Redox-Sensitive Reversible Self-Assembly of Amino Acid-Naphthalene Diimide Conjugates

*Wathsala Liyanage, Paul W. Rubeo, and Bradley L. Nilsson**

Department of Chemistry, University of Rochester, Rochester, NY, 14627-0216, USA.

E-mail: nilsson@chem.rochester.edu

Fax: +1 585 276-0205; Tel. +1 585 276-3053

Supporting Information

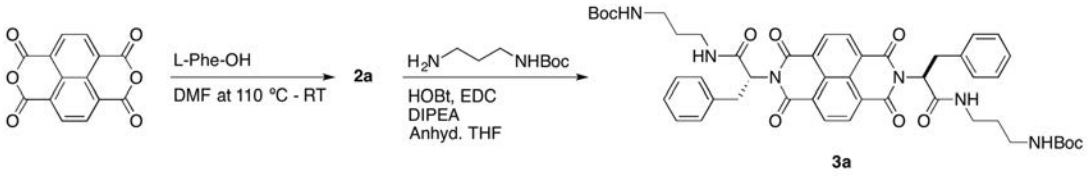
Table of Contents

General information

Unless stated otherwise, reactions were performed in flame-dried glassware under a positive pressure of nitrogen using dry solvents. Commercial grade solvents were used without further purification except where noted. Diethyl ether (Et_2O), dichloromethane (DCM), dimethylformamide (DMF), acetonitrile (ACN) and tetrahydrofuran (THF) were purified as described in: Pangborn, A. B.; Giardello, M. A.; Grubbs, R. H.; Rosen, R. K.; Timmers, F. J. *Organometallics* **1996**, *15*, 1518–1520. Reagents were purchased at highest available commercial quality and used without further purification unless otherwise stated. Thin-layer chromatography (TLC) was performed using silica gel 60 F254 pre-coated plates (0.25 mm). Flash chromatography was performed using silica gel (40 μm particle size). The purity of compounds was judged by TLC analysis (single spot/two solvent systems) using a UV lamp, ninhydrin, or basic $KMnO_4$ stain. NMR spectra were recorded on a Bruker Avance-400 MHz and 500 MHz spectrometers. NMR chemical shifts were reported as δ values relative to residual signals from deuterated solvents ($CDCl_3$ or DMSO-d_6). Water for the self-assembly experiments was purified with a Barnstead NANO pure system (0.2 μm filter, 18 Ω).

Synthesis of compounds

Compound 3a

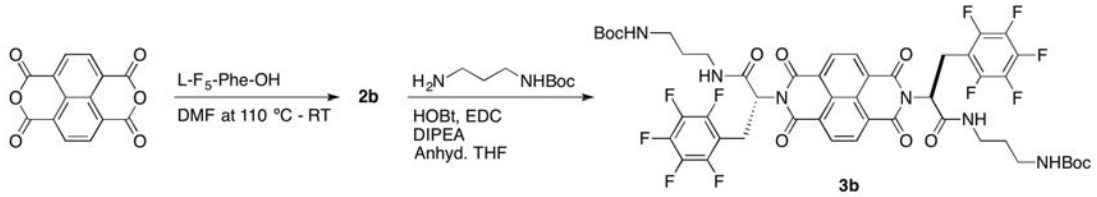


A solution of 1, 4, 5, 8-napthalenetetracarboxylic dianhydride (500 mg, 1.86 mmol) in dry DMF (10 mL) was treated with L-Phe-OH (616 mg, 3.73 mmol). The reaction was warmed to completely dissolve the substrate and the reaction mixture was stirred overnight at room temperature. The resulting crude product was poured into ice water and acidified to pH~3 and the resulting product **2a** was obtained by filtration. ^{1}H NMR: (500 MHz, DMSO-d_6): 13.11 (s, 2H), 8.70 (s, 4H), 7.15 (m, 10 H), 5.90 (m, 2H), 3.62 (dd, J = 7 Hz, 14 Hz, 2H), 3.36 (dd, J = 7 Hz, 22 Hz, 2H) ppm; ^{13}C NMR (125 MHz, DMSO-d_6) δ 170.72, 162.49, 138.28, 131.71, 129.39, 128.63, 126.82, 126.51, 126.13, 55.10, 34.83; HRMS (ESI-TOF) (*m/z*) $[M+Na]^+$ calcd for $C_{32}H_{23}N_2O_8$ 585.1274, found 585.1277.

Crude **2a** (400 mg, 0.70 mmol) was taken up directly in anhydrous THF and stirred at 0 ºC; 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide hydrochloride (EDC•HCl) (268 mg, 1.40 mmol) and *N*-hydroxybenzotriazole HOBt (228 mg, 1.7 mmol) were then added. The reaction was stirred 2 h at 0 ºC, then treated with 280 μL of N, N-diisopropylethylamine (DIPEA) and tert-butyl(3-aminopropyl)carbamate (244 mg, 1.40 mmol). The resulting reaction mixture was allowed to warm to room temperature and stirred for 3 h. The crude reaction was concentrated under reduced pressure and purified by flash chromatography (50% EtOAc/hexanes eluant) to obtain a **3a** as a pale yellow powder (143 mg, 23% yield). ^{1}H NMR: (500 MHz, DMSO-d_6): 8.60 (s, 4H), 7.52 (2H), 7.10 (m, 10H), 6.03 (t, J = 2H), 4.84 (m, 2H), 3.81 (dd, J = ,2H), 3.61 (dd, J =

2H), 3.40 (m, 2H), 3.10 (m, 6H), 1.63 (2H), ppm; ^{13}C NMR (125 MHz, DMSO-d_6): δ 168.59, 163.05, 157.17, 137.64, 130.82, 129.04, 128.53, 126.92, 126.72, 79.50, 56.22, 36.46, 35.05, 34.10, 29.55, 27.72 ppm; HRMS (ESI-TOF) (*m/z*) $[M+Na]^+$ calcd for $C_{48}H_{55}N_6O_{10}$ 897.3799, found 897.3795 .

Compound 3b

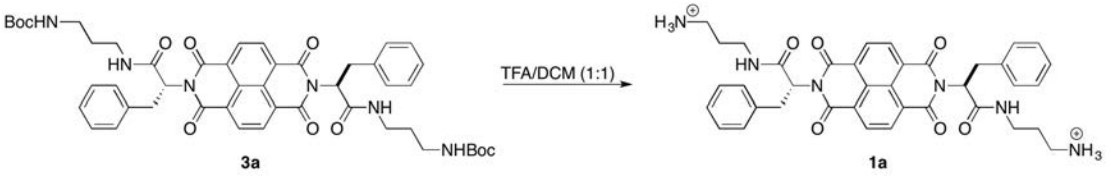


Compound **3b** was prepared by the same procedure described for **3a**, with L-F_5-Phe-OH (0.5741 g, 2.25 mmol) in place of L-Phe-OH. Compound **2b** was obtained as a brown powder (435 mg, 78%). ^{1}H NMR: (500 MHz, DMSO-d_6): 13.41 (s, 2H), 8.77 (s, 4H), 5.87 (2H), 3.74 (2H), 3.56 (2H) ppm; ^{13}C NMR (125 MHz, DMSO-d_6): δ 169.64, 162.64, 146.60, 144.20, 138.62, 136.09, 131. 91, 126.20, 111.94, 52.49, 22.55 ppm. ^{19}F NMR (376 MHz, DMSO-d_6) δ -80.34 (m, 2F), -93.42 (t, J = 18 Hz, 1F), -99.28 (m, 2F). HRMS (ESI-TOF) (*m/z*) $[M +Na^+]$ calcd for $C_{32}H_{13}F_{10}N_2O_8$ 765.0332 found 765.0315.

Crude **2b** (220 mg, 0.30 mmol) was taken up directly in anhydrous THF and stirred at 0 ºC; 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide hydrochloride (EDC•HCl) (50 mg, 0.26 mmol) and *N*-hydroxybenzotriazole (HOBt) (43 mg, 0.31 mmol) were then added. The reaction was stirred 2 h at 0 ºC, then treated with 54 μL of N, N-diisopropylethylamine (DIPEA) and tert-butyl(3-aminopropyl)carbamate (45 mg, 0.26 mmol). The resulting reaction mixture was allowed to warm to room temperature and stirred for 3 h. The crude reaction was concentrated under reduced pressure and purified by flash chromatography (50% EtOAc/hexanes eluant) to obtain a

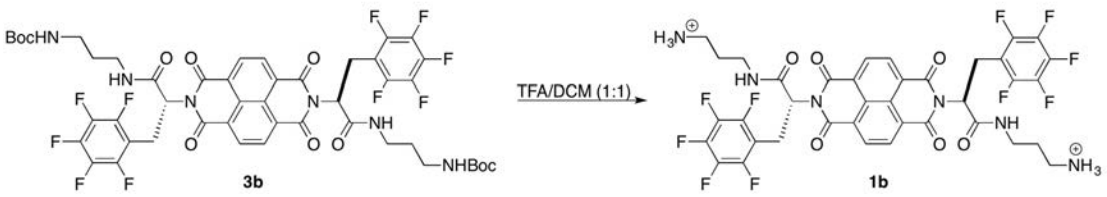
3b as a yellow powder (180 mg, 57%) ^{1}H NMR: (500 MHz, DMSO-d_6): 8.66 (s, 4H), 7.59 (s, 2H), 5.85 (2H), 4.51 (m, 2H), 3.93 (dd, J = 2H), 3.70 (dd, J = 2H), 3.48(m, 2H), 3.00 (m, 6H), 1.64 (m, 2H), 1.45 (m, 2H), 0.72 (s, 18H) ppm; ^{13}C NMR (125 MHz, DMSO-d_6): δ 167.15, 163.03, 157.44, 146.76, 144.81, 138.57, 136.540, 136.30, 131.23, 127.00, 112.04, 79.50, 54.54, 36.40, 34.92, 29.42, 27.47, 21.49 ppm; HRMS (ESI-TOF) (*m/z*) $[M+Na]^+$ calcd. for $C_{48}H_{45}F_{10}N_6O_{10}Na$ 1077.2857 found 1077.2897.

Compound 1a



A solution of **3a** (143 mg, 0.16 mmol) in 50% TFA/DCM solution was stirred at room temperature for 12 h. The reaction mixture was diluted with 5 mL of ethyl acetate, and concentrated in vacuo (this step is necessary to remove excess TFA). The crude residue was treated with Et_2O (precooled to 0 ºC) and the resulting precipitate was obtained by filtration, and then dried under vacuum. The desired product **1a** was obtained as a pale yellow powder (111 mg, 77%). ^{1}H NMR: (500 MHz, DMSO-d_6): 8.55 (s, 4H), 8.15 (s, 2H), 7.70 (s, 6H), 6.99 (m, 10H), 5.73 (t, J = 14 Hz, 4H), 3.60 (t, J = 10 Hz, 2H), 3.26 (m, 2H), 3.21 (m, 2H), 3.14 (m, 2H), 2.74 (m, 4H), 1.62 (s, 4H) ppm; ^{13}C NMR (125 MHz, DMSO-d_6): δ 169.08, 162.90, 138.41, 130.97, 129.35, 128.58, 126.72, 126.63, 126.40, 55.79, 37.14, 36.34, 34.21, 27.89 ppm; HRMS (ESI-TOF) (*m/z*) $[MH]^+$ calcd for $C_{38}H_{38}N_6O_6$ 675.2931 found 675.2931.

Compound 1b



Compound **3b** (177 mg, 0.17 mmol) was deprotected using the same procedure described for **3a.** The desired product **1b** (161 mg, 88%) was obtained as a pale yellow solid. ^{1}H NMR: (500 MHz, DMSO-d_6): 8.72 (s, 4H), 8.35 (s, 2H), 7.72 (s, 6H), 5.74-5.71 (J= 2H), 3.81-3.78 (J= 2H), 3.51-3.46 (J= 2H), 3.24-3.20 (J =, 4H), 2.80-2.79 (J =, 4H), 1.68-1.67(4H) ppm; ^{13}C NMR (125 MHz, DMSO-d_6):

δ 170.65, 169.92, 167.73, 162.92, 158.90, 158.66, 158.17, 146.52, 144.49, 140.56, 138.00, 135.86, 131.31,126.16, 118.52, 116.20, 112.78, 112.60, 112.36, 97.00 ppm;^{19}F NMR (376 MHz, DMSO-d_6) δ -80.85 (m, 2F), -93.13 (t, J = 22 Hz, 1F), -100.63(m, 2F). HRMS (ESI-TOF) (*m/z*) $[MH]^+$ calcd. for $C_{38}H_{29}F_{10}N_6O_6$ 855.1983 found 855.2000.

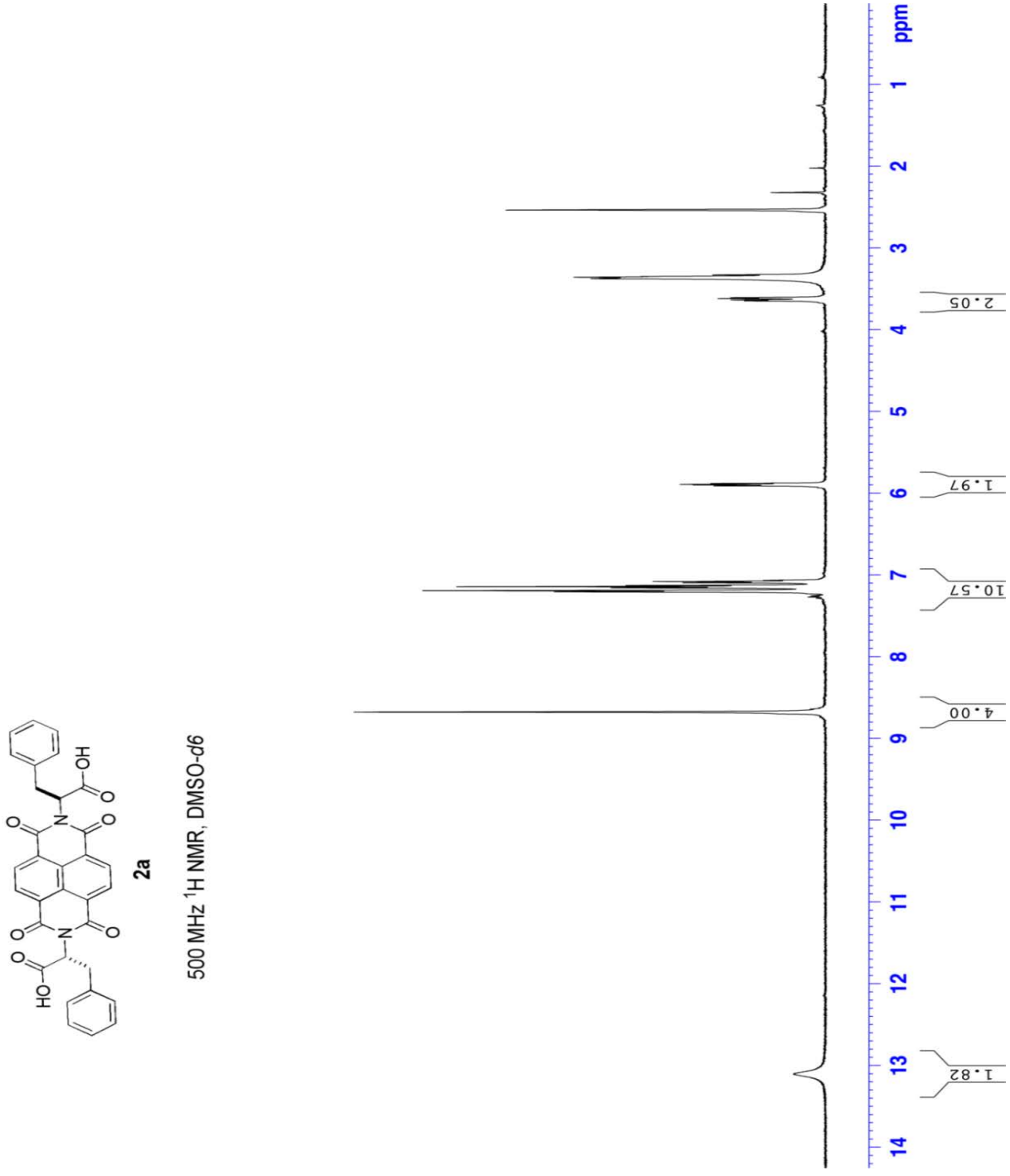


Figure S1. ^{1}H NMR of **2a**.

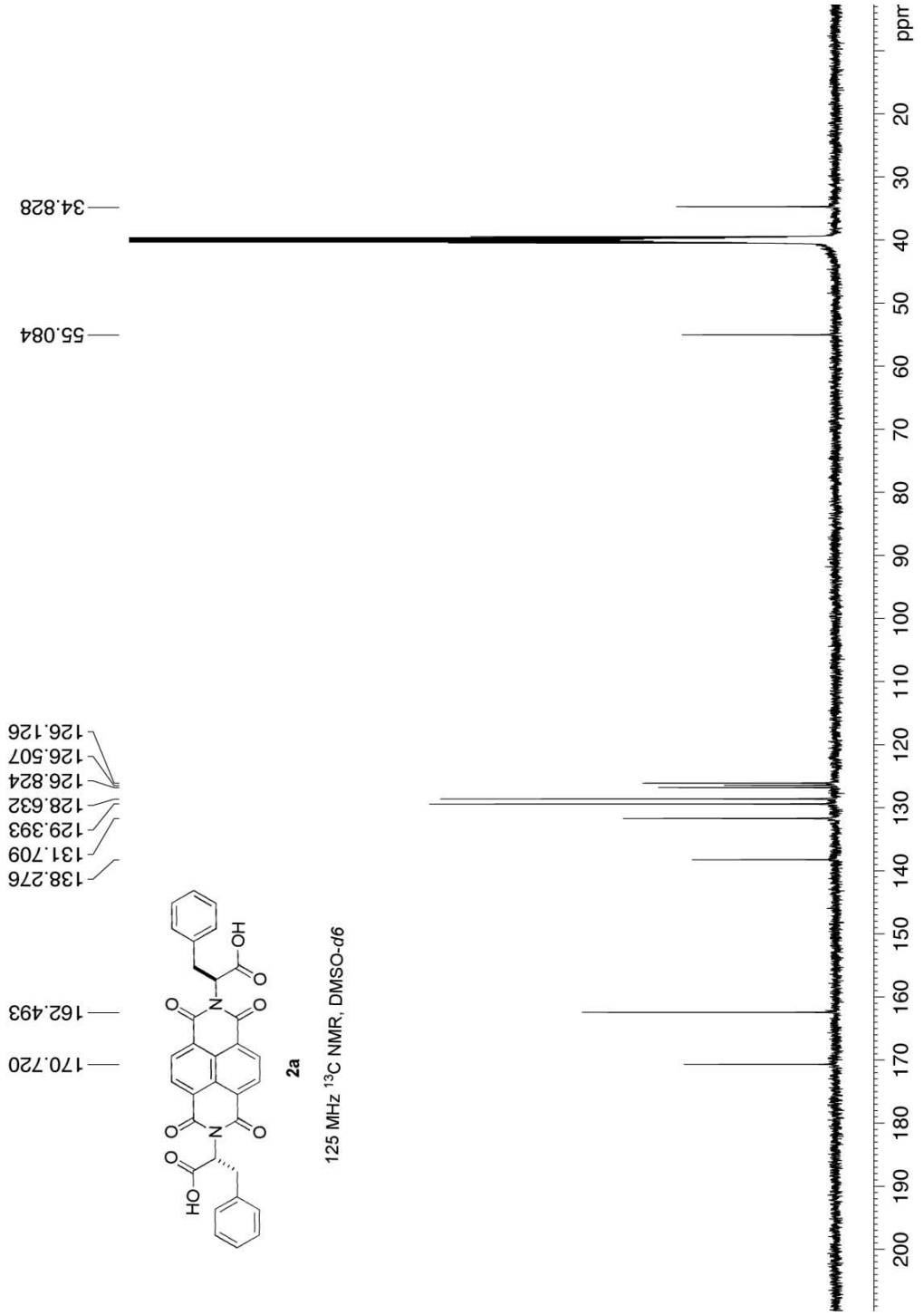


Figure S2. ^{13}C NMR of **2a**.

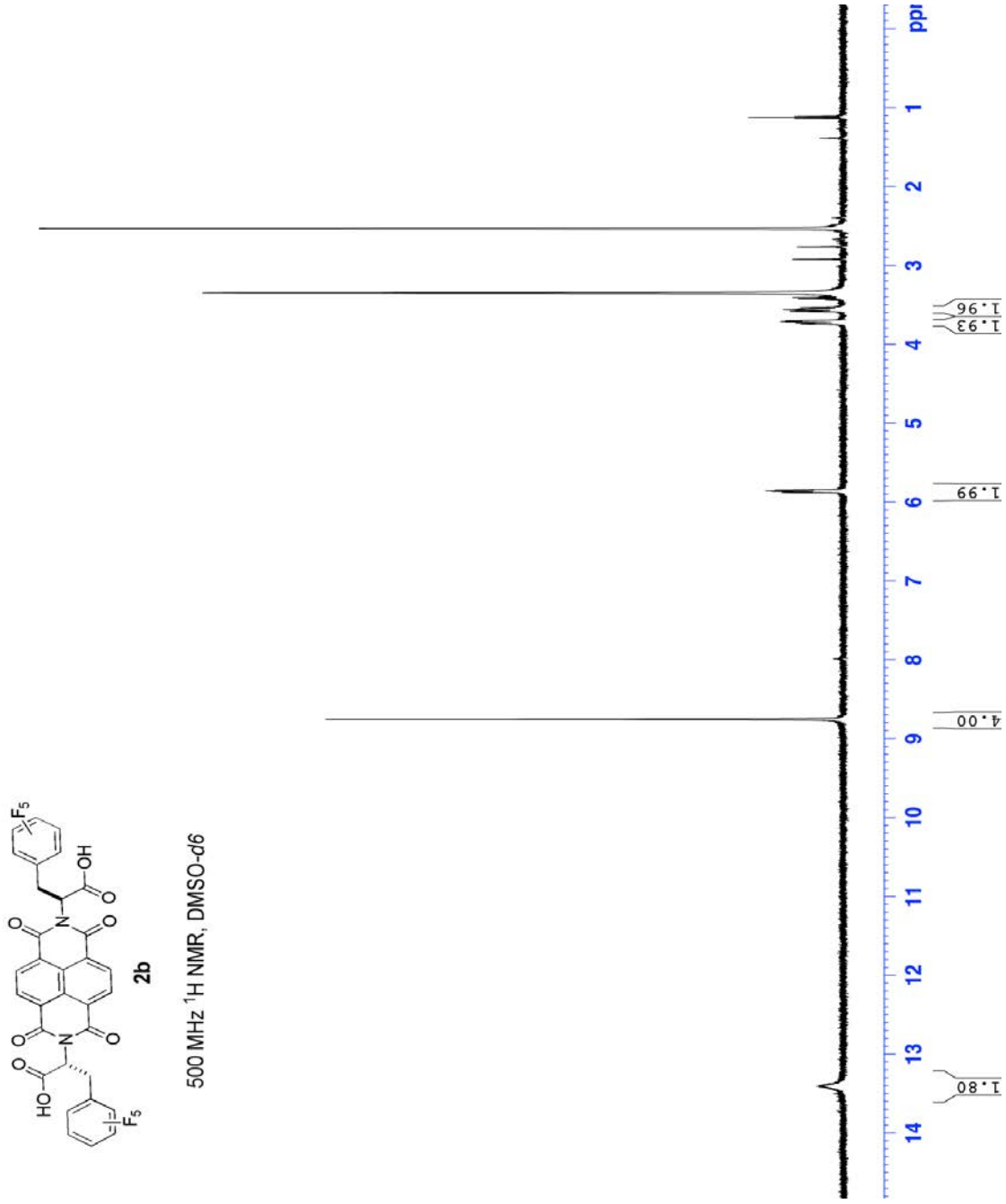


Figure S3. ^{1}H NMR of **2b**.

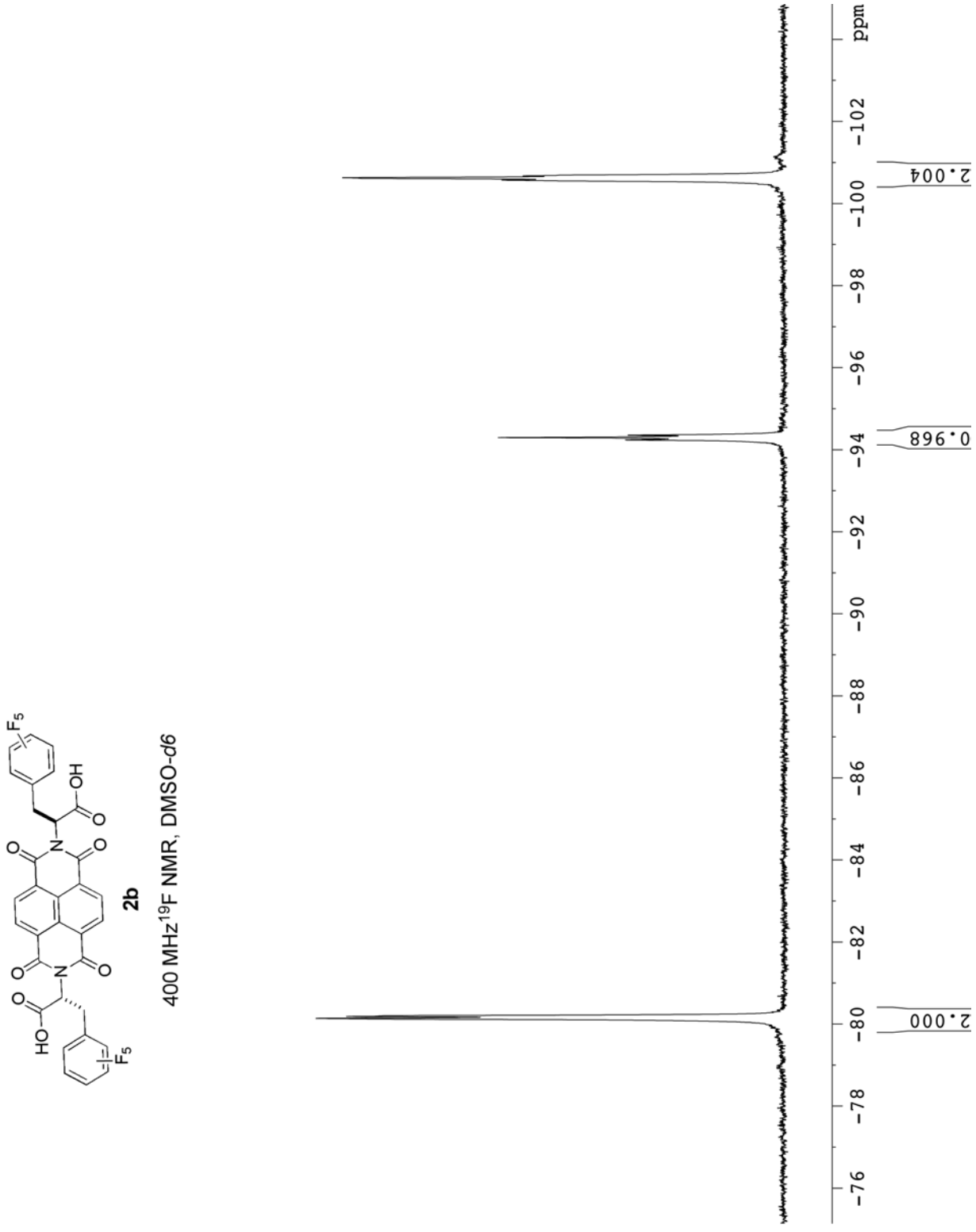


Figure S4. ^{19}F NMR of **2b**.

