Electronic Supplementary Material (ESI) for ChemComm.

Electronic Supplementary Information

Conformationally switchable non-cyclic tetrapyrrole receptors: Synthesis of tetrakis(1*H*-pyrrole-2-carbaldehyde) derivatives and their anion binding properties

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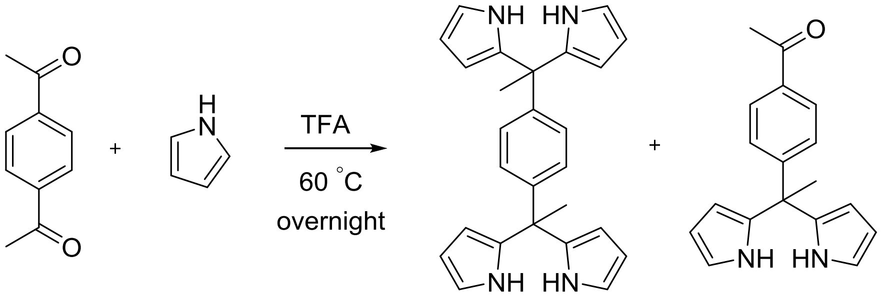


1
70%

1'
4%

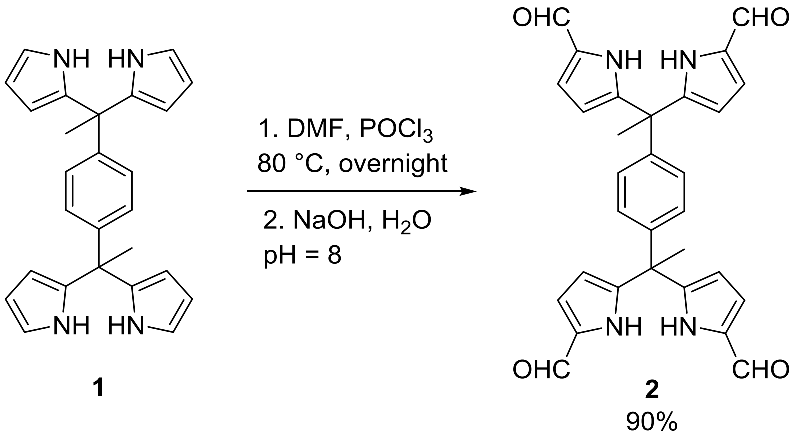
1,4-bis(1,1-di(1H-pyrrol-2-yl)ethyl)benzene (1):

Pyrrole was freshly distilled at 72 °C and 92 mbar. 1,4-Diacetylbenzene (1.45 g, 9 mmol) was dissolved in pyrrole (5 g, 75 mmol). Then, a catalytic amount of trifluoroacetic acid (TFA) (5 drops) was added. The mixture was stirred at 60 °C overnight. To the resulting mixture approximately 10 ml of methanol was added and the resulting pale green solution was filtered. The solid obtained in this way was collected and washed/refiltered from approximately 10 ml of methanol to give **1** as a white solid (2.45 g) in 70% yield. Based on an ^{1}H NMR spectral analysis, the monoDPM (**1'**) was present as a 6% impurity.

^{1}H NMR (400 MHz, DMSO-d_6 residual solvent peak set to 2.49 ppm) δ 10.28 (bs, 4H), 6.83 (s, 4H), 6.61 (m, 4H), 5.86 (m, 4H), 5.52 (m, 4H), 1.91 (s, 6H) ppm.

^{13}C NMR (100 MHz, DMSO-d_6 solvent peak set to 39.5 ppm) δ 146.3, 137.7, 126.4, 117.1, 106.2, 105.9, 43.9, 27.9 ppm.

HRMS (ESI) calcd for $C_{26}H_{26}N_4$ $(M+H)^+$ 395.22302, found 395.22355.



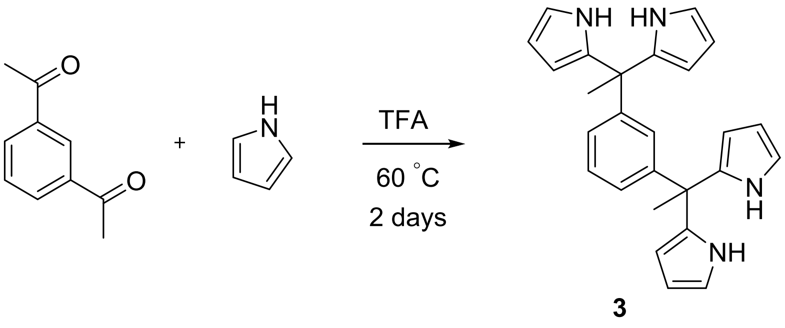
5,5',5'',5'''-(1,4-phenylenebis(ethane-1,1,1-triyl))tetrakis(1H-pyrrole-2-carbaldehyde) (2):

To a solution of **1** (3.8 g, 9.6 mmol) in 25 ml dimethylformamide (DMF), $POCl_3$ (6.5 ml, 69.5 mmol) was added slowly with the vessel held in a water bath. The dark red-colored reaction mixture was allowed to stir for an hour at room temperature and overnight at 80 °C. The mixture then was added to 100 ml water to quench the excess $POCl_3$. Concentrated aqueous NaOH solution (1-2 M) was added to the reaction mixture portion-wise until a pH of 8 was reached. The product precipitated out to give a solid containing an average of 2 DMF molecules per equivalent of **2** (5.58 g, 90% yield), as inferred from an integration of the ^1H NMR spectrum and from single crystal X-ray analysis. The precipitate obtained in this way was dissolved in DMF at 80 °C and allowed to cool. This gave **2**•2DMF for which the solvation was fully defined by *inter alia* a single crystal X-ray diffraction analysis (*vide infra*). The DMF present in this solid material was extracted out by sonicating the crystals in chloroform. The product (**2**) was collected as white powder from the surface of the $CHCl_3$ mixture after centrifugation.

^1H NMR (400 MHz, DMSO-d_6) δ 11.87 (bt, J = 2.2 Hz, 4H), 9.41 (s, 4H), 6.91 (dd, J = 3.8 Hz, J = 2.2 Hz, 4H), 6.90 (s, 4H), 5.89 (dd, J = 3.8 Hz, J = 2.3 Hz, 4H), 2.08 (s, 6H) ppm.

^{13}C NMR (100 MHz, DMSO-d_6) δ 179.5, 146.4, 145.0, 133.7, 127.2, 110.8, 45.43, 27.6 ppm.

HRMS (ESI$^+$) calcd for $C_{30}H_{26}N_4O_4$ $(M+H)^+$ 529.18460, found 529.18300.



3
20%

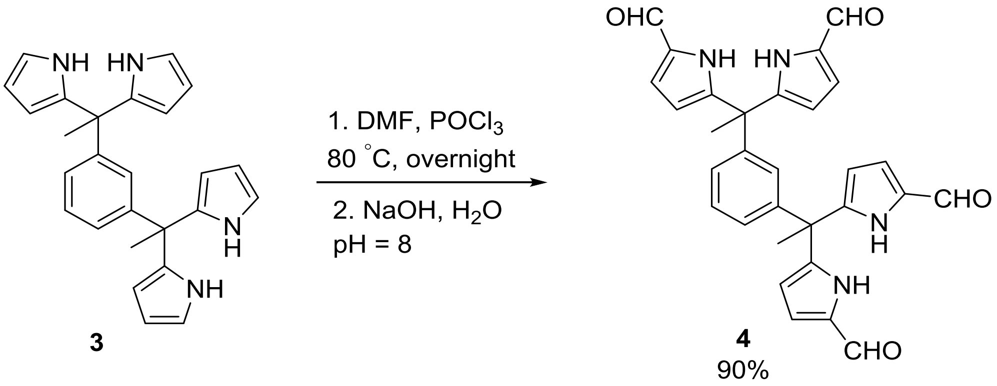
1,3-bis(1,1-di(1H-pyrrol-2-yl)ethyl)benzene (3):

1,3-Diacetylbenzene (650 mg, 4 mmol) was dissolved in freshly distilled pyrrole (1.5 g, 20 mmol). A catalytic amount of trifluoroacetic acid (TFA) (5 drops) was then added. The mixture was stirred at 60 °C for 2 days. To the resulting mixture, 0.2 ml of TEA was added and the resulting dark green solution was heated to distil off non-reacted pyrrole. The oily crude product obtained in this way was purified by column chromatography (silica gel/dichloromethane, $R_f = 0.4$). Product **3** was obtained in 20% yield as colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$ residual solvent peak set to 7.26 ppm) δ 7.75 (bs, 4H), 7.19 (t, *J* = 7.9 Hz, 1H), 7.09 (t, *J* = 7.9 Hz, 1H), 6.96 (dd, *J* = 7.9 Hz, 2H), 6.63 (m, 4H), 6.15 (m, 4H), 5.92 (m, 4H), 2.00 (s, 6H) ppm

^{13}C NMR (100 MHz, $CDCl_3$ solvent peak set to 77.0 ppm) δ 147.0, 137.3, 127.8, 126.8, 125.5, 116.9, 108.1, 106.2, 44.7, 28.6 ppm.

HRMS (ESI) calcd for $C_{26}H_{26}N_4$ $(M+H)^+$ 395.22302, found 395.22355.



3

4
90%

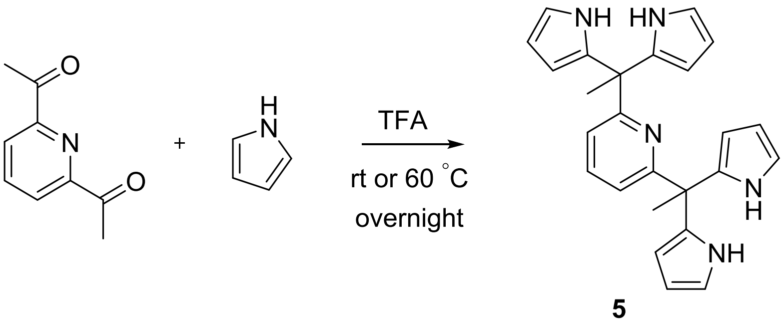
5,5',5'',5'''-(1,3-phenylenebis(ethane-1,1,1-triyl))tetrakis(1H-pyrrole-2-carbaldehyde) (4):

To a solution of **3** (400 mg, 1 mmol) in 5 ml DMF, $POCl_3$ (0.8 ml, 8 mmol) was added slowly with the reaction vessel held in a water bath. The dark red color reaction mixture was allowed to stir for an hour at room temperature and overnight at 80 °C. The mixture then was added to 100 ml water to quench the excess $POCl_3$. An aqueous concentrated NaOH solution (1-2 M) was added to the reaction portion-wise until a pH 8 was obtained. The product precipitated out under these conditions and was found to contain an average of 2 DMF molecules (5.58 g, 89% yield), as inferred from an integration of the ^1H NMR spectrum and from single crystal X-ray analysis. The precipitate was dissolved in DMF at 80 °C and allowed to cool to provide **4**•2DMF as a solid. The DMF was extracted out by sonicating the crystals in diethyl ether. The resulting product was collected in the form of an off-white crystalline solid.

^1H NMR (400 MHz, $CDCl_3$) δ 2.03 (s, 6H), 6.01 (dd, J = 4.0 Hz, J = 2.4 Hz, 4H), 6.77 (dd, J = 4.0 Hz, J = 2.4 Hz, 4H), 6.98 (t, J = 1.9 Hz, 1H), 7.07 (dd, J = 7.8 Hz, J=1.9 Hz, 2H), 7.20 (t, J = 7.8 Hz, 1H), 9.09 (s, 4H), 10.48 (bs, 4H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$) δ 28.0, 45.5, 110.5, 122.0, 125.5, 127.1, 128.6, 132.5, 145.0, 146.0, 179.1 ppm.

HRMS (ESI$^+$) calcd for $C_{30}H_{26}N_4O_4$ $(M+Na)^+$ 529.18460, found 529.18480.



5
65%

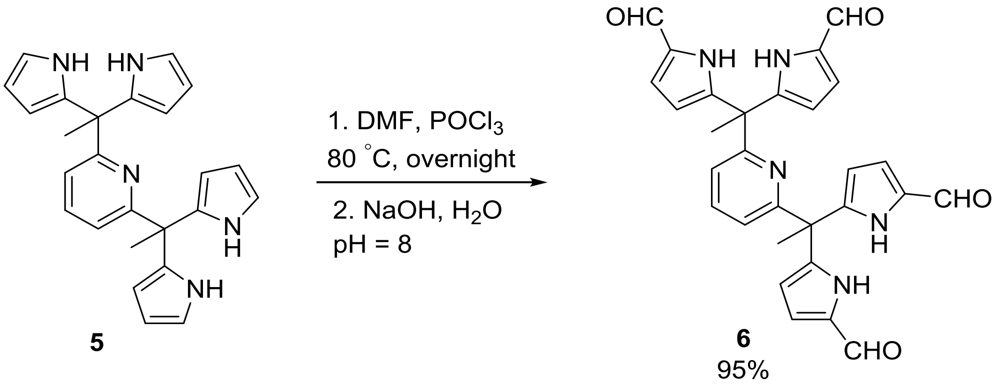
2,6-bis(1,1-di(1H-pyrrol-2-yl)ethyl)pyridine (5):

2,6-Diacetylpyridine (1.0 g, 2.5 mmol) was dissolved in freshly distilled pyrrole (16.7 g, 250 mmol). Then, a catalytic amount of trifluoroacetic acid (TFA) (10 drops) was added. The mixture was stirred at rt for one day. Precipitation occurred. To complete precipitatation about 50 ml of methanol was added to the pale green reaction mixture. The solid obtained in this way was washed with methanol to yield 1.55 g of **5** as a white solid, 65%.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.26 (bs, 4H), 7.70 (t, *J* = 7.9 Hz, 1H), 7.33 (d, *J* = 7.9 Hz, 2H), 6.57 (m, 4H), 6.14 (m, 4H), 5.89 (m, 4H), 2.11 (s, 6H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$) δ 164.4, 138.4, 136.8, 117.2, 117.1, 107.9, 105.0, 45.4, 25.6 ppm.

HRMS (ESI) calcd for $C_{25}H_{25}N_5$ $(M+Na)^+$ 418.20020, found 418.20050.



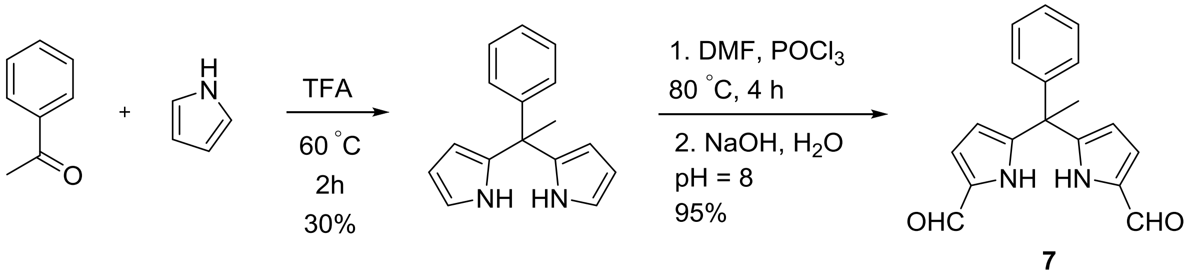
5,5',5'',5'''-(pyridine-2,6-diylbis(ethane-1,1,1-triyl))tetrakis(1H-pyrrole-2-carbaldehyde) (6):

To a solution of **5** (370 mg, 0.94 mmol) in 5 ml DMF, $POCl_3$ (0.5 ml, 5.3 mmol) was added slowly with the vessel held in a water bath. The dark red-colored reaction mixture was allowed to stir for an hour at room temperature and overnight at 80 °C. The mixture then was added to 100 ml water to quench the excess $POCl_3$. Concentrated aqueous NaOH (1-2 M) was added to the reaction portion-wise until a pH 8 was reached. Under these conditions, product **6** precipitates as off white/yellow solid (450 mg, 0.89 mmol). After purification by column chromatography (silica gel/EtOAc), product **6** was obtained as a yellow powder by treating the appropriate fractions with diethyl ether. The yield was 95% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 10.09 (bs, 4H), 9.29 (s, 4H), 7.68 (t, J = 7.9 Hz, 1H), 7.20 (d, J = 7.9 Hz, 2H), 6.85 (dd, J = 3.9 Hz, J = 2.5 Hz, 4H), 6.09 (d, J = 3.9 Hz, J = 2.5 Hz, 4H), 2.16 (s, 6H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$) δ 179.1, 161.9, 144.8, 138.3, 132.6, 121.7, 120.2, 110.2, 47.4, 27.1 ppm.

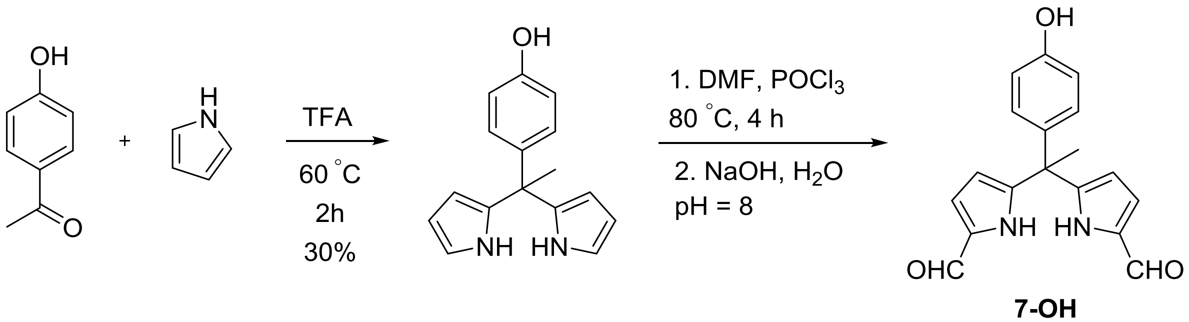
HRMS (ESI) calcd for $C_{29}H_{25}N_5O_4$ $(M+Na)^+$ 530.17990, found 530.18010.



7

5,5'-(1-phenylethane-1,1-diyl)bis(1H-pyrrole-2-carbaldehyde) (7) and

Pyrrole was freshly distilled at 72 °C and 92 mbar. Acetophenone (1.5 g, 12.5 mmol) was dissolved in pyrrole (18 g, 270 mmol). A catalytic amount of trifluoroacetic acid (TFA) (5 drops) was then added.[1] The resulting mixture was stirred at 60 °C for 2h. Excess pyrrole was removed under reduced pressure. The previously dipyrromethane (DPM) product[2] was passed through silica gel using dichloromethane as the eluent. The yellow oil that resulted upon removal of solvent was dissolved in DMF (20 ml). $POCl_3$ (4.5 g) added slowly with the reaction vessel held in a water bath. The dark red-colored reaction mixture was allowed to stir for an hour at room temperature and then 4 hours at 80 °C. The mixture then was added to 100 ml water to quench the excess $POCl_3$. Concentrated aqueous NaOH (1-2 M) was added to the reaction portion-wise until a pH of 8 was reached. This led to precipitation of a solid, which was collected and purified by column chromatography (silica gel/EtOAc). After removal of the volatiles, product **7**[3] was obtained as white solid.



7-OH

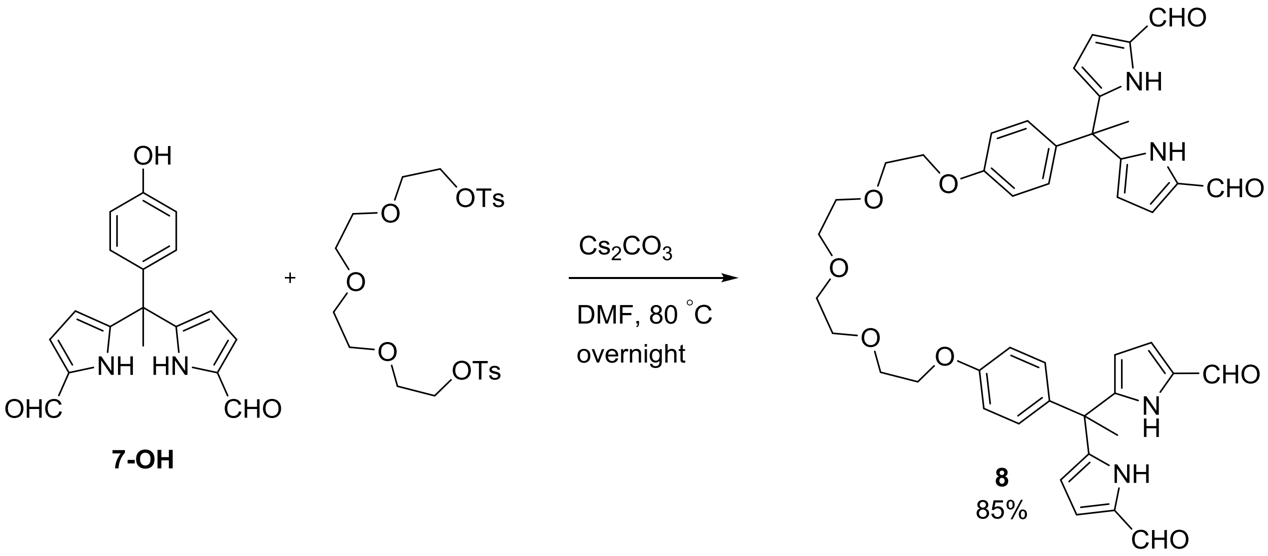
5,5'-(1-(4-hydroxyphenyl)ethane-1,1-diyl)bis(1H-pyrrole-2-carbaldehyde) 7-OH:

7-OH was prepared similarly. The first step is DPM synthesis[4] starting from 4-hydroxyacetophenone. **7-OH** is obtained by formylation of DPM in the second step using a modification of a procedure reported by Love and coworkers.[3]

^{1}H NMR (300 MHz, CD_3OD residual solvent peak set to 3.31 ppm) δ 9.33 (s, 2H), 6.94 (d, *J* = 4.0 Hz, 2H), 6.88 (m, 2H), 6.73 (m, 2H), 6.01 (d, *J* = 4.0 Hz, 2H), 2.09 (s, 3H) ppm.

^{13}C NMR (75 MHz, CD_3OD solvent peak set to 49.0 ppm) δ 180.6, 157.4, 148.4, 137.5, 134.2, 129.4, 116.0, 111.7, 46.2, 28.3,ppm.

HRMS (ESI) calcd for $C_{18}H_{16}N_2O_3$ $(M+H)^+$ 309.12387, found 309.12337.



5,5',5'',5'''-((((((oxybis(ethane-2,1-diyl))bis(oxy))bis(ethane-2,1-diyl))bis(oxy))bis(4,1-phenylene))bis(ethane-1,1,1-triyl))tetrakis(1H-pyrrole-2-carbaldehyde) (8):

Compound **7-OH** (310 mg, 1 mmol) and 1.2 equivalents Cs_2CO_3 (390 mg, 1.2 mmol) were dissolved in DMF (5 ml). The mixture was stirred for an hour. To this solution, one half of a molar equivalent of tetraethyleneglycol ditosylate (250 mg, 0.5 mmol) was added. The resulting mixture was stirred overnight at 80 °C. Then excess DMF was removed under reduced pressure. The resulting oily crude product was purified by column chromatography (silica gel/EOAc, Rf = 0.7) to give a yellow oil. Treatment with diethyl ether then gave **8** as a yellow powde**r** in 85% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 10.07 (bs, 4 H), 9.33 (s, 4 H), 6.92 (d, *J* = 8.9 Hz, 4 H), 6.89 (dd, J = 3.9 Hz, J = 2.4 Hz, 4H), 6.80 (d, J = 8.9 Hz, 4 H), 6.17 (dd, J = 3.9 Hz, J = 2.4 Hz, 4 H), 4.09 (dd, J = 5.2 Hz, J = 4.6 Hz, 4H), 3.87 (dd, J = 5.2 Hz, J = 4.6 Hz, 4 H), 3.68 (m, 8 H), 2.06 (s, 6 H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$) δ 178.9, 157.4, 146.1, 137.0, 132.6, 128.2, 121.2, 114.5, 110.3, 70.8, 70.7, 69.7, 67.4, 44.9, 28.6.

HRMS (ESI$^+$) calcd for $C_{44}H_{46}O_9$ $(M+Na)^+$ 797.31570, found 797.31670.

LC Chromatograms for Receptors 2,4,6,7, and 8

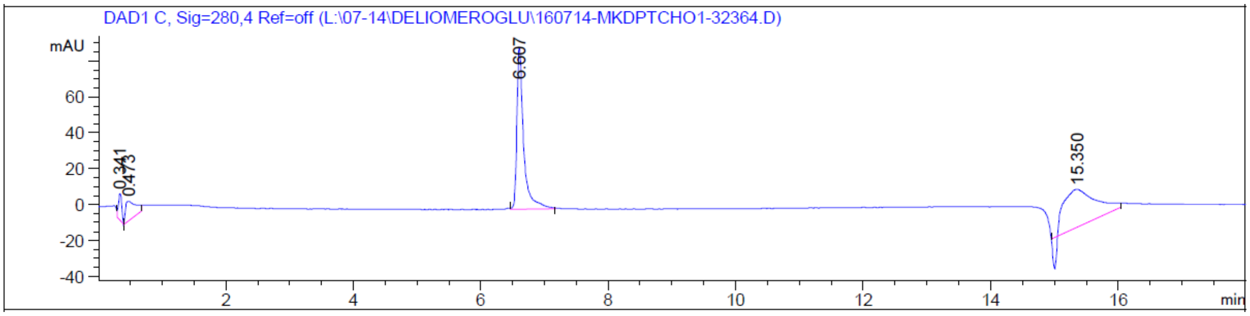


Figure S1 LCMS chromatogram for compound **2**.

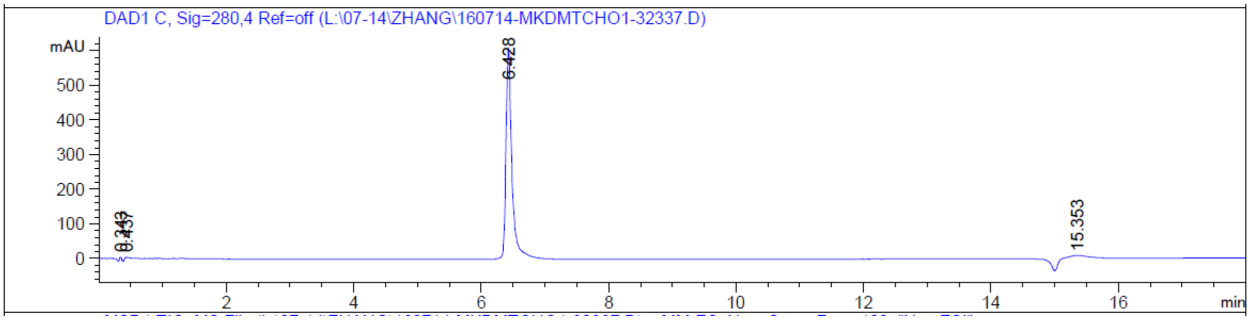


Figure S2 LCMS chromatogram for compound **4**.

