Protonation-triggered Conformational Modulation of an *N,N´*-Dialkylbispidine: First observation of the elusive boat-boat conformer.

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Supplementary material

1. ^{1}H and ^{13}C NMR data for 1, $[1{\cdot}H]^{+}$, $[1{\cdot}2H]^{2+}$ BC and $[1{\cdot}2H]^{2+}$ BB

1.1. Bispidine 1 CC

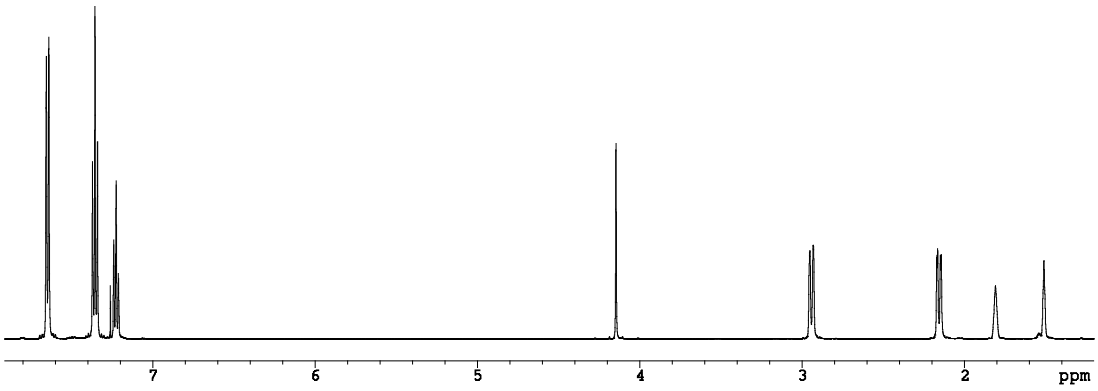

Figure S 1: ^{1}H NMR spectrum of **1** (500 MHz, $CDCl_3$ solution, 25 °C).

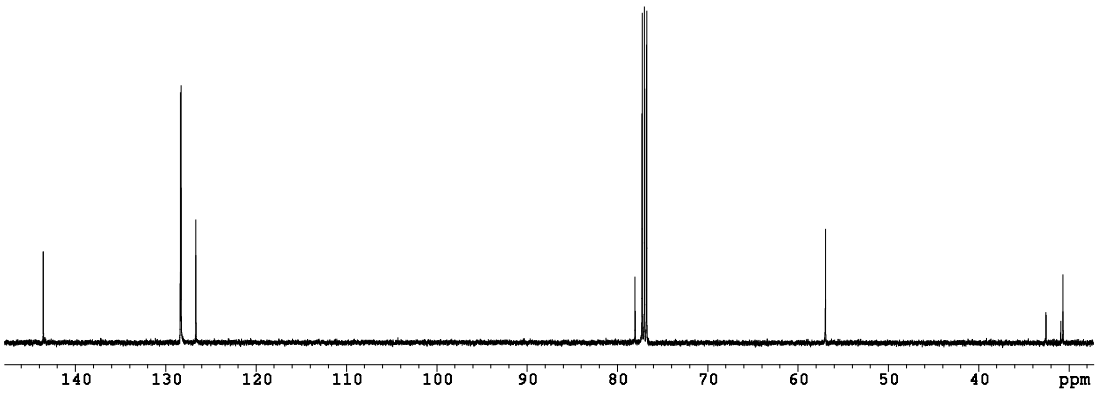

Figure S 2: ^{13}C NMR spectrum of **1** (125.7 MHz, $CDCl_3$ solution, 25 °C).

^{1}H NMR (500 MHz, $CDCl_3$ solution, 25 °C): δ = 7.65 (m, 8H, ortho-H); 7.35 (dm, J = 7.4 Hz, 8H, meta-H), 7.22 (dm, J = 7.4 Hz, 4H, para-H), 4.15 (s, 2H, $Ph_2C\underline{H}$), 2.94 (dm, J =11.1 Hz, 4H, 2,4,6,8-CH_2-eq), 2.16 (dm, J = 11.1 Hz, 4H, 2,4,6,8-CH_2-ax), 1.81 (m, 2H, 1,5-CH), 1.51 (m, 2H, 9-CH_2).

^{13}C NMR (125.7 MHz, $CDCl_3$ solution, 25 ^{o}C): δ = 143.6 (C-*ipso*), 128.34 (Ph), 128.28 (Ph), 126.6 (Ph), 78.0 ($Ph_2\underline{C}H$), 57.0 (2,4,6,8-CH_2), 32.6 (9-CH_2), 30.7 (1,5-CH).

1.2. Bispidine $[1{\cdot}H]^+$ CC

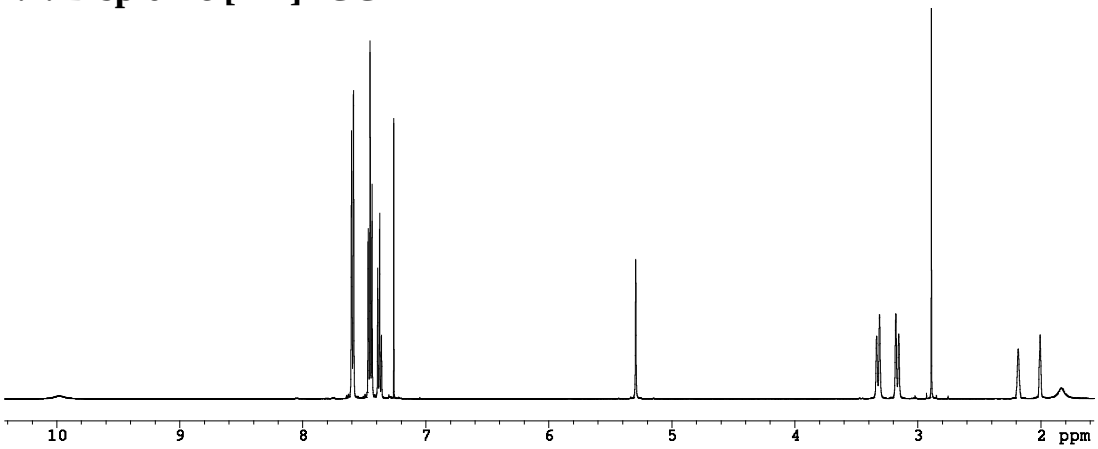

Figure S 3: ^{1}H NMR spectrum of $[\mathbf{1}{\cdot}H]^+$ protonated by aliquots of $MeSO_3H$ (500 MHz, $CDCl_3$ solution, 25 °C).

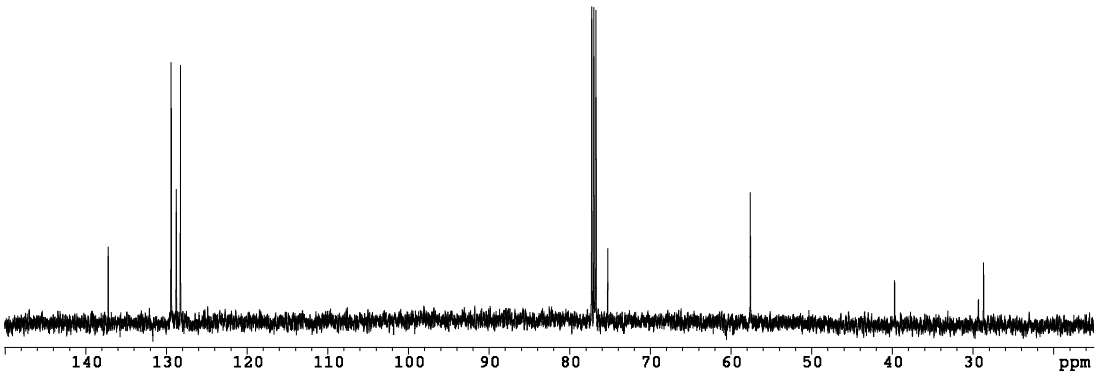

Figure S 4: ^{13}C NMR spectrum of $[\mathbf{1}{\cdot}H]+$ protonated by aliquots of $MeSO_3H$ (125.7 MHz, $CDCl_3$ solution, 25 °C).

^{1}H NMR (500 MHz, $CDCl_3$ solution, 25 ^{o}C): δ = 9.99 (br s, 1H, NH), 7.59 (m, 8H, ortho-H), 7.45 (m, 8H, meta-H), 7.37 (m, 4H, para-H), 5.29 (s, 2H, $Ph_2C\underline{H}$), 3.32 (dm, J = 12.0 Hz, 4H, 2,4,6,8-CH_2-eq), 3.17 (dm, J = 12.0 Hz, 4H, 2,4,6,8-CH_2-ax), 2.18 (m, 2H, 1,5-CH), 2.01 (m, 2H, 9-CH_2).

^{13}C NMR (125.7 MHz, $CDCl_3$ solution, 25 ^{o}C): δ = 137.2 (C-*ipso*), 129.4 (Ph), 129.8 (Ph), 128.2 (Ph), 75.3 ($Ph_2\underline{C}H$), 57.6 (2,4,6,8-CH_2), 39.7 (1,5-CH), 28.7 (9-CH_2).

1.3. Bispidine $[1{\cdot}2H]^{2+}$ BC

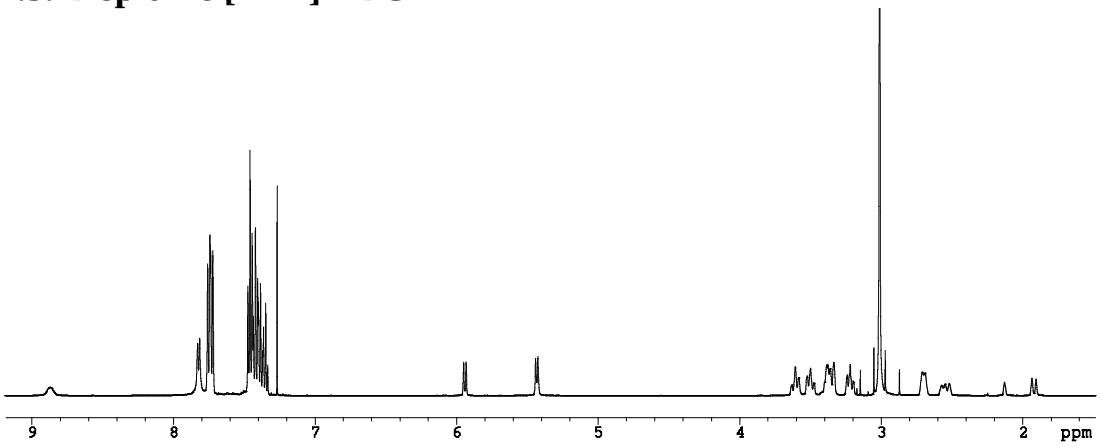

Figure S 5: ^{1}H NMR spectrum of $[1{\cdot}2H]^{2+}$ BC protonated by aliquots of $MeSO_3H$ (500 MHz, $CDCl_3$ solution, 25 °C).

^{1}H NMR (500 MHz, $CDCl_3$, 25 ^{o}C): δ = 9.33 (br s, 1H, chair-side NH), 8.32 (br s, 1H, boat-side NH), 7.80-7.70 (several multiplets), 7.49-7.33 (several multiplets), 5.94 (d, J = 9.0 Hz, 1H, boat-side $Ph_2C\underline{H}$), 5.43 (d, J = 8.1 Hz, 1H, chair-side $Ph_2C\underline{H}$), 3.60 (m, 2H, boat-side CH_2-eq), 3.50 (m, 2H, boat-side CH_2-ax), 3.36 (m, 2H, chair-side CH_2-eq), 3.21 (m, 2H, chair-side CH_2-ax), 2.70 (m, 2H, 1,5-CH), 2.55 (m, 1H, boat-side 9-CH_2), 1.92 (m, 1H, chair-side 9-CH_2).

^{13}C NMR (125.7 MHz, $CDCl_3$, 25 ^{o}C): δ = 134.3, 134.2, 133.6, 129.9, 129.6, 129.2, 129.1, 128.9, 80.2 (chair-side $Ph_2\underline{C}H$), 75.9 (boat-side $Ph_2\underline{C}H$), 56.9 (chair-side CH_2), 51.5 (boat-side CH_2), 24.5 (1,5-CH), 20.6 (9-CH_2).

1.4. Bispidine $[1{\cdot}2H]^{2+}$ BB

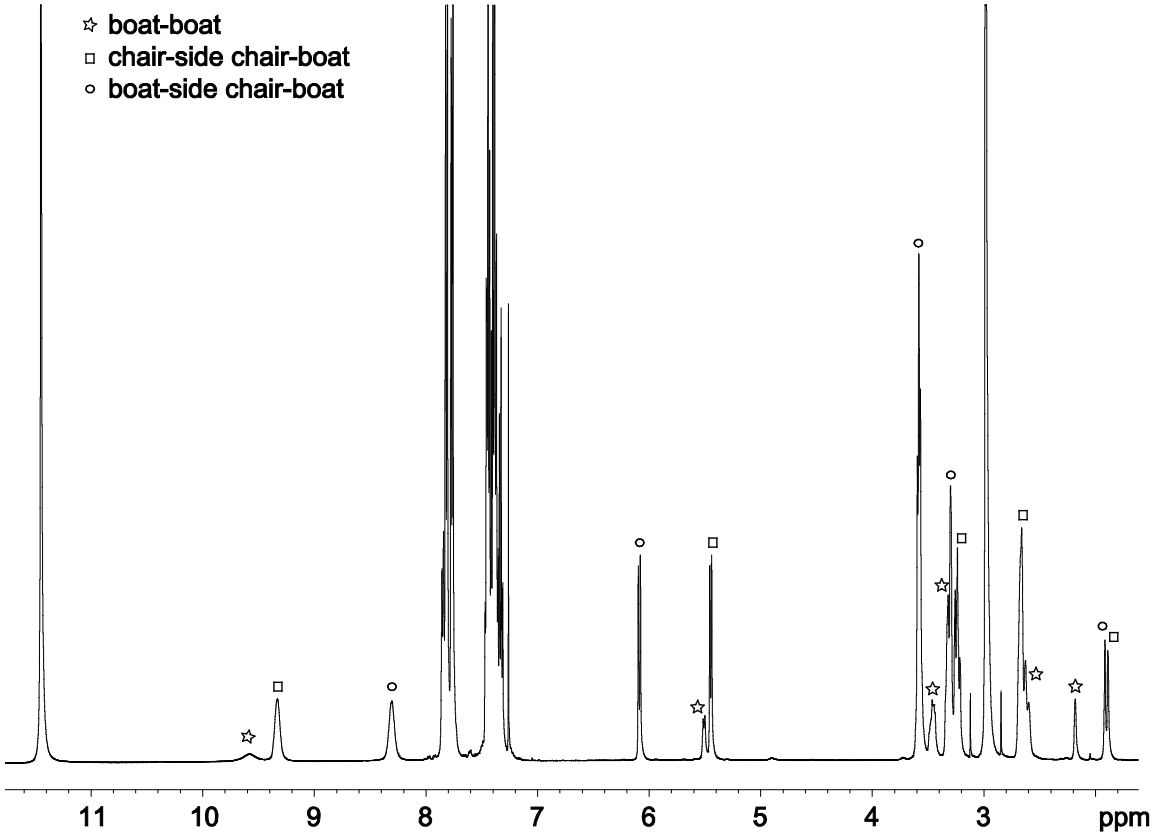

Figure S 6: ^{1}H NMR spectrum of a mixture of $[\mathbf{1}{\cdot}2H]^{2+}$ BC and $[\mathbf{1}{\cdot}2H]^{2+}$ BB protonated by an excess of $MeSO_3H$ (500 MHz, $CDCl_3$ solution, 25 °C).

^{1}H NMR (900 MHz, $CDCl_3$ solution, 25 ^{o}C): δ = 9.58 (br s, NH), 5.52 (d, J = 7.6 Hz, 2H, $Ph_2C\underline{H}$), 3.47 (m, 4H, CH_2-eq), 3.28 (m, 4H, CH_2-ax), 2.61 (m, 2H, 1,5-CH), 2.18 (m, 2H, 9-CH_2).

^{13}C NMR (125.7 MHz, $CDCl_3$, 25 ^{o}C): δ = 133.5, 130.1, 129.9, 129.5, 81.8 ($Ph_2\underline{C}H$), 55.8 (2,4,5,8-CH_2), 27.4 (m, 2H, 1,5-CH), 20.4 (m, 2H, 9-CH_2).

1.5. ^{1}H NMR comparison of 1 CC, [1·H]$^+$ CC and [1·2H]$^{2+}$ BC

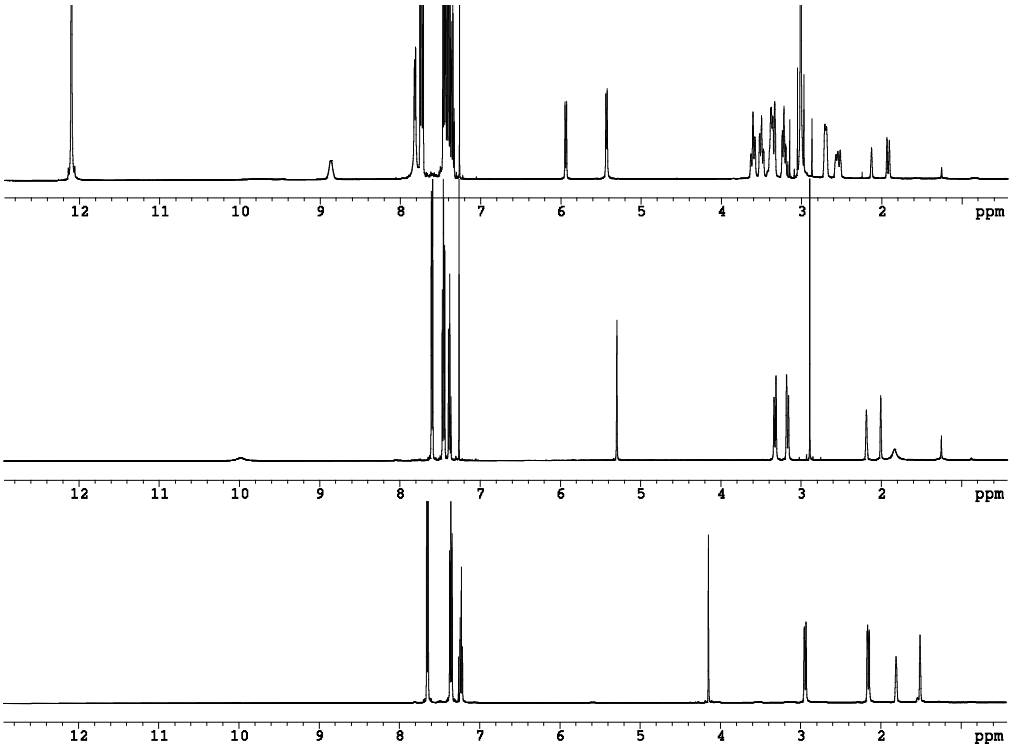

Figure S 7: ^{1}H NMR spectrum of **1** (bottom), [**1**·H]$^+$ (middle) and [**1**·2H]$^{2+}$ (top, mixture of BC and BB isomers), (500 MHz, $CDCl_3$ solution, 25 °C).

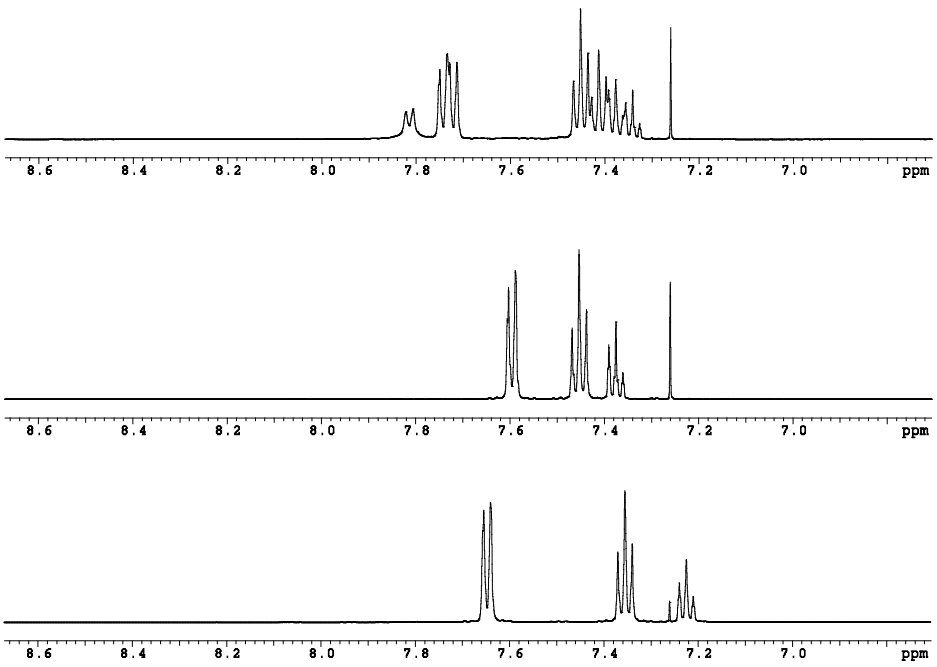

Figure S 8: Expansion of the aromatic region from ^{1}H NMR spectrum of **1** (bottom), [**1**·H]$^+$ (middle) and [**1**·2H]$^{2+}$ BC (top) (500 MHz, $CDCl_3$ solution, 25 °C).

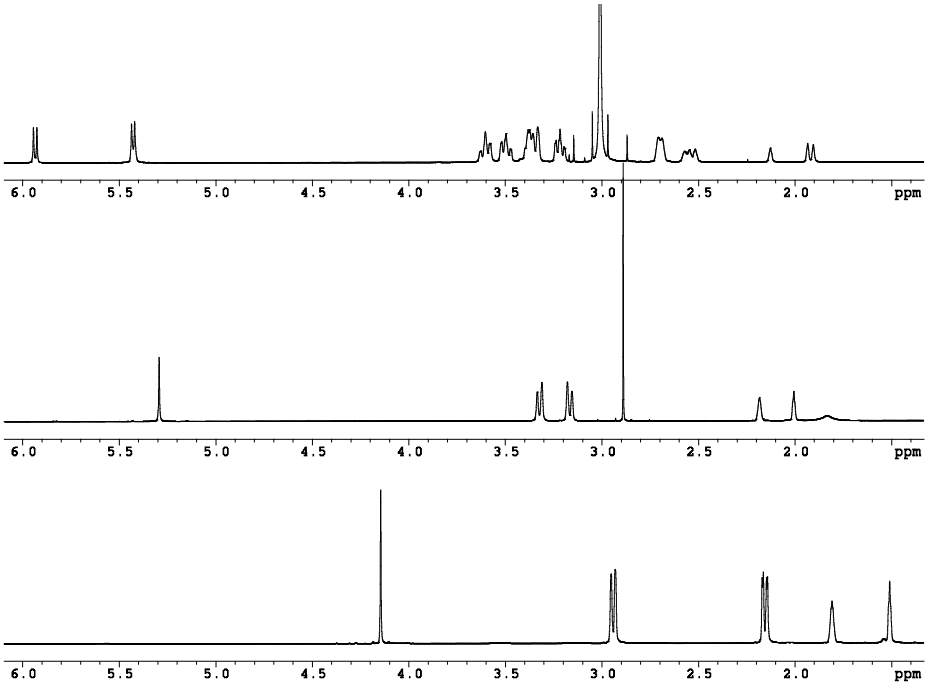

Figure S 9: Expansion of the aliphatic region from ^{1}H NMR spectrum of **1** (bottom), [**1**·H]$^{+}$ (middle) and [**1**·2H]$^{2+}$ BC (top) (500 MHz, $CDCl_3$ solution, 25 °C).