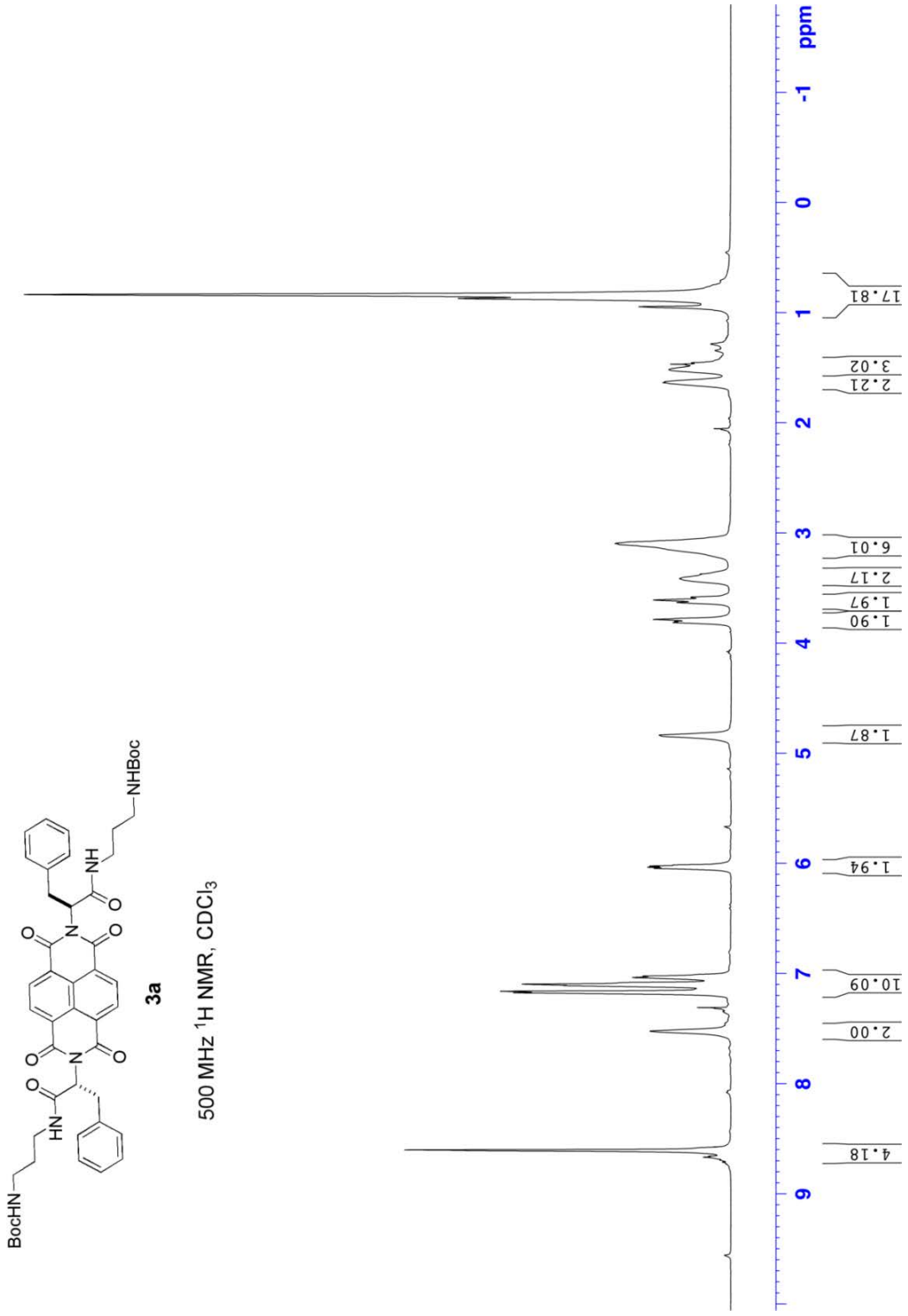


Figure S5. ^{1}H NMR of **3a**.

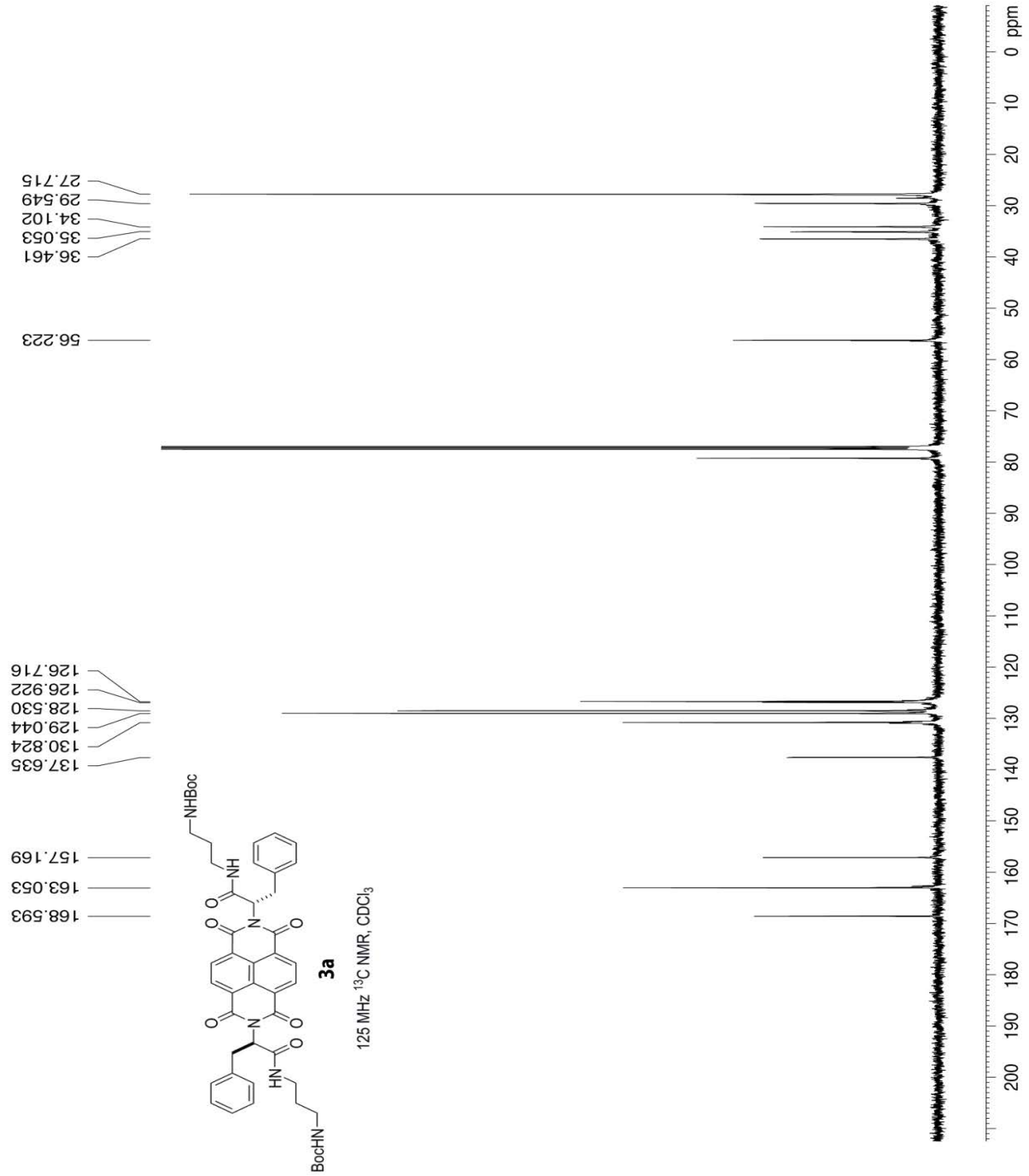


Figure S6. ^{13}C NMR of **3a**.

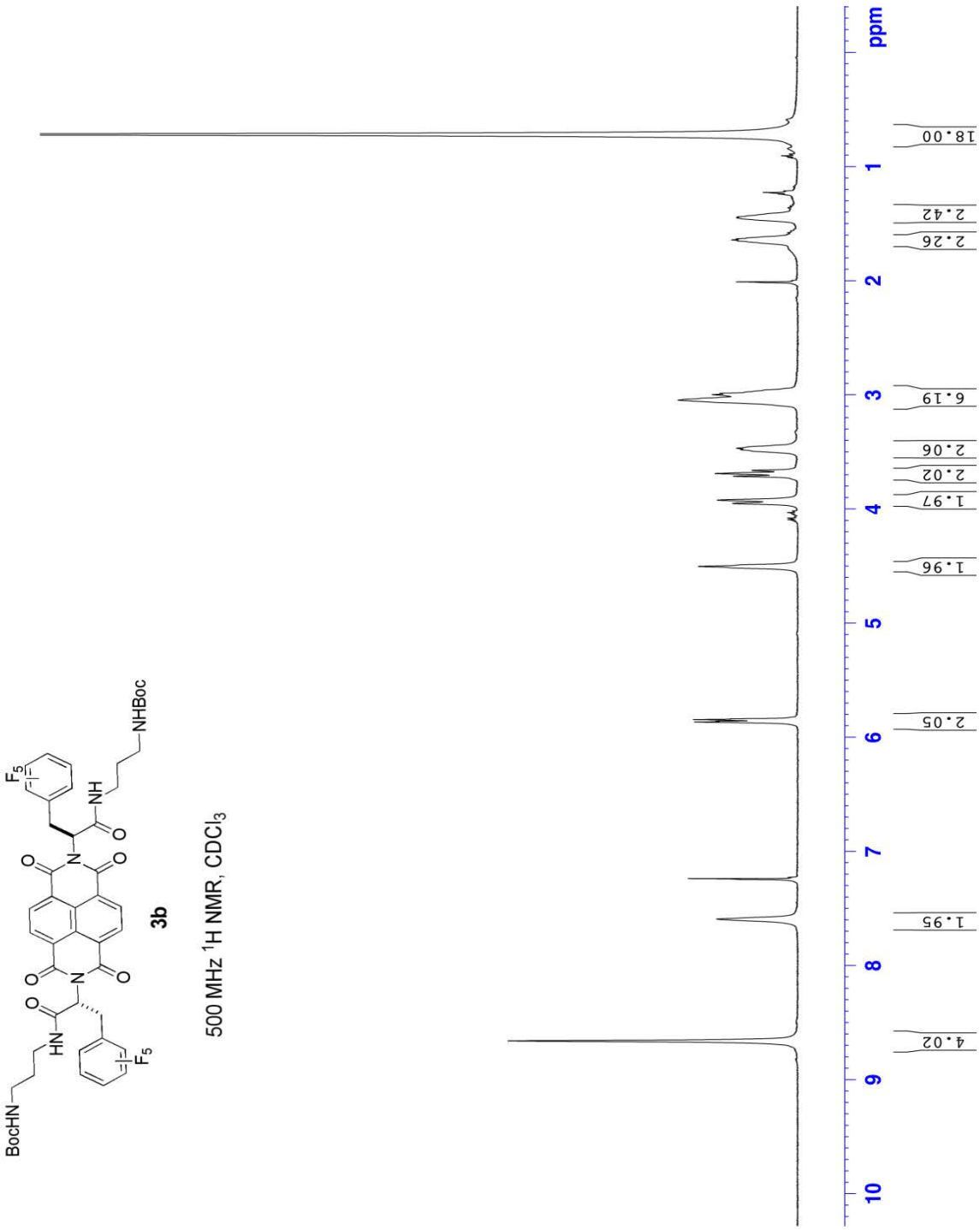


Figure S7. ^{1}H NMR of 3b.

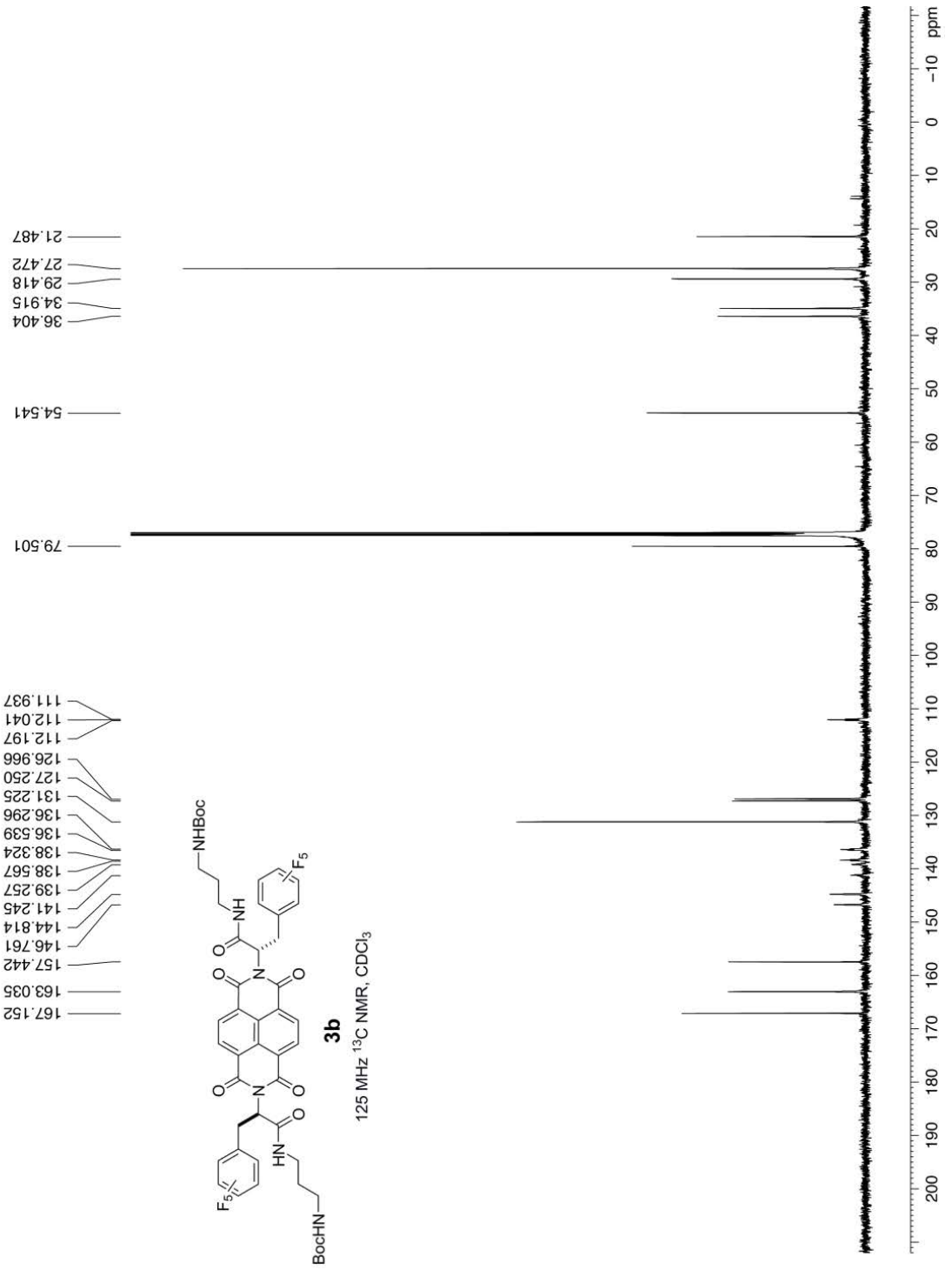


Figure S8. ^{13}C NMR of **3b**.

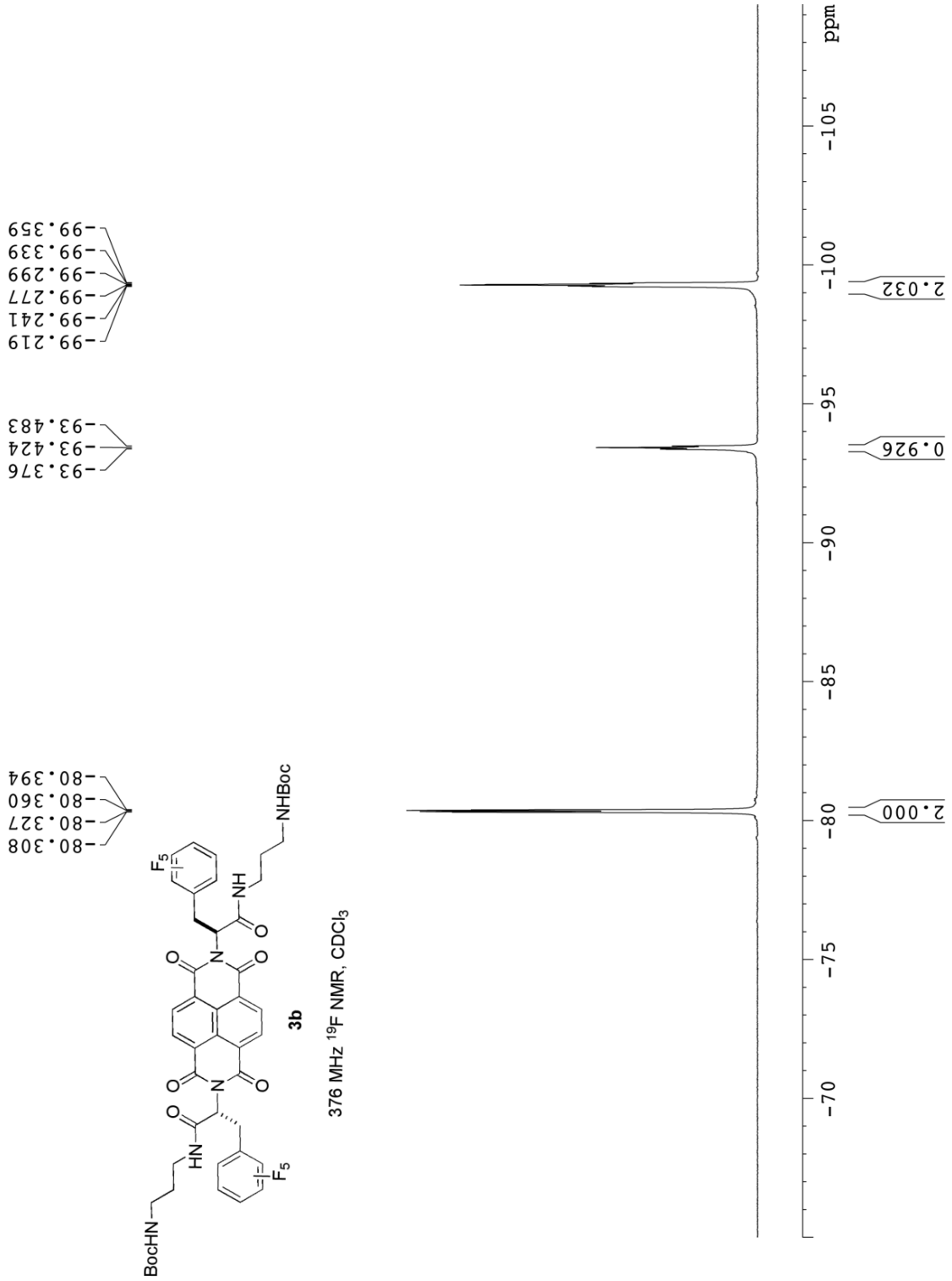


Figure S9. ^{19}F NMR of **3b**.

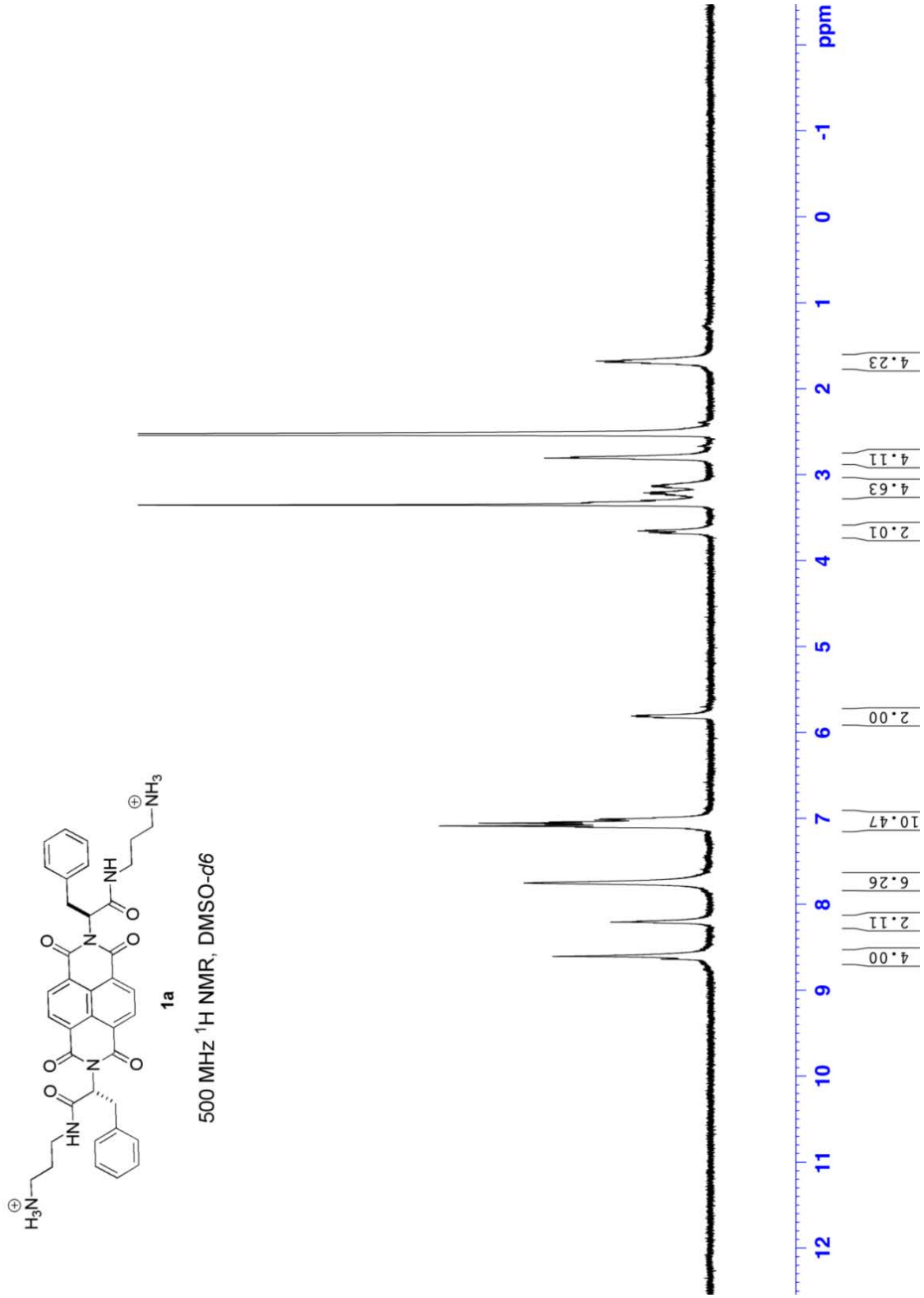


Figure S10. ^{1}H NMR of **1a**.

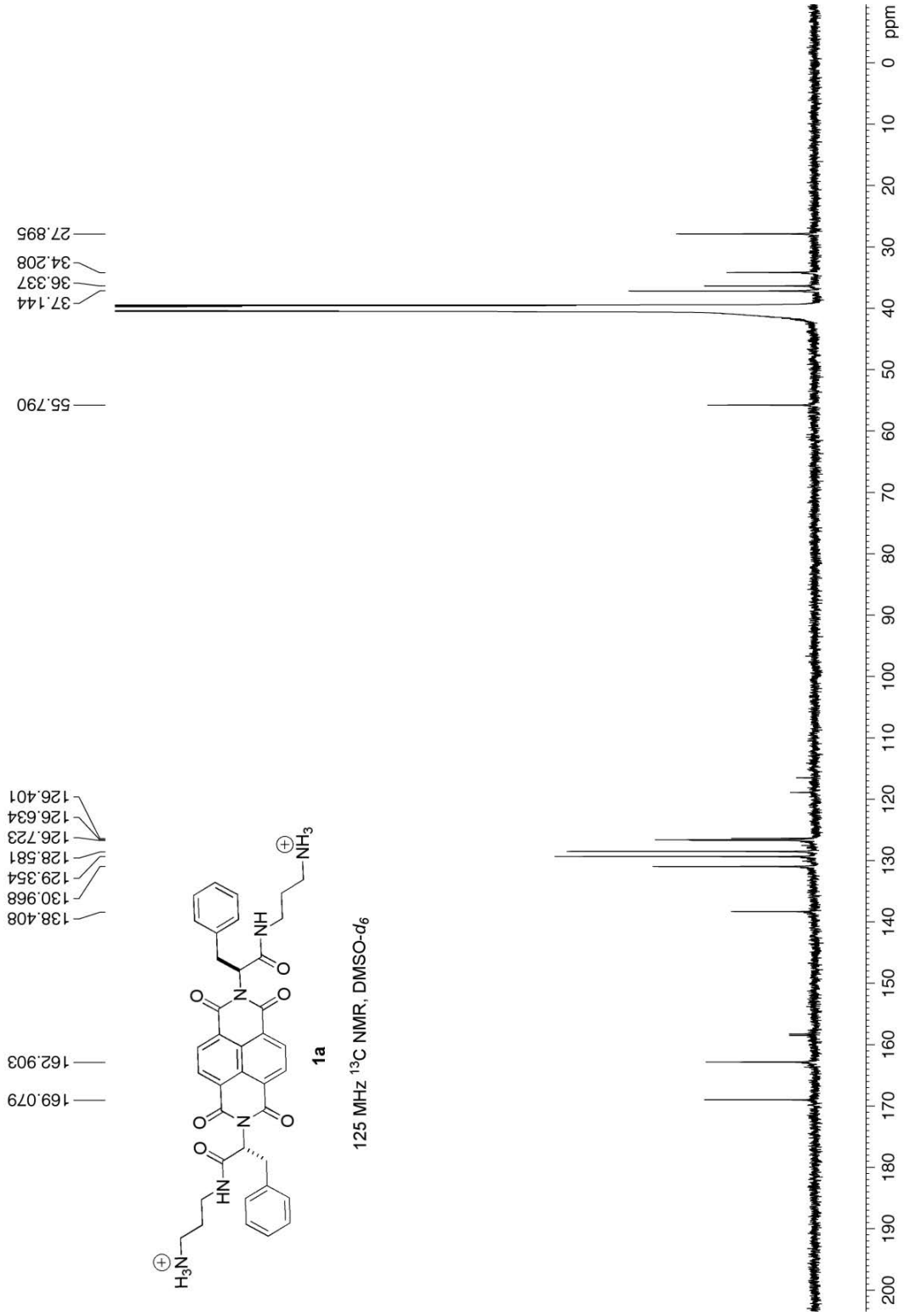


Figure S11. ^{13}C NMR of **1a**.