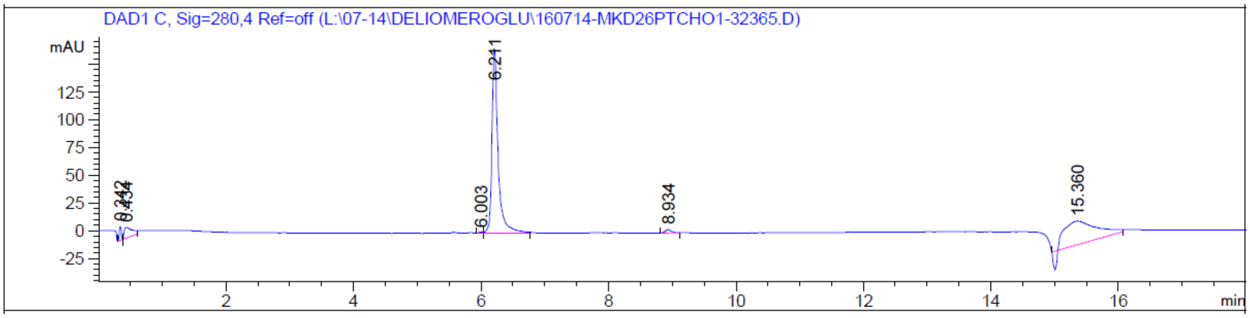


Figure S3 LCMS chromatogram for compound **6**.

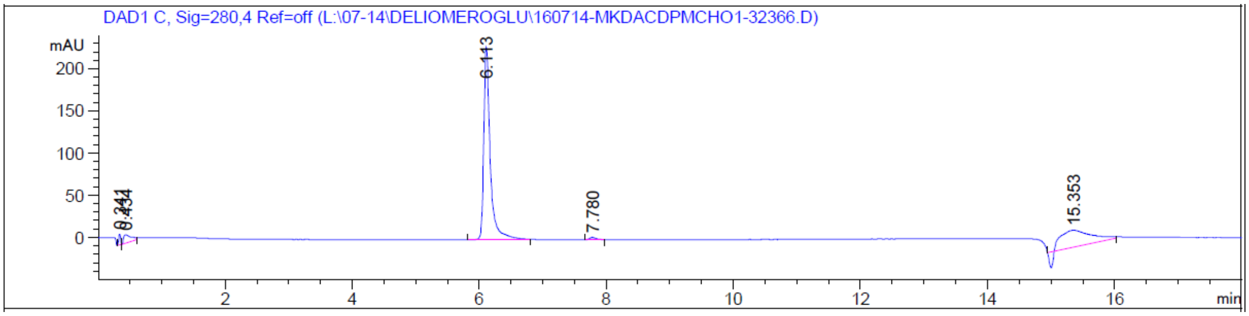


Figure S4 LCMS chromatogram for compound **7**.

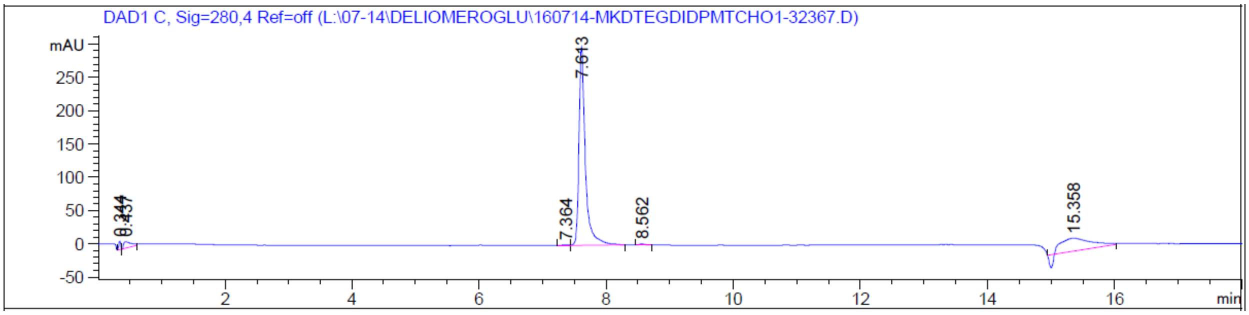


Figure S5 LCMS chromatogram for compound **8**.

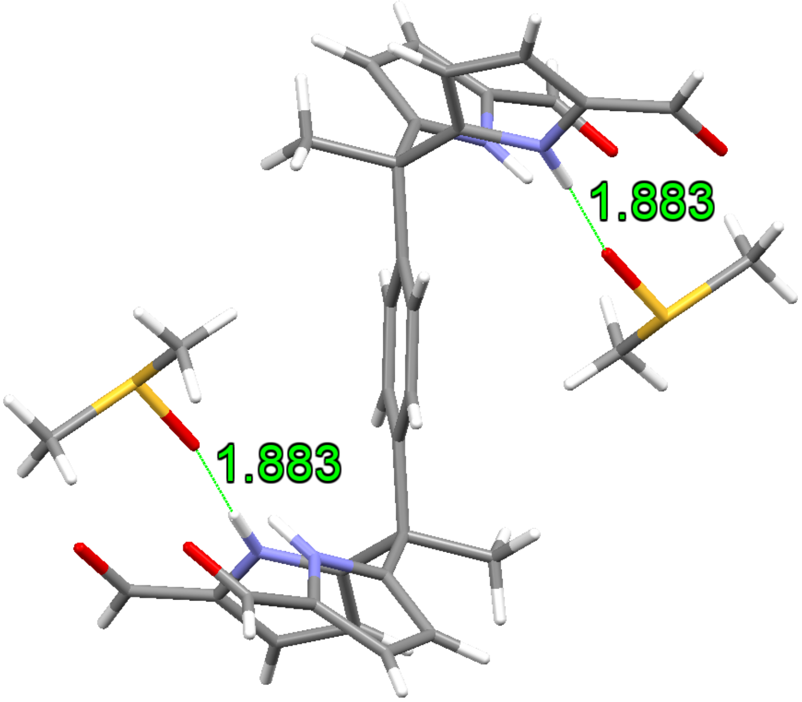


Figure S6 Single crystal X-ray crystallography structure of **2**•2DMSO. Distances were shown in Å.

Anion Binding Studies

UV-Vis Spectroscopy

All binding studies reported in Table 1 were carried out in commercially available Fisher Scientific $CHCl_3$ containing approximately 0.75% ethanol as a preservative. To observe better the absorbance changes, various initial receptor concentrations were chosen to obtain an A_{max} (maximum absorption) for each individual receptor (**2**, **4**, **6**) of 0.9. All anions were studied in the form of their commercially available tetrabutylammonium salts. Binding stoichiometries were determined by the Job plot method. In Job plot experiments, the total concentration of receptor and the salt of interest was kept constant by varying the fraction of receptor from 0 to 1. In the case of titrations carried out with intention of determining binding affinities, the receptor concentration was kept constant (by adding appropriate amounts of the guest salt solutions to the receptor solution). The following equation was used to determine the binding affinities

$$\Delta A = (1 + a*K + x*K - \surd(-4*a*x*K^2 + (-1 - a*K - x*K)^2))*(\Delta E)/(2*K)$$

where ΔA (measured change in absorbance relative to the initial solution) is the y variable; x is concentration of guest (TBA salt) added; a is the initial concentration of receptor (remains constant over the course of titration); ΔE is the extinction coefficient difference between free receptor and receptor-guest complex; K is the binding affinity of receptor for the guest in question.

OriginPro 9.0 was used to fit data in a non-linear fashion in accord with the above equation. Iterations (choosing a fixed a value and changing ΔE and K) were performed until an acceptable level of convergence was reached (chi-square tolerance value, $1x10^{-9}$).

The K values obtained in this way are listed in Table 1. Detailed UV-Vis studies for compound **2** are listed in the following pages (page-S13 to S16). Binding curve fittings for compound **2, 4** and **6** are provided under Table S22 on page S54-56.

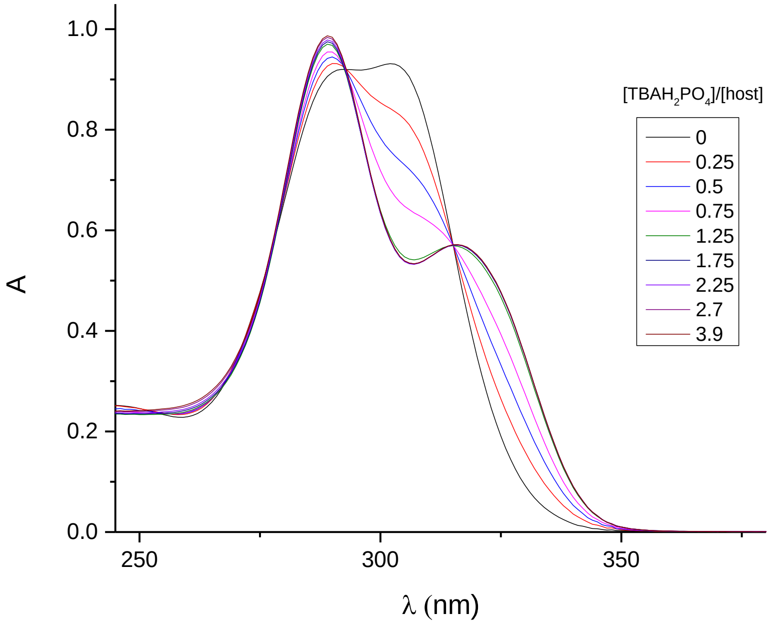


Figure S7 Stacked UV-Vis spectra for **2** recorded upon the addition of increasing quantities of TBAH$_2$PO$_4$ in CHCl$_3$. [**2**] = 1.2 x 10^{-5} M, [TBA H$_2$PO$_4$]$_0$ = 1.0 x 10^{-3} M, in CHCl$_3$.

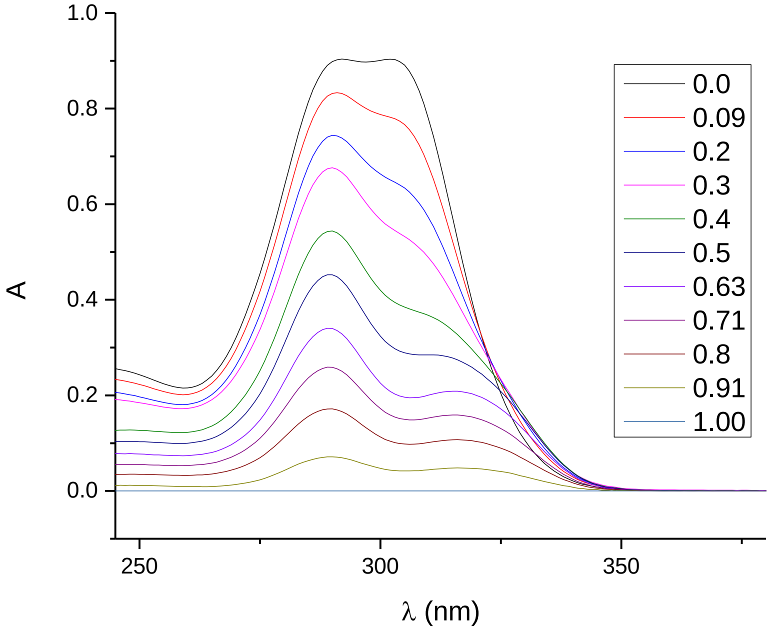
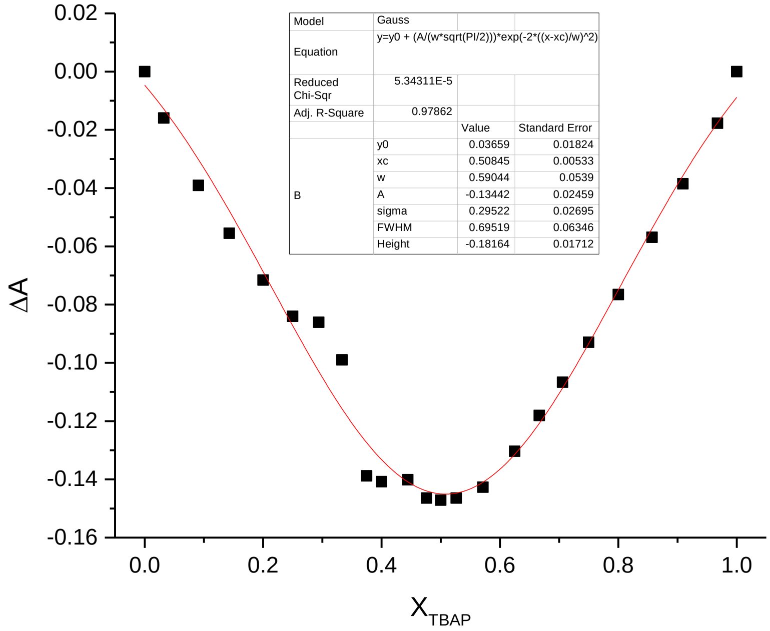
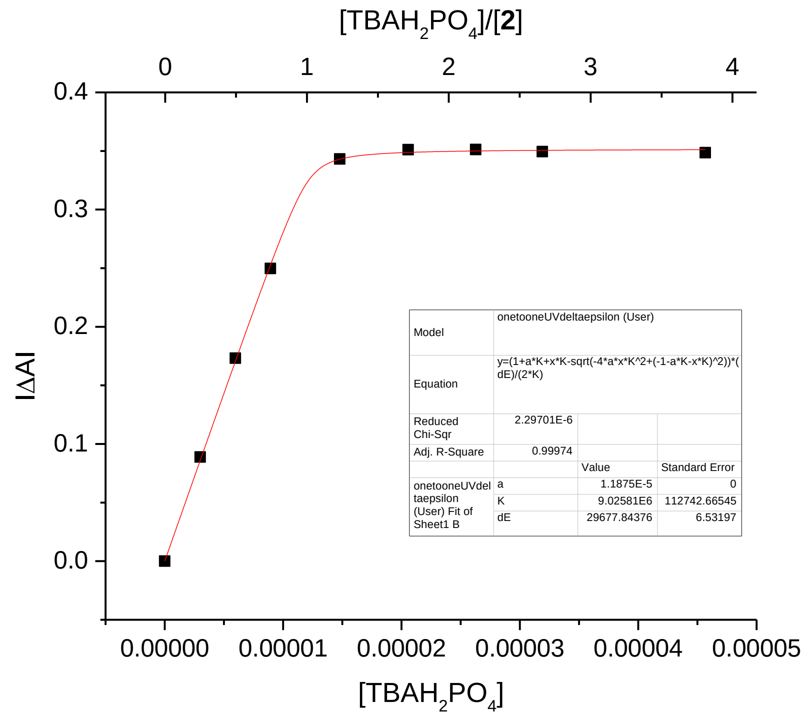


Figure S8 Stacked UV-Vis spectra for Job plot of **2** with TBAH$_2$PO$_4$ in CHCl$_3$. Fraction of TBAH$_2$PO$_4$ is varied from 0 to 1 at [**2**] + [TBAH$_2$PO$_4$] = 1.2 x 10^{-5} M.



Model	Gauss		
Equation	y=y0 + (A/(w*sqrt(PI/2)))*exp(-2*((x-xc)/w)^2)		
Reduced Chi-Sqr	5.34311E-5		
Adj. R-Square	0.97862		
		Value	Standard Error
B	y0	0.03659	0.01824
	xc	0.50845	0.00533
	w	0.59044	0.0539
	A	-0.13442	0.02459
	sigma	0.29522	0.02695
	FWHM	0.69519	0.06346
	Height	-0.18164	0.01712

Figure S9 Job plot for **2** with TBAH$_2$PO$_4$ in CHCl$_3$. [**2**] + [TBAH$_2$PO$_4$] = 1.2 x 10^{-5} M, ΔA at 302 nm.



Model	onetooneUVdeltaepsilon (User)		
Equation	y=(1+a*K+x*K-sqrt(-4*a*x*K^2+(-1-a*K-x*K)^2))*(dE)/(2*K)		
Reduced Chi-Sqr	2.29701E-6		
Adj. R-Square	0.99974		
		Value	Standard Error
onetooneUVdeltaepsilon (User) Fit of Sheet1 B	a	1.1875E-5	0
	K	9.02581E6	112742.66545
	dE	29677.84376	6.53197

Figure S10 Binding curve fitting for compound **2** with TBAH$_2$PO$_4$ in CHCl$_3$. Absorbance change at 302 nm in figure-S7 was plotted against [TBAH$_2$PO$_4$]. K = (8±2) x 10^6 M^{-1}.

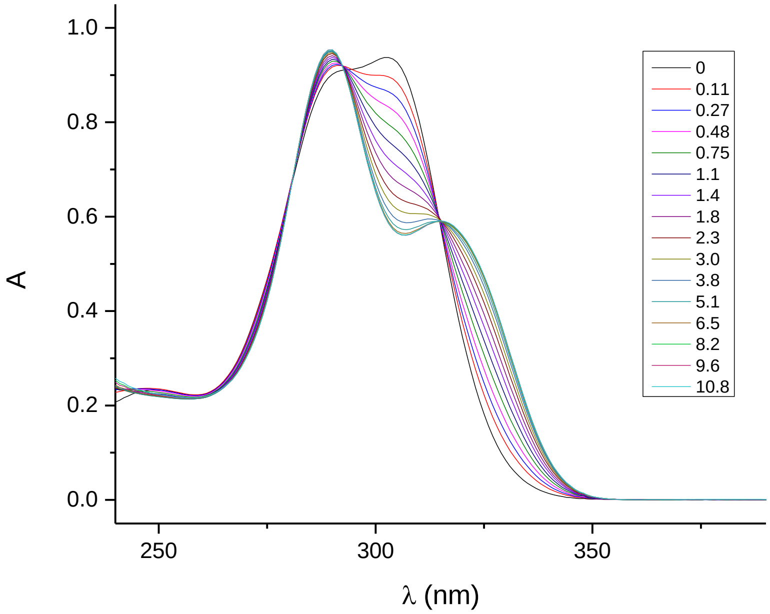


Figure S11 Stacked UV-Vis spectra recorded upon the titration of **2** with increasing quantities of $(TBA)_3HP_2O_7$ in $CHCl_3$. [**2**] = 1.2 x 10^{-5} M, $[(TBA)_3HP_2O_7]_0$ = 3.9 x 10^{-4} M, in $CHCl_3$. Binding curve fitting can be found at page-S52.

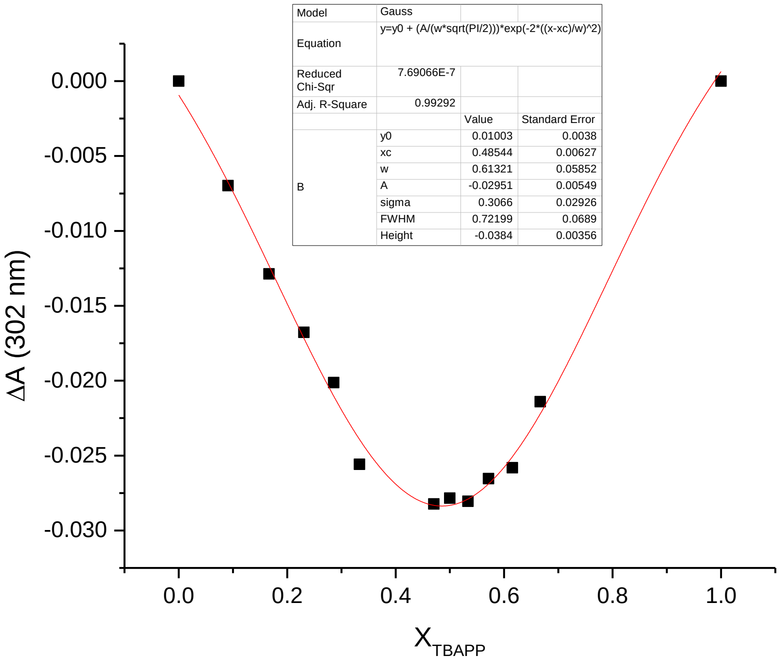


Figure S12 Job plot for **2** with $(TBA)_3HP_2O_7$ in $CHCl_3$. [**2**] + $[(TBA)_3HP_2O_7]$ = 1.2 x 10^{-5} M, ΔA at 302 nm.

^{1}H NMR Spectroscopy

All binding studies reported in Table 2 were carried out in commercially available Cambridge Isotope Laboratories, Inc. $CDCl_3$ (D, 99.8%) and DMSO-*d*$_6$ (D, 99.9%). All spectra were recorded in 400 MHz (Varian or Agilent). Various initial receptor concentrations were chosen based on their solubilities e.g. 1.0 mM in $CDCl_3$, 10 mM in $CDCl_3$/DMSO-*d*$_6$ (8/1) mixture. All anions were studied in the form of their commercially available tetrabutylammonium salts. In the case of titrations carried out with intention of determining binding affinities, the receptor concentration was kept constant (by adding appropriate amounts of the guest salt solutions to the receptor solution). The following equation was used to determine the binding affinities

$$\Delta\delta = (1 + a{*}K + x{*}K - \sqrt{}(-4{*}a{*}x{*}K^{2} + (-1 - a{*}K - x{*}K)^{2}))*(\delta_{complex}-\delta_{host})/(2{*}K)$$

where $\Delta\delta$ (measured change in chemical shift of a hydrogen of interest relative to the chemical shift of the same hydrogen of interest in host) is the y variable; x is concentration of guest (TBA salt) added; a is the initial concentration of receptor (remains constant over the course of titration); $\delta_{complex}$ is the chemical shift of the hydrogen of interest in receptor-guest complex and δ_{host} is the chemical shift of the same hydrogen of interest in receptor; K is the binding affinity of receptor for the guest in question.

OriginPro 9.0 was used to fit data in a non-linear fashion in accord with the above equation. Iterations (choosing a fixed a value and changing $\delta_{complex}$-δ_{host} and K) were performed until an acceptable level of convergence was reached (chi-square tolerance value, $1x10^{-9}$).

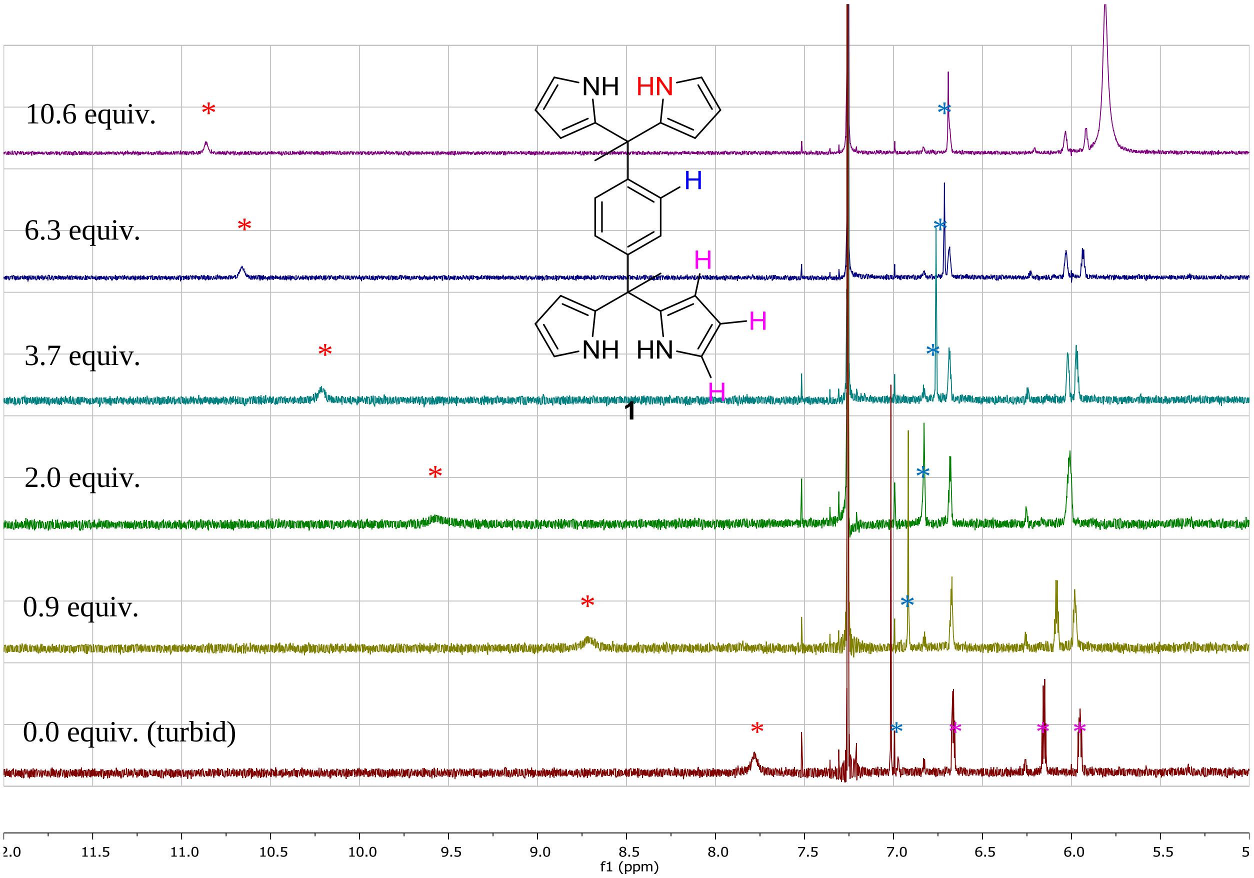


Figure S13 ^{1}H NMR spectrum of a turbid mixture of compound **1** (<0.6 mM) in $CDCl_3$ (bottom) and stacked spectra recorded upon the addition of $TBAH_2PO_4$. Proton signals from **1** shift from 7.8 ppm to 10.9 ppm in the presence of >7 equivalent of $TBAH_2PO_4$.

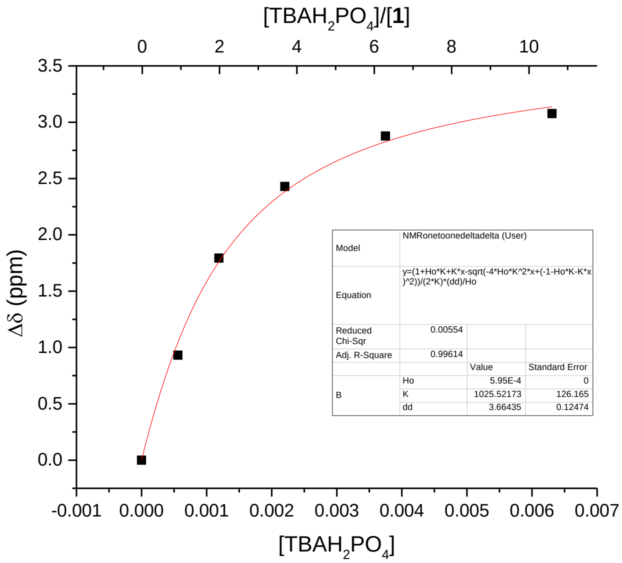


Figure S14 Binding curve fitting corresponding to the titration of compound **1** with $TBAH_2PO_4$ in $CDCl_3$. The chemical shift change of pyrrole NH was plotted against [$TBAH_2PO_4$]. K = 1026 ± 126 M^{-1}.