Further protonation attempts in different solvents to facilitate a larger temperature range were unsuccessful, as either no formation of [**1**·2H]$^{2+}$ was observed (dimethyl formamide, o-dichlorobenzene), or the protonated species was insoluble (toluene).

1.6. Ratio of Boat-Boat:Boat-Chair conformers

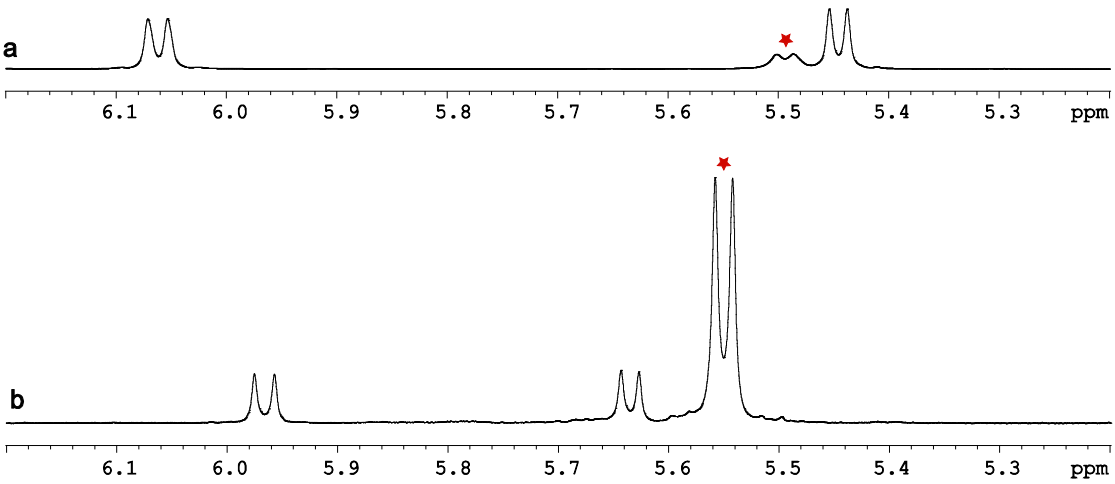

Figure S 10: Expansion of the C<u>H</u>Ph$_2$ protons of [**1**·2H]$^{2+}$ BC and BB (denoted by *). a) Stepwise addition of excess $MeSO_3H$, 18 % BB conformer b) Direct addition of excess $MeSO_3H$, 74 % BB conformer.

The BB conformer is so far observed only in a mixture with the BC conformer. The ratio can be tuned by the rate of acid addition. When stepwise addition to a solution of **1** is carried out generally a ratio of 8:2 of BC:BB is observed. When an excess of acid is added directly (in a single portion) to a solution of **1**, a ratio of up to 3:7 BC:BB has been observed.

2. Variable temperature NMR of a mixture of $[\mathbf{1}\cdot H]^+$ and $[\mathbf{1}\cdot 2H]^{2+}$ BC

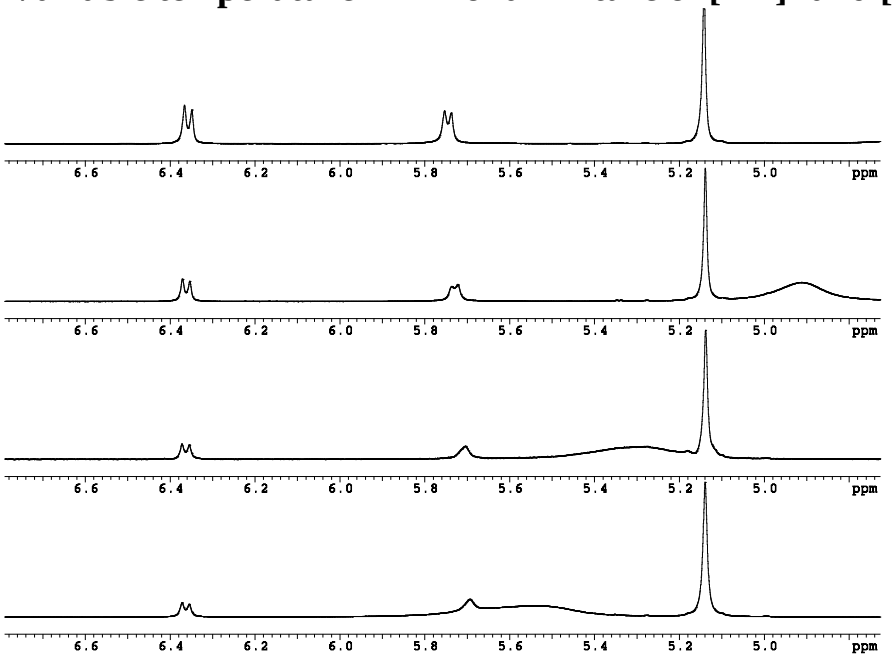

Figure S 11: Expansion of the $Ph_2C\underline{H}$ region from ^1H NMR spectrum (500 MHz, $CDCl_3$ solution) of a mixture of $[\mathbf{1}\cdot H]^+$ and $[\mathbf{1}\cdot 2H]^{2+}$ at various temperatures. From top: 25 °C, 45 °C, 55 °C and 60 °C.

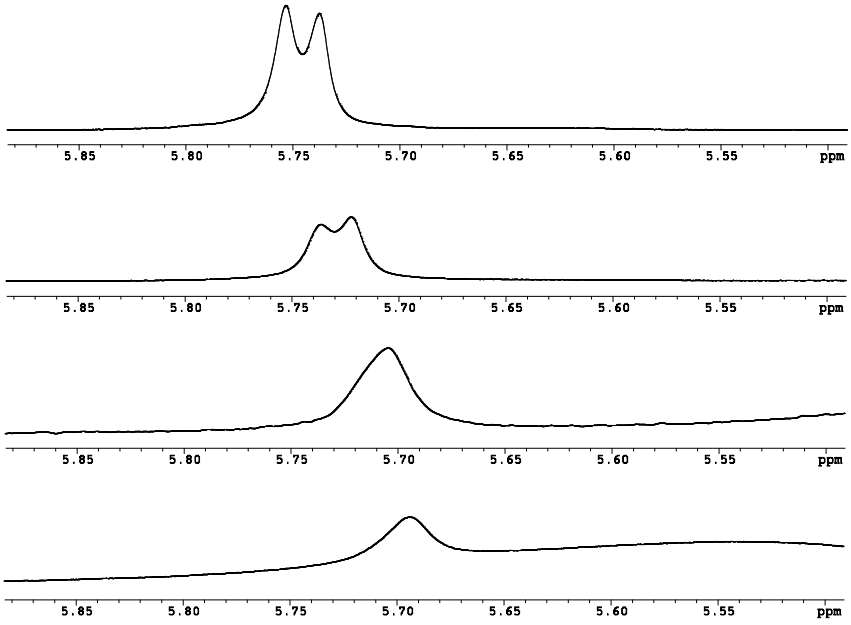

Figure S 12: Expansion of $[\mathbf{1}\cdot 2H]^{2+}$ BC chair $Ph_2C\underline{H}$ from ^1H NMR spectrum (500 MHz, $CDCl_3$ solution) at various temperatures. From top: 25 °C, 45 °C, 55 °C and 60 °C.

Broadening (loss of coupling to NH) of the chair-side $Ph_2C\underline{H}$ proton of $[\mathbf{1}\cdot 2H]^{2+}$ is due to NH exchange with free acid. Absence of significant chemical shift change indicates that ring flip does not occure.

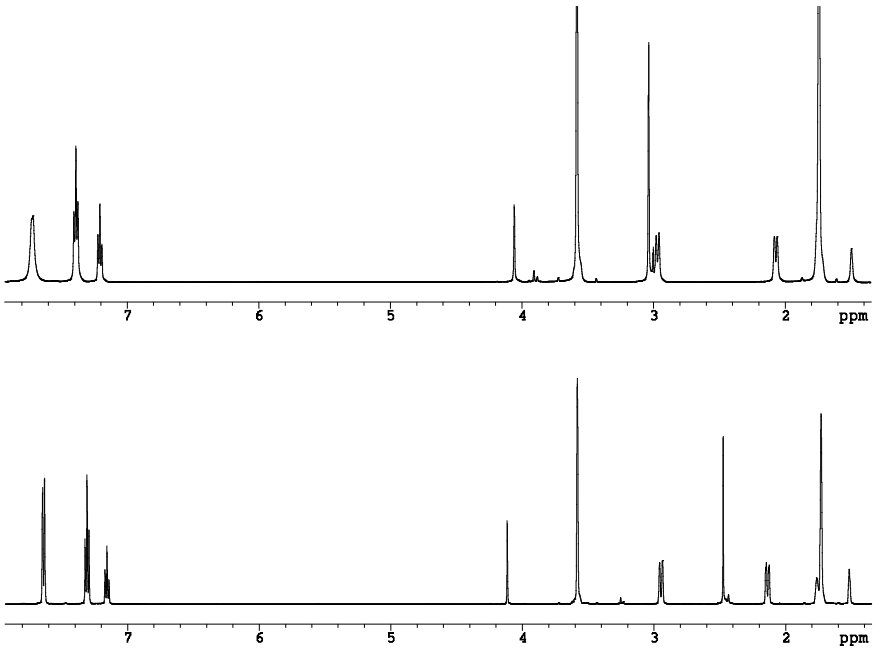

Figure S 13: Variable temperature ^{1}H NMR spectrum (500 MHz, THF-d_8) of **1**. Top: -80 °C Bottom: 25°C.

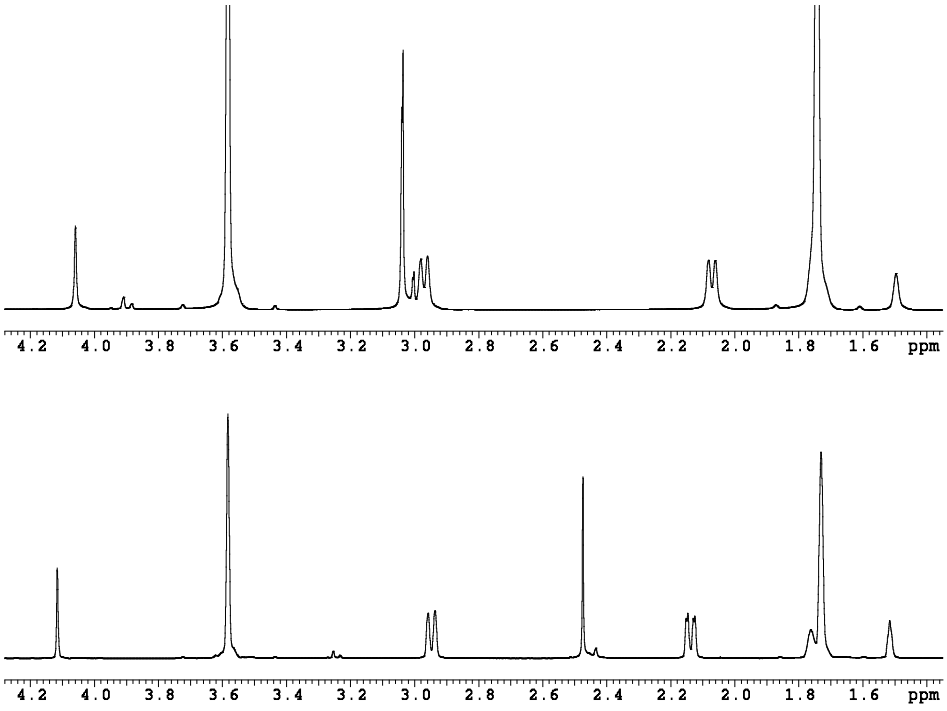

Figure S 14: Expansion of aliphatic signals, variable temperature ^{1}H NMR spectrum (500 MHz, THF-d_8) of **1**. Top: -80 °C Bottom: 25 °C.

Note that chemical shifts remain almost constant, excluding the presence of conformational dynamics.

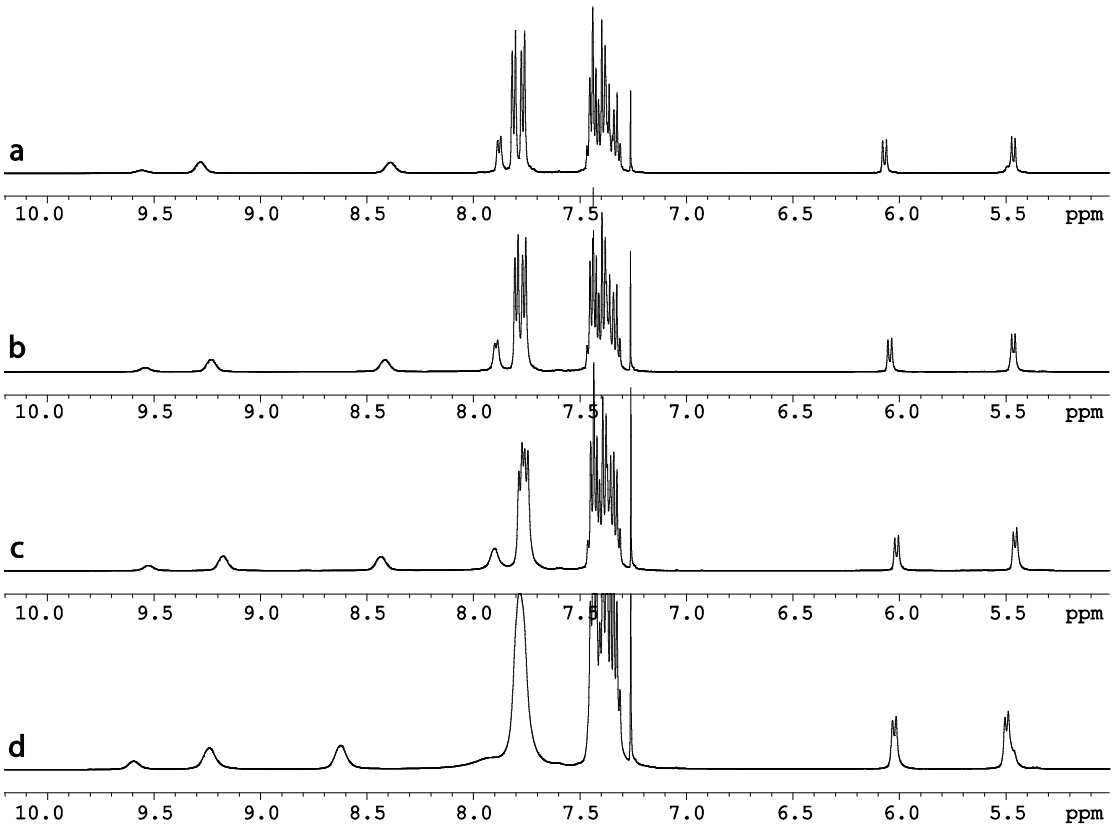

Figure S 15: Variable temperature ^{1}H NMR spectrum of a [**1**·2H]$^{2+}$ BC/BB mixture (~20 % BB) (500 MHz, $CDCl_3$ solution). Expansion of aromatic and benzhydryl region. a) 0 °C, b) -20 °C, c) -40 °C, d) -55 °C.

Broadening of ortho-Ph protons of the BB isomer ($\delta \approx 7.88$) indicates hindered phenyl rotation.

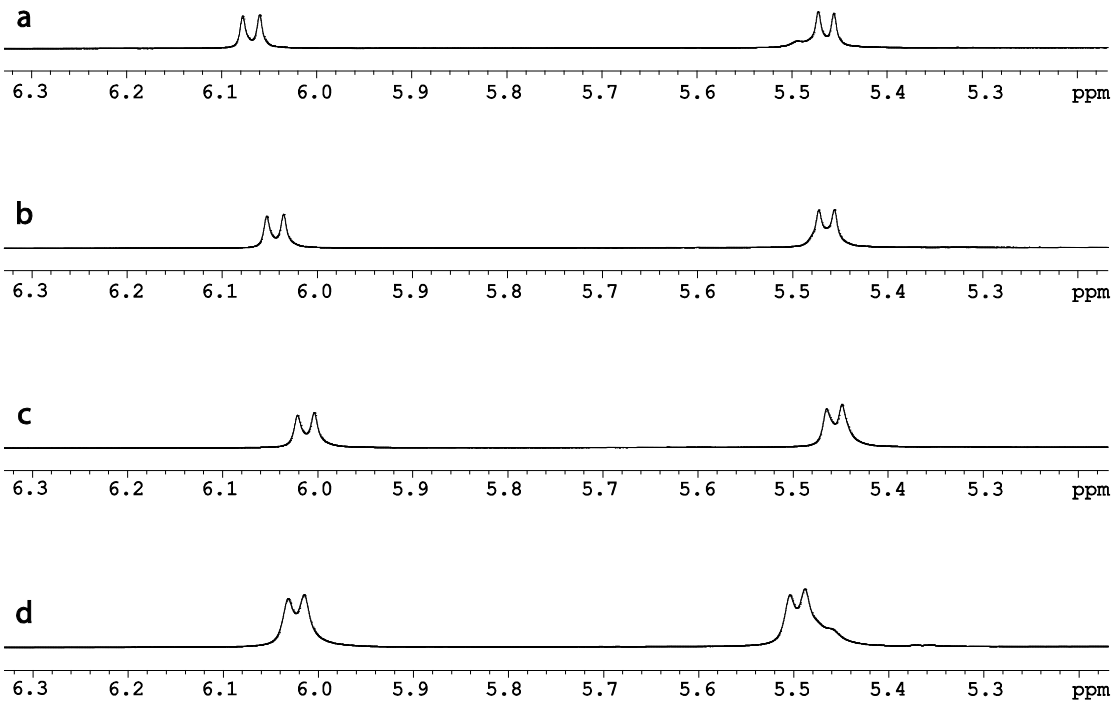

Figure S 16: Variable temperature ^{1}H NMR spectrum of a [**1**·2H]$^{2+}$ BC/BB mixture (~20 % BB) (500 MHz, $CDCl_3$ solution), expansion of $Ph_2C\underline{H}$ protons. a) 0 °C, b) -20 °C, c) -40 °C, d) -55 °C.

3. Saturation transfer spectra for [1·2H]$^{2+}$ N-H and benzhydryl protons

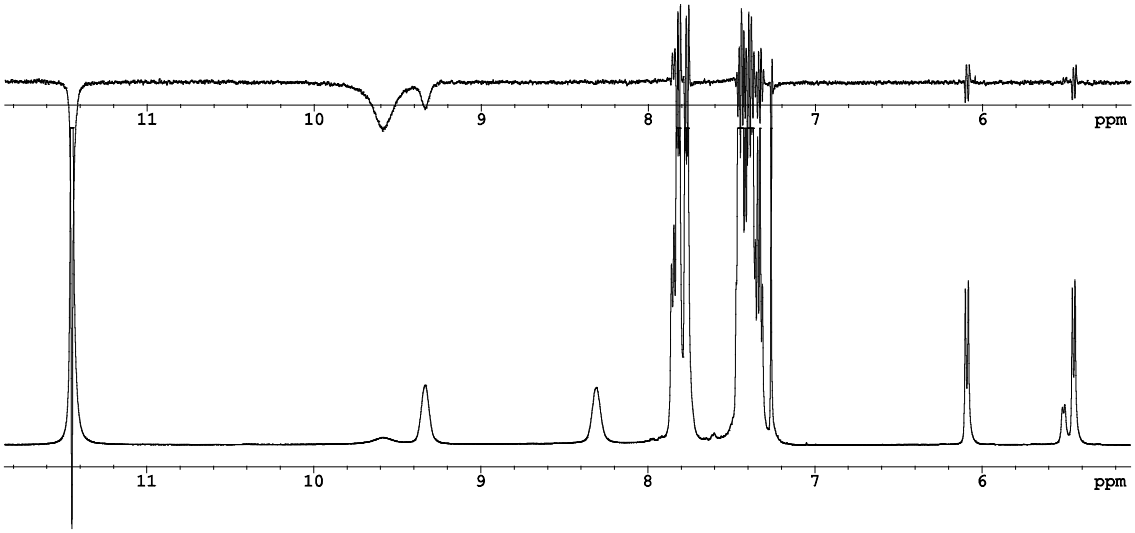

Figure S 17: Expansion from saturation transfer spectrum of [*N,N'*-dibenzhydrylbispidine·2H]$^{2+}$ (500 MHz, $CDCl_3$ solution, 25°C). Saturation time = 5 s.

The BB-NH signal (δ = 9.59) is saturated, resulting in saturation transfer to the free acid (δ = 11.46) and indirect transfer (via free acid) to the BC-NH chair-side (δ = 9.33). Note the absence of transfer to the BC-NH boat-side (δ = 8.31). A NOE to ortho-Ph protons is also detected.

