)	17.4(15)	-2.7(14)
C42	30.0(17)	41.8(18)	44.4(19)	3.1(16)	8.5(15)	-3.8(15)
C43	66(3)	71(3)	66(3)	27(2)	-3(2)	-15(2)
C44	49(2)	80(3)	72(3)	-12(2)	31(2)	-14(2)
C45	46(2)	65(3)	64(3)	-17(2)	13(2)	-14.4(19)
C47	29.7(17)	40.7(19)	31.0(17)	-2.4(15)	5.9(14)	-6.1(14)
C48	60(2)	39.9(19)	33.7(19)	2.8(15)	14.5(17)	-4.6(16)
C49	73(3)	61(3)	38(2)	-0.6(18)	23(2)	-11(2)
C50	54(2)	54(2)	48(2)	-14.0(18)	16.4(19)	-8.1(18)
C51	50(2)	33.3(19)	57(2)	-8.0(17)	15.5(19)	-7.6(16)
C52	42(2)	39(2)	39(2)	5.6(15)	10.6(17)	-8.2(15)
C53	107(4)	86(3)	70(3)	-33(3)	42(3)	-10(3)

Table S7. Bond Lengths for **3a**.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
S17	O27	1.434(3)	S46	O54	1.426(2)
S17	O28	1.428(3)	S46	O55	1.426(2)
S17	N6	1.645(3)	S46	N35	1.636(3)
S17	C18	1.773(4)	S46	C47	1.763(3)
O2	C1	1.440(5)	O3	C40	1.212(4)
O2	C3	1.340(4)	O5	C32	1.195(4)
O12	C11	1.351(4)	O31	C30	1.435(5)
O12	C13	1.466(4)	O31	C32	1.345(4)
O25	C3	1.197(4)	O41	C40	1.345(4)
O26	C11	1.213(4)	O41	C42	1.471(4)
N6	C5	1.476(4)	N35	C34	1.470(4)
N6	C7	1.480(4)	N35	C36	1.473(4)
N10	C9	1.459(4)	N39	C38	1.454(4)
N10	C11	1.337(4)	N39	C40	1.337(4)
C3	C4	1.511(5)	C32	C33	1.510(4)
C4	C5	1.525(4)	C33	C34	1.536(4)
C4	C9	1.525(4)	C33	C38	1.529(4)
C7	C8	1.519(4)	C36	C37	1.519(4)
C8	C9	1.520(4)	C37	C38	1.520(4)
C13	C14	1.511(5)	C42	C43	1.506(5)
C13	C15	1.519(5)	C42	C44	1.502(5)
C13	C16	1.513(5)	C42	C45	1.519(5)
C18	C19	1.376(5)	C47	C48	1.384(4)
C18	C23	1.366(5)	C47	C52	1.386(4)
C19	C20	1.396(6)	C48	C49	1.370(5)
C20	C21	1.373(6)	C49	C50	1.384(5)
C21	C22	1.371(6)	C50	C51	1.379(5)
C21	C24	1.509(6)	C50	C53	1.506(5)
C22	C23	1.383(6)	C51	C52	1.391(5)

Table S8. Bond Angles for **3a**.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
O27	S17	N6	111.58(15)	O54	S46	N35	106.57(14)
O27	S17	C18	107.88(17)	O54	S46	C47	108.17(15)
O28	S17	O27	118.13(18)	O55	S46	O54	120.20(16)
O28	S17	N6	107.36(14)	O55	S46	N35	106.31(14)
O28	S17	C18	109.60(17)	O55	S46	C47	107.97(15)
N6	S17	C18	100.93(15)	N35	S46	C47	106.93(14)
C3	O2	C1	116.7(3)	C32	O31	C30	116.1(3)
C11	O12	C13	121.0(2)	C40	O41	C42	121.4(2)
C5	N6	S17	112.34(18)	C34	N35	S46	117.79(19)
C5	N6	C7	113.5(2)	C34	N35	C36	111.3(2)
C7	N6	S17	116.1(2)	C36	N35	S46	117.5(2)
C11	N10	C9	120.2(3)	C40	N39	C38	122.5(3)
O2	C3	C4	110.3(3)	O5	C32	O31	122.9(3)
O25	C3	O2	122.7(3)	O5	C32	C33	127.0(3)
O25	C3	C4	127.0(3)	O31	C32	C33	110.1(3)
C3	C4	C5	110.9(3)	C32	C33	C34	109.3(3)
C3	C4	C9	114.9(3)	C32	C33	C38	114.3(2)
C5	C4	C9	108.3(2)	C38	C33	C34	109.5(3)
N6	C5	C4	109.2(2)	N35	C34	C33	108.2(2)
N6	C7	C8	108.7(3)	N35	C36	C37	108.4(2)
C7	C8	C9	111.5(3)	C36	C37	C38	111.5(3)
N10	C9	C4	113.6(3)	N39	C38	C33	112.7(3)
N10	C9	C8	111.2(2)	N39	C38	C37	110.1(3)
C8	C9	C4	110.6(3)	C37	C38	C33	111.9(3)
O26	C11	O12	124.8(3)	O3	C40	O41	125.3(3)
O26	C11	N10	125.0(3)	O3	C40	N39	124.7(3)
N10	C11	O12	110.2(3)	N39	C40	O41	110.0(3)
O12	C13	C14	109.8(3)	O41	C42	C43	109.6(3)
O12	C13	C15	101.7(3)	O41	C42	C44	110.5(3)
O12	C13	C16	110.3(3)	O41	C42	C45	102.6(3)
C14	C13	C15	110.3(3)	C43	C42	C45	110.8(3)
C14	C13	C16	113.4(3)	C44	C42	C43	113.1(3)
C16	C13	C15	110.6(3)	C44	C42	C45	109.7(3)
C19	C18	S17	119.6(3)	C48	C47	S46	119.6(3)
C23	C18	S17	120.1(3)	C48	C47	C52	120.1(3)
C23	C18	C19	120.3(4)	C52	C47	S46	120.2(3)
C18	C19	C20	118.5(4)	C49	C48	C47	119.7(3)
C21	C20	C19	122.2(4)	C48	C49	C50	121.6(4)
C20	C21	C24	120.5(5)	C49	C50	C53	121.2(4)
C22	C21	C20	117.3(4)	C51	C50	C49	118.1(3)
C22	C21	C24	122.2(5)	C51	C50	C53	120.6(4)
C21	C22	C23	121.8(4)	C50	C51	C52	121.5(3)
C18	C23	C22	119.8(4)	C47	C52	C51	118.9(3)

Table S9. Torsion Angles for **3a**.

A	B	C	D	Angle/°	A	B	C	D	Angle/°
S17	N6	C5	C4	-164.4(2)	S46	N35	C34	C33	-154.3(2)
S17	N6	C7	C8	169.7(2)	S46	N35	C36	C37	156.0(2)
S17	C18	C19	C20	178.8(3)	S46	C47	C48	C49	179.6(3)
S17	C18	C23	C22	-179.1(3)	S46	C47	C52	C51	-179.2(2)
O2	C3	C4	C5	56.5(3)	O5	C32	C33	C34	-115.6(3)

O2	C3	C4	C9	179.7(3)	O5	C32	C33	C38	7.5(5)
O25	C3	C4	C5	-125.4(4)	O31	C32	C33	C34	64.3(3)
O25	C3	C4	C9	-2.2(5)	O31	C32	C33	C38	-172.6(3)
O27	S17	N6	C5	-41.3(3)	O54	S46	N35	C34	46.8(3)
O27	S17	N6	C7	91.6(3)	O54	S46	N35	C36	-175.8(2)
O27	S17	C18	C19	-3.8(3)	O54	S46	C47	C48	166.3(3)
O27	S17	C18	C23	176.6(3)	O54	S46	C47	C52	-15.9(3)
O28	S17	N6	C5	-172.2(2)	O55	S46	N35	C34	176.1(2)
O28	S17	N6	C7	-39.3(3)	O55	S46	N35	C36	-46.4(3)
O28	S17	C18	C19	126.1(3)	O55	S46	C47	C48	34.8(3)
O28	S17	C18	C23	-53.5(3)	O55	S46	C47	C52	-147.4(3)
N6	S17	C18	C19	-120.9(3)	N35	S46	C47	C48	-79.3(3)
N6	S17	C18	C23	59.5(3)	N35	S46	C47	C52	98.6(3)
N6	C7	C8	C9	54.4(4)	N35	C36	C37	C38	55.6(3)
C1	O2	C3	O25	0.0(5)	C30	O31	C32	O5	3.7(5)
C1	O2	C3	C4	178.1(3)	C30	O31	C32	C33	-176.3(3)
C3	C4	C5	N6	67.7(3)	C32	C33	C34	N35	67.7(3)
C3	C4	C9	N10	59.0(4)	C32	C33	C38	N39	54.3(3)
C3	C4	C9	C8	-66.8(3)	C32	C33	C38	C37	-70.5(3)
C5	N6	C7	C8	-57.9(3)	C34	N35	C36	C37	-64.0(3)
C5	C4	C9	N10	-176.3(3)	C34	C33	C38	N39	177.2(2)
C5	C4	C9	C8	57.8(3)	C34	C33	C38	C37	52.5(3)
C7	N6	C5	C4	61.4(3)	C36	N35	C34	C33	65.7(3)
C7	C8	C9	N10	176.3(3)	C36	C37	C38	N39	-177.9(3)
C7	C8	C9	C4	-56.5(4)	C36	C37	C38	C33	-51.7(3)
C9	N10	C11	O12	177.9(3)	C38	N39	C40	O3	-8.9(5)
C9	N10	C11	O26	-1.7(5)	C38	N39	C40	O41	171.1(3)
C9	C4	C5	N6	-59.3(3)	C38	C33	C34	N35	-58.3(3)
C11	O12	C13	C14	-65.9(4)	C40	O41	C42	C43	-65.4(4)
C11	O12	C13	C15	177.3(3)	C40	O41	C42	C44	60.0(4)
C11	O12	C13	C16	59.8(4)	C40	O41	C42	C45	176.9(3)
C11	N10	C9	C4	83.4(4)	C40	N39	C38	C33	96.9(4)
C11	N10	C9	C8	-151.1(3)	C40	N39	C38	C37	-137.4(3)
C13	O12	C11	O26	0.7(5)	C42	O41	C40	O3	-1.4(5)
C13	O12	C11	N10	-178.9(3)	C42	O41	C40	N39	178.5(3)
C18	S17	N6	C5	73.1(2)	C47	S46	N35	C34	-68.7(2)
C18	S17	N6	C7	-154.1(2)	C47	S46	N35	C36	68.7(2)
C18	C19	C20	C21	0.0(6)	C47	C48	C49	C50	-0.5(6)
C19	C18	C23	C22	1.3(6)	C48	C47	C52	C51	-1.4(5)
C19	C20	C21	C22	1.8(6)	C48	C49	C50	C51	-1.0(6)
C19	C20	C21	C24	-178.2(4)	C48	C49	C50	C53	178.5(4)
C20	C21	C22	C23	-2.1(6)	C49	C50	C51	C52	1.3(6)
C21	C22	C23	C18	0.6(6)	C50	C51	C52	C47	-0.1(5)
C23	C18	C19	C20	-1.6(5)	C52	C47	C48	C49	1.7(5)
C24	C21	C22	C23	177.9(4)	C53	C50	C51	C52	-178.1(4)

Table S10. Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for **3a**.

Atom	***x***	***y***	***z***	**U(eq)**
H1A	13316	150	5486	117
H1B	12505	119	6250	117
H1C	12678	-692	5631	117
H4	15723	-383	9027	41

H5A	17521	-927	8830	42
H5B	16322	-1106	7701	42
H7A	18730	744	7711	55
H7B	19072	205	8820	55
H8A	16990	1342	7975	54
H8B	18211	1462	9102	54
H9	17611	322	9906	42
H14A	13562	1025	11195	103
H14B	14049	959	12520	103
H14C	14672	398	11858	103
H15A	15346	2876	12057	83
H15B	14480	2499	12657	83
H15C	13966	2529	11328	83
H16A	16876	951	12993	100
H16B	16333	1529	13700	100
H16C	17118	1919	13034	100
H19	16862	-2378	6052	69
H20	14944	-2783	4633	85
H22	14137	-436	3686	86
H23	16022	-13	5096	77
H24A	13137	-1931	2411	153
H24B	12393	-1558	3123	153
H24C	12875	-2488	3311	153
H30A	10148	2699	9533	113
H30B	11377	2690	10667	113
H30C	10575	1868	10232	113
H33	13476	2096	8757	41
H34A	12380	1758	6862	43
H34B	11438	1606	7493	43
H36A	11027	3600	5517	46
H36B	12114	2934	5659	46
H37A	12112	4067	7359	47
H37B	13069	4106	6729	47
H38	14054	2892	7564	43
H43A	17376	3454	11996	114
H43B	18790	3422	12032	114
H43C	17699	2886	11137	114
H44A	18148	3569	9560	97
H44B	19236	4119	10433	97
H44C	18079	4547	9456	97
H45A	17662	5388	10798	92
H45B	18688	4967	11879	92
H45C	17231	4995	11723	92
H48	10029	2610	3694	55
H49	10370	1793	2372	68
H51	10160	-248	4053	58
H52	9793	560	5395	50
H53A	10886	477	1782	128
H53B	9657	-46	1662	128
H53C	11019	-315	2544	128
H10	16120(30)	1680(20)	9400(30)	40(9)
H39	14090(30)	4140(20)	8920(30)	39(9)

• Compound **4**

Data Collection

A colorless crystal with approximate dimensions 0.1 × 0.04 × 0.03 mm^3 was selected under oil under ambient conditions and attached to the tip of a MiTeGen MicroMount©. The crystal was mounted in a stream of cold nitrogen at 150 K and centered in the X-ray beam by using a video camera.

The crystal evaluation and data collection were performed on a Bruker D8 Venture diffractometer with Cu K_α (λ = 1.54178 Å) radiation and the diffractometer to crystal distance of 4.00 cm.

The initial cell constants were obtained from three series of ω scans at different starting angles. Each series consisted of 20-30 frames collected at intervals of 0.5º in 10-15º range about ω with the exposure time of 20 seconds per frame. The reflections were successfully indexed by an automated indexing routine built in the APEXII program. The final cell constants were calculated from a set of 1198 strong reflections from the actual data collection.

The data were collected by using the half sphere data collection routine to survey the reciprocal space to the extent of a half sphere to a resolution of 0.81 Å. A total of 14985 data were harvested by collecting 16 sets of frames with 1º scans in ω and φ with an exposure time 20-30 sec per frame. These highly redundant datasets were corrected for Lorentz and polarization effects. The absorption correction was based on fitting a function to the empirical transmission surface as sampled by multiple equivalent measurements. [S1]

Structure Solution and Refinement

The systematic absences in the diffraction data were uniquely consistent for the space group $P2_12_12_1$ that yielded chemically reasonable and computationally stable results of refinement [S2-3].

