Supporting Information

For

N-Tosylpyrrolidine Calix[4]pyrrole: Synthesis and Ion Binding Studies

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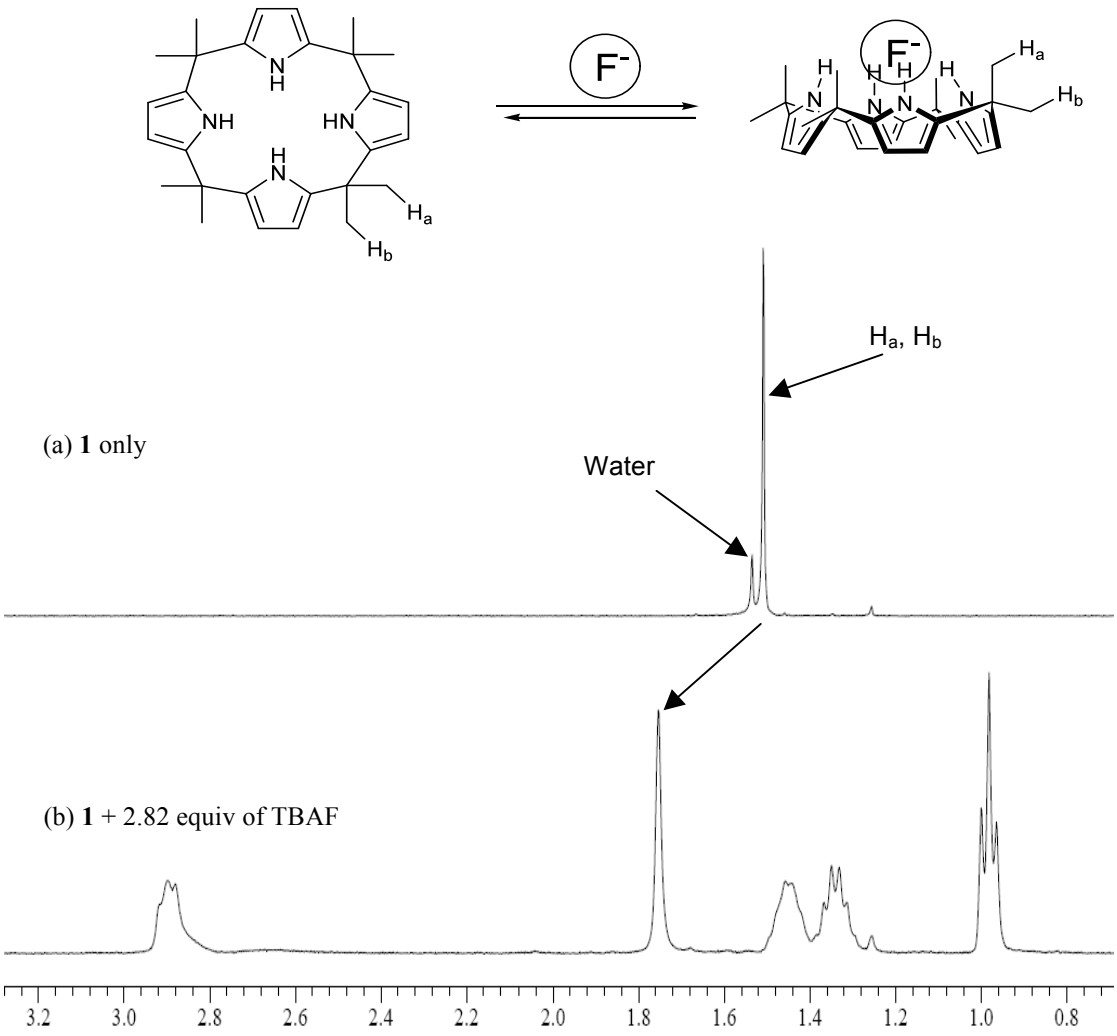


Figure S1. Partial ^{1}H NMR spectra of (a) free **1** and (b) **1** + 2.82 equiv of TBAF in CD_3Cl.

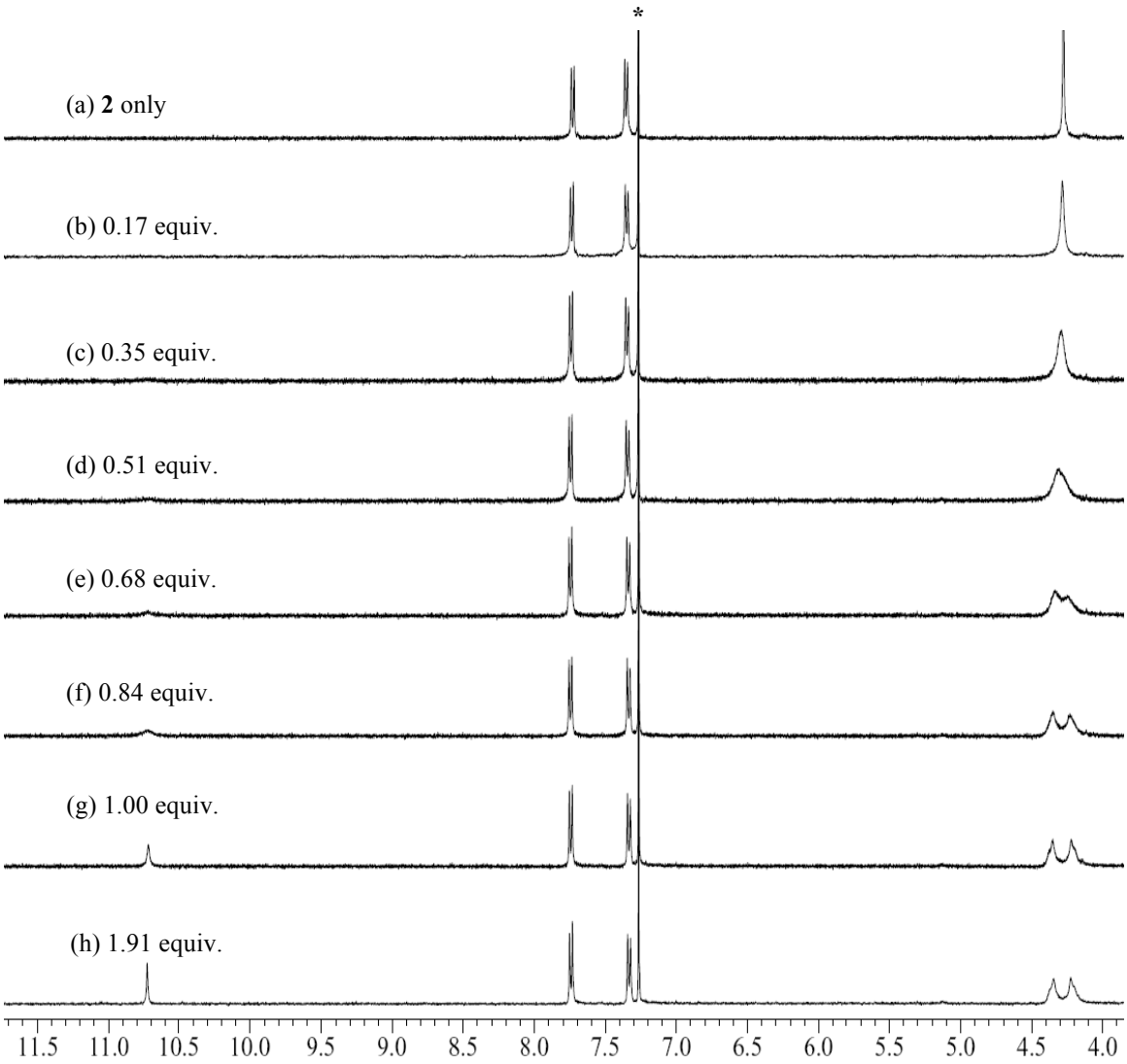


Figure S2. Partial ^{1}H NMR spectra obtained by subjecting **2** to titration with TBACl in $CDCl_3$. *Denotes a peak due to the NMR solvent.

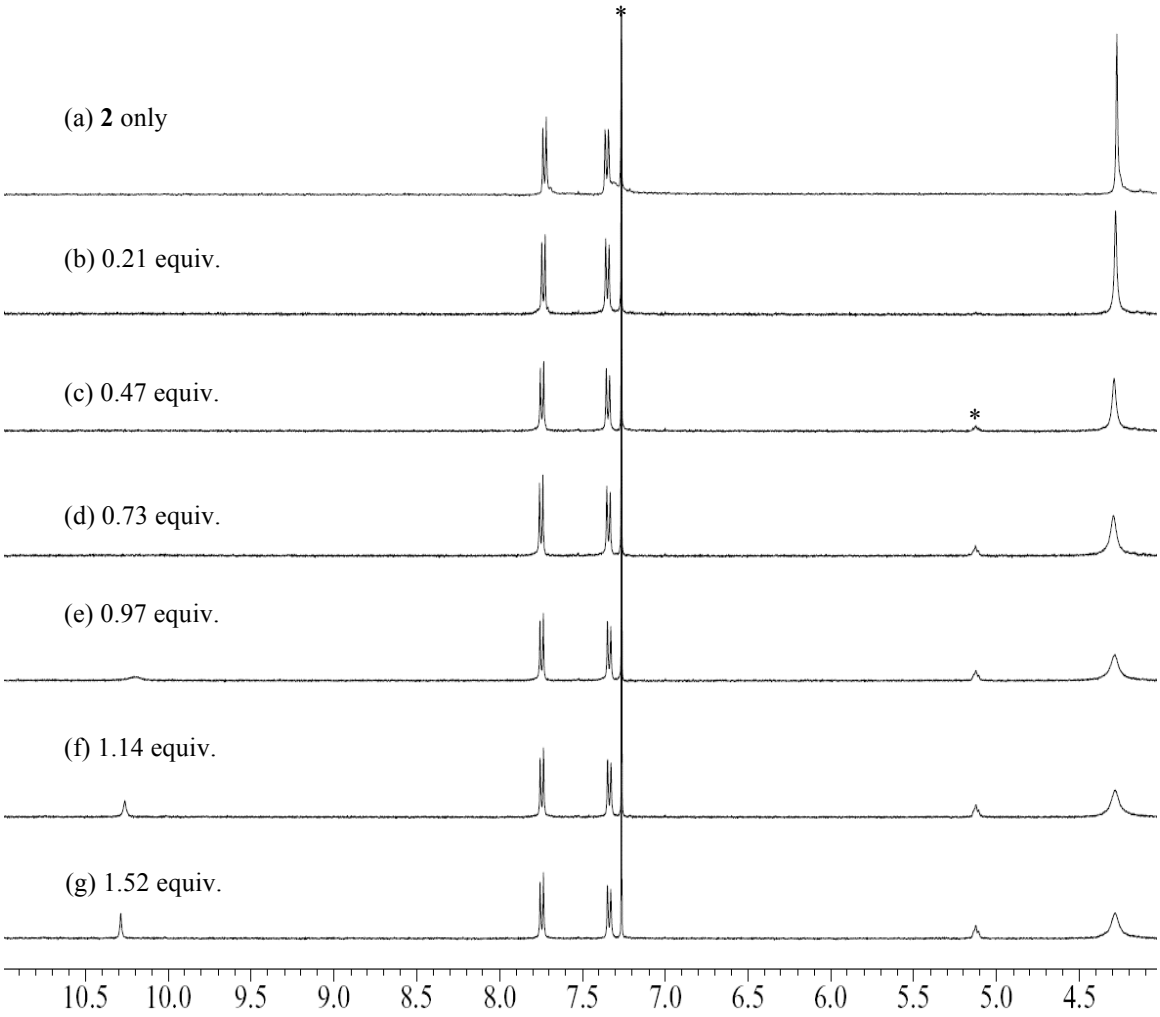


Figure S3. Partial ^{1}H NMR spectra corresponding to the titration of **2** with TBABr in $CDCl_3$. *Denotes a peak due to the NMR solvent or residual solvent.