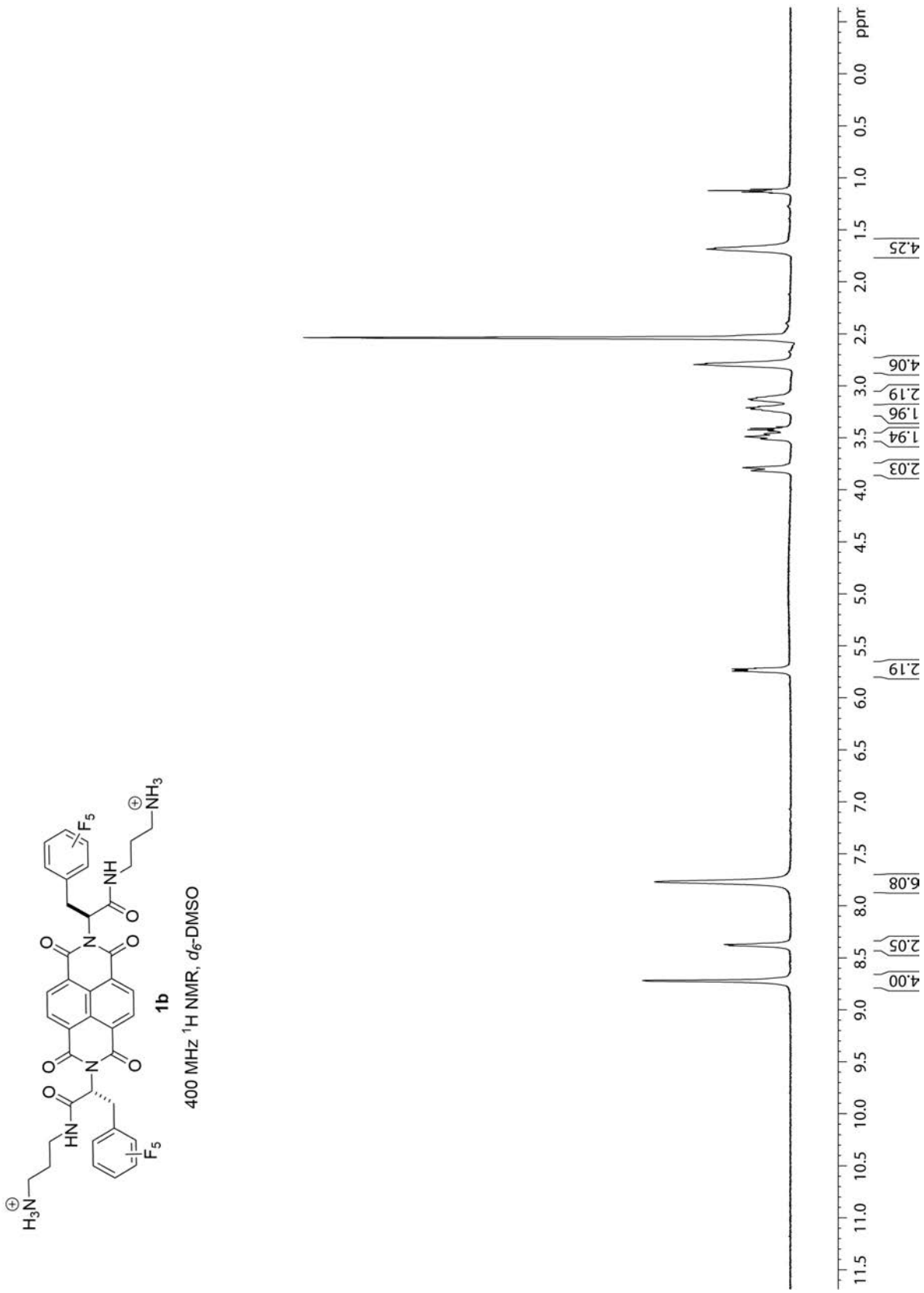


Figure S12. ^{1}H NMR of **1b**.

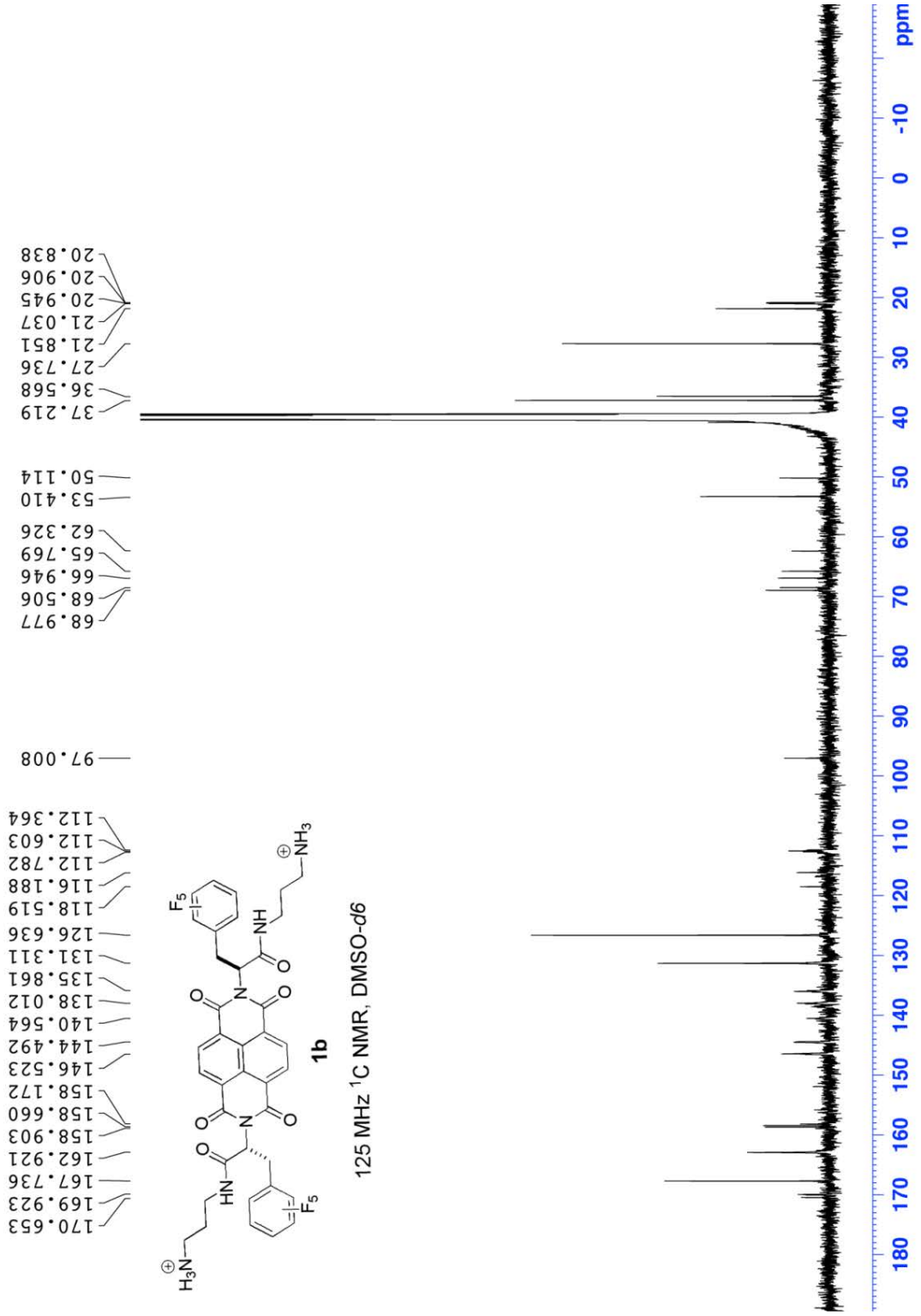


Figure S13. ^{13}C NMR of **1b**.

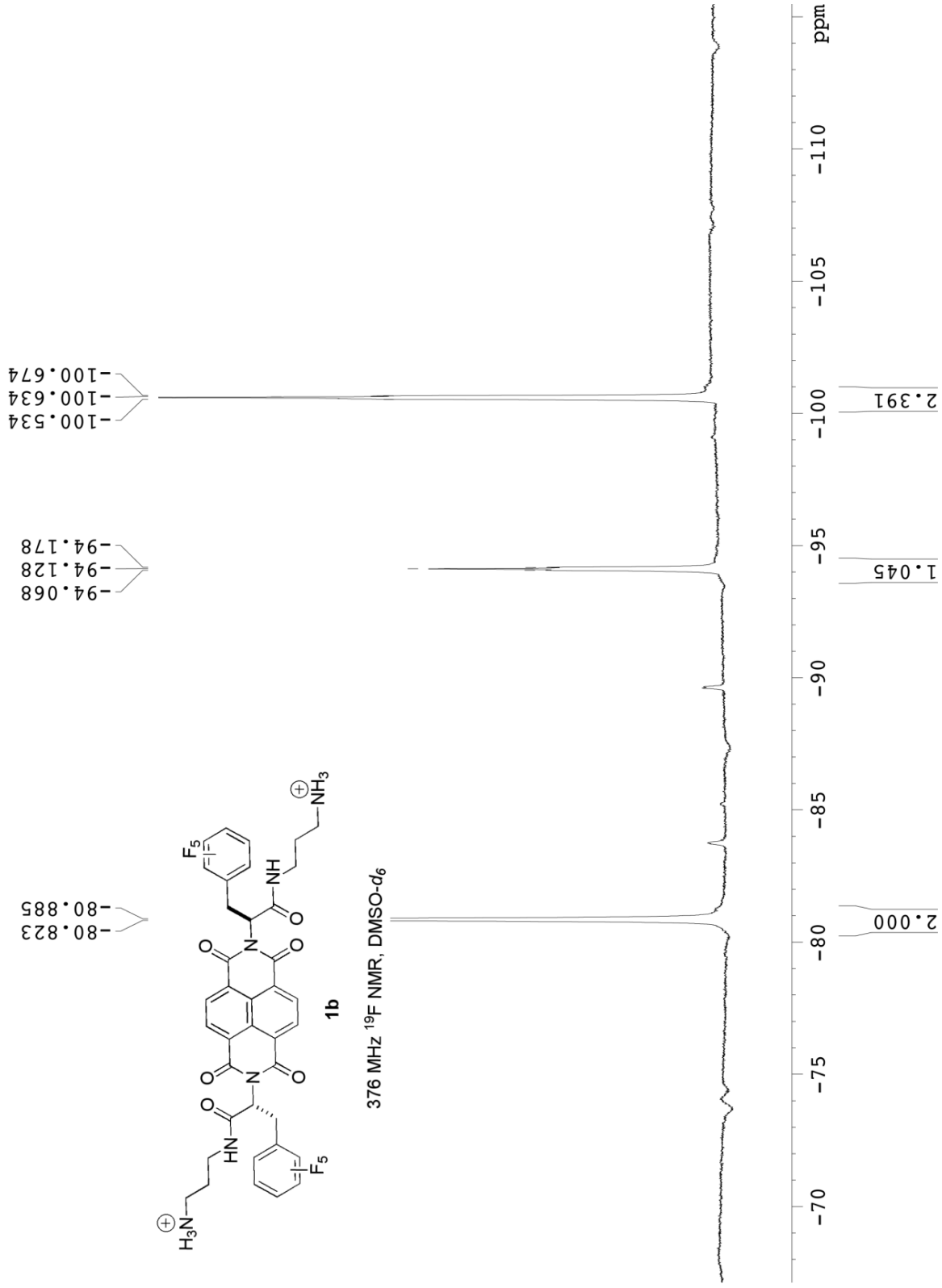


Figure S14. ^{19}F NMR of **1b.**

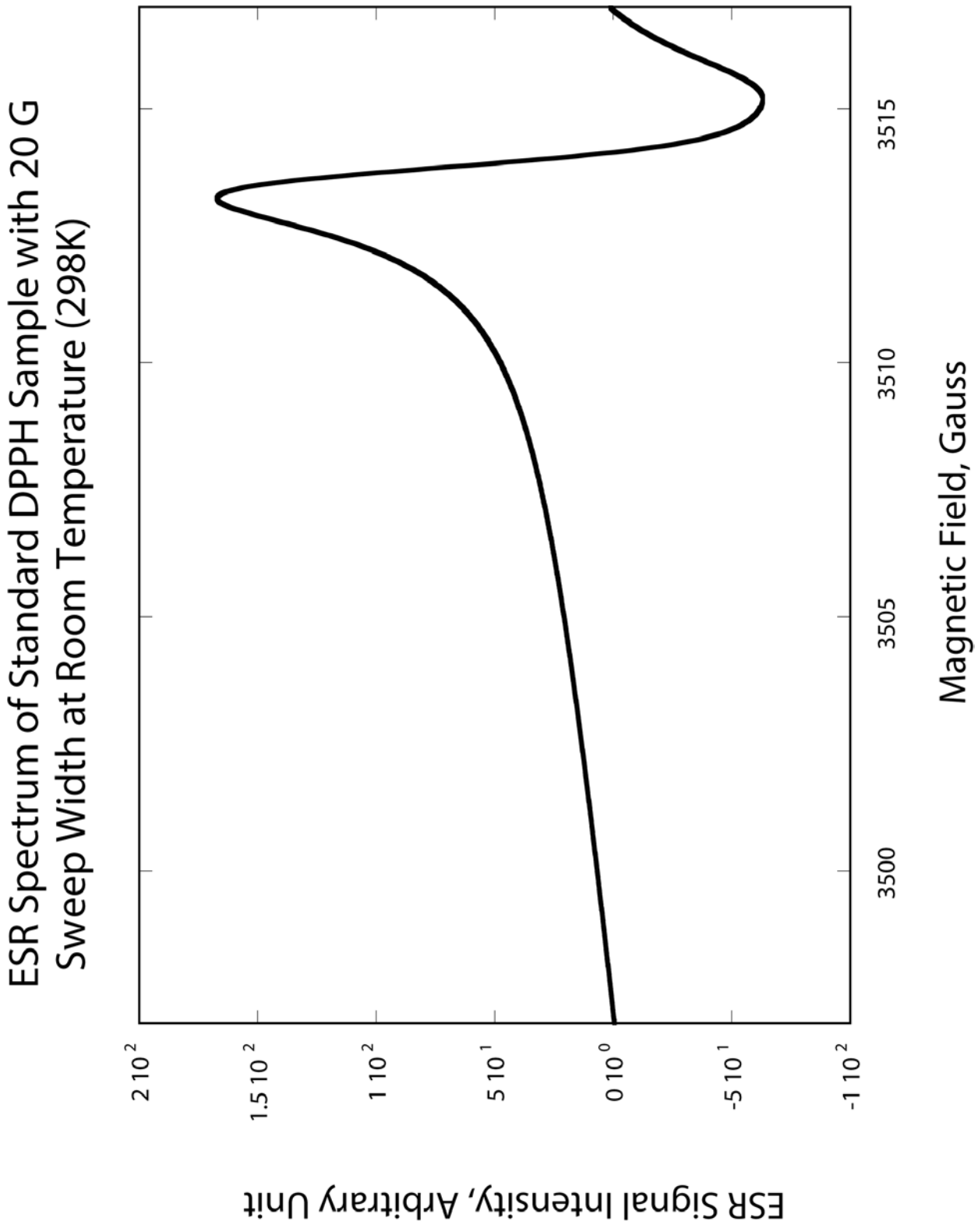


Figure S15. ESR spectrum of DPPH standard

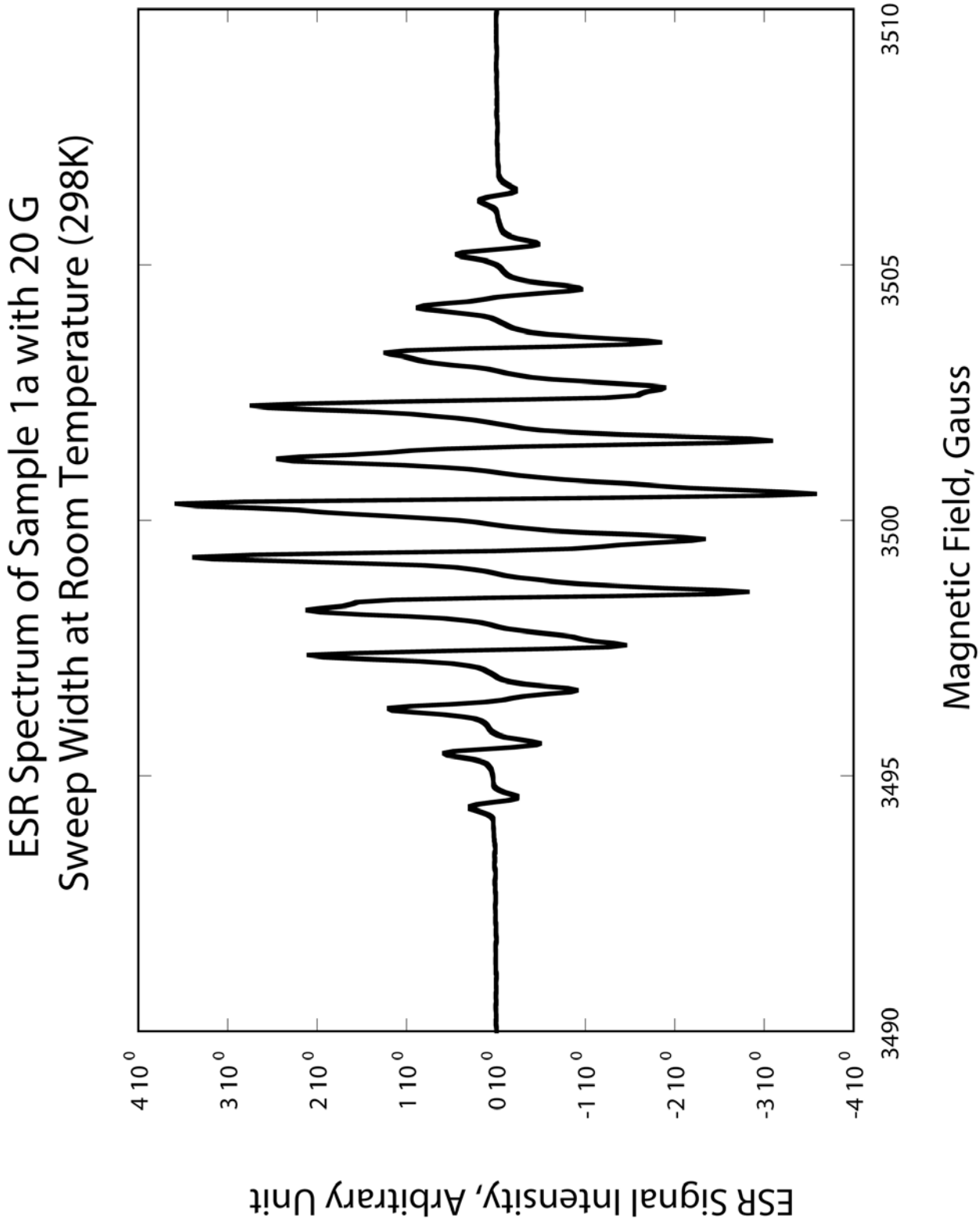


Figure S16. ESR Spectrum of compound **1a**.

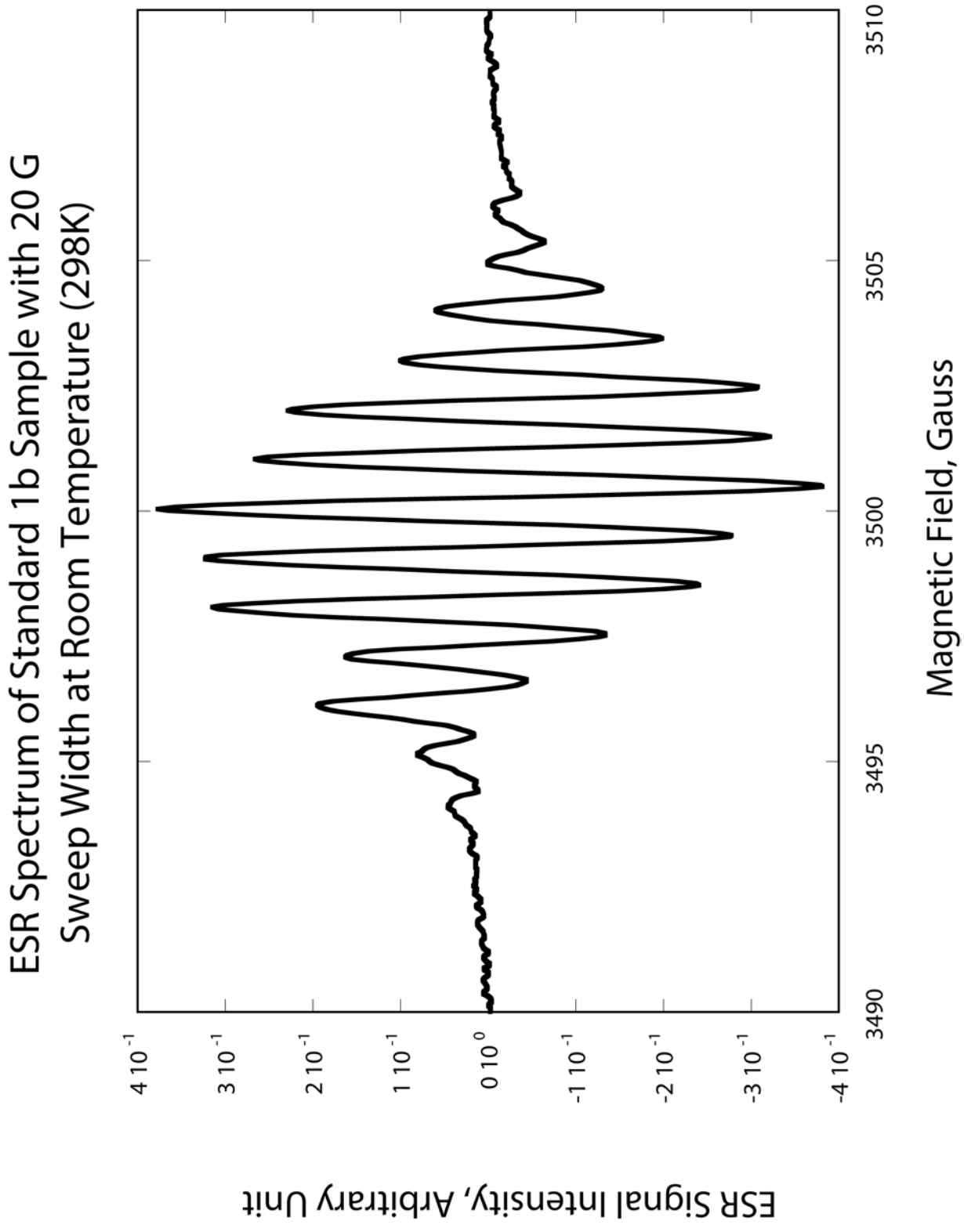


Figure S17. ESR Spectrum of compound **1b**

Table S1. EPR g values, hyperfine coupling and line widths at half height of radical anions in aqueous solution at room temperature (~296 K).

Compound	g-value	Hyperfine Coupling		EPR Line width ($\Delta H_{1/2}$, Gauss)	Comment
		a_N, Gauss	a_H, Gauss		
1a	1.9956	1.0	2.0	0.19	Aqueous Solution Strong signal at g~2.0
1b	1.9956	1.0	2.0	0.22	Aqueous Solution Strong signal at g~2.0

The observed EPR spectra from these radical anions can be described as a thirteen-line ESR signal centered at g ~2.0 Gauss. The EPR line widths and nitrogen (^{14}N, I =1) and proton (^{1}H, I =1/2) isotropic hyperfine coupling constants (a_N and a_H) of the samples were calculated from the EPR spectra and are reported here.

Typical EPR measurement parameters

Microwave Frequency:	9.86 GHz
Modulation Frequency:	100 KHz
Modulation Amplitude:	9.8 Gauss
Microwave Power:	25 dB or 0.63 mwatts
Center Field	3500 Gauss
Sweep Width:	20 or 200 Gauss
Conversion Time:	167 ms
Number of digital points:	1200
Receiver Gain	30 dB

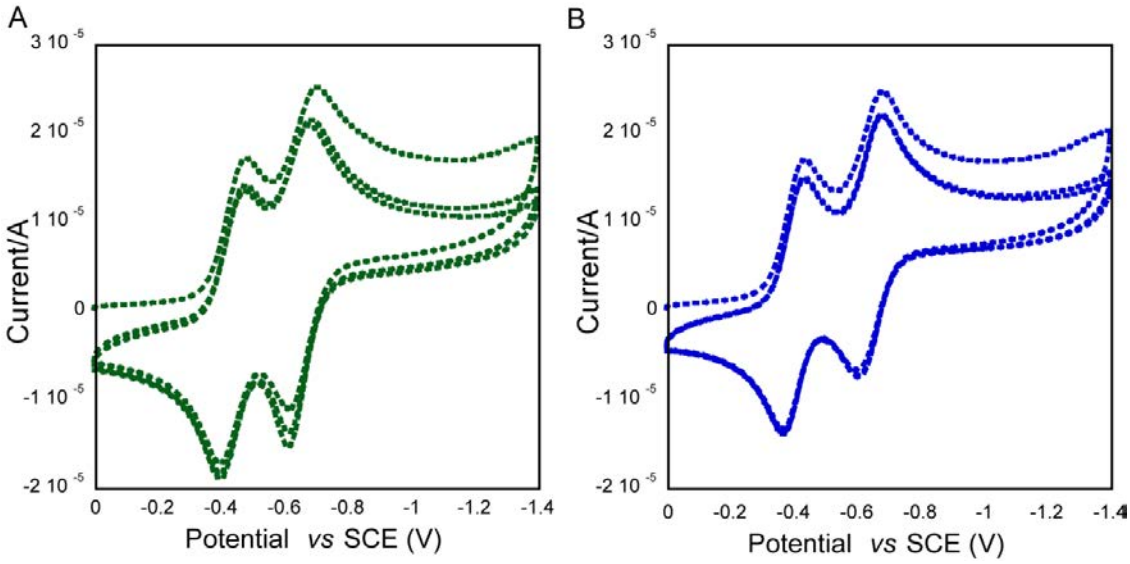


Figure S18. Multiple CV measurements in acetonitrile/H_2O (1:1) with tetra-N-butylammonium perchlorate (TBAPC) as the supporting electrolyte at 20 ºC at a glassy carbon working electrode at scan rate of 200 mV s^{-1} (A) **1a** and (B) **1b**.