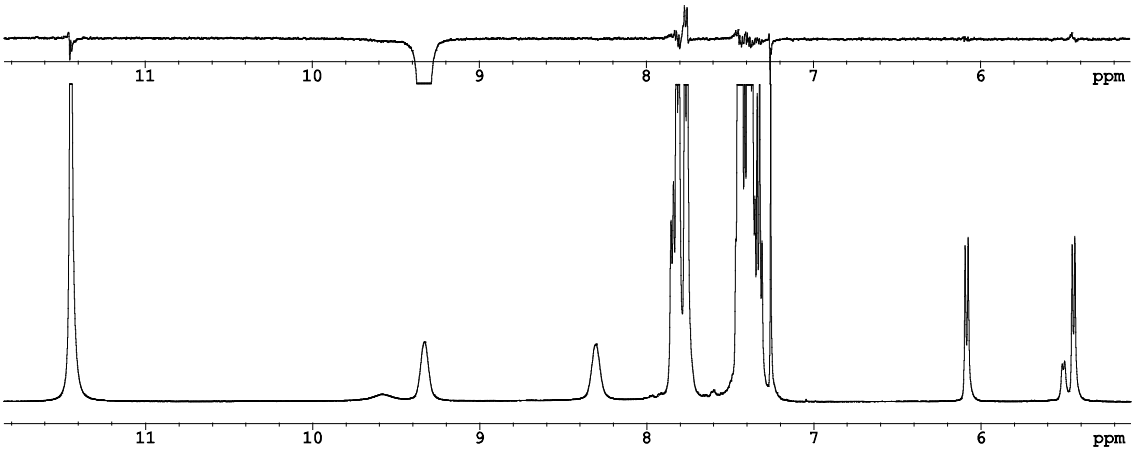

Figure S 18: Expansion from saturation transfer spectrum of [*N,N'*-dibenzhydrylbispidine·2H]$^{2+}$ (500 MHz, $CDCl_3$ solution, 25°C). Saturation time = 5 s.

The BC-NH signal (δ = 9.33) is saturated. Note the absence of transfer to any other signal. A NOE to ortho-Ph protons is detected.

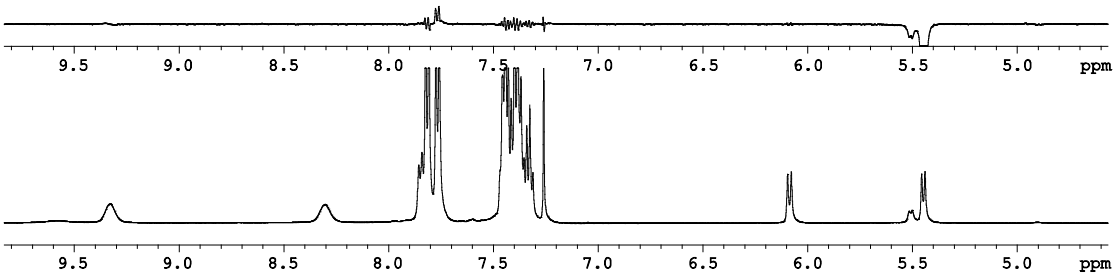

Figure S 19: Expansion from saturation transfer spectrum of [*N,N'*-dibenzhydrylbispidine·2H]$^{2+}$ (500 MHz, $CDCl_3$ solution, 25°C). Saturation time = 30 s.

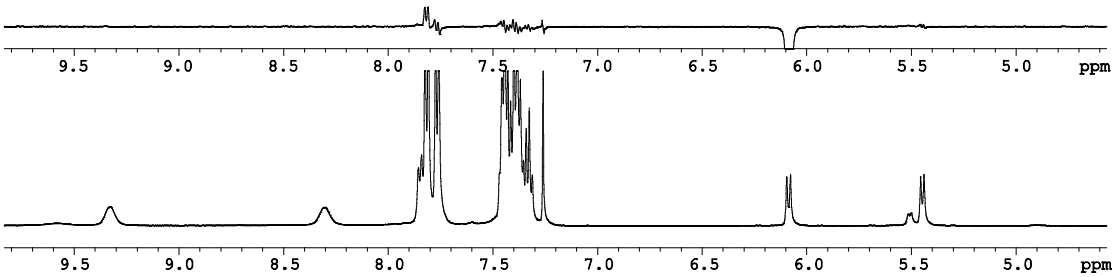

Figure S 20: Expansion from saturation transfer spectrum of [*N,N'*-dibenzhydrylbispidine·2H]$^{2+}$ (500 MHz, $CDCl_3$ solution, 25°C). Saturation time = 30 s.

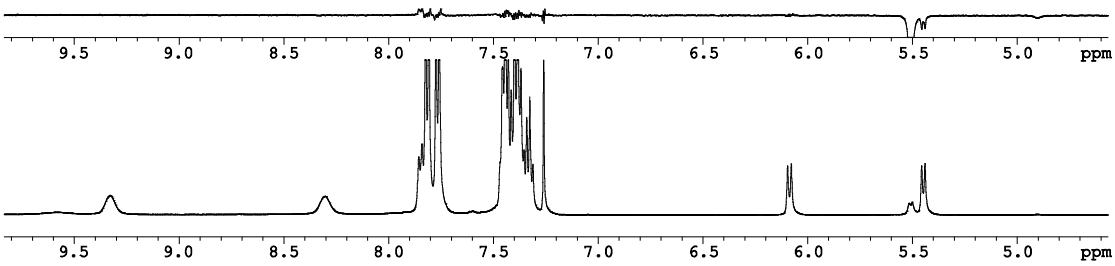

Figure S 21: Expansion from saturation transfer spectrum of [*N,N'*-dibenzhydrylbispidine·2H]$^{2+}$ (500 MHz, $CDCl_3$ solution, 25°C). Saturation time = 30 s.

4. NOE difference spectrum for [1·2H]$^{2+}$

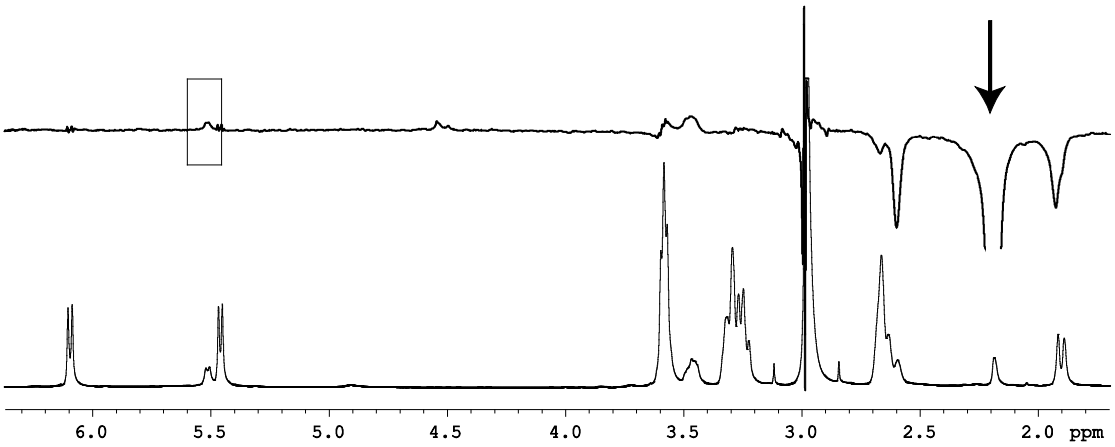

Figure S 22: Expansion from NOE difference spectrum of [*N,N'*-dibenzhydrylbispidine·2H]$^{2+}$, mixture of BC and BB isomers (500 MHz, $CDCl_3$ solution, 25°C). Saturation time = 8 s.

Saturation of the BB bridge protons (arrow) results in a small NOE for the benzhydryl protons (box).

5. 2D NMR spectra of 1, $[1 \cdot H]^{+}$ and $[1 \cdot 2H]^{2+}$

5.1. 2D NMR spectra of 1

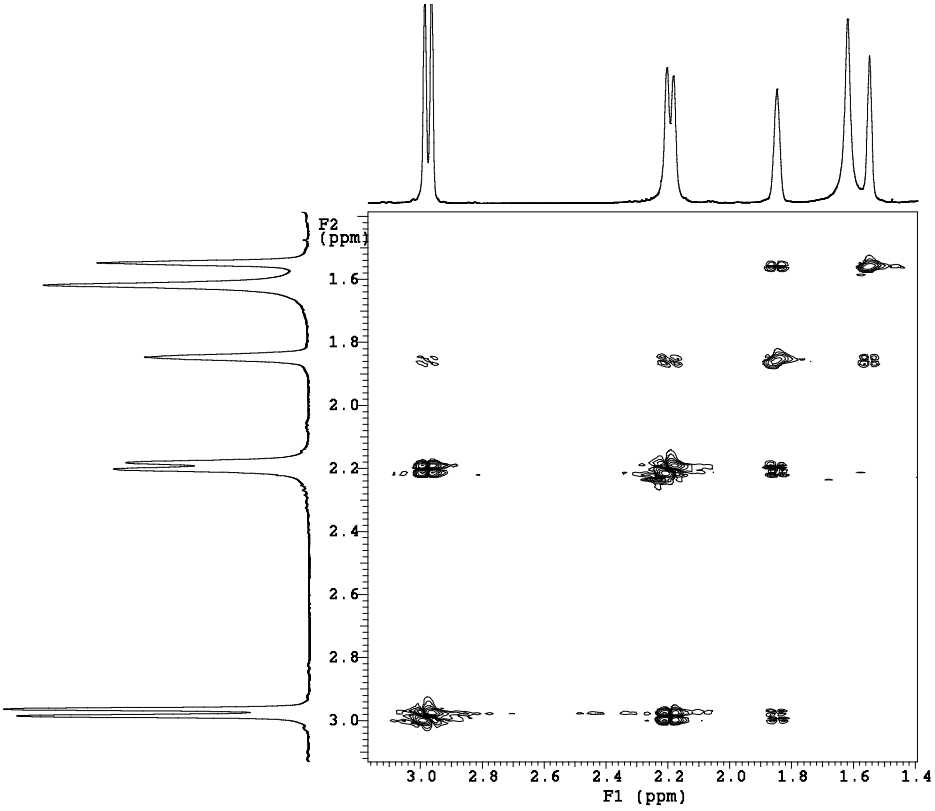

Figure S 23: Expansion from P.E. COSY spectrum of **1**, aliphatic region (500 MHz, $CDCl_3$, 25°C).

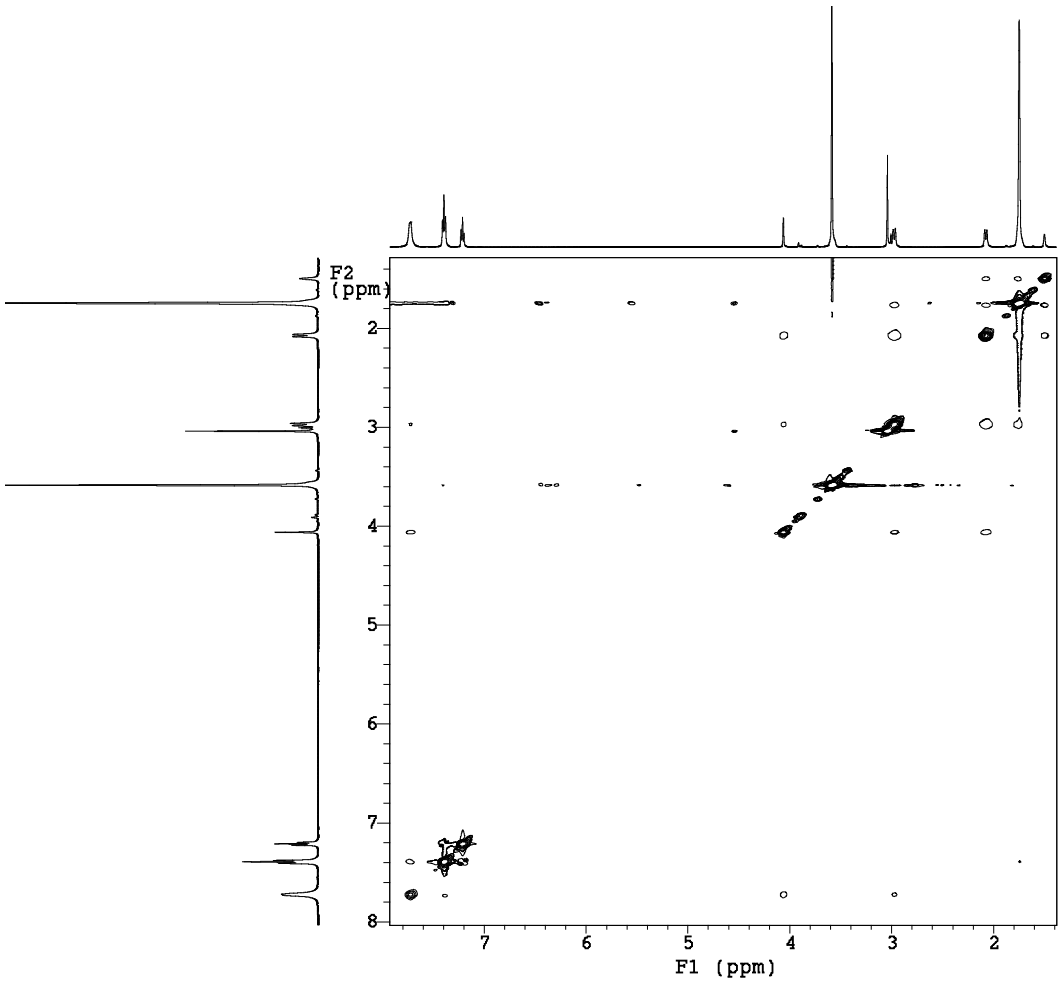

Figure S 24: ROESY spectrum of **1** (500 MHz, THF-d_8, -80 °C).

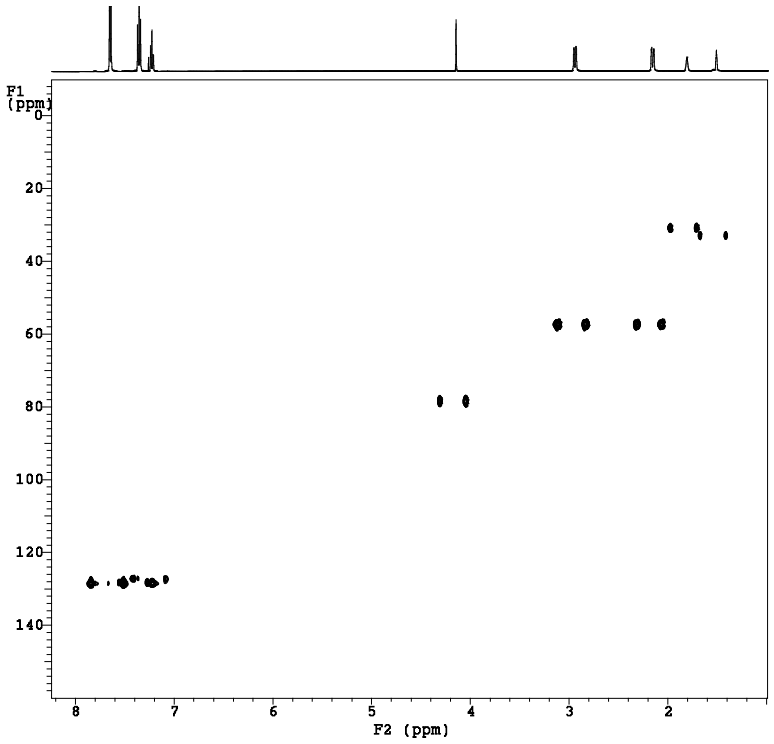

Figure S 25: HSQC spectrum of **1** (500 MHz, $CDCl_3$ solution, 25 °C).

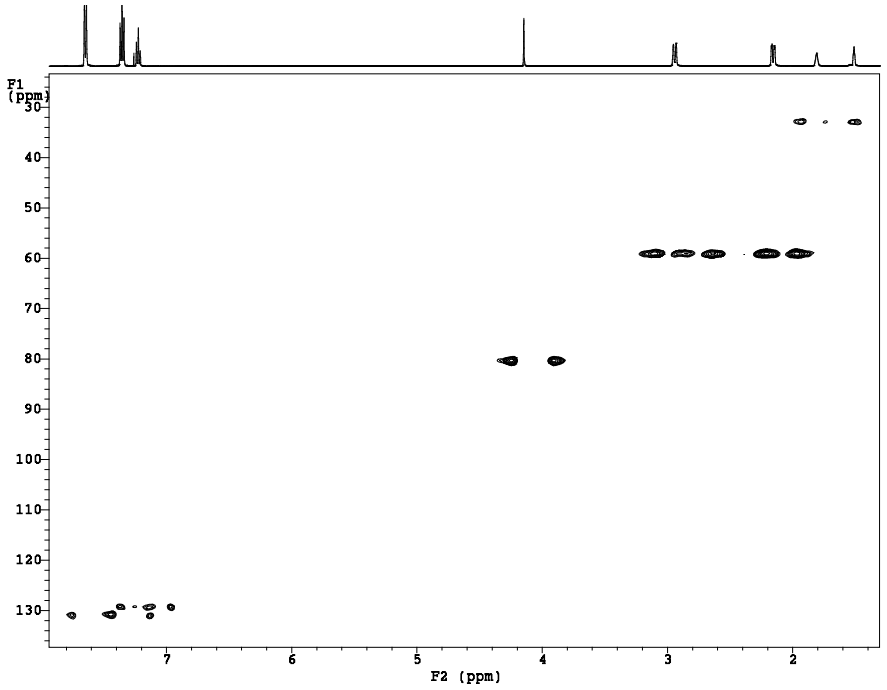

Figure S 26: HSQC spectrum of **1** (9 mg) and PBLG (77 mg) in 0.7 mL $CDCl_3$ solution (500 MHz, 25 °C) (1D trace for **1** in isotropic solution).

5.2. 2D NMR spectra of Bispidine $[1{\cdot}H]^+$

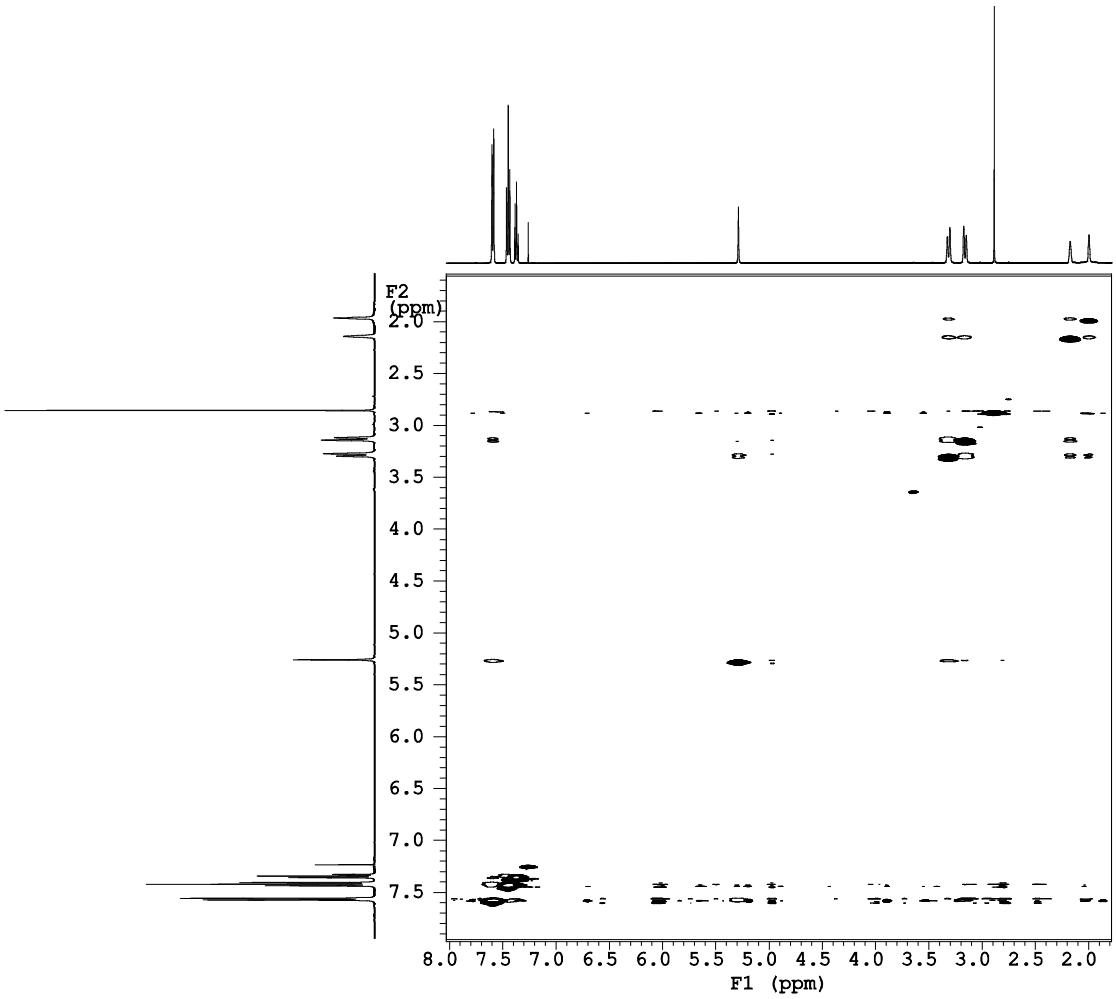

Figure S 27: NOESY spectrum of $[\mathbf{1}{\cdot}H]^+$ (500 MHz, $CDCl_3$, 25°C).

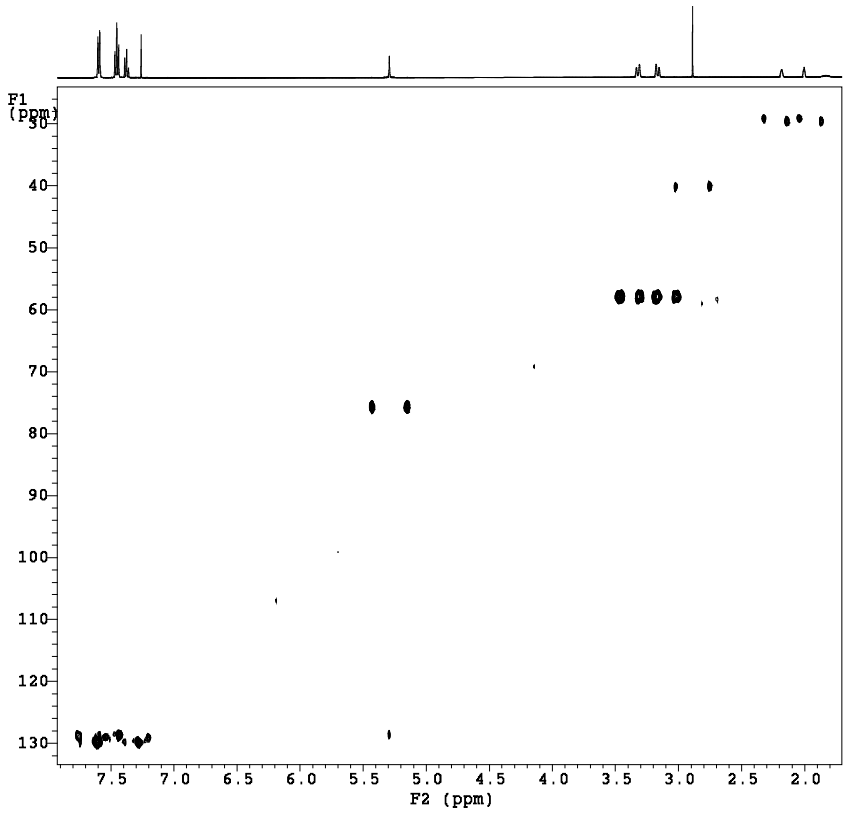

Figure S 28: HSQC spectrum of $[\mathbf{1}\cdot H]^+$ (8 mg) with 1 eq CH_3SO_3H added in $CDCl_3$ solution (900 MHz, 25 °C).