A successful solution by the direct methods provided most non-hydrogen atoms from the *E*-map. The solvent molecules, chloroform were found to be disordered, and were modeled in two different orientations. The remaining non-hydrogen atoms were located in an alternating series of least-squares cycles and difference Fourier maps. All non-hydrogen atoms were refined with anisotropic displacement coefficients. All hydrogen atoms were included in the structure factor calculation at idealized positions and were allowed to ride on the neighboring atoms with relative isotropic displacement coefficients.

The final least-squares refinement of 550 parameters against 8006 data resulted in residuals *R* (based on F^2 for $I \geq 2\sigma$) and *wR* (based on F^2 for all data) of 0.0643 and 0.1602, respectively. The final difference Fourier map was featureless.

Summary

Crystal Data for $C_{36}H_{55}Cl_3N_6O_{10}S$ (M =870.27): orthorhombic, space group $P2_12_12_1$ (no. 19), a = 9.6129(8) Å, b = 16.6129(6) Å, c = 27.4345(16) Å, V = 4381.2(5) $Å^3$, Z = 4, T = 150.0 K, μ(CuKα) = 2.834 mm^{-1}, *Dcalc* = 1.319 g/mm^3, 14985 reflections measured (6.2 ≤ 2Θ ≤ 145.3), 8006 unique (R_{int} = 0.0547, R_{sigma} = 0.0869) which were used in all calculations. The final R_1 was 0.0643 (I > 2σ(I)) and wR_2 was 0.1602 (all data).

Table S11. Crystal data and structure refinement for **4**.

Empirical formula	$C_{36}H_{55}Cl_3N_6O_{10}S$
Formula weight	870.27
Temperature/K	150.0
Crystal system	orthorhombic
Space group	$P2_12_12_1$
a/Å	9.6129(8)
b/Å	16.6129(6)
c/Å	27.4345(16)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	4381.2(5)
Z	4
ρ_{calc}mg/mm^3	1.319
m/mm^{-1}	2.834
F(000)	1840.0
Crystal size/mm^3	0.1 × 0.04 × 0.03
Radiation	CuKα (λ = 1.54178)
2Θ range for data collection	6.22 to 145.33°
Index ranges	$-11 \leq h \leq 11$, $-19 \leq k \leq 15$, $-33 \leq l \leq 25$
Reflections collected	14985
Independent reflections	8006 [R_{int} = 0.0547, R_{sigma} = 0.0869]
Data/restraints/parameters	8006/432/550
Goodness-of-fit on F^2	1.034
Final R indexes [I>=2σ (I)]	R_1 = 0.0643, wR_2 = 0.1405
Final R indexes [all data]	R_1 = 0.1044, wR_2 = 0.1602
Largest diff. peak/hole / e Å^{-3}	0.33/-0.30
Flack parameter	0.045(15)

Table S12. Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for **4**. U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{IJ} tensor.

Atom	***x***	***y***	***z***	**U(eq)**
S1	-140.2(19)	3087.7(10)	1782.0(6)	44.6(4)
O9	1267(5)	3333(3)	1852.7(19)	56.0(13)
O5	2801(4)	807(3)	-449.1(17)	43.6(11)
O2	-2788(7)	-211(4)	1604(3)	99(2)
O7	-1103(4)	-1219(3)	-813.6(16)	43.9(11)
O8	-2820(5)	-2150(3)	-937.1(16)	47.7(12)
O10	-745(6)	2498(3)	2093.9(17)	54.0(12)
O3	-754(5)	377(2)	706.1(16)	46.2(11)
O4	83(5)	2269(3)	-684.0(16)	48.1(11)
O1	-1273(6)	-1045(3)	1914(2)	67.5(16)
O6	551(4)	-2143(2)	-68.4(16)	39.3(10)
N6	-2267(5)	-1814(3)	-190.6(19)	36.2(12)
N3	-367(5)	1401(3)	-70.1(17)	35.7(12)
N2	-265(5)	2729(3)	1235.1(18)	37.6(12)
N4	832(5)	158(3)	-627.8(17)	30.9(11)
N1	-802(6)	951(3)	1436.0(18)	41.7(13)
N5	835(5)	-920(3)	282.7(17)	30.8(11)
C23	-1910(7)	-1794(5)	676(2)	51.7(18)
C12	261(6)	864(4)	-868(2)	33.2(13)
C14	2156(6)	172(4)	-455(2)	33.5(13)
C29	-1193(7)	3947(4)	1822(2)	45.2(16)
C7	-1654(6)	2470(4)	1064(2)	32.6(13)
C30	-2460(8)	3927(5)	2058(3)	58.9(19)
C15	2772(6)	-627(4)	-289(2)	35.3(14)
C28	-3776(9)	-2813(6)	-1600(3)	69(2)
C6	-1492(6)	1752(4)	723(2)	31.3(13)
C27	-2717(9)	-1480(5)	-1728(3)	63(2)
C4	42(11)	427(5)	2212(3)	73(3)
C26	-1191(8)	-2656(5)	-1534(3)	58(2)
C20	2345(6)	-884(4)	230(2)	36.8(14)
C16	4383(7)	-630(5)	-316(3)	54.3(19)
C13	-1068(7)	648(4)	-1139(3)	42.7(16)
C17	5069(7)	-138(5)	84(3)	62(2)
C19	2981(7)	-338(4)	611(3)	48.3(17)
C18	4560(8)	-386(5)	583(3)	65(2)
C21	69(6)	-1534(3)	112(2)	30.9(12)
C9	826(7)	2353(4)	476(2)	41.0(15)
C24	-1987(6)	-1684(4)	-662(2)	35.6(14)
C5	-969(6)	976(4)	951(2)	30.9(13)
C25	-2583(7)	-2254(4)	-1458(2)	47.1(16)
C31	-3260(9)	4614(5)	2077(3)	69(2)
C2	-1631(9)	-348(5)	1734(3)	55.9(18)
C32	-2838(10)	5323(5)	1868(3)	69(2)
C8	619(7)	3032(4)	843(2)	39.0(14)
C1	-2340(11)	-1613(6)	2016(3)	85(3)
C10	-562(6)	2027(4)	294(2)	33.7(13)
C11	-2(7)	1574(4)	-526(2)	37.0(14)
C33	-3717(11)	6082(6)	1877(4)	99(4)
C22	-1485(6)	-1425(4)	192(2)	34.4(14)

C34	-1580(10)	5326(5)	1626(3)	67(2)
C35	-741(9)	4649(4)	1605(3)	54.4(18)
C3	-429(8)	220(4)	1697(3)	46.8(16)
Cl5S	2726(3)	1482(2)	1598.7(15)	85.9(12)
Cl6S	5608(3)	1131.7(19)	1675.5(13)	75.3(11)
Cl4S	4542(3)	2592.6(19)	2091.2(12)	70.7(10)
C2S	4386(13)	1926(8)	1620(4)	54(3)
Cl2S	3972(11)	469(7)	1786(5)	123(4)
Cl3S	5968(9)	1701(7)	2053(3)	95(3)
Cl1S	3242(10)	2159(6)	1750(4)	106(4)
C1S	4560(40)	1500(30)	1637(17)	91(9)

Table S13. Anisotropic Displacement Parameters ($Å^2 \times 10^3$) for **4**. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
S1	61.2(11)	36.3(8)	36.4(8)	-5.5(8)	-9.9(8)	6.7(8)
O9	59(3)	53(3)	56(3)	-13(3)	-23(2)	5(2)
O5	42(2)	31(2)	58(3)	8(2)	-3(2)	-4.6(19)
O2	68(4)	82(5)	147(7)	14(5)	-6(4)	-3(3)
O7	43(2)	45(3)	44(3)	8(2)	-5(2)	-12(2)
O8	50(3)	58(3)	35(2)	-2(2)	-4.3(19)	-22(2)
O10	82(3)	45(3)	35(2)	-5(2)	-3(2)	6(3)
O3	77(3)	26(2)	36(2)	-5(2)	7(2)	7(2)
O4	76(3)	30(2)	39(2)	5(2)	4(2)	6(2)
O1	99(4)	42(3)	61(3)	3(3)	12(3)	-7(3)
O6	40(2)	32(2)	46(2)	-9(2)	-4(2)	7.0(18)
N6	32(2)	38(3)	39(3)	-3(2)	-2(2)	-7(2)
N3	50(3)	28(3)	29(2)	4(2)	1(2)	4(2)
N2	40(3)	36(3)	37(3)	-6(2)	-2(2)	1(2)
N4	34(2)	27(2)	31(3)	3(2)	-1(2)	0(2)
N1	66(4)	27(3)	32(3)	-5(2)	-7(2)	10(3)
N5	33(2)	24(2)	35(3)	-3(2)	-1(2)	4.0(19)
C23	47(4)	67(5)	42(4)	-10(4)	6(3)	-8(4)
C12	41(3)	30(3)	28(3)	2(2)	-2(2)	5(2)
C14	33(3)	31(3)	36(3)	2(3)	3(3)	-2(2)
C29	67(4)	36(3)	32(3)	-12(3)	-10(3)	7(3)
C7	39(3)	29(3)	30(3)	0(3)	0(2)	6(2)
C30	59(4)	58(4)	60(5)	-20(4)	0(4)	0(3)
C15	35(3)	28(3)	42(3)	-1(3)	-1(3)	2(2)
C28	74(5)	90(6)	42(4)	-5(4)	-11(4)	-31(5)
C6	33(3)	31(3)	30(3)	0(2)	-2(2)	4(2)
C27	69(5)	67(5)	53(5)	10(4)	-15(4)	-6(4)
C4	113(7)	53(5)	52(4)	15(4)	-29(5)	4(5)
C26	65(4)	50(4)	58(5)	3(4)	2(4)	-7(4)
C20	32(3)	33(3)	46(3)	1(3)	-5(2)	-1(2)
C16	36(3)	52(4)	75(5)	17(4)	5(3)	5(3)
C13	47(4)	41(4)	40(4)	-2(3)	-7(3)	5(3)
C17	38(3)	57(5)	92(5)	20(4)	-13(4)	1(3)
C19	49(4)	48(4)	48(4)	0(3)	-17(3)	-11(3)
C18	50(4)	68(5)	76(5)	16(4)	-24(4)	-7(4)
C21	35(3)	28(3)	29(3)	1(2)	-1(2)	5(2)
C9	41(3)	43(4)	39(3)	-5(3)	-1(3)	3(3)
C24	31(3)	33(3)	43(3)	0(3)	-4(2)	-2(2)

C5	37(3)	28(3)	28(3)	-4(2)	1(2)	2(2)
C25	55(4)	55(4)	31(3)	0(3)	-5(3)	-16(3)
C31	64(5)	62(4)	81(6)	-34(4)	-7(4)	11(4)
C2	59(4)	50(4)	59(5)	-1(4)	8(4)	6(3)
C32	79(5)	61(4)	67(5)	-30(4)	-34(4)	21(4)
C8	40(3)	38(3)	38(3)	-2(3)	0(3)	4(3)
C1	124(8)	73(6)	59(6)	8(5)	6(5)	-38(6)
C10	41(3)	33(3)	27(3)	0(2)	0(2)	5(3)
C11	47(3)	35(3)	29(3)	4(2)	-1(3)	8(3)
C33	100(7)	78(6)	120(9)	-35(6)	-28(6)	39(6)
C22	37(3)	30(3)	37(3)	-8(3)	-3(2)	3(2)
C34	90(5)	45(4)	67(5)	-11(4)	-28(4)	16(4)
C35	72(4)	42(4)	49(4)	-7(3)	-10(4)	9(3)
C3	62(4)	34(3)	45(4)	5(3)	-4(3)	9(3)
Cl5S	57.5(18)	80(2)	120(3)	-21(2)	-16.9(18)	5.0(17)
Cl6S	59.8(17)	62.7(19)	103(3)	9.5(19)	11.5(17)	19.6(15)
Cl4S	70.8(19)	66.0(19)	75.3(19)	-8.9(16)	-5.3(15)	-0.3(15)
C2S	54(6)	58(6)	51(6)	11(5)	14(4)	16(5)
Cl2S	101(7)	109(7)	160(10)	-39(7)	0(7)	15(5)
Cl3S	83(5)	139(9)	63(5)	-13(6)	2(4)	-17(5)
Cl1S	80(6)	96(7)	142(9)	31(7)	14(6)	13(5)
C1S	64(12)	110(13)	98(19)	-29(12)	-17(11)	19(10)

Table S14. Bond Lengths for **4**.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
S1	O9	1.426(5)	C29	C30	1.379(10)
S1	O10	1.425(5)	C29	C35	1.379(10)
S1	N2	1.619(5)	C7	C6	1.523(8)
S1	C29	1.753(7)	C30	C31	1.377(11)
O5	C14	1.223(7)	C15	C20	1.542(9)
O2	C2	1.190(10)	C15	C16	1.550(9)
O7	C24	1.222(7)	C28	C25	1.526(10)
O8	C24	1.346(7)	C6	C5	1.520(8)
O8	C25	1.458(8)	C6	C10	1.546(8)
O3	C5	1.219(7)	C27	C25	1.491(10)
O4	C11	1.235(7)	C4	C3	1.523(10)
O1	C2	1.305(9)	C26	C25	1.510(11)
O1	C1	1.422(10)	C20	C19	1.514(9)
O6	C21	1.218(7)	C16	C17	1.518(11)
N6	C24	1.338(8)	C17	C18	1.511(11)
N6	C22	1.444(7)	C19	C18	1.522(10)
N3	C10	1.454(7)	C21	C22	1.520(8)
N3	C11	1.331(7)	C9	C8	1.526(9)
N2	C7	1.479(8)	C9	C10	1.524(9)
N2	C8	1.461(8)	C31	C32	1.371(13)
N4	C12	1.453(7)	C2	C3	1.495(11)
N4	C14	1.359(8)	C32	C33	1.517(12)
N1	C5	1.340(7)	C32	C34	1.380(13)
N1	C3	1.454(8)	C34	C35	1.386(11)
N5	C20	1.460(7)	Cl5S	C2S	1.758(13)
N5	C21	1.343(7)	Cl6S	C2S	1.773(13)
C23	C22	1.517(9)	Cl4S	C2S	1.709(14)
C12	C13	1.521(8)	Cl2S	C1S	1.85(5)

C12	C11		1.528(8)	Cl3S	C1S		1.80(4)
C14	C15		1.523(8)	Cl1S	C1S		1.70(4)