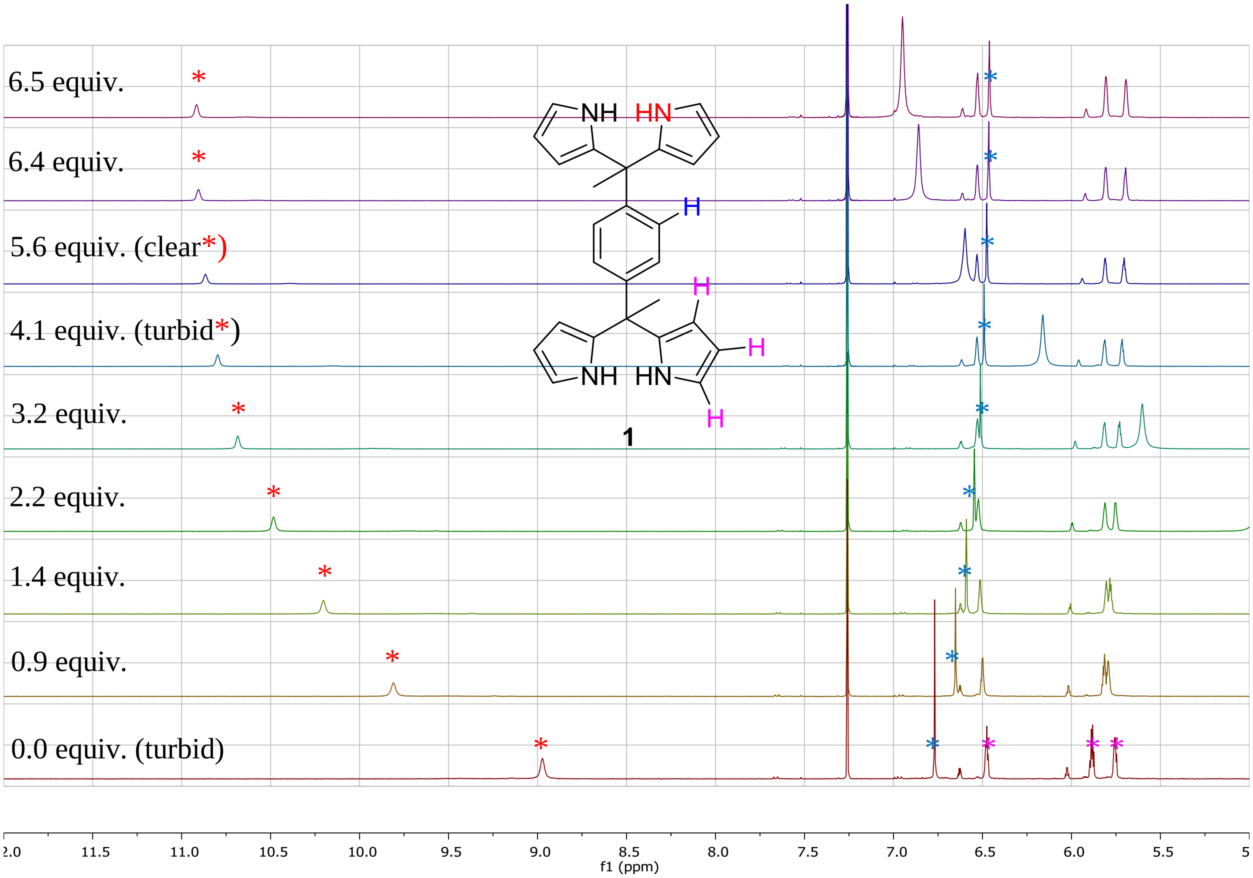
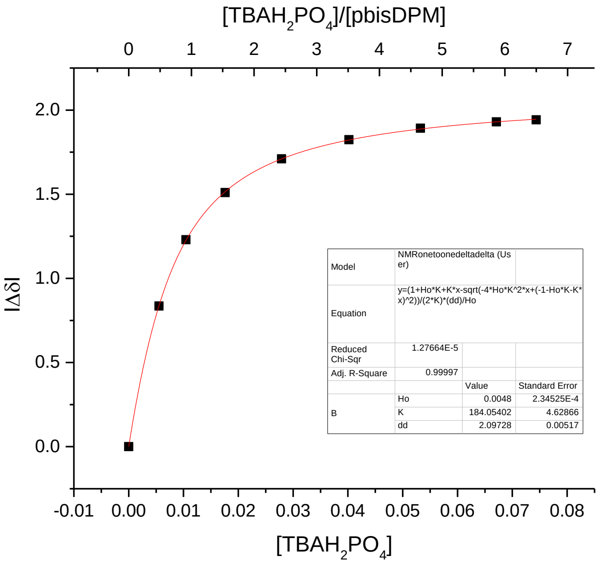


Figure S15 ^{1}H NMR spectrum of a turbid mixture of compound **1** in $CDCl_3$/DMSO-d_6 (8/1) (bottom) and stacked spectra recorded upon the addition of $TBAH_2PO_4$. Proton signals from **1** shift from 9.0 ppm to 10.9 ppm in the presence of ~7 equivalent of $TBAH_2PO_4$. Initial turbid mixture of **1** was prepared to be 11.4 mM were full solubility achieved. Compound **1** became completely soluble after >5 equivalent of $TBAH_2PO_4$ was added. Ratio of compound **1** to $TBAH_2PO_4$ was inferred from an integration of the ^{1}H NMR spectrum.



Model	NMRonetoonedeltadelta (User)		
Equation	y=(1+Ho*K+K*x-sqrt(-4*Ho*K^2*x+(-1-Ho*K-K*x)^2))/(2*K)*(dd)/Ho		
Reduced Chi-Sqr	1.27664E-5		
Adj. R-Square	0.99997		
		Value	Standard Error
B	Ho	0.0048	2.34525E-4
	K	184.05402	4.62866
	dd	2.09728	0.00517

Figure S16 Binding profile and curve fit for the titration of compound **1** with $TBAH_2PO_4$ in $CDCl_3$/DMSO-d_6 (8/1). The chemical shift change of pyrrole NH was plotted against [$TBAH_2PO_4$]. K = 184 ± 5 M^{-1}.

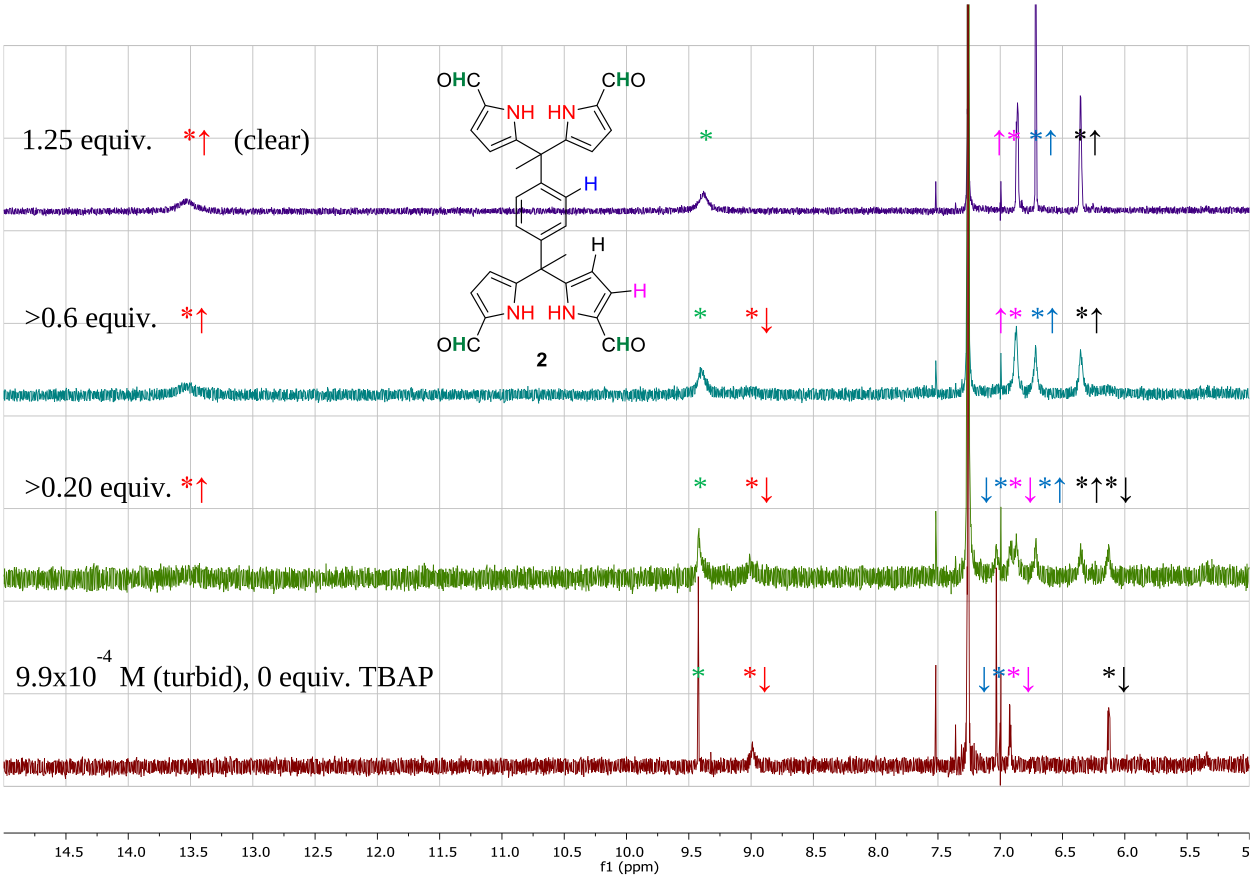


Figure S17 1H NMR Spectrum of a turbid mixture of compound **2** in $CDCl_3$ (bottom) and stacked spectra obtained upon addition of increasing quantities of $TBAH_2PO_4$. The proton signals from **2** become split as $TBAH_2PO_4$ is added up to <1 equivalent. When >1 equivalent of $TBAH_2PO_4$ is added, only a single set of newly emerged signals is observed and the solution becomes clear.

Diffusion Ordered NMR Spectroscopic (DOSY) Analysis

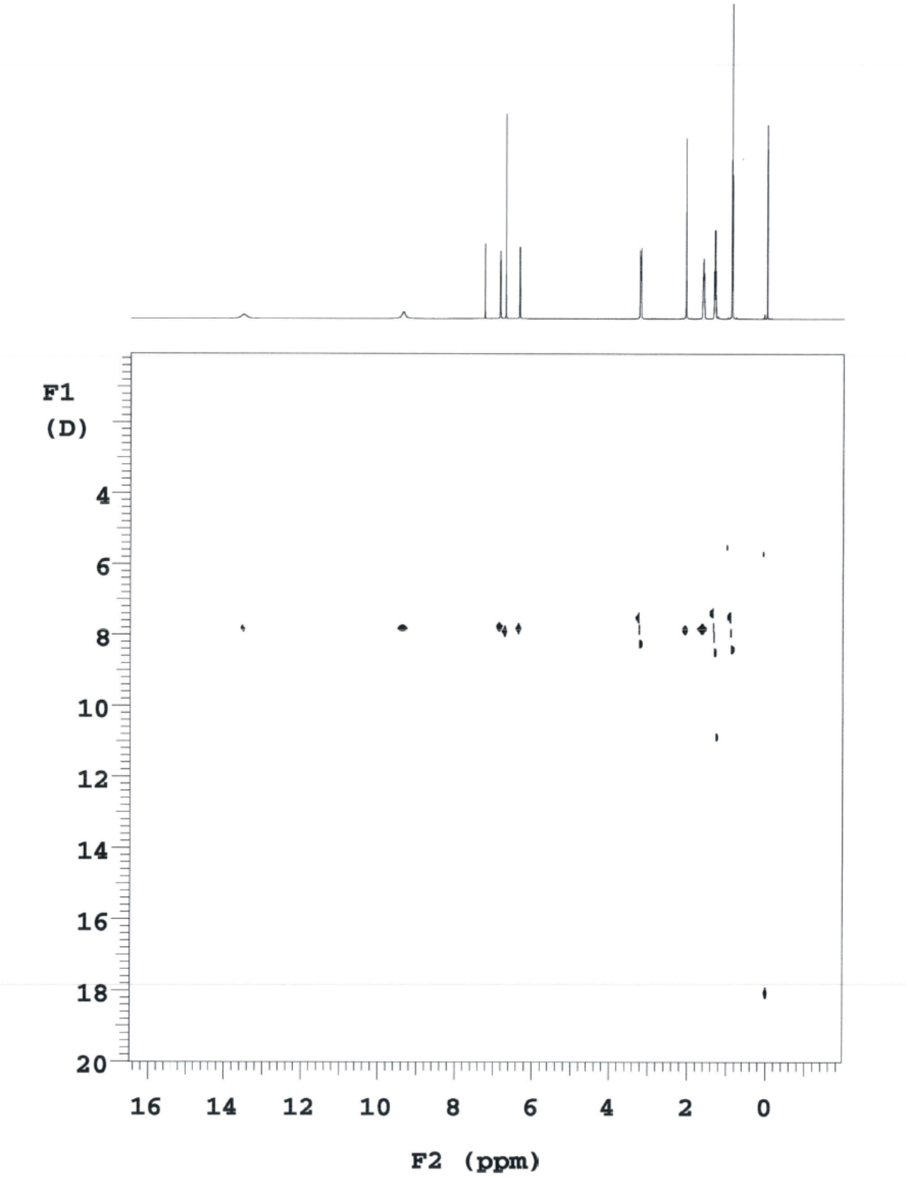


Figure S18 An example DOSY spectrum of **2**•TBAH_2PO_4 recorded at a concentration of 0.025 M in $CDCl_3$.

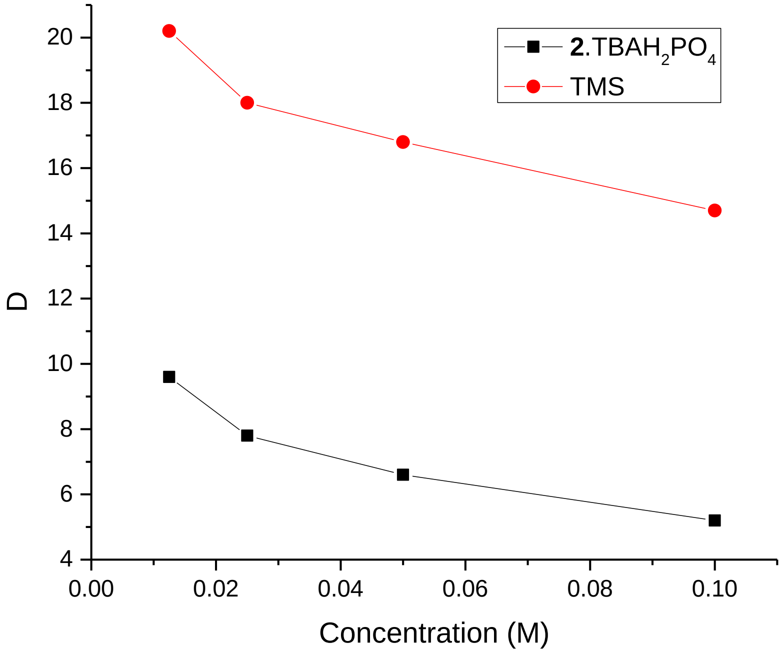


Figure S19 Summary of DOSY spectral results for **2**•TBAH$_2$PO$_4$ recorded at various concentrations (from 0.0125 M to 0.1 M) in CDCl$_3$.

X-ray Experimental for 2•2DMF

Table S1 Crystal data and structure refinement for **2**•2DMF.

Empirical formula	C36 H40 N6 O6	
Formula weight	652.74	
Temperature	153(2) K	
Wavelength	0.71073 Å	
Crystal system	monoclinic	
Space group	P 21/c	
Unit cell dimensions	a = 8.3870(4) Å	α = 90°.
	b = 14.2432(5) Å	β = 104.354(2)°.
	c = 14.6816(7) Å	γ = 90°.
Volume	1699.08(13) Å^3	
Z	2	
Density (calculated)	1.276 Mg/m^3	
Absorption coefficient	0.088 mm^{-1}	
F(000)	692	
Crystal size	0.320 x 0.300 x 0.250 mm	
Theta range for data collection	2.860 to 27.494°.	
Index ranges	-10<=h<=10, -18<=k<=18, -19<=l<=19	
Reflections collected	29051	
Independent reflections	3904 [R(int) = 0.0546]	
Completeness to theta = 25.242°	99.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	1.00 and 0.873	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3904 / 38 / 247	
Goodness-of-fit on F^2	1.027	
Final R indices [I>2sigma(I)]	R1 = 0.0437, wR2 = 0.0989	
R indices (all data)	R1 = 0.0696, wR2 = 0.1163	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.256 and -0.394 e.Å^{-3}	
CCDC Number	1012700	

Table S2 Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^2 x 10^3) for **2**•2DMF. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
C1	3813(2)	8276(1)	3291(1)	27(1)
C2	4270(2)	8884(1)	4040(1)	34(1)
C3	5414(2)	8422(1)	4754(1)	33(1)
C4	5642(2)	7534(1)	4428(1)	23(1)
C5	6801(2)	6754(1)	4894(1)	24(1)
C6	8149(2)	6664(1)	4376(1)	25(1)
C7	9778(2)	6957(1)	4650(1)	36(1)
C8	10475(2)	6802(1)	3897(1)	39(1)
C9	9301(2)	6400(1)	3181(1)	29(1)
C10	2664(2)	8399(1)	2401(1)	39(1)
C11	9478(2)	6075(1)	2295(1)	35(1)
C12	7590(2)	7026(1)	5920(1)	36(1)
C13	5852(2)	5833(1)	4911(1)	22(1)
C14	6534(2)	4962(1)	4809(1)	25(1)
C15	4316(2)	5858(1)	5107(1)	25(1)
N1	4668(2)	7453(1)	3546(1)	24(1)
N2	7882(2)	6324(1)	3489(1)	24(1)
O1	2306(2)	7796(1)	1798(1)	60(1)
O2	8449(2)	5654(1)	1706(1)	43(1)
O3	4668(6)	5787(3)	2457(2)	35(1)
N3	2521(3)	4910(1)	1642(1)	26(1)
C16	2121(3)	5561(2)	852(2)	39(1)
C17	1557(3)	4055(2)	1557(2)	38(1)
C18	3770(2)	5077(1)	2369(2)	30(1)
O3A	4730(30)	5689(17)	2616(11)	32
N3A	2665(13)	5105(7)	1448(6)	32
C16A	2465(11)	4287(6)	2010(6)	32
C17A	1626(11)	5182(7)	511(6)	32
C18A	3819(10)	5734(5)	1800(6)	32

Table S3 Bond lengths [Å] and angles [°] for **2•**2DMF .

C1-N1	1.3766(19)	C14-C15#1	1.389(2)
C1-C2	1.378(2)	C14-H14	0.971(18)
C1-C10	1.430(2)	C15-C14#1	1.389(2)
C2-C3	1.398(3)	C15-H15	0.968(17)
C2-H2	0.95	N1-H1	0.88
C3-C4	1.382(2)	N2-H2A	0.88
C3-H3	0.95	O3-C18	1.248(5)
C4-N1	1.354(2)	N3-C18	1.319(3)
C4-C5	1.522(2)	N3-C17	1.450(3)
C5-C6	1.517(2)	N3-C16	1.458(3)
C5-C12	1.538(2)	C16-H16A	0.98
C5-C13	1.538(2)	C16-H16B	0.98
C6-N2	1.355(2)	C16-H16C	0.98
C6-C7	1.389(2)	C17-H17A	0.98
C7-C8	1.390(3)	C17-H17B	0.98
C7-H7	0.95	C17-H17C	0.98
C8-C9	1.374(3)	C18-H18	0.95
C8-H8	0.95	O3A-C18A	1.254(9)
C9-N2	1.378(2)	N3A-C18A	1.326(8)
C9-C11	1.422(3)	N3A-C17A	1.438(8)
C10-O1	1.216(2)	N3A-C16A	1.461(8)
C10-H10	0.95	C16A-H16D	0.98
C11-O2	1.218(2)	C16A-H16E	0.98
C11-H11	0.95	C16A-H16F	0.98
C12-H12A	0.98	C17A-H17D	0.98
C12-H12B	0.98	C17A-H17E	0.98
C12-H12C	0.98	C17A-H17F	0.98
C13-C15	1.388(2)	C18A-H18A	0.95
C13-C14	1.390(2)		
N1-C1-C2	107.18(14)	C1-C2-H2	126.1
N1-C1-C10	122.76(15)	C3-C2-H2	126.1
C2-C1-C10	130.05(16)	C4-C3-C2	107.45(15)
C1-C2-C3	107.80(14)	C4-C3-H3	126.3

C2-C3-H3	126.3	C14-C13-C5	122.07(13)
N1-C4-C3	107.82(14)	C15#1-C14-C13	120.42(14)
N1-C4-C5	122.30(13)	C15#1-C14-H14	118.9(10)
C3-C4-C5	129.81(15)	C13-C14-H14	120.7(10)
C6-C5-C4	107.98(12)	C13-C15-C14#1	121.32(14)
C6-C5-C12	108.66(13)	C13-C15-H15	119.5(10)
C4-C5-C12	109.12(13)	C14#1-C15-H15	119.2(10)
C6-C5-C13	112.93(13)	C4-N1-C1	109.75(13)
C4-C5-C13	110.75(12)	C4-N1-H1	125.1
C12-C5-C13	107.32(12)	C1-N1-H1	125.1
N2-C6-C7	107.59(15)	C6-N2-C9	109.64(13)
N2-C6-C5	123.09(13)	C6-N2-H2A	125.2
C7-C6-C5	129.15(15)	C9-N2-H2A	125.2
C6-C7-C8	107.42(16)	C18-N3-C17	122.39(19)
C6-C7-H7	126.3	C18-N3-C16	120.59(19)
C8-C7-H7	126.3	C17-N3-C16	116.89(19)
C9-C8-C7	108.15(15)	N3-C16-H16A	109.5
C9-C8-H8	125.9	N3-C16-H16B	109.5
C7-C8-H8	125.9	H16A-C16-H16B	109.5
C8-C9-N2	107.18(16)	N3-C16-H16C	109.5
C8-C9-C11	128.15(16)	H16A-C16-H16C	109.5
N2-C9-C11	124.62(16)	H16B-C16-H16C	109.5
O1-C10-C1	124.55(17)	N3-C17-H17A	109.5
O1-C10-H10	117.7	N3-C17-H17B	109.5
C1-C10-H10	117.7	H17A-C17-H17B	109.5
O2-C11-C9	126.43(17)	N3-C17-H17C	109.5
O2-C11-H11	116.8	H17A-C17-H17C	109.5
C9-C11-H11	116.8	H17B-C17-H17C	109.5
C5-C12-H12A	109.5	O3-C18-N3	124.6(2)
C5-C12-H12B	109.5	O3-C18-H18	117.7
H12A-C12-H12B	109.5	N3-C18-H18	117.7
C5-C12-H12C	109.5	C18A-N3A-C17A	122.2(8)
H12A-C12-H12C	109.5	C18A-N3A-C16A	119.5(8)
H12B-C12-H12C	109.5	C17A-N3A-C16A	118.3(7)
C15-C13-C14	118.25(14)	N3A-C16A-H16D	109.5
C15-C13-C5	119.48(13)	N3A-C16A-H16E	109.5

H16D-C16A-H16E	109.5	N3A-C17A-H17F	109.5
N3A-C16A-H16F	109.5	H17D-C17A-H17F	109.5
H16D-C16A-H16F	109.5	H17E-C17A-H17F	109.5
H16E-C16A-H16F	109.5	O3A-C18A-N3A	123.6(12)
N3A-C17A-H17D	109.5	O3A-C18A-H18A	118.2
N3A-C17A-H17E	109.5	N3A-C18A-H18A	118.2
H17D-C17A-H17E	109.5		

Symmetry transformations used to generate equivalent atoms:

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

Table S4 Anisotropic displacement parameters ($Å^2$x 10^3) for **2•**2DMF . 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}
C1	25(1)	23(1)	35(1)	7(1)	13(1)	1(1)
C2	45(1)	20(1)	43(1)	3(1)	21(1)	3(1)
C3	45(1)	24(1)	31(1)	-3(1)	14(1)	-3(1)
C4	26(1)	20(1)	26(1)	2(1)	10(1)	-5(1)
C5	25(1)	21(1)	24(1)	2(1)	4(1)	-4(1)
C6	21(1)	22(1)	28(1)	6(1)	2(1)	-3(1)
C7	25(1)	42(1)	34(1)	7(1)	-3(1)	-8(1)
C8	19(1)	50(1)	47(1)	14(1)	5(1)	-3(1)
C9	20(1)	29(1)	40(1)	12(1)	9(1)	4(1)
C10	35(1)	37(1)	44(1)	12(1)	7(1)	9(1)
C11	30(1)	33(1)	47(1)	11(1)	18(1)	7(1)
C12	43(1)	35(1)	26(1)	0(1)	2(1)	-9(1)
C13	23(1)	21(1)	21(1)	4(1)	3(1)	-2(1)
C14	21(1)	26(1)	30(1)	6(1)	7(1)	1(1)
C15	26(1)	20(1)	30(1)	5(1)	8(1)	3(1)
N1	24(1)	19(1)	28(1)	1(1)	7(1)	0(1)
N2	17(1)	24(1)	31(1)	3(1)	5(1)	-2(1)
O1	62(1)	58(1)	46(1)	-2(1)	-14(1)	12(1)
O2	47(1)	39(1)	47(1)	-1(1)	19(1)	0(1)
O3	27(1)	34(2)	40(2)	-9(1)	1(1)	-3(1)
N3	26(1)	25(1)	25(1)	-4(1)	4(1)	-1(1)
C16	44(1)	41(1)	31(1)	-1(1)	8(1)	-6(1)
C17	36(1)	32(1)	43(1)	-9(1)	6(1)	-5(1)
C18	28(1)	29(1)	32(1)	-5(1)	7(1)	3(1)

Table S5 Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^2 x 10 ^{3}) for **2**•2DMF .

	x	y	z	U(eq)
H2	3878	9507	4066	41
H3	5937	8672	5354	39
H7	10317	7215	5242	43
H8	11573	6948	3880	47
H10	2144	8994	2271	47
H11	10499	6199	2149	42
H12A	8343	6529	6222	54
H12B	6726	7110	6257	54
H12C	8201	7615	5935	54
H1	4593	6950	3190	28
H2A	6945	6090	3159	29
H16A	2801	6126	1005	59
H16B	956	5734	724	59
H16C	2339	5260	294	59
H17A	1991	3654	2105	57
H17B	1621	3721	984	57
H17C	407	4212	1525	57
H18	4003	4625	2860	36
H16D	2584	3713	1666	48
H16E	1369	4301	2135	48
H16F	3306	4299	2607	48
H17D	476	5246	542	48
H17E	1745	4618	152	48
H17F	1948	5735	202	48
H18A	3962	6245	1413	38
H15	3840(20)	6457(12)	5201(12)	25(4)
H14	7620(20)	4915(12)	4685(12)	29(4)

Table S6 Torsion angles [°] for **2**•2DMF.