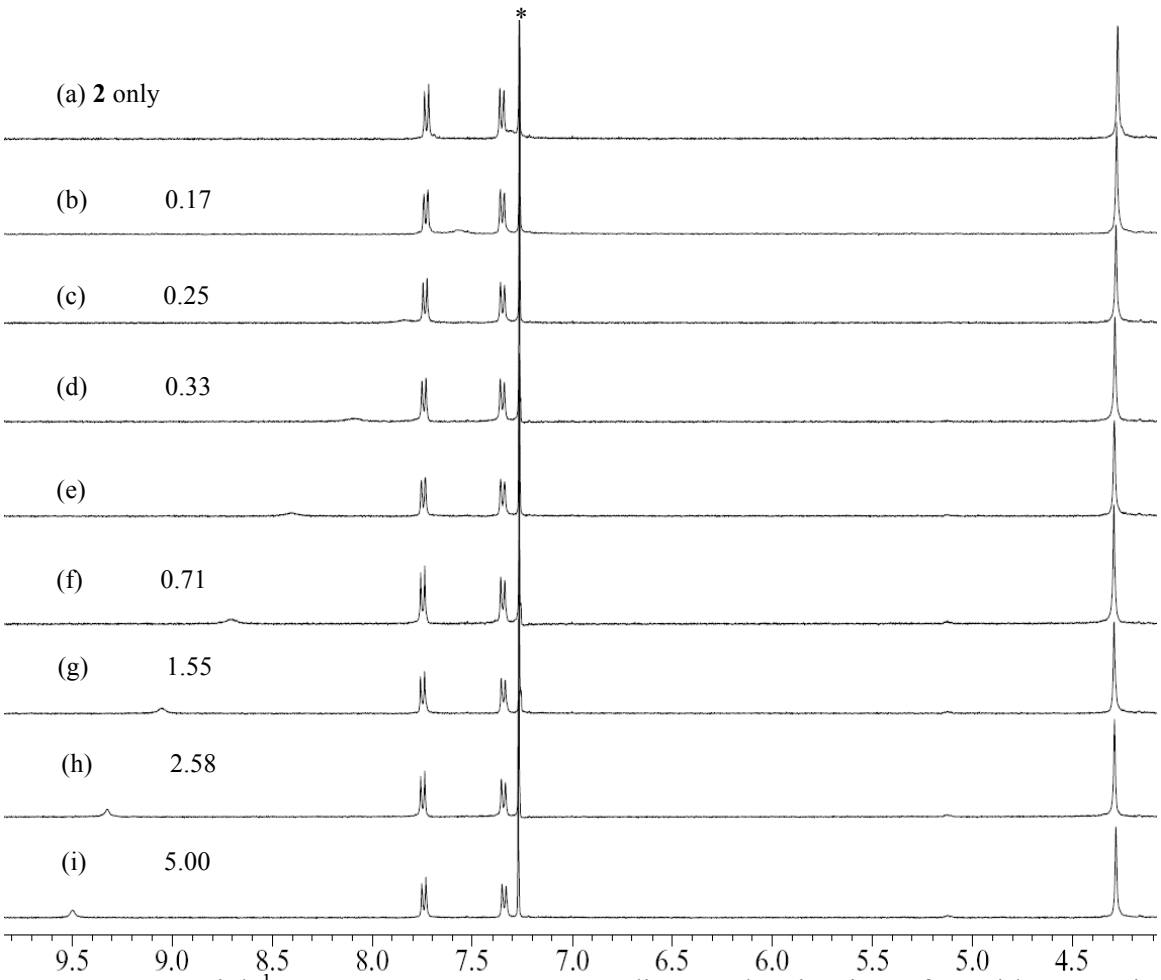


Figure S4. Partial ^{1}H NMR spectra corresponding to the titration of **2** with TBAI in $CDCl_3$. *Denotes a peak due to the NMR solvent.

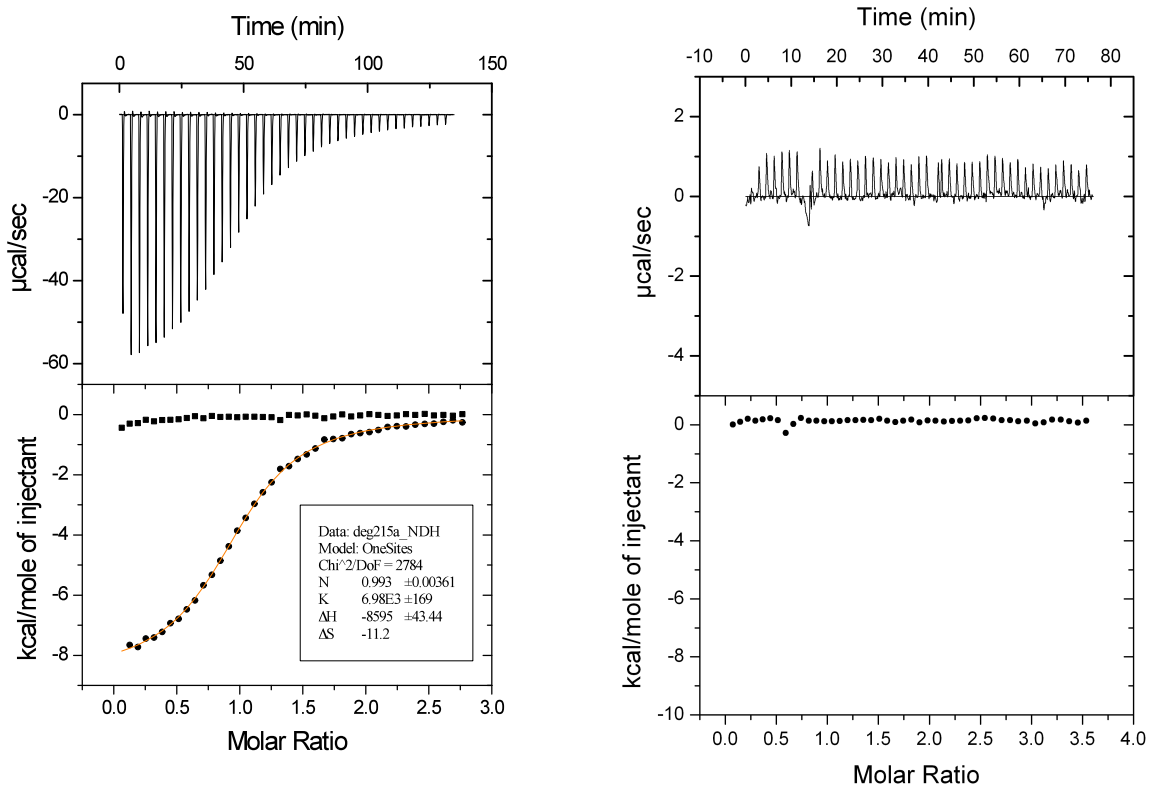


Figure S5. ITC plots showing titrations of calix[4]pyrrole **1** (initial concentrations: 1.64 mM for TEACl, 1.10 mM for TBACl) with TEACl (left, 21.03 mM) and TBACl (right, 23.07 mM).

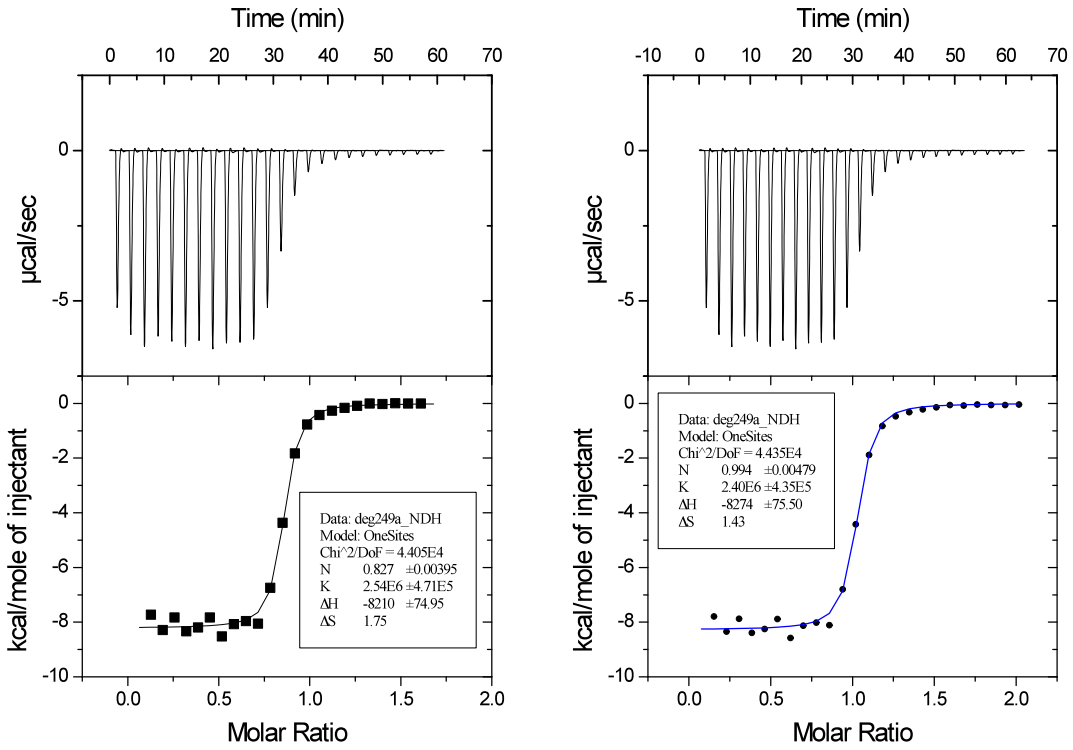


Figure S6. Original ITC plots (left) obtained by subjecting calix[4]pyrrole **2** (0.21 mM) to titration with TBACl (2.71 mM), as well as the corresponding plots (right) obtained after adjusting the host concentration to obtain a value of 1 for N.

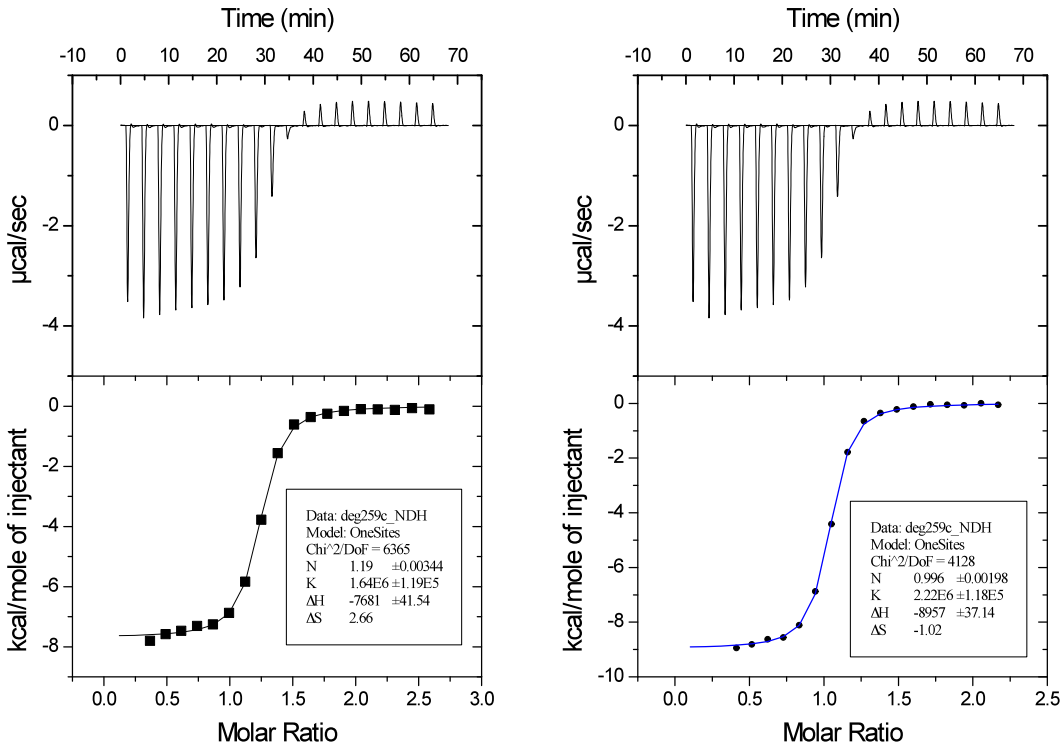


Figure S7. Original ITC plots (left) obtained by subjecting calix[4]pyrrole **2** (1.57 mM) to titration with TBACl (0.09 mM), as well as the corresponding plots (right) obtained after adjusting the host concentration to obtain a value of 1 for N.

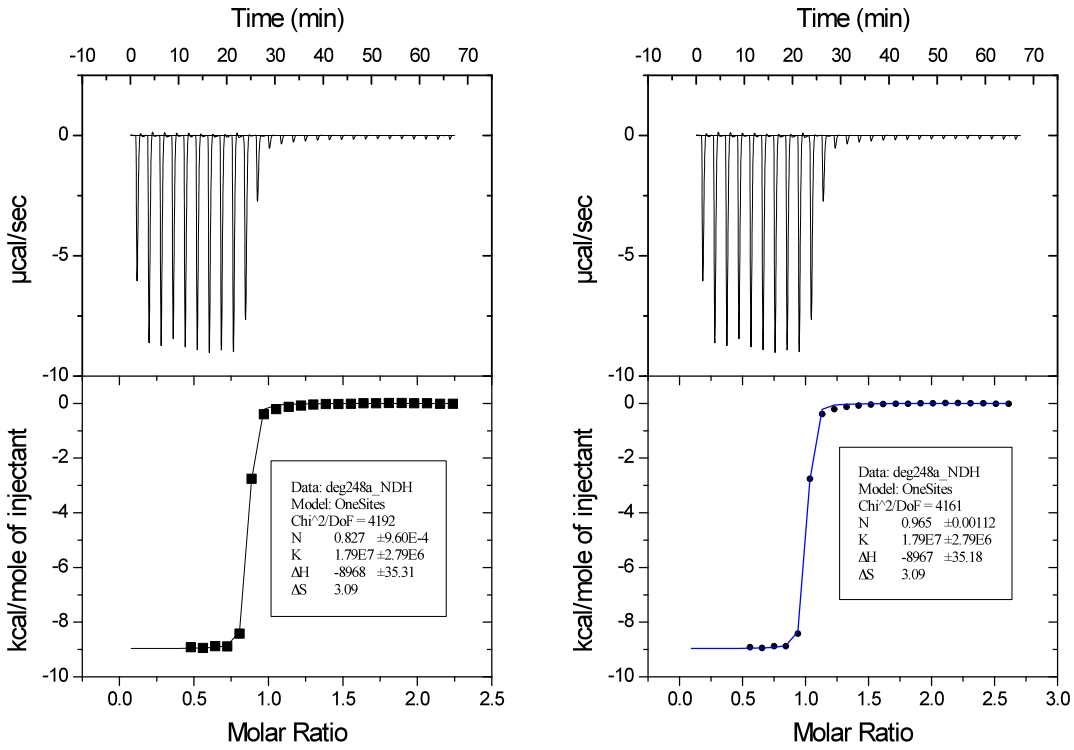


Figure S8. Original ITC plots (left) obtained by subjecting calix[4]pyrrole **2** (0.21 mM) to titration with TEACl (4.74 mM), as well as the corresponding plots (right) obtained after adjusting the host concentration to obtain a value of 1 for N.