5.3. 2D NMR spectra of $[1{\cdot}2H]^{2+}$

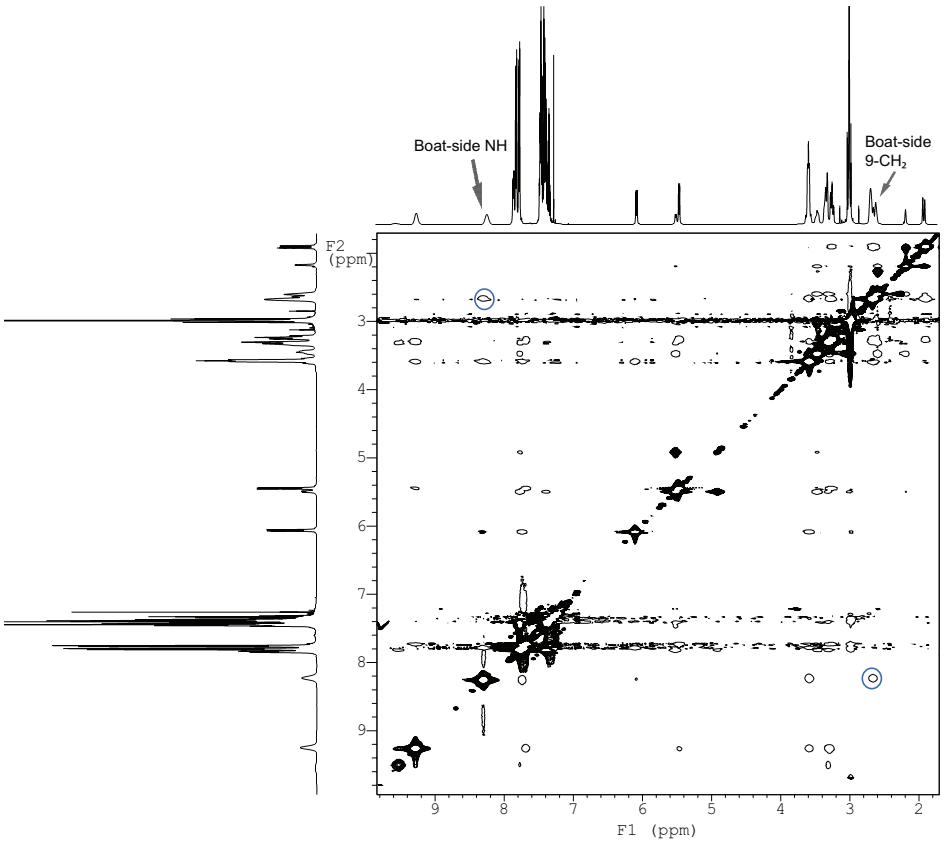

Figure S 29: gNOESY spectrum of a $[\mathbf{2}{\cdot}H]^{2+}$ BC/BB mixture with excess CH_3SO_3H (500 MHz, $CDCl_3$ solution, 25 °C, mix=0.5).

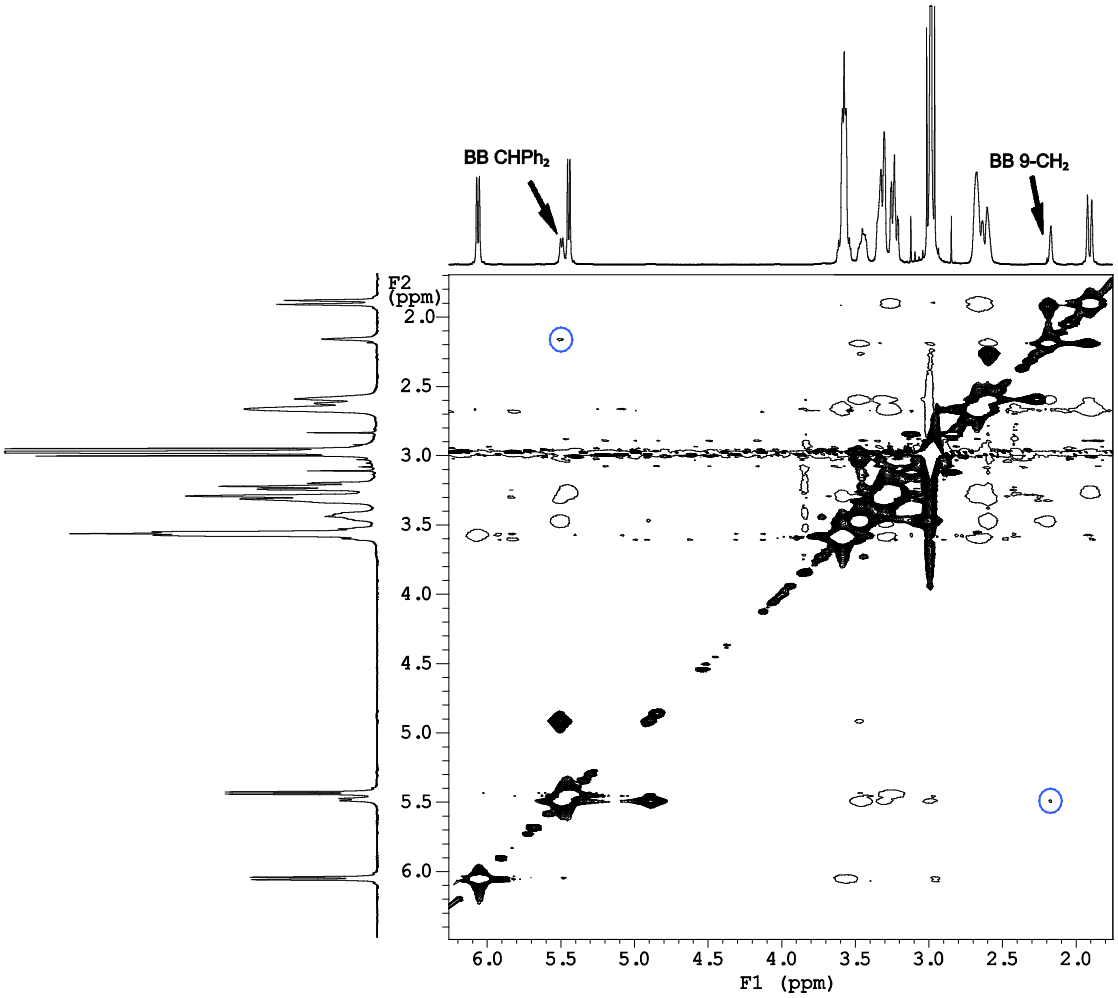

Figure S 30: Expansion from gNOESY spectrum of a $[\mathbf{2}\cdot H]^{2+}$ BC/BB mixture with excess CH_3SO_3H (500 MHz, $CDCl_3$ solution,25 °C, mix=0.5).

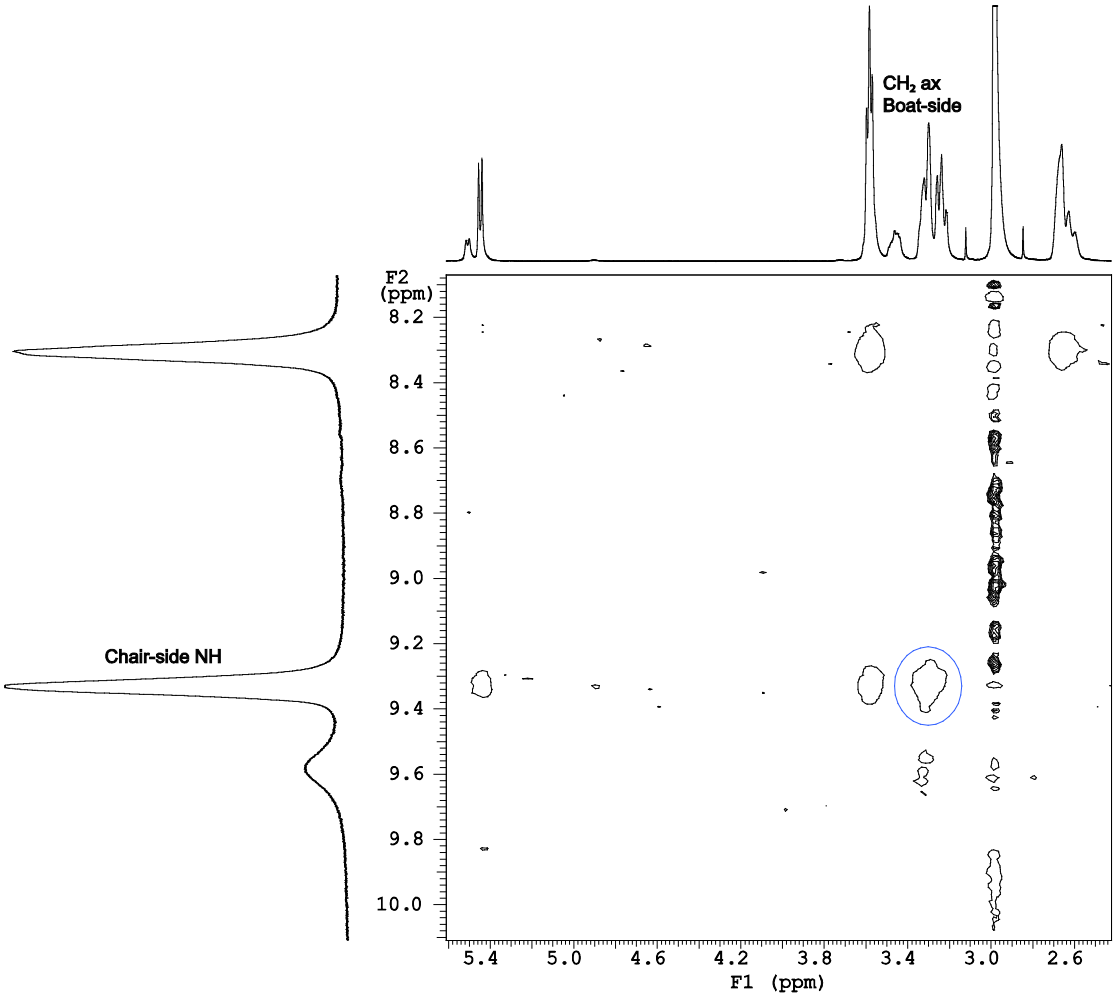

Figure S 31: Expansion from gNOESY spectrum of [*N,N'*-dibenzhydrylbispidine·2H]$^{2+}$ (500 MHz, $CDCl_3$ solution, 25°C).

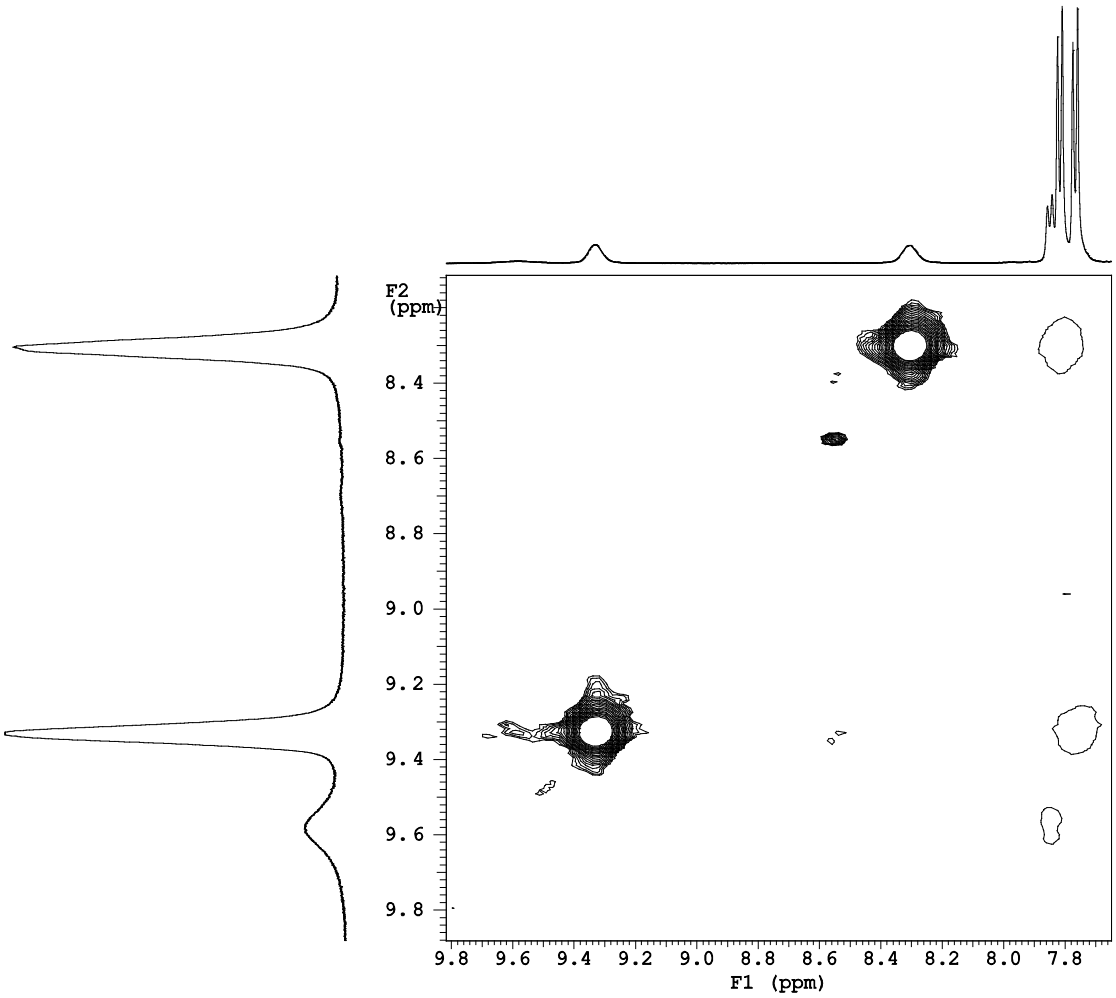

Figure S 32: Expansion from gNOESY spectrum of [*N,N'*-dibenzhydrylbispidine·2H]$^{2+}$ (500 MHz, $CDCl_3$ solution, 25°C).

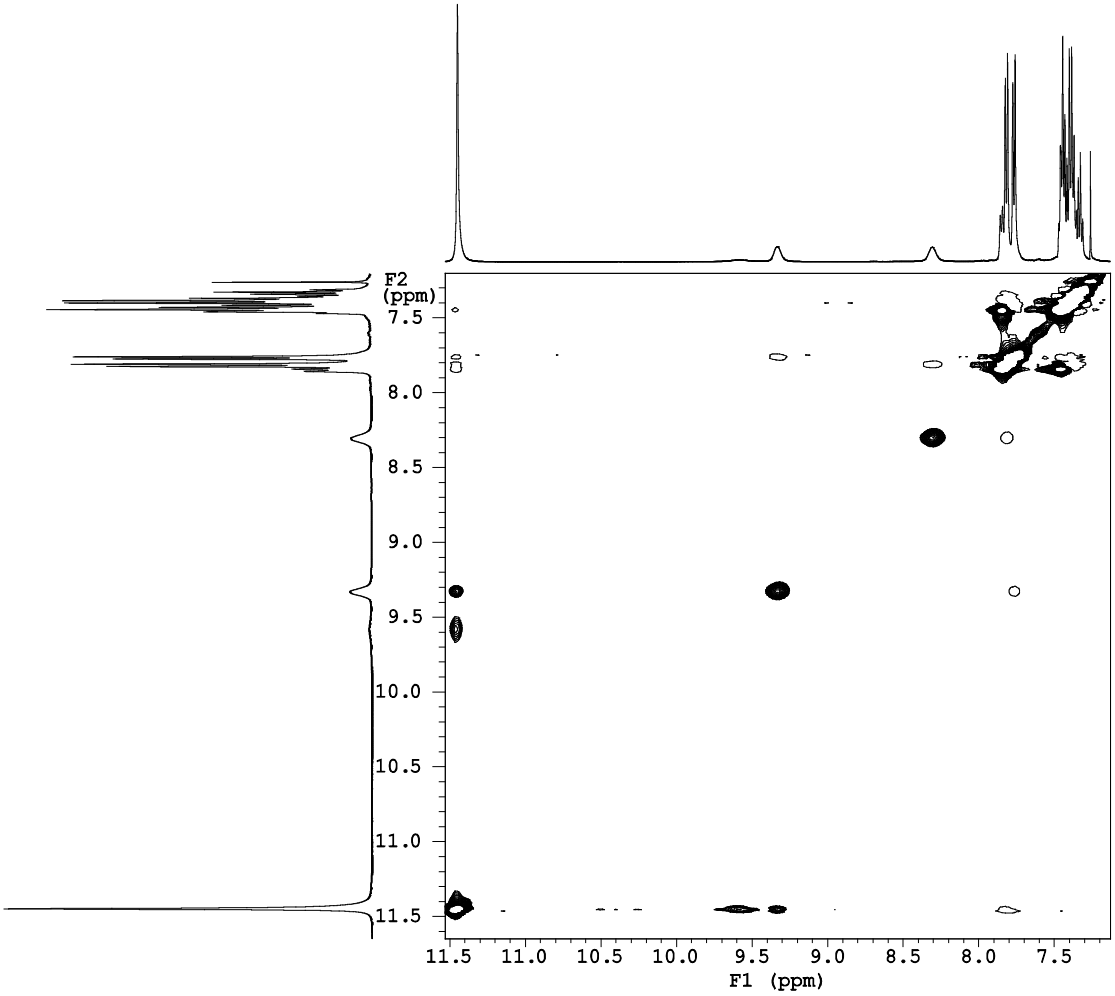

Figure S 33: Expansion from gNOESY spectrum of [*N,N'*-dibenzhydrylbispidine·2H]$^{2+}$ (500 MHz, $CDCl_3$ solution, 25°C).

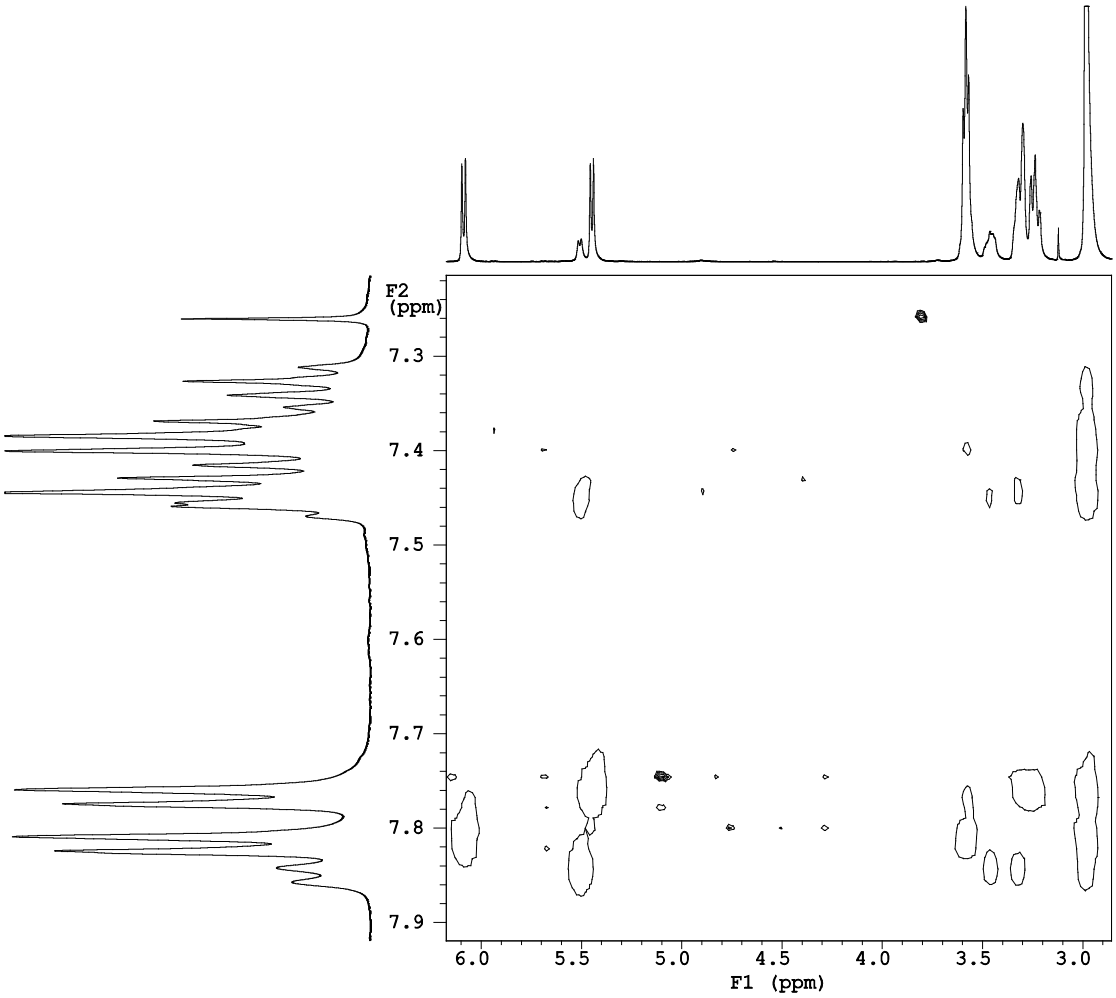

Figure S 34: Expansion from gNOESY spectrum of [*N,N'*-dibenzhydrylbispidine·2H]$^{2+}$ (500 MHz, $CDCl_3$ solution, 25°C).