N1-C1-C2-C3	0.00(18)	C8-C9-C11-O2	173.69(18)
C10-C1-C2-C3	178.82(17)	N2-C9-C11-O2	-3.4(3)
C1-C2-C3-C4	0.14(19)	C6-C5-C13-C15	-161.41(13)
C2-C3-C4-N1	-0.23(18)	C4-C5-C13-C15	-40.16(19)
C2-C3-C4-C5	176.92(15)	C12-C5-C13-C15	78.86(17)
N1-C4-C5-C6	67.79(17)	C6-C5-C13-C14	23.8(2)
C3-C4-C5-C6	-108.99(18)	C4-C5-C13-C14	145.00(15)
N1-C4-C5-C12	-174.26(14)	C12-C5-C13-C14	-95.98(17)
C3-C4-C5-C12	8.9(2)	C15-C13-C14-C15#1	0.6(3)
N1-C4-C5-C13	-56.33(19)	C5-C13-C14-C15#1	175.54(14)
C3-C4-C5-C13	126.88(17)	C14-C13-C15-C14#1	-0.7(3)
C4-C5-C6-N2	-69.89(17)	C5-C13-C15-C14#1	-175.69(14)
C12-C5-C6-N2	171.87(14)	C3-C4-N1-C1	0.24(17)
C13-C5-C6-N2	52.91(19)	C5-C4-N1-C1	-177.17(13)
C4-C5-C6-C7	104.85(18)	C2-C1-N1-C4	-0.15(17)
C12-C5-C6-C7	-13.4(2)	C10-C1-N1-C4	-179.07(15)
C13-C5-C6-C7	-132.35(17)	C7-C6-N2-C9	-0.62(17)
N2-C6-C7-C8	1.23(19)	C5-C6-N2-C9	175.10(13)
C5-C6-C7-C8	-174.15(15)	C8-C9-N2-C6	-0.23(18)
C6-C7-C8-C9	-1.4(2)	C11-C9-N2-C6	177.37(15)
C7-C8-C9-N2	0.99(19)	C17-N3-C18-O3	177.4(4)
C7-C8-C9-C11	-176.50(16)	C16-N3-C18-O3	1.6(5)
N1-C1-C10-O1	1.6(3)	C17A-N3A-C18A-O3A	179.3(19)
C2-C1-C10-O1	-177.08(19)	C16A-N3A-C18A-O3A	-3(2)

Symmetry transformations used to generate equivalent atoms:

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

Table S7 Hydrogen bonds for **2**•2DMF [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
C2-H2...O2#2	0.95	2.58	3.393(2)	144
C7-H7...O1#3	0.95	2.47	3.354(2)	155
N1-H1...O3	0.88	1.98	2.861(6)	174
N1-H1...O3A	0.88	2.00	2.87(3)	168
N2-H2A...O3	0.88	1.98	2.850(4)	170
N2-H2A...O3A	0.88	1.92	2.785(17)	169
C2-H2...O2#2	0.95	2.58	3.393(2)	144
C7-H7...O1#3	0.95	2.47	3.354(2)	155
N1-H1...O3	0.88	1.98	2.861(6)	174
N1-H1...O3A	0.88	2.00	2.87(3)	168
N2-H2A...O3	0.88	1.98	2.850(4)	170
N2-H2A...O3A	0.88	1.92	2.785(17)	169

Symmetry transformations used to generate equivalent atoms:

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

X-ray Experimental for 4•2DMF

Table S8 Crystal data and structure refinement for **4**•2DMF

Empirical formula	C36 H40 N6 O6	
Formula weight	652.74	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	orthorhombic	
Space group	P b c a	
Unit cell dimensions	a = 15.1665(12) Å	α= 90°.
	b = 17.7506(16) Å	β= 90°.
	c = 24.997(2) Å	γ = 90°.
Volume	6729.5(10) $Å^3$	
Z	8	
Density (calculated)	1.289 Mg/m^3	
Absorption coefficient	0.089 mm^{-1}	
F(000)	2768	
Crystal size	0.200 x 0.110 x 0.100 mm	
Theta range for data collection	3.016 to 27.481°.	
Index ranges	-19<=h<=19, -23<=k<=23, -31<=l<=32	
Reflections collected	81471	
Independent reflections	7708 [R(int) = 0.0981]	
Completeness to theta = 25.242°	99.8 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	1.00 and 0.774	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	7708 / 0 / 455	
Goodness-of-fit on F^2	1.134	
Final R indices [I>2sigma(I)]	R1 = 0.0676, wR2 = 0.1114	
R indices (all data)	R1 = 0.1068, wR2 = 0.1226	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.253 and -0.266 e.$Å^{-3}$	
CCDC Number	1012699	

Table S9 Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$ x 10^3) for **4**•2DMF. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
C1	2100(2)	3543(2)	1153(1)	28(1)
C2	2940(1)	3373(1)	918(1)	19(1)
C3	3679(2)	3818(1)	876(1)	23(1)
C4	4336(2)	3393(1)	624(1)	20(1)
C5	3986(1)	2691(1)	515(1)	16(1)
C6	4416(1)	2000(1)	267(1)	16(1)
C7	3995(1)	1837(1)	-275(1)	16(1)
C8	4336(1)	1920(1)	-787(1)	19(1)
C9	3678(1)	1698(1)	-1148(1)	19(1)
C10	2948(1)	1486(1)	-855(1)	17(1)
C11	2116(2)	1209(1)	-1046(1)	22(1)
C12	5404(1)	2166(1)	184(1)	21(1)
C13	4352(1)	1318(1)	646(1)	15(1)
C14	4322(1)	1412(1)	1200(1)	16(1)
C15	4318(1)	798(1)	1548(1)	16(1)
C16	4342(1)	74(1)	1332(1)	19(1)
C17	4380(1)	-27(1)	783(1)	20(1)
C18	4384(1)	590(1)	442(1)	18(1)
C19	4218(1)	915(1)	2156(1)	16(1)
C20	4590(1)	252(1)	2464(1)	17(1)
C21	4212(2)	-200(1)	2852(1)	23(1)
C22	4839(2)	-733(1)	3010(1)	25(1)
C23	5599(2)	-600(1)	2717(1)	20(1)
C24	6428(2)	-988(1)	2705(1)	26(1)
C25	4682(1)	1624(1)	2347(1)	14(1)
C26	4401(1)	2172(1)	2705(1)	20(1)
C27	5103(1)	2670(1)	2784(1)	21(1)
C28	5797(1)	2431(1)	2475(1)	16(1)
C29	6655(1)	2760(1)	2396(1)	20(1)
C30	3221(1)	983(1)	2275(1)	21(1)
C31	6678(1)	505(1)	1144(1)	22(1)

C32	7374(2)	571(2)	273(1)	31(1)
C33	7530(2)	1615(1)	926(1)	34(1)
C34	1362(2)	1054(1)	524(1)	23(1)
C35	-95(2)	678(2)	818(1)	54(1)
C36	1047(2)	1101(2)	1464(1)	43(1)
N1	3134(1)	2685(1)	689(1)	17(1)
N2	3154(1)	1575(1)	-322(1)	17(1)
N3	5434(1)	7(1)	2388(1)	17(1)
N4	5531(1)	1785(1)	2213(1)	16(1)
N5	7173(1)	878(1)	796(1)	20(1)
N6	798(1)	937(1)	915(1)	23(1)
O1	1460(1)	3126(1)	1160(1)	38(1)
O2	1496(1)	1012(1)	-765(1)	30(1)
O3	7064(1)	-799(1)	2435(1)	36(1)
O4	7214(1)	2514(1)	2090(1)	28(1)
O5	6495(1)	722(1)	1600(1)	26(1)
O6	2121(1)	1297(1)	576(1)	27(1)

Table S10 Bond lengths [Å] and angles [°] for **4•**2DMF.

C1-O1	1.220(3)	C16-H16	0.95
C1-C2	1.435(3)	C17-C18	1.388(3)
C1-H1	0.95	C17-H17	0.95
C2-C3	1.375(3)	C18-H18	0.95
C2-N1	1.380(3)	C19-C20	1.517(3)
C3-C4	1.400(3)	C19-C25	1.519(3)
C3-H3	0.95	C19-C30	1.545(3)
C4-C5	1.381(3)	C20-N3	1.365(3)
C4-H4	0.95	C20-C21	1.382(3)
C5-N1	1.363(3)	C21-C22	1.398(3)
C5-C6	1.521(3)	C21-H21	0.95
C6-C7	1.527(3)	C22-C23	1.387(3)
C6-C13	1.539(3)	C22-H22	0.95
C6-C12	1.543(3)	C23-N3	1.377(3)
C7-N2	1.362(3)	C23-C24	1.433(3)
C7-C8	1.388(3)	C24-O3	1.224(3)
C8-C9	1.403(3)	C24-H24	0.95
C8-H8	0.95	C25-N4	1.361(3)
C9-C10	1.381(3)	C25-C26	1.388(3)
C9-H9	0.95	C26-C27	1.398(3)
C10-N2	1.377(3)	C26-H26	0.95
C10-C11	1.435(3)	C27-C28	1.373(3)
C11-O2	1.224(3)	C27-H27	0.95
C11-H11	0.95	C28-N4	1.382(3)
C12-H12A	0.98	C28-C29	1.439(3)
C12-H12B	0.98	C29-O4	1.223(3)
C12-H12C	0.98	C29-H29	0.95
C13-C18	1.390(3)	C30-H30A	0.98
C13-C14	1.395(3)	C30-H30B	0.98
C14-C15	1.395(3)	C30-H30C	0.98
C14-H14	0.95	C31-O5	1.235(3)
C15-C16	1.393(3)	C31-N5	1.324(3)
C15-C19	1.542(3)	C31-H31	0.95
C16-C17	1.386(3)	C32-N5	1.450(3)

C32-H32A	0.98	C35-H35A	0.98
C32-H32B	0.98	C35-H35B	0.98
C32-H32C	0.98	C35-H35C	0.98
C33-N5	1.452(3)	C36-N6	1.453(3)
C33-H33A	0.98	C36-H36A	0.98
C33-H33B	0.98	C36-H36B	0.98
C33-H33C	0.98	C36-H36C	0.98
C34-O6	1.236(3)	N1-H1N	0.89(3)
C34-N6	1.315(3)	N2-H2N	0.88(2)
C34-H34	0.95	N3-H3N	0.92(3)
C35-N6	1.451(3)	N4-H4N	0.92(2)

O1-C1-C2	125.8(2)	C7-C8-C9	107.35(19)
O1-C1-H1	117.1	C7-C8-H8	126.3
C2-C1-H1	117.1	C9-C8-H8	126.3
C3-C2-N1	107.65(19)	C10-C9-C8	107.79(18)
C3-C2-C1	129.3(2)	C10-C9-H9	126.1
N1-C2-C1	123.0(2)	C8-C9-H9	126.1
C2-C3-C4	107.7(2)	N2-C10-C9	107.44(18)
C2-C3-H3	126.2	N2-C10-C11	124.15(19)
C4-C3-H3	126.2	C9-C10-C11	128.40(19)
C5-C4-C3	107.61(19)	O2-C11-C10	125.6(2)
C5-C4-H4	126.2	O2-C11-H11	117.2
C3-C4-H4	126.2	C10-C11-H11	117.2
N1-C5-C4	107.90(19)	C6-C12-H12A	109.5
N1-C5-C6	122.01(18)	C6-C12-H12B	109.5
C4-C5-C6	130.07(19)	H12A-C12-H12B	109.5
C5-C6-C7	109.61(16)	C6-C12-H12C	109.5
C5-C6-C13	110.87(16)	H12A-C12-H12C	109.5
C7-C6-C13	111.81(16)	H12B-C12-H12C	109.5
C5-C6-C12	108.48(17)	C18-C13-C14	118.41(19)
C7-C6-C12	108.80(17)	C18-C13-C6	120.19(18)
C13-C6-C12	107.16(16)	C14-C13-C6	121.25(18)
N2-C7-C8	107.83(18)	C13-C14-C15	121.74(19)
N2-C7-C6	122.16(18)	C13-C14-H14	119.1
C8-C7-C6	130.01(19)	C15-C14-H14	119.1

C16-C15-C14	118.59(19)	C25-C26-C27	107.50(18)
C16-C15-C19	120.63(18)	C25-C26-H26	126.3
C14-C15-C19	120.62(18)	C27-C26-H26	126.3
C17-C16-C15	120.32(19)	C28-C27-C26	107.96(19)
C17-C16-H16	119.8	C28-C27-H27	126.0
C15-C16-H16	119.8	C26-C27-H27	126.0
C16-C17-C18	120.4(2)	C27-C28-N4	107.43(18)
C16-C17-H17	119.8	C27-C28-C29	130.2(2)
C18-C17-H17	119.8	N4-C28-C29	122.36(19)
C17-C18-C13	120.58(19)	O4-C29-C28	124.7(2)
C17-C18-H18	119.7	O4-C29-H29	117.6
C13-C18-H18	119.7	C28-C29-H29	117.6
C20-C19-C25	108.08(16)	C19-C30-H30A	109.5
C20-C19-C15	111.00(17)	C19-C30-H30B	109.5
C25-C19-C15	112.12(16)	H30A-C30-H30B	109.5
C20-C19-C30	109.09(17)	C19-C30-H30C	109.5
C25-C19-C30	109.21(17)	H30A-C30-H30C	109.5
C15-C19-C30	107.30(16)	H30B-C30-H30C	109.5
N3-C20-C21	107.60(19)	O5-C31-N5	125.2(2)
N3-C20-C19	121.75(18)	O5-C31-H31	117.4
C21-C20-C19	130.65(19)	N5-C31-H31	117.4
C20-C21-C22	107.9(2)	N5-C32-H32A	109.5
C20-C21-H21	126.0	N5-C32-H32B	109.5
C22-C21-H21	126.0	H32A-C32-H32B	109.5
C23-C22-C21	107.54(19)	N5-C32-H32C	109.5
C23-C22-H22	126.2	H32A-C32-H32C	109.5
C21-C22-H22	126.2	H32B-C32-H32C	109.5
N3-C23-C22	107.26(19)	N5-C33-H33A	109.5
N3-C23-C24	121.5(2)	N5-C33-H33B	109.5
C22-C23-C24	131.2(2)	H33A-C33-H33B	109.5
O3-C24-C23	124.8(2)	N5-C33-H33C	109.5
O3-C24-H24	117.6	H33A-C33-H33C	109.5
C23-C24-H24	117.6	H33B-C33-H33C	109.5
N4-C25-C26	107.60(18)	O6-C34-N6	125.6(2)
N4-C25-C19	122.39(18)	O6-C34-H34	117.2
C26-C25-C19	129.78(18)	N6-C34-H34	117.2

N6-C35-H35A	109.5	C7-N2-C10	109.60(18)
N6-C35-H35B	109.5	C7-N2-H2N	125.2(15)
H35A-C35-H35B	109.5	C10-N2-H2N	125.0(15)
N6-C35-H35C	109.5	C20-N3-C23	109.68(18)
H35A-C35-H35C	109.5	C20-N3-H3N	126.5(16)
H35B-C35-H35C	109.5	C23-N3-H3N	123.4(16)
N6-C36-H36A	109.5	C25-N4-C28	109.50(17)
N6-C36-H36B	109.5	C25-N4-H4N	127.3(15)
H36A-C36-H36B	109.5	C28-N4-H4N	123.2(15)
N6-C36-H36C	109.5	C31-N5-C32	121.54(19)
H36A-C36-H36C	109.5	C31-N5-C33	120.95(19)
H36B-C36-H36C	109.5	C32-N5-C33	117.51(19)
C5-N1-C2	109.16(18)	C34-N6-C35	122.2(2)
C5-N1-H1N	127.0(17)	C34-N6-C36	120.1(2)
C2-N1-H1N	123.0(16)	C35-N6-C36	117.7(2)

Table S11 Anisotropic displacement parameters ($Å^2 \times 10^3$) for **4**•2DMF. 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}
C1	28(1)	36(1)	22(1)	-1(1)	-5(1)	10(1)
C2	20(1)	22(1)	15(1)	-3(1)	-2(1)	6(1)
C3	28(1)	19(1)	21(1)	-4(1)	-5(1)	2(1)
C4	20(1)	20(1)	22(1)	2(1)	-1(1)	-4(1)
C5	15(1)	19(1)	14(1)	3(1)	-2(1)	0(1)
C6	15(1)	16(1)	16(1)	1(1)	2(1)	0(1)
C7	16(1)	14(1)	18(1)	1(1)	0(1)	0(1)
C8	18(1)	20(1)	19(1)	3(1)	3(1)	0(1)
C9	26(1)	18(1)	13(1)	3(1)	2(1)	2(1)
C10	20(1)	15(1)	15(1)	1(1)	-3(1)	2(1)
C11	25(1)	23(1)	16(1)	-1(1)	-3(1)	4(1)
C12	18(1)	23(1)	22(1)	1(1)	0(1)	-2(1)
C13	12(1)	16(1)	17(1)	1(1)	-1(1)	0(1)
C14	14(1)	15(1)	19(1)	-3(1)	-2(1)	1(1)
C15	12(1)	17(1)	18(1)	-1(1)	-2(1)	0(1)
C16	20(1)	17(1)	19(1)	2(1)	-4(1)	-2(1)
C17	24(1)	16(1)	21(1)	-1(1)	-2(1)	1(1)
C18	19(1)	22(1)	13(1)	-1(1)	-2(1)	1(1)
C19	15(1)	19(1)	15(1)	2(1)	0(1)	-1(1)
C20	18(1)	18(1)	15(1)	-2(1)	-3(1)	-2(1)
C21	22(1)	26(1)	21(1)	3(1)	1(1)	-4(1)
C22	33(1)	20(1)	22(1)	9(1)	-5(1)	-6(1)
C23	26(1)	17(1)	18(1)	2(1)	-8(1)	-2(1)
C24	32(1)	19(1)	27(1)	-1(1)	-10(1)	1(1)
C25	13(1)	17(1)	13(1)	1(1)	-2(1)	0(1)
C26	17(1)	23(1)	21(1)	-2(1)	4(1)	0(1)
C27	24(1)	20(1)	19(1)	-4(1)	0(1)	-2(1)
C28	20(1)	15(1)	15(1)	1(1)	-1(1)	-3(1)
C29	22(1)	18(1)	20(1)	1(1)	-2(1)	-2(1)
C30	16(1)	26(1)	22(1)	-1(1)	0(1)	-3(1)
C31	22(1)	17(1)	28(1)	2(1)	2(1)	-1(1)

C32	35(1)	36(1)	22(1)	-2(1)	4(1)	-1(1)
C33	32(1)	27(1)	42(2)	-4(1)	10(1)	-10(1)
C34	26(1)	26(1)	17(1)	4(1)	0(1)	-1(1)
C35	20(1)	89(3)	53(2)	25(2)	-3(1)	-13(2)
C36	50(2)	51(2)	29(2)	-8(1)	17(1)	-17(2)
N1	17(1)	18(1)	17(1)	0(1)	-1(1)	1(1)
N2	16(1)	21(1)	13(1)	2(1)	2(1)	-1(1)
N3	18(1)	18(1)	15(1)	2(1)	-2(1)	0(1)
N4	16(1)	16(1)	16(1)	-2(1)	1(1)	-1(1)
N5	23(1)	17(1)	21(1)	-1(1)	4(1)	-2(1)
N6	17(1)	30(1)	23(1)	6(1)	4(1)	-1(1)
O1	22(1)	53(1)	38(1)	2(1)	2(1)	3(1)
O2	21(1)	45(1)	25(1)	-1(1)	0(1)	-5(1)
O3	29(1)	29(1)	52(1)	1(1)	-1(1)	6(1)
O4	22(1)	31(1)	31(1)	-2(1)	5(1)	-2(1)
O5	30(1)	22(1)	26(1)	0(1)	11(1)	1(1)
O6	23(1)	33(1)	26(1)	-1(1)	4(1)	-10(1)

Table S12 Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^2 x 10^3) for **4**•2DMF.

	x	y	z	U(eq)
H1	2036	4022	1318	34
H3	3733	4324	997	28
H4	4916	3557	543	24
H8	4910	2095	-876	23
H9	3726	1695	-1527	23
H11	2041	1176	-1423	26
H12A	5471	2593	-62	32
H12B	5694	1721	32	32
H12C	5676	2291	528	32
H14	4305	1907	1344	19
H16	4331	-351	1563	23
H17	4404	-522	639	24
H18	4408	514	66	21
H21	3628	-157	2986	28
H22	4758	-1117	3270	30
H24	6488	-1423	2923	31
H26	3836	2202	2867	24
H27	5100	3099	3011	25
H29	6796	3198	2596	24
H30A	3133	1064	2659	32
H30B	2922	518	2166	32
H30C	2975	1410	2076	32
H31	6445	34	1033	26
H32A	7090	78	234	47
H32B	8014	514	235	47
H32C	7154	913	-4	47
H33A	7294	1782	1272	50
H33B	7362	1976	648	50
H33C	8174	1584	948	50
H34	1168	944	171	28

H35A	-514	1056	948	81
H35B	-192	201	1007	81
H35C	-181	602	433	81
H36A	953	653	1686	65
H36B	685	1516	1600	65
H36C	1671	1245	1477	65
H1N	2779(17)	2290(15)	712(10)	36(8)
H3N	5824(17)	176(15)	2133(10)	41(8)
H4N	5886(15)	1526(13)	1978(9)	27(7)
H2N	2811(16)	1446(13)	-53(10)	28(7)

Table S13 Torsion angles [°] for **4**•2DMF.

O1-C1-C2-C3	177.4(2)	C13-C14-C15-C16	-0.2(3)
O1-C1-C2-N1	-3.2(4)	C13-C14-C15-C19	-175.58(18)
N1-C2-C3-C4	-0.7(2)	C14-C15-C16-C17	0.8(3)
C1-C2-C3-C4	178.8(2)	C19-C15-C16-C17	176.23(19)
C2-C3-C4-C5	0.0(2)	C15-C16-C17-C18	-0.9(3)
C3-C4-C5-N1	0.7(2)	C16-C17-C18-C13	0.3(3)
C3-C4-C5-C6	-177.3(2)	C14-C13-C18-C17	0.4(3)
N1-C5-C6-C7	68.5(2)	C6-C13-C18-C17	176.09(19)
C4-C5-C6-C7	-113.7(2)	C16-C15-C19-C20	27.7(3)
N1-C5-C6-C13	-55.4(2)	C14-C15-C19-C20	-156.98(18)
C4-C5-C6-C13	122.4(2)	C16-C15-C19-C25	148.70(19)
N1-C5-C6-C12	-172.80(18)	C14-C15-C19-C25	-36.0(3)
C4-C5-C6-C12	4.9(3)	C16-C15-C19-C30	-91.4(2)
C5-C6-C7-N2	-70.3(2)	C14-C15-C19-C30	83.9(2)
C13-C6-C7-N2	53.1(3)	C25-C19-C20-N3	-68.9(2)
C12-C6-C7-N2	171.22(18)	C15-C19-C20-N3	54.4(2)
C5-C6-C7-C8	108.9(2)	C30-C19-C20-N3	172.45(18)
C13-C6-C7-C8	-127.7(2)	C25-C19-C20-C21	110.4(2)
C12-C6-C7-C8	-9.5(3)	C15-C19-C20-C21	-126.3(2)
N2-C7-C8-C9	-0.1(2)	C30-C19-C20-C21	-8.3(3)
C6-C7-C8-C9	-179.5(2)	N3-C20-C21-C22	-0.4(2)
C7-C8-C9-C10	0.1(2)	C19-C20-C21-C22	-179.8(2)
C8-C9-C10-N2	0.0(2)	C20-C21-C22-C23	0.1(3)
C8-C9-C10-C11	-179.2(2)	C21-C22-C23-N3	0.2(2)
N2-C10-C11-O2	-0.8(4)	C21-C22-C23-C24	-177.7(2)
C9-C10-C11-O2	178.3(2)	N3-C23-C24-O3	4.3(4)
C5-C6-C13-C18	155.49(19)	C22-C23-C24-O3	-178.0(2)
C7-C6-C13-C18	32.8(3)	C20-C19-C25-N4	73.3(2)
C12-C6-C13-C18	-86.3(2)	C15-C19-C25-N4	-49.3(3)
C5-C6-C13-C14	-28.9(3)	C30-C19-C25-N4	-168.12(18)
C7-C6-C13-C14	-151.57(19)	C20-C19-C25-C26	-100.4(2)
C12-C6-C13-C14	89.3(2)	C15-C19-C25-C26	136.9(2)
C18-C13-C14-C15	-0.4(3)	C30-C19-C25-C26	18.1(3)
C6-C13-C14-C15	-176.09(18)	N4-C25-C26-C27	0.1(2)

C19-C25-C26-C27	174.5(2)	C11-C10-N2-C7	179.17(19)
C25-C26-C27-C28	0.4(2)	C21-C20-N3-C23	0.6(2)
C26-C27-C28-N4	-0.7(2)	C19-C20-N3-C23	-179.98(18)
C26-C27-C28-C29	177.3(2)	C22-C23-N3-C20	-0.5(2)
C27-C28-C29-O4	-176.5(2)	C24-C23-N3-C20	177.68(19)
N4-C28-C29-O4	1.3(3)	C26-C25-N4-C28	-0.5(2)
C4-C5-N1-C2	-1.2(2)	C19-C25-N4-C28	-175.49(17)
C6-C5-N1-C2	177.03(18)	C27-C28-N4-C25	0.8(2)
C3-C2-N1-C5	1.2(2)	C29-C28-N4-C25	-177.44(19)
C1-C2-N1-C5	-178.35(19)	O5-C31-N5-C32	178.3(2)
C8-C7-N2-C10	0.1(2)	O5-C31-N5-C33	-2.1(3)
C6-C7-N2-C10	179.50(18)	O6-C34-N6-C35	177.5(3)
C9-C10-N2-C7	0.0(2)	O6-C34-N6-C36	0.6(4)

Table S14 Hydrogen bonds for **4•**2DMF [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
C4-H4...O2#1	0.95	2.58	3.461(3)	155
C8-H8...O1#1	0.95	2.49	3.355(3)	152
C26-H26...O4#2	0.95	2.52	3.411(3)	156
C29-H29...O3#3	0.95	2.51	3.215(3)	131
C33-H33A...O4	0.98	2.43	3.352(3)	157
C34-H34...O2	0.95	2.40	3.231(3)	146
N1-H1N...O6	0.89(3)	2.05(3)	2.918(2)	165(2)
N3-H3N...O5	0.92(3)	1.94(3)	2.844(2)	168(2)
N4-H4N...O5	0.92(2)	1.94(2)	2.836(2)	163(2)
N2-H2N...O6	0.88(2)	1.91(2)	2.782(2)	172(2)

Symmetry transformations used to generate equivalent atoms:

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

X-ray Experimental for 2•2DMSO

Table S15 Crystal data and structure refinement for **2**•2DMSO.