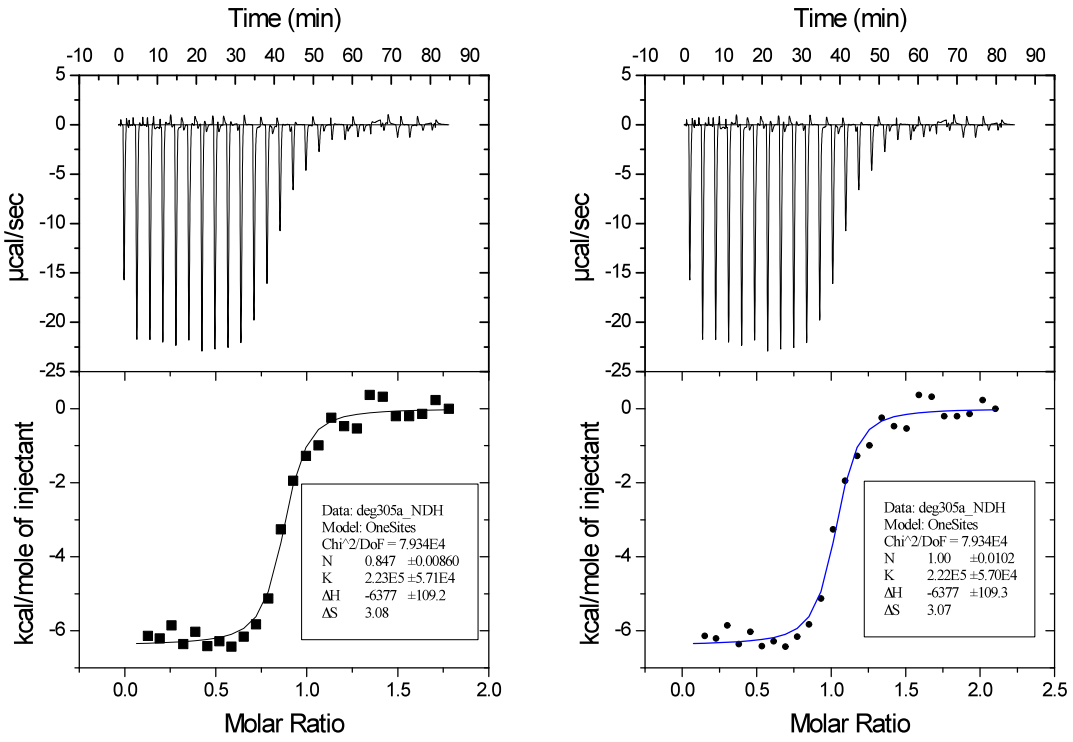


Figure S9. Original ITC plots (left) obtained by subjecting calix[4]pyrrole **2** (1.00 mM) to titration with TBABr (10.3 mM), as well as the corresponding plots (right) obtained after adjusting the host concentration to obtain a value of 1 for N.

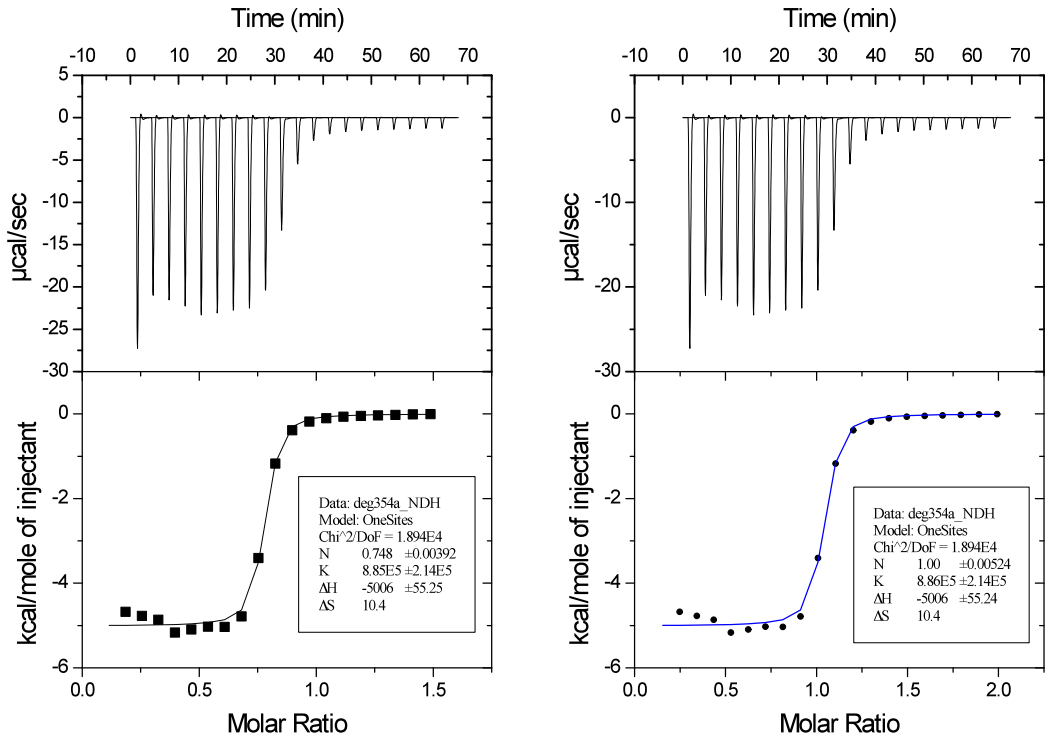


Figure S10. Original ITC plots (left) obtained by subjecting calix[4]pyrrole **2** (1.00 mM) to titration with TEABr (16.4 mM), as well as the corresponding plots (right) obtained after adjusting the host concentration to obtain a value of 1 for N.

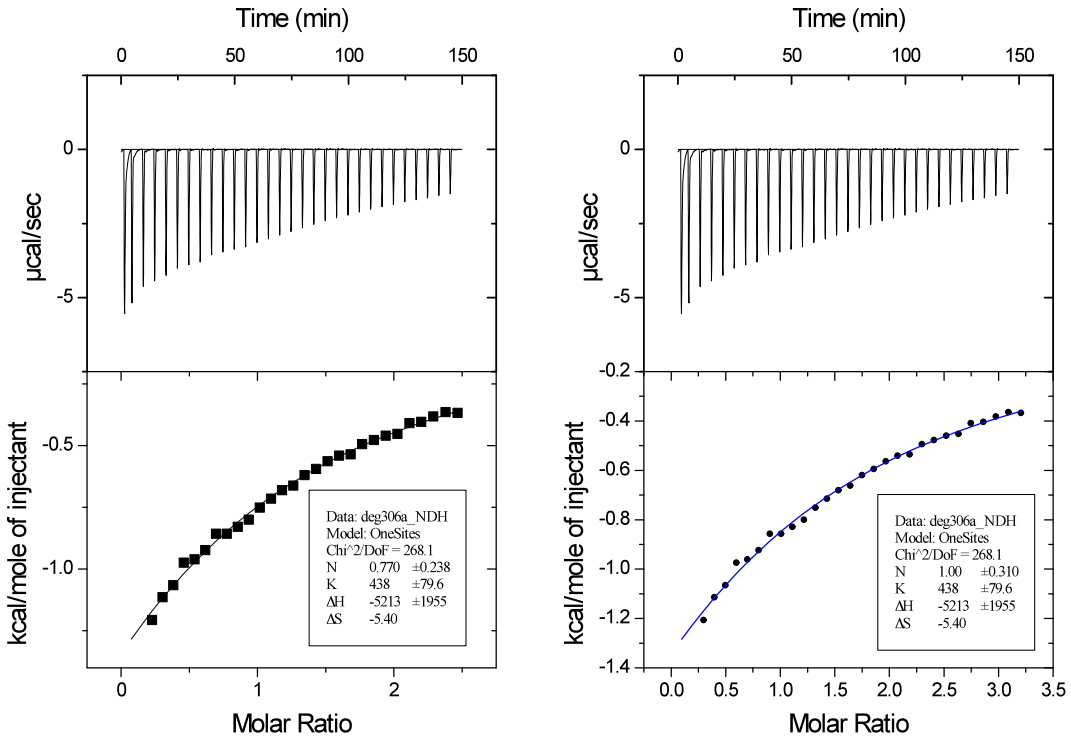


Figure S11. Original ITC plots (left) obtained by subjecting calix[4]pyrrole **2** (1.00 mM) to titration with TBAI (11.9 mM), as well as the corresponding plots (right) obtained after adjusting the host concentration to obtain a value of 1 for N.

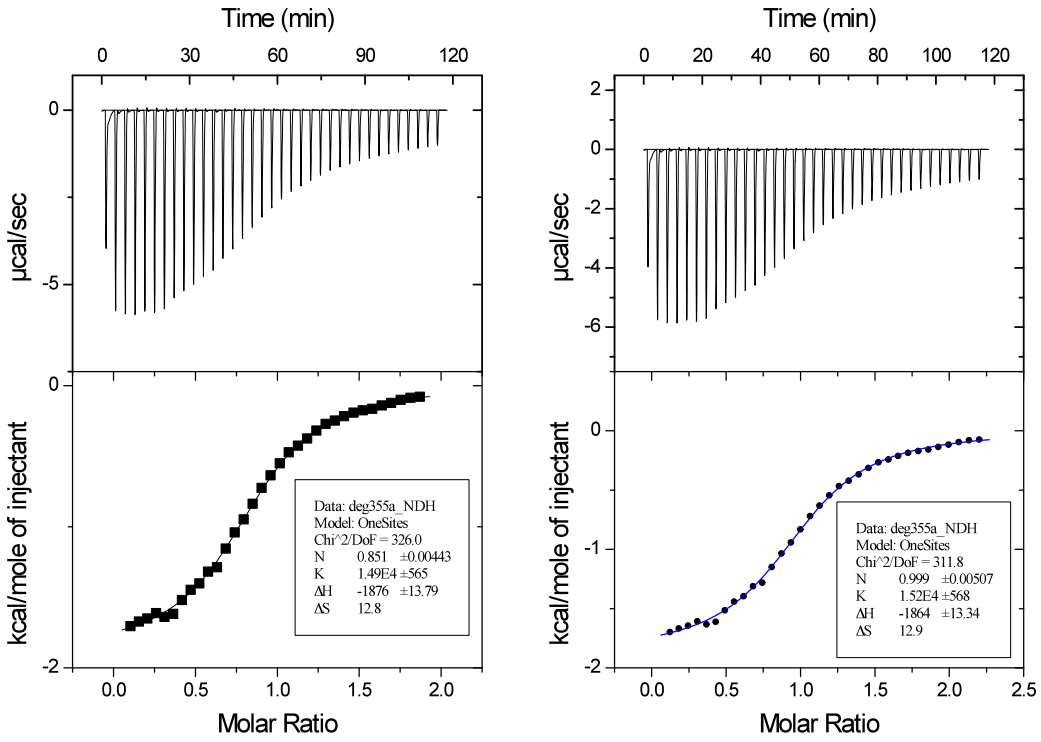


Figure S12. Original ITC plots (left) obtained by subjecting calix[4]pyrrole **2** (1.00 mM) to titration with TEAI (12.2 mM), as well as the corresponding plots (right) obtained after adjusting the host concentration to obtain a value of 1 for N.

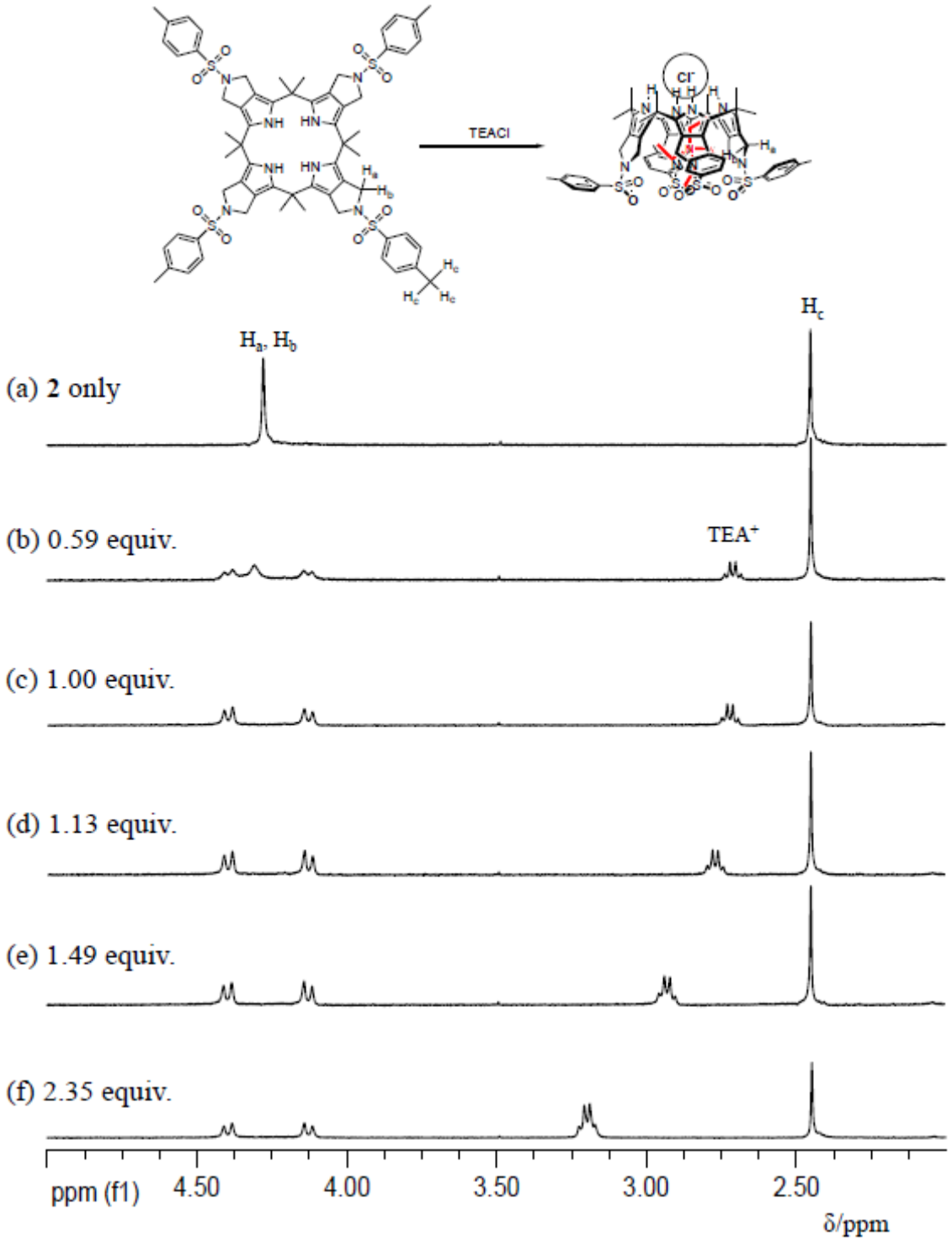


Figure S13. Partial ^{1}H NMR spectra corresponding to the titration of **2** with TEACl in $CDCl_3$.