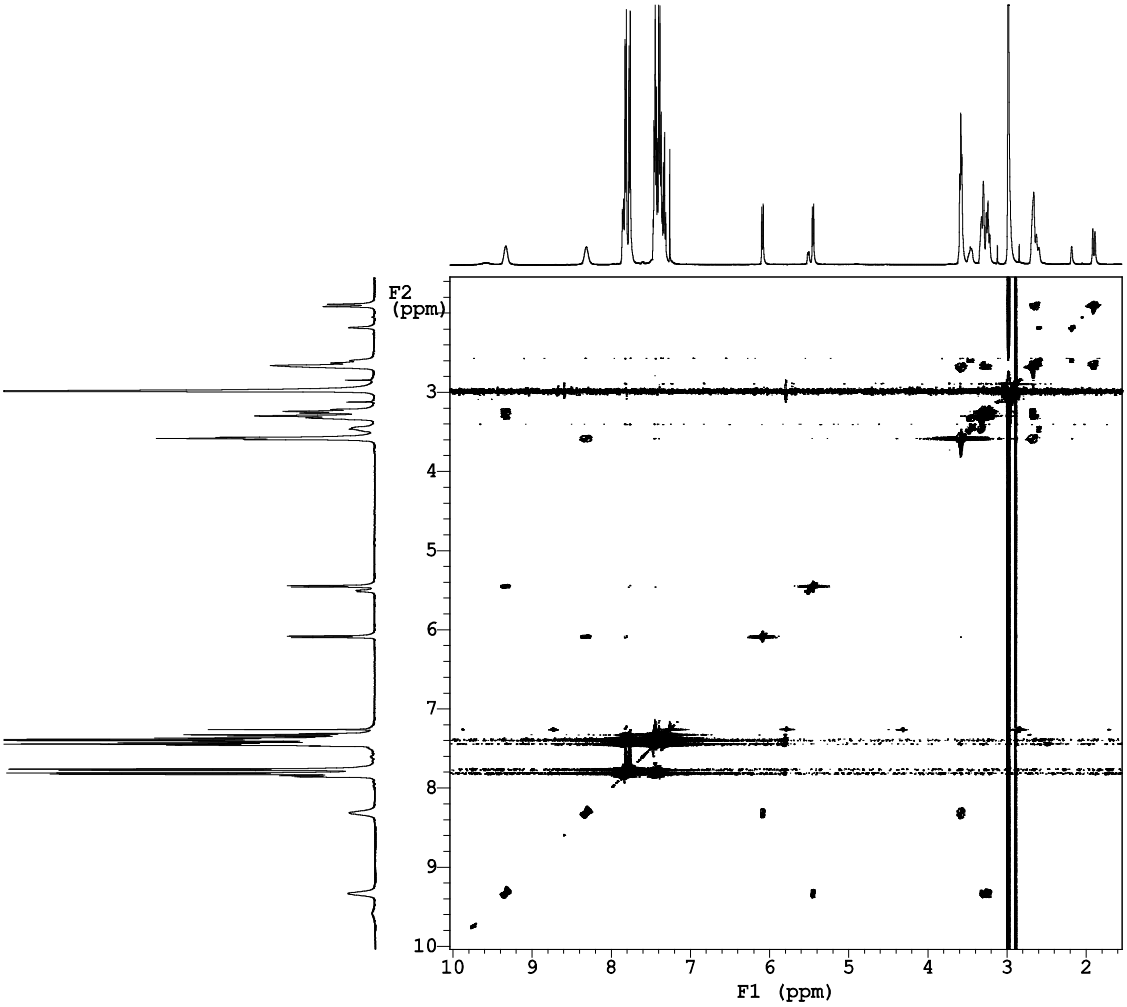

Figure S 35: P.E. COSY spectrum of a $[\mathbf{2}\cdot H]^{2+}$ BC/BB mixture with excess CH_3SO_3H (500 MHz, $CDCl_3$ solution, 25 °C).

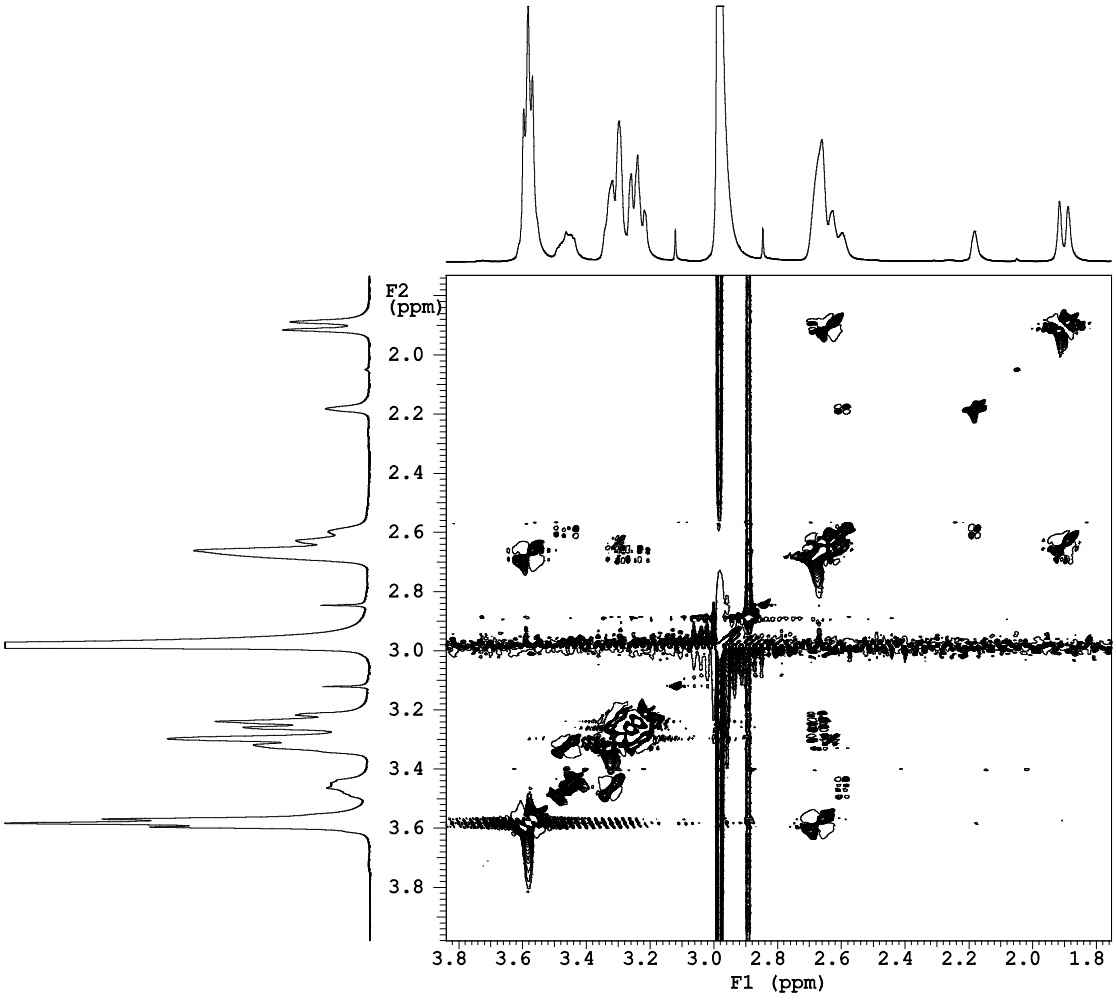

Figure S 36: Expansion from P.E. COSY spectrum of the aliphatic region of a $[\mathbf{2}\cdot H]^{2+}$ BC/BB mixture with excess CH_3SO_3H (500 MHz, $CDCl_3$ solution, 25 °C).

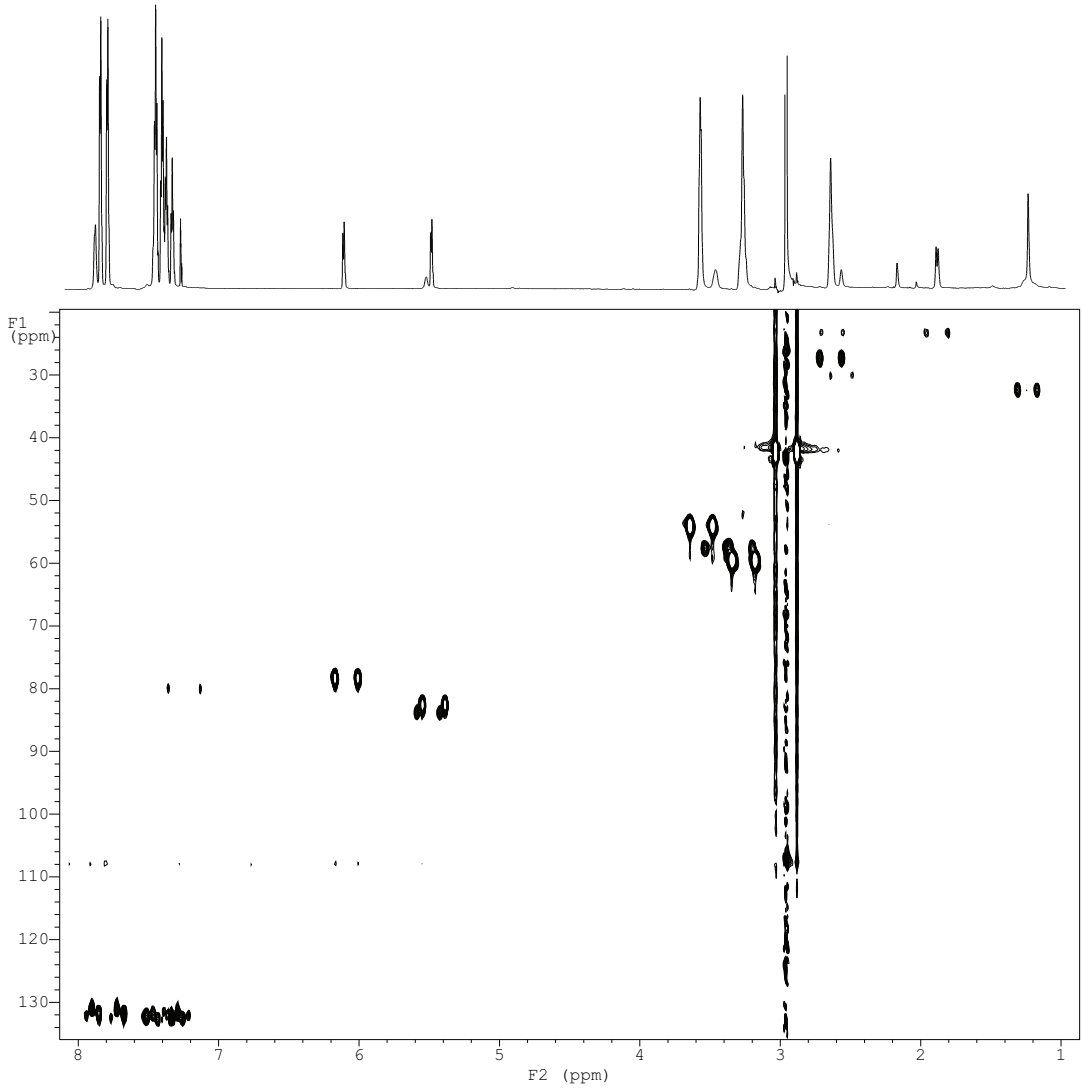

Figure S 37: HSQC spectrum of a $[\mathbf{1}\cdot 2H]^{2+}$ (6 mg) BC/BB mixture with excess CH_3SO_3H (900 MHz, $CDCl_3$ solution, 25 °C).

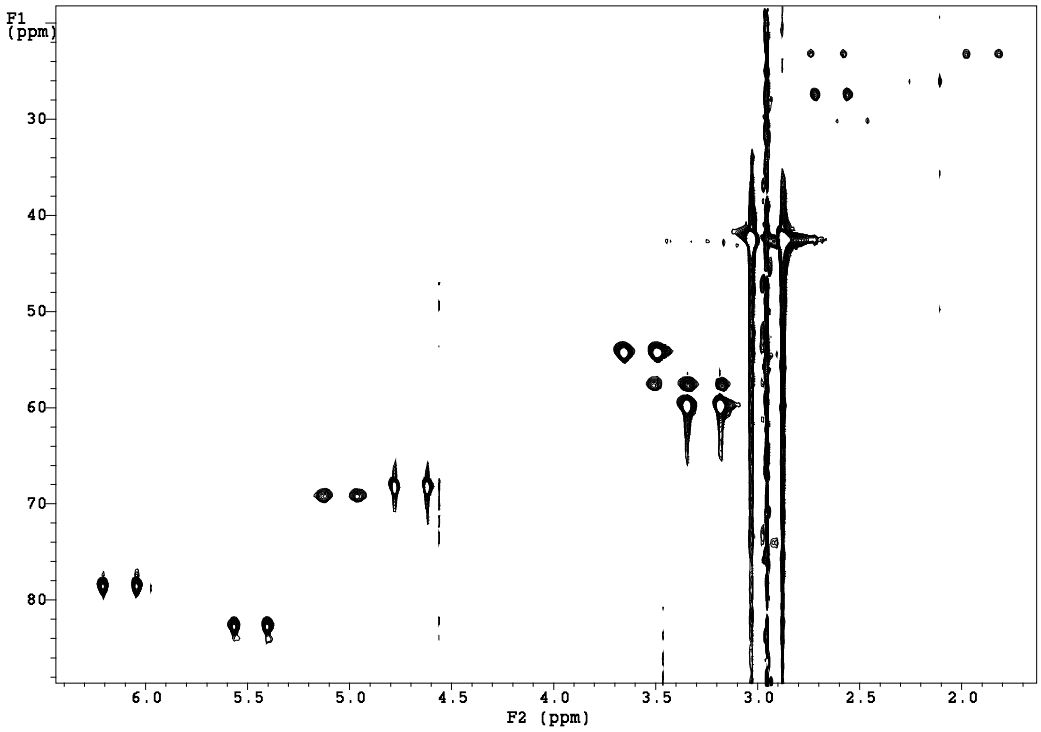

Figure S 38: CLIP-HSQC spectrum of a $[\mathbf{2}\cdot H]^{2+}$ (6 mg) BC/BB mixture with excess CH_3SO_3H and PBLG (75 mg) in 0.7 mL $CDCl_3$ (900 MHz, 25 °C).

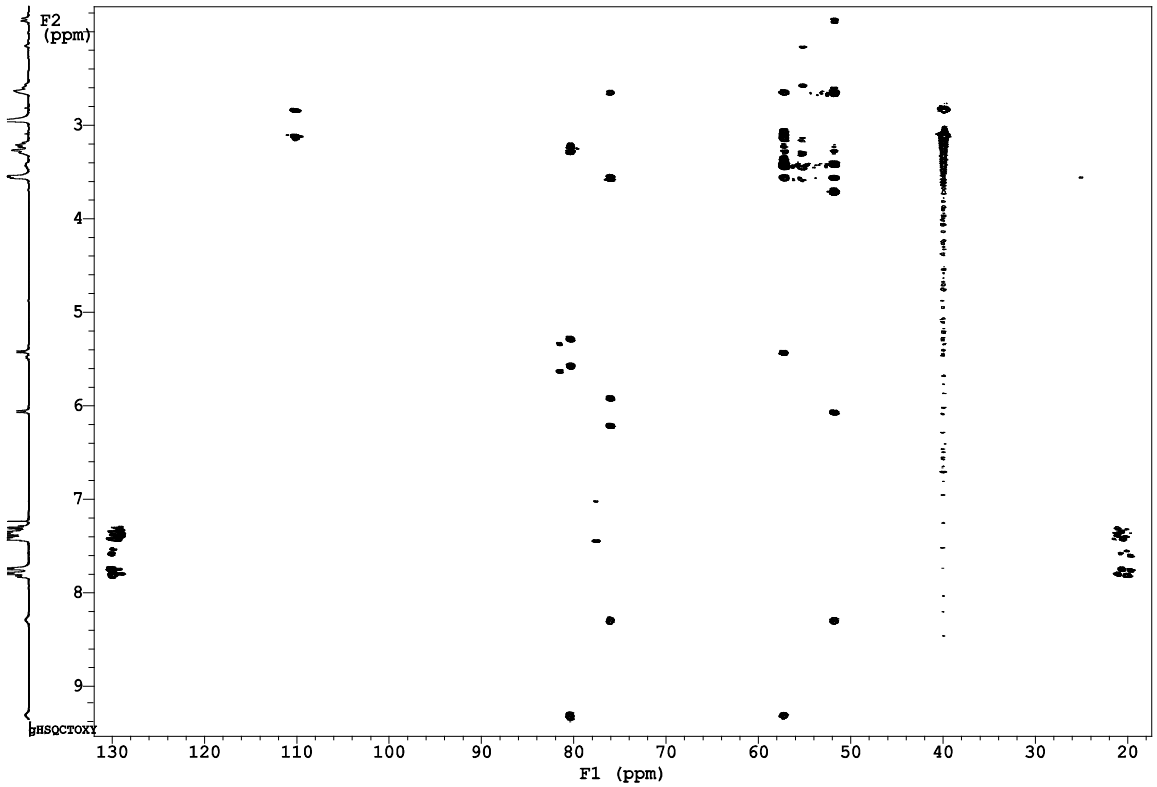

Figure S 39: gHSQC-TOCSY spectrum of [*N,N'*-dibenzhydrylbispidine·2H]$^{2+}$ (500 MHz, $CDCl_3$ solution, 25°C).

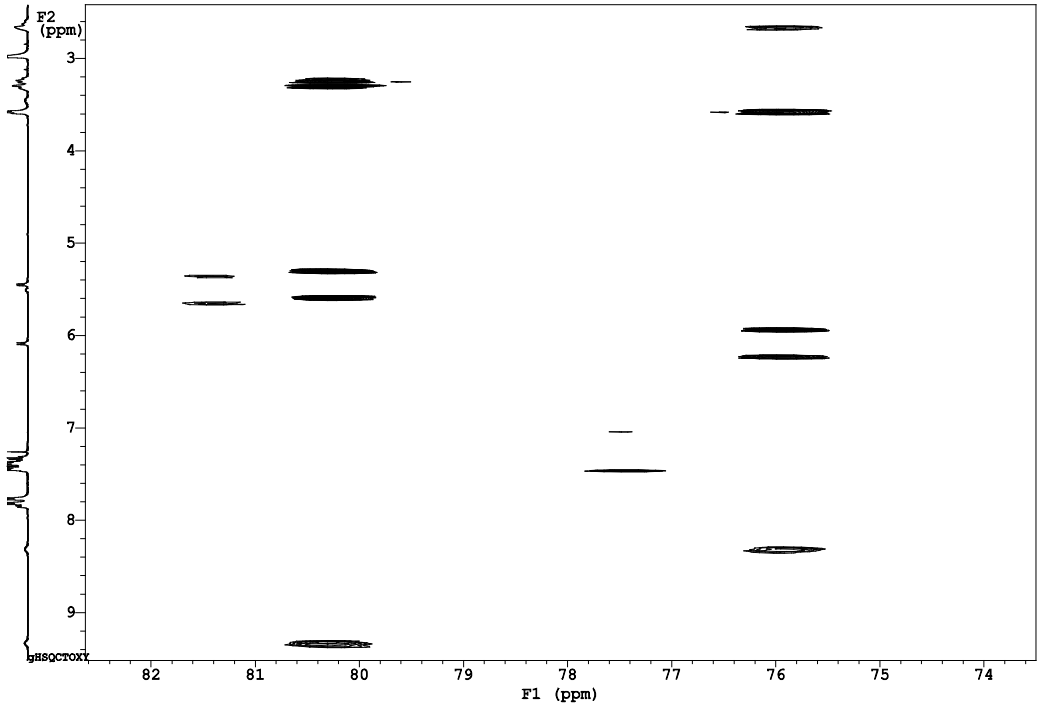

Figure S 40: Expansion from gHSQC-TOCSY spectrum of [*N,N'*-dibenzhydrylbispidine·2H]$^{2+}$ (500 MHz, $CDCl_3$ solution, 25°C).

Cross peaks with chair-side $Ph_2C\underline{H}$ (δ = 80.2) and boat-side $Ph_2C\underline{H}$ (δ = 75.9) identify protons in the two rings of the BC isomer.

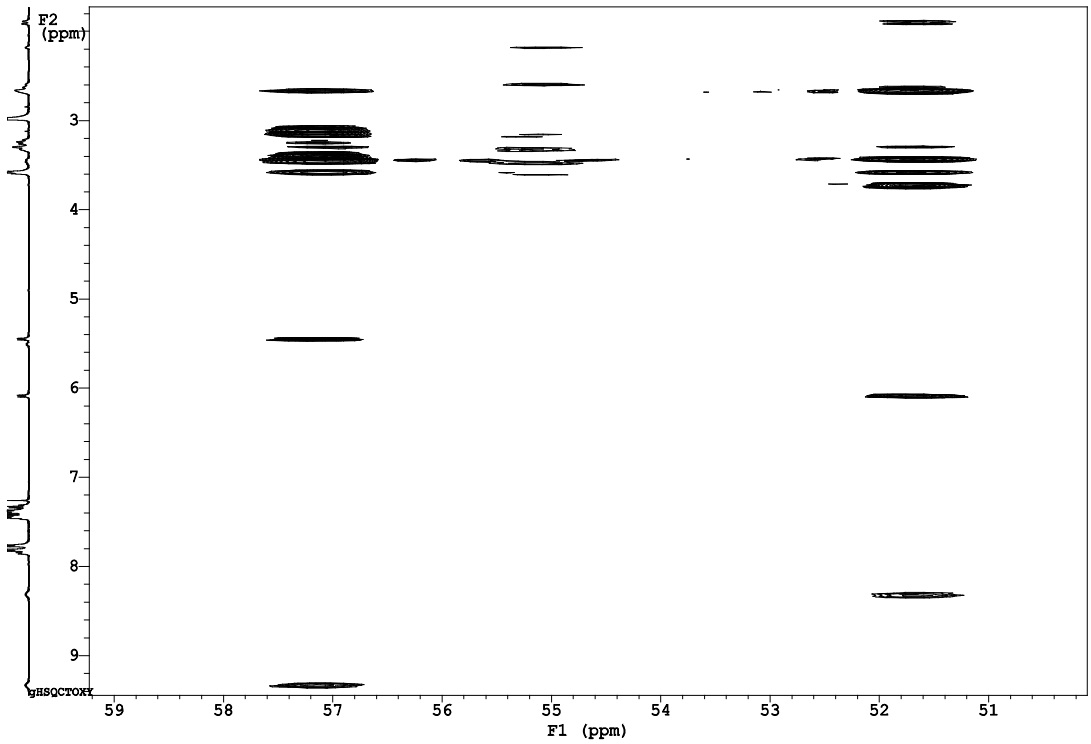

Figure S 41: Expansion from gHSQC-TOCSY spectrum of [*N,N'*-dibenzhydrylbispidine·2H]$^{2+}$ (500 MHz, $CDCl_3$ solution, 25°C).

Cross peaks with chair-side CH_2 ($\delta = 56.9$) and boat-side CH_2 ($\delta = 51.5$) identify protons in the two rings of the BC isomer. Cross peaks with BB CH_2 ($\delta = 55.8$) are also present.