Table S15. Bond Angles for **4**.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
O9	S1	N2	107.6(3)	N5	C21	C22	113.4(5)
O9	S1	C29	107.9(3)	C10	C9	C8	111.4(5)
O10	S1	O9	120.1(3)	O7	C24	O8	125.9(6)
O10	S1	N2	105.9(3)	O7	C24	N6	124.9(6)
O10	S1	C29	106.7(3)	N6	C24	O8	109.3(5)
N2	S1	C29	108.3(3)	O3	C5	N1	120.1(6)
C24	O8	C25	121.7(5)	O3	C5	C6	121.4(5)
C2	O1	C1	118.3(7)	N1	C5	C6	118.4(5)
C24	N6	C22	121.7(5)	O8	C25	C28	101.9(5)
C11	N3	C10	121.7(5)	O8	C25	C27	111.8(6)
C7	N2	S1	118.0(4)	O8	C25	C26	109.1(6)
C8	N2	S1	120.8(4)	C27	C25	C28	109.5(6)
C8	N2	C7	113.0(5)	C27	C25	C26	112.9(6)
C14	N4	C12	119.9(5)	C26	C25	C28	111.2(6)
C5	N1	C3	123.0(5)	C32	C31	C30	122.0(9)
C21	N5	C20	122.8(5)	O2	C2	O1	121.9(8)
N4	C12	C13	110.4(5)	O2	C2	C3	125.6(8)
N4	C12	C11	114.0(5)	O1	C2	C3	112.4(7)
C13	C12	C11	110.1(5)	C31	C32	C33	122.8(10)
O5	C14	N4	119.5(6)	C31	C32	C34	117.7(8)
O5	C14	C15	123.5(5)	C34	C32	C33	119.5(10)
N4	C14	C15	117.0(5)	N2	C8	C9	107.9(5)
C30	C29	S1	121.3(6)	N3	C10	C6	112.7(5)
C35	C29	S1	118.7(6)	N3	C10	C9	111.4(5)
C35	C29	C30	120.0(7)	C9	C10	C6	111.3(5)
N2	C7	C6	109.4(5)	O4	C11	N3	123.2(6)
C31	C30	C29	119.5(8)	O4	C11	C12	119.7(5)
C14	C15	C20	114.4(5)	N3	C11	C12	117.0(5)
C14	C15	C16	112.1(5)	N6	C22	C23	108.3(5)
C20	C15	C16	108.0(5)	N6	C22	C21	110.7(5)
C7	C6	C10	107.2(5)	C23	C22	C21	110.0(5)
C5	C6	C7	116.4(5)	C32	C34	C35	121.7(9)
C5	C6	C10	111.9(5)	C29	C35	C34	119.1(8)
N5	C20	C15	111.5(5)	N1	C3	C4	110.0(6)
N5	C20	C19	110.9(5)	N1	C3	C2	111.7(6)
C19	C20	C15	111.4(5)	C2	C3	C4	108.1(7)
C17	C16	C15	113.4(6)	Cl5S	C2S	Cl6S	107.0(7)
C18	C17	C16	111.5(6)	Cl4S	C2S	Cl5S	112.1(7)
C20	C19	C18	109.6(6)	Cl4S	C2S	Cl6S	111.0(7)
C17	C18	C19	110.8(6)	Cl3S	C1S	Cl2S	105(2)
O6	C21	N5	124.4(5)	Cl1S	C1S	Cl2S	109(2)
O6	C21	C22	122.1(5)	Cl1S	C1S	Cl3S	109(2)

Table S16. Torsion Angles for **4**.

A	B	C	D	Angle/°	A	B	C	D	Angle/°
S1	N2	C7	C6	-146.4(4)	C30	C31	C32	C33	178.7(8)
S1	N2	C8	C9	151.3(4)	C30	C31	C32	C34	1.1(13)
S1	C29	C30	C31	-179.5(6)	C15	C20	C19	C18	-61.3(7)
S1	C29	C35	C34	178.6(6)	C15	C16	C17	C18	53.2(8)
O9	S1	N2	C7	-177.0(4)	C20	N5	C21	O6	5.6(9)
O9	S1	N2	C8	-30.5(5)	C20	N5	C21	C22	-177.8(5)
O9	S1	C29	C30	-139.8(6)	C20	C15	C16	C17	-53.0(8)
O9	S1	C29	C35	41.2(6)	C20	C19	C18	C17	59.2(9)
O5	C14	C15	C20	100.1(7)	C16	C15	C20	N5	-178.4(5)
O5	C14	C15	C16	-23.3(9)	C16	C15	C20	C19	57.1(7)
O2	C2	C3	N1	-5.7(12)	C16	C17	C18	C19	-55.1(9)
O2	C2	C3	C4	115.4(10)	C13	C12	C11	O4	-85.4(8)
O10	S1	N2	C7	53.5(5)	C13	C12	C11	N3	92.1(7)
O10	S1	N2	C8	-160.1(5)	C21	N5	C20	C15	77.9(7)
O10	S1	C29	C30	-9.5(7)	C21	N5	C20	C19	-157.3(6)
O10	S1	C29	C35	171.5(5)	C24	O8	C25	C28	-179.6(6)
O1	C2	C3	N1	172.2(6)	C24	O8	C25	C27	-62.8(8)
O1	C2	C3	C4	-66.7(8)	C24	O8	C25	C26	62.8(8)
O6	C21	C22	N6	-33.9(8)	C24	N6	C22	C23	-171.5(6)
O6	C21	C22	C23	85.8(7)	C24	N6	C22	C21	-50.8(8)
N2	S1	C29	C30	104.0(6)	C5	N1	C3	C4	165.4(7)
N2	S1	C29	C35	-75.0(6)	C5	N1	C3	C2	-74.6(8)
N2	C7	C6	C5	67.0(7)	C5	C6	C10	N3	53.4(6)
N2	C7	C6	C10	-59.0(6)	C5	C6	C10	C9	-72.6(6)
N4	C12	C11	O4	149.9(6)	C25	O8	C24	O7	11.2(10)
N4	C12	C11	N3	-32.6(8)	C25	O8	C24	N6	-168.3(6)
N4	C14	C15	C20	-81.6(7)	C31	C32	C34	C35	-2.1(12)
N4	C14	C15	C16	155.0(6)	C32	C34	C35	C29	1.7(12)
N5	C20	C19	C18	173.8(6)	C8	N2	C7	C6	64.6(6)
N5	C21	C22	N6	149.3(5)	C8	C9	C10	N3	177.8(5)
N5	C21	C22	C23	-91.0(6)	C8	C9	C10	C6	-55.5(7)
C12	N4	C14	O5	8.8(9)	C1	O1	C2	O2	-8.4(13)
C12	N4	C14	C15	-169.5(5)	C1	O1	C2	C3	173.6(7)
C14	N4	C12	C13	165.9(5)	C10	N3	C11	O4	-6.3(10)
C14	N4	C12	C11	-69.6(7)	C10	N3	C11	C12	176.3(5)
C14	C15	C20	N5	56.0(7)	C10	C6	C5	O3	-53.5(8)
C14	C15	C20	C19	-68.5(7)	C10	C6	C5	N1	129.3(6)
C14	C15	C16	C17	73.9(8)	C10	C9	C8	N2	55.4(7)
C29	S1	N2	C7	-60.6(5)	C11	N3	C10	C6	158.1(5)
C29	S1	N2	C8	85.8(5)	C11	N3	C10	C9	-75.9(7)
C29	C30	C31	C32	0.1(13)	C33	C32	C34	C35	-179.7(8)
C7	N2	C8	C9	-60.7(6)	C22	N6	C24	O7	-2.5(10)
C7	C6	C5	O3	-177.2(6)	C22	N6	C24	O8	177.0(5)
C7	C6	C5	N1	5.7(8)	C35	C29	C30	C31	-0.5(11)
C7	C6	C10	N3	-177.9(5)	C3	N1	C5	O3	-2.9(10)
C7	C6	C10	C9	56.1(6)	C3	N1	C5	C6	174.3(6)
C30	C29	C35	C34	-0.4(11)					

Table S17. Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for **4**.

Atom	*x*	*y*	*z*	U(eq)
H6A	-2946	-2145	-112	43
H3A	-493	895	13	43
H4	321	-278	-594	37
H1	-924	1396	1604	50
H5	409	-521	432	37
H23A	-1630	-2361	683	78
H23B	-2921	-1755	713	78
H23C	-1453	-1504	942	78
H12	956	1044	-1117	40
H7A	-2116	2918	890	39
H7B	-2239	2318	1346	39
H30	-2779	3444	2205	71
H15	2428	-1051	-518	42
H28A	-4664	-2562	-1514	103
H28B	-3680	-3326	-1426	103
H28C	-3749	-2911	-1952	103
H6	-2434	1636	584	38
H27A	-2714	-1586	-2080	95
H27B	-1934	-1128	-1645	95
H27C	-3591	-1216	-1637	95
H4A	-716	698	2386	109
H4B	851	785	2197	109
H4C	295	-68	2385	109
H26A	-1146	-3150	-1340	87
H26B	-446	-2290	-1432	87
H26C	-1076	-2788	-1880	87
H20	2716	-1439	286	44
H16A	4716	-1192	-294	65
H16B	4674	-414	-637	65
H13A	-1773	467	-905	64
H13B	-876	215	-1372	64
H13C	-1413	1122	-1314	64
H17A	6090	-210	66	75
H17B	4863	440	32	75
H19A	2665	-504	940	58
H19B	2675	224	556	58
H18A	4974	-29	832	78
H18B	4864	-944	652	78
H9A	1373	2555	195	49
H9B	1360	1912	630	49
H31	-4131	4596	2241	83
H8A	1529	3206	976	47
H8B	173	3500	683	47
H1A	-2736	-1810	1710	128
H1B	-3071	-1355	2210	128
H1C	-1948	-2066	2200	128
H10	-1054	2483	130	40
H33A	-4249	6122	1574	149
H33B	-3109	6553	1910	149
H33C	-4358	6061	2155	149

H22	-1710	-837	195	41
H34	-1281	5806	1469	81
H35	133	4667	1444	65
H3	351	-53	1522	56
H2S	4558	2216	1306	65
H1S	4880	1540	1291	109

Table S18. Atomic Occupancy for **4**.

Atom	***Occupancy***	**Atom**	***Occupancy***	**Atom**	***Occupancy***
Cl5S	0.706(4)	Cl6S	0.706(4)	Cl4S	0.706(4)
C2S	0.706(4)	H2S	0.706(4)	Cl2S	0.294(4)
Cl3S	0.294(4)	Cl1S	0.294(4)	C1S	0.294(4)
H1S	0.294(4)				

• Compound **7**

Data Collection

The diffraction data from yellow crystals (0.012 × 0.011 × 0.013 mm^3) mounted on a MiTeGen MicroMount© were collected at 100 on a ADSC Quantum 210 CCD diffractometer with synchrotron radiation (0.7000 Å) at Supramolecular Crystallography 2D, Pohang Accelerator Laboratory (PAL), Pohang, Korea. The ADSC Q210 ADX program[S4] was used for data collection (detector distance is 63 mm, omega scan; $\Delta\omega = 1^o$, exposure time is 1 sec/frame and HKL3000sm (Ver. 703r)[S5] was used for cell refinement, reduction and absorption correction. The crystal structure was solved by the direct method with SHELX-XT (Ver. 2014/5) [3] and refined by full-matrix least-squares calculations with the SHELX-XL (Ver. 2016/4)[S6] program package.

Structure Solution and Refinement

The systematic absences in the diffraction data were uniquely consistent for the monoclinic space group C2 that yielded chemically reasonable and computationally stable results of refinement [S3, S7].

A successful solution by the direct methods provided most non-hydrogen atoms from the *E*-map. The remaining non-hydrogen atoms were located in an alternating series of least-squares cycles and difference Fourier maps. All non-hydrogen atoms were refined with anisotropic displacement coefficients. All hydrogen atoms were included in the structure factor calculation at idealized positions and were allowed to ride on the neighboring atoms with relative isotropic displacement coefficients.

The final least-squares refinement of 581 parameters against 112496 data resulted in residuals *R* (based on F^2 for $I \geq 2\sigma$) and *wR* (based on F^2 for all data) of 0.0455 and 0.1281 respectively. The final difference Fourier map was featureless.

Summary

Crystal Data for $C_{48}H_{73}N_7O_9$ (M =892.13 g/mol): monoclinic, space group C2 (no. 5), a = 43.685(9) Å, b = 10.180(2) Å, c = 12.884(3) Å, β = 103.50(3)°, V = 5571(2) $Å^3$, Z = 4, T = 100 K, μ(synchrotron) = 0.074 mm^{-1}, *Dcalc* = 1.064 g/cm^3, 12496 reflections measured (3.25° ≤ 2Θ ≤ 55.992°), 12496 unique (R_{int} = 0.034, R_{sigma} = 0.0272) which were used in all calculations. The final R_1 was 0.0455 (I > 2σ(I)) and wR_2 was 0.1281 (all data).

Table S19. Crystal data and structure refinement for **7**.

Empirical formula	$C_{48}H_{73}N_7O_9$
Formula weight	892.13
Temperature/K	100
Crystal system	monoclinic
Space group	C2
a/Å	43.685(9)
b/Å	10.180(2)
c/Å	12.884(3)
α/°	90
β/°	103.50(3)
γ/°	90
Volume/Å^3	5571(2)
Z	4
ρ_{calc}g/cm^3	1.064
μ/mm^{-1}	0.074
F(000)	1928.0
Crystal size/mm^3	0.23 × 0.09 × 0.07
Radiation	synchrotron (λ = 0.70000)
2Θ range for data collection/°	3.25 to 55.992
Index ranges	? ≤ h ≤ ?, ? ≤ k ≤ ?, ? ≤ l ≤ ?
Reflections collected	12496
Independent reflections	12496 [R_{int} = 0.034, R_{sigma} = 0.0272]
Data/restraints/parameters	12496/1/581
Goodness-of-fit on F^2	1.036
Final R indexes [I>=2σ (I)]	R_1 = 0.0455, wR_2 = 0.1252
Final R indexes [all data]	R_1 = 0.0483, wR_2 = 0.1281
Largest diff. peak/hole / e Å^{-3}	0.28/-0.29
Flack parameter	0.04(18)

Table S20. Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for **7**. U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{IJ} tensor.