Table S2. Cyclic voltammetric data obtained for reduction of **1a** and **1b** in acetonitrile/H_2O at a scan rate of 200 mV s-1 (0.1 M TBAPC).

	E_{PC}/V	E_{PA}/V	ΔE_p [V][a]	E^o_f [V][b]
1a	-0.444 -0.668	-0.451 -0.666	0.007 0.002	-0.447 -0.667
1b	-0.386 -0.612	-0.428 -0.673	0.042 0.061	-0.407 -0.642

[a]$\Delta E_p = E_{PA} - E_{PC}$, [b]the reversible potential E^o_f calculated as $(E_{PC} + E_{PA})/2$, where E_{PC} reduction potential, E_{PA} oxidation potential. E_{PC}, E_{PA}, and ΔE_p(V) refer potential vs SCE.

Quantum yield calculation

A TECAN Infinite plate reader fluorimeter was used for these photophysical measurements. Fluorescein solution (0.1 M NaOH) (Φ_{std} = 0.92) used as a quantum yield standard. Peptide-π conjugates **1a** and **1b** (50 μM in mM $Na_2S_2O_4$) were prepared in unbuffered water for the photophysical characterization. The quantum yields were calculated using equation **1** below. The quantum yield is reported as the average of three measurements.

$$\Phi_x = \Phi_{std}\left[\frac{I_x}{I_{std}}\right]\left[\frac{A_{std}}{A_x}\right]\left[\frac{\eta_x^2}{\eta_{std}^2}\right] \quad \textbf{1}$$

Where

Φ - quantum yield, I-integrated emission, A-absorption at the excitation wavelength

η- refractive index, x- sample, std- standard sample.

Single crystal X-ray structure for 3a

A crystal of **3a** (0.28 x 0.24 x 0.10 mm^3) was placed onto the tip of a 0.1 mm diameter glass capillary tube or fiber and mounted on a Bruker SMART APEX II CCD Platform diffractometer for a data collection at 100.0(5) K (*APEX2*, version 2011.4-1; Bruker AXS: Madison, WI, 2011). A preliminary set of cell constants and an orientation matrix were calculated from reflections harvested from three orthogonal wedges of reciprocal space. The full data collection was carried out using MoKα radiation (graphite monochromator) with a frame time of 60 seconds and a detector distance of 4.01 cm. A randomly oriented region of reciprocal space was surveyed: six major sections of frames were collected with 0.50º steps in ω at six different ϕ settings and a detector position of -38º in 2θ. The intensity data were corrected for absorption (Sheldrick, G. M. *SADABS*, version 2008/1; University of Göttingen: Göttingen, Germany, 2008). Final cell constants were calculated from the xyz centroids of 4082 strong reflections from the actual data collection after integration (*SAINT*, version 7.68A; Bruker AXS: Madison, WI, 2009). See Table 1 for additional crystal and refinement information.

Single crystal X-ray structure for 3b

A crystal of **3b** (0.32 x 0.16 x 0.08 mm^3) was placed onto the tip of a 0.1 mm diameter glass capillary tube or fiber and mounted on a Bruker SMART APEX II CCD Platform diffractometer for a data collection at 100.0(5) K (*APEX2*, version 2011.4-1; Bruker AXS: Madison, WI, 2011). A preliminary set of cell constants and an orientation matrix were calculated from reflections harvested from three orthogonal wedges of reciprocal space. The full data collection was carried out using MoKα radiation (graphite monochromator) with a frame time of 90 seconds and a detector distance of 4.01 cm. A randomly oriented region of reciprocal space was surveyed: six

major sections of frames were collected with 0.50º steps in ω at six different ϕ settings and a detector position of -38º in 2θ. The intensity data were corrected for absorption (Sheldrick, G. M. *SADABS*, version 2008/1; University of Göttingen: Göttingen, Germany, 2008). Final cell constants were calculated from the xyz centroids of 4083 strong reflections from the actual data collection after integration (*SAINT*, version 7.68A; Bruker AXS: Madison, WI, 2009). See Table 1 for additional crystal and refinement information.

Structure solution and refinement for 3a and 3b

The structures were solved using SIR97 (Altomare, A.; Burla, M. C.; Camalli, M.; Cascarano, G. L.; Giacovazzo, C.; Guagliardi, A.; Moliterni, A. G. G.; Polidori, G.; Spagna, R. *SIR97: A new program for solving and refining crystal structures*; Istituto di Cristallografia, CNR: Bari, Italy, 1999) and refined using SHELXL-97(Sheldrick, G. M. *Acta. Cryst.* **2008***, A64*, 112-122). The space group $P2_1/n$ was determined based on systematic absences. A direct-methods solution was calculated which provided most non-hydrogen atoms from the E-map. Full-matrix least squares / difference Fourier cycles were performed which located the remaining non-hydrogen atoms. All non-hydrogen atoms were refined with anisotropic displacement parameters. The amine hydrogen atoms were found from the difference Fourier map, and their positional and isotropic displacement parameters were refined independently from those of their respective bonded nitrogen atoms. All other hydrogen atoms were placed in ideal positions and refined as riding atoms with relative isotropic displacement parameters. The final full matrix least squares refinement converged to $R1 = 0.0476$ (F^2, $I > 2\sigma(I)$) and $wR2 = 0.1120$ (F^2, all data).

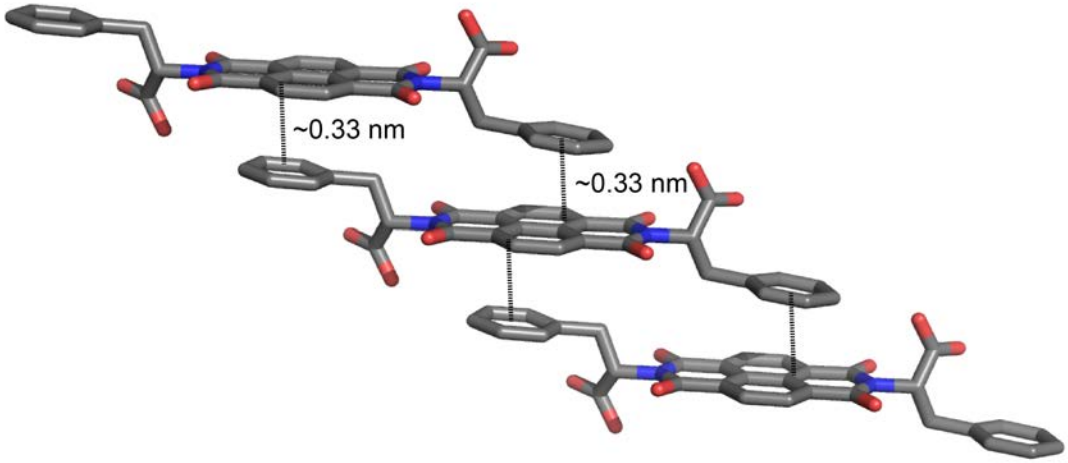


Figure S19. Crystal packing of **2a**.

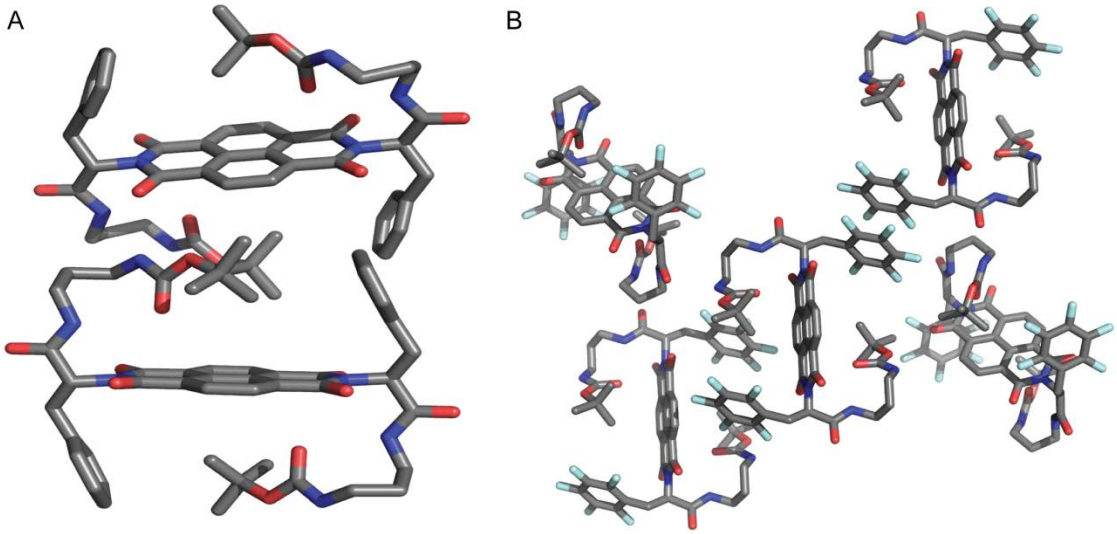


Figure S20. Crystal packing of (A) **3a** (B) **3b**.

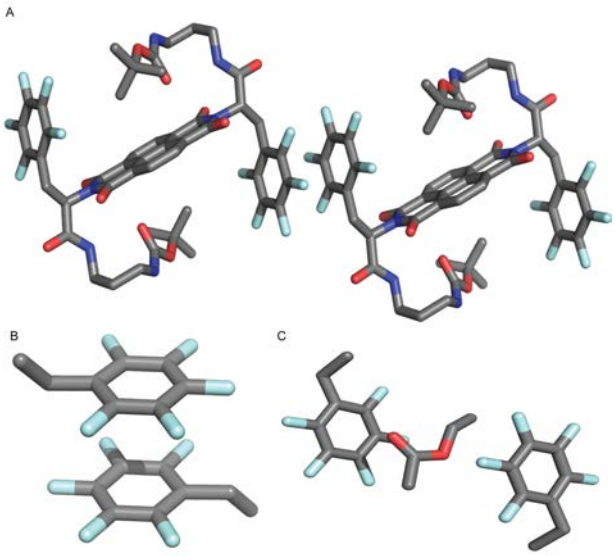


Figure S21. Crystal packing mode of (A) **3b**. (B) Local dipole interaction between opposing F_5-Phe rings of **3b.** (C) Solvent assisted aromatic interactions in **3b.**

Appendix 1. Crystal Structure Report for **2a**

CRYSTAL STRUCTURE REPORT

$C_{40}\ H_{42}\ N_2\ O_{10}$

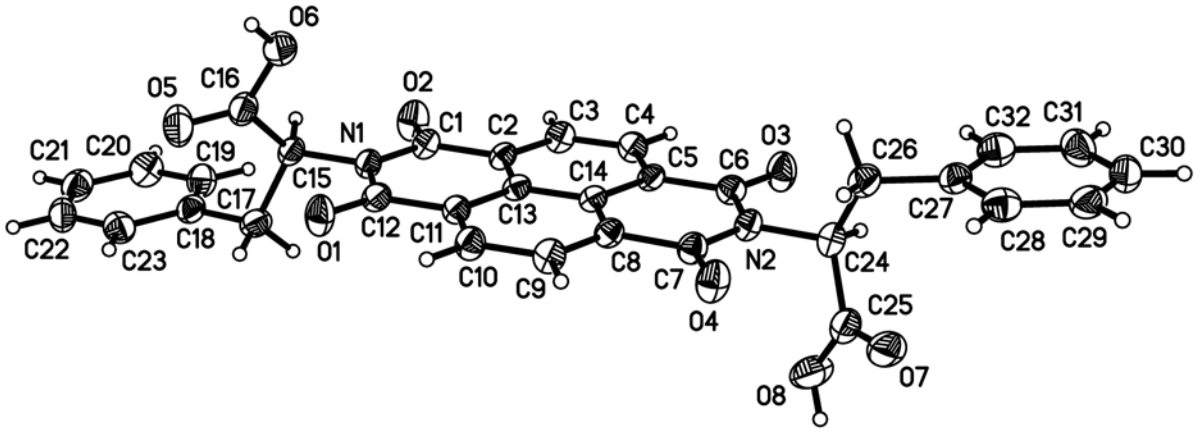
or

$C_{32}H_{22}N_2O_8 \cdot 2Et_2O$

Report prepared for:

W. Liyanage, Prof. B. Nilsson

October 24, 2011



William W. Brennessel

X-ray Crystallographic Facility

Department of Chemistry, University of Rochester

120 Trustee Road

Rochester, NY 14627

Data collection

A crystal (0.44 x 0.28 x 0.14 mm^3) was placed onto the tip of a 0.1 mm diameter glass capillary tube or fiber and mounted on a Bruker SMART APEX II CCD Platform diffractometer for a data collection at 173(2) K.[1] A preliminary set of cell constants and an orientation matrix were calculated from reflections harvested from three orthogonal wedges of reciprocal space. The full data collection was carried out using MoKα radiation (graphite monochromator) with a frame time of 60 seconds and a detector distance of 3.99 cm. A randomly oriented region of reciprocal space was surveyed: four major sections of frames were collected with 0.50º steps in ω at four different ϕ settings and a detector position of -38º in 2θ. The intensity data were corrected for absorption.[2] Final cell constants were calculated from the xyz centroids of 3773 strong reflections from the actual data collection after integration.[3] See Table 1 for additional crystal and refinement information.

Structure solution and refinement

The structure was solved using SIR97[4] and refined using SHELXL-97.[5] The space group $P2_1$ was determined based on systematic absences and intensity statistics. A direct-methods solution was calculated which provided most non-hydrogen atoms from the E-map. Full-matrix least squares / difference Fourier cycles were performed which located the remaining non-hydrogen atoms. All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were placed in ideal positions and refined as riding atoms with relative isotropic displacement parameters. Due to the lack of significant anomalous dispersion effects, the absolute configuration could not be determined from the experiment. However, the chemist provided the absolute configuration based on the synthetic procedure. Friedel opposites were merged in the final refinement. The final full matrix least squares refinement converged to $R1 = 0.0573$ (F^2, $I > 2\sigma(I)$) and $wR2 = 0.1767$ (F^2, all data).

Structure description

The structure is the one suggested with all atoms in general positions. There are two hydrogen-bonded (see Table 7) co-crystallized diethyl ether solvent molecules per featured organic molecule; each is modeled as disordered over two positions (73:27 and 88:12). Pi-stacking on the order of ~3.3 Å is likely responsible for one-dimensional stacks of molecules (see diagram).

Unless noted otherwise all structural diagrams containing thermal displacement ellipsoids are drawn at the 50 % probability level.

Data collection, structure solution, and structure refinement were conducted at the X-ray Crystallographic Facility, B51 Hutchison Hall, Department of Chemistry, University of Rochester. All publications arising from this report MUST either 1) include William W. Brennessel as a coauthor or 2) acknowledge William W. Brennessel and the X-ray Crystallographic Facility of the Department of Chemistry at the University of Rochester.

---

[1] *APEX2*, version 2011.4-1; Bruker AXS: Madison, WI, 2011.

[2] Sheldrick, G. M. *SADABS*, version 2008/1; University of Göttingen: Göttingen, Germany, 2008.

[3] *SAINT*, version 7.68A; Bruker AXS: Madison, WI, 2009.

[4] Altomare, A.; Burla, M. C.; Camalli, M.; Cascarano, G. L.; Giacovazzo, C.; Guagliardi, A.; Moliterni, A. G. G.; Polidori, G.; Spagna, R. *SIR97: A new program for solving and refining crystal structures*; Istituto di Cristallografia, CNR: Bari, Italy, 1999.

[5] Sheldrick, G. M. *Acta. Cryst.* **2008***, A64*, 112-122.

Some equations of interest:

$$R_{int} = \Sigma\, |F_o^2 - < F_o^2 >| \,/\, \Sigma |F_o^2|$$

$$R1 = \Sigma ||F_o| - |F_c|| \,/\, \Sigma |F_o|$$

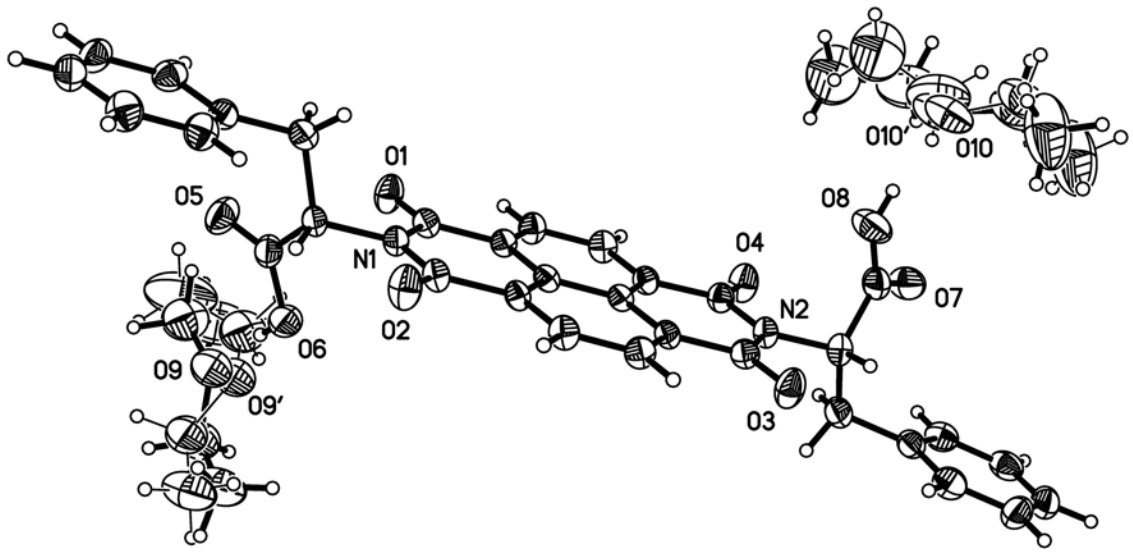
$$wR2 = [\Sigma [w(F_o^2 - F_c^2)^2] \,/\, \Sigma\, [w(F_o^2)^2]]^{1/2}$$

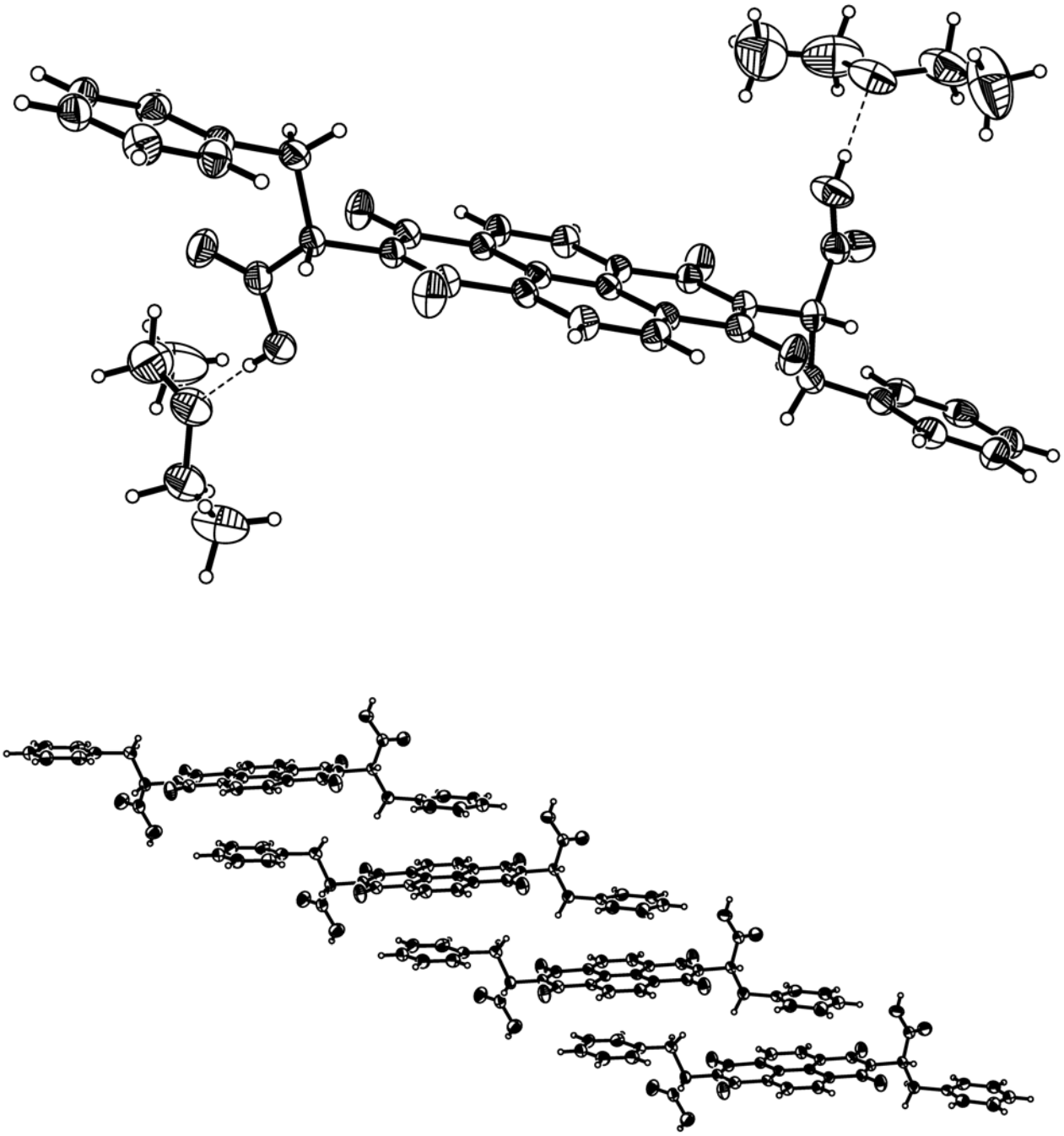
where $w = 1 \,/\, [\sigma^2 (F_o^2) + (aP)^2 + bP]$ and

$$P = 1/3 \max (0, F_o^2) + 2/3\, F_c^2$$

$$\text{GOF} = S = [\Sigma [w(F_o^2 - F_c^2)^2] \,/\, (m-n)]^{1/2}$$

where m = number of reflections and n = number of parameters





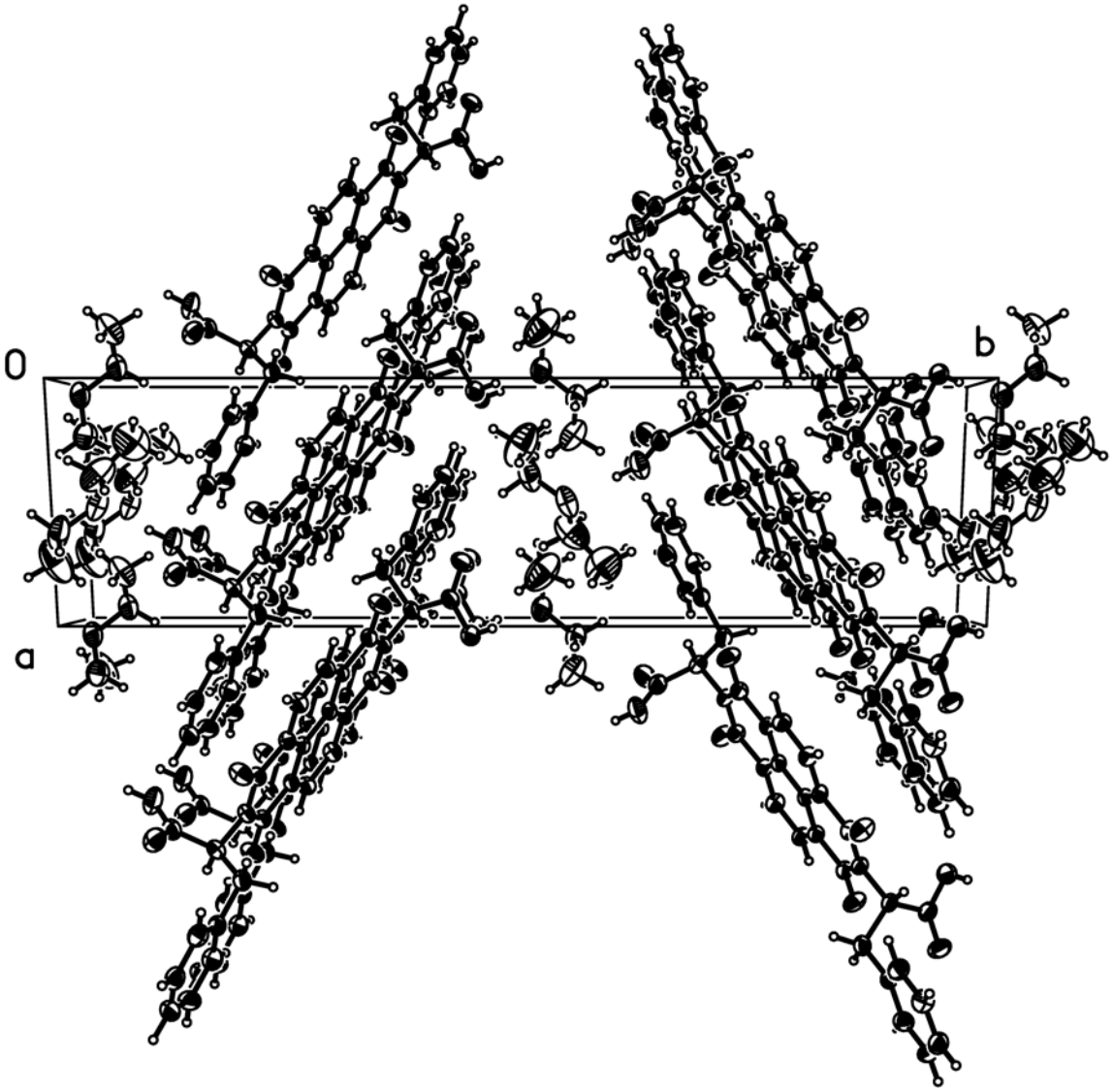

0
b
a

Table 1. Crystal data and structure refinement for nilwl03.