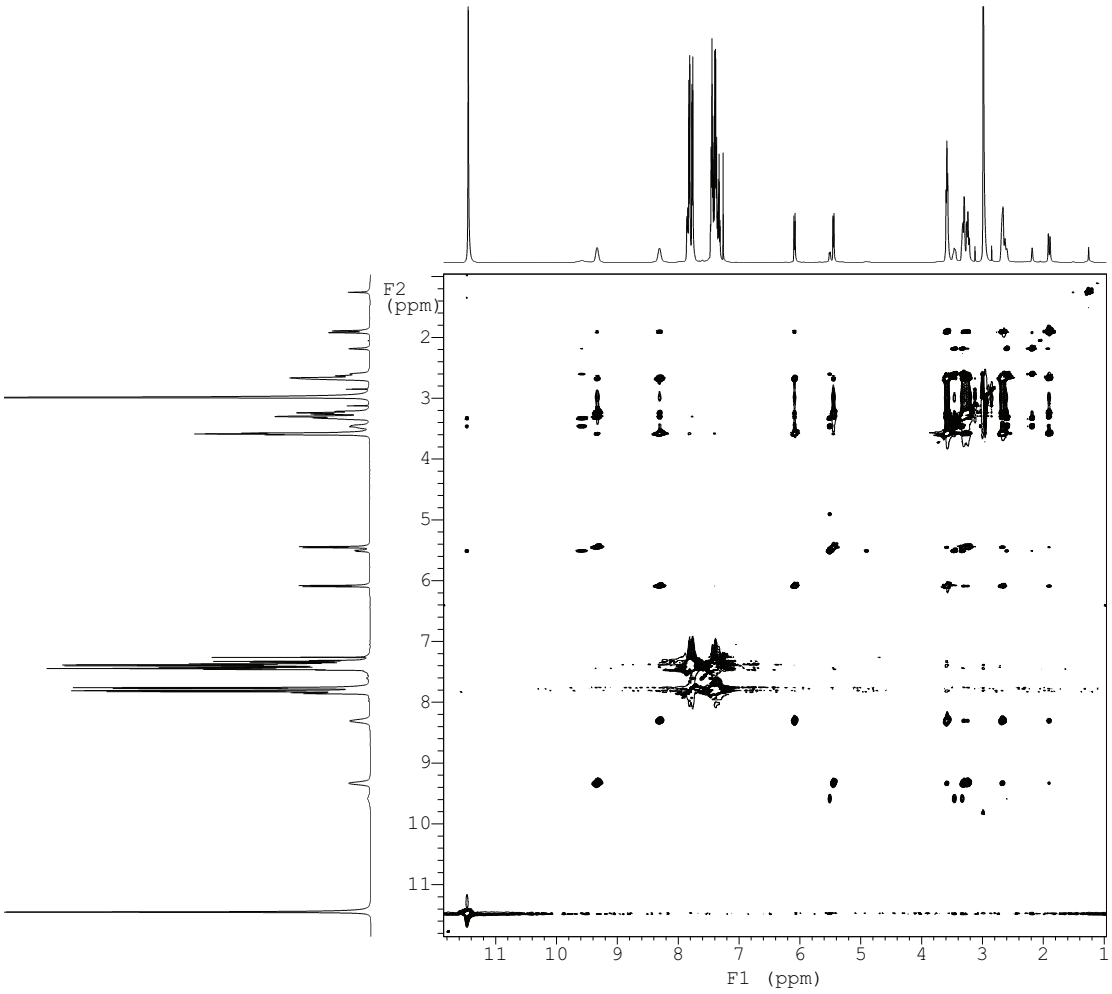

Figure S 42: TOCSY spectrum of [*N,N'*-dibenzhydrylbispidine·2H]$^{2+}$ (500 MHz, $CDCl_3$ solution, 25°C).

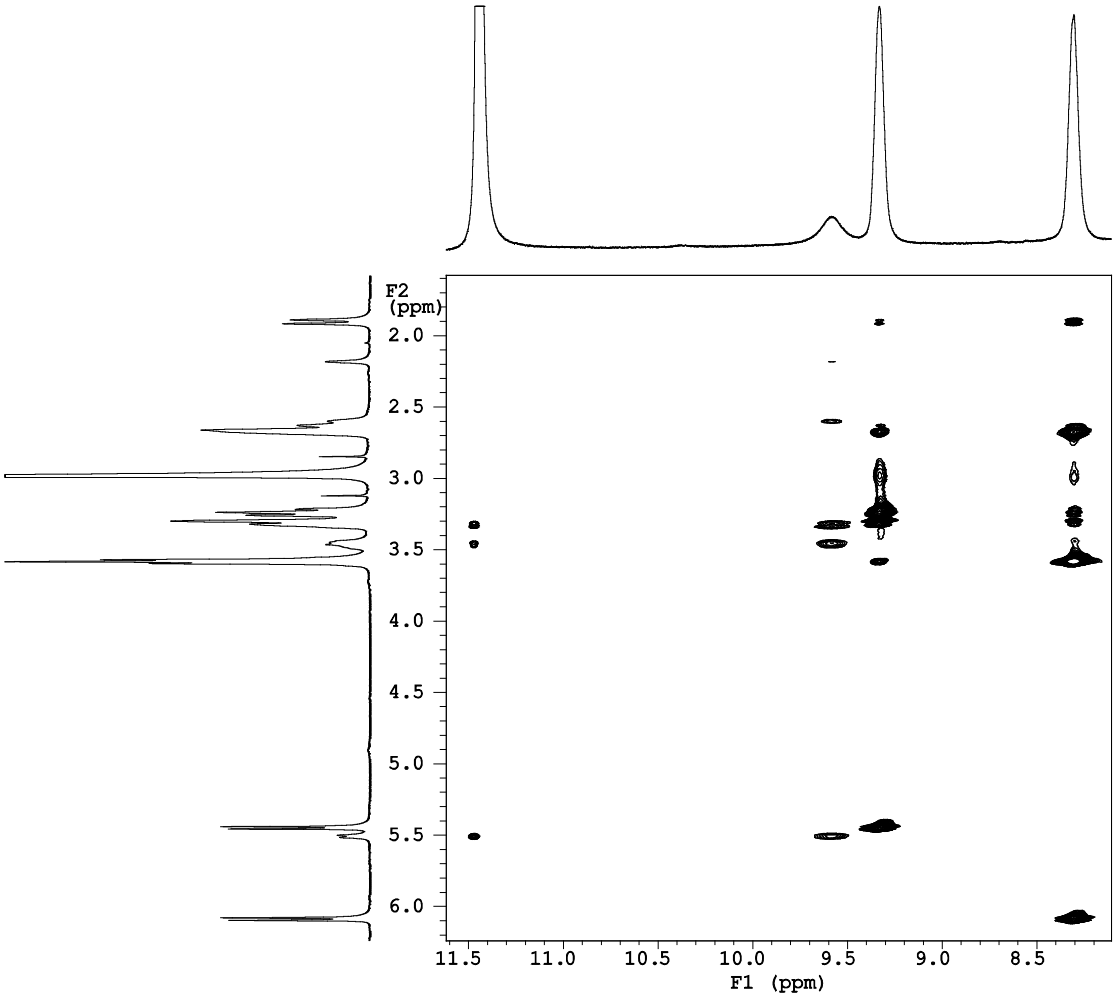

Figure S 43: Expansion from TOCSY spectrum of [*N,N'*-dibenzhydrylbispidine·2H]$^{2+}$ (500 MHz, $CDCl_3$ solution, 25°C).

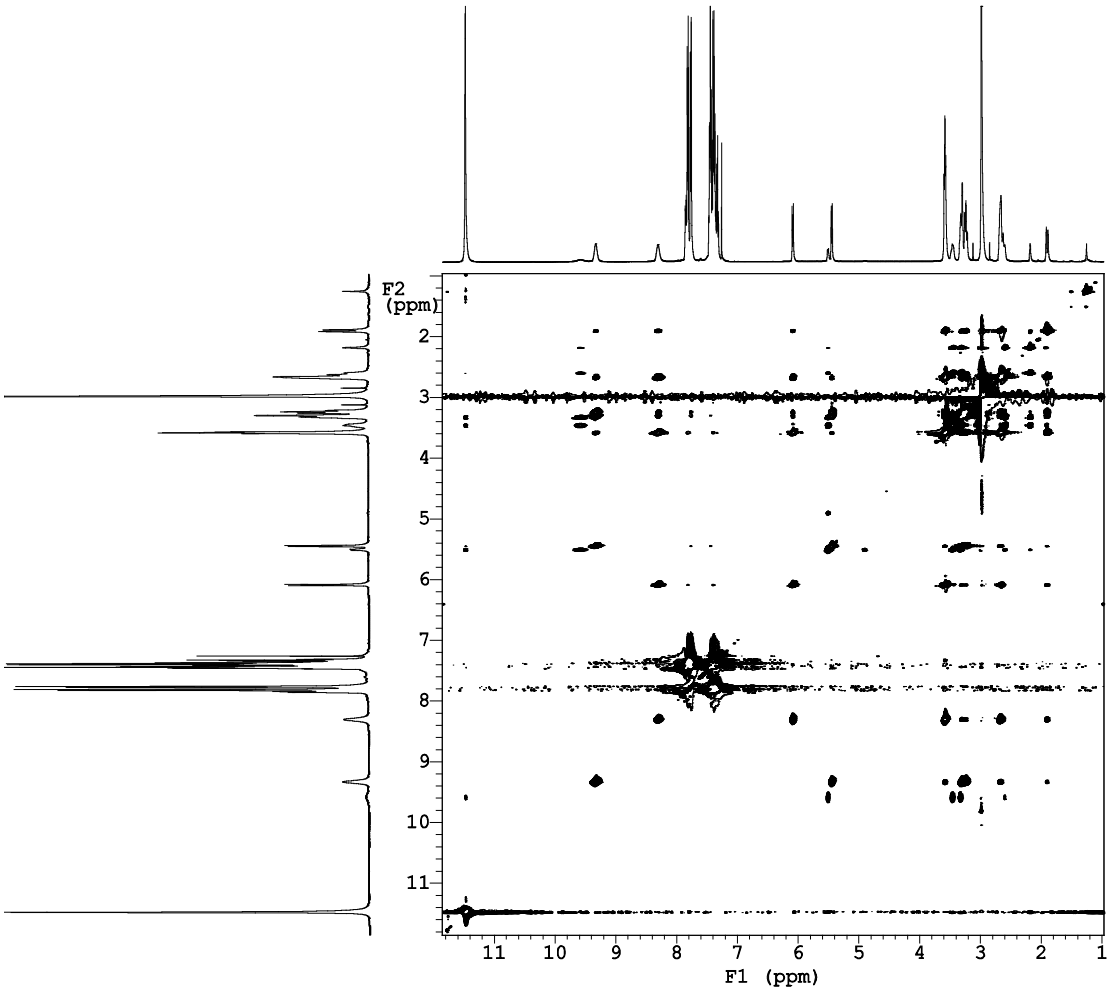

Figure S 44: Expansion from TOCSY spectrum of [*N,N'*-dibenzhydrylbispidine·2H]$^{2+}$ (500 MHz, $CDCl_3$ solution, 25°C).

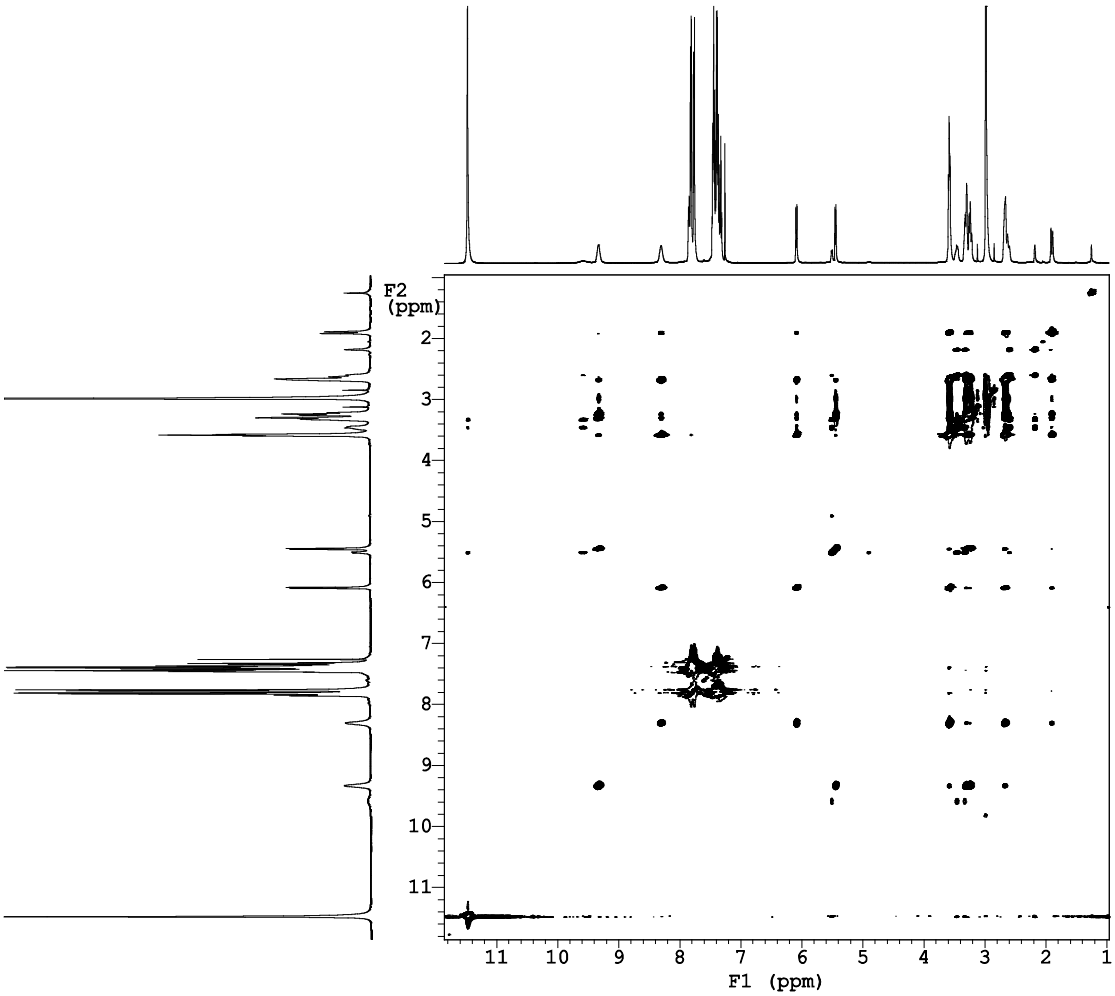

Figure S 45: Expansion from TOCSY spectrum of [*N,N'*-dibenzhydrylbispidine·2H]$^{2+}$ (500 MHz, $CDCl_3$ solution, 25°C).

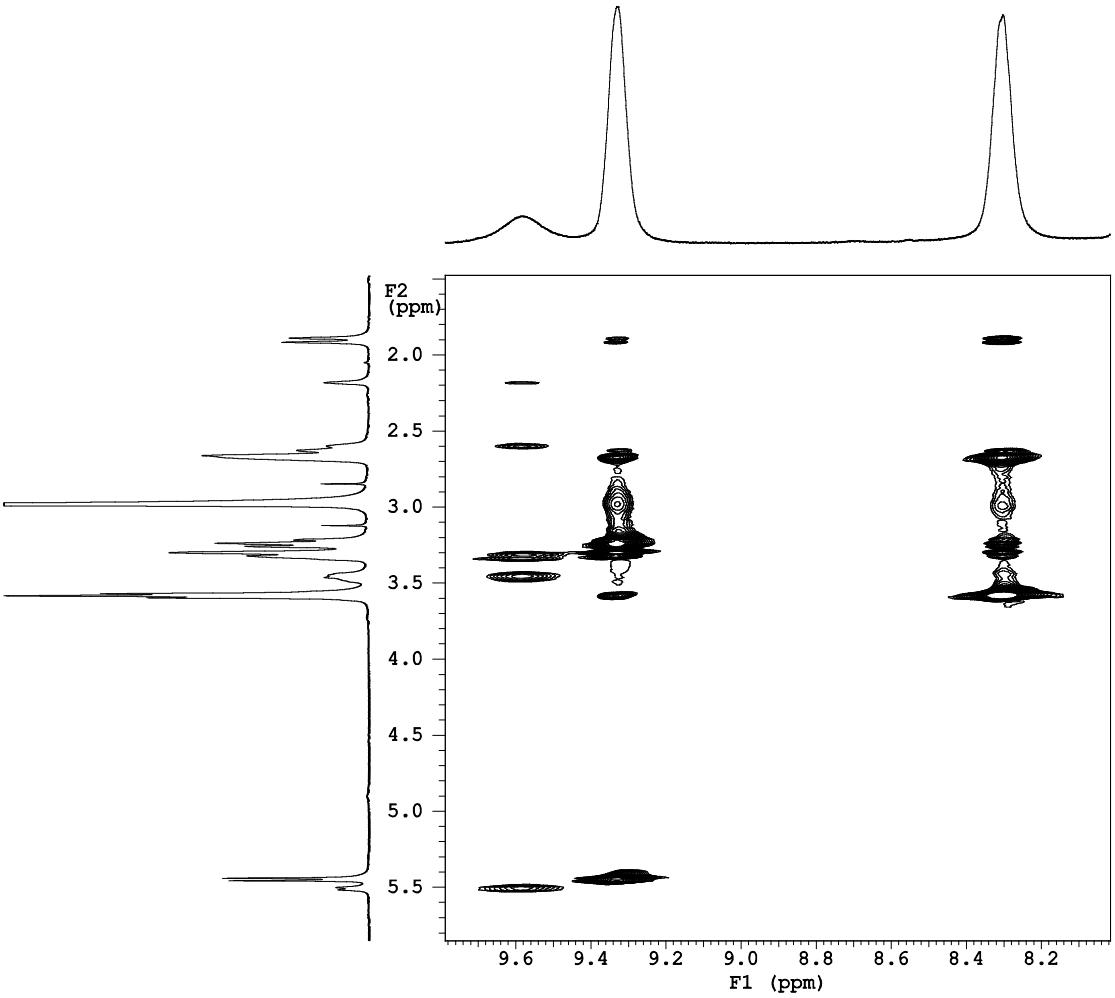

Figure S 46: Expansion from TOCSY spectrum of [*N,N'*-dibenzhydrylbispidine·2H]$^{2+}$ (500 MHz, $CDCl_3$ solution, 25°C).

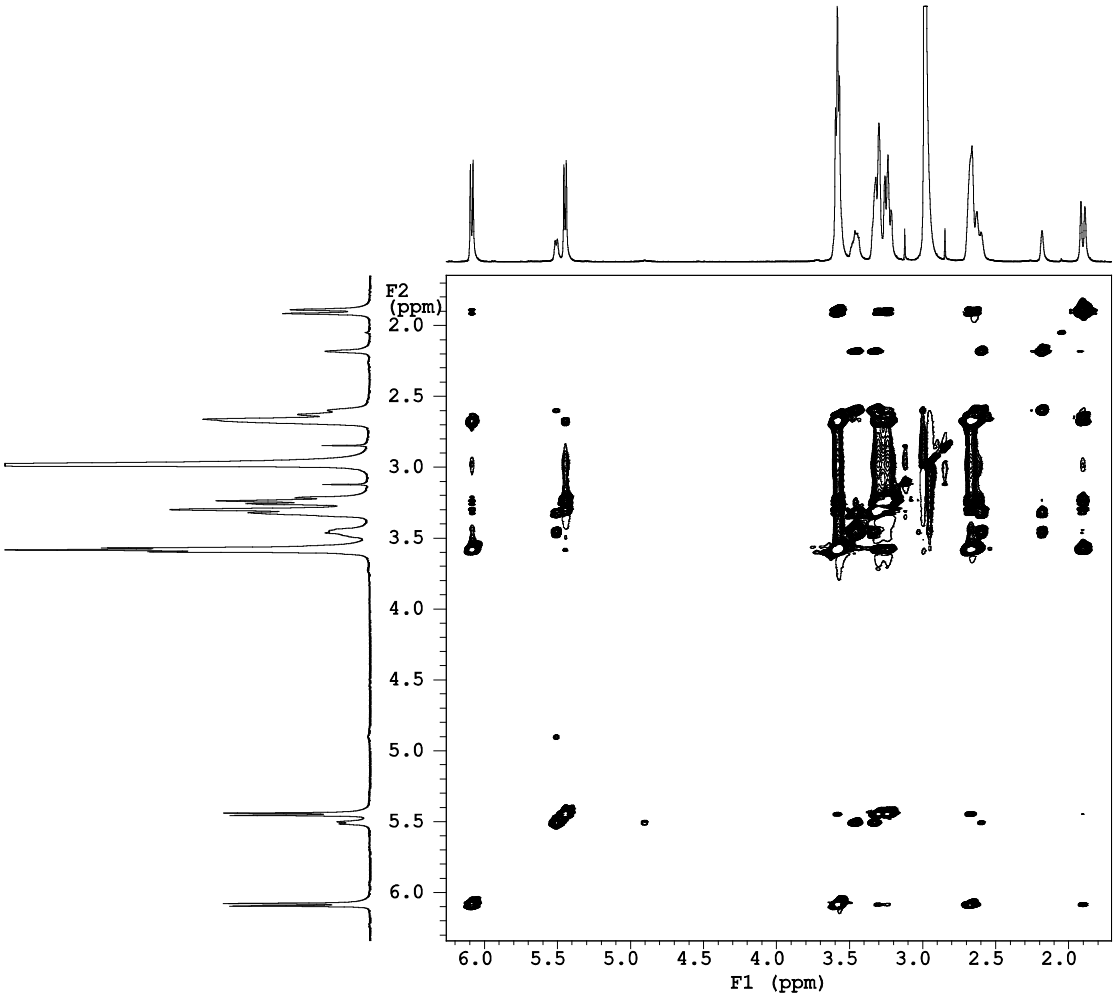

Figure S 47: Expansion from TOCSY spectrum of [*N,N'*-dibenzhydrylbispidine·2H]$^{2+}$ (500 MHz, $CDCl_3$ solution, 25°C).