Empirical formula	C34 H38 N4 O6 S2	
Formula weight	662.80	
Temperature	153(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	C2/c	
Unit cell dimensions	a = 22.6373(7) Å	α= 90°.
	b = 9.5570(3) Å	β= 105.708(2)°.
	c = 16.0764(5) Å	γ = 90°.
Volume	3348.15(18) $Å^3$	
Z	4	
Density (calculated)	1.315 Mg/m^3	
Absorption coefficient	0.209 mm^{-1}	
F(000)	1400	
Crystal size	0.22 x 0.20 x 0.14 mm	
Theta range for data collection	1.87 to 27.50°.	
Index ranges	-29<=h<=29, -12<=k<=12, -20<=l<=20	
Reflections collected	52202	
Independent reflections	3843 [R(int) = 0.0505]	
Completeness to theta = 27.50°	99.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	1.00 and 0.857	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3843 / 3 / 259	
Goodness-of-fit on F^2	1.046	
Final R indices [I>2sigma(I)]	R1 = 0.0391, wR2 = 0.0975	
R indices (all data)	R1 = 0.0512, wR2 = 0.1070	
Largest diff. peak and hole	0.324 and -0.252 e.$Å^{-3}$	
CCDC Number	1012698	

Table S16 Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^2 x 10^3) for **2**•2DMSO. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
O1	773(1)	7401(1)	4991(1)	41(1)
O2	1415(1)	3841(1)	8051(1)	52(1)
O3	1836(1)	4982(1)	6275(1)	38(1)
S1A	2250(1)	6158(1)	6582(1)	45(1)
C16A	2303(3)	7090(7)	5644(5)	74(2)
C17A	1812(5)	7395(8)	6972(5)	102(3)
S1B	2088(1)	6147(1)	6934(1)	41(1)
C16B	2283(2)	7478(4)	6268(4)	71(1)
C17B	1456(2)	7010(4)	7153(3)	49(1)
N1	863(1)	4446(1)	4763(1)	20(1)
N2	1255(1)	2493(1)	6410(1)	20(1)
C1	389(1)	6766(2)	4447(1)	30(1)
C2	409(1)	5301(2)	4280(1)	24(1)
C3	31(1)	4489(2)	3649(1)	34(1)
C4	262(1)	3121(2)	3750(1)	30(1)
C5	779(1)	3124(1)	4449(1)	20(1)
C6	1198(1)	1929(1)	4861(1)	18(1)
C7	1088(1)	1599(1)	5731(1)	18(1)
C8	795(1)	463(1)	5984(1)	24(1)
C9	786(1)	702(2)	6840(1)	27(1)
C10	1071(1)	1968(2)	7095(1)	24(1)
C11	1168(1)	2705(2)	7895(1)	36(1)
C12	1042(1)	628(2)	4278(1)	27(1)
C13	1877(1)	2280(1)	4954(1)	18(1)
C14	2050(1)	3258(1)	4422(1)	21(1)
C15	2336(1)	1531(1)	5531(1)	21(1)

Table S17 Bond lengths [Å] and angles [°] for **2**•2DMSO.

O1-C1	1.216(2)	C1-H1	0.95
O2-C11	1.216(2)	C2-C3	1.376(2)
O3-S1A	1.4618(17)	C3-C4	1.401(2)
O3-S1B	1.5365(15)	C3-H3	0.95
S1A-C17A	1.765(6)	C4-C5	1.3864(19)
S1A-C16A	1.783(6)	C4-H4	0.95
C16A-H16A	0.98	C5-C6	1.5175(18)
C16A-H16B	0.98	C6-C7	1.5186(17)
C16A-H16C	0.98	C6-C13	1.5391(17)
C17A-H17A	0.98	C6-C12	1.5404(18)
C17A-H17B	0.98	C7-C8	1.3887(18)
C17A-H17C	0.98	C8-C9	1.402(2)
S1B-C17B	1.767(4)	C8-H8	0.95
S1B-C16B	1.792(5)	C9-C10	1.382(2)
C16B-H16D	0.98	C9-H9	0.95
C16B-H16E	0.98	C10-C11	1.430(2)
C16B-H16F	0.98	C11-H11	0.95
C17B-H17D	0.98	C12-H12A	0.98
C17B-H17E	0.98	C12-H12B	0.98
C17B-H17F	0.98	C12-H12C	0.98
N1-C5	1.3542(18)	C13-C15	1.3891(18)
N1-C2	1.3764(17)	C13-C14	1.3929(18)
N1-H1N	0.894(18)	C14-C15#1	1.3880(18)
N2-C7	1.3561(17)	C14-H14	0.940(17)
N2-C10	1.3735(17)	C15-C14#1	1.3879(18)
N2-H2N	0.883(19)	C15-H15	0.966(16)
C1-C2	1.429(2)		
O3-S1A-C17A	105.3(4)	S1B-C16B-H16D	109.5
O3-S1A-C16A	106.4(3)	S1B-C16B-H16E	109.5
C17A-S1A-C16A	97.9(4)	H16D-C16B-H16E	109.5
O3-S1B-C17B	107.80(15)	S1B-C16B-H16F	109.5
O3-S1B-C16B	102.0(2)	H16D-C16B-H16F	109.5
C17B-S1B-C16B	97.5(2)	H16E-C16B-H16F	109.5

S1B-C17B-H17D	109.5	C13-C6-C12	107.08(10)
S1B-C17B-H17E	109.5	N2-C7-C8	107.95(11)
H17D-C17B-H17E	109.5	N2-C7-C6	122.03(11)
S1B-C17B-H17F	109.5	C8-C7-C6	129.95(12)
H17D-C17B-H17F	109.5	C7-C8-C9	107.20(12)
H17E-C17B-H17F	109.5	C7-C8-H8	126.4
C5-N1-C2	109.61(12)	C9-C8-H8	126.4
C5-N1-H1N	127.4(11)	C10-C9-C8	107.68(12)
C2-N1-H1N	123.0(11)	C10-C9-H9	126.2
C7-N2-C10	109.70(12)	C8-C9-H9	126.2
C7-N2-H2N	125.6(11)	N2-C10-C9	107.47(12)
C10-N2-H2N	124.7(11)	N2-C10-C11	122.40(14)
O1-C1-C2	124.86(14)	C9-C10-C11	130.10(13)
O1-C1-H1	117.6	O2-C11-C10	125.11(15)
C2-C1-H1	117.6	O2-C11-H11	117.4
C3-C2-N1	107.55(13)	C10-C11-H11	117.4
C3-C2-C1	130.24(14)	C6-C12-H12A	109.5
N1-C2-C1	122.19(14)	C6-C12-H12B	109.5
C2-C3-C4	107.62(13)	H12A-C12-H12B	109.5
C2-C3-H3	126.2	C6-C12-H12C	109.5
C4-C3-H3	126.2	H12A-C12-H12C	109.5
C5-C4-C3	107.36(14)	H12B-C12-H12C	109.5
C5-C4-H4	126.3	C15-C13-C14	118.16(12)
C3-C4-H4	126.3	C15-C13-C6	119.93(11)
N1-C5-C4	107.86(12)	C14-C13-C6	121.69(11)
N1-C5-C6	122.10(11)	C15#1-C14-C13	120.60(12)
C4-C5-C6	130.02(13)	C15#1-C14-H14	118.1(10)
C5-C6-C7	108.60(10)	C13-C14-H14	121.3(10)
C5-C6-C13	111.62(10)	C14#1-C15-C13	121.24(12)
C7-C6-C13	111.36(10)	C14#1-C15-H15	119.8(9)
C5-C6-C12	109.15(11)	C13-C15-H15	119.0(9)
C7-C6-C12	108.98(11)		

Symmetry transformations used to generate equivalent atoms:

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

Table S18 Anisotropic displacement parameters ($Å^2$x 10^3) for **2**•2DMSO. 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	51(1)	27(1)	46(1)	4(1)	16(1)	8(1)
O2	80(1)	46(1)	32(1)	-12(1)	18(1)	-4(1)
O3	40(1)	28(1)	38(1)	0(1)	0(1)	-10(1)
S1A	42(1)	28(1)	52(1)	0(1)	-11(1)	-6(1)
C16A	59(3)	63(4)	98(5)	30(4)	16(4)	-21(3)
C17A	175(10)	72(5)	48(4)	-9(3)	11(5)	53(6)
S1B	37(1)	27(1)	44(1)	-5(1)	-11(1)	-4(1)
C16B	50(2)	45(2)	112(4)	14(2)	11(3)	-18(2)
C17B	65(2)	37(2)	35(2)	-7(1)	-3(2)	10(2)
N1	19(1)	23(1)	20(1)	3(1)	6(1)	4(1)
N2	23(1)	20(1)	19(1)	1(1)	8(1)	0(1)
C1	32(1)	32(1)	33(1)	14(1)	18(1)	13(1)
C2	21(1)	32(1)	23(1)	10(1)	11(1)	8(1)
C3	25(1)	46(1)	27(1)	10(1)	3(1)	7(1)
C4	26(1)	39(1)	23(1)	0(1)	1(1)	-2(1)
C5	18(1)	26(1)	17(1)	1(1)	8(1)	0(1)
C6	19(1)	19(1)	18(1)	-2(1)	7(1)	-1(1)
C7	17(1)	18(1)	21(1)	1(1)	7(1)	3(1)
C8	24(1)	19(1)	29(1)	3(1)	9(1)	1(1)
C9	28(1)	27(1)	30(1)	10(1)	14(1)	4(1)
C10	24(1)	29(1)	21(1)	6(1)	10(1)	8(1)
C11	46(1)	41(1)	23(1)	4(1)	14(1)	11(1)
C12	31(1)	26(1)	25(1)	-8(1)	10(1)	-5(1)
C13	19(1)	19(1)	18(1)	-3(1)	8(1)	1(1)
C14	22(1)	23(1)	19(1)	4(1)	7(1)	5(1)
C15	24(1)	20(1)	22(1)	5(1)	11(1)	2(1)

Table S19 Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^2 x 10^3) for **2**•2DMSO.

	x	y	z	U(eq)
H16A	2534	6532	5328	111
H16B	2514	7982	5817	111
H16C	1890	7269	5271	111
H17A	1452	7662	6505	153
H17B	2062	8226	7178	153
H17C	1677	6985	7448	153
H16D	2620	7148	6044	107
H16E	2410	8326	6612	107
H16F	1924	7686	5785	107
H17D	1158	7256	6607	73
H17E	1598	7864	7485	73
H17F	1263	6390	7487	73
H1	50	7282	4107	36
H3	-322	4799	3221	40
H4	96	2336	3402	37
H8	632	-328	5640	29
H9	613	100	7183	32
H11	1029	2273	8340	43
H12A	1300	-158	4552	40
H12B	1117	829	3717	40
H12C	609	385	4191	40
H15	2222(7)	871(17)	5917(10)	23(4)
H14	1757(8)	3814(18)	4037(11)	29(4)
H2N	1465(8)	3270(20)	6422(11)	31(4)
H1N	1164(8)	4757(18)	5208(11)	30(4)

Table S20 Torsion angles [°] for **2**•2DMSO.

S1B-O3-S1A-C17A	-39.6(3)	C13-C6-C7-N2	54.24(15)
S1B-O3-S1A-C16A	-142.9(3)	C12-C6-C7-N2	172.14(12)
S1A-O3-S1B-C17B	134.2(2)	C5-C6-C7-C8	107.56(15)
S1A-O3-S1B-C16B	32.2(2)	C13-C6-C7-C8	-129.15(14)
C5-N1-C2-C3	0.17(15)	C12-C6-C7-C8	-11.24(18)
C5-N1-C2-C1	-178.28(12)	N2-C7-C8-C9	0.39(15)
O1-C1-C2-C3	-174.72(15)	C6-C7-C8-C9	-176.59(12)
O1-C1-C2-N1	3.3(2)	C7-C8-C9-C10	-0.10(15)
N1-C2-C3-C4	-0.30(16)	C7-N2-C10-C9	0.48(15)
C1-C2-C3-C4	177.98(14)	C7-N2-C10-C11	-178.11(13)
C2-C3-C4-C5	0.32(17)	C8-C9-C10-N2	-0.22(15)
C2-N1-C5-C4	0.04(15)	C8-C9-C10-C11	178.22(15)
C2-N1-C5-C6	-178.48(11)	N2-C10-C11-O2	0.1(3)
C3-C4-C5-N1	-0.22(16)	C9-C10-C11-O2	-178.18(16)
C3-C4-C5-C6	178.14(13)	C5-C6-C13-C15	160.94(12)
N1-C5-C6-C7	69.78(15)	C7-C6-C13-C15	39.38(16)
C4-C5-C6-C7	-108.37(15)	C12-C6-C13-C15	-79.66(14)
N1-C5-C6-C13	-53.35(15)	C5-C6-C13-C14	-24.48(16)
C4-C5-C6-C13	128.49(14)	C7-C6-C13-C14	-146.03(12)
N1-C5-C6-C12	-171.53(11)	C12-C6-C13-C14	94.92(14)
C4-C5-C6-C12	10.32(18)	C15-C13-C14-C15#1	0.2(2)
C10-N2-C7-C8	-0.54(15)	C6-C13-C14-C15#1	-174.44(12)
C10-N2-C7-C6	176.73(11)	C14-C13-C15-C14#1	-0.2(2)
C5-C6-C7-N2	-69.05(15)	C6-C13-C15-C14#1	174.54(12)

Symmetry transformations used to generate equivalent atoms:

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

Table S21 Hydrogen bonds for **2•**2DMSO [Å and °].

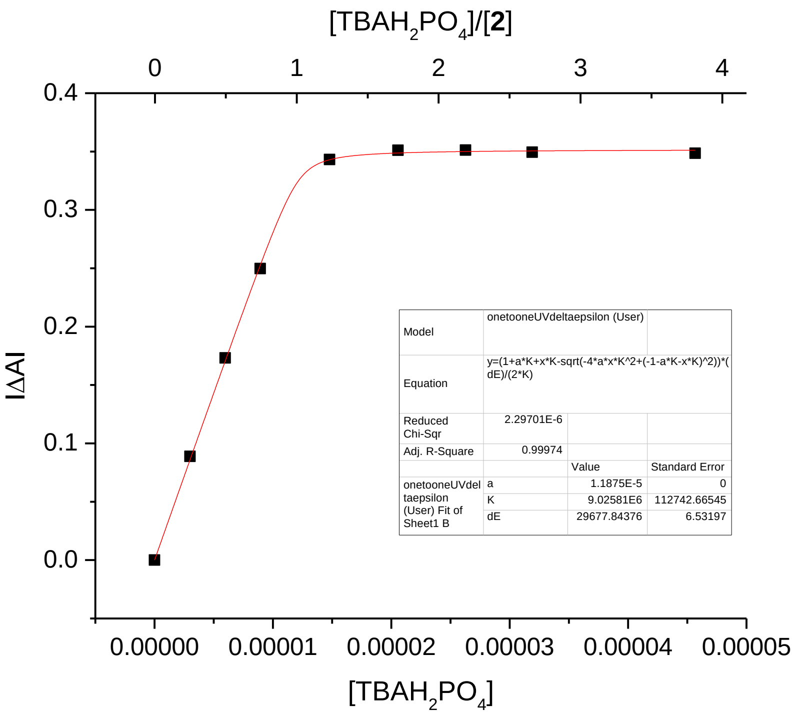
D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
N2-H2N...O3	0.883(19)	1.879(19)	2.7552(16)	171.1(17)
N1-H1N...O3	0.894(18)	1.973(18)	2.8504(16)	166.5(16)

Symmetry transformations used to generate equivalent atoms:

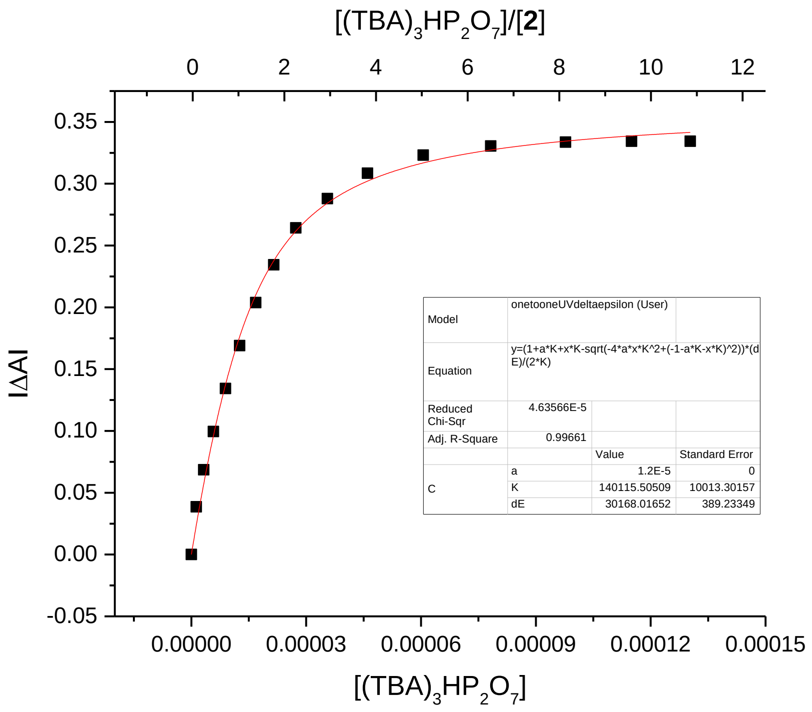
#1 -x+1/2,-y+1/2,-z+1

Anion Binding Fitting Curves for Compounds 2, 4, and 6

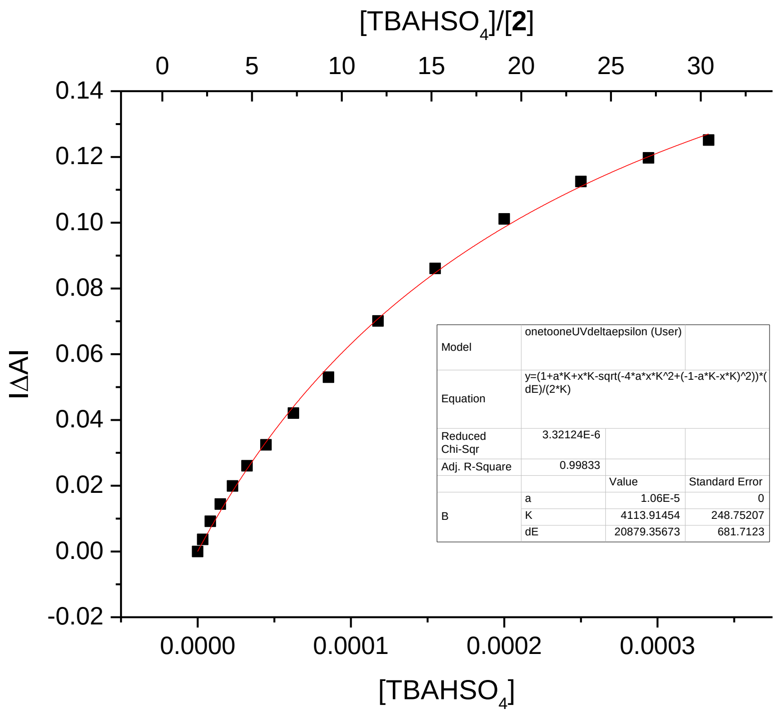
Table S22 Binding curve fittings for compound **2**, **4**, and **6** with $TBAH_2PO_4$, $(TBA)_3HP_2O_7$, $TBAHSO_4$, $TBAC_6H_5CO_2$ in $CHCl_3$ as determined by UV-Vis spectroscopy. Binding affinities (in unit M^{-1}) obtained here by non-linear curve fitting are listed in Table 1.



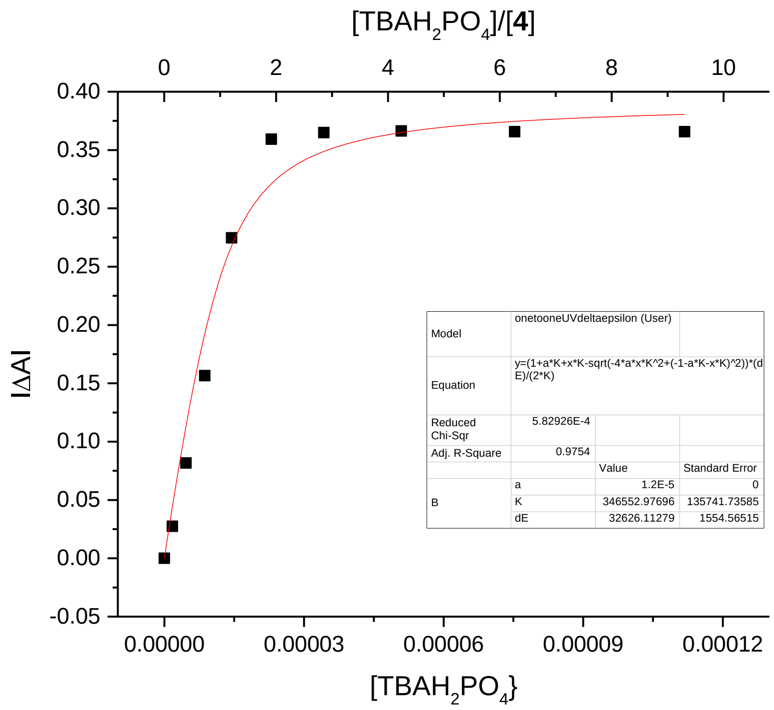
Model	onetooneUVdeltaepsilon (User)		
Equation	y=(1+a*K+x*K-sqrt(-4*a*x*K^2+(-1-a*K-x*K)^2))*(dE)/(2*K)		
Reduced Chi-Sqr	2.29701E-6		
Adj. R-Square	0.99974		
		Value	Standard Error
onetooneUVdeltaepsilon (User) Fit of Sheet1 B	a	1.1875E-5	0
	K	9.02581E6	112742.66545
	dE	29677.84376	6.53197



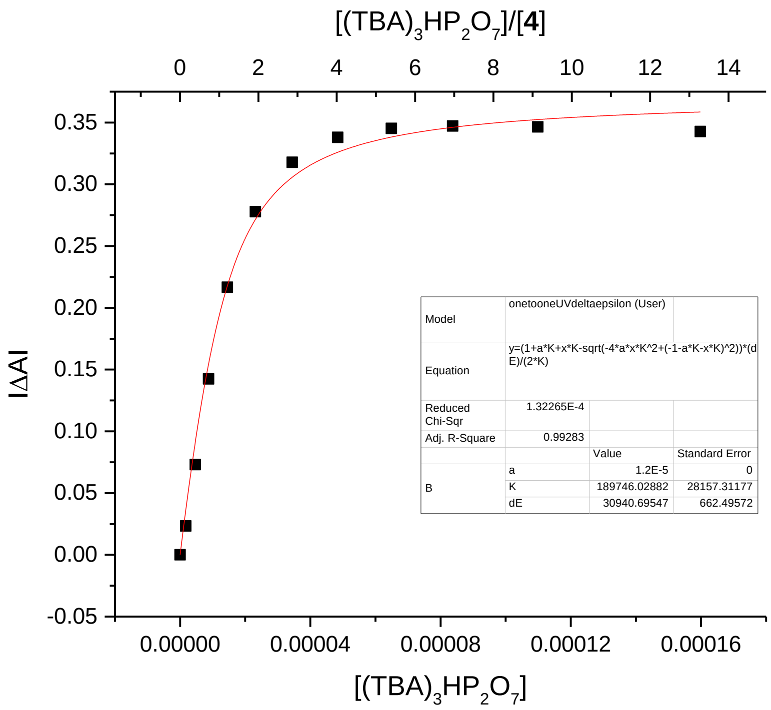
Model	onetooneUVdeltaepsilon (User)		
Equation	y=(1+a*K+x*K-sqrt(-4*a*x*K^2+(-1-a*K-x*K)^2))*(dE)/(2*K)		
Reduced Chi-Sqr	4.63566E-5		
Adj. R-Square	0.99661		
		Value	Standard Error
C	a	1.2E-5	0
	K	140115.50509	10013.30157
	dE	30168.01652	389.23349



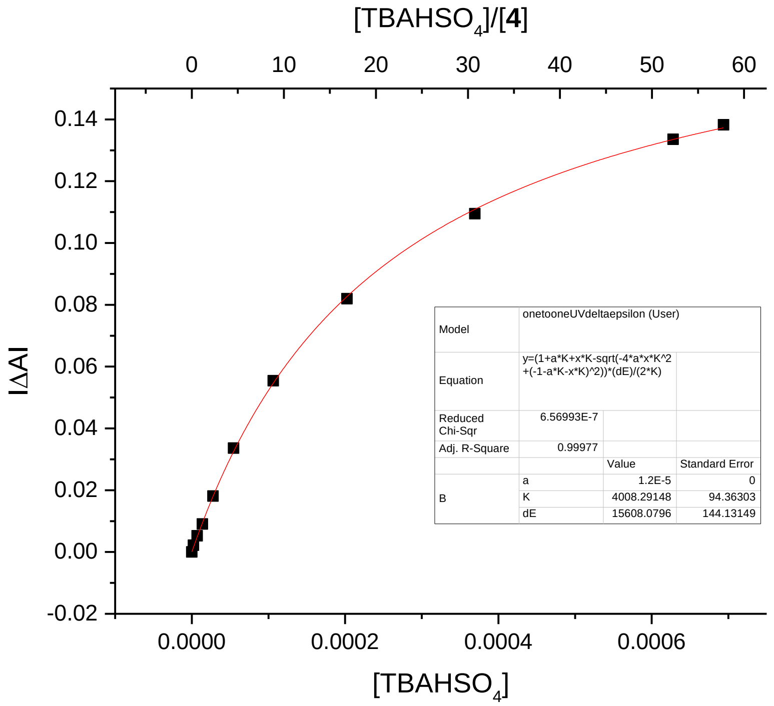
Model	onetooneUVdeltaepsilon (User)		
Equation	y=(1+a*K+x*K-sqrt(-4*a*x*K^2+(-1-a*K-x*K)^2))*(dE)/(2*K)		
Reduced Chi-Sqr	3.32124E-6		
Adj. R-Square	0.99833		
		Value	Standard Error
B	a	1.06E-5	0
	K	4113.91454	248.75207
	dE	20879.35673	681.7123



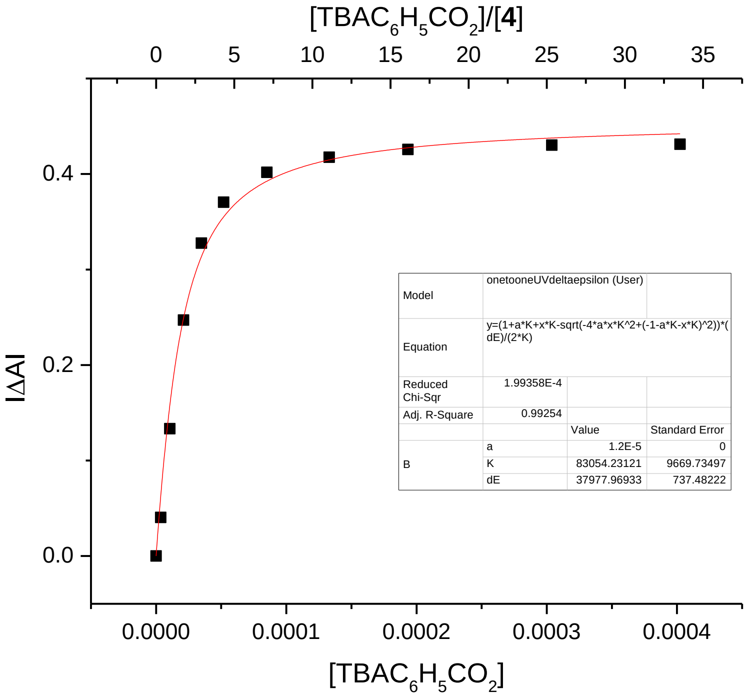
Model	onetooneUVdeltaepsilon (User)		
Equation	y=(1+a*K+x*K-sqrt(-4*a*x*K^2+(-1-a*K-x*K)^2))*(dE)/(2*K)		
Reduced Chi-Sqr	5.82926E-4		
Adj. R-Square	0.9754		
		Value	Standard Error
B	a	1.2E-5	0
	K	346552.97696	135741.73585
	dE	32626.11279	1554.56515