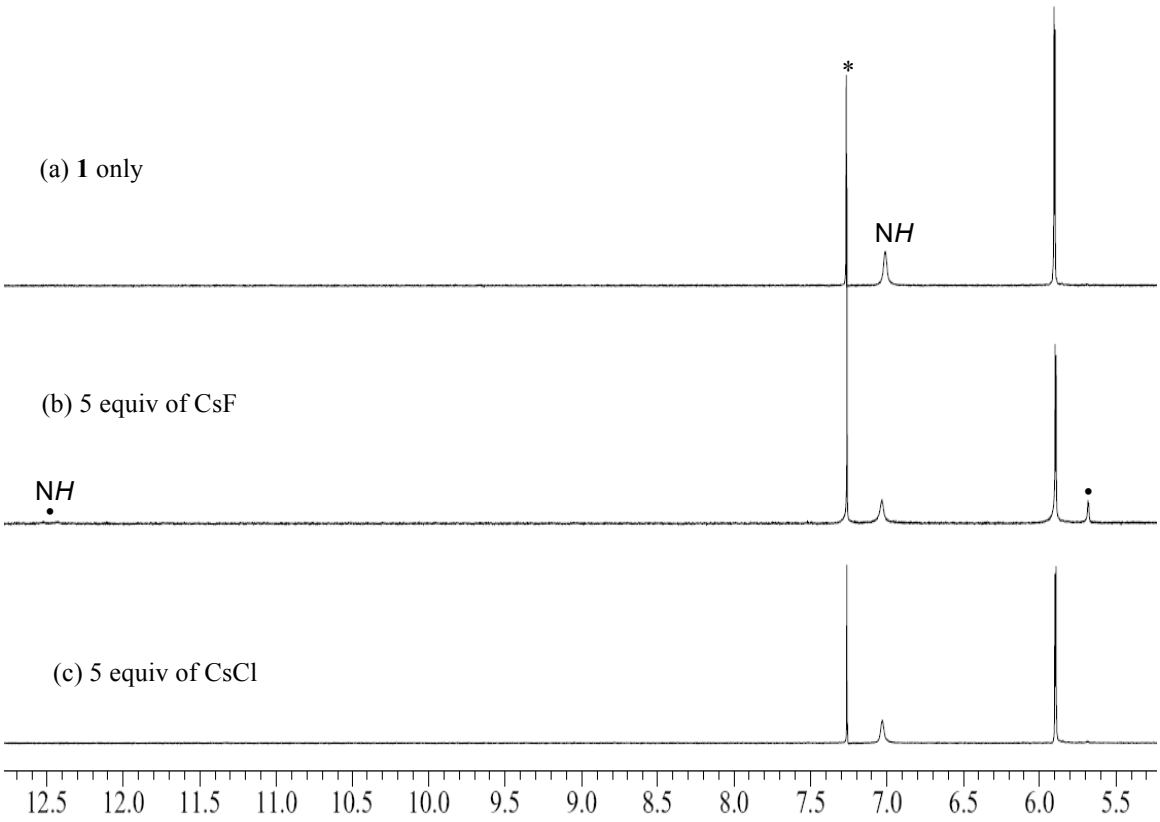
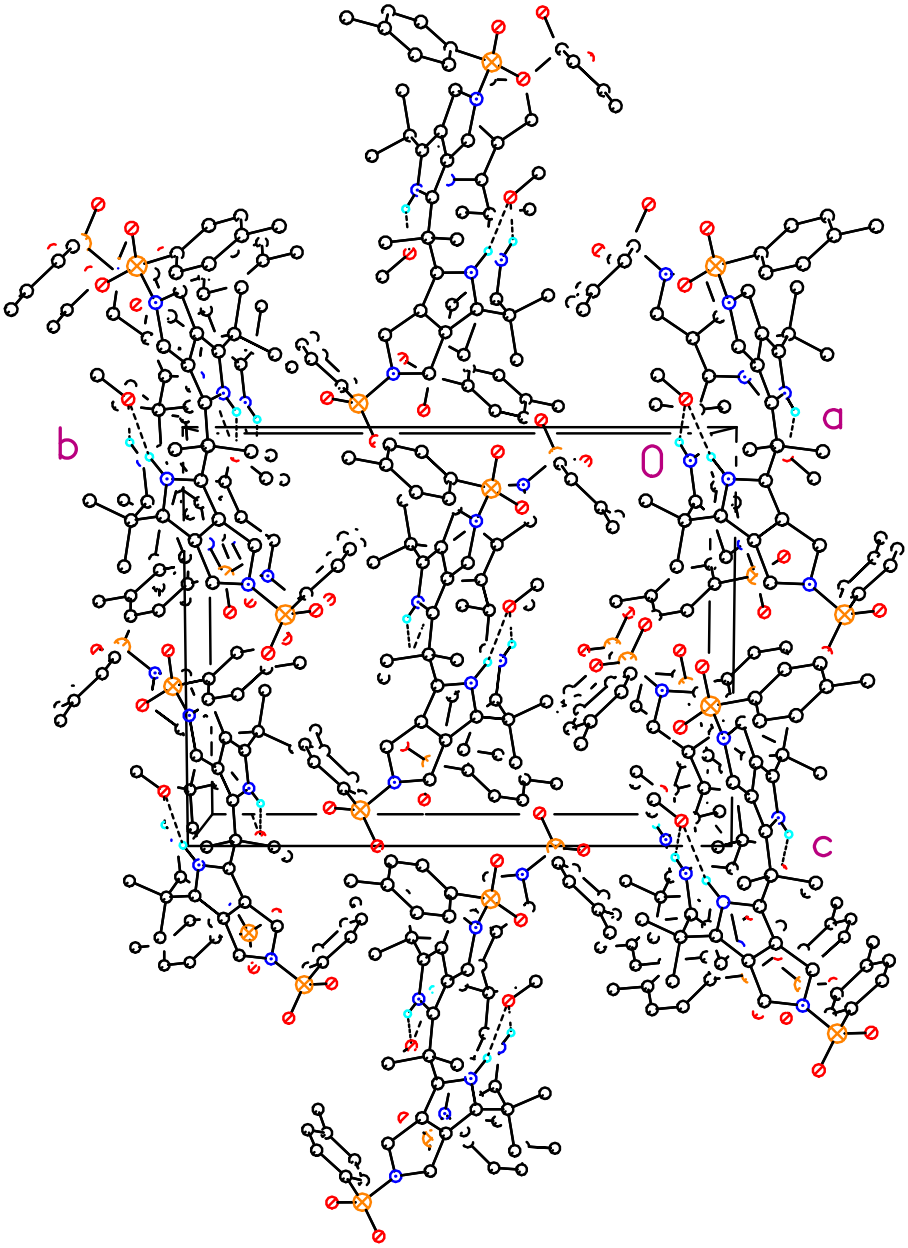


Figure S14. Chemical shift changes of **1** observed upon the addition of CsF and CsCl in $CDCl_3$. * and • denote peaks due to the NMR solvent and the complex **1**·CsF, respectively.

Figure S15. Unit cell packing diagram for **2**·$(CH_3OH)_2$. The view is approximately down the **a** axis.



X-ray Experimental for **2**·$(CH_3OH)_2$: Crystals grew as long, colorless laths by slow evaporation from methanol. The data crystal was cut from a larger crystal and had approximate dimensions; 0.30 × 0.07 × 0.04 mm. The data were collected on a Nonius Kappa CCD diffractometer using a graphite monochromator with MoKα radiation (λ = 0.71073 Å). A total of 311 frames of data were collected using ω-scans with a scan range of 0.9° and a counting time of 239 seconds per frame. The data were collected at 153 K using an Oxford Cryostream low temperature device. Details of crystal data, data collection and structure refinement are listed in Table S1. Data reduction were performed using DENZO-SMN.[1] The structure was solved by direct methods using SIR97[2] and refined by full-matrix least-squares on F^2 with anisotropic displacement parameters for the non-H atoms using SHELXL-97.[3] The hydrogen atoms were calculated in ideal positions with isotropic displacement parameters set to 1.2 × Ueq of the attached atom (1.5 × Ueq for methyl hydrogen atoms). The hydrogen atom on the methanol oxygen atom, O1a, could not be located in a ΔF map and was not included in the final refinement model. The function, $\Sigma w(|Fo|^2 - |Fc|^2)^2$, was minimized, where $w = 1/[(\sigma(Fo))^2 + (0.0606*P)^2 + (2.5237*P)]$ and $P = (|Fo|^2 + 2|Fc|^2)/3$. $Rw(F^2)$ refined to 0.237, with R(F) equal to 0.0922 and a goodness of fit, S, = 1.007. Definitions used for calculating R(F), $Rw(F^2)$ and the goodness of fit, S, are given below.[4] The data were checked for secondary extinction effects but no correction was necessary. Neutral atom scattering factors and values used to calculate the linear absorption coefficient are from the International Tables for X-ray Crystallography (1992).[5] All figures were generated using SHELXTL/PC.[6]

Table S1. Crystal data and structure refinement for **2**·$(CH_3OH)_2$.

Empirical formula	C33 H40 N4 O5 S2	
Formula weight	636.81	
Temperature	153(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P21/n	
Unit cell dimensions	a = 12.817(3) Å	α= 90°.
	b = 17.885(6) Å	β= 98.261(11)°.
	c = 13.861(5) Å	γ = 90°.
Volume	3144.4(17) $Å^3$	
Z	4	
Density (calculated)	1.345 Mg/m^3	
Absorption coefficient	0.217 mm^{-1}	
F(000)	1352	
Crystal size	0.30 × 0.07 × 0.04 mm	
Theta range for data collection	2.32 to 25.00°.	
Index ranges	-15<=h<=15, -21<=k<=19, -16<=l<=16	
Reflections collected	8959	
Independent reflections	5356 [R(int) = 0.1094]	
Completeness to theta = 25.00°	96.6 %	
Absorption correction	None	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	5356 / 0 / 403	
Goodness-of-fit on F^2	1.007	
Final R indices [I>2sigma(I)]	R1 = 0.0922, wR2 = 0.1696	
R indices (all data)	R1 = 0.2844, wR2 = 0.2370	
Largest diff. peak and hole	0.303 and -0.192 $e.Å^{-3}$	

X-ray Experimental for **2**·$(DMF)_4$·$(CH_2Cl_2)_{½}$: Crystals grew as clusters of colorless needles by slow evaporation from DMF and dichloromethnae. The data crystal was cut from a large cluster and had approximate dimensions; 0.28 × 0.18 × 0.05 mm. The data were collected on a Nonius Kappa CCD diffractometer using a graphite monochromator with MoKα radiation (λ = 0.71073 Å). A total of 205 frames of data were collected using ω-scans with a scan range of 2° and a counting time of 222 seconds per frame. The data were collected at 153 K using an Oxford Cryostream low temperature device. Details of crystal data, data collection and structure refinement are listed in Table S2. Data reduction were performed using DENZO-SMN.[1] The structure was solved by direct methods using SIR97[2] and refined by full-matrix least-squares on F^2 with anisotropic displacement parameters for the non-H atoms using SHELXL-97.[3] The hydrogen atoms on carbon were calculated in ideal positions with isotropic displacement parameters set to 1.2 × Ueq of the attached atom (1.5 × Ueq for methyl hydrogen atoms). The hydrogen atoms on the pyrrolic nitrogen atoms, N1 and N2, were observed in a ΔF map and refined with isotropic displacement parameters.

There were two regions of disordered solvent in the lattice. One, near a crystallographic inversion center, appeared to be due to dichloromethane. Two peaks, about 3 Å apart, were thought to be due to a partially occupied dichloromethane molecule. A second solvate molecule that was clearly DMF was located near the dichloromethane molecule. Both solvate molecules were badly disordered. The contribution to the structure factors due to these molecules was removed by use of the utility Squeeze in PLATON98.[7] PLATON98 was used as incorporated in WinGX.[8]

The macrocycle is located around a crystallographic inversion center at ½, ½, ½. The macrocycle is H-bound to two molecules of DMF. The DMF molecules are disordered about two orientations. The disorder was modeled by assigning the site occupancy factor of one orientation to the variable x. The site occupancy factor for the second orientation was assigned to (1 - x). A common site occupancy factor was refined for all atoms of the two orientations. In this way, the site occupancy of the major component was 69(2)%. The geometry of the disordered molecules was restrained to be equivalent throughout the refinement. Anisotropic displacement parameters were used for the major component of the disorder. The atoms of the minor component were refined isotropically.