Atom	***x***	***y***	***z***	**U(eq)**
O4	5178.3(4)	6401.1(19)	8918.8(13)	31.1(4)
O13	4227.2(4)	3485.1(19)	7999.0(14)	32.0(4)
O22	4197.2(3)	6682.4(19)	6836.9(14)	31.8(4)
O30	4512.4(4)	7470(2)	4572.5(16)	35.1(4)
O31	4185.3(3)	8857.5(17)	5176.9(14)	27.8(3)
O38	3258.3(3)	2885.6(18)	5198.2(13)	26.5(3)
O47	3195.2(3)	4713.1(18)	7245.0(13)	27.2(3)
O56	2585.4(4)	6331(2)	3463.5(15)	38.2(4)
O57	3028.6(4)	5219(2)	3388.7(14)	36.7(4)
N2	5333.6(4)	7079(2)	7460.6(17)	29.8(4)
N11	4653.0(4)	4765(2)	8622.7(15)	27.7(4)
N20	3823.6(4)	6013(2)	7681.7(14)	24.8(4)
N25	3999.6(4)	6924(2)	4475.8(16)	26.6(4)
N36	3746.8(4)	3558.5(19)	6047.5(15)	22.4(4)
N45	3023.8(4)	2607(2)	7175.9(15)	25.5(4)
N54	2844.1(4)	5070(2)	4846.6(16)	28.4(4)
C1	5528.6(6)	8135(3)	8000(2)	38.9(6)
C3	5165.9(5)	6304(2)	7961.9(18)	26.4(4)
C5	4950.0(5)	5315(3)	7245.5(18)	28.3(5)

C6	5105.5(6)	4633(3)	6431(2)	37.0(6)
C7	5373.6(7)	3733(3)	6982(2)	40.3(6)
C8	5257.2(7)	2691(3)	7650(2)	41.7(6)
C9	5095.6(6)	3318(3)	8455(2)	34.3(5)
C10	4829.7(5)	4242(3)	7886.0(18)	28.1(5)
C12	4359.6(5)	4382(2)	8595.9(17)	26.5(4)
C14	4191.2(5)	5104(3)	9333.7(18)	28.9(5)
C15	3975.9(6)	4179(3)	9762(2)	40.5(6)
C16	3788.4(7)	4895(4)	10457(2)	51.7(8)
C17	3593.9(7)	5998(4)	9829(2)	51.2(8)
C18	3810.3(7)	6962(3)	9435(2)	42.3(6)
C19	4015.0(5)	6315(3)	8746.5(18)	29.8(5)
C21	3932.6(4)	6261(2)	6802.7(17)	22.9(4)
C23	3702.4(4)	5972(2)	5743.1(16)	20.0(4)
C24	3719.7(4)	7042(2)	4905.9(17)	24.0(4)
C26	4041.4(6)	5629(3)	4043(2)	31.4(5)
C27	4059.9(5)	4566(3)	4894(2)	28.8(5)
C28	3756.0(4)	4614(2)	5291.3(17)	22.7(4)
C29	4255.4(5)	7725(3)	4748.1(18)	26.6(4)
C32	4436.6(5)	9807(3)	5625(2)	31.3(5)
C33	4262.7(6)	10769(3)	6190(3)	45.3(7)
C34	4703.7(5)	9148(3)	6423(2)	36.3(6)
C35	4547.1(6)	10485(3)	4719(3)	41.7(6)
C37	3493.3(4)	2771(2)	5934.3(17)	22.0(4)
C39	3513.4(5)	1681(2)	6757.3(18)	25.2(4)
C40	3384.1(5)	409(3)	6173(2)	32.7(5)
C41	3386.3(6)	-719(3)	6943(3)	40.3(6)
C42	3192.8(6)	-352(3)	7749(3)	44.5(7)
C43	3322.5(6)	895(3)	8358(2)	38.6(6)
C44	3338.6(5)	2076(2)	7631.3(18)	27.2(4)
C46	2981.8(5)	3893(2)	6967.3(16)	22.7(4)
C48	2648.6(4)	4268(2)	6366.2(17)	25.2(4)
C49	2441.3(5)	4610(3)	7143(2)	37.9(6)
C50	2519.9(7)	5948(3)	7679(2)	44.0(7)
C51	2499.8(7)	7023(3)	6850(2)	45.7(7)
C52	2717.7(6)	6729(3)	6109(2)	34.0(5)
C53	2641.0(5)	5390(2)	5567.4(18)	26.6(4)
C55	2799.3(5)	5598(3)	3874.5(19)	30.1(5)
C58	3010.2(6)	5755(4)	2333(2)	41.5(6)
C59	2816.1(7)	4890(3)	1478(2)	39.5(6)
C60	2492.1(7)	5064(4)	1146(2)	48.9(8)
C61	2310.5(8)	4250(4)	380(2)	53.5(8)
C62	2451.1(10)	3266(5)	-65(3)	61.2(10)
C63	2770.8(11)	3057(6)	277(4)	78.0(13)
C64	2954.5(9)	3875(5)	1050(4)	67.1(11)

Table S21. Anisotropic Displacement Parameters ($Å^2 \times 10^3$) for **7**. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
O4	23.6(7)	39.3(10)	25.6(8)	1.2(7)	-3.6(6)	-6.2(7)
O13	17.3(7)	33.9(10)	38.4(9)	-2.1(7)	-6.6(6)	-3.1(6)
O22	14.3(7)	42.5(11)	34.5(9)	7.9(7)	-2.7(6)	-5.6(6)
O30	23.3(8)	39.8(11)	46.5(10)	-3.4(7)	16.6(7)	-2.3(7)
O31	12.9(6)	28.1(9)	41.9(9)	1.8(6)	5.3(6)	-0.4(6)
O38	14.3(6)	31.8(9)	29.2(8)	-1.0(6)	-3.1(5)	-0.9(6)
O47	13.3(6)	34.6(9)	30.7(8)	-3.2(6)	-1.0(6)	-0.8(6)
O56	35.0(9)	42.1(11)	32.4(9)	3.2(7)	-2.4(7)	13.5(8)
O57	27.9(8)	51.2(12)	30.3(9)	4.2(7)	5.1(7)	6.8(8)
N2	19.1(8)	36.0(12)	33.7(10)	0.0(8)	4.8(7)	-0.6(7)
N11	14.8(8)	39.0(12)	25.0(9)	1.3(7)	-4.1(6)	-4.3(7)
N20	13.4(7)	34.9(11)	22.5(8)	-1.2(7)	-3.3(6)	-0.3(6)
N25	18.9(8)	31.2(11)	29.6(9)	0.4(7)	5.7(7)	-2.9(7)
N36	11.7(7)	23.9(10)	28.9(9)	1.2(7)	-0.5(6)	-0.7(6)
N45	12.4(7)	30.3(11)	32.5(9)	0.3(7)	2.5(6)	1.0(6)
N54	16.6(8)	36.5(12)	28.5(9)	2.5(8)	-1.9(7)	6.2(7)
C1	29.0(12)	39.2(16)	48.7(15)	-2.7(11)	9.6(11)	-10.6(10)
C3	12.7(8)	33.4(13)	28.9(10)	5.0(9)	-3.4(7)	3.9(8)
C5	16.3(9)	40.6(14)	23.3(10)	3.2(9)	-5.1(7)	-3.0(8)
C6	34.9(12)	48.9(17)	26.2(11)	-7.9(10)	5.4(9)	-14.0(11)
C7	38.0(13)	40.9(17)	44.8(14)	-10.1(11)	15.4(11)	-3.8(11)
C8	38.2(14)	34.2(16)	52.8(16)	-3.6(12)	10.9(12)	1.4(11)
C9	30.1(12)	34.2(14)	35.6(12)	4.8(10)	1.5(9)	-0.3(9)
C10	18.7(9)	36.5(13)	25.5(10)	0.2(8)	-2.0(8)	-5.3(8)
C12	15.4(9)	32.9(13)	25.6(10)	6.9(8)	-6.3(7)	-0.8(8)
C14	16.3(9)	40.4(14)	25.0(10)	2.6(9)	-4.8(7)	-5.0(8)
C15	24.8(11)	56.7(18)	37.6(13)	9.1(12)	2.8(10)	-5.4(11)
C16	33.9(14)	86(3)	35.1(14)	8.4(15)	8.6(11)	-1.8(14)
C17	29.4(13)	89(3)	34.8(14)	-6.1(14)	7.4(11)	7.7(14)
C18	34.3(13)	59.3(19)	28.1(12)	-10.8(11)	-3.3(10)	8.5(12)
C19	19.3(9)	41.2(14)	24.4(10)	-3.1(9)	-4.2(8)	-0.3(9)
C21	11.2(8)	26.7(12)	27.4(10)	0.7(8)	-2.5(7)	1.7(7)
C23	9.5(8)	25.6(11)	23.0(9)	2.1(7)	0.1(7)	0.2(6)
C24	12.6(8)	31.6(12)	25.5(10)	4.1(8)	-0.4(7)	-0.8(7)
C26	28.7(11)	35.9(14)	32.6(11)	-4.5(9)	13.3(9)	-4.6(9)
C27	18.3(9)	32.0(13)	37.2(12)	-2.4(9)	8.8(8)	0.3(8)
C28	12.3(8)	29.5(12)	24.4(9)	-0.4(8)	0.8(7)	-3.7(7)
C29	16.9(9)	35.1(13)	28.2(10)	6.8(9)	6.0(8)	-0.3(8)
C32	14.6(9)	27.7(13)	51.6(14)	-1.1(10)	7.5(9)	-1.6(8)
C33	20.9(11)	36.3(16)	79(2)	-14.3(13)	11.6(12)	1.2(10)
C34	17.5(10)	38.3(15)	49.7(15)	-0.6(11)	0.8(9)	-0.5(9)
C35	24.1(11)	35.7(16)	65.8(18)	12.3(12)	11.7(11)	-4.9(9)
C37	12.0(8)	23.5(11)	28.4(10)	-4.4(8)	0.7(7)	0.2(7)
C39	12.3(8)	26.5(12)	34.7(11)	0.9(8)	1.2(7)	0.8(7)
C40	19.2(10)	29.4(13)	46.8(14)	0.4(10)	2.3(9)	-1.5(8)
C41	27.2(12)	28.5(15)	65.7(18)	5.8(11)	12.0(12)	0.6(9)
C42	28.3(12)	39.4(16)	68.3(19)	19.0(13)	16.6(12)	4.0(10)
C43	25.2(11)	49.0(17)	41.7(14)	15.6(11)	8.2(10)	5.9(10)
C44	14.7(9)	33.6(13)	31.0(11)	2.3(9)	0.4(8)	0.9(8)
C46	13.4(8)	29.5(12)	24.3(9)	-3.1(8)	2.8(7)	-0.3(7)

C48	11.8(8)	34.2(13)	27.3(10)	-3.6(8)	0.1(7)	0.3(7)
C49	18.5(10)	55.4(18)	41.7(13)	-0.8(12)	10.6(9)	6.7(10)
C50	38.6(14)	56(2)	37.7(14)	-12.6(12)	9.5(11)	13.8(12)
C51	42.4(15)	43.5(17)	44.7(15)	-14.1(12)	-3.1(12)	14.2(12)
C52	31.9(12)	29.4(14)	34.3(12)	-2.1(9)	-5.5(9)	5.2(9)
C53	14.6(9)	33.6(13)	26.8(10)	-3.5(8)	-5.0(7)	3.3(8)
C55	18.9(10)	38.7(14)	28.1(11)	-4.0(9)	-3.8(8)	1.3(8)
C58	28.8(12)	58.6(19)	37.2(13)	11.7(12)	8.0(10)	-2.3(11)
C59	36.1(13)	54.9(18)	30.2(12)	9.4(11)	13.2(10)	1.8(11)
C60	36.3(14)	72(2)	35.1(14)	-1.7(13)	0.8(11)	5.1(14)
C61	44.1(16)	82(3)	31.9(13)	-2.1(14)	2.7(12)	2.9(16)
C62	67(2)	78(3)	40.0(16)	-12.7(16)	14.3(15)	-8.5(19)
C63	73(3)	89(4)	79(3)	-28(2)	33(2)	5(2)
C64	41.9(17)	84(3)	81(3)	-10(2)	24.6(17)	-2.3(17)

Table S22. Bond Lengths for **7**.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
O4	C3	1.226(3)	C14	C19	1.553(3)
O13	C12	1.245(3)	C15	C16	1.532(5)
O22	C21	1.224(3)	C16	C17	1.522(5)
O30	C29	1.224(3)	C17	C18	1.529(5)
O31	C29	1.344(3)	C18	C19	1.546(4)
O31	C32	1.475(3)	C21	C23	1.523(3)
O38	C37	1.229(3)	C23	C24	1.547(3)
O47	C46	1.240(3)	C23	C28	1.539(3)
O56	C55	1.216(3)	C26	C27	1.528(4)
O57	C55	1.355(3)	C27	C28	1.531(3)
O57	C58	1.450(3)	C32	C33	1.525(4)
N2	C1	1.445(3)	C32	C34	1.519(3)
N2	C3	1.341(3)	C32	C35	1.528(4)
N11	C10	1.457(3)	C37	C39	1.523(3)
N11	C12	1.333(3)	C39	C40	1.537(3)
N20	C19	1.463(3)	C39	C44	1.554(3)
N20	C21	1.351(3)	C40	C41	1.516(4)
N25	C24	1.460(3)	C41	C42	1.530(4)
N25	C26	1.460(3)	C42	C43	1.529(5)
N25	C29	1.362(3)	C43	C44	1.535(4)
N36	C28	1.457(3)	C46	C48	1.529(3)
N36	C37	1.348(3)	C48	C49	1.538(3)
N45	C44	1.467(3)	C48	C53	1.532(3)
N45	C46	1.340(3)	C49	C50	1.530(4)
N54	C53	1.463(3)	C50	C51	1.518(5)
N54	C55	1.335(3)	C51	C52	1.527(4)
C3	C5	1.532(3)	C52	C53	1.532(4)
C5	C6	1.542(4)	C58	C59	1.507(5)
C5	C10	1.534(3)	C59	C60	1.391(4)
C6	C7	1.525(4)	C59	C64	1.376(5)
C7	C8	1.526(4)	C60	C61	1.387(5)
C8	C9	1.524(4)	C61	C62	1.368(6)
C9	C10	1.541(3)	C62	C63	1.379(7)
C12	C14	1.520(3)	C63	C64	1.399(7)
C14	C15	1.523(4)			