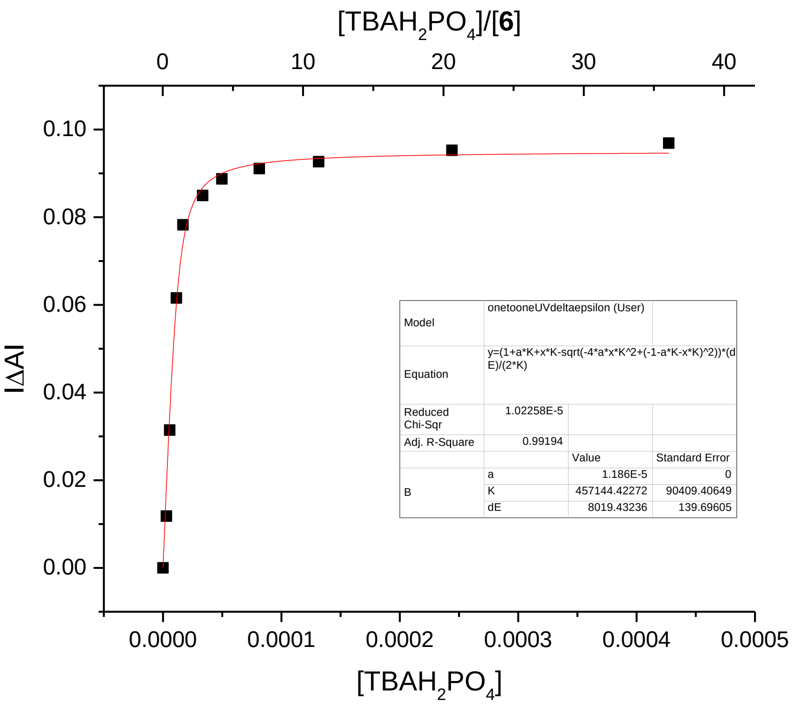
Model	onetooneUVdeltaepsilon (User)		
Equation	y=(1+a*K+x*K-sqrt(-4*a*x*K^2+(-1-a*K-x*K)^2))*(dE)/(2*K)		
Reduced Chi-Sqr	1.32265E-4		
Adj. R-Square	0.99283		
		Value	Standard Error
B	a	1.2E-5	0
	K	189746.02882	28157.31177
	dE	30940.69547	662.49572



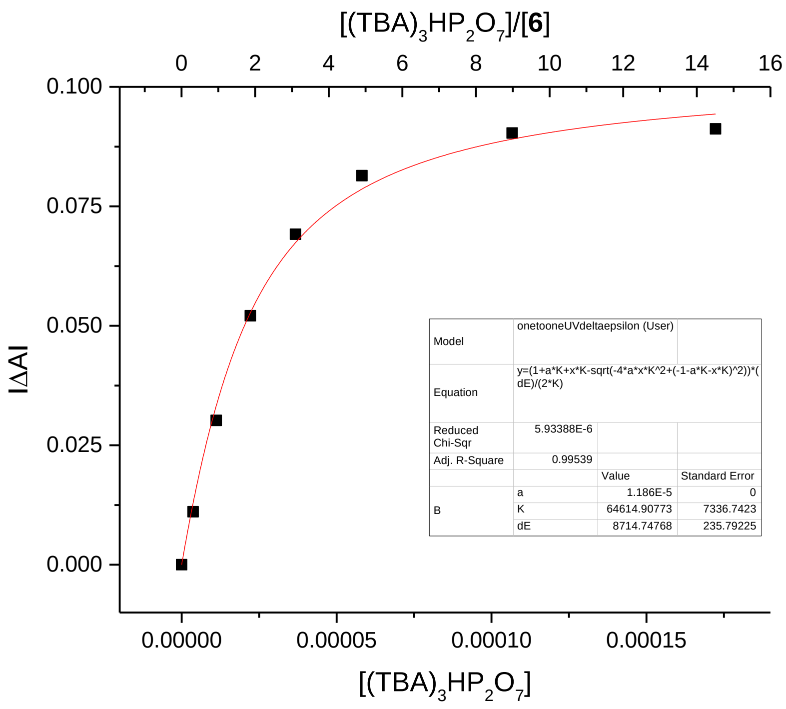
Model	onetooneUVdeltaepsilon (User)		
Equation	y=(1+a*K+x*K-sqrt(-4*a*x*K^2+(-1-a*K-x*K)^2))*(dE)/(2*K)		
Reduced Chi-Sqr	6.56993E-7		
Adj. R-Square	0.99977		
		Value	Standard Error
B	a	1.2E-5	0
	K	4008.29148	94.36303
	dE	15608.0796	144.13149



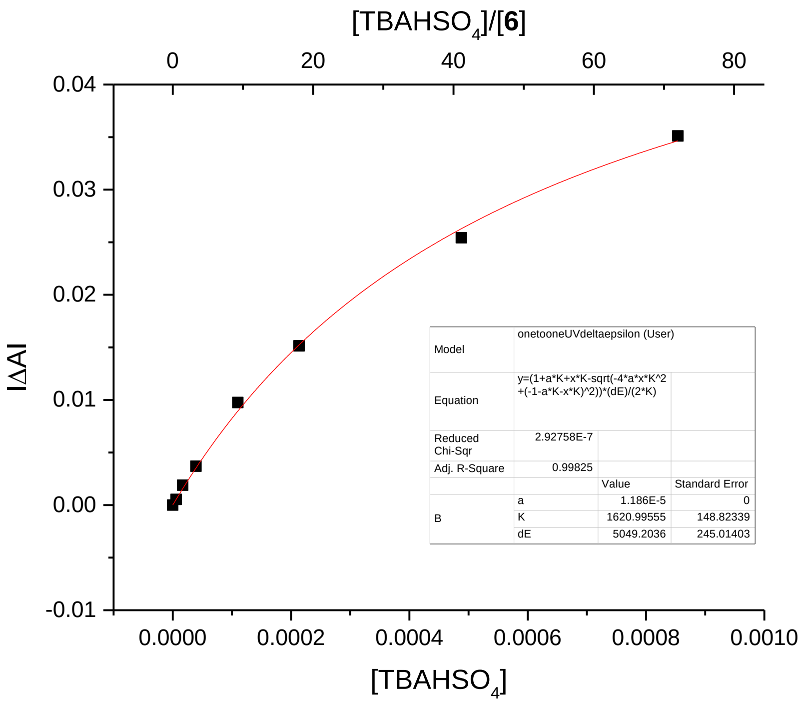
Model	onetooneUVdeltaepsilon (User)		
Equation	y=(1+a*K+x*K-sqrt(-4*a*x*K^2+(-1-a*K-x*K)^2))*(dE)/(2*K)		
Reduced Chi-Sqr	1.99358E-4		
Adj. R-Square	0.99254		
		Value	Standard Error
B	a	1.2E-5	0
	K	83054.23121	9669.73497
	dE	37977.96933	737.48222



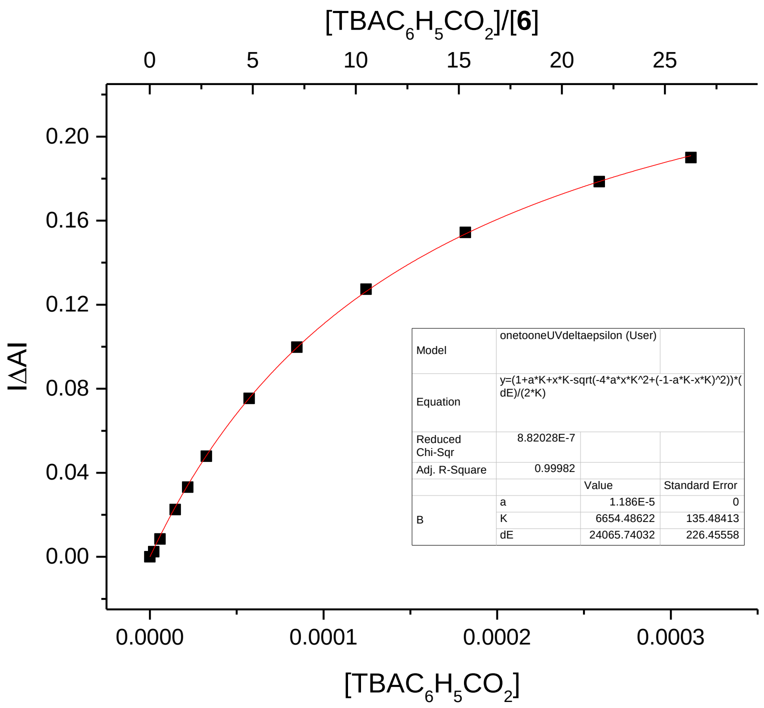
Model	onetooneUVdeltaepsilon (User)		
Equation	y=(1+a*K+x*K-sqrt(-4*a*x*K^2+(-1-a*K-x*K)^2))*(dE)/(2*K)		
Reduced Chi-Sqr	1.02258E-5		
Adj. R-Square	0.99194		
		Value	Standard Error
B	a	1.186E-5	0
	K	457144.42272	90409.40649
	dE	8019.43236	139.69605



Model	onetooneUVdeltaepsilon (User)		
Equation	y=(1+a*K+x*K-sqrt(-4*a*x*K^2+(-1-a*K-x*K)^2))*(dE)/(2*K)		
Reduced Chi-Sqr	5.93388E-6		
Adj. R-Square	0.99539		
		Value	Standard Error
B	a	1.186E-5	0
	K	64614.90773	7336.7423
	dE	8714.74768	235.79225



Model	onetooneUVdeltaepsilon (User)		
Equation	y=(1+a*K+x*K-sqrt(-4*a*x*K^2+(-1-a*K-x*K)^2))*(dE)/(2*K)		
Reduced Chi-Sqr	2.92758E-7		
Adj. R-Square	0.99825		
		Value	Standard Error
B	a	1.186E-5	0
	K	1620.99555	148.82339
	dE	5049.2036	245.01403



Model	onetooneUVdeltaepsilon (User)		
Equation	y=(1+a*K+x*K-sqrt(-4*a*x*K^2+(-1-a*K-x*K)^2))*(dE)/(2*K)		
Reduced Chi-Sqr	8.82028E-7		
Adj. R-Square	0.99982		
		Value	Standard Error
B	a	1.186E-5	0
	K	6654.48622	135.48413
	dE	24065.74032	226.45558

NMR Spectral Data for Compounds 1-8

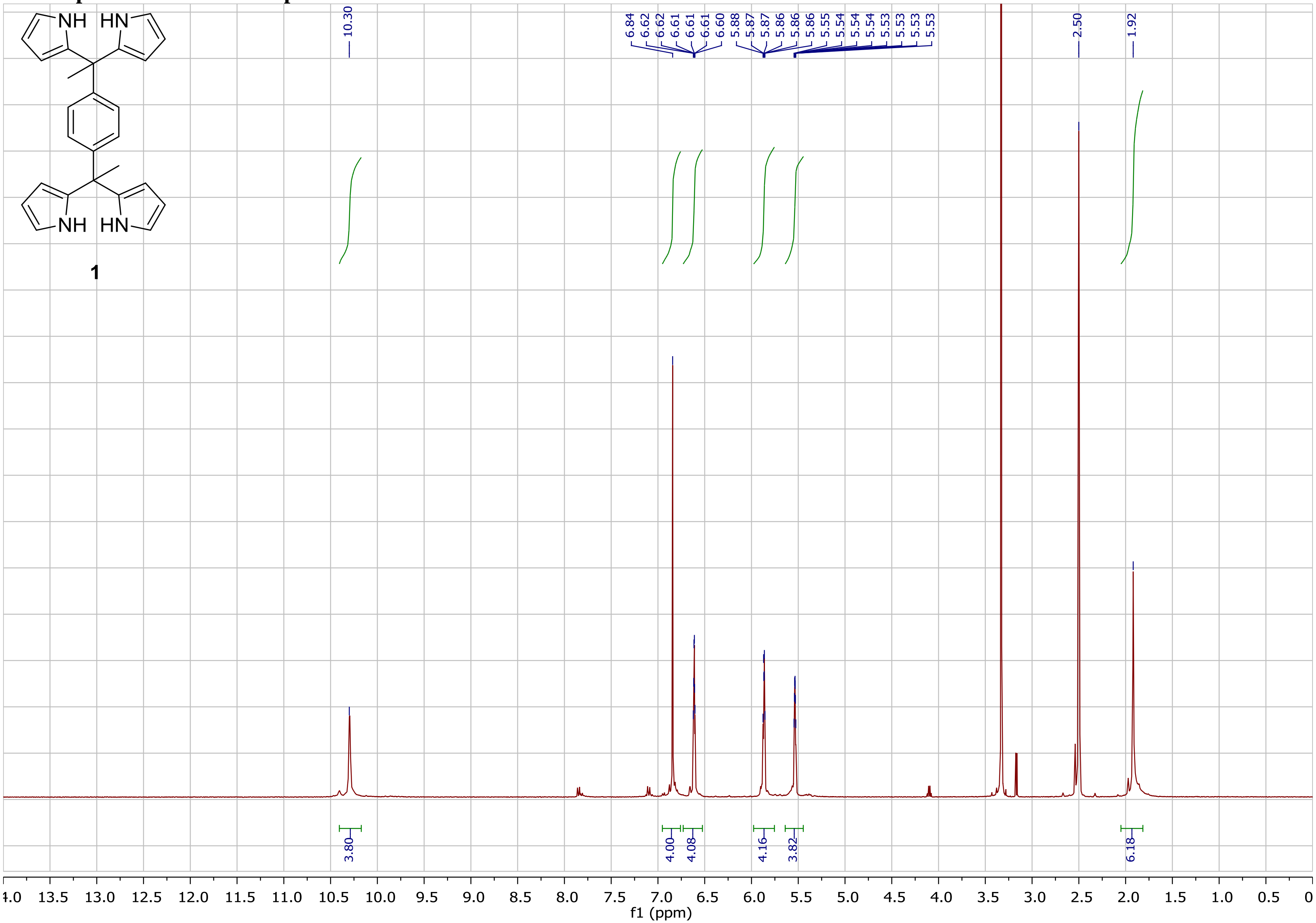
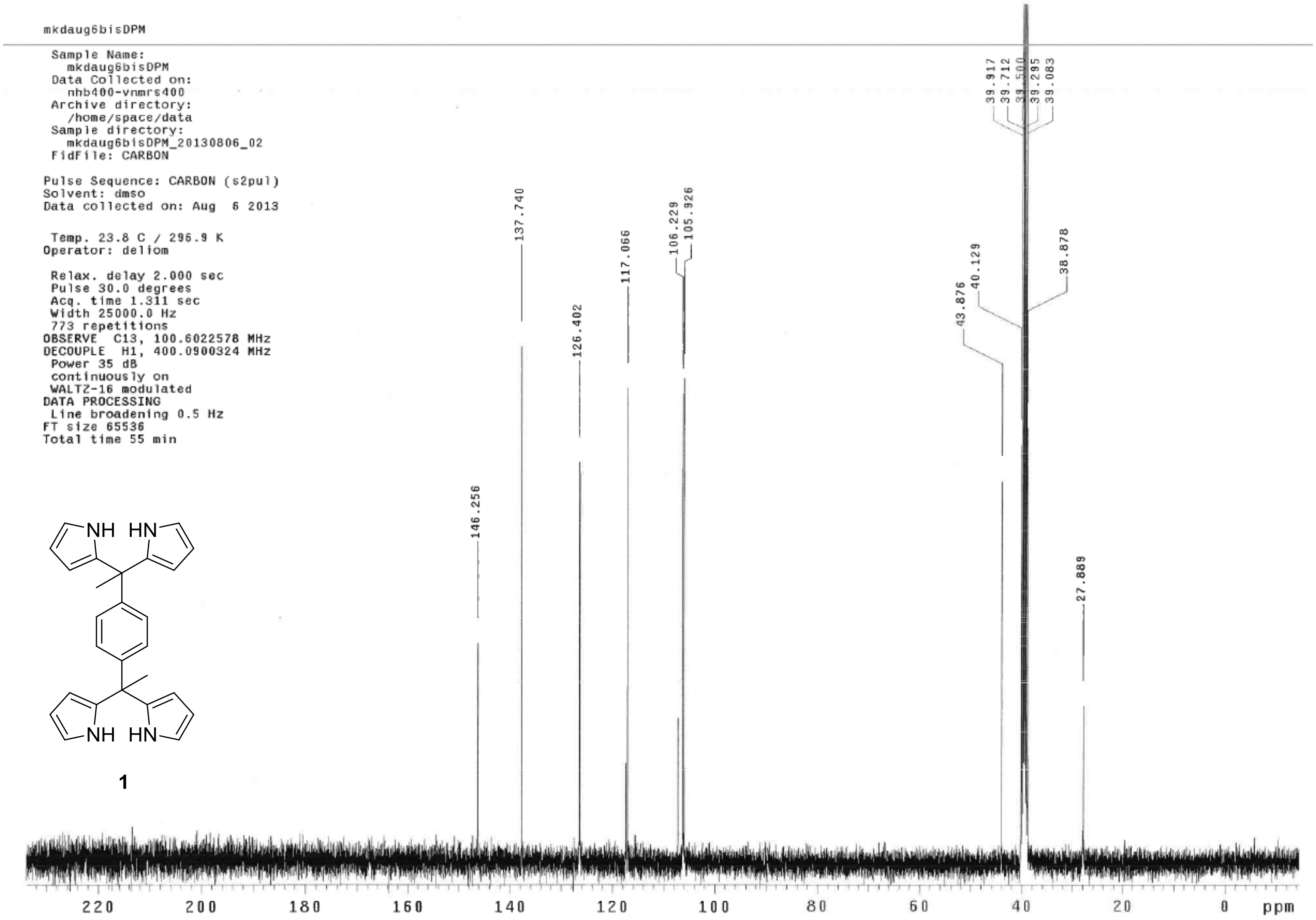


Figure S20 ^{1}H NMR (400 MHz) spectrum of **1** in DMSO- d_6.



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mkdaug6bisDPM

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   mkdaug6bisDPM
 Data Collected on:
   nhb400-vnmrs400
 Archive directory:
   /home/space/data
 Sample directory:
   mkdaug6bisDPM_20130806_02
 FidFile: CARBON

Pulse Sequence: CARBON (s2pul)
Solvent: dmso
Data collected on: Aug  6 2013

 Temp. 23.8 C / 296.9 K
Operator: deliom

 Relax. delay 2.000 sec
 Pulse 30.0 degrees
 Acq. time 1.311 sec
 Width 25000.0 Hz
 773 repetitions
OBSERVE  C13, 100.6022578 MHz
DECOUPLE  H1, 400.0900324 MHz
 Power 35 dB
 continuously on
 WALTZ-16 modulated
DATA PROCESSING
 Line broadening 0.5 Hz
FT size 65536
Total time 55 min
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Figure S21 ^{13}C NMR (100 MHz) spectrum of **1** in DMSO-d_6.

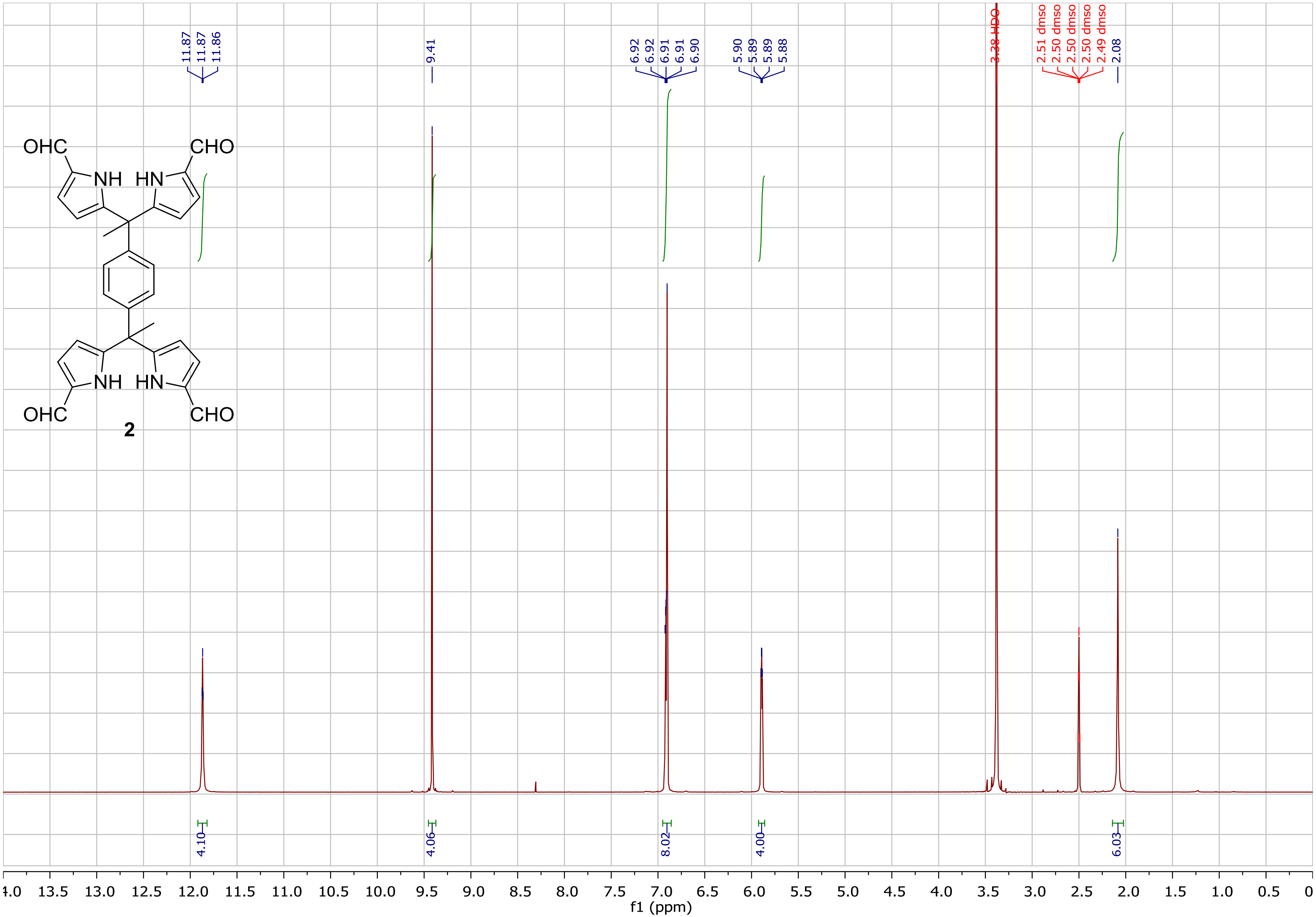

Figure S22 ^{1}H NMR (400 MHz) spectrum of **2** in DMSO- d_6.

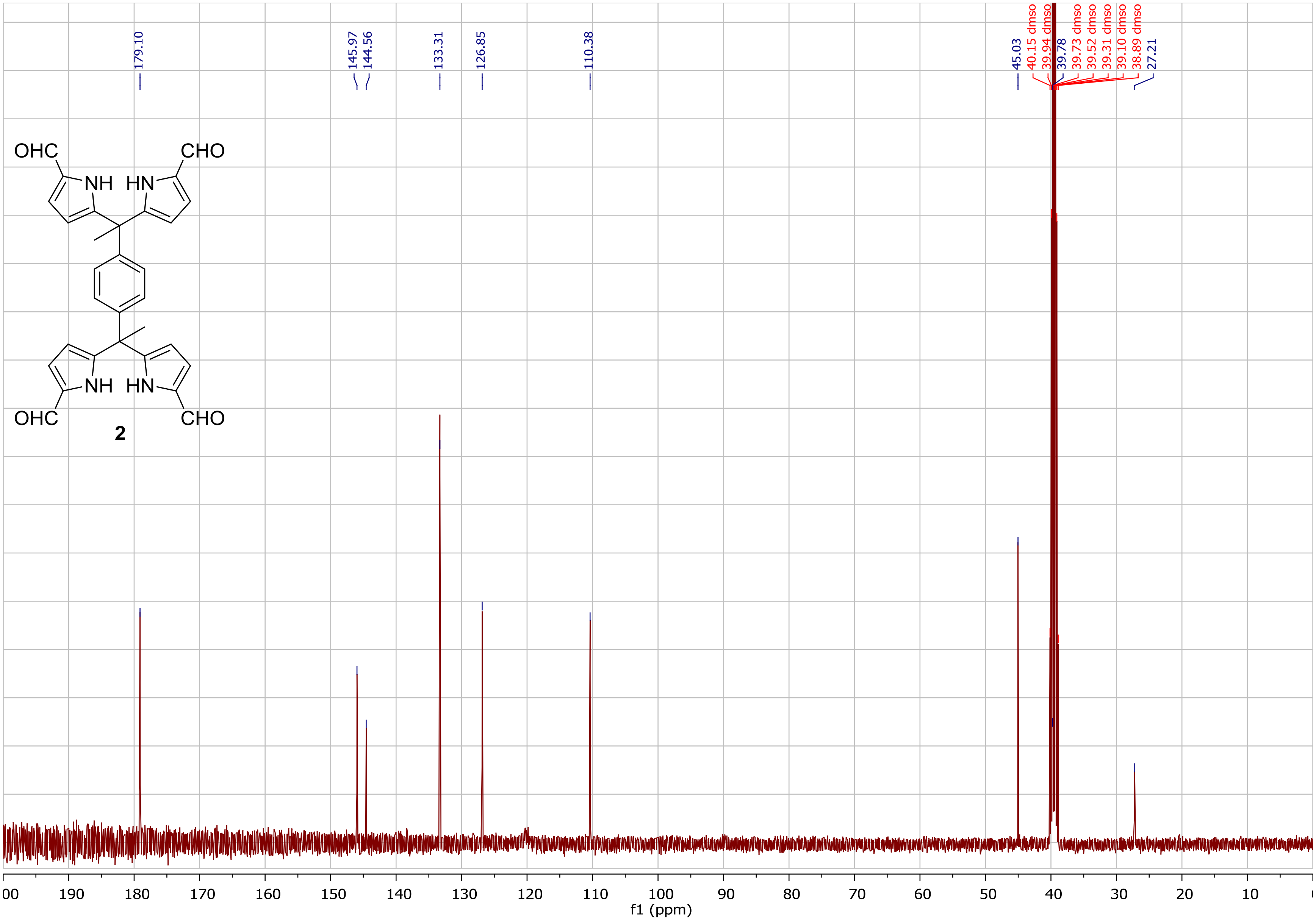

Figure S23 ^{13}C NMR (100 MHz) spectrum of **2** in DMSO- d_6.