The function, $\Sigma w(|F_O|^2 - |F_C|^2)^2$, was minimized, where $w = 1/[(\sigma(F_O))^2 + (0.0533*P)^2 + (0.281*P)]$ and $P = (|F_O|^2 + 2|F_C|^2)/3$. $R_w(F^2)$ refined to 0.134, with R(F) equal to 0.0525 and a goodness of fit, S, = 1.14. Definitions used for calculating R(F),

$R_w(F^2)$ and the goodness of fit, S, are given below.[4] The data were corrected for secondary extinction effects. The correction takes the form: $F_{corr} = kF_c/[1 + (5.0(11) \times 10^{-6})* F_c^2 \lambda^3/(\sin 2\theta)]^{0.25}$ where k is the overall scale factor. Neutral atom scattering factors and values used to calculate the linear absorption coefficient are from the International Tables for X-ray Crystallography (1992).[5] All figures were generated using SHELXTL/PC.[6]

Table S2. Crystal data and structure refinement for **2**·$(DMF)_4$·$(CH_2Cl_2)_{½}$.

Empirical formula	C76.50 H101 Cl N12 O12 S4	
Formula weight	1544.38	
Temperature	153(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 11.4296(6) Å	α = 105.0390(10)°.
	b = 12.6286(6) Å	β = 90.9620(10)°.
	c = 15.0391(9) Å	γ = 107.6010(10)°.
Volume	1987.52(18) $Å^3$	
Z	2	
Density (calculated)	2.581 Mg/m^3	
Absorption coefficient	0.440 mm^{-1}	
F(000)	1642	
Crystal size	0.28 × 0.18 × 0.05 mm	
Theta range for data collection	1.93 to 27.50°.	
Index ranges	-14<=h<=14, -16<=k<=16, -19<=l<=19	
Reflections collected	15170	
Independent reflections	8976 [R(int) = 0.0290]	
Completeness to theta = 27.50°	98.2 %	
Absorption correction	None	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	8976 / 38 / 459	
Goodness-of-fit on F^2	1.140	
Final R indices [I>2sigma(I)]	R1 = 0.0525, wR2 = 0.1250	
R indices (all data)	R1 = 0.0855, wR2 = 0.1341	
Extinction coefficient	5.0(11) × 10^{-6}	
Largest diff. peak and hole	0.353 and -0.393 e.$Å^{-3}$	

X-ray Experimental for **2**·TBACl: Crystals grew as colorless prisms by slow evaporation from Methanol and dichloromethane. The data crystal was a prism that had approximate dimensions; 0.13 × 0.10 × 0.08 mm. The data were collected on a Nonius Kappa CCD diffractometer using a graphite monochromator with MoKα radiation (λ = 0.71073 Å). A total of 151 frames of data were collected using ω-scans with a scan range of 1.2° and a counting time of 531 seconds per frame. The data were collected at 153 K using an Oxford Cryostream low temperature device. Details of crystal data, data collection and structure refinement are listed in Table S3. Data reduction were performed using DENZO-SMN.[1] The structure was solved by direct methods using SIR97[2] and refined by full-matrix least-squares on F^2 with anisotropic displacement parameters for the non-H atoms using SHELXL-97.[3] The hydrogen atoms were calculated in ideal positions with isotropic displacement parameters set to 1.2 × Ueq of the attached atom (1.5 × Ueq for methyl hydrogen atoms).

The *tetrakis*-n-butylammonium ion was disordered. The disorder could not be adequately modeled. As a result, the utility, SQUEEZE in Platon98[7] was used to remove the cationic contribution to the scattering. Platon98 was used as incorporated in WinGX.[8]

The function, $\Sigma w(|F_O|^2 - |F_C|^2)^2$, was minimized, where $w = 1/[(\sigma(F_O))^2 + (0.11*P)^2]$ and $P = (|F_O|^2 + 2|F_C|^2)/3$. $R_w(F^2)$ refined to 0.229, with R(F) equal to 0.0861 and a goodness of fit, S, = 1.124. Definitions used for calculating R(F), $R_w(F^2)$ and the goodness of fit, S, are given below.[4] The data were checked for secondary extinction effects but no correction was necessary. Neutral atom scattering factors and values used to calculate the linear absorption coefficient are from the International Tables for X-ray Crystallography (1992).[5] All figures were generated using SHELXTL/PC.[6]

Table S3. Crystal data and structure refinement for **2**·TBACl.

Empirical formula	C80 H108 Cl N9 O8 S4	
Formula weight	1487.44	
Temperature	153(2) K	
Wavelength	0.71073 Å	
Crystal system	Tetragonal	
Space group	I-4/1md	
Unit cell dimensions	a = 23.5509(15) Å	α = 90°.
	b = 23.5509(15) Å	β = 90°.
	c = 14.5959(9) Å	γ = 90°.
Volume	8095.5(9) $Å^3$	
Z	4	
Density (calculated)	1.220 Mg/m^3	
Absorption coefficient	0.209 mm^{-1}	
F(000)	3184	
Crystal size	0.15 × 0.10 × 0.08 mm	
Theta range for data collection	2.38 to 25.02°.	
Index ranges	-27<=h<=28, -26<=k<=28, -17<=l<=17	
Reflections collected	12049	
Independent reflections	3746 [R(int) = 0.1141]	
Completeness to theta = 25.02°	99.8 %	
Absorption correction	None	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3746 / 1 / 205	
Goodness-of-fit on F^2	1.124	
Final R indices [I>2sigma(I)]	R1 = 0.0861, wR2 = 0.2084	
R indices (all data)	R1 = 0.1379, wR2 = 0.2295	
Absolute structure parameter	0.21(18)	
Largest diff. peak and hole	0.626 and -0.459 $e.Å^{-3}$	

References for Supporting Material

(1) DENZO-SMN. (1997). Z. Otwinowski and W. Minor, Methods in Enzymology, **276**: Macromolecular Crystallography, part A, 307 – 326, C. W. Carter, Jr. and R. M. Sweets, Editors, Academic Press.

(2) SIR97. (1999). A program for crystal structure solution. Altomare, A.; Burla, M. C.; Camalli, M.; Cascarano, G. L.; Giacovazzo, C.; Guagliardi, A.; Moliterni, A. G. G.; Polidori, G.; Spagna, R. *J. Appl. Cryst.* **1999**, *32*, 115.

(3) Sheldrick, G. M. (1994). SHELXL97. Program for the Refinement of Crystal Structures. University of Gottingen, Germany.

(4) Spek, A. L. (1998). PLATON, A Multipurpose Crystallographic Tool. Utrecht University, The Netherlands.

(5) WinGX 1.64. (1999). An Integrated System of Windows Programs for the Solution, Refinement and Analysis of Single Crystal X-ray Diffraction Data. Farrugia, L. J. *J. Appl. Cryst.* **1999**, *32*. 837-838.

(6) $R_w(F^2) = \{\Sigma w(|Fo|^2 - |Fc|^2)^2/\Sigma w(|Fo|)^4\}^{1/2}$ where w is the weight given each reflection. $R(F) = \Sigma (|Fo| - |Fc|)/\Sigma|Fo|\}$ for reflections with $Fo > 4(\sigma(Fo))$. $S = [\Sigma w(|Fo|^2 - |Fc|^2)^2/(n - p)]^{1/2}$, where n is the number of reflections and p is the number of refined parameters.

(7) International Tables for X-ray Crystallography (1992). Vol. C, Tables 4.2.6.8 and 6.1.1.4, A. J. C. Wilson, editor, Boston: Kluwer Academic Press.

(8) Sheldrick, G. M. (1994). SHELXTL/PC (Version 5.03). Siemens Analytical X-ray Instruments, Inc., Madison, Wisconsin, USA.

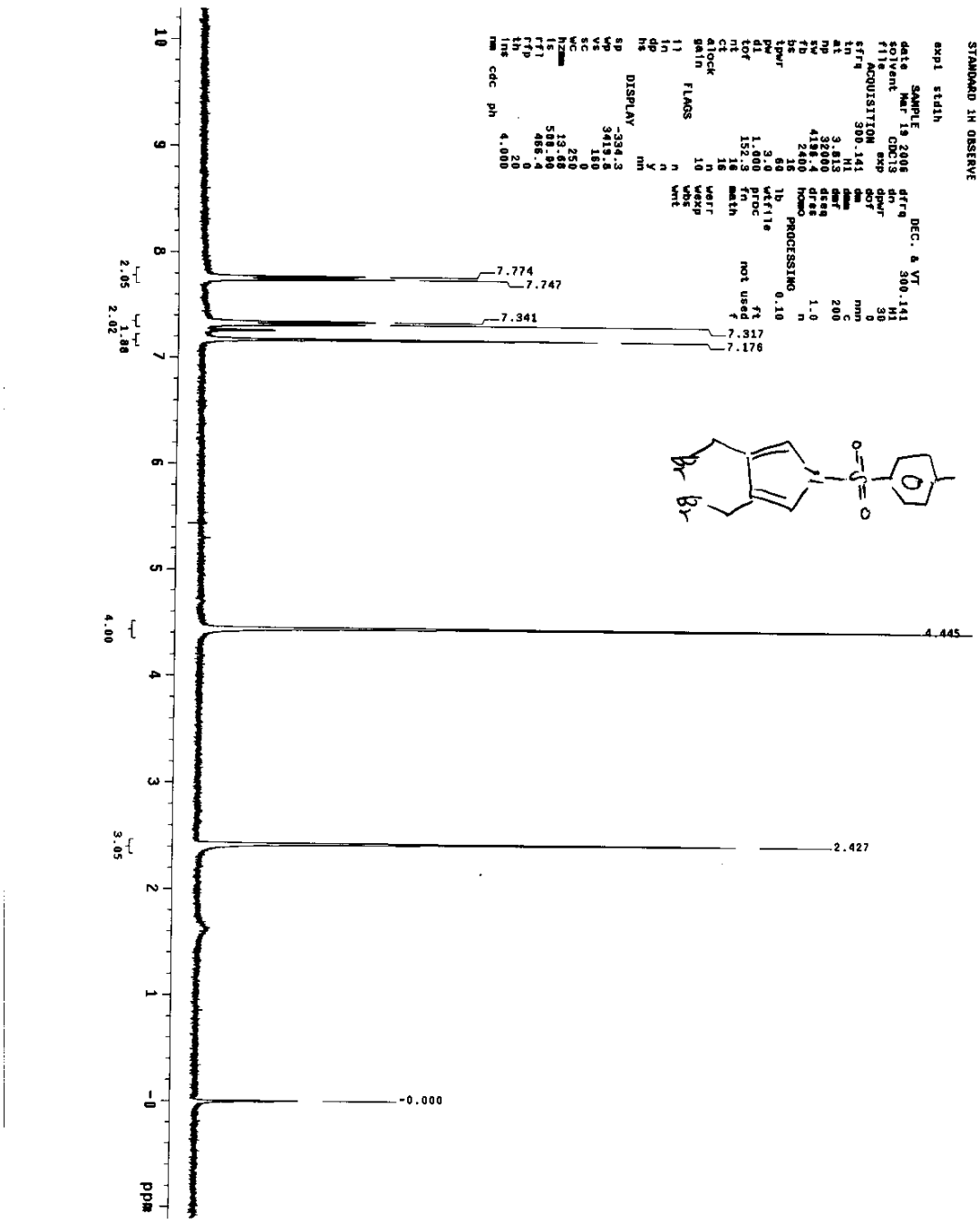


Figure S16. ^{1}H NMR spectrum of **6** recorded in $CDCl_3$.