Table S23. Bond Angles for **7**.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C29	O31	C32	120.17(17)	C27	C28	C23	112.04(17)
C55	O57	C58	116.1(2)	O30	C29	O31	124.4(2)
C3	N2	C1	122.2(2)	O30	C29	N25	124.0(2)
C12	N11	C10	121.9(2)	O31	C29	N25	111.57(18)
C21	N20	C19	120.71(18)	O31	C32	C33	101.52(18)
C26	N25	C24	114.20(18)	O31	C32	C34	111.1(2)
C29	N25	C24	124.2(2)	O31	C32	C35	109.6(2)
C29	N25	C26	118.11(19)	C33	C32	C35	110.9(2)
C37	N36	C28	121.11(17)	C34	C32	C33	110.5(2)
C46	N45	C44	120.83(19)	C34	C32	C35	112.7(2)
C55	N54	C53	121.88(19)	O38	C37	N36	122.9(2)
O4	C3	N2	122.4(2)	O38	C37	C39	120.55(19)
O4	C3	C5	122.4(2)	N36	C37	C39	116.48(18)
N2	C3	C5	115.2(2)	C37	C39	C40	108.51(19)
C3	C5	C6	113.49(19)	C37	C39	C44	110.96(18)
C3	C5	C10	112.56(18)	C40	C39	C44	112.74(19)
C10	C5	C6	107.8(2)	C41	C40	C39	111.8(2)
C7	C6	C5	111.5(2)	C40	C41	C42	109.9(2)
C6	C7	C8	111.0(2)	C43	C42	C41	110.7(2)
C9	C8	C7	111.2(2)	C42	C43	C44	113.7(2)
C8	C9	C10	110.5(2)	N45	C44	C39	112.27(18)
N11	C10	C5	113.0(2)	N45	C44	C43	111.15(19)
N11	C10	C9	111.63(19)	C43	C44	C39	109.8(2)
C5	C10	C9	112.07(19)	O47	C46	N45	122.74(19)
O13	C12	N11	122.4(2)	O47	C46	C48	122.7(2)
O13	C12	C14	121.19(19)	N45	C46	C48	114.53(19)
N11	C12	C14	116.4(2)	C46	C48	C49	111.25(18)
C12	C14	C15	110.9(2)	C46	C48	C53	113.27(17)
C12	C14	C19	109.65(18)	C53	C48	C49	110.2(2)
C15	C14	C19	112.9(2)	C50	C49	C48	113.0(2)
C14	C15	C16	112.2(3)	C51	C50	C49	110.7(2)
C17	C16	C15	110.4(2)	C50	C51	C52	110.9(2)
C16	C17	C18	109.8(2)	C51	C52	C53	110.9(2)
C17	C18	C19	113.7(3)	N54	C53	C48	109.83(19)
N20	C19	C14	113.6(2)	N54	C53	C52	112.7(2)
N20	C19	C18	110.31(18)	C52	C53	C48	112.90(19)
C18	C19	C14	110.2(2)	O56	C55	O57	123.3(2)
O22	C21	N20	123.38(19)	O56	C55	N54	125.8(2)
O22	C21	C23	121.3(2)	N54	C55	O57	110.9(2)
N20	C21	C23	115.29(17)	O57	C58	C59	111.4(2)
C21	C23	C24	111.08(17)	C60	C59	C58	120.6(3)
C21	C23	C28	112.67(16)	C64	C59	C58	120.4(3)
C28	C23	C24	109.40(17)	C64	C59	C60	118.9(3)
N25	C24	C23	112.84(17)	C61	C60	C59	121.0(3)
N25	C26	C27	110.82(19)	C62	C61	C60	119.8(3)
C26	C27	C28	108.22(19)	C61	C62	C63	120.0(4)
N36	C28	C23	112.29(17)	C62	C63	C64	120.4(4)
N36	C28	C27	111.20(18)	C59	C64	C63	120.0(4)

Table S24. Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for **7**.

Atom	***x***	***y***	***z***	**U(eq)**
H2	5325	6940	6780	36
H11	4743	5351	9099	33
H20	3635	5667	7613	30
H36	3910	3433	6587	27
H45	2861	2076	7038	31
H54	3000	4514	5060	34
H1A	5734	8108	7818	58
H1B	5557	8035	8774	58
H1C	5427	8979	7775	58
H5	4763	5809	6834	34
H6A	4945	4111	5928	44
H6B	5188	5307	6015	44
H7A	5541	4263	7448	48
H7B	5465	3299	6437	48
H8A	5107	2100	7173	50
H8B	5438	2156	8033	50
H9A	5252	3821	8988	41
H9B	5007	2623	8836	41
H10	4679	3693	7357	34
H14	4355	5434	9956	35
H15A	4104	3479	10189	49
H15B	3828	3755	9155	49
H16A	3647	4265	10701	62
H16B	3935	5262	11095	62
H17A	3477	6464	10290	61
H17B	3439	5628	9212	61
H18A	3950	7386	10061	51
H18B	3680	7658	9011	51
H19	4178	6971	8660	36
H23	3485	5985	5868	24
H24A	3530	6981	4312	29
H24B	3719	7918	5239	29
H26A	4237	5620	3781	38
H26B	3863	5440	3431	38
H27A	4244	4724	5494	35
H27B	4084	3691	4587	35
H28	3578	4460	4658	27
H33A	4074	11094	5685	68
H33B	4401	11509	6467	68
H33C	4201	10322	6783	68
H34A	4617	8592	6905	55
H34B	4840	9821	6838	55
H34C	4827	8606	6040	55
H35A	4655	9846	4360	63
H35B	4692	11198	5011	63
H35C	4365	10845	4205	63
H39	3740	1538	7109	30
H40A	3166	562	5758	39
H40B	3513	171	5664	39
H41A	3606	-917	7324	48

H41B	3296	-1513	6543	48
H42A	2971	-209	7370	53
H42B	3199	-1083	8260	53
H43A	3537	711	8795	46
H43B	3188	1127	8851	46
H44	3465	2778	8079	33
H48	2554	3480	5950	30
H49A	2218	4607	6748	46
H49B	2468	3923	7701	46
H50A	2371	6141	8132	53
H50B	2735	5925	8144	53
H51A	2559	7874	7213	55
H51B	2280	7096	6424	55
H52A	2939	6735	6525	41
H52B	2694	7423	5557	41
H53	2421	5443	5122	32
H58A	3225	5841	2215	50
H58B	2915	6642	2286	50
H60	2394	5749	1448	59
H61	2089	4375	164	64
H62	2329	2727	-608	73
H63	2867	2355	-15	94
H64	3175	3729	1281	81

References

[S1] Bruker-AXS. (2007-2013) APEX2 (Ver. 2013.2-0), SADABS (2012-1), and SAINT+ (Ver. 8.30C) Software Reference Manuals. Bruker-AXS, Madison, Wisconsin, USA.

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[S7] Sheldrick, G. M. *Acta. Cryst*. **2015**, *C71*, 3-8.

Copies of NMR spectra

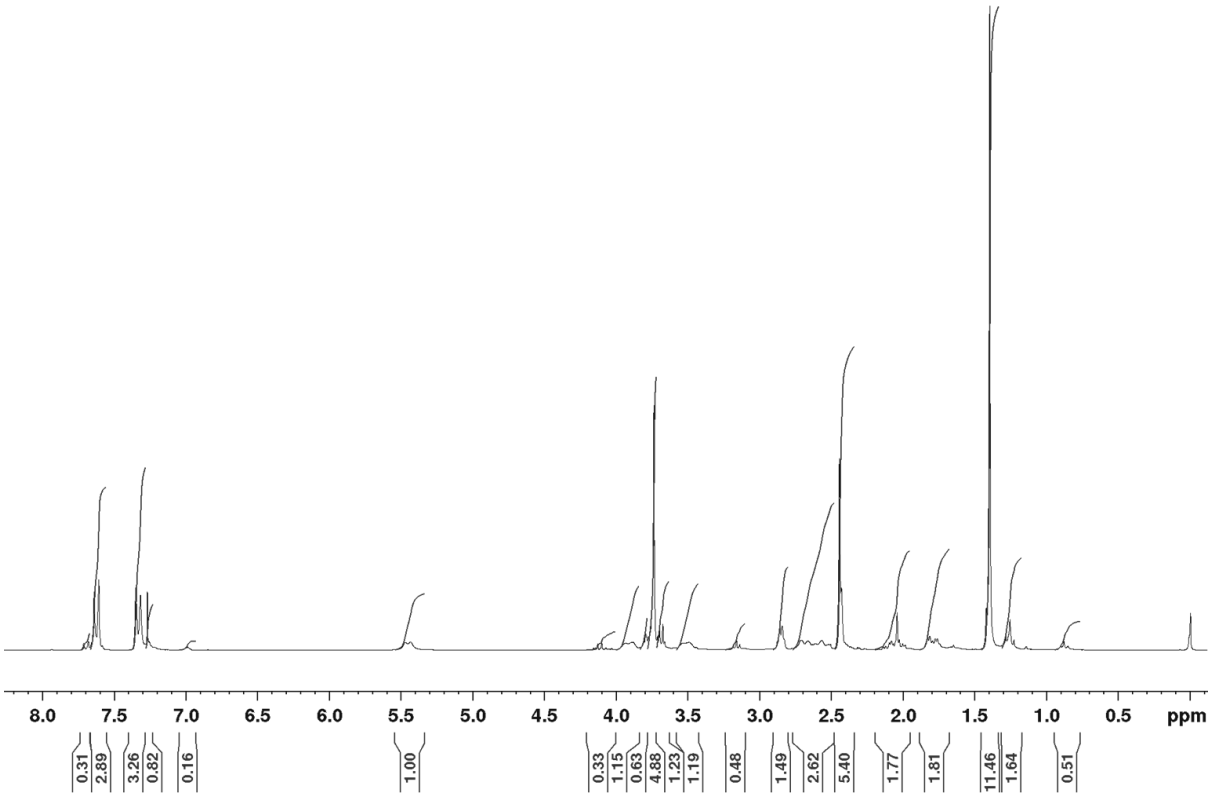

Figure S1. H-NMR spectrum of **3a**.

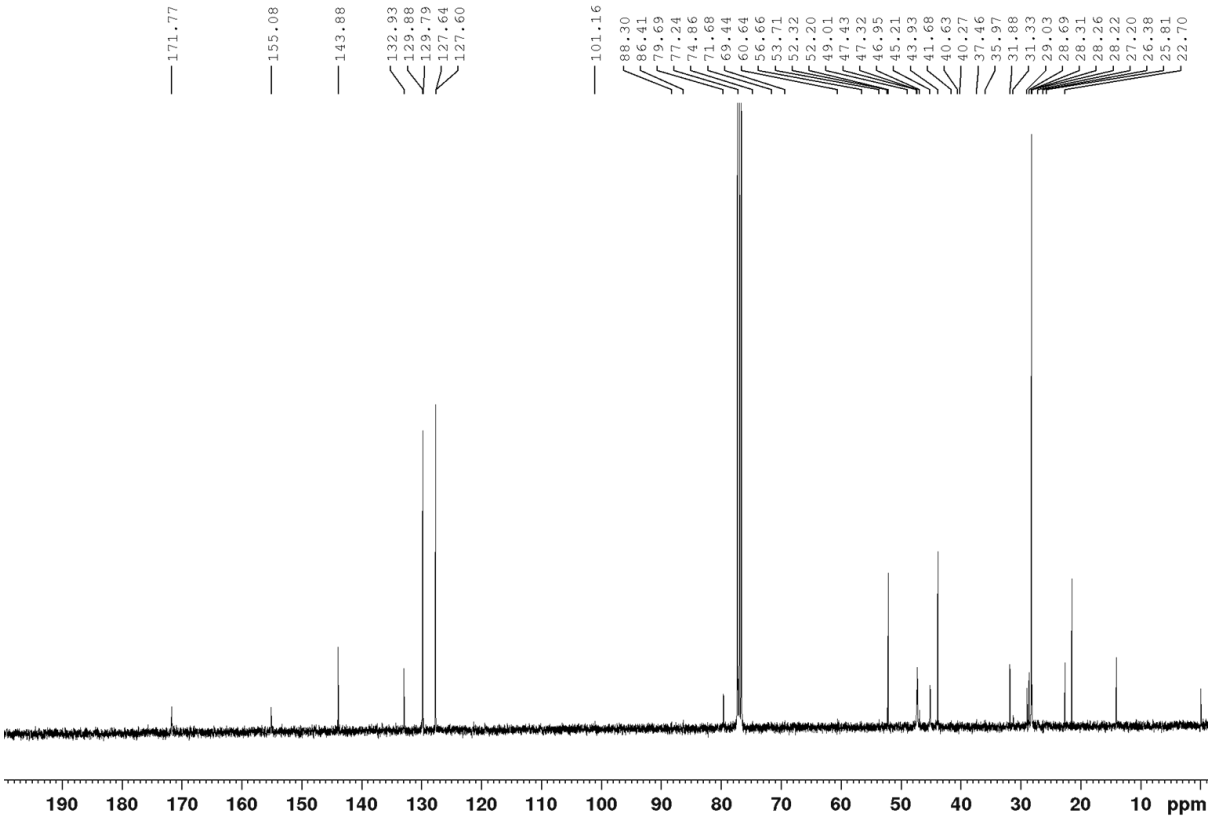

Figure S2. C-NMR spectrum of **3a**.

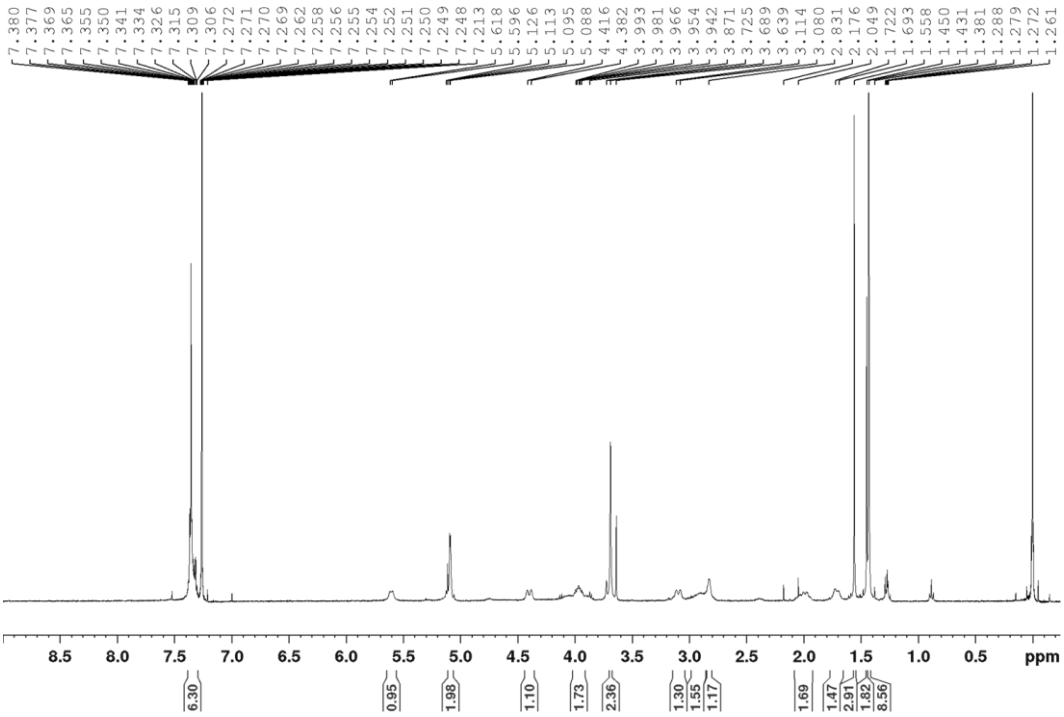

Figure S3. H-NMR spectrum of **3b**.