Identification code	nilwl03	
Empirical formula	C40 H42 N2 O10	
Formula weight	710.76	
Temperature	173(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	$P2_1$	
Unit cell dimensions	a = 8.1121(12) Å	α = 90°
	b = 28.530(4) Å	β = 111.988(3)°
	c = 8.3555(12) Å	γ = 90°
Volume	1793.1(5) Å^3	
Z	2	
Density (calculated)	1.316 Mg/m^3	
Absorption coefficient	0.095 mm^{-1}	
F(000)	752	
Crystal color, morphology	yellow, plate	
Crystal size	0.44 x 0.28 x 0.14 mm^3	
Theta range for data collection	1.43 to 31.51°	
Index ranges	$-11 \le h \le 11$, $-41 \le k \le 41$, $-12 \le l \le 12$	
Reflections collected	31686	
Independent reflections	6065 [R(int) = 0.0584]	
Observed reflections	4392	
Completeness to theta = 31.51°	100.0%	
Absorption correction	Multi-scan	
Max. and min. transmission	0.9868 and 0.9595	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	6065 / 39 / 509	
Goodness-of-fit on F^2	1.033	
Final R indices [I>2sigma(I)]	R1 = 0.0573, wR2 = 0.1549	
R indices (all data)	R1 = 0.0854, wR2 = 0.1767	
Largest diff. peak and hole	0.338 and -0.279 e.Å^{-3}	

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for nilwl03. U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U_{eq}
O1	-1044(3)	3530(1)	3930(3)	39(1)
O2	2323(3)	3505(1)	646(3)	41(1)
O3	8845(3)	2191(1)	7111(3)	41(1)
O4	5363(3)	2187(1)	10287(3)	39(1)
O5	-2673(3)	4376(1)	1539(3)	47(1)
O6	266(3)	4463(1)	2907(3)	43(1)
O7	7813(4)	1340(1)	11912(3)	47(1)
O8	6536(4)	1244(1)	9066(3)	53(1)
N1	666(3)	3532(1)	2324(3)	26(1)
N2	7088(3)	2185(1)	8685(3)	27(1)
C1	2170(4)	3399(1)	1989(4)	28(1)
C2	3523(4)	3116(1)	3346(3)	24(1)
C3	5059(4)	2979(1)	3133(4)	29(1)
C4	6347(4)	2720(1)	4412(4)	29(1)
C5	6103(4)	2593(1)	5901(4)	24(1)
C6	7455(4)	2312(1)	7240(4)	27(1)
C7	5567(4)	2315(1)	8978(4)	28(1)
C8	4237(4)	2605(1)	7646(3)	25(1)
C9	2713(4)	2734(1)	7867(4)	29(1)
C10	1422(4)	3000(1)	6579(4)	30(1)
C11	1683(4)	3126(1)	5112(4)	24(1)
C12	317(4)	3407(1)	3787(4)	27(1)
C13	3240(3)	2993(1)	4848(3)	22(1)
C14	4542(4)	2729(1)	6148(3)	23(1)
C15	-695(4)	3820(1)	1015(4)	28(1)
C16	-1175(4)	4246(1)	1853(4)	33(1)
C17	-2316(4)	3526(1)	-62(4)	34(1)
C18	-3457(4)	3769(1)	-1714(4)	30(1)
C19	-2857(4)	3826(1)	-3049(4)	36(1)
C20	-3888(5)	4038(1)	-4580(5)	41(1)
C21	-5561(5)	4203(1)	-4797(4)	40(1)

C22	-6196(4)	4145(1)	-3473(5)	39(1)
C23	-5159(4)	3928(1)	-1958(4)	35(1)
C24	8406(4)	1900(1)	10036(4)	30(1)
C25	7545(4)	1469(1)	10476(4)	37(1)
C26	9455(4)	2195(1)	11621(4)	35(1)
C27	11122(4)	1958(1)	12809(4)	31(1)
C28	11293(5)	1814(1)	14450(4)	36(1)
C29	12832(5)	1600(1)	15545(4)	40(1)
C30	14213(5)	1519(1)	14983(5)	42(1)
C31	14066(4)	1665(1)	13368(5)	41(1)
C32	12545(5)	1882(1)	12294(4)	37(1)
C33	2150(16)	5549(4)	4660(20)	85(3)
C34	630(20)	5583(4)	5160(30)	72(3)
O9	-529(8)	5200(2)	4391(8)	57(1)
C35	-2203(10)	5227(3)	4568(11)	73(2)
C36	-2155(18)	5211(5)	6326(15)	119(4)
C37	2505(14)	870(4)	9660(14)	120(4)
C38	3843(13)	534(4)	10580(11)	100(3)
O10	5069(7)	480(1)	9749(6)	61(1)
C39	6175(10)	81(2)	10409(9)	81(2)
C40	7338(18)	0(4)	9458(14)	126(4)
C33'	1810(50)	5714(11)	4380(70)	85(3)
C34'	340(70)	5621(10)	4920(90)	72(3)
O9'	-70(20)	5136(7)	4910(30)	57(1)
C35'	-1260(30)	5020(7)	5740(30)	73(2)
C36'	-3030(30)	5215(11)	4970(40)	119(4)
C37'	2730(70)	540(30)	9770(100)	120(4)
C38'	4590(80)	410(30)	10500(60)	100(3)
O10'	5420(50)	421(11)	9280(50)	61(1)
C39'	6320(60)	-5(13)	9270(70)	81(2)
C40'	8110(70)	-30(30)	10540(100)	126(4)

Table 3. Bond lengths [Å] and angles [°] for nilwl03.

O(1)-C(12)	1.206(3)	C(13)-C(14)	1.416(3)
O(2)-C(1)	1.213(4)	C(15)-C(16)	1.524(4)
O(3)-C(6)	1.222(4)	C(15)-C(17)	1.535(4)
O(4)-C(7)	1.222(4)	C(15)-H(15)	1.0000
O(5)-C(16)	1.202(4)	C(17)-C(18)	1.512(4)
O(6)-C(16)	1.324(4)	C(17)-H(17A)	0.9900
O(6)-H(6)	0.8400	C(17)-H(17B)	0.9900
O(7)-C(25)	1.195(4)	C(18)-C(19)	1.384(4)
O(8)-C(25)	1.322(4)	C(18)-C(23)	1.394(4)
O(8)-H(8)	0.8400	C(19)-C(20)	1.379(5)
N(1)-C(12)	1.400(4)	C(19)-H(19)	0.9500
N(1)-C(1)	1.402(4)	C(20)-C(21)	1.383(5)
N(1)-C(15)	1.479(3)	C(20)-H(20)	0.9500
N(2)-C(7)	1.394(4)	C(21)-C(22)	1.394(6)
N(2)-C(6)	1.394(4)	C(21)-H(21)	0.9500
N(2)-C(24)	1.475(4)	C(22)-C(23)	1.377(5)
C(1)-C(2)	1.486(4)	C(22)-H(22)	0.9500
C(2)-C(3)	1.381(4)	C(23)-H(23)	0.9500
C(2)-C(13)	1.402(3)	C(24)-C(25)	1.526(4)
C(3)-C(4)	1.394(4)	C(24)-C(26)	1.530(4)
C(3)-H(3)	0.9500	C(24)-H(24)	1.0000
C(4)-C(5)	1.380(4)	C(26)-C(27)	1.505(4)
C(4)-H(4)	0.9500	C(26)-H(26A)	0.9900
C(5)-C(14)	1.411(4)	C(26)-H(26B)	0.9900
C(5)-C(6)	1.476(4)	C(27)-C(28)	1.387(4)
C(7)-C(8)	1.479(4)	C(27)-C(32)	1.392(5)
C(8)-C(9)	1.368(4)	C(28)-C(29)	1.384(5)
C(8)-C(14)	1.408(4)	C(28)-H(28)	0.9500
C(9)-C(10)	1.409(4)	C(29)-C(30)	1.387(6)
C(9)-H(9)	0.9500	C(29)-H(29)	0.9500
C(10)-C(11)	1.368(4)	C(30)-C(31)	1.374(5)
C(10)-H(10)	0.9500	C(30)-H(30)	0.9500
C(11)-C(13)	1.413(3)	C(31)-C(32)	1.372(5)
C(11)-C(12)	1.477(4)	C(31)-H(31)	0.9500

C(32)-H(32)	0.9500	O(9')-C(35')	1.419(15)
C(33)-C(34)	1.446(10)	C(35')-C(36')	1.448(17)
C(33)-H(33A)	0.9800	C(35')-H(35C)	0.9900
C(33)-H(33B)	0.9800	C(35')-H(35D)	0.9900
C(33)-H(33C)	0.9800	C(36')-H(36D)	0.9800
C(34)-O(9)	1.427(11)	C(36')-H(36E)	0.9800
C(34)-H(34A)	0.9900	C(36')-H(36F)	0.9800
C(34)-H(34B)	0.9900	C(37')-C(38')	1.45(2)
O(9)-C(35)	1.422(9)	C(37')-H(37D)	0.9800
C(35)-C(36)	1.455(11)	C(37')-H(37E)	0.9800
C(35)-H(35A)	0.9900	C(37')-H(37F)	0.9800
C(35)-H(35B)	0.9900	C(38')-O(10')	1.416(18)
C(36)-H(36A)	0.9800	C(38')-H(38C)	0.9900
C(36)-H(36B)	0.9800	C(38')-H(38D)	0.9900
C(36)-H(36C)	0.9800	O(10')-C(39')	1.422(17)
C(37)-C(38)	1.437(12)	C(39')-C(40')	1.444(19)
C(37)-H(37A)	0.9800	C(39')-H(39C)	0.9900
C(37)-H(37B)	0.9800	C(39')-H(39D)	0.9900
C(37)-H(37C)	0.9800	C(40')-H(40D)	0.9800
C(38)-O(10)	1.419(9)	C(40')-H(40E)	0.9800
C(38)-H(38A)	0.9900	C(40')-H(40F)	0.9800
C(38)-H(38B)	0.9900	C(16)-O(6)-H(6)	109.5
O(10)-C(39)	1.427(8)	C(25)-O(8)-H(8)	109.5
C(39)-C(40)	1.461(12)	C(12)-N(1)-C(1)	125.5(2)
C(39)-H(39A)	0.9900	C(12)-N(1)-C(15)	116.6(2)
C(39)-H(39B)	0.9900	C(1)-N(1)-C(15)	117.9(2)
C(40)-H(40A)	0.9800	C(7)-N(2)-C(6)	125.0(2)
C(40)-H(40B)	0.9800	C(7)-N(2)-C(24)	116.5(2)
C(40)-H(40C)	0.9800	C(6)-N(2)-C(24)	118.5(2)
C(33')-C(34')	1.448(16)	O(2)-C(1)-N(1)	121.0(3)
C(33')-H(33D)	0.9800	O(2)-C(1)-C(2)	122.6(3)
C(33')-H(33E)	0.9800	N(1)-C(1)-C(2)	116.4(2)
C(33')-H(33F)	0.9800	C(3)-C(2)-C(13)	120.2(2)
C(34')-O(9')	1.422(16)	C(3)-C(2)-C(1)	120.0(2)
C(34')-H(34C)	0.9900	C(13)-C(2)-C(1)	119.8(2)
C(34')-H(34D)	0.9900	C(2)-C(3)-C(4)	120.3(3)

C(2)-C(3)-H(3)	119.8	N(1)-C(15)-C(17)	111.6(2)
C(4)-C(3)-H(3)	119.8	C(16)-C(15)-C(17)	113.3(2)
C(5)-C(4)-C(3)	120.7(3)	N(1)-C(15)-H(15)	107.0
C(5)-C(4)-H(4)	119.6	C(16)-C(15)-H(15)	107.0
C(3)-C(4)-H(4)	119.6	C(17)-C(15)-H(15)	107.0
C(4)-C(5)-C(14)	120.0(2)	O(5)-C(16)-O(6)	124.7(3)
C(4)-C(5)-C(6)	120.6(2)	O(5)-C(16)-C(15)	123.9(3)
C(14)-C(5)-C(6)	119.4(2)	O(6)-C(16)-C(15)	111.4(3)
O(3)-C(6)-N(2)	120.5(3)	C(18)-C(17)-C(15)	112.4(2)
O(3)-C(6)-C(5)	122.3(3)	C(18)-C(17)-H(17A)	109.1
N(2)-C(6)-C(5)	117.2(2)	C(15)-C(17)-H(17A)	109.1
O(4)-C(7)-N(2)	120.2(3)	C(18)-C(17)-H(17B)	109.1
O(4)-C(7)-C(8)	122.4(3)	C(15)-C(17)-H(17B)	109.1
N(2)-C(7)-C(8)	117.4(2)	H(17A)-C(17)-H(17B)	107.9
C(9)-C(8)-C(14)	121.4(2)	C(19)-C(18)-C(23)	118.2(3)
C(9)-C(8)-C(7)	119.4(2)	C(19)-C(18)-C(17)	120.6(3)
C(14)-C(8)-C(7)	119.2(2)	C(23)-C(18)-C(17)	121.2(3)
C(8)-C(9)-C(10)	119.5(2)	C(20)-C(19)-C(18)	121.6(3)
C(8)-C(9)-H(9)	120.2	C(20)-C(19)-H(19)	119.2
C(10)-C(9)-H(9)	120.2	C(18)-C(19)-H(19)	119.2
C(11)-C(10)-C(9)	120.4(3)	C(19)-C(20)-C(21)	119.8(3)
C(11)-C(10)-H(10)	119.8	C(19)-C(20)-H(20)	120.1
C(9)-C(10)-H(10)	119.8	C(21)-C(20)-H(20)	120.1
C(10)-C(11)-C(13)	121.1(2)	C(20)-C(21)-C(22)	119.4(3)
C(10)-C(11)-C(12)	119.4(2)	C(20)-C(21)-H(21)	120.3
C(13)-C(11)-C(12)	119.5(2)	C(22)-C(21)-H(21)	120.3
O(1)-C(12)-N(1)	120.3(3)	C(23)-C(22)-C(21)	120.2(3)
O(1)-C(12)-C(11)	122.8(3)	C(23)-C(22)-H(22)	119.9
N(1)-C(12)-C(11)	116.9(2)	C(21)-C(22)-H(22)	119.9
C(2)-C(13)-C(11)	121.9(2)	C(22)-C(23)-C(18)	120.8(3)
C(2)-C(13)-C(14)	119.7(2)	C(22)-C(23)-H(23)	119.6
C(11)-C(13)-C(14)	118.5(2)	C(18)-C(23)-H(23)	119.6
C(8)-C(14)-C(5)	121.8(2)	N(2)-C(24)-C(25)	111.3(2)
C(8)-C(14)-C(13)	119.1(2)	N(2)-C(24)-C(26)	111.6(2)
C(5)-C(14)-C(13)	119.1(2)	C(25)-C(24)-C(26)	113.0(3)
N(1)-C(15)-C(16)	110.6(2)	N(2)-C(24)-H(24)	106.8

C(25)-C(24)-H(24)	106.8	O(9)-C(35)-C(36)	115.9(8)
C(26)-C(24)-H(24)	106.8	O(9)-C(35)-H(35A)	108.3
O(7)-C(25)-O(8)	124.3(3)	C(36)-C(35)-H(35A)	108.3
O(7)-C(25)-C(24)	124.3(3)	O(9)-C(35)-H(35B)	108.3
O(8)-C(25)-C(24)	111.3(3)	C(36)-C(35)-H(35B)	108.3
C(27)-C(26)-C(24)	113.3(2)	H(35A)-C(35)-H(35B)	107.4
C(27)-C(26)-H(26A)	108.9	O(10)-C(38)-C(37)	109.8(8)
C(24)-C(26)-H(26A)	108.9	O(10)-C(38)-H(38A)	109.7
C(27)-C(26)-H(26B)	108.9	C(37)-C(38)-H(38A)	109.7
C(24)-C(26)-H(26B)	108.9	O(10)-C(38)-H(38B)	109.7
H(26A)-C(26)-H(26B)	107.7	C(37)-C(38)-H(38B)	109.7
C(28)-C(27)-C(32)	118.1(3)	H(38A)-C(38)-H(38B)	108.2
C(28)-C(27)-C(26)	121.2(3)	C(38)-O(10)-C(39)	110.6(6)
C(32)-C(27)-C(26)	120.7(3)	O(10)-C(39)-C(40)	110.9(6)
C(29)-C(28)-C(27)	121.1(3)	O(10)-C(39)-H(39A)	109.5
C(29)-C(28)-H(28)	119.5	C(40)-C(39)-H(39A)	109.5
C(27)-C(28)-H(28)	119.5	O(10)-C(39)-H(39B)	109.5
C(28)-C(29)-C(30)	119.5(3)	C(40)-C(39)-H(39B)	109.5
C(28)-C(29)-H(29)	120.2	H(39A)-C(39)-H(39B)	108.1
C(30)-C(29)-H(29)	120.2	O(9')-C(34')-C(33')	113(2)
C(31)-C(30)-C(29)	119.9(3)	O(9')-C(34')-H(34C)	108.9
C(31)-C(30)-H(30)	120.1	C(33')-C(34')-H(34C)	108.9
C(29)-C(30)-H(30)	120.1	O(9')-C(34')-H(34D)	108.9
C(32)-C(31)-C(30)	120.3(3)	C(33')-C(34')-H(34D)	108.9
C(32)-C(31)-H(31)	119.8	H(34C)-C(34')-H(34D)	107.7
C(30)-C(31)-H(31)	119.8	C(35')-O(9')-C(34')	115.1(19)
C(31)-C(32)-C(27)	121.0(3)	O(9')-C(35')-C(36')	115.8(19)
C(31)-C(32)-H(32)	119.5	O(9')-C(35')-H(35C)	108.3
C(27)-C(32)-H(32)	119.5	C(36')-C(35')-H(35C)	108.3
O(9)-C(34)-C(33)	108.0(10)	O(9')-C(35')-H(35D)	108.3
O(9)-C(34)-H(34A)	110.1	C(36')-C(35')-H(35D)	108.3
C(33)-C(34)-H(34A)	110.1	H(35C)-C(35')-H(35D)	107.4
O(9)-C(34)-H(34B)	110.1	O(10')-C(38')-C(37')	113(3)
C(33)-C(34)-H(34B)	110.1	O(10')-C(38')-H(38C)	109.0
H(34A)-C(34)-H(34B)	108.4	C(37')-C(38')-H(38C)	109.0
C(35)-O(9)-C(34)	113.9(7)	O(10')-C(38')-H(38D)	109.0

C(37')-C(38')-H(38D)	109.0	C(40')-C(39')-H(39C)	108.7
H(38C)-C(38')-H(38D)	107.8	O(10')-C(39')-H(39D)	108.7
C(38')-O(10')-C(39')	112(3)	C(40')-C(39')-H(39D)	108.7
O(10')-C(39')-C(40')	114(3)	H(39C)-C(39')-H(39D)	107.6
O(10')-C(39')-H(39C)	108.7		

Table 4. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for nilwl03. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U_{11} + ... + 2\ h\ k\ a^*\ b^*\ U_{12}\ ]$

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
O1	34(1)	47(1)	40(1)	10(1)	19(1)	14(1)
O2	46(1)	51(1)	33(1)	13(1)	23(1)	14(1)
O3	33(1)	50(1)	46(1)	16(1)	22(1)	13(1)
O4	42(1)	48(1)	34(1)	14(1)	22(1)	12(1)
O5	34(1)	45(1)	50(1)	-9(1)	4(1)	11(1)
O6	38(1)	32(1)	50(1)	-11(1)	6(1)	1(1)
O7	51(1)	46(1)	35(1)	14(1)	7(1)	-10(1)
O8	70(2)	34(1)	41(1)	5(1)	5(1)	-15(1)
N1	26(1)	25(1)	26(1)	4(1)	9(1)	4(1)
N2	29(1)	25(1)	28(1)	4(1)	13(1)	6(1)
C1	32(1)	24(1)	29(1)	3(1)	13(1)	5(1)
C2	29(1)	21(1)	24(1)	3(1)	13(1)	2(1)
C3	34(1)	31(1)	27(1)	4(1)	17(1)	3(1)
C4	28(1)	32(1)	33(1)	3(1)	18(1)	2(1)
C5	26(1)	20(1)	29(1)	2(1)	14(1)	2(1)
C6	28(1)	27(1)	29(1)	2(1)	14(1)	1(1)
C7	29(1)	28(1)	27(1)	4(1)	12(1)	3(1)
C8	28(1)	24(1)	25(1)	1(1)	12(1)	2(1)
C9	33(1)	33(1)	28(1)	3(1)	19(1)	5(1)
C10	30(1)	32(1)	32(1)	4(1)	16(1)	5(1)
C11	25(1)	24(1)	26(1)	1(1)	12(1)	2(1)
C12	29(1)	24(1)	30(1)	2(1)	14(1)	2(1)
C13	26(1)	19(1)	25(1)	0(1)	14(1)	1(1)
C14	26(1)	20(1)	24(1)	1(1)	12(1)	0(1)
C15	29(1)	22(1)	29(1)	4(1)	8(1)	4(1)
C16	34(1)	29(1)	32(1)	1(1)	7(1)	5(1)
C17	37(2)	26(1)	34(2)	4(1)	7(1)	-3(1)
C18	32(1)	23(1)	30(1)	-2(1)	7(1)	1(1)
C19	36(2)	36(2)	37(2)	-1(1)	15(1)	5(1)
C20	46(2)	42(2)	36(2)	1(1)	17(1)	2(1)
C21	43(2)	32(2)	36(2)	1(1)	6(1)	2(1)

C22	30(1)	35(2)	44(2)	-6(1)	5(1)	6(1)
C23	33(1)	35(2)	35(2)	-7(1)	11(1)	-2(1)
C24	31(1)	29(1)	29(1)	4(1)	10(1)	6(1)
C25	38(2)	31(2)	35(2)	6(1)	7(1)	4(1)
C26	38(2)	26(1)	38(2)	-1(1)	9(1)	2(1)
C27	34(1)	25(1)	31(1)	-1(1)	9(1)	-1(1)
C28	41(2)	35(2)	33(2)	-2(1)	16(1)	-6(1)
C29	48(2)	33(2)	30(2)	5(1)	6(1)	-9(1)
C30	38(2)	32(2)	44(2)	-1(1)	1(1)	4(1)
C31	30(2)	42(2)	49(2)	-5(2)	12(1)	3(1)
C32	42(2)	36(2)	35(2)	0(1)	18(1)	-3(1)
C33	92(7)	70(7)	94(7)	-10(6)	36(6)	-32(6)
C34	67(7)	41(3)	91(8)	-16(4)	9(7)	-5(3)
O9	66(3)	41(2)	59(4)	-18(3)	19(3)	-3(2)
C35	70(4)	61(4)	90(5)	-25(3)	30(4)	2(3)
C36	144(10)	122(8)	119(9)	-60(7)	82(8)	-60(7)
C37	134(8)	122(8)	91(6)	-34(6)	27(5)	20(6)
C38	107(7)	112(7)	91(5)	-16(5)	49(5)	-43(6)
O10	89(3)	44(2)	54(2)	-6(2)	31(2)	-22(2)
C39	109(5)	46(3)	68(4)	9(3)	9(4)	-22(3)
C40	176(11)	105(7)	100(7)	-3(5)	53(8)	61(7)
C33'	92(7)	70(7)	94(7)	-10(6)	36(6)	-32(6)
C34'	67(7)	41(3)	91(8)	-16(4)	9(7)	-5(3)
O9'	66(3)	41(2)	59(4)	-18(3)	19(3)	-3(2)
C35'	70(4)	61(4)	90(5)	-25(3)	30(4)	2(3)
C36'	144(10)	122(8)	119(9)	-60(7)	82(8)	-60(7)
C37'	134(8)	122(8)	91(6)	-34(6)	27(5)	20(6)
C38'	107(7)	112(7)	91(5)	-16(5)	49(5)	-43(6)
O10'	89(3)	44(2)	54(2)	-6(2)	31(2)	-22(2)
C39'	109(5)	46(3)	68(4)	9(3)	9(4)	-22(3)
C40'	176(11)	105(7)	100(7)	-3(5)	53(8)	61(7)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$ x 10^3) for nilwl03.

	x	y	z	U(eq)
H6	-34	4695	3353	64
H8	6083	1008	9343	79
H3	5239	3061	2108	35
H4	7406	2630	4257	35
H9	2526	2645	8882	35
H10	364	3092	6730	36
H15	-145	3941	205	33
H17A	-1903	3222	-349	41
H17B	-3044	3460	635	41
H19	-1705	3715	-2907	43
H20	-3451	4070	-5482	50
H21	-6272	4354	-5840	48
H22	-7347	4256	-3616	47
H23	-5610	3886	-1069	42
H24	9278	1784	9542	36
H26A	9777	2497	11233	42
H26B	8684	2264	12272	42
H28	10338	1863	14827	43
H29	12942	1509	16675	48
H30	15258	1362	15713	51
H31	15023	1615	12993	49
H32	12462	1981	11182	44
H33A	2924	5293	5298	127
H33B	2812	5845	4921	127
H33C	1744	5486	3418	127
H34A	1020	5569	6431	87
H34B	4	5884	4757	87
H35A	-2953	4965	3913	88
H35B	-2791	5522	4026	88
H36A	-1381	4955	6954	178

H36B	-3359	5160	6301	178
H36C	-1693	5509	6905	178
H37A	3076	1165	9559	180
H37B	1717	925	10289	180
H37C	1809	750	8505	180
H38A	4477	641	11782	120
H38B	3277	229	10616	120
H39A	5423	-199	10314	98
H39B	6907	130	11645	98
H40A	6620	-19	8220	190
H40B	7986	-295	9842	190
H40C	8186	259	9673	190
H33D	2427	5420	4363	127
H33E	2633	5934	5181	127
H33F	1349	5850	3214	127
H34C	638	5746	6102	87
H34D	-726	5790	4146	87
H35C	-730	5127	6951	88
H35D	-1362	4675	5752	88
H36D	-2979	5512	4397	178
H36E	-3508	5271	5867	178
H36F	-3801	4995	4115	178
H37D	2165	401	8629	180
H37E	2629	887	9659	180
H37F	2134	436	10529	180
H38C	5231	630	11456	120
H38D	4694	94	10991	120
H39C	6365	-48	8108	98
H39D	5632	-268	9473	98
H40D	8956	51	9990	190
H40E	8355	-342	11027	190
H40F	8242	201	11460	190

Table 6. Torsion angles [°] for nilwl03.