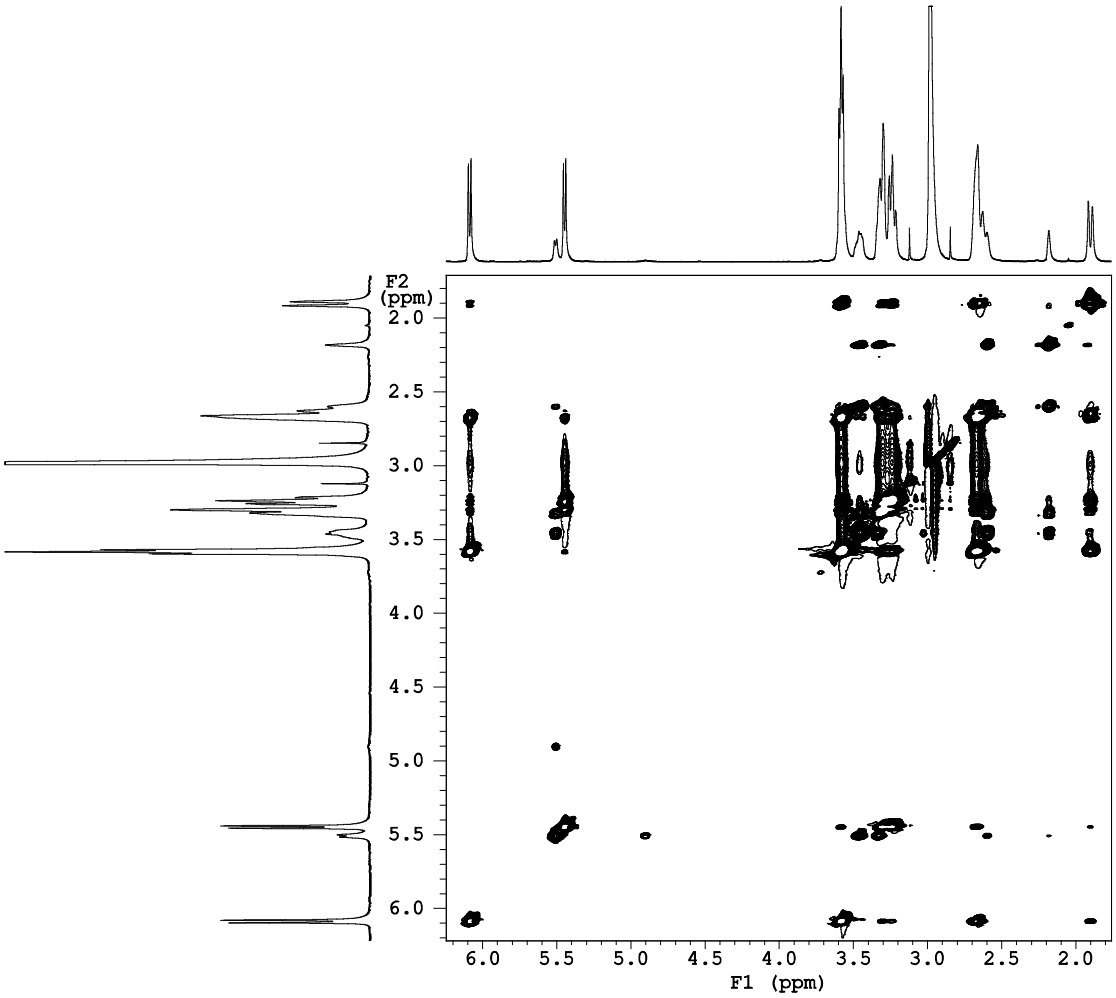

Figure S 48: Expansion from TOCSY spectrum of [*N,N'*-dibenzhydrylbispidine·2H]$^{2+}$ (500 MHz, $CDCl_3$ solution, 25°C).

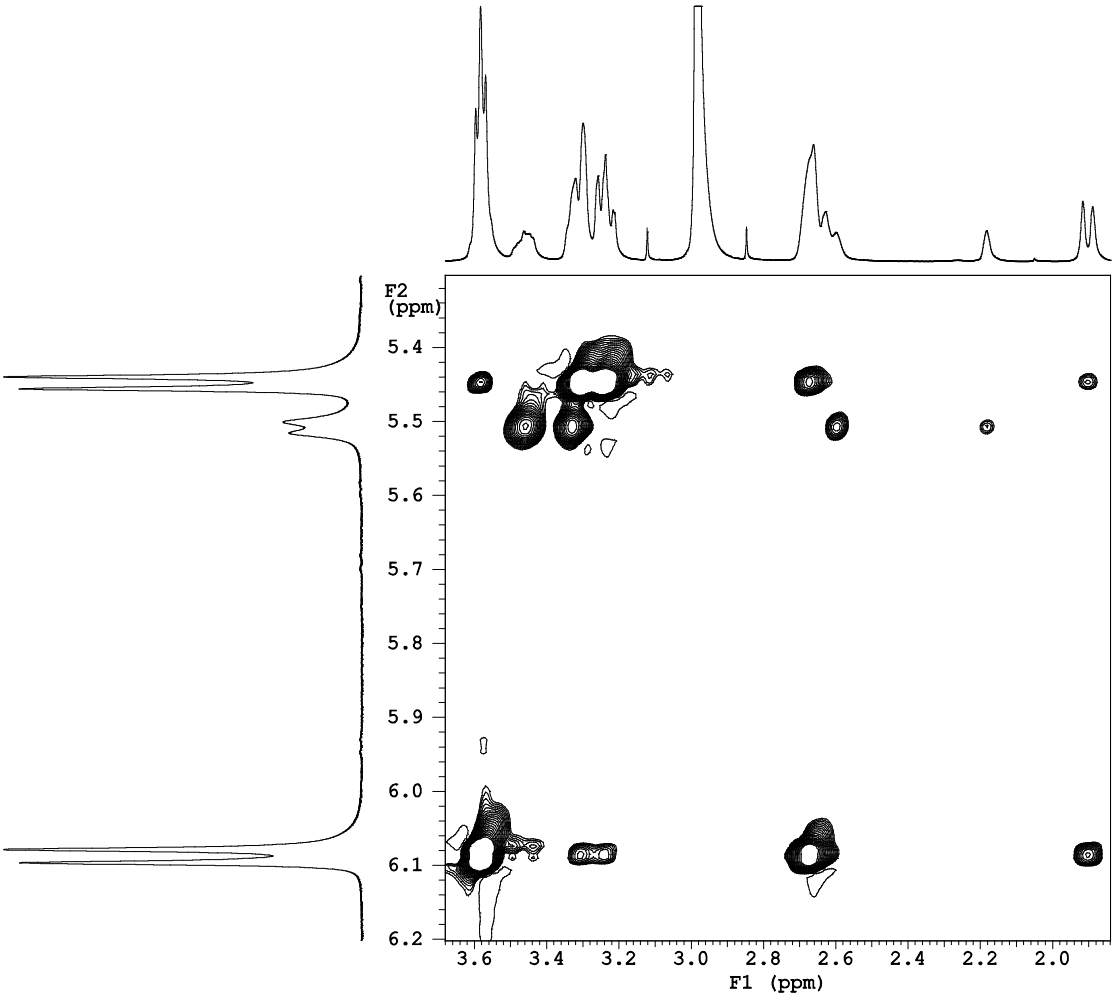

Figure S 49: Expansion from TOCSY spectrum of [*N,N'*-dibenzhydrylbispidine·2H]$^{2+}$ (500 MHz, $CDCl_3$ solution, 25°C).

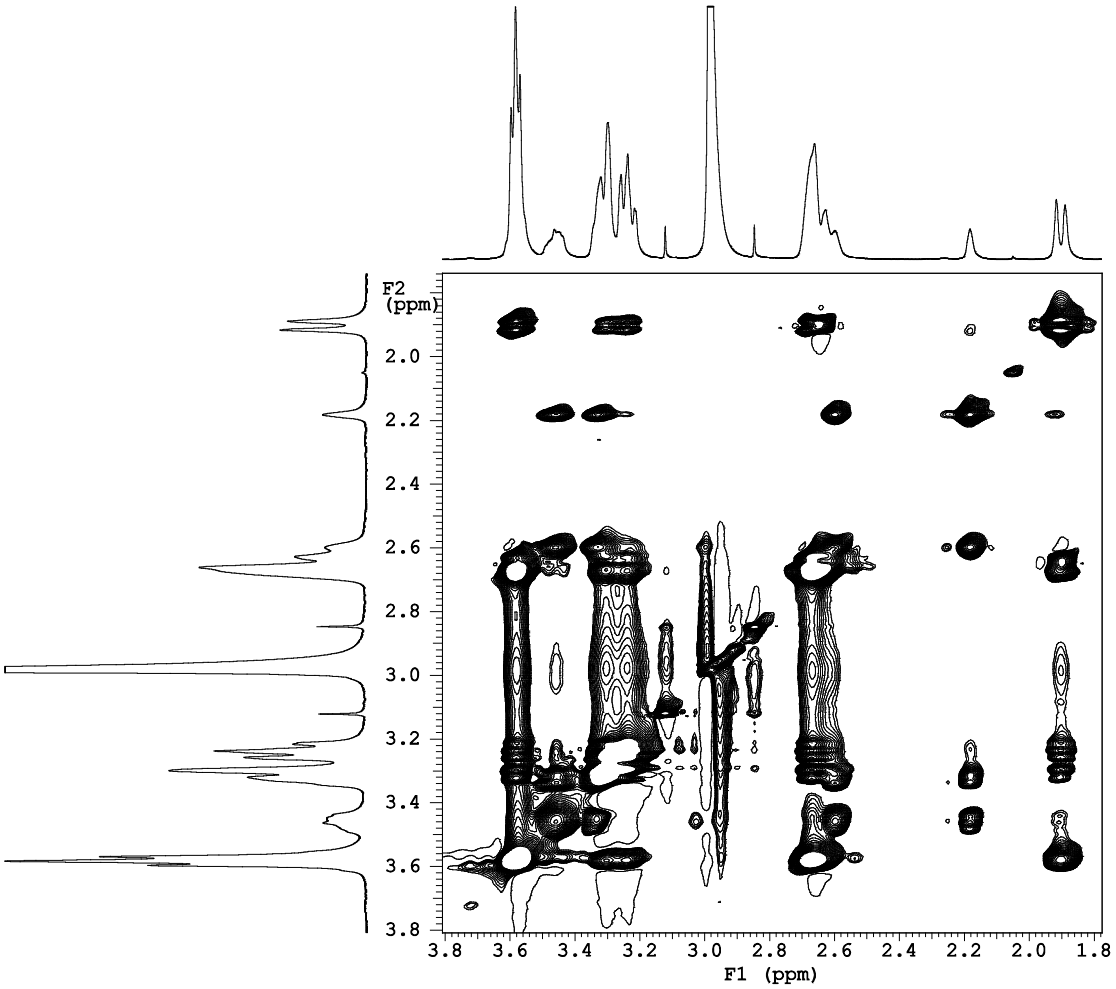

Figure S 50: Expansion from TOCSY spectrum of [*N,N'*-dibenzhydrylbispidine·2H]$^{2+}$ (500 MHz, $CDCl_3$ solution, 25°C).

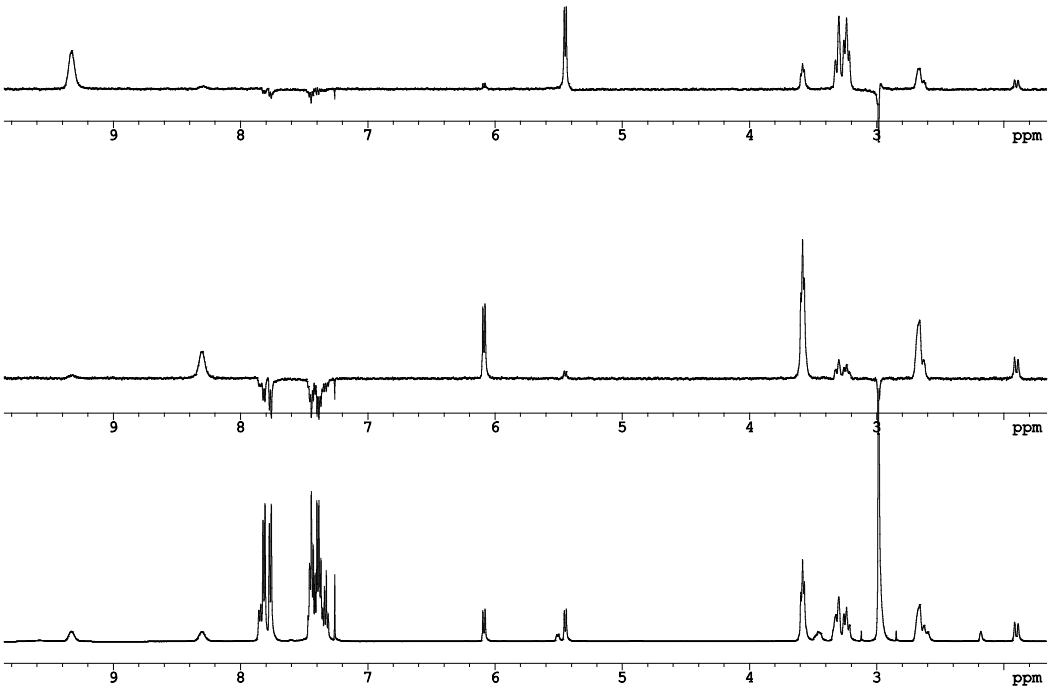

Figure S 51: Expansion from selective TOCSY spectrum of [*N,N'*-dibenzhydrylbispidine·2H]$^{2+}$ (500 MHz, $CDCl_3$ solution, 25°C).

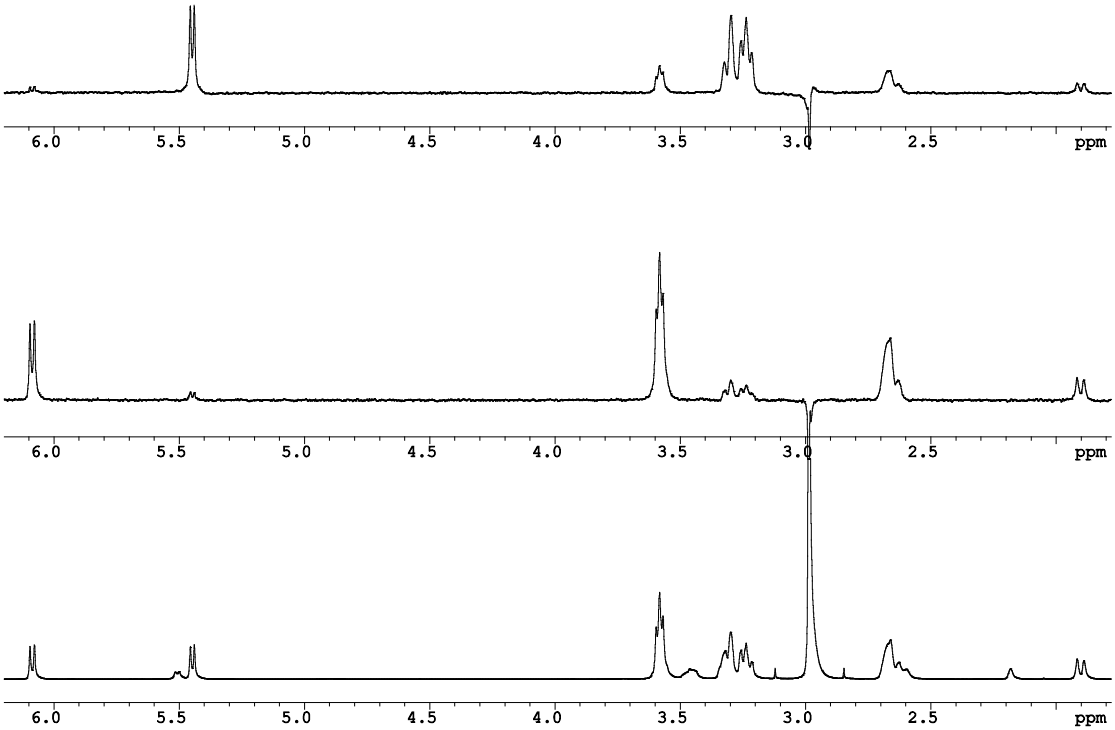

Figure S 52: Expansion from selective TOCSY spectrum of [*N,N'*-dibenzhydrylbispidine·2H]$^{2+}$ (500 MHz, $CDCl_3$ solution, 25°C).

6. RDC matching data from MSpin for 1, $[1{\cdot}H]^+$, $[1{\cdot}2H]^{2+}$ BC and $[1{\cdot}2H]^{2+}$ BB

6.1. Bispidine 1

Alignment vector
Axx=-0.000308253
Ayy=-0.000976435
Azz=0.00128469
(0.660072,0.710576,-0.243693,)
(-0.630045,0.700333,0.335524,)
(0.409082,-0.0679329,0.909965,)
SVD condition number is 15.1214
Axial component Aa=0.00192703
rhombic component
Ar=0.000668182
rhombicity R=0.346742
Asimmetry parameter
etha=0.520113
GDO=0.00237086
Euler Angles
Set 1
(-4.26946,-24.1472,-43.6667)
Set 2
(175.731,204.147,136.333)
Q=0.197

	Exp. Hz	Comp. Hz
C9,H56	-19.3	-16.9
C9,H57	-19.3	-17.0
C1,H63	-24.9	-19.2
C7,H66	-24.9	-20.8
C3,H64	-24.9	-20.8
C5,H59	-24.9	-19.2
C1,H62	13.3	13.5
C7,H67	13.3	13.1
C3,H65	13.3	13.2
C5,H60	13.3	13.4
C2,H61	11	17.8
C6,H58	11	18.0
C10,H69	29.2	32.9
C11,H68	29.2	32.4

6.2. Bispidine $[1{\cdot}H]^+$

Alignment vector
Axx=-0.000252672
Ayy=-0.000969229
Azz=0.0012219
(0.822019,0.455908,-0.341222,)
(-0.386504,0.886723,0.25365,)
(0.41821,-0.0766214,0.905113,)
SVD condition number is 14.8397
Axial component Aa=0.00183285
rhombic component
Ar=0.000716557
rhombicity R=0.390952
Asimmetry parameter
etha=0.586428
GDO=0.00229114
Euler Angles
Set 1
(-4.83878,-24.7216,-25.1823)
Set 2
(175.161,204.722,154.818)
Q=0.274

	Exp. Hz	Comp. Hz
C11,H68	21.8	16.69
C10,H69	21.8	28.96
C5,H60	7	10.72
C3,H65	7	7.21
C7,H67	7	10.82
C1,H62	7	7.08
C5,H59	-21	-13.13
C3,H64	-21	-18.79
C1,H63	-21	-12.01
C7,H66	-21	-18.67
C9,H56	-7.4	-12.11
C9,H57	-7.4	-12.74
C2,H61	14.6	14.82
C6,H58	14.6	11.28

6.3. Bispidine $[1{\cdot}2H]^{2+}$ BC

Alignment vector
Axx=-3.11468e-06
Ayy=-0.000211625
Azz=0.000214739
(0.967144,-0.224763,-0.118802,)
(-0.0185878,0.403538,-0.914774,)
(0.253548,0.886927,0.386101,)
SVD condition number is 6.17112
Axial component
Aa=0.000322109
rhombic component
Ar=0.00020851
rhombicity R=0.647327
Asimmetry parameter
etha=0.970991
GDO=0.000451169
Euler Angles
Set 1
(66.4753,-14.6876,-1.10105)
Set 2
(-113.525,194.688,178.899)
Q = 0.237

	Exp. Hz	Comp. Hz
C11,H68	4.6	5.04
C10,H69	4.9	5.62
C5,H59	4.4	5.21
C3,H64	4.4	3.88
C3,H65	6.2	5.06
C5,H60	6.2	5.08
C9,H57	2.4	-0.09
C9,H56	-5.2	-6.59
C2,H61	4.8	4.22
C6,H58	4.8	3.85

6.4. Bispidine $[1{\cdot}2H]^{2+}$ BB

Alignment vector
Axx=-4.6736e-05
Ayy=-0.000161289
Azz=0.000208025
(0.42003,0.648441,0.634901,)
(-0.861865,0.0659438,0.502832,)
(0.284189,-0.758403,0.586567,)
SVD condition number is 1.96304
Axial component
Aa=0.000312037
rhombic component
Ar=0.000114553
rhombicity R=0.367112
Asimmetry parameter
etha=0.550668
GDO=0.00038666
Euler Angles
Set 1
(-52.2808,-16.5104,-64.0177)
Set 2
(127.719,196.51,115.982)
Q = 0.293

	Exp.	Comp.
C9,H60	-0.8	0.48
C10,H59	-0.8	0.88
C3,H68	6	5.06
C3,H69	4.2	2.47
C4,H70	4.2	3.13
C1,H65	6	4.99
C1,H65	4.2	4.99
C4,H71	6	5.1
C6,H66	6	4.66
C6,H67	4.2	2.6
C8,H55	-8.6	-7.15
C8,H56	-8.6	-6.74
C2,H58	5.8	8.28
C5,H57	5.8	8.79

7. X-ray crystallographic data

Table S 1: Crystal data and structure refinement details.

Identification code	**2011com0554**	
Empirical formula	$C_{53.15}H_{62.30}N_2O_{8.05}S_2$ $C_{33}H_{36}N_2$, $2(C_7H_7O_3S)$, $2.05(C_3H_6O)$	
Formula weight	922.07	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	*P*–1	
Unit cell dimensions	a = 8.574(4) Å	α = 65.791(16)°
	b = 17.686(5) Å	β = 85.89(2)°
	c = 18.241(6) Å	γ = 83.18(2)°
Volume	2504.1(16) $Å^3$	
Z	2	
Density (calculated)	1.223 Mg / m^3	
Absorption coefficient	0.161 mm^{-1}	
F(000)	983	
Crystal	Fragment; Colourless	
Crystal size	0.080 × 0.030 × 0.020 mm^3	
θ range for data collection	3.107 – 25.027°	
Index ranges	$-10 \le h \le 9$, $-21 \le k \le 21$, $-21 \le l \le 21$	
Reflections collected	19192	
Independent reflections	8806 [R_{int} = 0.1252]	
Completeness to θ = 27.500°	76.6 %	
Absorption correction	Semi–empirical from equivalents	
Max. and min. transmission	1.000 and 0.666	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	8806 / 19 / 441	
Goodness-of-fit on F^2	1.141	
Final *R* indices [$F^2 > 2\sigma(F^2)$]	*R1* = 0.1561, *wR2* = 0.3119	
R indices (all data)	*R1* = 0.2367, *wR2* = 0.3626	
Extinction coefficient	n/a	
Largest diff. peak and hole	1.635 and –0.770 e $Å^{-3}$	

Diffractometer: *Rigaku AFC12* goniometer equipped with an enhanced sensitivity (HG) *Saturn724+* detector mounted at the window of an *FR-E+ SuperBright* molybdenum rotating anode generator with HF *Varimax* optics (100µm focus). **Cell determination, Data collection, Data reduction and cell refinement & Absorption correction**: CrystalClear-SM Expert 2.0 r7 (Rigaku, 2011) , **Structure solution**: SHELXS97 (Sheldrick, G.M. (2008). *Acta Cryst*. **A64**, 112-122). S**tructure refinement**: SHELXL2012 (G. M. Sheldrick (2012), University of Göttingen, Germany). **Graphics:** CrystalMaker: a crystal and molecular structures program for Mac and Windows. CrystalMaker Software Ltd, Oxford, England (www.crystalmaker.com)

Special details: The structure contains large solvent filled channels extending along the a-axis. The solvent is modelled as 5 discrete orientations of partially occupied acetone molecules. These were restrained using the shelx FRAG instruction and a fragment taken from an earlier structure. Modelling of the structure using the SQUEEZE (Sluis, P. v.d. & Spek, A. L. (1990) Acta Cryst. A46, 194-201.) algorithm as implemented in platon (Spek, A. L. (1990) Acta Cryst. A46, C34) reduces the R-factor by 5%

Table S 2: Atomic coordinates [$\times 10^4$], equivalent isotropic displacement parameters [$Å^2 \times 10^3$] and site occupancy factors. U_{eq} is defined as one third of the trace of the orthogonalized U^{ij} tensor.