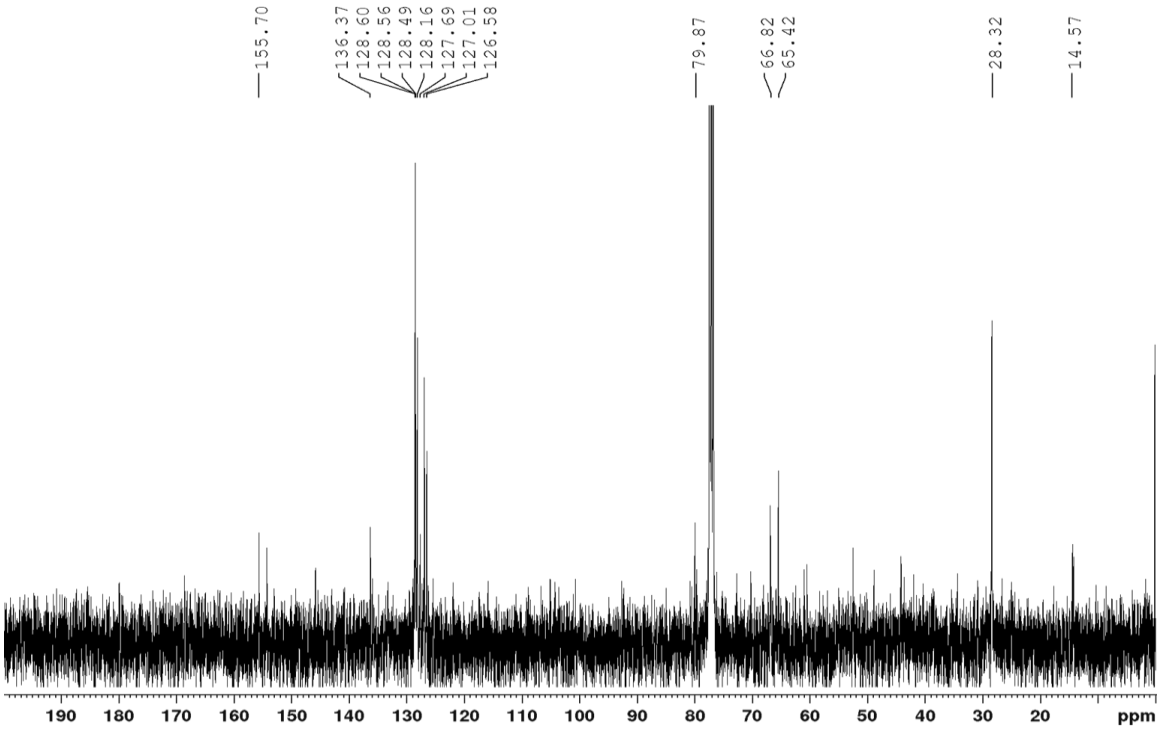

Figure S4. C-NMR spectrum of **3b**.

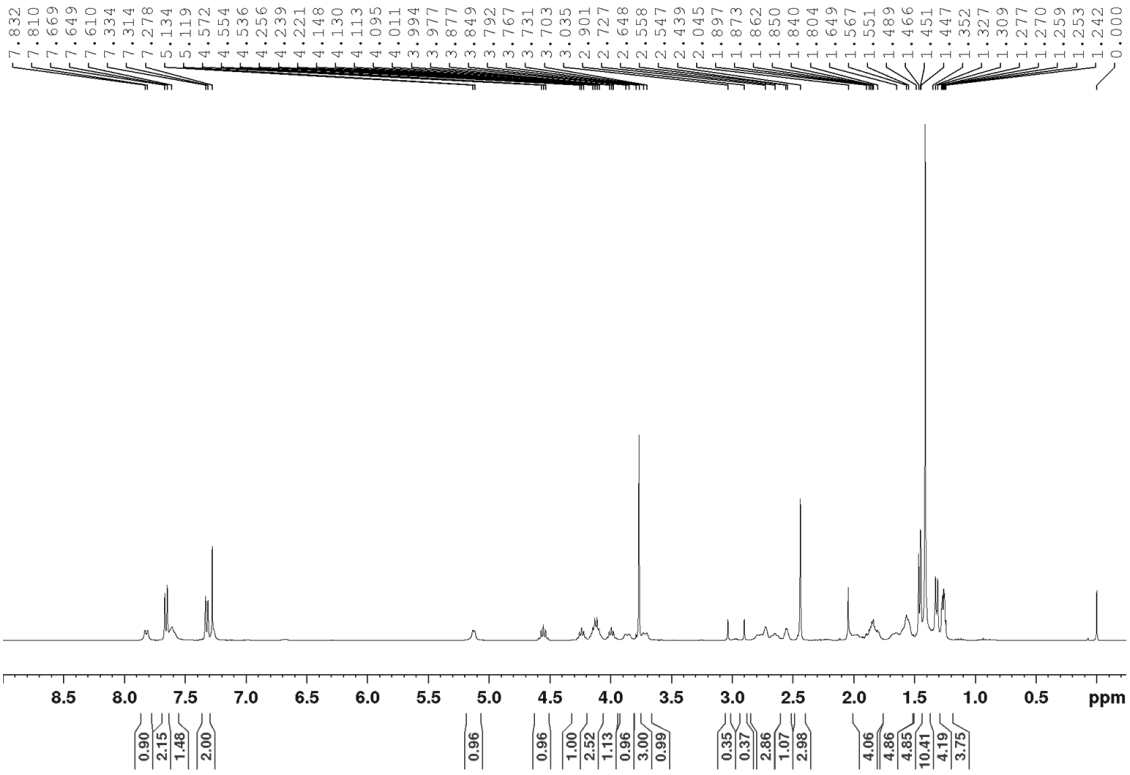

Figure S5. H-NMR spectrum of **4**.

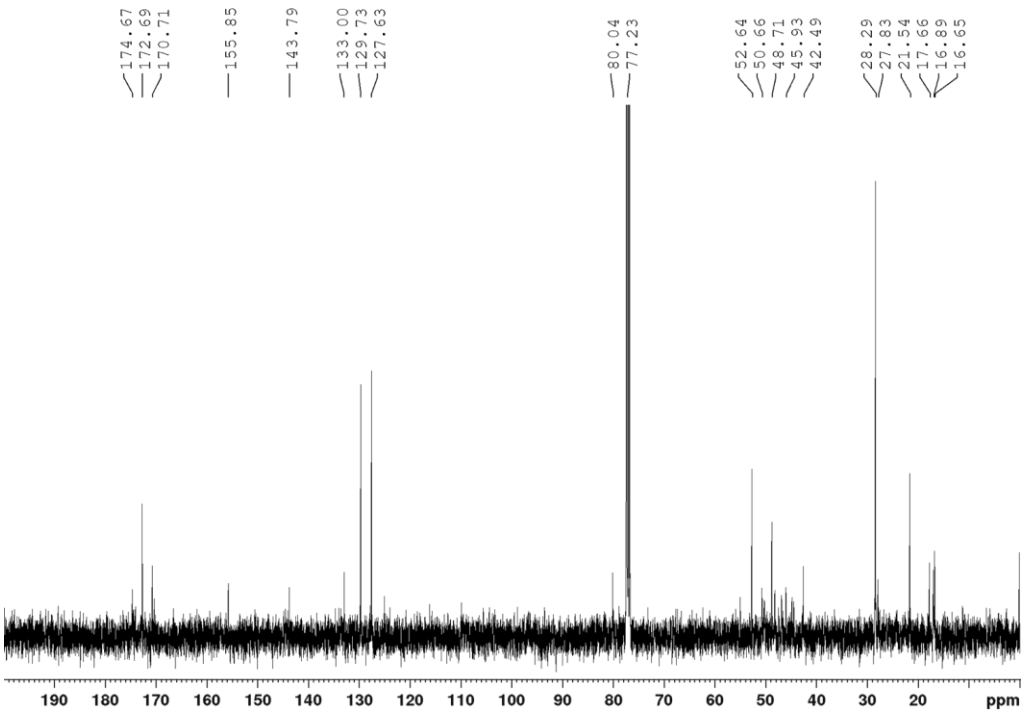

Figure S6. C-NMR spectrum of **4**.

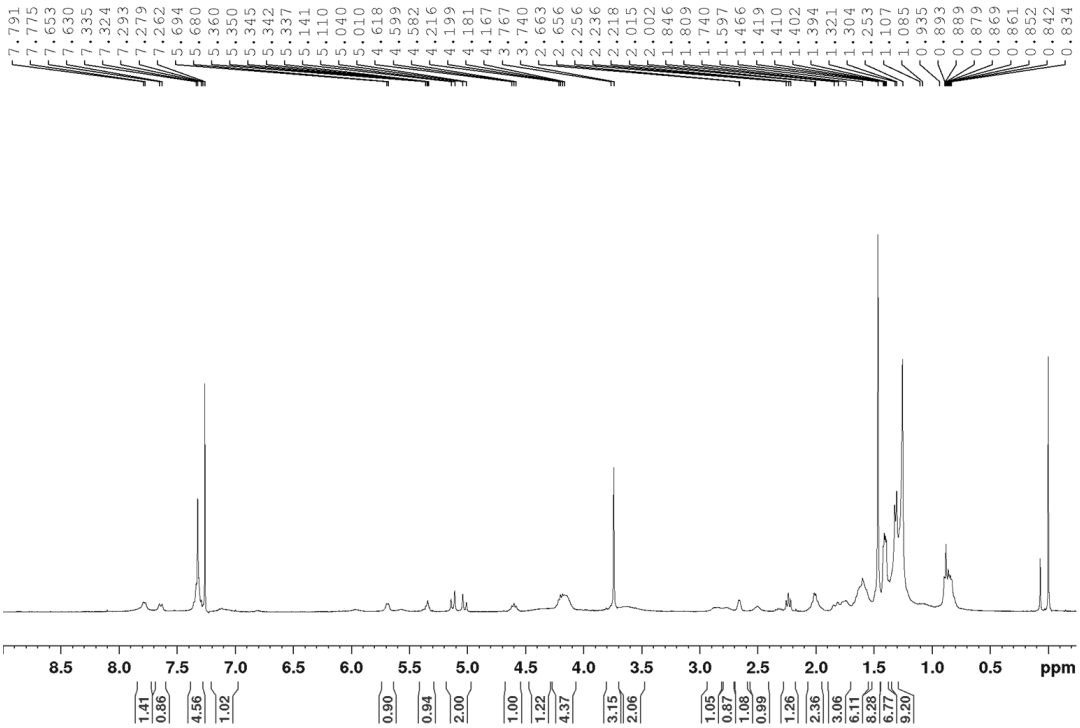

Figure S7. H-NMR spectrum of **5**.

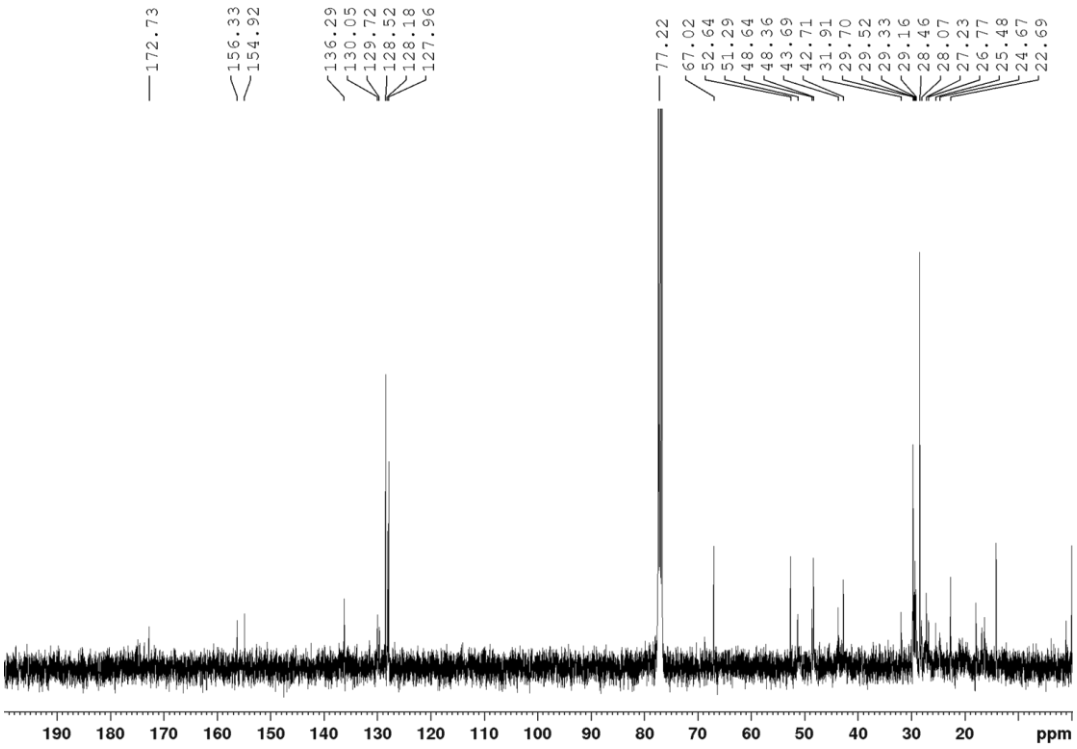

Figure S8. C-NMR spectrum of **5**.