C12-N1-C1-O2	176.4(3)	C1-N1-C12-O1	-178.0(3)
C15-N1-C1-O2	-2.2(4)	C15-N1-C12-O1	0.6(4)
C12-N1-C1-C2	-2.4(4)	C1-N1-C12-C11	2.2(4)
C15-N1-C1-C2	179.0(2)	C15-N1-C12-C11	-179.1(2)
O2-C1-C2-C3	2.5(4)	C10-C11-C12-O1	-0.6(4)
N1-C1-C2-C3	-178.7(3)	C13-C11-C12-O1	179.7(3)
O2-C1-C2-C13	-178.0(3)	C10-C11-C12-N1	179.1(3)
N1-C1-C2-C13	0.8(4)	C13-C11-C12-N1	-0.6(4)
C13-C2-C3-C4	-0.6(4)	C3-C2-C13-C11	-179.8(3)
C1-C2-C3-C4	179.0(3)	C1-C2-C13-C11	0.7(4)
C2-C3-C4-C5	0.7(4)	C3-C2-C13-C14	0.3(4)
C3-C4-C5-C14	-0.6(4)	C1-C2-C13-C14	-179.2(2)
C3-C4-C5-C6	178.9(3)	C10-C11-C13-C2	179.5(3)
C7-N2-C6-O3	178.3(3)	C12-C11-C13-C2	-0.8(4)
C24-N2-C6-O3	-0.7(4)	C10-C11-C13-C14	-0.6(4)
C7-N2-C6-C5	-1.7(4)	C12-C11-C13-C14	179.1(2)
C24-N2-C6-C5	179.4(2)	C9-C8-C14-C5	-179.3(3)
C4-C5-C6-O3	1.8(4)	C7-C8-C14-C5	-1.5(4)
C14-C5-C6-O3	-178.6(3)	C9-C8-C14-C13	0.0(4)
C4-C5-C6-N2	-178.2(3)	C7-C8-C14-C13	177.9(2)
C14-C5-C6-N2	1.3(4)	C4-C5-C14-C8	179.8(3)
C6-N2-C7-O4	180.0(3)	C6-C5-C14-C8	0.2(4)
C24-N2-C7-O4	-1.1(4)	C4-C5-C14-C13	0.4(4)
C6-N2-C7-C8	0.5(4)	C6-C5-C14-C13	-179.1(2)
C24-N2-C7-C8	179.4(2)	C2-C13-C14-C8	-179.6(3)
O4-C7-C8-C9	-0.5(4)	C11-C13-C14-C8	0.5(3)
N2-C7-C8-C9	179.1(3)	C2-C13-C14-C5	-0.3(3)
O4-C7-C8-C14	-178.4(3)	C11-C13-C14-C5	179.9(2)
N2-C7-C8-C14	1.2(4)	C12-N1-C15-C16	51.0(3)
C14-C8-C9-C10	-0.4(4)	C1-N1-C15-C16	-130.2(3)
C7-C8-C9-C10	-178.3(3)	C12-N1-C15-C17	-76.0(3)
C8-C9-C10-C11	0.4(4)	C1-N1-C15-C17	102.7(3)
C9-C10-C11-C13	0.1(4)	N1-C15-C16-O5	-135.2(3)
C9-C10-C11-C12	-179.5(3)	C17-C15-C16-O5	-9.1(4)

N1-C15-C16-O6	47.5(3)	C37-C38-O10-C39	-167.7(7)
C17-C15-C16-O6	173.6(3)	C38-O10-C39-C40	175.2(8)
N1-C15-C17-C18	-163.1(2)	C33'-C34'-O9'-C35'	169(4)
C16-C15-C17-C18	71.4(3)	C34'-O9'-C35'-C36'	63(4)
C15-C17-C18-C19	70.3(4)	C37'-C38'-O10'-C39'	-129(6)
C15-C17-C18-C23	-111.9(3)	C38'-O10'-C39'-C40'	-85(6)
C23-C18-C19-C20	0.8(5)		
C17-C18-C19-C20	178.7(3)		
C18-C19-C20-C21	0.5(5)		
C19-C20-C21-C22	-1.1(5)		
C20-C21-C22-C23	0.4(5)		
C21-C22-C23-C18	0.9(5)		
C19-C18-C23-C22	-1.5(4)		
C17-C18-C23-C22	-179.4(3)		
C7-N2-C24-C25	52.6(4)		
C6-N2-C24-C25	-128.4(3)		
C7-N2-C24-C26	-74.7(3)		
C6-N2-C24-C26	104.4(3)		
N2-C24-C25-O7	-134.7(3)		
C26-C24-C25-O7	-8.2(5)		
N2-C24-C25-O8	48.5(4)		
C26-C24-C25-O8	175.0(3)		
N2-C24-C26-C27	-164.1(3)		
C25-C24-C26-C27	69.5(4)		
C24-C26-C27-C28	-112.8(3)		
C24-C26-C27-C32	67.7(4)		
C32-C27-C28-C29	-0.1(5)		
C26-C27-C28-C29	-179.5(3)		
C27-C28-C29-C30	-1.4(5)		
C28-C29-C30-C31	2.1(5)		
C29-C30-C31-C32	-1.4(5)		
C30-C31-C32-C27	-0.1(5)		
C28-C27-C32-C31	0.8(5)		
C26-C27-C32-C31	-179.7(3)		
C33-C34-O9-C35	-171.3(11)		
C34-O9-C35-C36	-63.1(13)		

Table 7. Hydrogen bonds and close contacts for nilwl03 [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
O6-H6...O9	0.84	1.80	2.640(7)	176.3
O6-H6...O9'	0.84	1.82	2.63(2)	161.6
O8-H8...O10	0.84	1.81	2.646(5)	174.9
O8-H8...O10'	0.84	1.75	2.55(3)	156.7

Appendix 2. Crystal Structure Report for **3a**

REFERENCE NUMBER: nilwl05

CRYSTAL STRUCTURE REPORT

$C_{50}\ H_{58}\ Cl_4\ N_6\ O_{10}$

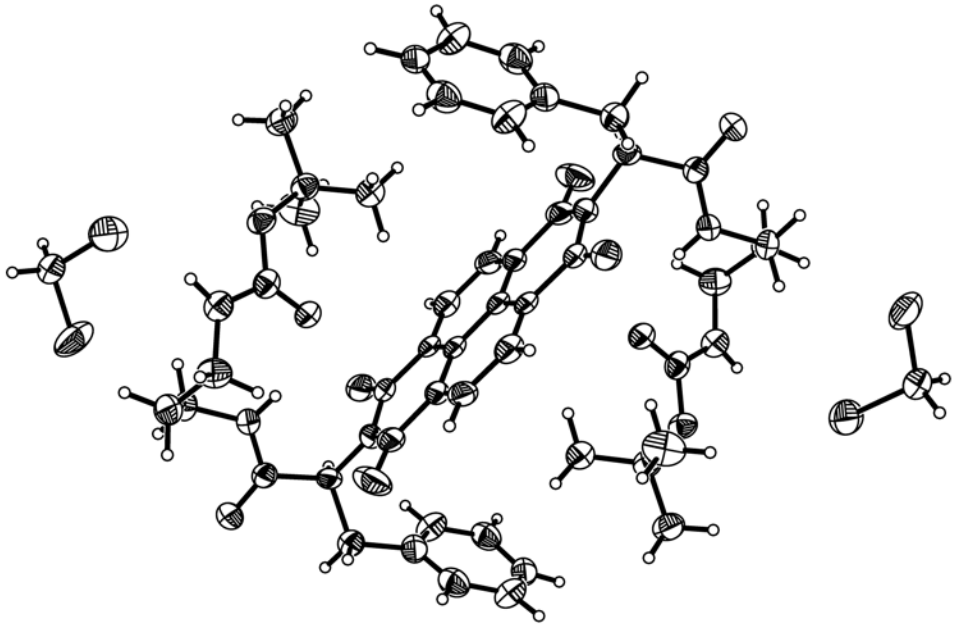
or

$C_{48}H_{54}N_6O_{10} \cdot CH_2Cl_2$

Report prepared for:

W. Liyanage, Prof. B. Nilsson

February 27, 2012



William W. Brennessel

X-ray Crystallographic Facility

Department of Chemistry, University of Rochester

120 Trustee Road

Rochester, NY 14627

Data collection

A crystal (0.28 x 0.24 x 0.10 mm^3) was placed onto the tip of a 0.1 mm diameter glass capillary tube or fiber and mounted on a Bruker SMART APEX II CCD Platform diffractometer for a data collection at 100.0(5) K.[1] A preliminary set of cell constants and an orientation matrix were calculated from reflections harvested from three orthogonal wedges of reciprocal space. The full data collection was carried out using MoKα radiation (graphite monochromator) with a frame time of 60 seconds and a detector distance of 4.01 cm. A randomly oriented region of reciprocal space was surveyed: six major sections of frames were collected with 0.50º steps in ω at six different ϕ settings and a detector position of -38º in 2θ. The intensity data were corrected for absorption.[2] Final cell constants were calculated from the xyz centroids of 4082 strong reflections from the actual data collection after integration.[3] See Table 1 for additional crystal and refinement information.

Structure solution and refinement

The structure was solved using SIR97[4] and refined using SHELXL-97.[5] The space group $P2_1/c$ was determined based on systematic absences. A direct-methods solution was calculated which provided most non-hydrogen atoms from the E-map. Full-matrix least squares / difference Fourier cycles were performed which located the remaining non-hydrogen atoms. All non-hydrogen atoms were refined with anisotropic displacement parameters. The positional parameters for the amine hydrogen atoms were refined independently from those of their respective bonded nitrogen atoms. All other hydrogen atoms were placed in ideal positions and refined as riding atoms with relative isotropic displacement parameters. The final full matrix least squares refinement converged to $R1 = 0.0652$ (F^2, $I > 2\sigma(I)$) and $wR2 = 0.1421$ (F^2, all data).

Structure description

The structure is the one suggested. The molecule lies in a crystallographic inversion center, and thus one half is unique. The benzyl moiety is modeled as disordeded over two positions (50:50, due to the nearby crystallographic inversion center). There are also two (one unique) cocrystallized dichloromethane solvent molecules per featured molecule. Intermolecular hydrogen bonding links neighboring molecules and intramolecular hydrogen bonding is present within each molecule (see diagram and Table 7). The long chains may be oriented such that the C=O group is aimed at the electropositive center of the aromatic rings (see diagram, distance 2.95 Å).

Unless noted otherwise all structural diagrams containing thermal displacement ellipsoids are drawn at the 50 % probability level.

Data collection, structure solution, and structure refinement were conducted at the X-ray Crystallographic Facility, B51 Hutchison Hall, Department of Chemistry, University of Rochester. All publications arising from this report MUST either 1) include William W. Brennessel as a coauthor or 2) acknowledge William W. Brennessel and the X-ray Crystallographic Facility of the Department of Chemistry at the University of Rochester.

[1] *APEX2*, version 2011.4-1; Bruker AXS: Madison, WI, 2011.

[2] Sheldrick, G. M. *SADABS*, version 2008/1; University of Göttingen: Göttingen, Germany, 2008.

[3] *SAINT*, version 7.68A; Bruker AXS: Madison, WI, 2009.

[4] Altomare, A.; Burla, M. C.; Camalli, M.; Cascarano, G. L.; Giacovazzo, C.; Guagliardi, A.; Moliterni, A. G. G.; Polidori, G.; Spagna, R. *SIR97: A new program for solving and refining crystal structures*; Istituto di Cristallografia, CNR: Bari, Italy, 1999.

[5] Sheldrick, G. M. *Acta. Cryst.* **2008***, A64*, 112-122.

Some equations of interest:

$$R_{int} = \Sigma\, |F_o^2 - < F_o^2 >| \,/\, \Sigma |F_o^2|$$

$$R1 = \Sigma ||F_o| - |F_c|| \,/\, \Sigma |F_o|$$

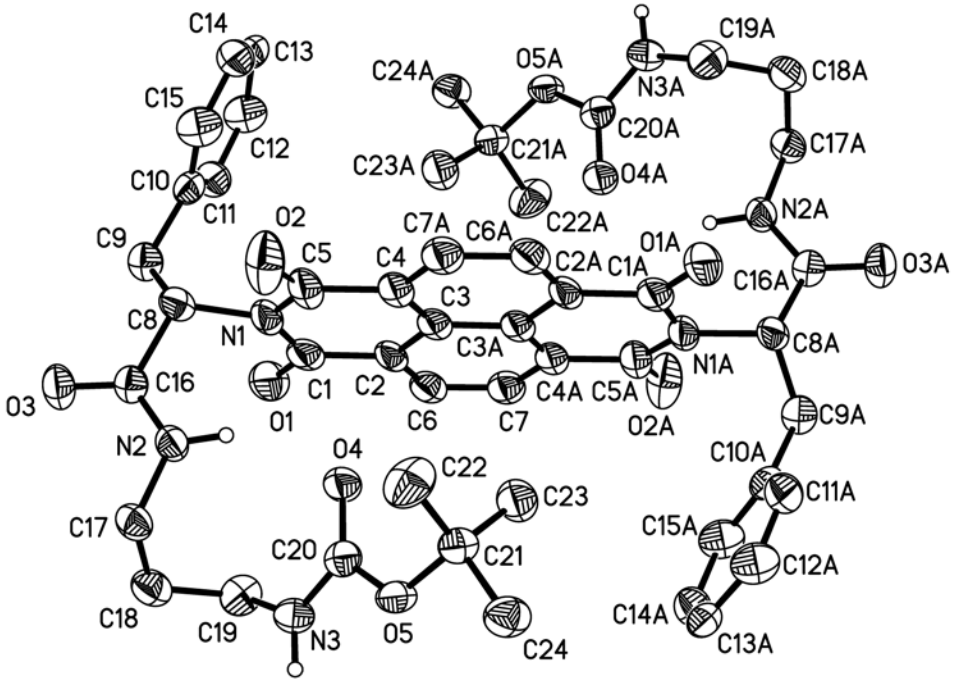
$$wR2 = [\Sigma [w(F_o^2 - F_c^2)^2] \,/\, \Sigma\, [w(F_o^2)^2]]^{1/2}$$

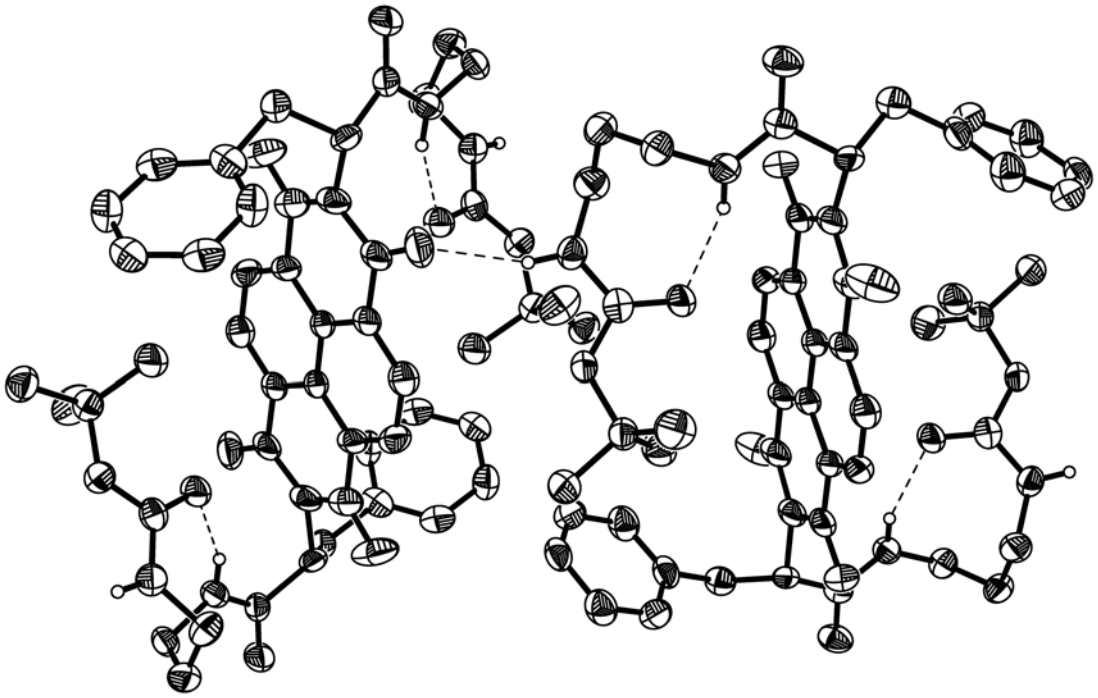
where $w = 1 \,/\, [\sigma^2 (F_o^2) + (aP)^2 + bP]$ and

$$P = 1/3 \max (0, F_o^2) + 2/3\, F_c^2$$

$$\text{GOF} = S = [\Sigma [w(F_o^2 - F_c^2)^2] \,/\, (m-n)]^{1/2}$$

where m = number of reflections and n = number of parameters





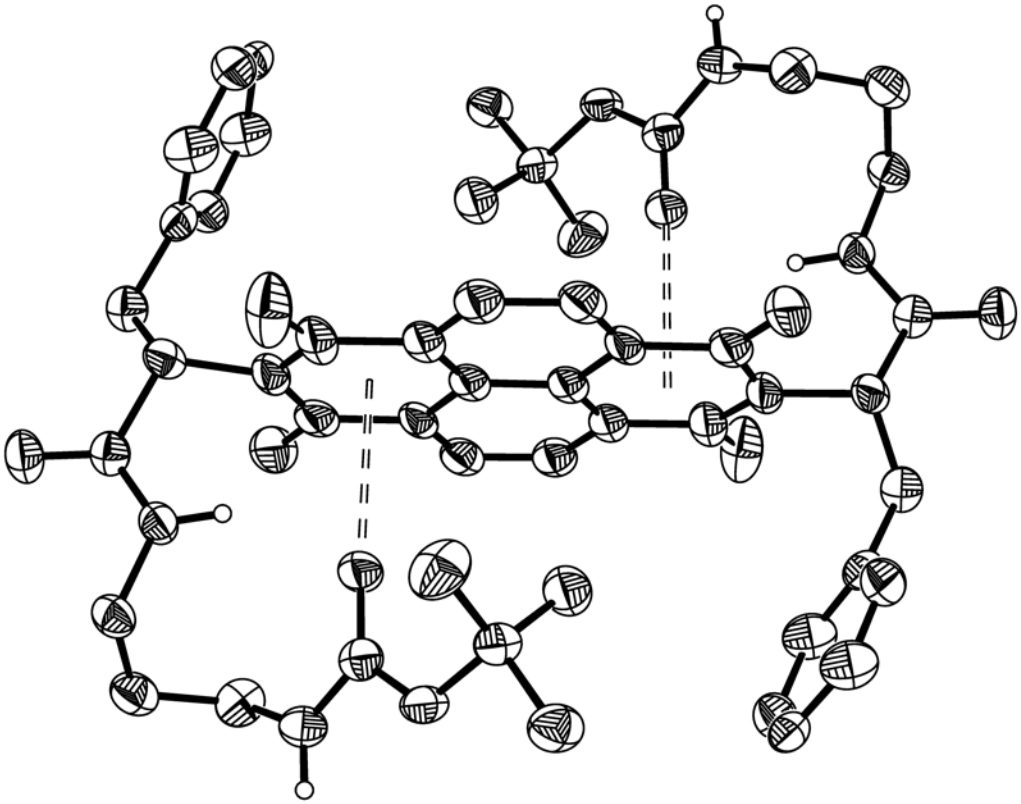


Table 1. Crystal data and structure refinement for nilwl05.

Identification code	nilwl05	
Empirical formula	C50 H58 Cl4 N6 O10	
Formula weight	1044.82	
Temperature	100.0(5) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	$P2_1/c$	
Unit cell dimensions	a = 14.567(3) Å	α = 90°
	b = 15.967(3) Å	β = 109.917(3)°
	c = 11.502(2) Å	γ = 90°
Volume	2515.2(9) Å^3	
Z	2	
Density (calculated)	1.380 Mg/m^3	
Absorption coefficient	0.299 mm^{-1}	
F(000)	1096	
Crystal color, morphology	colorless, plate	
Crystal size	0.28 x 0.24 x 0.10 mm^3	
Theta range for data collection	1.96 to 25.02°	
Index ranges	$-17 \le h \le 17$, $-19 \le k \le 19$, $-13 \le l \le 13$	
Reflections collected	37000	
Independent reflections	4440 [R(int) = 0.1261]	
Observed reflections	2717	
Completeness to theta = 25.02°	100.0%	
Absorption correction	Multi-scan	
Max. and min. transmission	0.9707 and 0.9208	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4440 / 19 / 331	
Goodness-of-fit on F^2	1.080	
Final R indices [I>2sigma(I)]	$R1$ = 0.0652, $wR2$ = 0.1236	
R indices (all data)	$R1$ = 0.1167, $wR2$ = 0.1421	
Largest diff. peak and hole	0.311 and -0.473 e.Å^{-3}	

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for nilwl05. U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U_{eq}
O1	2780(2)	5168(2)	2659(3)	65(1)
O2	2277(2)	4480(2)	-1319(4)	64(1)
O3	5010(2)	4107(2)	1815(3)	46(1)
O4	1538(2)	3125(2)	974(3)	41(1)
O5	829(2)	1838(2)	843(2)	36(1)
N1	2537(2)	4910(2)	641(4)	44(1)
N2	3562(3)	3453(2)	1401(3)	36(1)
N3	2159(3)	2114(2)	2419(3)	38(1)
C1	2204(3)	5065(3)	1626(5)	48(1)
C2	1139(3)	5116(2)	1344(4)	38(1)
C3	505(3)	4975(2)	129(4)	34(1)
C4	870(3)	4774(2)	-818(4)	39(1)
C5	1929(3)	4703(3)	-556(5)	47(1)
C6	768(3)	5297(3)	2258(4)	42(1)
C7	-234(3)	5364(3)	2000(4)	43(1)
C8	3584(5)	4873(5)	684(10)	36(3)
C9	4143(6)	5676(5)	1228(8)	39(2)
C10	3630(8)	6458(6)	584(10)	42(1)
C11	3518(11)	7110(7)	1303(10)	47(2)
C12	3130(17)	7869(8)	779(16)	48(2)
C13	2883(9)	7982(8)	-485(17)	42(1)
C14	2935(7)	7314(7)	-1210(13)	47(2)
C15	3346(9)	6565(7)	-662(10)	48(2)
C8'	3628(5)	4971(5)	1145(11)	36(3)
C9'	3938(6)	5488(5)	259(8)	39(2)
C10'	3488(9)	6356(5)	29(10)	42(1)
C11'	3646(11)	6940(7)	955(10)	47(2)
C12'	3272(17)	7741(8)	715(16)	48(2)
C13'	2680(9)	7961(8)	-461(17)	42(1)
C14'	2552(7)	7385(7)	-1390(12)	47(2)
C15'	2935(8)	6588(6)	-1133(9)	48(2)

C16	4122(3)	4115(3)	1430(4)	34(1)
C17	3949(3)	2641(2)	1882(4)	37(1)
C18	3921(3)	2472(3)	3151(4)	44(1)
C19	2925(3)	2622(3)	3269(4)	44(1)
C20	1518(3)	2422(3)	1382(4)	35(1)
C21	61(3)	2000(3)	-350(4)	36(1)
C22	518(4)	2139(3)	-1326(4)	59(1)
C23	-560(3)	2728(3)	-219(4)	50(1)
C24	-513(3)	1192(3)	-574(4)	46(1)
C25	3792(3)	15(3)	614(4)	45(1)
Cl1	2662(1)	339(1)	705(1)	68(1)
Cl2	4537(1)	862(1)	575(2)	80(1)

Table 3. Bond lengths [Å] and angles [°] for nilwl05.