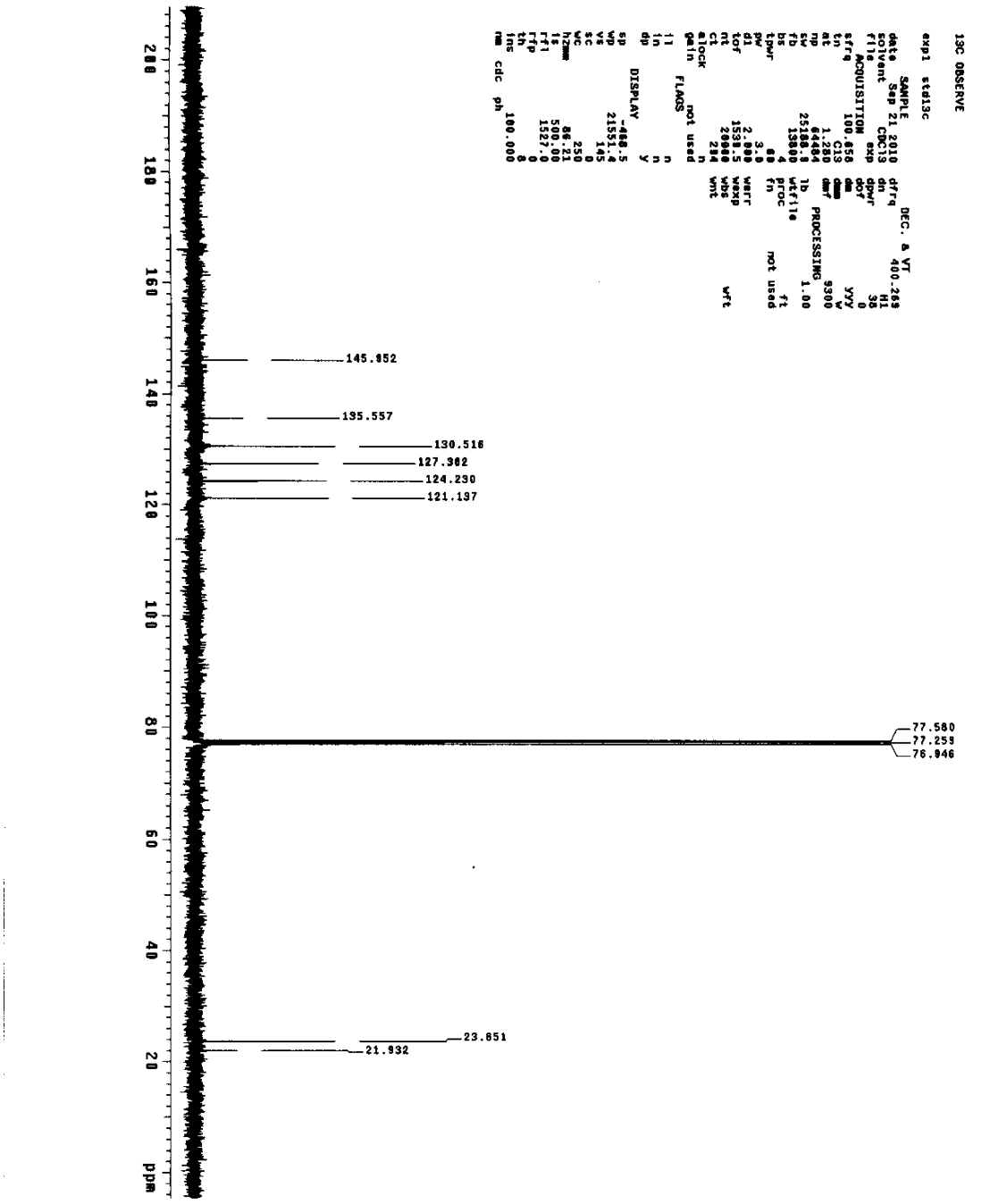
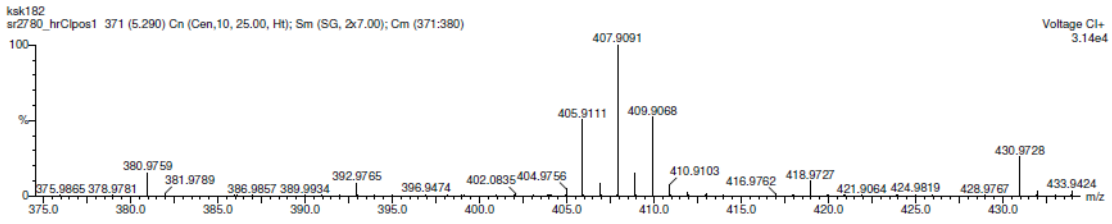


Figure S17. ^{13}C NMR spectrum of **6** recorded in $CDCl_3$.

Elemental Composition Report **Page 1**

Single Mass Analysis (displaying only valid results)
Tolerance = 5.0 PPM / DBE: min = -6.0, max = 9.0
Selected filters: None

Monoisotopic Mass, Odd and Even Electron Ions
165 formula(e) evaluated with 1 results within limits (all results (up to 1000) for each mass)
Elements Used:
C: 0-100 H: 0-100 N: 0-2 O: 0-6 S: 1-1 Br: 1-2



Minimum:				-6.0		
Maximum:		1000.0	5.0	9.0		
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Formula
405.9111	405.9112	-0.1	-0.2	6.5	1.0	C13 H14 N O2 S Br2

Figure S18. CI-HRMS of compound **6**.

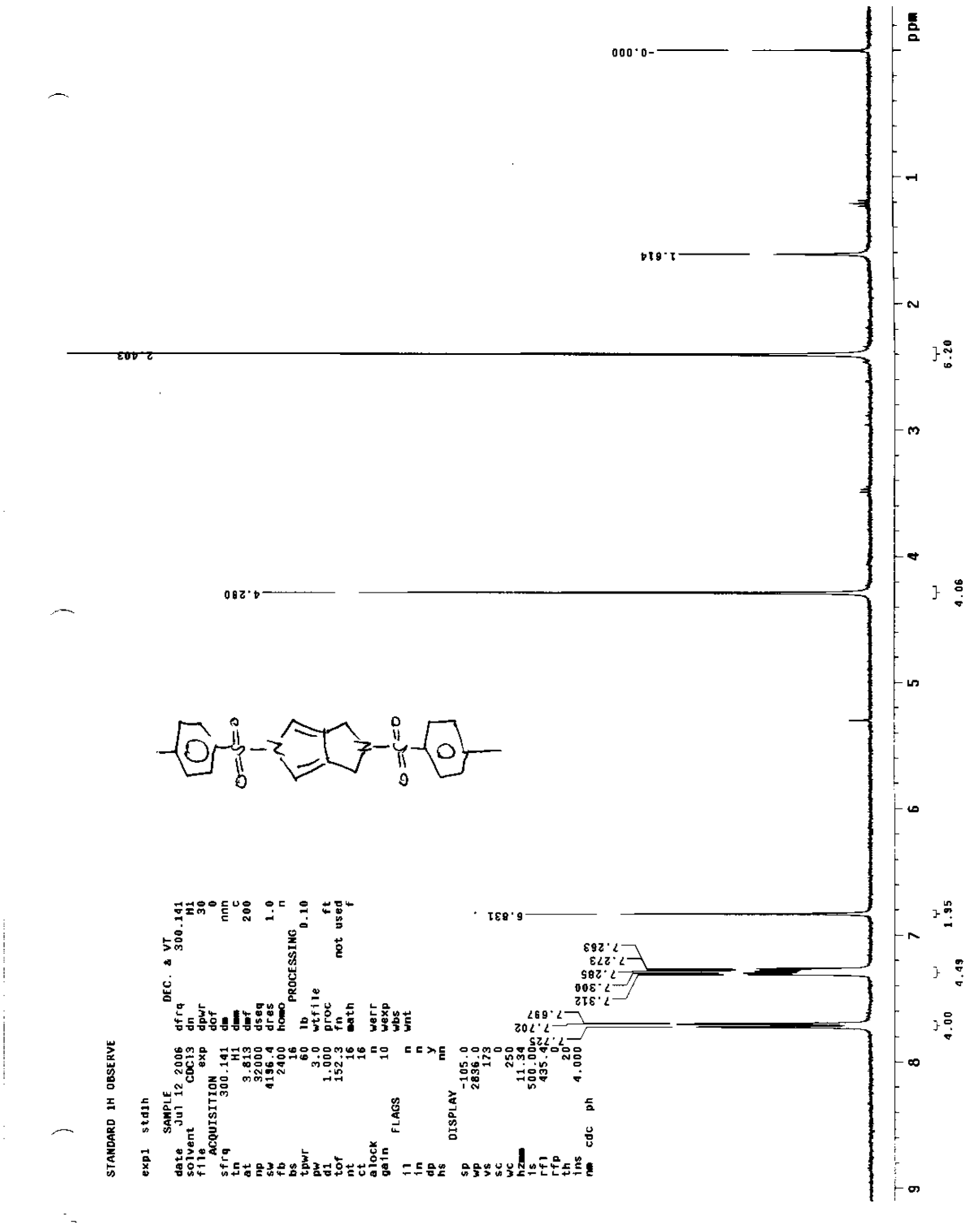


Figure S19. ^{1}H NMR spectrum of **7** recorded in $CDCl_3$.

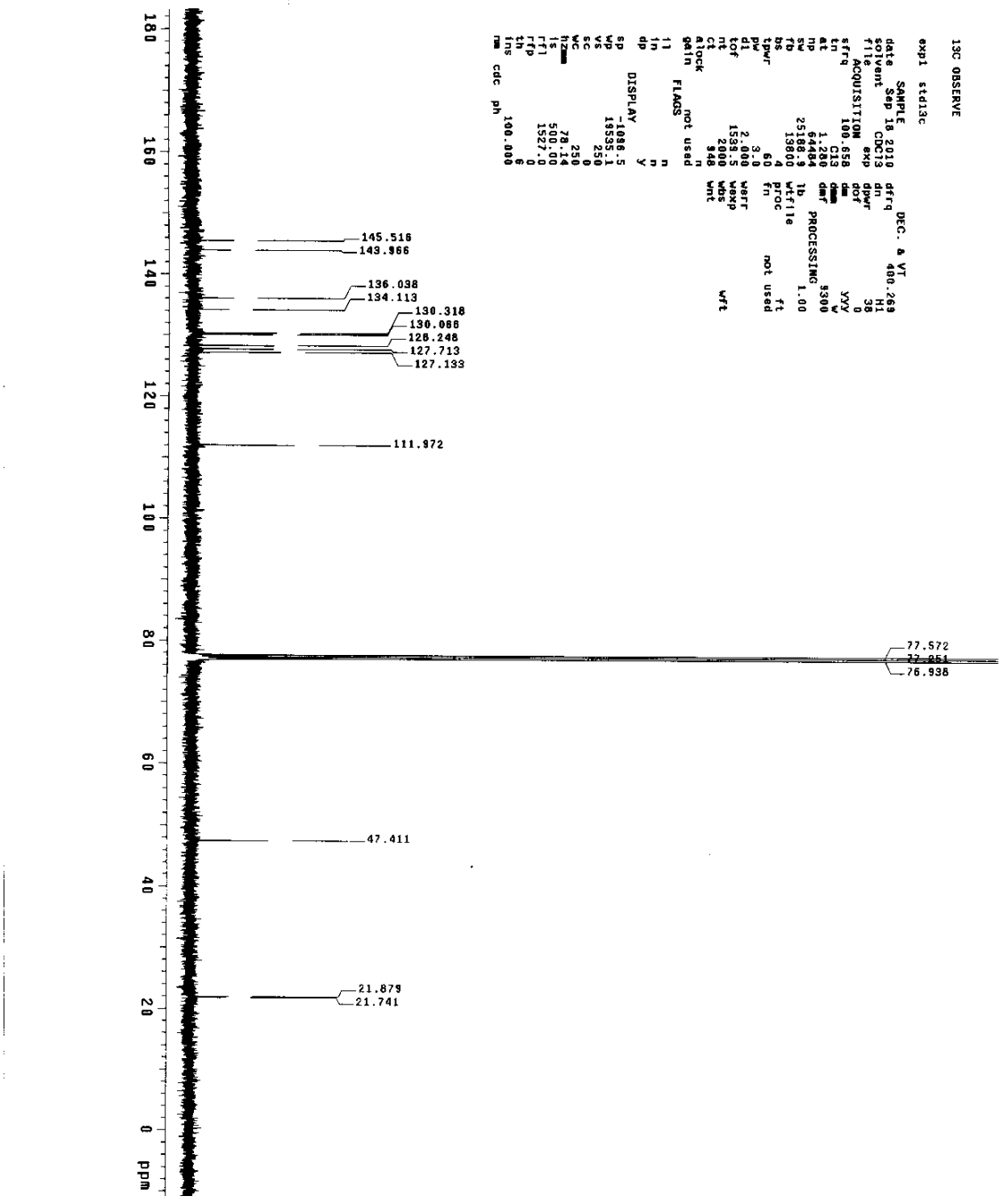


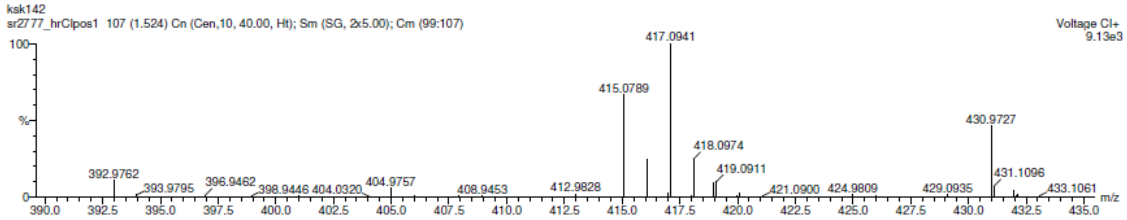
Figure S20. ^{13}C NMR spectrum of **7** recorded in $CDCl_3$.

Elemental Composition Report **Page 1**

Single Mass Analysis (displaying only valid results)
Tolerance = 5.0 PPM / DBE: min = -1000.0, max = 1000.0
Selected filters: None

Monoisotopic Mass, Odd and Even Electron Ions
131 formula(e) evaluated with 1 results within limits (all results (up to 1000) for each mass)
Elements Used:
C: 0-100 H: 0-100 N: 0-2 O: 0-4 S: 2-2

ksk142
sr2777_hrClpos1 107 (1.524) Cn (Cen,10, 40.00, Ht); Sm (SG, 2x5.00); Cm (99:107)



Minimum:				-1000.0		
Maximum:		1000.0	5.0	1000.0		
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Formula
417.0941	417.0943	-0.2	-0.5	11.5	30.7	C20 H21 N2 O4 S2

Figure S21. CI-HRMS spectrum of compound **7**.