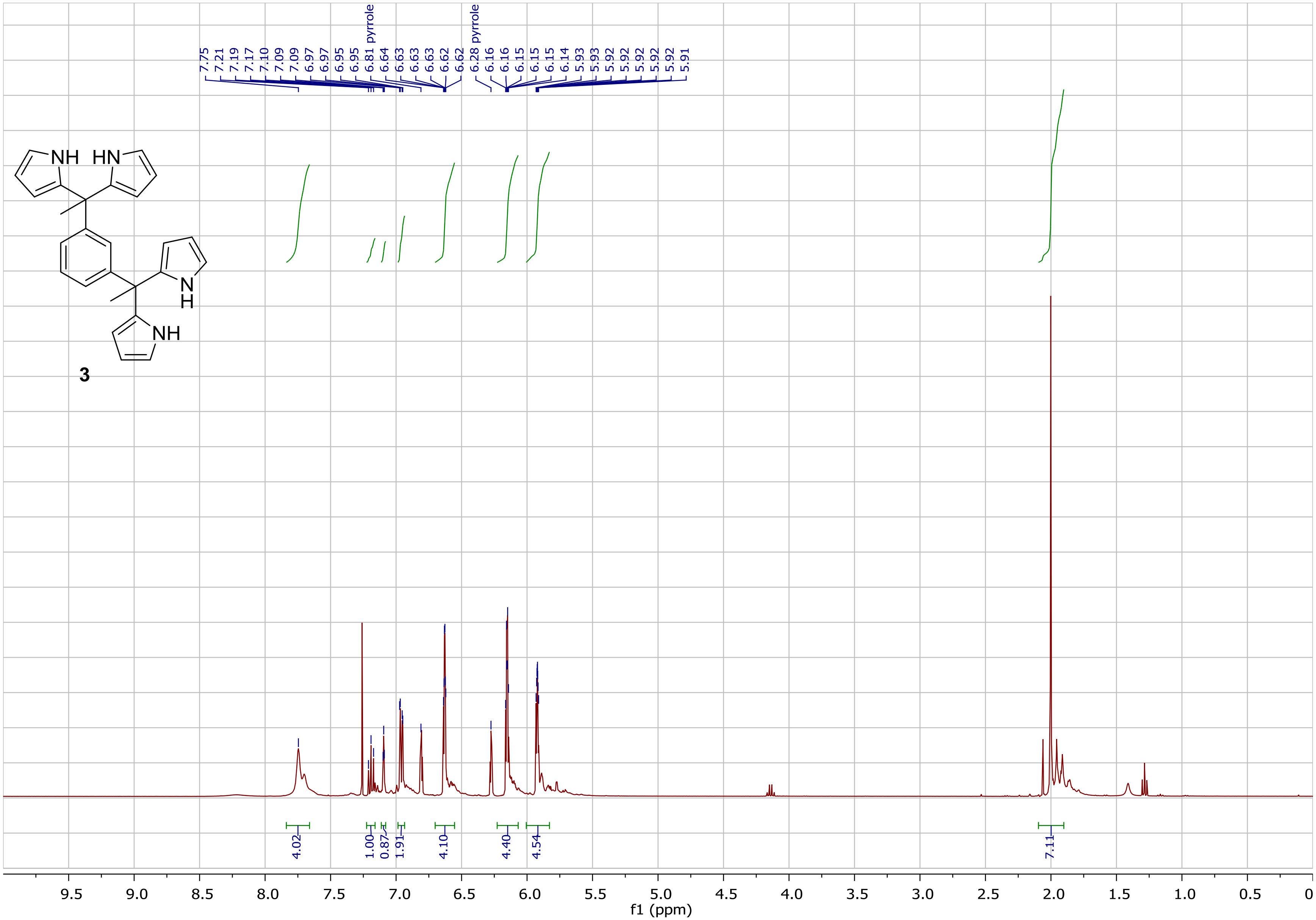

Figure S24 ^{1}H NMR (400 MHz) spectrum of **3** in $CDCl_3$.

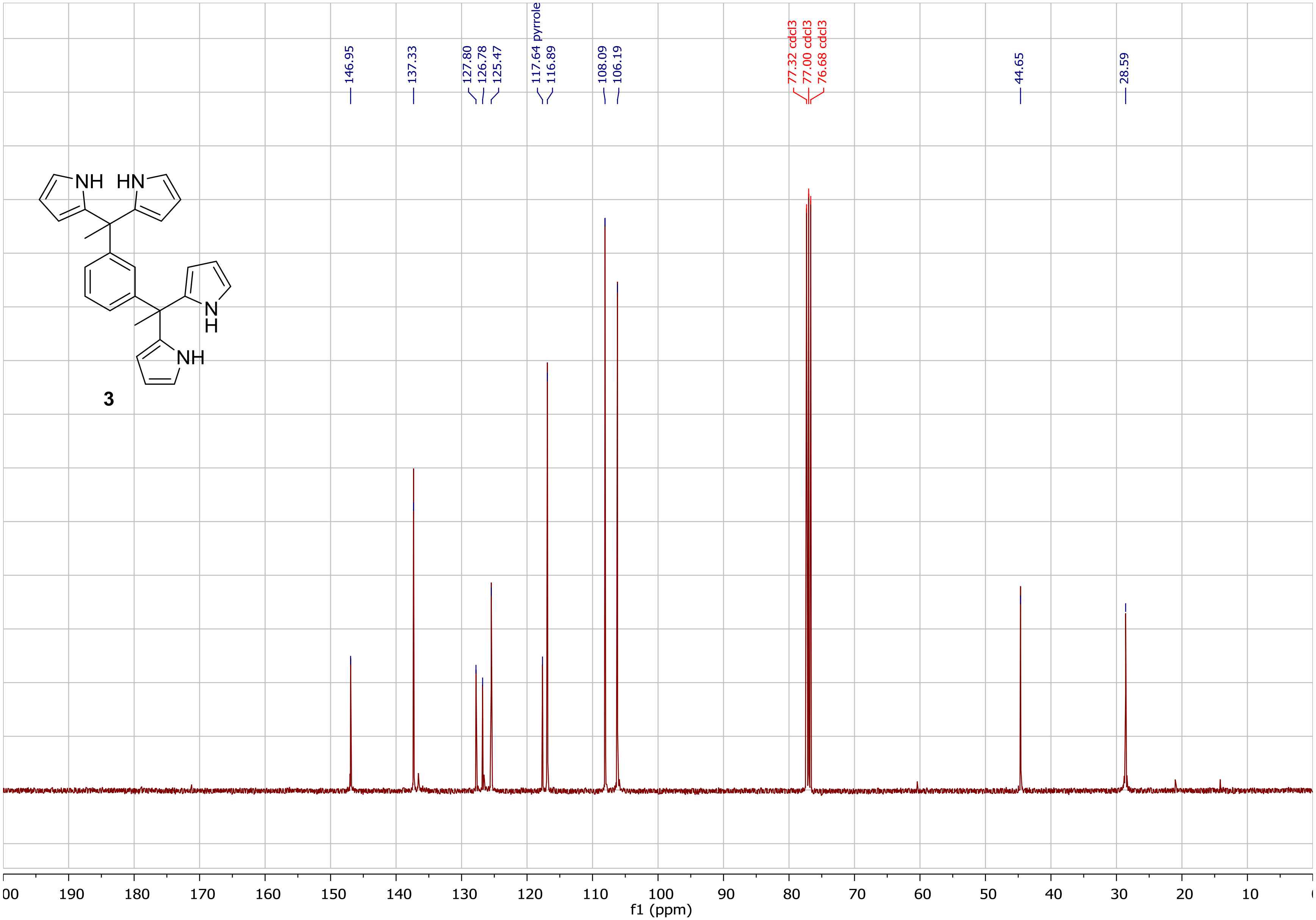

Figure S25 ^{13}C NMR (100 MHz) spectrum of **3** in $CDCl_3$.

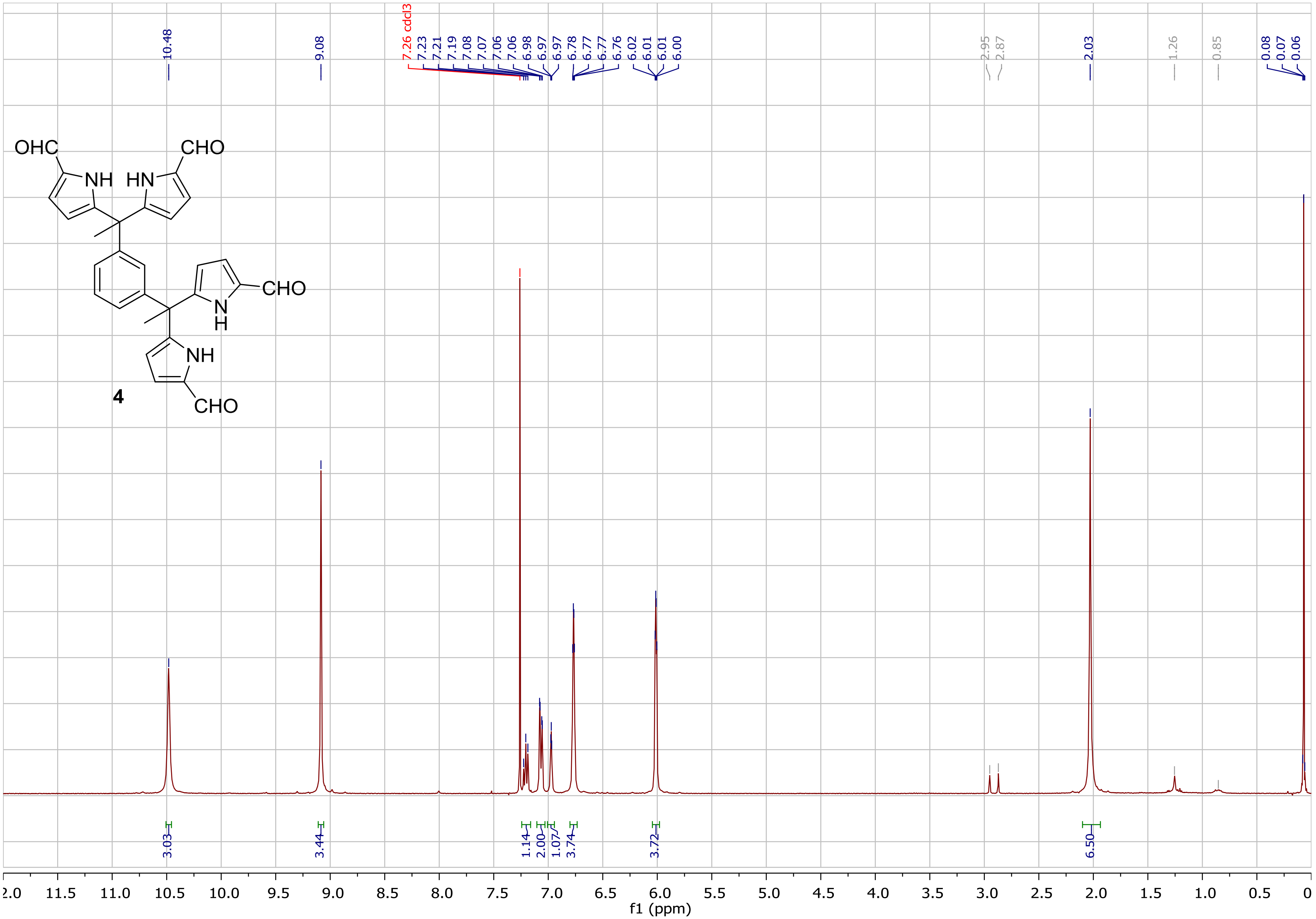

Figure S26 ^{1}H NMR (400 MHz) spectrum of **4** in CDCl$_3$.

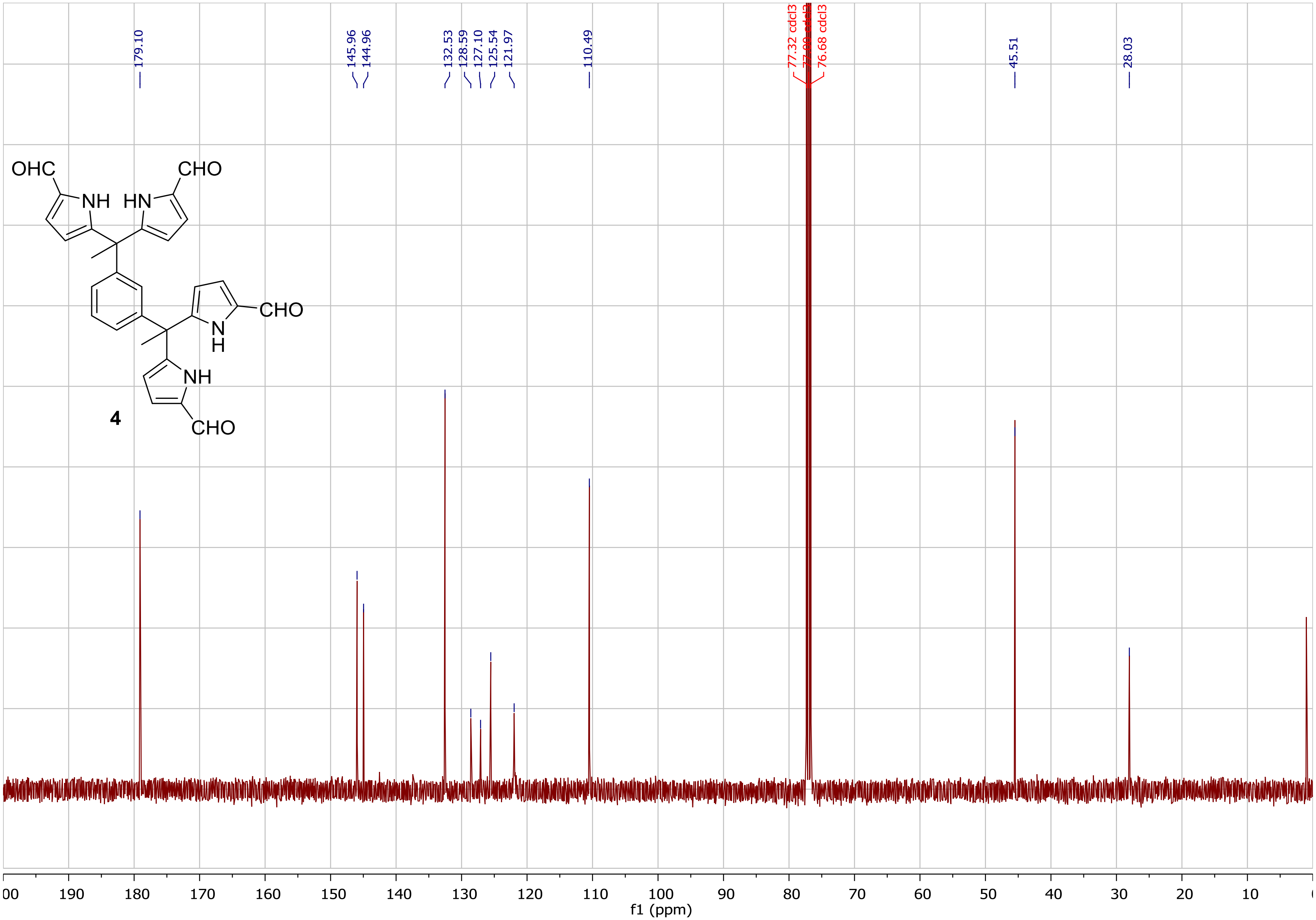

Figure S27 ^{13}C NMR (100 MHz) spectrum of **4** in CDCl$_3$.

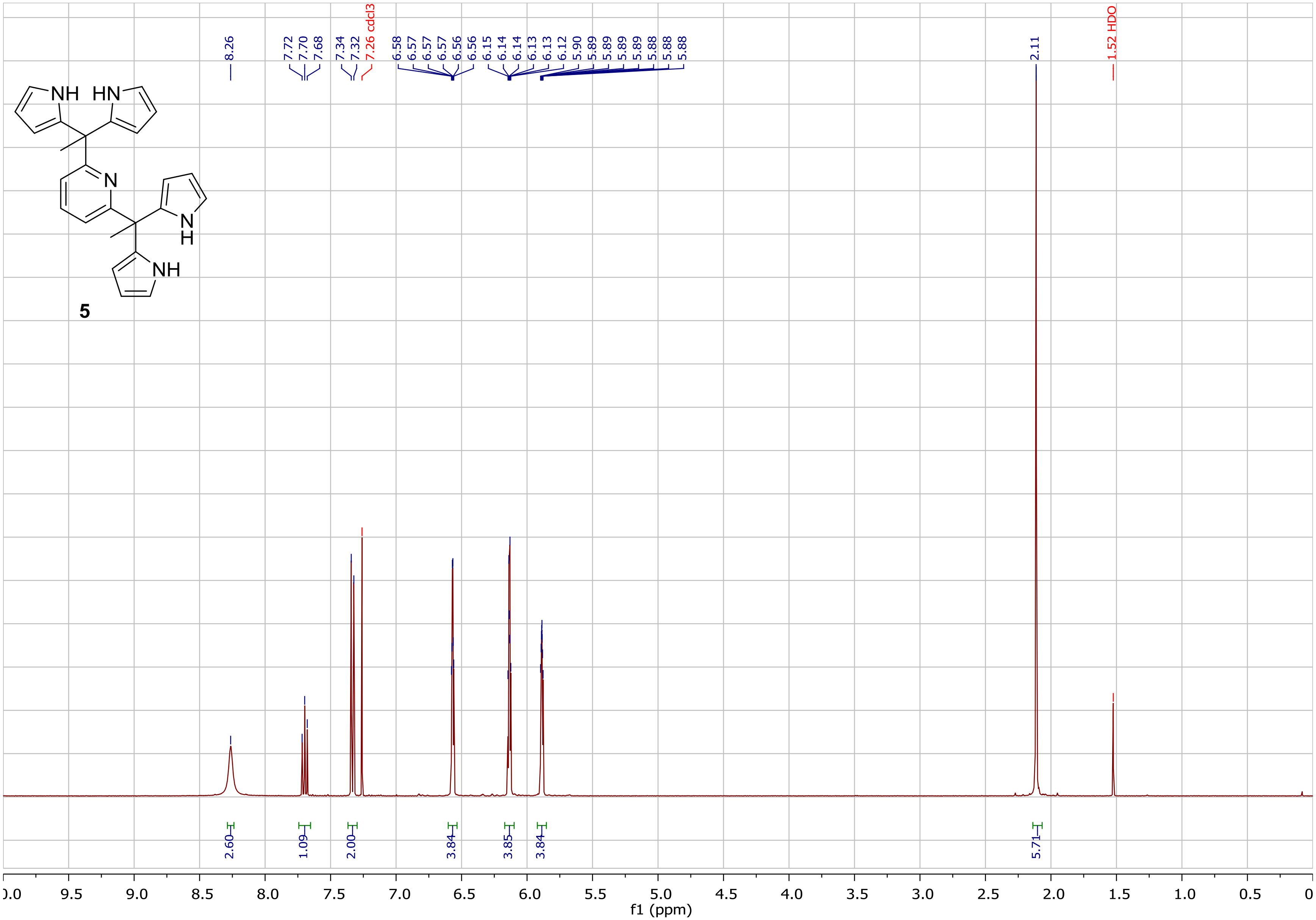

Figure S28 ^{1}H NMR (400 MHz) spectrum of **5** in $CDCl_3$.

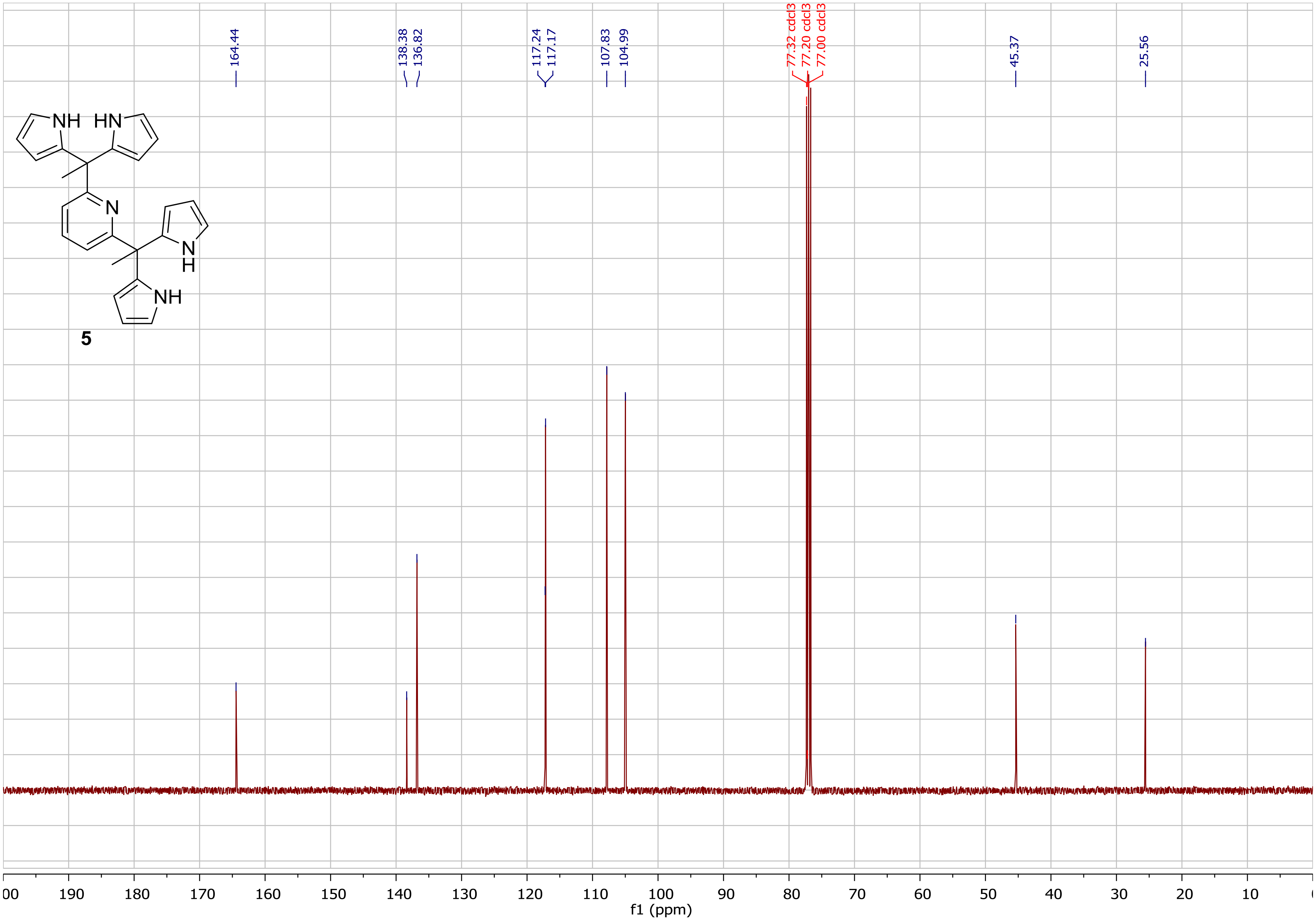

Figure S29 ^{13}C NMR (100 MHz) spectrum of **5** in CDCl$_3$.

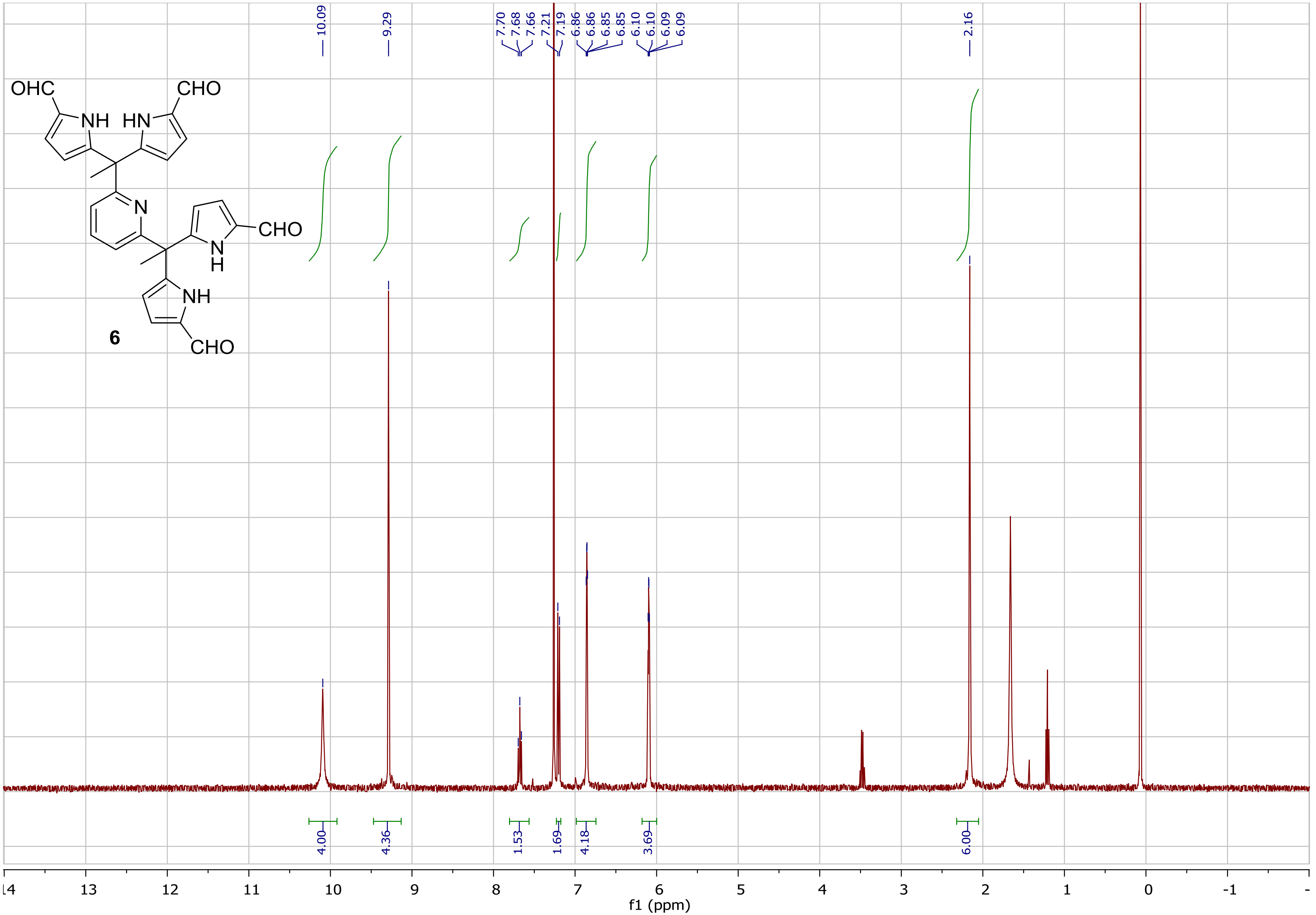

Figure S30 ^{1}H NMR (400 MHz) spectrum of **6** in CDCl$_3$.