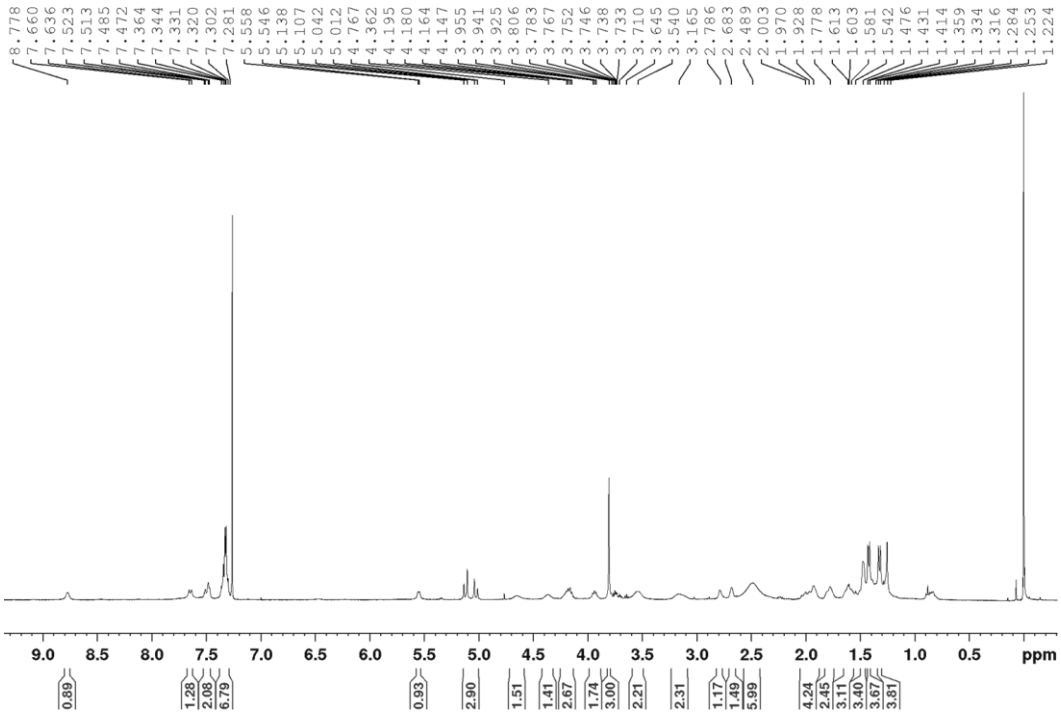

Figure S9. H-NMR spectrum of **6**.

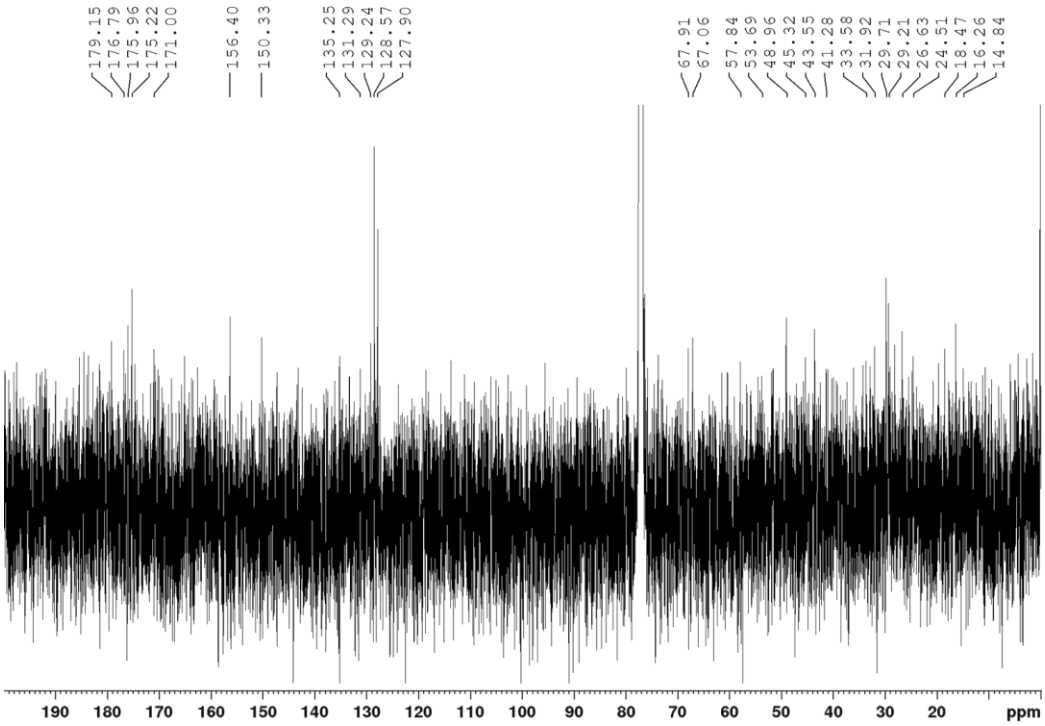

Figure S10. C-NMR spectrum of **6**.

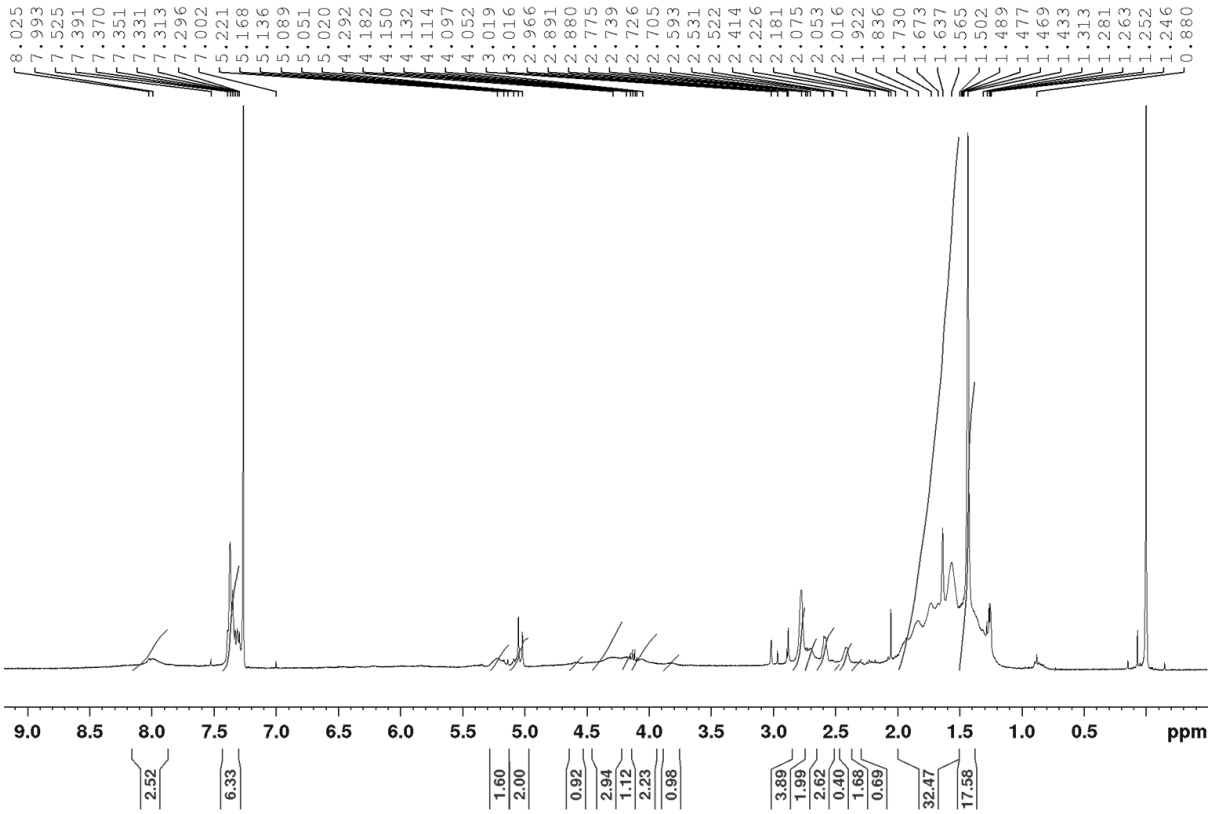

Figure S11. H-NMR spectrum of **7**.

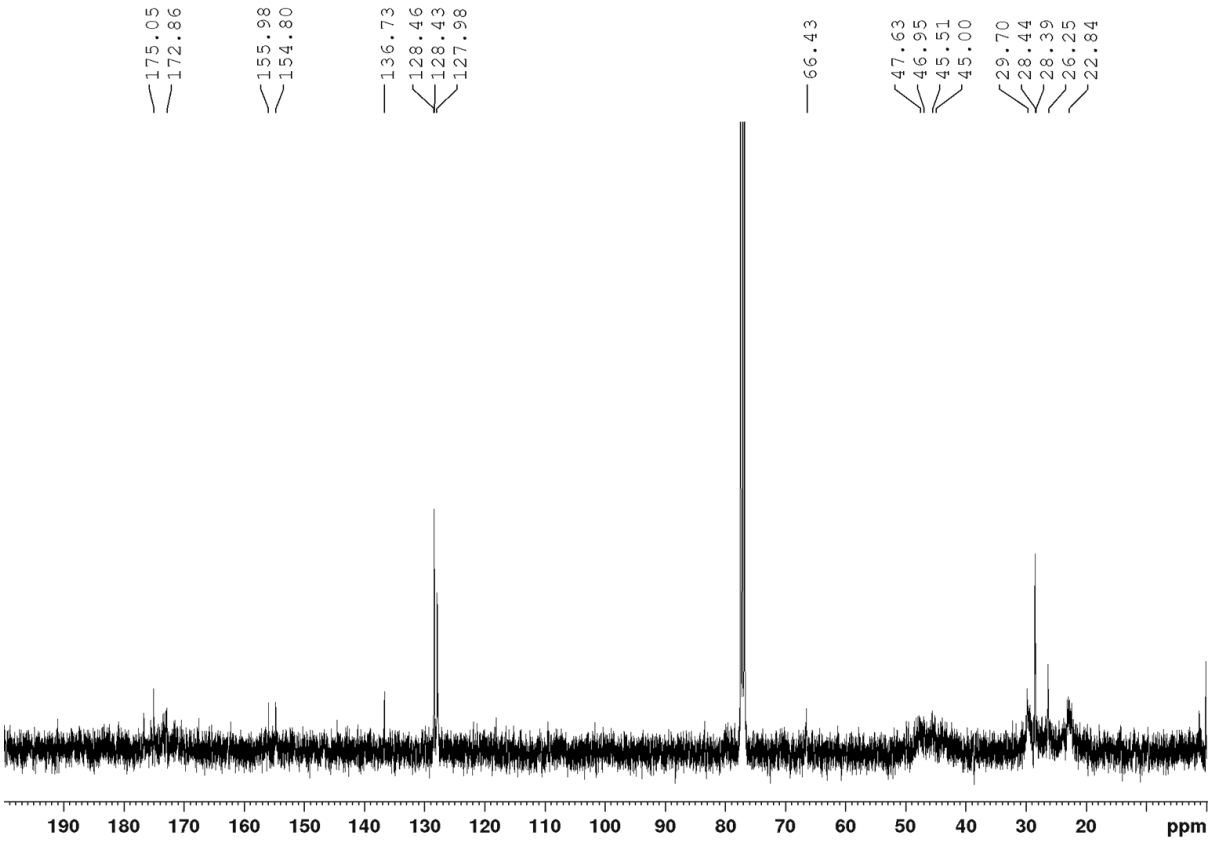

Figure S12. C-NMR spectrum of **7**.

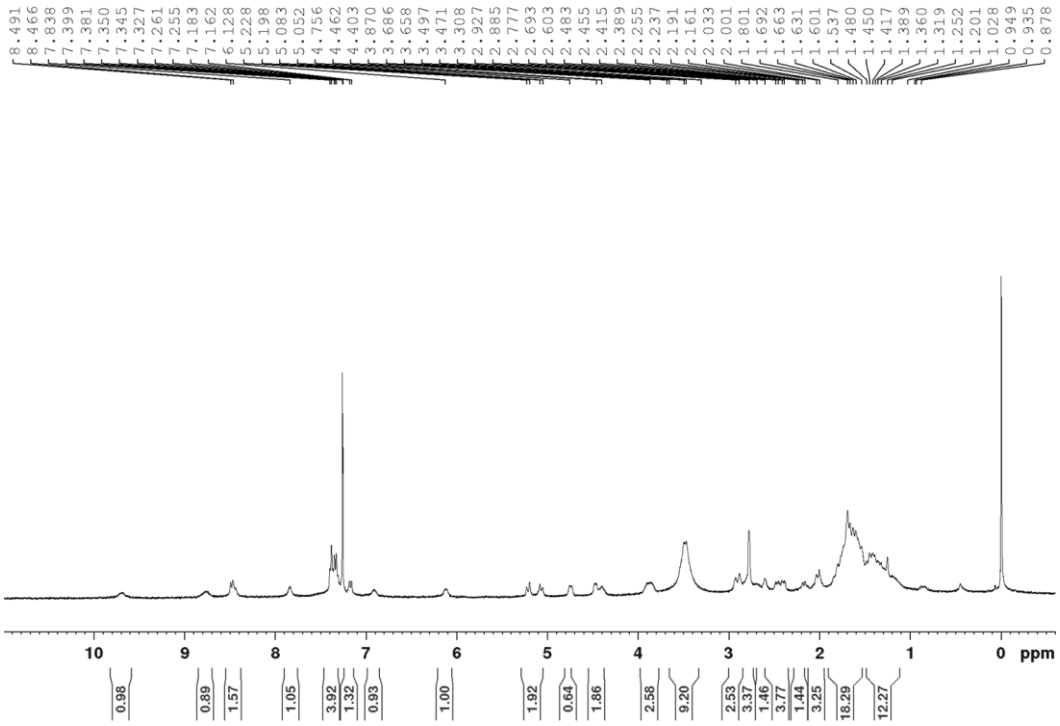

Figure S13. H-NMR spectrum of **8**.

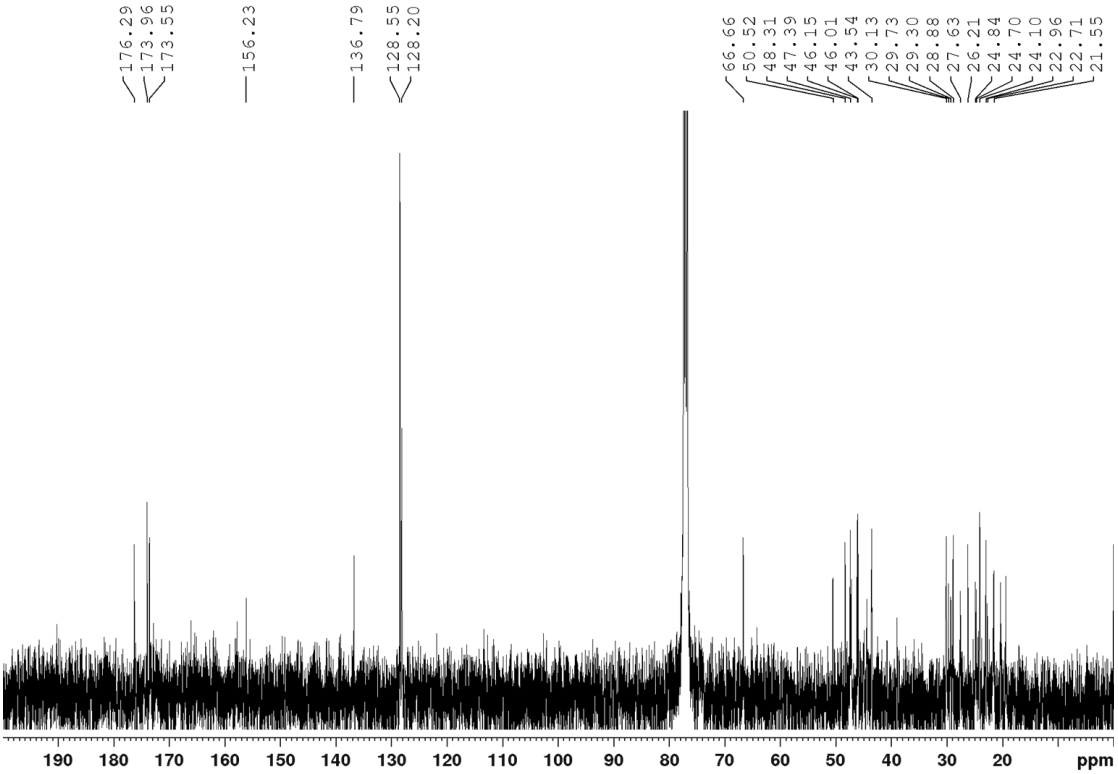

Figure S14. C-NMR spectrum of **8**.