O(1)-C(1)	1.209(5)	C(10)-C(11)	1.374(11)
O(2)-C(5)	1.208(5)	C(11)-C(12)	1.386(12)
O(3)-C(16)	1.216(4)	C(11)-H(11)	0.9500
O(4)-C(20)	1.220(5)	C(12)-C(13)	1.385(12)
O(5)-C(20)	1.356(5)	C(12)-H(12)	0.9500
O(5)-C(21)	1.469(5)	C(13)-C(14)	1.372(11)
N(1)-C(1)	1.398(6)	C(13)-H(13)	0.9500
N(1)-C(5)	1.399(6)	C(14)-C(15)	1.389(12)
N(1)-C(8')	1.498(7)	C(14)-H(14)	0.9500
N(1)-C(8)	1.510(8)	C(15)-H(15)	0.9500
N(2)-C(16)	1.329(5)	C(8')-C(9')	1.495(11)
N(2)-C(17)	1.446(5)	C(8')-C(16)	1.528(8)
N(2)-H(2)	0.88(4)	C(8')-H(8')	1.0000
N(3)-C(20)	1.333(5)	C(9')-C(10')	1.518(10)
N(3)-C(19)	1.454(5)	C(9')-H(9C)	0.9900
N(3)-H(3)	0.86(4)	C(9')-H(9D)	0.9900
C(1)-C(2)	1.475(6)	C(10')-C(15')	1.356(11)
C(2)-C(6)	1.367(6)	C(10')-C(11')	1.375(12)
C(2)-C(3)	1.406(5)	C(11')-C(12')	1.380(11)
C(3)-C(3)#1	1.401(8)	C(11')-H(11')	0.9500
C(3)-C(4)	1.402(6)	C(12')-C(13')	1.379(12)
C(4)-C(7)#1	1.377(6)	C(12')-H(12')	0.9500
C(4)-C(5)	1.471(6)	C(13')-C(14')	1.374(12)
C(6)-C(7)	1.391(6)	C(13')-H(13')	0.9500
C(6)-H(6)	0.9500	C(14')-C(15')	1.381(11)
C(7)-C(4)#1	1.377(6)	C(14')-H(14')	0.9500
C(7)-H(7)	0.9500	C(15')-H(15')	0.9500
C(8)-C(9)	1.534(11)	C(17)-C(18)	1.499(5)
C(8)-C(16)	1.535(8)	C(17)-H(17A)	0.9900
C(8)-H(8)	1.0000	C(17)-H(17B)	0.9900
C(9)-C(10)	1.513(10)	C(18)-C(19)	1.521(6)
C(9)-H(9A)	0.9900	C(18)-H(18A)	0.9900
C(9)-H(9B)	0.9900	C(18)-H(18B)	0.9900
C(10)-C(15)	1.359(12)	C(19)-H(19A)	0.9900

C(19)-H(19B)	0.9900	C(3)#1-C(3)-C(2)	119.3(5)
C(21)-C(22)	1.504(6)	C(4)-C(3)-C(2)	120.9(4)
C(21)-C(24)	1.511(6)	C(7)#1-C(4)-C(3)	119.8(4)
C(21)-C(23)	1.511(6)	C(7)#1-C(4)-C(5)	119.7(4)
C(22)-H(22A)	0.9800	C(3)-C(4)-C(5)	120.4(4)
C(22)-H(22B)	0.9800	O(2)-C(5)-N(1)	120.1(4)
C(22)-H(22C)	0.9800	O(2)-C(5)-C(4)	123.0(4)
C(23)-H(23A)	0.9800	N(1)-C(5)-C(4)	116.9(4)
C(23)-H(23B)	0.9800	C(2)-C(6)-C(7)	120.9(4)
C(23)-H(23C)	0.9800	C(2)-C(6)-H(6)	119.6
C(24)-H(24A)	0.9800	C(7)-C(6)-H(6)	119.6
C(24)-H(24B)	0.9800	C(4)#1-C(7)-C(6)	120.2(4)
C(24)-H(24C)	0.9800	C(4)#1-C(7)-H(7)	119.9
C(25)-Cl(2)	1.745(4)	C(6)-C(7)-H(7)	119.9
C(25)-Cl(1)	1.761(4)	N(1)-C(8)-C(9)	111.7(7)
C(25)-H(25A)	0.9900	N(1)-C(8)-C(16)	111.6(5)
C(25)-H(25B)	0.9900	C(9)-C(8)-C(16)	109.4(6)
C(20)-O(5)-C(21)	121.0(3)	N(1)-C(8)-H(8)	108.0
C(1)-N(1)-C(5)	124.1(4)	C(9)-C(8)-H(8)	108.0
C(1)-N(1)-C(8')	106.8(6)	C(16)-C(8)-H(8)	108.0
C(5)-N(1)-C(8')	129.0(6)	C(10)-C(9)-C(8)	112.7(7)
C(1)-N(1)-C(8)	127.3(5)	C(10)-C(9)-H(9A)	109.1
C(5)-N(1)-C(8)	108.5(6)	C(8)-C(9)-H(9A)	109.1
C(16)-N(2)-C(17)	123.2(3)	C(10)-C(9)-H(9B)	109.1
C(16)-N(2)-H(2)	121(3)	C(8)-C(9)-H(9B)	109.1
C(17)-N(2)-H(2)	115(3)	H(9A)-C(9)-H(9B)	107.8
C(20)-N(3)-C(19)	122.7(4)	C(15)-C(10)-C(11)	118.9(8)
C(20)-N(3)-H(3)	117(3)	C(15)-C(10)-C(9)	122.8(10)
C(19)-N(3)-H(3)	120(3)	C(11)-C(10)-C(9)	118.1(9)
O(1)-C(1)-N(1)	120.3(4)	C(10)-C(11)-C(12)	121.0(9)
O(1)-C(1)-C(2)	122.3(5)	C(10)-C(11)-H(11)	119.5
N(1)-C(1)-C(2)	117.4(4)	C(12)-C(11)-H(11)	119.5
C(6)-C(2)-C(3)	120.0(4)	C(13)-C(12)-C(11)	119.5(10)
C(6)-C(2)-C(1)	120.3(4)	C(13)-C(12)-H(12)	120.3
C(3)-C(2)-C(1)	119.7(4)	C(11)-C(12)-H(12)	120.3
C(3)#1-C(3)-C(4)	119.8(5)	C(14)-C(13)-C(12)	119.2(11)

C(14)-C(13)-H(13)	120.4	C(10')-C(15')-H(15')	119.3
C(12)-C(13)-H(13)	120.4	C(14')-C(15')-H(15')	119.3
C(13)-C(14)-C(15)	119.8(10)	O(3)-C(16)-N(2)	124.7(4)
C(13)-C(14)-H(14)	120.1	O(3)-C(16)-C(8')	116.8(4)
C(15)-C(14)-H(14)	120.1	N(2)-C(16)-C(8')	117.8(4)
C(10)-C(15)-C(14)	121.1(9)	O(3)-C(16)-C(8)	119.3(4)
C(10)-C(15)-H(15)	119.5	N(2)-C(16)-C(8)	114.9(4)
C(14)-C(15)-H(15)	119.5	N(2)-C(17)-C(18)	113.5(3)
C(9')-C(8')-N(1)	107.4(6)	N(2)-C(17)-H(17A)	108.9
C(9')-C(8')-C(16)	114.3(7)	C(18)-C(17)-H(17A)	108.9
N(1)-C(8')-C(16)	112.6(5)	N(2)-C(17)-H(17B)	108.9
C(9')-C(8')-H(8')	107.4	C(18)-C(17)-H(17B)	108.9
N(1)-C(8')-H(8')	107.4	H(17A)-C(17)-H(17B)	107.7
C(16)-C(8')-H(8')	107.4	C(17)-C(18)-C(19)	113.7(3)
C(8')-C(9')-C(10')	114.2(7)	C(17)-C(18)-H(18A)	108.8
C(8')-C(9')-H(9C)	108.7	C(19)-C(18)-H(18A)	108.8
C(10')-C(9')-H(9C)	108.7	C(17)-C(18)-H(18B)	108.8
C(8')-C(9')-H(9D)	108.7	C(19)-C(18)-H(18B)	108.8
C(10')-C(9')-H(9D)	108.7	H(18A)-C(18)-H(18B)	107.7
H(9C)-C(9')-H(9D)	107.6	N(3)-C(19)-C(18)	112.9(4)
C(15')-C(10')-C(11')	117.8(8)	N(3)-C(19)-H(19A)	109.0
C(15')-C(10')-C(9')	119.8(9)	C(18)-C(19)-H(19A)	109.0
C(11')-C(10')-C(9')	122.4(9)	N(3)-C(19)-H(19B)	109.0
C(10')-C(11')-C(12')	121.5(10)	C(18)-C(19)-H(19B)	109.0
C(10')-C(11')-H(11')	119.3	H(19A)-C(19)-H(19B)	107.8
C(12')-C(11')-H(11')	119.3	O(4)-C(20)-N(3)	125.6(4)
C(13')-C(12')-C(11')	120.4(11)	O(4)-C(20)-O(5)	124.6(4)
C(13')-C(12')-H(12')	119.8	N(3)-C(20)-O(5)	109.8(4)
C(11')-C(12')-H(12')	119.8	O(5)-C(21)-C(22)	109.5(3)
C(14')-C(13')-C(12')	117.7(10)	O(5)-C(21)-C(24)	102.1(3)
C(14')-C(13')-H(13')	121.1	C(22)-C(21)-C(24)	111.0(4)
C(12')-C(13')-H(13')	121.1	O(5)-C(21)-C(23)	109.5(3)
C(13')-C(14')-C(15')	120.9(10)	C(22)-C(21)-C(23)	113.2(4)
C(13')-C(14')-H(14')	119.5	C(24)-C(21)-C(23)	111.1(4)
C(15')-C(14')-H(14')	119.5	C(21)-C(22)-H(22A)	109.5
C(10')-C(15')-C(14')	121.5(9)	C(21)-C(22)-H(22B)	109.5

H(22A)-C(22)-H(22B)	109.5	C(21)-C(24)-H(24B)	109.5
C(21)-C(22)-H(22C)	109.5	H(24A)-C(24)-H(24B)	109.5
H(22A)-C(22)-H(22C)	109.5	C(21)-C(24)-H(24C)	109.5
H(22B)-C(22)-H(22C)	109.5	H(24A)-C(24)-H(24C)	109.5
C(21)-C(23)-H(23A)	109.5	H(24B)-C(24)-H(24C)	109.5
C(21)-C(23)-H(23B)	109.5	Cl(2)-C(25)-Cl(1)	112.0(2)
H(23A)-C(23)-H(23B)	109.5	Cl(2)-C(25)-H(25A)	109.2
C(21)-C(23)-H(23C)	109.5	Cl(1)-C(25)-H(25A)	109.2
H(23A)-C(23)-H(23C)	109.5	Cl(2)-C(25)-H(25B)	109.2
H(23B)-C(23)-H(23C)	109.5	Cl(1)-C(25)-H(25B)	109.2
C(21)-C(24)-H(24A)	109.5	H(25A)-C(25)-H(25B)	107.9

Symmetry transformations used to generate equivalent atoms:

#1 -x,-y+1,-z

Table 4. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for nilwl05. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U_{11} + ... + 2\ h\ k\ a^*\ b^*\ U_{12}\ ]$

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
O1	40(2)	72(3)	60(2)	20(2)	-10(2)	-16(2)
O2	42(2)	47(2)	103(3)	-34(2)	25(2)	-2(2)
O3	30(2)	42(2)	63(2)	-6(2)	11(2)	2(1)
O4	38(2)	28(2)	54(2)	5(1)	10(1)	-2(1)
O5	42(2)	31(2)	34(2)	6(1)	9(1)	-5(1)
N1	28(2)	26(2)	68(3)	10(2)	4(2)	-1(2)
N2	31(2)	30(2)	43(2)	2(2)	9(2)	2(2)
N3	46(2)	36(2)	32(2)	2(2)	14(2)	0(2)
C1	39(3)	26(2)	65(3)	14(2)	0(3)	-7(2)
C2	31(2)	22(2)	50(3)	8(2)	-1(2)	-2(2)
C3	34(2)	15(2)	44(2)	1(2)	4(2)	-2(2)
C4	34(2)	15(2)	59(3)	3(2)	4(2)	-3(2)
C5	32(2)	19(2)	78(4)	3(2)	5(2)	0(2)
C6	41(3)	30(2)	44(3)	5(2)	-2(2)	-7(2)
C7	47(3)	29(2)	51(3)	2(2)	13(2)	-2(2)
C8	31(3)	30(3)	35(8)	1(4)	-3(3)	-6(2)
C9	38(3)	36(4)	43(4)	-5(3)	13(3)	0(3)
C10	33(3)	36(2)	60(3)	11(2)	21(3)	-1(2)
C11	40(4)	55(3)	40(4)	7(2)	7(3)	-2(4)
C12	63(6)	35(3)	49(3)	-6(3)	21(3)	-5(3)
C13	33(3)	36(2)	60(3)	11(2)	21(3)	-1(2)
C14	40(4)	55(3)	40(4)	7(2)	7(3)	-2(4)
C15	63(6)	35(3)	49(3)	-6(3)	21(3)	-5(3)
C8'	31(3)	30(3)	35(8)	1(4)	-3(3)	-6(2)
C9'	38(3)	36(4)	43(4)	-5(3)	13(3)	0(3)
C10'	33(3)	36(2)	60(3)	11(2)	21(3)	-1(2)
C11'	40(4)	55(3)	40(4)	7(2)	7(3)	-2(4)
C12'	63(6)	35(3)	49(3)	-6(3)	21(3)	-5(3)
C13'	33(3)	36(2)	60(3)	11(2)	21(3)	-1(2)
C14'	40(4)	55(3)	40(4)	7(2)	7(3)	-2(4)
C15'	63(6)	35(3)	49(3)	-6(3)	21(3)	-5(3)

C16	33(2)	31(2)	37(2)	-6(2)	12(2)	0(2)
C17	39(2)	31(2)	42(2)	1(2)	14(2)	8(2)
C18	44(3)	41(3)	39(2)	5(2)	6(2)	3(2)
C19	48(3)	50(3)	33(2)	-5(2)	12(2)	-7(2)
C20	40(2)	33(3)	37(2)	-1(2)	20(2)	3(2)
C21	41(2)	34(2)	35(2)	2(2)	13(2)	-2(2)
C22	64(3)	83(4)	35(3)	-1(3)	24(2)	-15(3)
C23	43(3)	36(3)	65(3)	1(2)	9(2)	-1(2)
C24	52(3)	37(3)	44(3)	0(2)	9(2)	-6(2)
C25	48(3)	36(3)	52(3)	-1(2)	17(2)	2(2)
Cl1	61(1)	65(1)	88(1)	-22(1)	40(1)	-4(1)
Cl2	84(1)	37(1)	146(2)	-21(1)	74(1)	-9(1)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$ x 10^3) for nilwl05.

	x	y	z	U(eq)
H2	2930(30)	3510(30)	1230(40)	43
H3	2070(30)	1610(30)	2620(40)	45
H6	1201	5378	3081	51
H7	-480	5506	2640	51
H8	3581	4812	-183	43
H9A	4224	5710	2117	47
H9B	4802	5650	1160	47
H11	3710	7040	2173	56
H12	3033	8309	1282	58
H13	2680	8516	-846	50
H14	2691	7364	-2086	56
H15	3429	6120	-1165	58
H8'	3808	5288	1941	43
H9C	3760	5187	-540	47
H9D	4657	5545	583	47
H11'	4020	6789	1780	56
H12'	3423	8142	1362	58
H13'	2370	8494	-622	50
H14'	2196	7537	-2220	56
H15'	2807	6192	-1786	58
H17A	4634	2603	1906	45
H17B	3570	2202	1311	45
H18A	4407	2835	3751	52
H18B	4114	1882	3373	52
H19A	2963	2495	4127	53
H19B	2752	3221	3111	53
H22A	908	2653	-1142	88
H22B	4	2191	-2136	88
H22C	939	1663	-1337	88
H23A	-162	3238	-28	76

H23B	-814	2612	452	76
H23C	-1106	2805	-995	76
H24A	-797	1113	77	69
H24B	-77	723	-565	69
H24C	-1036	1217	-1380	69
H25A	4132	-341	1338	54
H25B	3675	-328	-140	54

Table 6. Torsion angles [°] for nilwl05.

C5-N1-C1-O1	173.5(4)	C5-N1-C8-C16	-108.4(7)
C8'-N1-C1-O1	-3.9(6)	N1-C8-C9-C10	-52.9(10)
C8-N1-C1-O1	-1.7(7)	C16-C8-C9-C10	-177.0(7)
C5-N1-C1-C2	-8.0(6)	C8-C9-C10-C15	-53.4(14)
C8'-N1-C1-C2	174.6(4)	C8-C9-C10-C11	131.8(11)
C8-N1-C1-C2	176.8(4)	C15-C10-C11-C12	-1(2)
O1-C1-C2-C6	1.0(6)	C9-C10-C11-C12	174.5(14)
N1-C1-C2-C6	-177.5(4)	C10-C11-C12-C13	-2(3)
O1-C1-C2-C3	-178.9(4)	C11-C12-C13-C14	7(2)
N1-C1-C2-C3	2.7(6)	C12-C13-C14-C15	-7.9(19)
C6-C2-C3-C3#1	0.2(7)	C11-C10-C15-C14	-0.9(17)
C1-C2-C3-C3#1	-180.0(4)	C9-C10-C15-C14	-175.7(10)
C6-C2-C3-C4	-178.9(4)	C13-C14-C15-C10	5.2(17)
C1-C2-C3-C4	0.9(6)	C1-N1-C8'-C9'	-134.2(6)
C3#1-C3-C4-C7#1	0.6(7)	C5-N1-C8'-C9'	48.5(8)
C2-C3-C4-C7#1	179.7(4)	C1-N1-C8'-C16	99.2(7)
C3#1-C3-C4-C5	-178.8(4)	C5-N1-C8'-C16	-78.1(8)
C2-C3-C4-C5	0.3(6)	N1-C8'-C9'-C10'	57.4(10)
C1-N1-C5-O2	-171.0(4)	C16-C8'-C9'-C10'	-176.9(7)
C8'-N1-C5-O2	5.8(7)	C8'-C9'-C10'-C15'	-120.6(12)
C8-N1-C5-O2	5.0(6)	C8'-C9'-C10'-C11'	61.7(13)
C1-N1-C5-C4	9.1(6)	C15'-C10'-C11'-C12'	-1(2)
C8'-N1-C5-C4	-174.1(5)	C9'-C10'-C11'-C12'	176.5(14)
C8-N1-C5-C4	-174.9(4)	C10'-C11'-C12'-C13'	4(2)
C7#1-C4-C5-O2	-4.3(6)	C11'-C12'-C13'-C14'	-6(2)
C3-C4-C5-O2	175.1(4)	C12'-C13'-C14'-C15'	5.5(19)
C7#1-C4-C5-N1	175.5(4)	C11'-C10'-C15'-C14'	1.0(18)
C3-C4-C5-N1	-5.1(5)	C9'-C10'-C15'-C14'	-176.8(10)
C3-C2-C6-C7	-1.5(6)	C13'-C14'-C15'-C10'	-3.3(17)
C1-C2-C6-C7	178.6(4)	C17-N2-C16-O3	2.8(6)
C2-C6-C7-C4#1	1.8(6)	C17-N2-C16-C8'	-167.4(6)
C1-N1-C8-C9	-55.4(8)	C17-N2-C16-C8	170.3(6)
C5-N1-C8-C9	128.7(7)	C9'-C8'-C16-O3	55.4(9)
C1-N1-C8-C16	67.4(9)	N1-C8'-C16-O3	178.3(6)

C9'-C8'-C16-N2	-133.5(6)
N1-C8'-C16-N2	-10.7(10)
N1-C8-C16-O3	-161.5(5)
C9-C8-C16-O3	-37.4(9)
N1-C8-C16-N2	30.2(9)
C9-C8-C16-N2	154.4(6)
C16-N2-C17-C18	99.1(5)
N2-C17-C18-C19	51.2(5)
C20-N3-C19-C18	-102.4(5)
C17-C18-C19-N3	58.4(5)
C19-N3-C20-O4	6.2(6)
C19-N3-C20-O5	-173.4(3)
C21-O5-C20-O4	3.5(6)
C21-O5-C20-N3	-176.8(3)
C20-O5-C21-C22	62.0(5)
C20-O5-C21-C24	179.7(3)
C20-O5-C21-C23	-62.5(4)

Symmetry transformations used to generate equivalent atoms:

#1 -x,-y+1,-z

Table 7. Hydrogen bonds and close contacts for nilwl05 [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
N2-H2...O4	0.88(4)	2.04(4)	2.867(4)	156(4)
N3-H3...O2#2	0.86(4)	2.09(4)	2.907(5)	159(4)

Symmetry transformations used to generate equivalent atoms:

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

Appendix 3. Crystal Structure Report for **3b**

REFERENCE NUMBER: nilwl04

CRYSTAL STRUCTURE REPORT

$C_{52}\ H_{52}\ F_{10}\ N_6\ O_{12}$

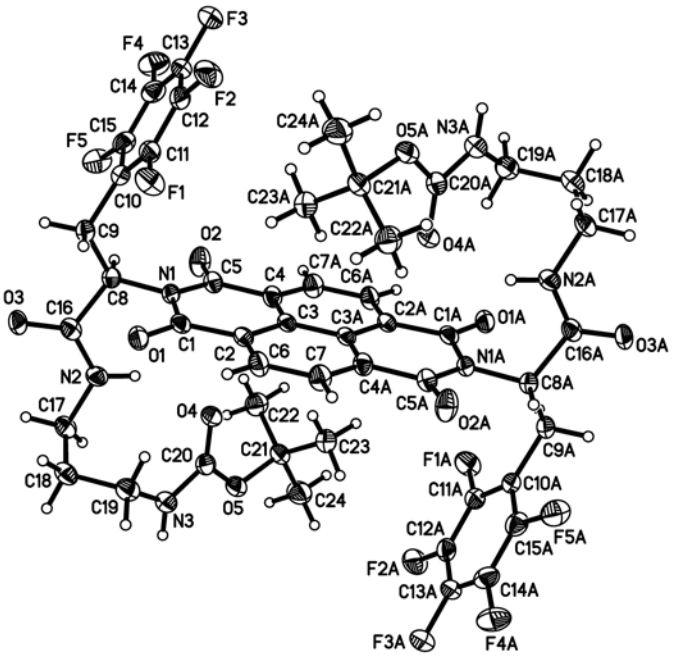
or

$C_{48}H_{44}F_{10}N_6O_{10}$ · ethyl acetate solvate

Report prepared for:

W. Liyanage, Prof. B. Nilsson

December 26, 2011



William W. Brennessel

X-ray Crystallographic Facility

Department of Chemistry, University of Rochester

120 Trustee Road

Rochester, NY 14627

Data collection

A crystal (0.32 x 0.16 x 0.08 mm^3) was placed onto the tip of a 0.1 mm diameter glass capillary tube or fiber and mounted on a Bruker SMART APEX II CCD Platform diffractometer for a data collection at 100.0(5) K.[1] A preliminary set of cell constants and an orientation matrix were calculated from reflections harvested from three orthogonal wedges of reciprocal space. The full data collection was carried out using MoKα radiation (graphite monochromator) with a frame time of 90 seconds and a detector distance of 4.01 cm. A randomly oriented region of reciprocal space was surveyed: six major sections of frames were collected with 0.50º steps in ω at six different ϕ settings and a detector position of -38º in 2θ. The intensity data were corrected for absorption.[2] Final cell constants were calculated from the xyz centroids of 4083 strong reflections from the actual data collection after integration.[3] See Table 1 for additional crystal and refinement information.

Structure solution and refinement

The structure was solved using SIR97[4] and refined using SHELXL-97.[5] The space group $P2_1/n$ was determined based on systematic absences. A direct-methods solution was calculated which provided most non-hydrogen atoms from the E-map. Full-matrix least squares / difference Fourier cycles were performed which located the remaining non-hydrogen atoms. All non-hydrogen atoms were refined with anisotropic displacement parameters. The amine hydrogen atoms were found from the difference Fourier map, and their positional and isotropic displacement parameters were refined independently from those of their respective bonded nitrogen atoms. All other hydrogen atoms were placed in ideal positions and refined as riding atoms with relative isotropic displacement parameters. The final full matrix least squares refinement converged to $R1 = 0.0476$ (F^2, $I > 2\sigma(I)$) and $wR2 = 0.1120$ (F^2, all data).

Structure description

The structure is the one suggested. The featured molecule and the co-crystallized ethyl acetate solvent molecule lie in crystallographic inversion centers; the latter is modeled as disordered over the center (50:50). Intramolecular and intermolecular hydrogen bonding are present (see diagram and Table 7). The intermolecular hydrogen bonding links molecules in one direction, while pi-stacking (~3.2 Å) links molecules in a second (orthogonal) direction (see diagrams).

Unless noted otherwise all structural diagrams containing thermal displacement ellipsoids are drawn at the 50 % probability level.

Data collection, structure solution, and structure refinement were conducted at the X-ray Crystallographic Facility, B51 Hutchison Hall, Department of Chemistry, University of Rochester. All publications arising from this report MUST either 1) include William W. Brennessel as a coauthor or 2) acknowledge William W. Brennessel and the X-ray Crystallographic Facility of the Department of Chemistry at the University of Rochester.

---

[1] *APEX2*, version 2011.4-1; Bruker AXS: Madison, WI, 2011.

[2] Sheldrick, G. M. *SADABS*, version 2008/1; University of Göttingen: Göttingen, Germany, 2008.

[3] *SAINT*, version 7.68A; Bruker AXS: Madison, WI, 2009.

[4] Altomare, A.; Burla, M. C.; Camalli, M.; Cascarano, G. L.; Giacovazzo, C.; Guagliardi, A.; Moliterni, A. G. G.; Polidori, G.; Spagna, R. *SIR97: A new program for solving and refining crystal structures*; Istituto di Cristallografia, CNR: Bari, Italy, 1999.

[5] Sheldrick, G. M. *Acta. Cryst.* **2008***, A64*, 112-122.