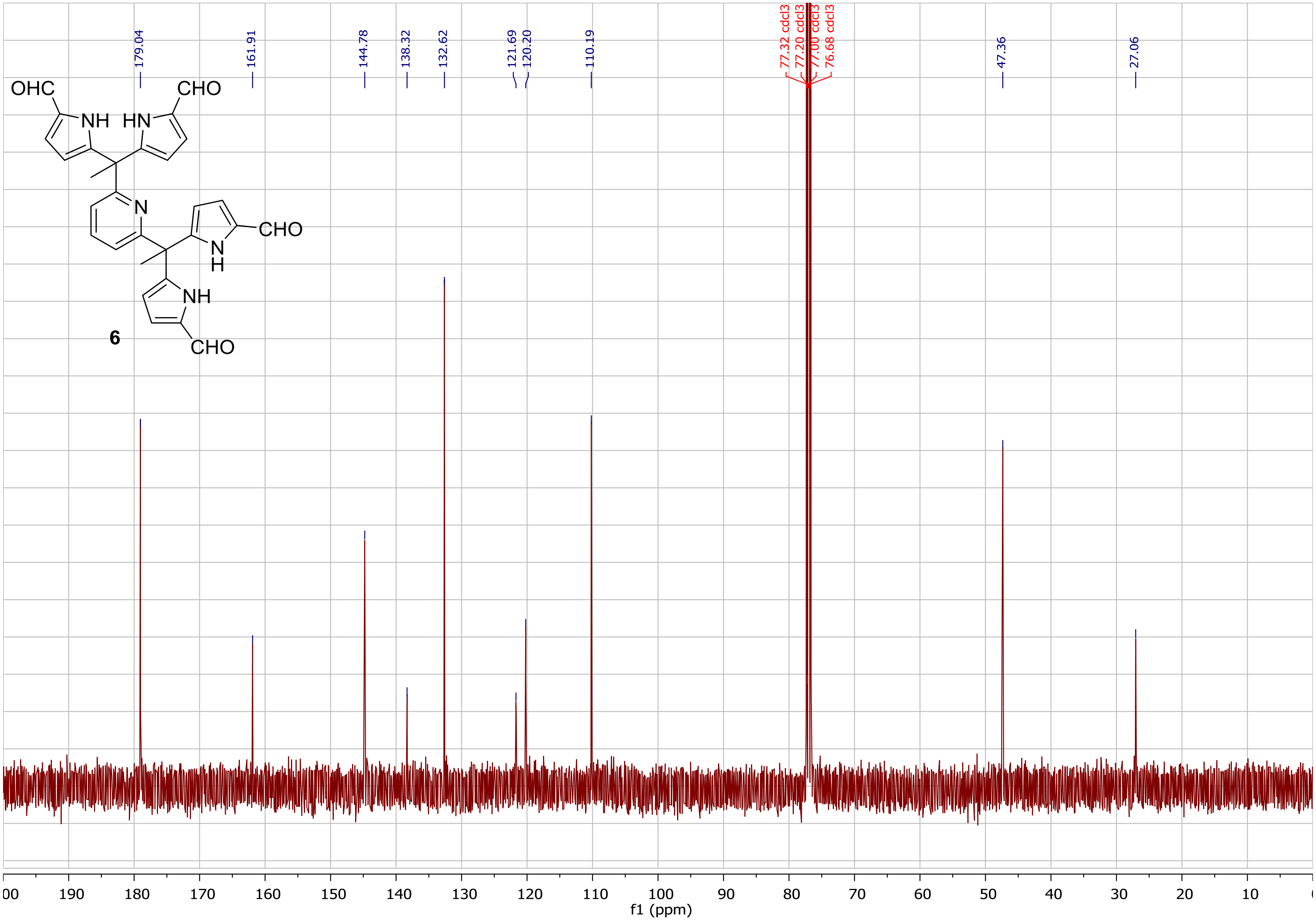

Figure S31 Figure S26 ^{13}C NMR (100 MHz) spectrum of **6** in CDCl$_3$.

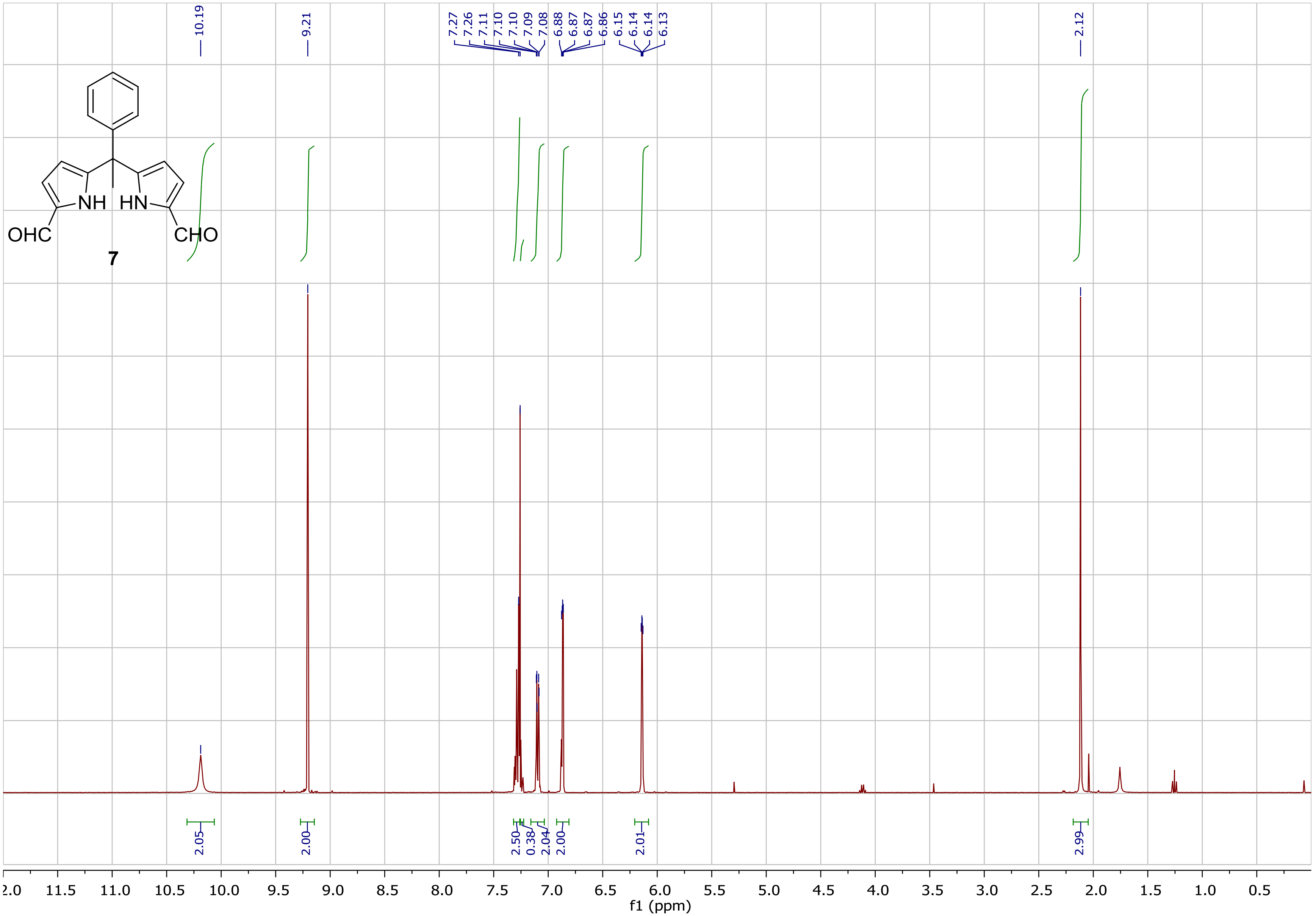

Figure S32 ^{1}H NMR (400 MHz) spectrum of **7** in $CDCl_3$.

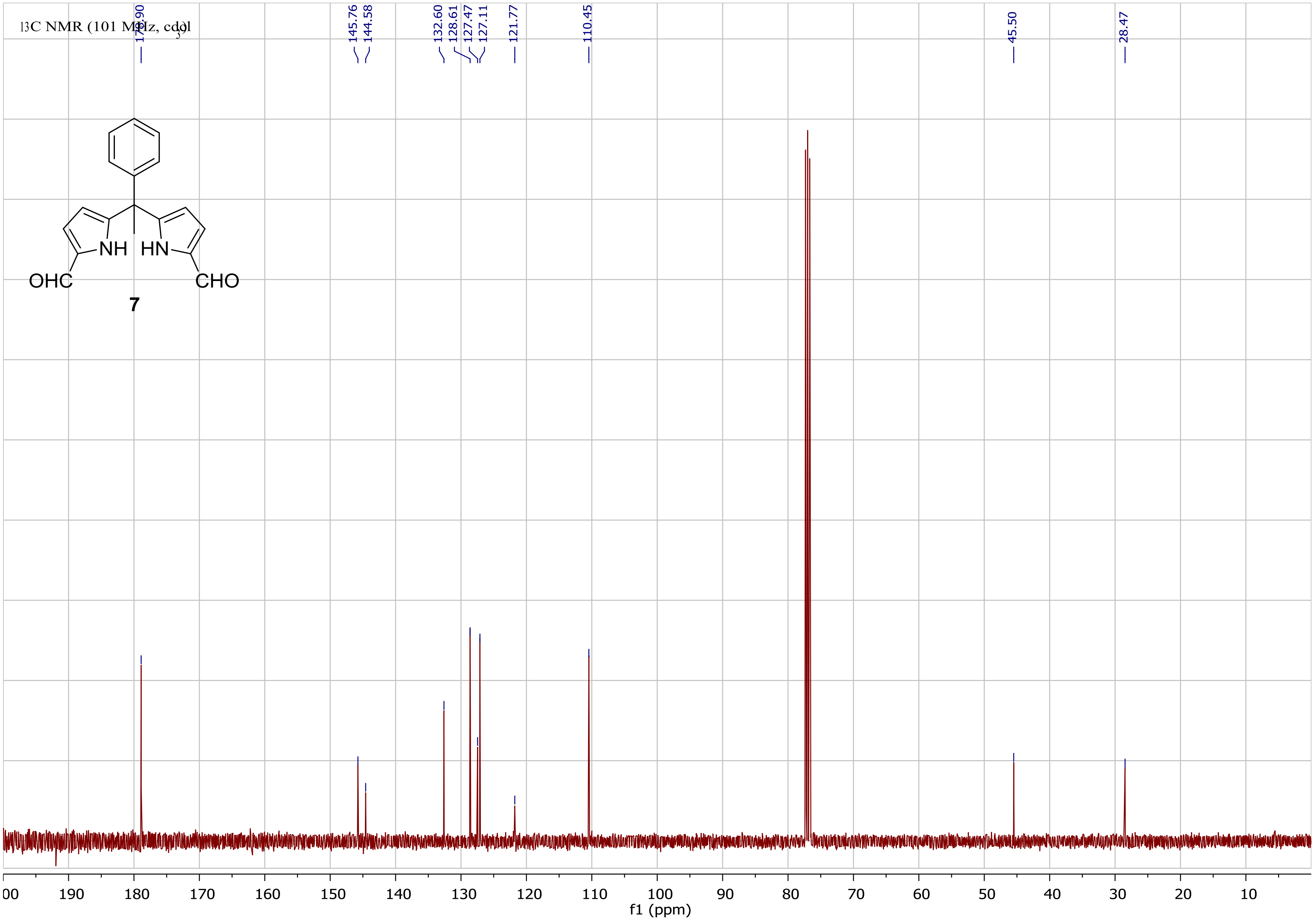

Figure S33 ^{13}C NMR (100 MHz) spectrum of **7** in $CDCl_3$.

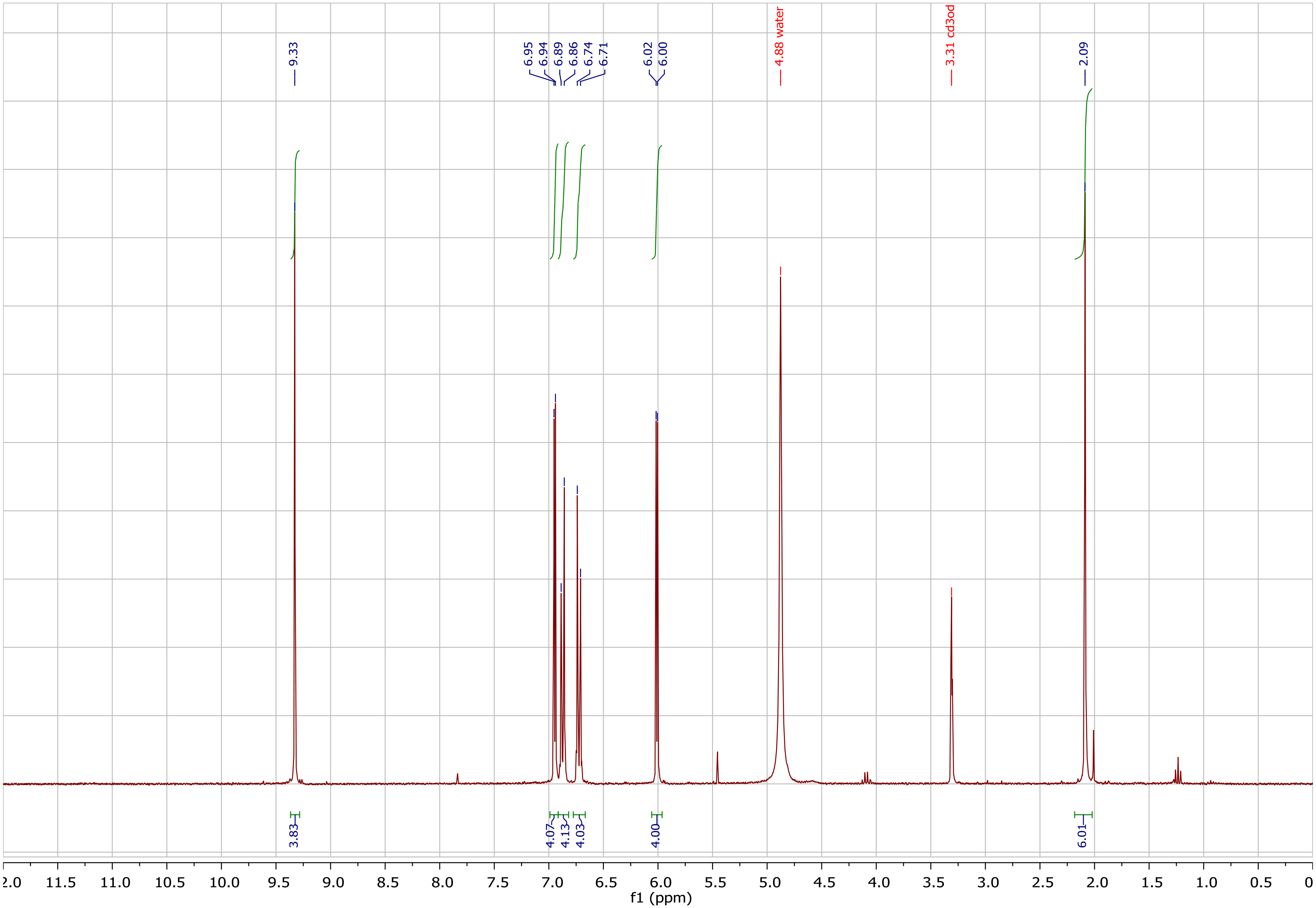

Figure S34 ^{1}H NMR (300 MHz) spectrum of **7-OH** in CD_3OD.

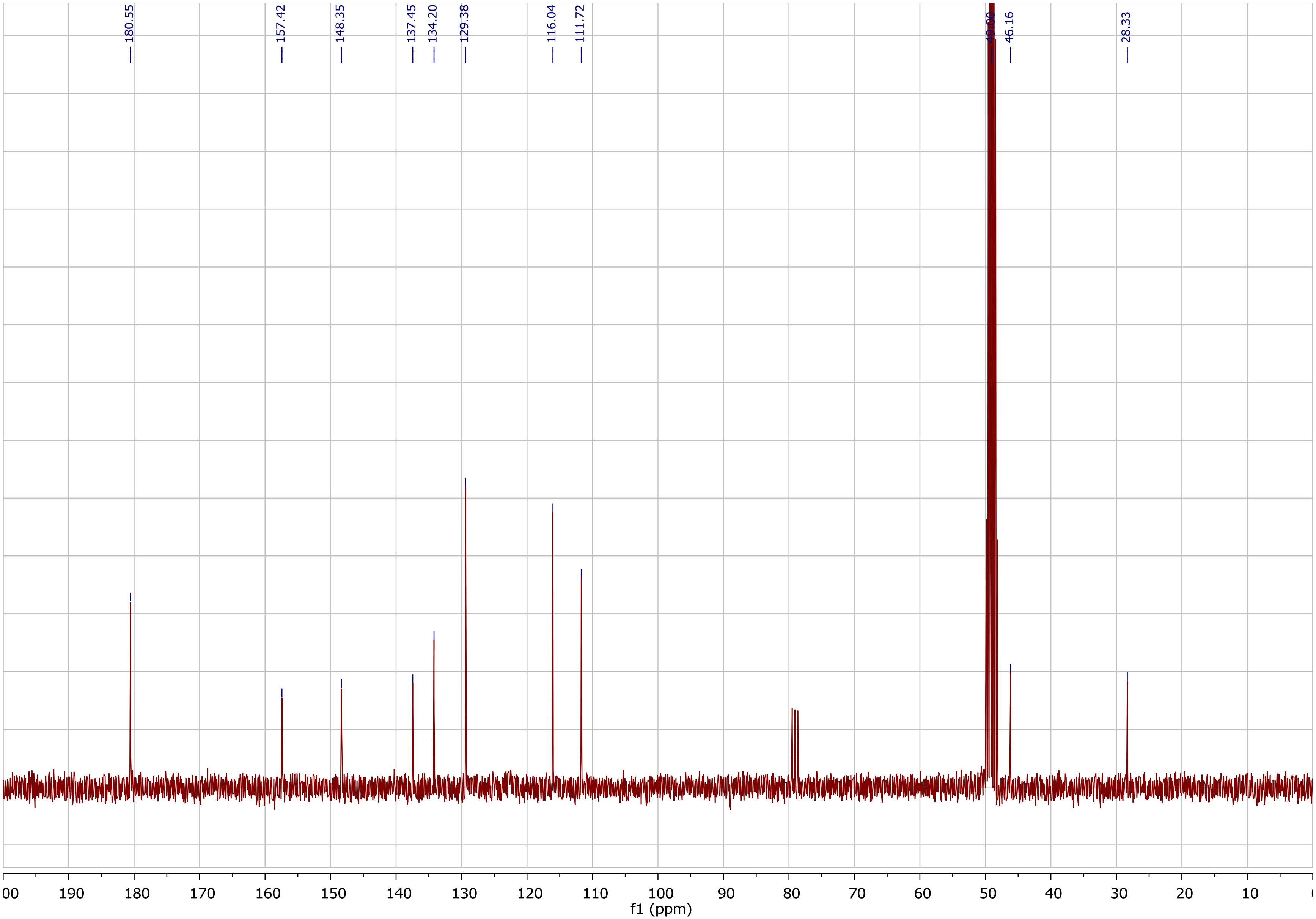

Figure S35 ^{13}C NMR (75 MHz) spectrum of **7-OH** in CD_3OD.

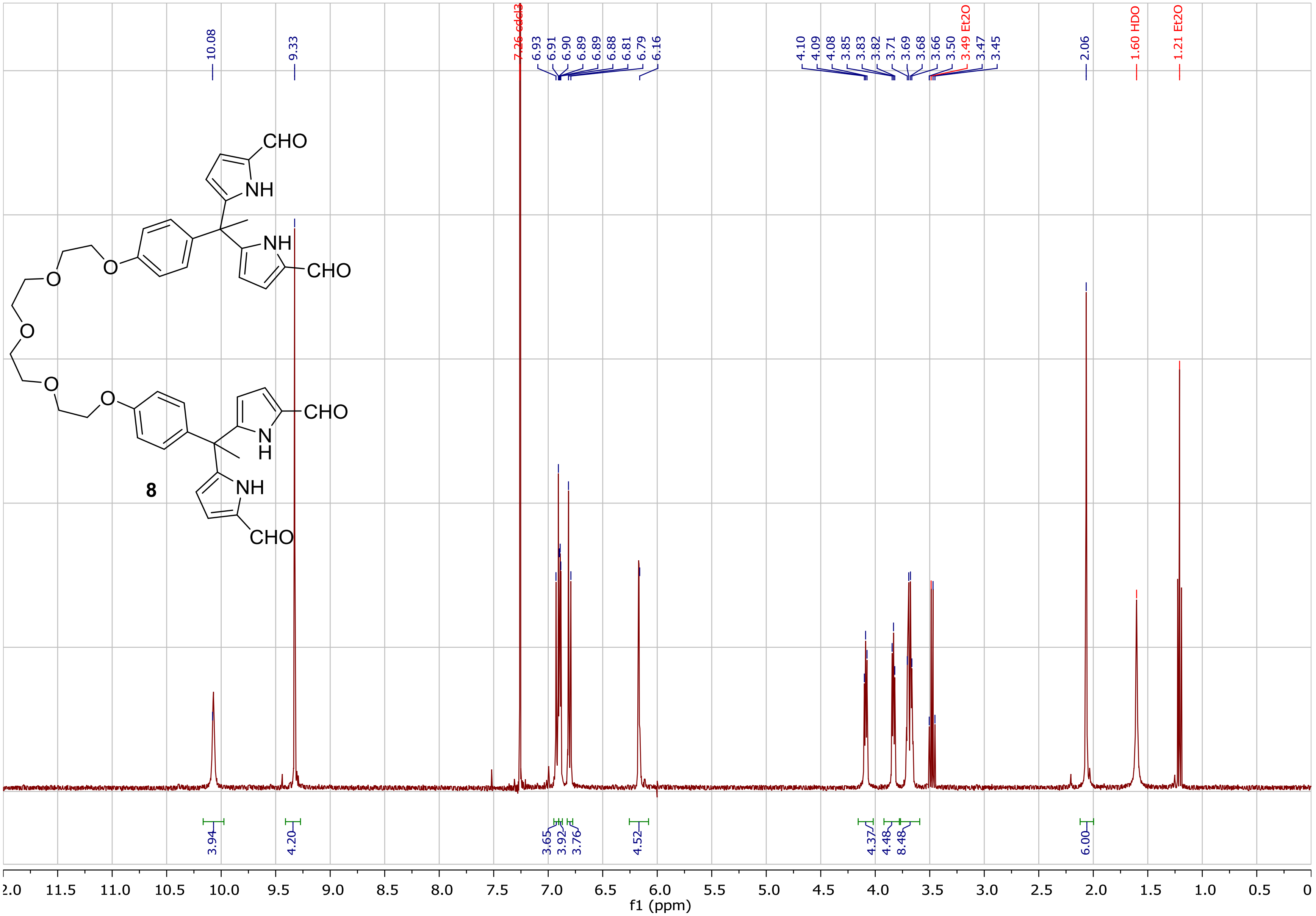

Figure S36 ^{1}H NMR (400 MHz) spectrum of **8** in $CDCl_3$.

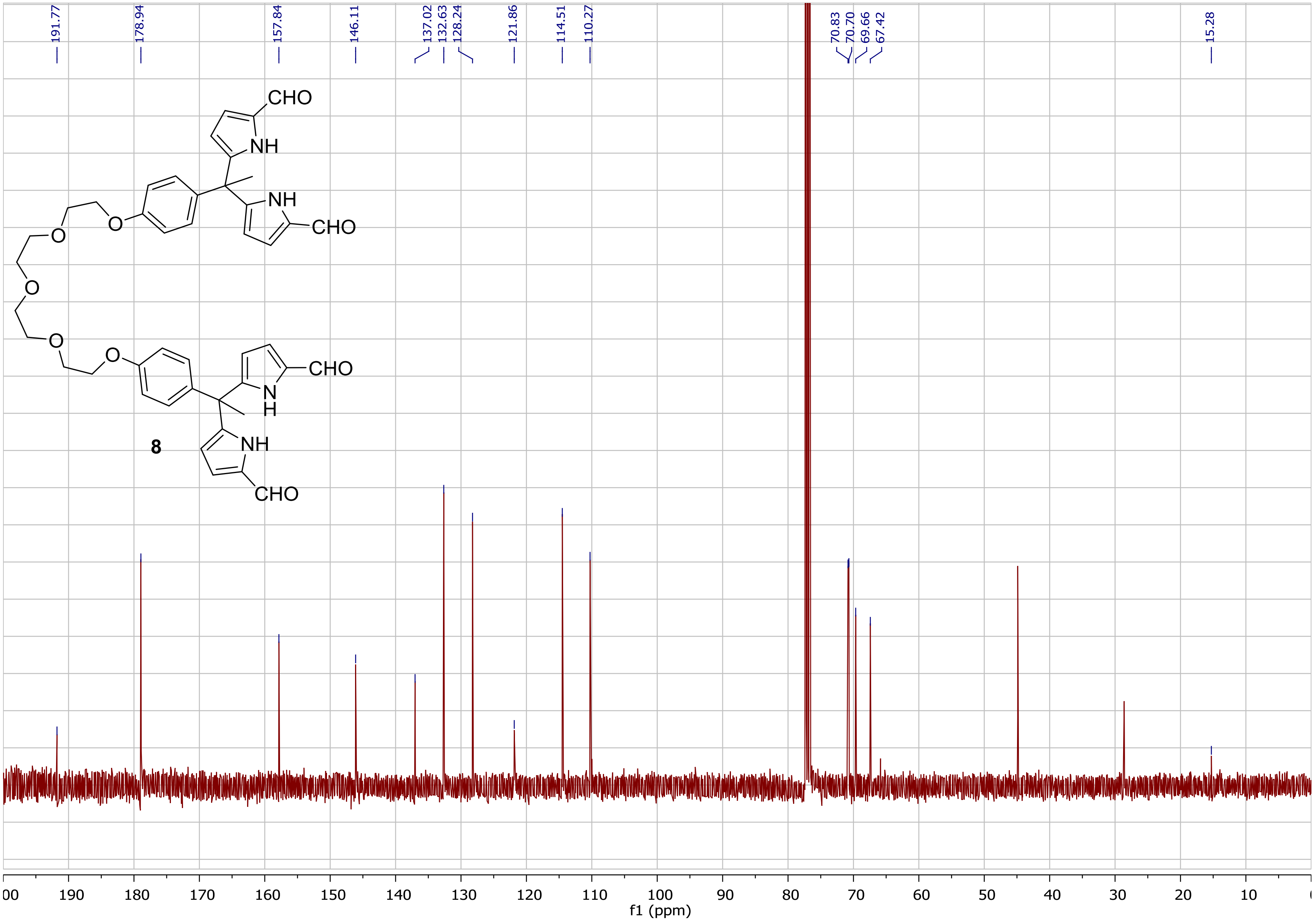

Figure S37 ^{13}C NMR (100 MHz) spectrum of **8** in $CDCl_3$.

References:

1. J. K. Laha, S. Dhanalekshmi, M. Taniguchi, A. Ambroise and J. S. Lindsey *Org. Proc. Res. Dev.*, 2003, **6**, 799–812.
2. L. Adriaenssens, C. Estarellas, A. V. Jentzsch, M. M. Belmonte, S. Matile, and P. Ballester, *J. Am. Chem. Soc.*, 2013, **135**, 8324–8330.
3. J. B. Love, A. J. Blake, C. Wilson, S. D. Reid, A. Novaka and P. B. Hitchcock, *Chem. Commun.*, 2003, **14**, 1682-1683.
4. J. Yoo, I.-W. Park, T.-Y. Kim and C.-H Lee, *Bull. Korean Chem. Soc.*, 2010, **31**, 630-634.