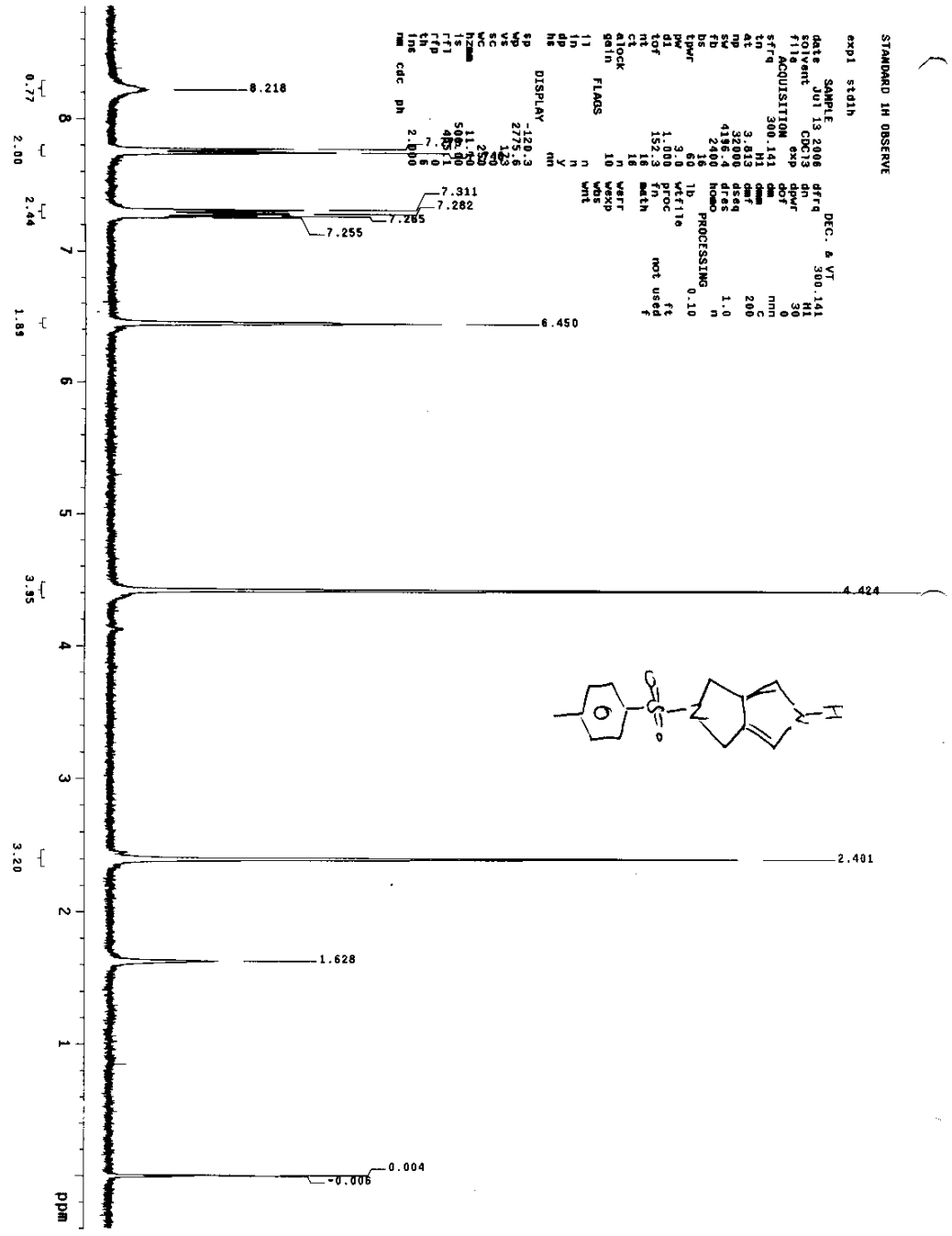


Figure S22. ^{1}H NMR spectrum of **8** recorded in $CDCl_3$.

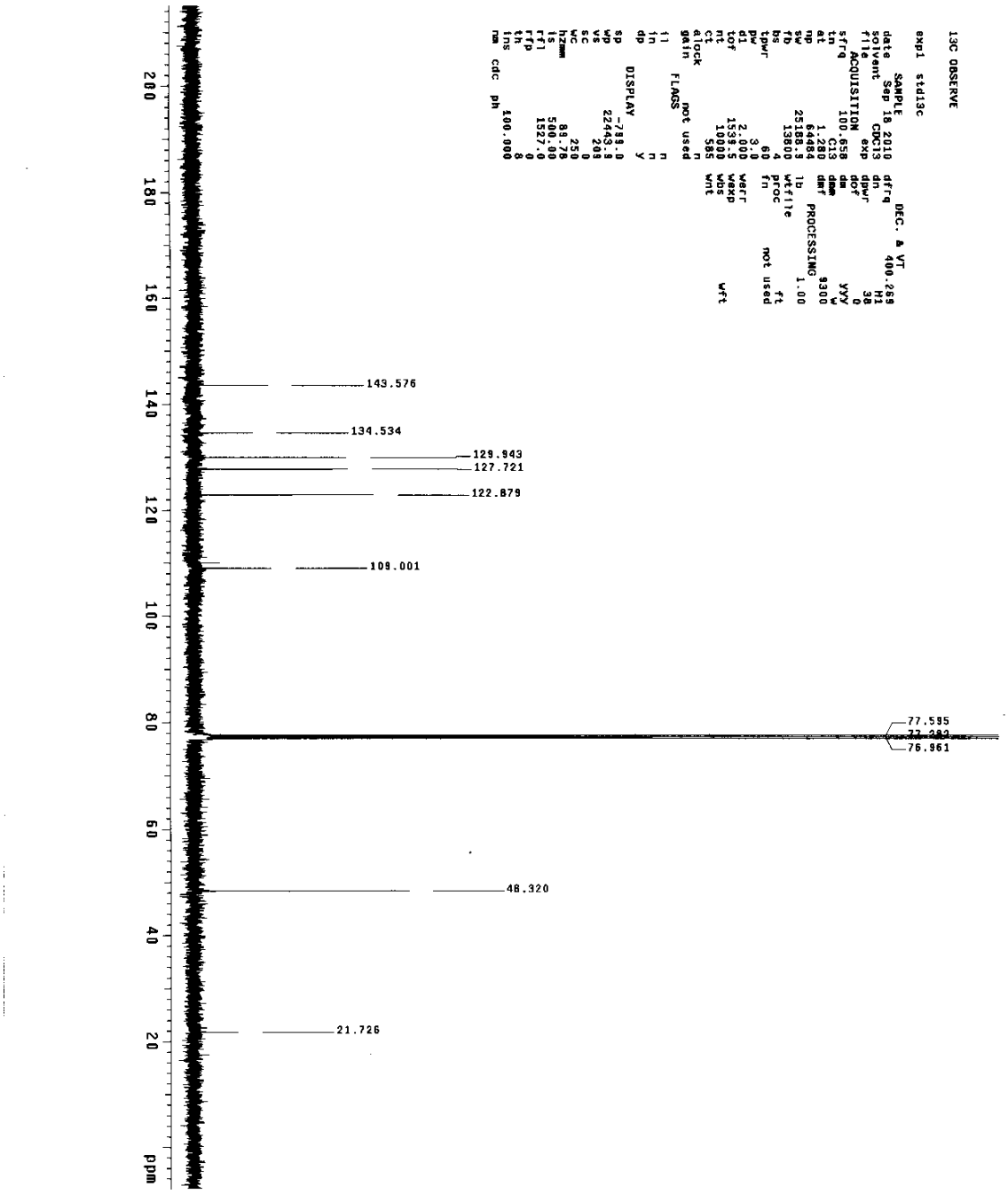


Figure S23. ^{13}C NMR spectrum of **8** recorded in $CDCl_3$.

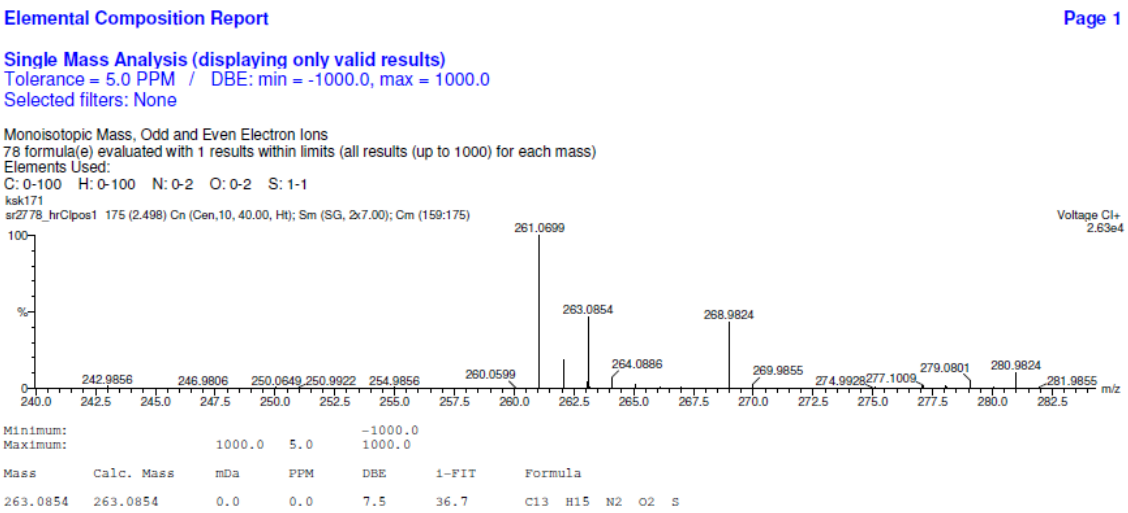


Figure S24. CI-HRMS spectrum of compound **8**.

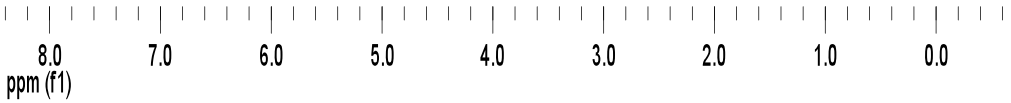


Figure S25. ^{1}H NMR spectrum of **2** recorded in $CDCl_3$.

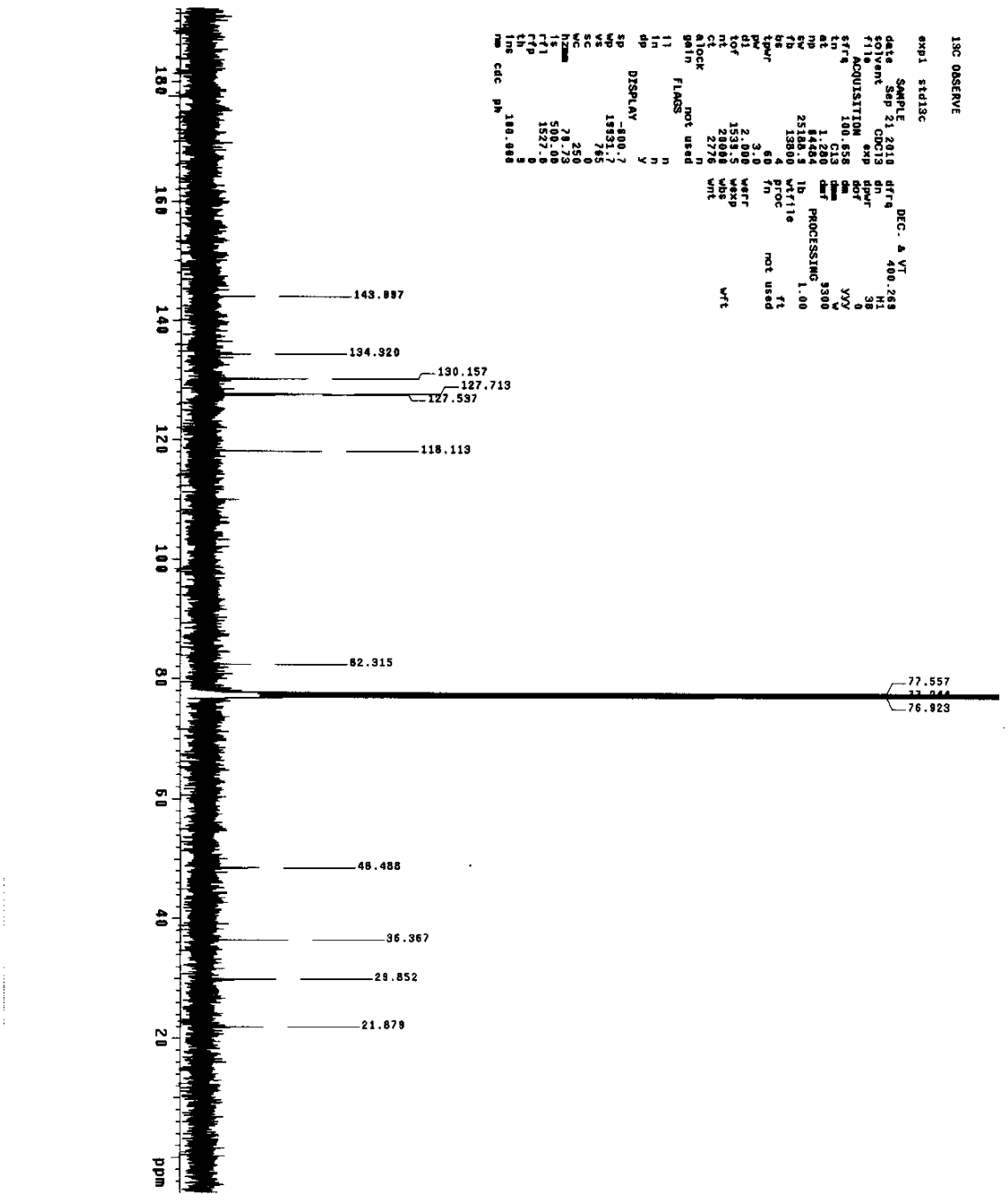


Figure S26. ^{1}H NMR spectrum of **2** recorded in $CDCl_3$.