Some equations of interest:

$$R_{int} = \Sigma\, |F_o^2 - < F_o^2 >| \,/\, \Sigma |F_o^2|$$

$$R1 = \Sigma ||F_o| - |F_c|| \,/\, \Sigma |F_o|$$

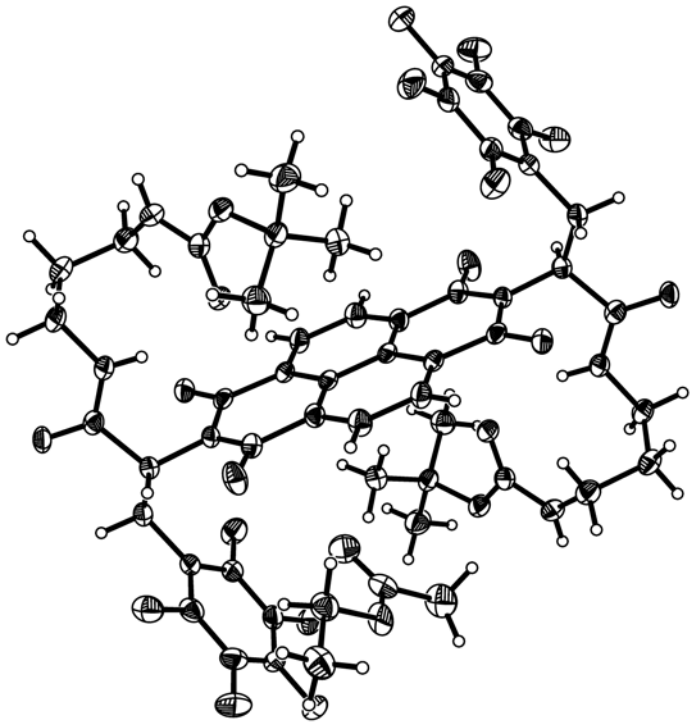
$$wR2 = [\Sigma [w(F_o^2 - F_c^2)^2] \,/\, \Sigma\, [w(F_o^2)^2]]^{1/2}$$

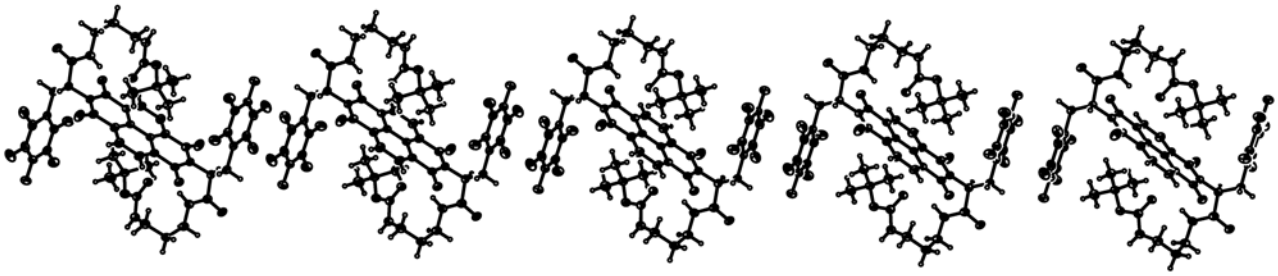
where $w = 1 \,/\, [\sigma^2 (F_o^2) + (aP)^2 + bP]$ and

$$P = 1/3 \max (0, F_o^2) + 2/3\, F_c^2$$

$$\text{GOF} = S = [\Sigma [w(F_o^2 - F_c^2)^2] \,/\, (m-n)]^{1/2}$$

where m = number of reflections and n = number of parameters





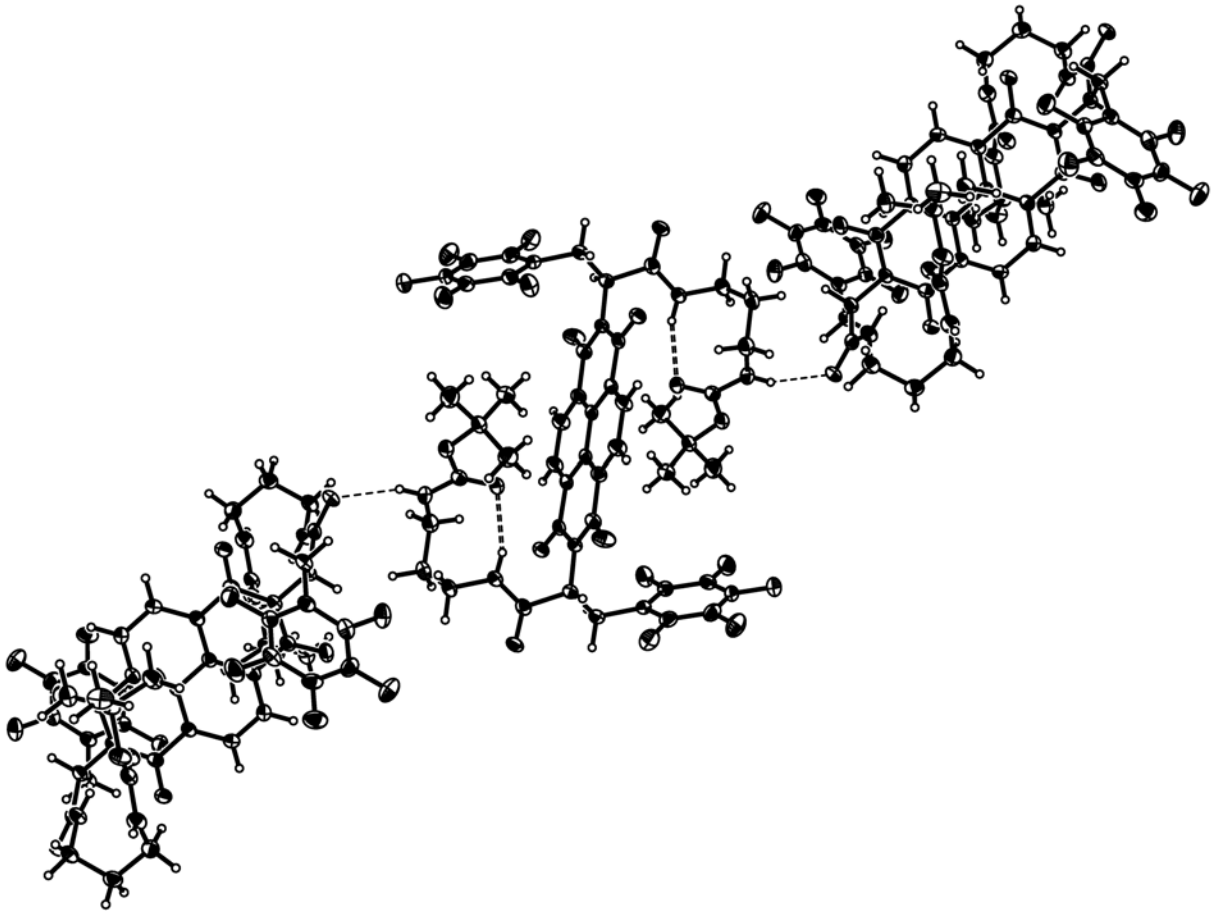


Table 1. Crystal data and structure refinement for nilwl04.

Identification code	nilwl04	
Empirical formula	C52 H52 F10 N6 O12	
Formula weight	1143.00	
Temperature	100.0(5) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	$P2_1/n$	
Unit cell dimensions	a = 10.637(2) Å	α = 90°
	b = 11.266(2) Å	β = 103.619(4)°
	c = 21.887(5) Å	γ = 90°
Volume	2549.0(9) Å^3	
Z	2	
Density (calculated)	1.489 Mg/m^3	
Absorption coefficient	0.130 mm^{-1}	
F(000)	1184	
Crystal color, morphology	colorless, needle	
Crystal size	0.32 x 0.16 x 0.08 mm^3	
Theta range for data collection	1.91 to 28.28°	
Index ranges	$-14 \le h \le 14$, $-15 \le k \le 15$, $-29 \le l \le 29$	
Reflections collected	47284	
Independent reflections	6316 [R(int) = 0.1051]	
Observed reflections	3828	
Completeness to theta = 28.28°	100.0%	
Absorption correction	Multi-scan	
Max. and min. transmission	0.9897 and 0.9597	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	6316 / 0 / 401	
Goodness-of-fit on F^2	1.010	
Final R indices [I>2sigma(I)]	R1 = 0.0476, wR2 = 0.0941	
R indices (all data)	R1 = 0.0972, wR2 = 0.1120	
Largest diff. peak and hole	0.331 and -0.220 e.Å^{-3}	

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for nilwl04. U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U_{eq}
F1	5296(1)	2970(1)	4305(1)	37(1)
F2	5727(1)	1244(1)	3542(1)	41(1)
F3	6726(1)	-868(1)	4022(1)	39(1)
F4	7196(1)	-1257(1)	5285(1)	42(1)
F5	6687(1)	449(1)	6054(1)	37(1)
O1	6377(1)	5249(1)	5438(1)	26(1)
O2	9281(2)	2362(1)	6226(1)	35(1)
O3	5452(1)	3843(1)	6758(1)	28(1)
O4	9627(1)	5738(1)	6537(1)	28(1)
O5	11215(1)	6653(1)	7270(1)	30(1)
N1	7785(2)	3748(1)	5787(1)	21(1)
N2	7412(2)	4743(2)	6893(1)	26(1)
N3	9188(2)	7272(2)	7130(1)	29(1)
C1	7414(2)	4795(2)	5442(1)	21(1)
C2	8336(2)	5285(2)	5095(1)	20(1)
C3	9556(2)	4755(2)	5161(1)	20(1)
C4	9929(2)	3749(2)	5548(1)	23(1)
C5	9013(2)	3219(2)	5882(1)	24(1)
C6	7996(2)	6255(2)	4714(1)	26(1)
C7	8865(2)	6735(2)	4388(1)	28(1)
C8	6846(2)	3208(2)	6101(1)	23(1)
C9	5654(2)	2727(2)	5636(1)	25(1)
C10	5987(2)	1782(2)	5210(1)	24(1)
C11	5769(2)	1934(2)	4568(1)	25(1)
C12	5995(2)	1058(2)	4167(1)	28(1)
C13	6491(2)	-9(2)	4408(1)	28(1)
C14	6735(2)	-205(2)	5045(1)	30(1)
C15	6479(2)	683(2)	5433(1)	28(1)
C16	6485(2)	4003(2)	6604(1)	24(1)
C17	7283(2)	5524(2)	7404(1)	28(1)
C18	6909(2)	6789(2)	7183(1)	30(1)

C19	7820(2)	7348(2)	6818(1)	30(1)
C20	9986(2)	6491(2)	6946(1)	26(1)
C21	12268(2)	5891(2)	7148(1)	28(1)
C22	12027(2)	4599(2)	7281(1)	34(1)
C23	12417(2)	6086(2)	6483(1)	35(1)
C24	13450(2)	6355(2)	7624(1)	41(1)
O6	9033(3)	1600(3)	4765(2)	39(1)
O7	10124(14)	-61(13)	4925(5)	36(2)
C25	9774(6)	705(6)	3923(3)	45(1)
C26	9590(5)	805(4)	4580(2)	31(1)
C27	10095(5)	-49(5)	5599(2)	34(1)
C28	10464(6)	-1252(5)	5881(3)	42(1)

Table 3. Bond lengths [Å] and angles [°] for nilwl04.

F(1)-C(11)	1.346(2)	C(9)-C(10)	1.510(3)
F(2)-C(12)	1.346(2)	C(9)-H(9A)	0.9900
F(3)-C(13)	1.347(2)	C(9)-H(9B)	0.9900
F(4)-C(14)	1.341(2)	C(10)-C(11)	1.380(3)
F(5)-C(15)	1.352(2)	C(10)-C(15)	1.387(3)
O(1)-C(1)	1.214(2)	C(11)-C(12)	1.379(3)
O(2)-C(5)	1.215(2)	C(12)-C(13)	1.368(3)
O(3)-C(16)	1.235(2)	C(13)-C(14)	1.373(3)
O(4)-C(20)	1.227(2)	C(14)-C(15)	1.381(3)
O(5)-C(20)	1.344(3)	C(17)-C(18)	1.526(3)
O(5)-C(21)	1.484(3)	C(17)-H(17A)	0.9900
N(1)-C(1)	1.405(2)	C(17)-H(17B)	0.9900
N(1)-C(5)	1.406(3)	C(18)-C(19)	1.530(3)
N(1)-C(8)	1.471(2)	C(18)-H(18A)	0.9900
N(2)-C(16)	1.332(3)	C(18)-H(18B)	0.9900
N(2)-C(17)	1.454(3)	C(19)-H(19A)	0.9900
N(2)-H(2)	0.85(2)	C(19)-H(19B)	0.9900
N(3)-C(20)	1.349(3)	C(21)-C(23)	1.516(3)
N(3)-C(19)	1.456(3)	C(21)-C(22)	1.518(3)
N(3)-H(3)	0.86(3)	C(21)-C(24)	1.523(3)
C(1)-C(2)	1.481(3)	C(22)-H(22A)	0.9800
C(2)-C(6)	1.372(3)	C(22)-H(22B)	0.9800
C(2)-C(3)	1.405(3)	C(22)-H(22C)	0.9800
C(3)-C(4)	1.414(3)	C(23)-H(23A)	0.9800
C(3)-C(3)#1	1.417(4)	C(23)-H(23B)	0.9800
C(4)-C(7)#1	1.370(3)	C(23)-H(23C)	0.9800
C(4)-C(5)	1.477(3)	C(24)-H(24A)	0.9800
C(6)-C(7)	1.402(3)	C(24)-H(24B)	0.9800
C(6)-H(6A)	0.9500	C(24)-H(24C)	0.9800
C(7)-C(4)#1	1.370(3)	O(6)-C(26)	1.195(6)
C(7)-H(7A)	0.9500	O(7)-C(26)	1.282(16)
C(8)-C(9)	1.526(3)	O(7)-C(27)	1.483(8)
C(8)-C(16)	1.538(3)	C(25)-C(26)	1.502(7)
C(8)-H(8A)	1.0000	C(25)-H(25A)	0.9800

C(25)-H(25B)	0.9800	C(4)#1-C(7)-C(6)	120.47(19)
C(25)-H(25C)	0.9800	C(4)#1-C(7)-H(7A)	119.8
C(27)-C(28)	1.502(8)	C(6)-C(7)-H(7A)	119.8
C(27)-H(27A)	0.9900	N(1)-C(8)-C(9)	112.57(16)
C(27)-H(27B)	0.9900	N(1)-C(8)-C(16)	113.93(16)
C(28)-H(28A)	0.9800	C(9)-C(8)-C(16)	112.14(17)
C(28)-H(28B)	0.9800	N(1)-C(8)-H(8A)	105.8
C(28)-H(28C)	0.9800	C(9)-C(8)-H(8A)	105.8
C(20)-O(5)-C(21)	120.53(16)	C(16)-C(8)-H(8A)	105.8
C(1)-N(1)-C(5)	124.71(16)	C(10)-C(9)-C(8)	112.54(17)
C(1)-N(1)-C(8)	117.56(16)	C(10)-C(9)-H(9A)	109.1
C(5)-N(1)-C(8)	117.63(16)	C(8)-C(9)-H(9A)	109.1
C(16)-N(2)-C(17)	123.36(19)	C(10)-C(9)-H(9B)	109.1
C(16)-N(2)-H(2)	121.7(15)	C(8)-C(9)-H(9B)	109.1
C(17)-N(2)-H(2)	114.6(15)	H(9A)-C(9)-H(9B)	107.8
C(20)-N(3)-C(19)	121.87(18)	C(11)-C(10)-C(15)	115.34(18)
C(20)-N(3)-H(3)	117.8(17)	C(11)-C(10)-C(9)	122.19(18)
C(19)-N(3)-H(3)	120.4(17)	C(15)-C(10)-C(9)	122.41(18)
O(1)-C(1)-N(1)	119.80(18)	F(1)-C(11)-C(12)	116.91(18)
O(1)-C(1)-C(2)	123.33(18)	F(1)-C(11)-C(10)	119.94(18)
N(1)-C(1)-C(2)	116.88(17)	C(12)-C(11)-C(10)	123.14(19)
C(6)-C(2)-C(3)	120.40(18)	F(2)-C(12)-C(13)	119.98(19)
C(6)-C(2)-C(1)	119.86(18)	F(2)-C(12)-C(11)	120.55(19)
C(3)-C(2)-C(1)	119.75(17)	C(13)-C(12)-C(11)	119.46(19)
C(2)-C(3)-C(4)	121.66(17)	F(3)-C(13)-C(12)	120.03(19)
C(2)-C(3)-C(3)#1	119.4(2)	F(3)-C(13)-C(14)	120.16(19)
C(4)-C(3)-C(3)#1	118.9(2)	C(12)-C(13)-C(14)	119.80(19)
C(7)#1-C(4)-C(3)	120.36(18)	F(4)-C(14)-C(13)	120.24(19)
C(7)#1-C(4)-C(5)	119.93(18)	F(4)-C(14)-C(15)	120.4(2)
C(3)-C(4)-C(5)	119.71(18)	C(13)-C(14)-C(15)	119.30(19)
O(2)-C(5)-N(1)	120.26(18)	F(5)-C(15)-C(14)	117.91(19)
O(2)-C(5)-C(4)	122.80(19)	F(5)-C(15)-C(10)	119.13(19)
N(1)-C(5)-C(4)	116.94(17)	C(14)-C(15)-C(10)	122.93(19)
C(2)-C(6)-C(7)	120.42(19)	O(3)-C(16)-N(2)	124.69(19)
C(2)-C(6)-H(6A)	119.8	O(3)-C(16)-C(8)	119.89(18)
C(7)-C(6)-H(6A)	119.8	N(2)-C(16)-C(8)	115.00(18)

N(2)-C(17)-C(18)	112.78(16)	C(21)-C(22)-H(22B)	109.5
N(2)-C(17)-H(17A)	109.0	H(22A)-C(22)-H(22B)	109.5
C(18)-C(17)-H(17A)	109.0	C(21)-C(22)-H(22C)	109.5
N(2)-C(17)-H(17B)	109.0	H(22A)-C(22)-H(22C)	109.5
C(18)-C(17)-H(17B)	109.0	H(22B)-C(22)-H(22C)	109.5
H(17A)-C(17)-H(17B)	107.8	C(21)-C(23)-H(23A)	109.5
C(17)-C(18)-C(19)	113.52(18)	C(21)-C(23)-H(23B)	109.5
C(17)-C(18)-H(18A)	108.9	H(23A)-C(23)-H(23B)	109.5
C(19)-C(18)-H(18A)	108.9	C(21)-C(23)-H(23C)	109.5
C(17)-C(18)-H(18B)	108.9	H(23A)-C(23)-H(23C)	109.5
C(19)-C(18)-H(18B)	108.9	H(23B)-C(23)-H(23C)	109.5
H(18A)-C(18)-H(18B)	107.7	C(21)-C(24)-H(24A)	109.5
N(3)-C(19)-C(18)	114.65(18)	C(21)-C(24)-H(24B)	109.5
N(3)-C(19)-H(19A)	108.6	H(24A)-C(24)-H(24B)	109.5
C(18)-C(19)-H(19A)	108.6	C(21)-C(24)-H(24C)	109.5
N(3)-C(19)-H(19B)	108.6	H(24A)-C(24)-H(24C)	109.5
C(18)-C(19)-H(19B)	108.6	H(24B)-C(24)-H(24C)	109.5
H(19A)-C(19)-H(19B)	107.6	C(26)-O(7)-C(27)	117.9(8)
O(4)-C(20)-O(5)	125.12(19)	O(6)-C(26)-O(7)	124.0(5)
O(4)-C(20)-N(3)	124.0(2)	O(6)-C(26)-C(25)	124.5(5)
O(5)-C(20)-N(3)	110.88(18)	O(7)-C(26)-C(25)	111.5(5)
O(5)-C(21)-C(23)	110.04(18)	O(7)-C(27)-C(28)	109.6(7)
O(5)-C(21)-C(22)	110.55(17)	O(7)-C(27)-H(27A)	109.8
C(23)-C(21)-C(22)	112.57(17)	C(28)-C(27)-H(27A)	109.8
O(5)-C(21)-C(24)	102.44(16)	O(7)-C(27)-H(27B)	109.8
C(23)-C(21)-C(24)	110.50(19)	C(28)-C(27)-H(27B)	109.8
C(22)-C(21)-C(24)	110.29(19)	H(27A)-C(27)-H(27B)	108.2
C(21)-C(22)-H(22A)	109.5		

Symmetry transformations used to generate equivalent atoms:

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

Table 4. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for nilwl04. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U_{11} + ... + 2\ h\ k\ a^*\ b^*\ U_{12}\ ]$

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
F1	51(1)	30(1)	30(1)	5(1)	13(1)	10(1)
F2	61(1)	41(1)	24(1)	-2(1)	18(1)	-3(1)
F3	43(1)	31(1)	48(1)	-14(1)	21(1)	-2(1)
F4	46(1)	23(1)	52(1)	3(1)	3(1)	4(1)
F5	51(1)	32(1)	25(1)	5(1)	3(1)	-6(1)
O1	25(1)	28(1)	28(1)	-1(1)	11(1)	1(1)
O2	34(1)	40(1)	34(1)	18(1)	13(1)	5(1)
O3	29(1)	34(1)	24(1)	1(1)	14(1)	-1(1)
O4	31(1)	31(1)	22(1)	-8(1)	9(1)	-5(1)
O5	28(1)	34(1)	31(1)	-11(1)	10(1)	-5(1)
N1	23(1)	23(1)	18(1)	-1(1)	8(1)	-3(1)
N2	29(1)	30(1)	20(1)	-4(1)	11(1)	-4(1)
N3	34(1)	28(1)	26(1)	-8(1)	10(1)	-4(1)
C1	24(1)	24(1)	16(1)	-5(1)	6(1)	0(1)
C2	24(1)	23(1)	15(1)	-3(1)	6(1)	-1(1)
C3	24(1)	21(1)	14(1)	-3(1)	6(1)	-1(1)
C4	25(1)	27(1)	19(1)	1(1)	8(1)	-1(1)
C5	24(1)	27(1)	20(1)	1(1)	7(1)	1(1)
C6	24(1)	28(1)	29(1)	2(1)	11(1)	5(1)
C7	30(1)	28(1)	27(1)	7(1)	9(1)	4(1)
C8	27(1)	24(1)	21(1)	0(1)	11(1)	-3(1)
C9	26(1)	29(1)	24(1)	-1(1)	11(1)	-3(1)
C10	22(1)	24(1)	26(1)	-3(1)	9(1)	-5(1)
C11	27(1)	23(1)	27(1)	1(1)	9(1)	0(1)
C12	31(1)	33(1)	23(1)	-2(1)	12(1)	-6(1)
C13	27(1)	25(1)	36(1)	-10(1)	14(1)	-3(1)
C14	29(1)	20(1)	40(1)	2(1)	6(1)	0(1)
C15	29(1)	31(1)	23(1)	0(1)	4(1)	-8(1)
C16	32(1)	25(1)	16(1)	4(1)	8(1)	3(1)
C17	34(1)	33(1)	17(1)	-4(1)	10(1)	-1(1)
C18	33(1)	33(1)	24(1)	-6(1)	9(1)	3(1)

C19	36(1)	27(1)	27(1)	0(1)	9(1)	2(1)
C20	31(1)	27(1)	23(1)	-1(1)	11(1)	-3(1)
C21	28(1)	31(1)	26(1)	-7(1)	10(1)	-1(1)
C22	38(1)	34(1)	29(1)	3(1)	8(1)	-2(1)
C23	39(1)	34(1)	36(1)	-3(1)	18(1)	-6(1)
C24	33(1)	46(1)	43(1)	-15(1)	8(1)	-5(1)
O6	42(2)	34(2)	41(2)	4(2)	7(2)	4(2)
O7	52(5)	47(3)	12(5)	10(3)	13(2)	-4(3)
C25	56(4)	50(4)	29(3)	11(3)	7(3)	2(3)
C26	30(3)	27(2)	32(3)	6(2)	2(2)	-6(2)
C27	32(3)	38(3)	33(3)	-2(2)	7(2)	-6(2)
C28	41(3)	46(4)	39(4)	5(3)	8(3)	-5(3)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$ x 10^3) for nilwl04.

	x	y	z	U(eq)
H2	8100(20)	4846(19)	6763(10)	28(6)
H3	9510(20)	7730(20)	7439(12)	42(7)
H6A	7167	6605	4670	31
H7A	8615	7400	4120	33
H8A	7290	2500	6330	28
H9A	5050	2390	5872	30
H9B	5207	3389	5375	30
H17A	8113	5543	7723	33
H17B	6616	5199	7606	33
H18A	6901	7288	7555	35
H18B	6021	6782	6913	35
H19A	7683	6954	6404	36
H19B	7586	8195	6743	36
H22A	11269	4311	6971	50
H22B	11871	4528	7704	50
H22C	12785	4125	7256	50
H23A	11638	5808	6183	52
H23B	13170	5643	6421	52
H23C	12540	6934	6416	52
H24A	13305	6288	8048	61
H24B	13595	7189	7533	61
H24C	14210	5885	7596	61
H25A	8970	928	3622	68
H25B	9999	-114	3843	68
H25C	10472	1237	3873	68
H27A	9216	161	5642	41
H27B	10707	556	5825	41
H28A	10515	-1225	6333	63
H28B	11308	-1481	5810	63
H28C	9811	-1835	5682	63

Table 6. Torsion angles [°] for nilwl04.

C5-N1-C1-O1	-172.53(17)	C8-C9-C10-C15	66.7(3)
C8-N1-C1-O1	3.7(3)	C15-C10-C11-F1	-179.78(18)
C5-N1-C1-C2	7.6(3)	C9-C10-C11-F1	2.9(3)
C8-N1-C1-C2	-176.22(16)	C15-C10-C11-C12	1.2(3)
O1-C1-C2-C6	-4.6(3)	C9-C10-C11-C12	-176.1(2)
N1-C1-C2-C6	175.32(17)	F1-C11-C12-F2	-1.2(3)
O1-C1-C2-C3	175.30(18)	C10-C11-C12-F2	177.93(19)
N1-C1-C2-C3	-4.8(3)	F1-C11-C12-C13	179.19(19)
C6-C2-C3-C4	-179.50(19)	C10-C11-C12-C13	-1.7(3)
C1-C2-C3-C4	0.6(3)	F2-C12-C13-F3	0.9(3)
C6-C2-C3-C3#1	1.2(3)	C11-C12-C13-F3	-179.48(19)
C1-C2-C3-C3#1	-178.6(2)	F2-C12-C13-C14	-178.49(19)
C2-C3-C4-C7#1	-178.68(19)	C11-C12-C13-C14	1.2(3)
C3#1-C3-C4-C7#1	0.6(3)	F3-C13-C14-F4	-0.7(3)
C2-C3-C4-C5	1.3(3)	C12-C13-C14-F4	178.61(19)
C3#1-C3-C4-C5	-179.4(2)	F3-C13-C14-C15	-179.50(19)
C1-N1-C5-O2	174.55(18)	C12-C13-C14-C15	-0.1(3)
C8-N1-C5-O2	-1.6(3)	F4-C14-C15-F5	-1.0(3)
C1-N1-C5-C4	-5.7(3)	C13-C14-C15-F5	177.73(19)
C8-N1-C5-C4	178.08(16)	F4-C14-C15-C10	-179.15(19)
C7#1-C4-C5-O2	0.7(3)	C13-C14-C15-C10	-0.4(3)
C3-C4-C5-O2	-179.24(19)	C11-C10-C15-F5	-178.20(18)
C7#1-C4-C5-N1	-179.00(18)	C9-C10-C15-F5	-0.9(3)
C3-C4-C5-N1	1.0(3)	C11-C10-C15-C14	-0.1(3)
C3-C2-C6-C7	-0.4(3)	C9-C10-C15-C14	177.2(2)
C1-C2-C6-C7	179.42(18)	C17-N2-C16-O3	-4.4(3)
C2-C6-C7-C4#1	-0.9(3)	C17-N2-C16-C8	-176.90(17)
C1-N1-C8-C9	66.8(2)	N1-C8-C16-O3	157.14(17)
C5-N1-C8-C9	-116.68(19)	C9-C8-C16-O3	27.8(3)
C1-N1-C8-C16	-62.3(2)	N1-C8-C16-N2	-30.0(2)
C5-N1-C8-C16	114.20(19)	C9-C8-C16-N2	-159.32(17)
N1-C8-C9-C10	60.0(2)	C16-N2-C17-C18	-98.4(2)
C16-C8-C9-C10	-170.01(16)	N2-C17-C18-C19	-54.4(2)
C8-C9-C10-C11	-116.2(2)	C20-N3-C19-C18	104.1(2)

C17-C18-C19-N3	-50.8(2)
C21-O5-C20-O4	-0.1(3)
C21-O5-C20-N3	179.91(17)
C19-N3-C20-O4	-5.0(3)
C19-N3-C20-O5	175.02(17)
C20-O5-C21-C23	64.2(2)
C20-O5-C21-C22	-60.7(2)
C20-O5-C21-C24	-178.25(18)
C27-O7-C26-O6	-2.6(16)
C27-O7-C26-C25	176.3(8)
C26-O7-C27-C28	166.2(9)

Symmetry transformations used to generate equivalent atoms:

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

Table 7. Hydrogen bonds and close contacts for nilwl04 [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
N2-H2...O4	0.85(2)	2.07(2)	2.877(2)	158(2)
N3-H3...O3#2	0.86(3)	2.15(3)	2.960(2)	157(2)

Symmetry transformations used to generate equivalent atoms:

#1 -x+2,-y+1,-z+1 #2 -x+3/2,y+1/2,-z+3/2