Copies of mass data (HRMS & MALDI-TOF)

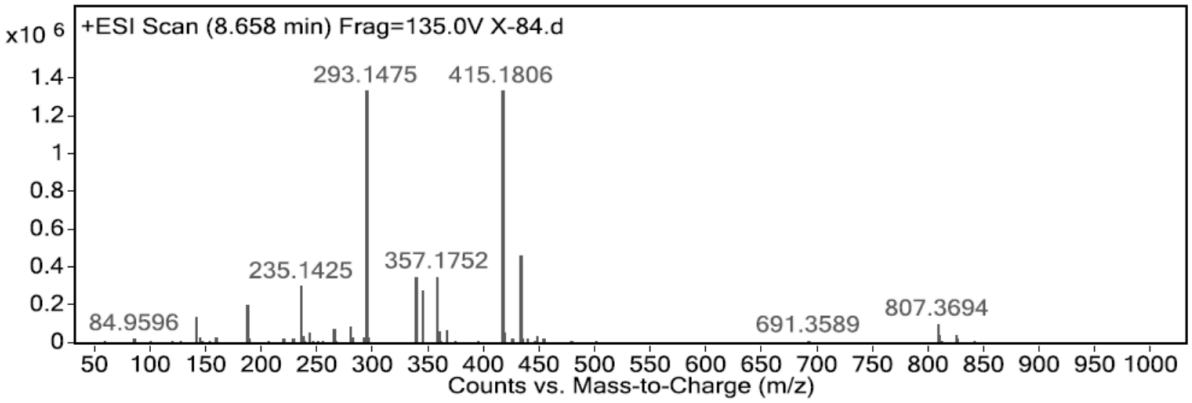

Figure S15. HRMS spectrum for **3b**.

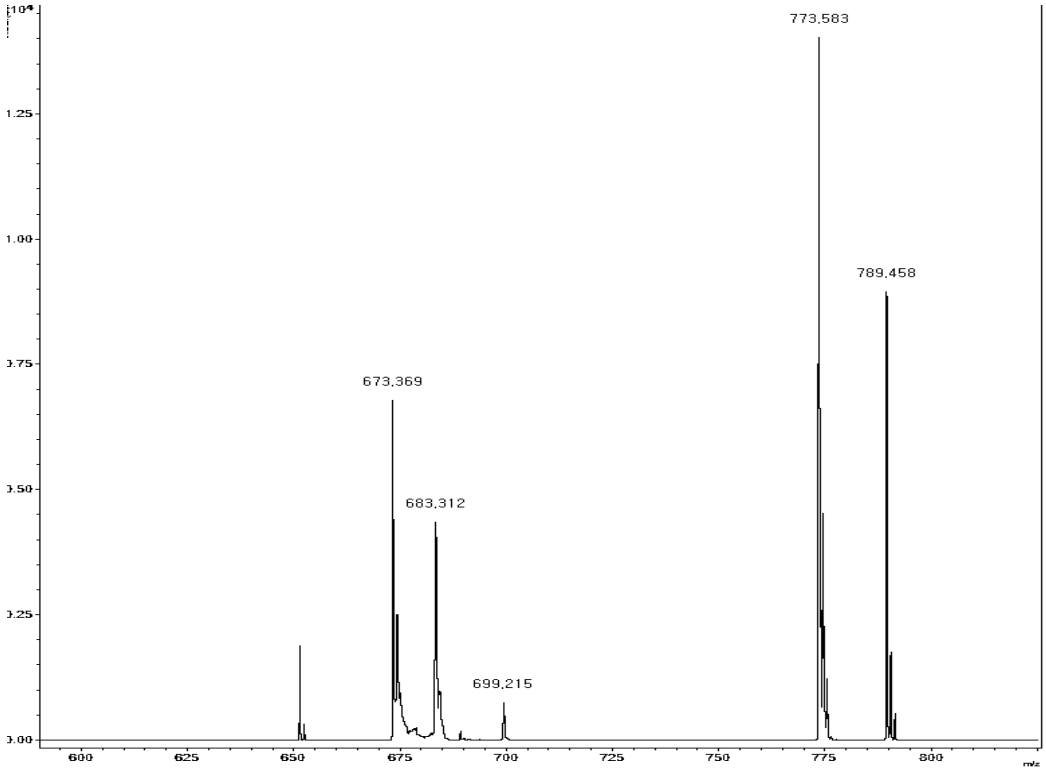

Figure S16. MALDI-TOF spectrum for **4**.

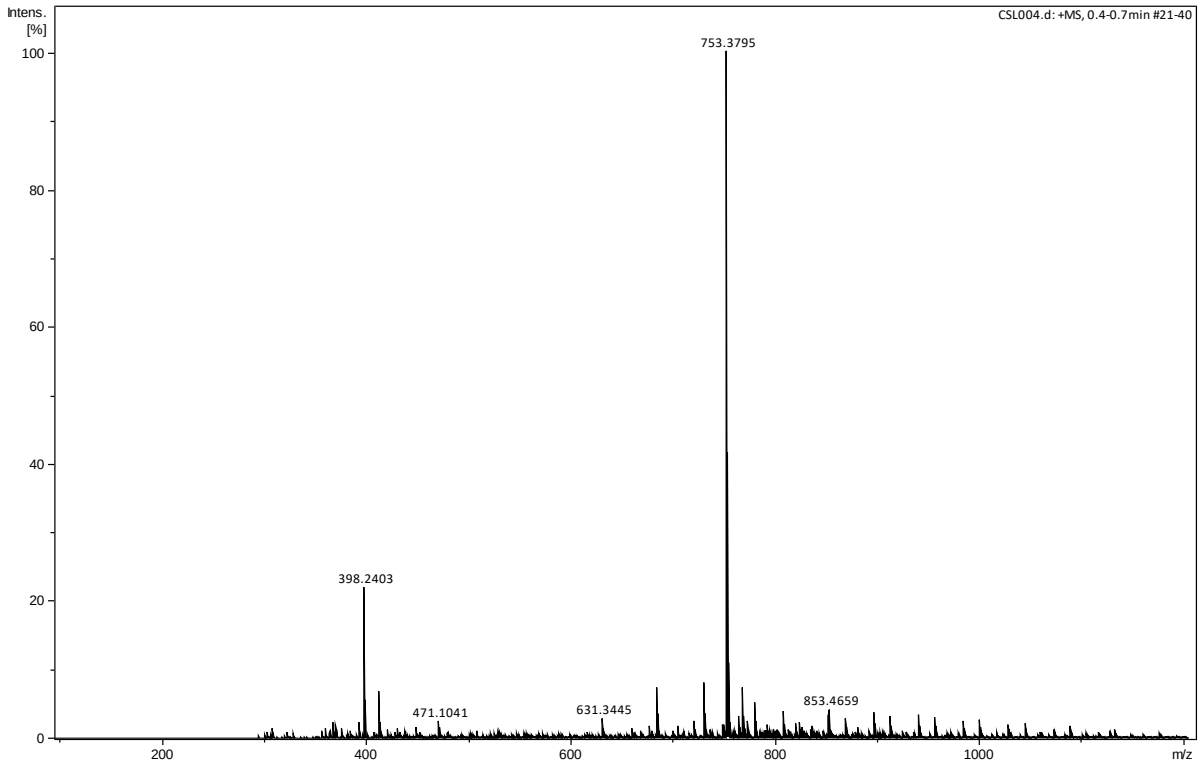

Figure S17. UHRMS spectrum for **5**.

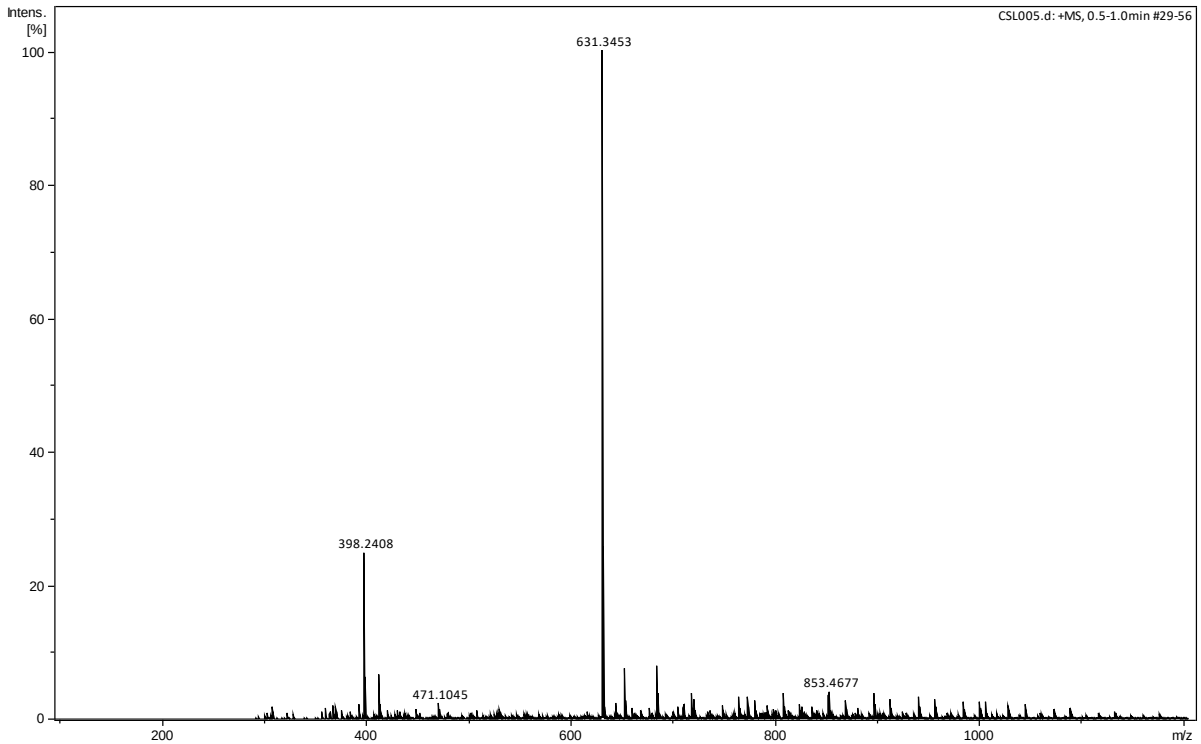

Figure S18. UHRMS spectrum for **6**.

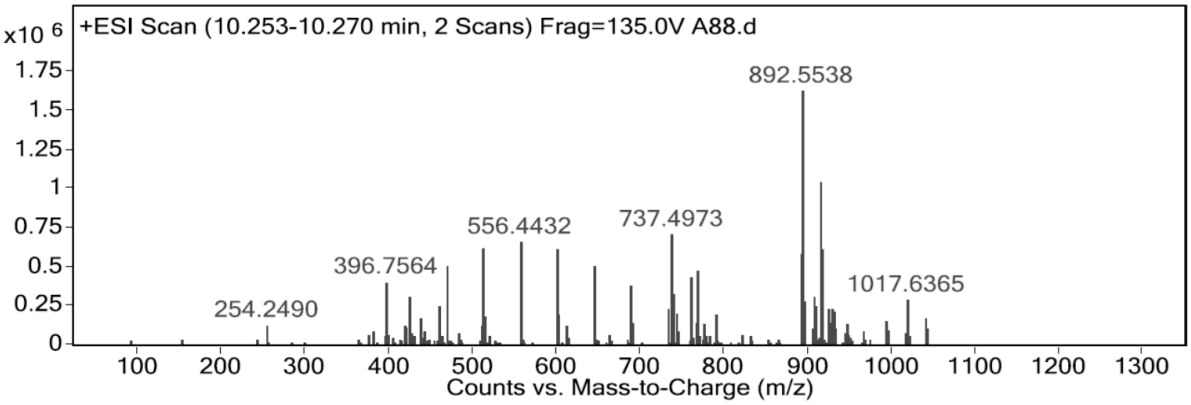

Figure S19. HRMS spectrum for **7**.

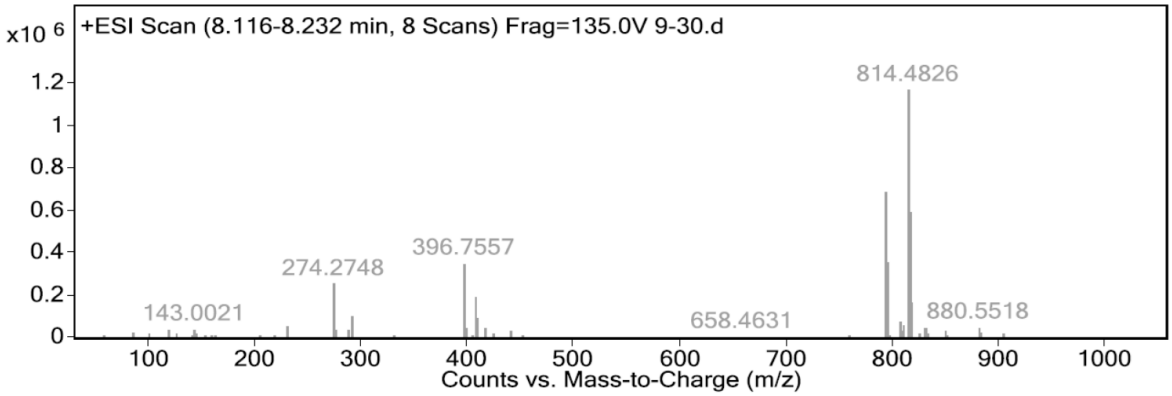

Figure S20. HRMS spectrum for **8**.