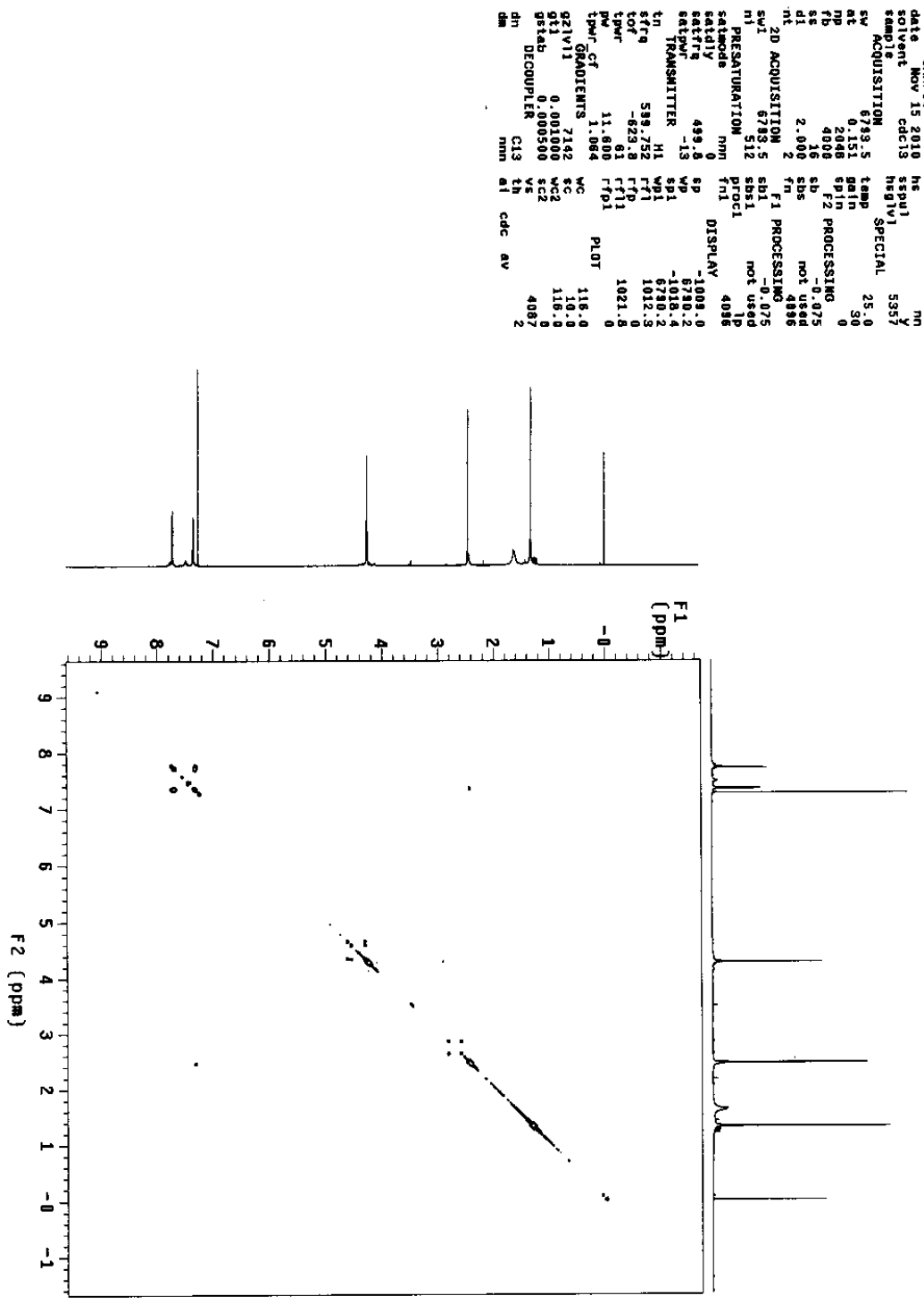


Figure S27. COSY NMR spectrum of **2** recorded in $CDCl_3$.

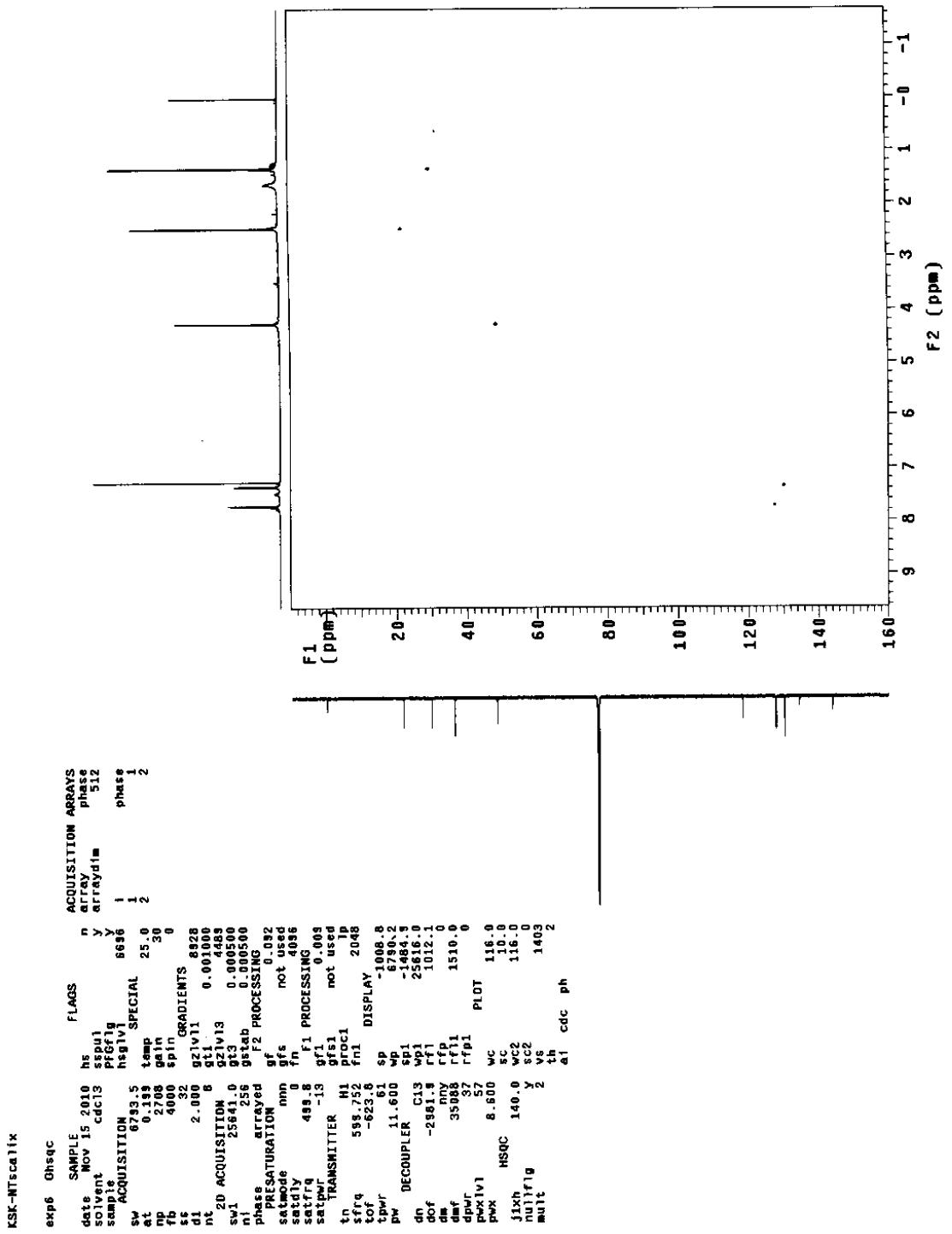


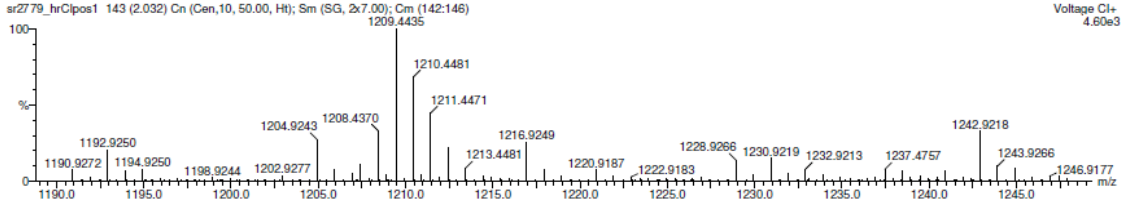
Figure S28. HSQC NMR spectrum of **2** recorded in $CDCl_3$.

Elemental Composition Report **Page 1**

Single Mass Analysis (displaying only valid results)
Tolerance = 3.0 PPM / DBE: min = -1000.0, max = 1000.0
Selected filters: None

Monoisotopic Mass, Odd and Even Electron Ions
211 formula(e) evaluated with 1 results within limits (all results (up to 1000) for each mass)
Elements Used:
C: 0-100 H: 0-100 N: 4-8 O: 4-8 S: 4-4

ksk159
sr2779_hrClpos1 143 (2.032) Cn (Cen,10, 50.00, Ht); Sm (SG, 2x7.00); Cm (142:146)



Minimum:				-1000.0		
Maximum:		1000.0	3.0	1000.0		
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Formula
1209.4435	1209.4434	0.1	0.1	32.5	20.9	C64 H73 N8 O8 S4

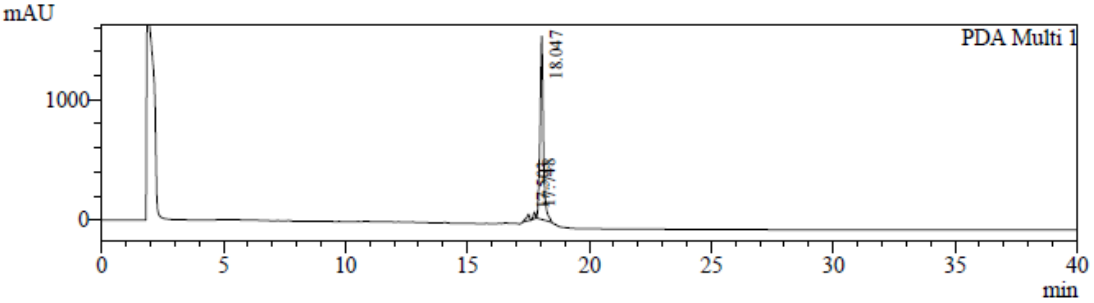
Figure S29. CI-HRMS of compound **2**.

Sample Information

Acquired by	: Admin
Sample Name	: SungKuk1inDMSO
Sample ID	: 1
Tray#	: 1
Vail#	: 31
Injection Volume	: 10 uL
Data Filename	: SungKuk3inDMSO.lcd
Method Filename	: Pic analytical A.lcm
Batch Filename	: run1.lcb
Report Filename	: Base General report2.lcr
Date Acquired	: 9/19/2010 3:24:12 PM
Data Processed	: 9/19/2010 4:04:14 PM

Chromatogram

SungKuk1inDMSO C:\Documents and Settings\User\Desktop\Group Files\Derric\091910\SungKuk3inDMSO.lcd



1 PDA Multi 1 / 230nm 4nm

PeakTable

PDA Ch1 230nm 4nm

Peak#	Ret. Time	Area	Area %
1	17.503	455589	3.007
2	17.748	317829	2.098
3	18.047	14377572	94.895
Total		15150990	100.000

Contour

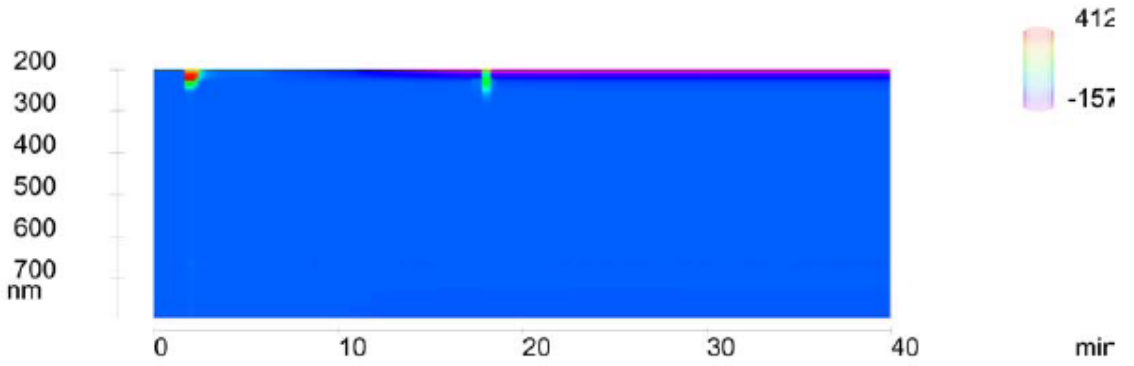


Figure S30. HPLC analysis of compound **2**.

Method

<<Comment>>
<<PDA>>

Model	:SPD-M20A
Lamp Type	:D2&W
Wavelength From	:200 nm
Wavelength To	:800 nm
Use Cell Temp.	:Use
Cell Temp.	:40 C
Slit Width	:1.2 nm
Reference correction	:Not Used
DA1 Wavelength	:470 nm
DA1 Bandwidth	:4 nm
DA1 Output Range	:4.0 AU/V
DA1 Polarity	:+
DA2 Wavelength	:750 nm
DA2 Bandwidth	:4 nm
DA2 Output Range	:4.0 AU/V
DA2 Polarity	:+
DA3 Wavelength	:250 nm
DA3 Bandwidth	:4 nm
DA3 Output Range	:1.0 AU/V
DA3 Polarity	:+
DA4 Wavelength	:250 nm
DA4 Bandwidth	:4 nm
DA4 Output Range	:1.0 AU/V
DA4 Polarity	:+

<<LC Program>>

Time	Unit	Command	Value
0.10	Pumps	B.Conc	10
15.00	Pumps	B.Conc	100
40.00	Controller	Stop	