Atom	*x*	*y*	*z*	U_{eq}	*S.o.f.*
C101	690(20)	4572(10)	3888(10)	120(2)	0.45
C102	–951(19)	4751(10)	4230(9)	120(2)	0.45
C103	–1880(30)	5540(13)	3690(14)	120(2)	0.45
O101	–1450(20)	4233(13)	4850(11)	120(2)	0.45
C201	1786(17)	8174(7)	1326(8)	120(2)	0.6
C202	1207(15)	7292(7)	1759(7)	120(2)	0.6
C203	2180(20)	6617(9)	1570(11)	120(2)	0.6
O201	144(18)	7175(9)	2263(9)	120(2)	0.6
C301	2610(20)	7215(12)	2589(11)	120(2)	0.4
C302	1940(20)	7423(11)	1750(11)	120(2)	0.4
C303	860(40)	6807(18)	1735(16)	120(2)	0.4
O301	2170(30)	8081(13)	1187(11)	120(2)	0.4
C401	3212(12)	6837(7)	3585(11)	120(2)	0.27
C402	2415(12)	6316(7)	4340(11)	120(2)	0.27
C403	3291(14)	5537(8)	4806(14)	120(2)	0.27
O401	1243(16)	6579(11)	4545(12)	120(2)	0.27
C501	2557(1)	7271(1)	2659(1)	120(2)	0.33
C502	2436(1)	6564(1)	3494(1)	120(2)	0.33
C503	1434(1)	5910(1)	3545(1)	120(2)	0.33
O501	3231(2)	6530(1)	4024(1)	120(2)	0.33
C1	7198(1)	386(1)	3361(1)	17(2)	1
C2	6730(1)	413(1)	2555(1)	20(2)	1
N3	4981(1)	396(1)	2501(1)	16(1)	1
C4	4063(1)	1068(1)	2716(1)	22(2)	1
C5	4597(1)	1031(1)	3527(1)	20(2)	1
C6	5282(1)	1815(1)	3464(1)	28(2)	1
N7	6876(1)	1938(1)	3022(1)	20(1)	1
C8	7981(1)	1141(1)	3289(1)	18(2)	1
C9	5779(2)	280(1)	3938(1)	19(2)	1
C10	4649(1)	501(1)	1645(1)	18(2)	1
C11	2850(1)	618(1)	1492(1)	18(2)	1
C12	2164(1)	1402(1)	1040(1)	22(2)	1
C13	615(2)	1531(1)	825(1)	25(2)	1
C14	–257(2)	868(1)	1059(1)	28(2)	1
C15	403(2)	69(1)	1520(1)	26(2)	1
C16	1978(2)	–54(1)	1729(1)	24(2)	1
C17	5526(2)	–193(1)	1465(1)	19(2)	1
C18	6309(2)	6(1)	722(1)	22(2)	1
C19	7165(2)	–595(1)	507(1)	32(2)	1
C20	7221(2)	–1418(1)	1058(1)	31(2)	1
C21	6458(2)	–1641(1)	1799(1)	34(2)	1
C22	5602(2)	–1031(1)	1996(1)	26(2)	1

C23	7623(1)	2593(1)	3213(1)	20(2)	1
C24	9210(1)	2795(1)	2771(1)	22(2)	1
C25	9601(1)	2837(1)	2008(1)	22(2)	1
C26	11059(1)	3068(1)	1655(1)	24(2)	1
C27	12135(1)	3276(1)	2055(1)	27(2)	1
C28	11733(1)	3246(1)	2818(1)	26(2)	1
C29	10291(1)	3007(1)	3190(1)	23(2)	1
C30	6511(1)	3379(1)	3038(1)	24(2)	1
C31	6110(1)	3943(1)	2268(1)	32(2)	1
C32	5130(1)	4663(1)	2142(1)	39(2)	1
C33	4560(1)	4836(1)	2796(1)	52(3)	1
C34	4932(1)	4286(1)	3564(1)	57(3)	1
C35	5928(1)	3543(1)	3690(1)	40(2)	1
S2	6353(1)	2814(1)	575(1)	23(1)	1
O1	6802(2)	866(1)	6483(1)	26(1)	1
O2	8451(2)	–32(1)	5962(1)	52(2)	1
O3	7138(2)	1277(1)	5051(1)	51(2)	1
C36	13658(2)	2522(1)	5732(1)	45(2)	1
C37	12219(8)	2102(5)	5748(5)	31(2)	1
C38	11062(9)	2013(5)	6355(4)	33(2)	1
C39	9710(9)	1633(4)	6370(4)	29(2)	1
C40	9512(8)	1327(4)	5805(4)	24(2)	1
C41	10663(8)	1422(4)	5198(4)	24(2)	1
C42	11989(9)	1797(4)	5183(4)	30(2)	1
S1	7849(2)	818(1)	5823(1)	26(1)	1
O4	7617(6)	3348(3)	294(3)	32(1)	1
O5	5932(6)	2591(3)	1439(3)	30(1)	1
O6	6597(5)	2080(3)	398(3)	30(1)	1
C43	436(10)	4808(5)	–1176(6)	63(3)	1
C44	1915(9)	4322(4)	–770(5)	30(2)	1
C45	2587(9)	3627(5)	–866(5)	38(2)	1
C46	3922(8)	3151(4)	–465(4)	27(2)	1
C47	4643(8)	3403(4)	40(4)	22(2)	1
C48	4030(8)	4115(4)	149(4)	27(2)	1
C49	2680(9)	4577(4)	–265(5)	34(2)	1

Table S 3: Bond lengths [Å] and angles [°].

C101–C102	1.548(8)
C101–H10A	0.9600
C101–H10B	0.9600
C101–H10C	0.9600
C102–O101	1.214(6)
C102–C103	1.508(8)
C103–H10D	0.9600
C103–H10E	0.9600
C103–H10F	0.9600
C201–C202	1.556(7)
C201–H20Z	0.9600
C201–H20Y	0.9600
C201–H20C	0.9600
C202–O201	1.220(6)
C202–C203	1.516(7)
C203–H20D	0.9600
C203–H20E	0.9600
C203–H20F	0.9600
C301–C302	1.559(9)
C301–H30A	0.9600
C301–H30B	0.9600
C301–H30C	0.9600
C302–O301	1.222(7)
C302–C303	1.518(8)
C303–H30D	0.9600
C303–H30E	0.9600
C303–H30F	0.9600
C401–C402	1.478(4)
C401–H40A	0.9600
C401–H40B	0.9600
C401–H40C	0.9600
C402–O401	1.159(3)
C402–C403	1.439(4)
C403–H40D	0.9599
C403–H40E	0.9599
C403–H40F	0.9599
C501–C502	1.5294
C501–H50A	0.9600
C501–H50B	0.9600
C501–H50C	0.9600
C502–O501	1.1996
C502–C503	1.4898
C503–H50D	0.9600
C503–H50E	0.9600
C503–H50F	0.9600

C1–C8	1.5181
C1–C9	1.5257
C1–C2	1.5334
C1–H1	0.9800
C2–N3	1.5143
C2–H2A	0.9700
C2–H2B	0.9700
N3–C4	1.5171
N3–C10	1.5383
N3–H3	0.9800
C4–C5	1.5531
C4–H4A	0.9700
C4–H4B	0.9700
C5–C9	1.5253
C5–C6	1.5282
C5–H5	0.9800
C6–N7	1.5276
C6–H6A	0.9700
C6–H6B	0.9700
N7–C8	1.5193
N7–C23	1.5530
N7–H7	0.9800
C8–H8A	0.9700
C8–H8B	0.9700
C9–H9A	0.9700
C9–H9B	0.9700
C10–C17	1.5022
C10–C11	1.5617
C10–H10	0.9800
C11–C12	1.3735
C11–C16	1.3795
C12–C13	1.3783
C12–H12	0.9300
C13–C14	1.3676
C13–H13	0.9300
C14–C15	1.3880
C14–H14	0.9300
C15–C16	1.3975
C15–H15	0.9300
C16–H16	0.9300
C17–C18	1.3945
C17–C22	1.3961
C18–C19	1.3914
C18–H18	0.9300
C19–C20	1.3859
C19–H19	0.9300
C20–C21	1.3816

C20–H20	0.9300
C21–C22	1.3868
C21–H21	0.9300
C22–H22	0.9300
C23–C30	1.5198
C23–C24	1.5331
C23–H23	0.9800
C24–C25	1.3813
C24–C29	1.4169
C25–C26	1.3904
C25–H25	0.9300
C26–C27	1.3848
C26–H26	0.9300
C27–C28	1.3912
C27–H27	0.9300
C28–C29	1.3916
C28–H28	0.9300
C29–H29	0.9300
C30–C35	1.3826
C30–C31	1.3865
C31–C32	1.3829
C31–H31	0.9300
C32–C33	1.3914
C32–H32	0.9300
C33–C34	1.3725
C33–H33	0.9300
C34–C35	1.4218
C34–H34	0.9300
C35–H35	0.9300
S2–O4	1.447(5)
S2–O6	1.450(5)
S2–O5	1.488(5)
S2–C47	1.788(7)
O1–S1	1.473(2)
O2–S1	1.454(2)
O3–S1	1.443(2)
C36–C37	1.507(8)
C36–H36A	0.9600
C36–H36B	0.9600
C36–H36C	0.9600
C37–C42	1.378(11)
C37–C38	1.405(10)
C38–C39	1.400(10)
C38–H38	0.9300
C39–C40	1.374(11)
C39–H39	0.9300
C40–C41	1.400(10)

C40–S1	1.765(7)
C41–C42	1.375(10)
C41–H41	0.9300
C42–H42	0.9300
C43–C44	1.499(10)
C43–H43A	0.9600
C43–H43B	0.9600
C43–H43C	0.9600
C44–C45	1.367(11)
C44–C49	1.407(12)
C45–C46	1.393(10)
C45–H45	0.9300
C46–C47	1.384(10)
C46–H46	0.9300
C47–C48	1.391(10)
C48–C49	1.404(10)
C48–H48	0.9300
C49–H49	0.9300

C102–C101–H10A	109.5
C102–C101–H10B	109.5
H10A–C101–H10B	109.5
C102–C101–H10C	109.5
H10A–C101–H10C	109.5
H10B–C101–H10C	109.5
O101–C102–C103	125.2
O101–C102–C101	119.7
C103–C102–C101	114.8
C102–C103–H10D	109.5
C102–C103–H10E	109.5
H10D–C103–H10E	109.5
C102–C103–H10F	109.5
H10D–C103–H10F	109.5
H10E–C103–H10F	109.5
C202–C201–H20Z	109.5
C202–C201–H20Y	109.5
H20Z–C201–H20Y	109.5
C202–C201–H20C	109.5
H20Z–C201–H20C	109.5
H20Y–C201–H20C	109.5
O201–C202–C203	125.2
O201–C202–C201	119.7
C203–C202–C201	114.7
C202–C203–H20D	109.5
C202–C203–H20E	109.5
H20D–C203–H20E	109.5
C202–C203–H20F	109.5

H20D–C203–H20F	109.5
H20E–C203–H20F	109.5
C302–C301–H30A	109.5
C302–C301–H30B	109.5
H30A–C301–H30B	109.5
C302–C301–H30C	109.5
H30A–C301–H30C	109.5
H30B–C301–H30C	109.5
O301–C302–C303	125.2
O301–C302–C301	119.7
C303–C302–C301	114.7
C302–C303–H30D	109.5
C302–C303–H30E	109.5
H30D–C303–H30E	109.5
C302–C303–H30F	109.5
H30D–C303–H30F	109.5
H30E–C303–H30F	109.5
C402–C401–H40A	109.5
C402–C401–H40B	109.5
H40A–C401–H40B	109.5
C402–C401–H40C	109.5
H40A–C401–H40C	109.5
H40B–C401–H40C	109.5
O401–C402–C403	125.2
O401–C402–C401	119.7
C403–C402–C401	114.8
C402–C403–H40D	109.5
C402–C403–H40E	109.5
H40D–C403–H40E	109.5
C402–C403–H40F	109.5
H40D–C403–H40F	109.5
H40E–C403–H40F	109.5
C502–C501–H50A	109.5
C502–C501–H50B	109.5
H50A–C501–H50B	109.5
C502–C501–H50C	109.5
H50A–C501–H50C	109.5
H50B–C501–H50C	109.5
O501–C502–C503	125.2
O501–C502–C501	119.7
C503–C502–C501	114.8
C502–C503–H50D	109.5
C502–C503–H50E	109.5
H50D–C503–H50E	109.5
C502–C503–H50F	109.5
H50D–C503–H50F	109.5
H50E–C503–H50F	109.5

C8–C1–C9	109.3
C8–C1–C2	114.0
C9–C1–C2	110.9
C8–C1–H1	107.4
C9–C1–H1	107.4
C2–C1–H1	107.4
N3–C2–C1	113.2
N3–C2–H2A	108.9
C1–C2–H2A	108.9
N3–C2–H2B	108.9
C1–C2–H2B	108.9
H2A–C2–H2B	107.8
C2–N3–C4	110.6
C2–N3–C10	108.1
C4–N3–C10	112.1
C2–N3–H3	108.7
C4–N3–H3	108.7
C10–N3–H3	108.7
N3–C4–C5	111.2
N3–C4–H4A	109.4
C5–C4–H4A	109.4
N3–C4–H4B	109.4
C5–C4–H4B	109.4
H4A–C4–H4B	108.0
C9–C5–C6	108.7
C9–C5–C4	111.9
C6–C5–C4	114.4
C9–C5–H5	107.1
C6–C5–H5	107.1
C4–C5–H5	107.1
N7–C6–C5	113.3
N7–C6–H6A	108.9
C5–C6–H6A	108.9
N7–C6–H6B	108.9
C5–C6–H6B	108.9
H6A–C6–H6B	107.7
C8–N7–C6	112.7
C8–N7–C23	108.7
C6–N7–C23	107.1
C8–N7–H7	109.4
C6–N7–H7	109.4
C23–N7–H7	109.4
C1–C8–N7	113.3
C1–C8–H8A	108.9
N7–C8–H8A	108.9
C1–C8–H8B	108.9
N7–C8–H8B	108.9

H8A–C8–H8B	107.7
C5–C9–C1	106.1
C5–C9–H9A	110.5
C1–C9–H9A	110.5
C5–C9–H9B	110.5
C1–C9–H9B	110.5
H9A–C9–H9B	108.7
C17–C10–N3	110.6
C17–C10–C11	113.7
N3–C10–C11	112.0
C17–C10–H10	106.7
N3–C10–H10	106.7
C11–C10–H10	106.7
C12–C11–C16	119.5
C12–C11–C10	118.7
C16–C11–C10	121.5
C11–C12–C13	121.2
C11–C12–H12	119.4
C13–C12–H12	119.4
C14–C13–C12	119.6
C14–C13–H13	120.2
C12–C13–H13	120.2
C13–C14–C15	120.4
C13–C14–H14	119.8
C15–C14–H14	119.8
C14–C15–C16	119.4
C14–C15–H15	120.3
C16–C15–H15	120.3
C11–C16–C15	119.9
C11–C16–H16	120.1
C15–C16–H16	120.1
C18–C17–C22	117.5
C18–C17–C10	118.5
C22–C17–C10	124.0
C19–C18–C17	122.5
C19–C18–H18	118.8
C17–C18–H18	118.8
C20–C19–C18	117.9
C20–C19–H19	121.1
C18–C19–H19	121.1
C21–C20–C19	121.5
C21–C20–H20	119.3
C19–C20–H20	119.3
C20–C21–C22	119.5
C20–C21–H21	120.3
C22–C21–H21	120.3
C21–C22–C17	121.1

C21–C22–H22	119.4
C17–C22–H22	119.4
C30–C23–C24	111.2
C30–C23–N7	111.7
C24–C23–N7	111.8
C30–C23–H23	107.3
C24–C23–H23	107.3
N7–C23–H23	107.3
C25–C24–C29	119.6
C25–C24–C23	126.1
C29–C24–C23	114.1
C24–C25–C26	120.7
C24–C25–H25	119.7
C26–C25–H25	119.7
C27–C26–C25	120.7
C27–C26–H26	119.7
C25–C26–H26	119.7
C26–C27–C28	118.7
C26–C27–H27	120.7
C28–C27–H27	120.7
C27–C28–C29	121.9
C27–C28–H28	119.1
C29–C28–H28	119.1
C28–C29–C24	118.4
C28–C29–H29	120.8
C24–C29–H29	120.8
C35–C30–C31	119.4
C35–C30–C23	117.0
C31–C30–C23	123.6
C32–C31–C30	121.2
C32–C31–H31	119.4
C30–C31–H31	119.4
C31–C32–C33	119.6
C31–C32–H32	120.2
C33–C32–H32	120.2
C34–C33–C32	120.4
C34–C33–H33	119.8
C32–C33–H33	119.8
C33–C34–C35	119.8
C33–C34–H34	120.1
C35–C34–H34	120.1
C30–C35–C34	119.7
C30–C35–H35	120.1
C34–C35–H35	120.1
O4–S2–O6	114.3(3)
O4–S2–O5	112.8(3)
O6–S2–O5	111.2(3)

O4–S2–C47	107.0(3)
O6–S2–C47	105.4(3)
O5–S2–C47	105.4(3)
C37–C36–H36A	109.5
C37–C36–H36B	109.5
H36A–C36–H36B	109.5
C37–C36–H36C	109.5
H36A–C36–H36C	109.5
H36B–C36–H36C	109.5
C42–C37–C38	118.2(7)
C42–C37–C36	122.3(6)
C38–C37–C36	119.5(7)
C39–C38–C37	120.1(8)
C39–C38–H38	120.0
C37–C38–H38	120.0
C40–C39–C38	120.7(7)
C40–C39–H39	119.6
C38–C39–H39	119.6
C39–C40–C41	118.9(7)
C39–C40–S1	121.9(5)
C41–C40–S1	119.2(6)
C42–C41–C40	120.2(7)
C42–C41–H41	119.9
C40–C41–H41	119.9
C41–C42–C37	121.8(7)
C41–C42–H42	119.1
C37–C42–H42	119.1
O3–S1–O2	113.73(15)
O3–S1–O1	111.58(16)
O2–S1–O1	112.62(14)
O3–S1–C40	105.8(2)
O2–S1–C40	105.5(3)
O1–S1–C40	107.0(3)
C44–C43–H43A	109.5
C44–C43–H43B	109.5
H43A–C43–H43B	109.5
C44–C43–H43C	109.5
H43A–C43–H43C	109.5
H43B–C43–H43C	109.5
C45–C44–C49	116.9(7)
C45–C44–C43	123.0(8)
C49–C44–C43	120.1(8)
C44–C45–C46	123.5(8)
C44–C45–H45	118.3
C46–C45–H45	118.3
C47–C46–C45	118.8(7)
C47–C46–H46	120.6

C45–C46–H46	120.6
C46–C47–C48	120.3(6)
C46–C47–S2	120.8(6)
C48–C47–S2	118.9(6)
C47–C48–C49	119.2(7)
C47–C48–H48	120.4
C49–C48–H48	120.4
C48–C49–C44	121.3(7)
C48–C49–H49	119.3
C44–C49–H49	119.3

Table S 4: Anisotropic displacement parameters [$Å^2 \times 10^3$]. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U^{11} + \cdots + 2\ h\ k\ a^*\ b^*\ U^{12}]$.

Atom	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
C101	148(6)	112(4)	113(5)	−63(3)	31(4)	−18(4)
C102	148(6)	112(4)	113(5)	−63(3)	31(4)	−18(4)
C103	148(6)	112(4)	113(5)	−63(3)	31(4)	−18(4)
O101	148(6)	112(4)	113(5)	−63(3)	31(4)	−18(4)
C201	148(6)	112(4)	113(5)	−63(3)	31(4)	−18(4)
C202	148(6)	112(4)	113(5)	−63(3)	31(4)	−18(4)
C203	148(6)	112(4)	113(5)	−63(3)	31(4)	−18(4)
O201	148(6)	112(4)	113(5)	−63(3)	31(4)	−18(4)
C301	148(6)	112(4)	113(5)	−63(3)	31(4)	−18(4)
C302	148(6)	112(4)	113(5)	−63(3)	31(4)	−18(4)
C303	148(6)	112(4)	113(5)	−63(3)	31(4)	−18(4)
O301	148(6)	112(4)	113(5)	−63(3)	31(4)	−18(4)
C401	148(6)	112(4)	113(5)	−63(3)	31(4)	−18(4)
C402	148(6)	112(4)	113(5)	−63(3)	31(4)	−18(4)
C403	148(6)	112(4)	113(5)	−63(3)	31(4)	−18(4)
O401	148(6)	112(4)	113(5)	−63(3)	31(4)	−18(4)
C501	148(6)	112(4)	113(5)	−63(3)	31(4)	−18(4)
C502	148(6)	112(4)	113(5)	−63(3)	31(4)	−18(4)
C503	148(6)	112(4)	113(5)	−63(3)	31(4)	−18(4)
O501	148(6)	112(4)	113(5)	−63(3)	31(4)	−18(4)
C1	7(3)	23(3)	19(3)	−8(3)	−1(3)	0(3)
C2	9(3)	28(4)	24(3)	−13(3)	0(3)	4(3)
N3	15(3)	15(3)	19(3)	−8(2)	−2(2)	−4(2)
C4	30(4)	17(3)	21(3)	−11(3)	−2(3)	0(3)
C5	27(4)	25(3)	14(3)	−12(2)	1(3)	−9(3)
C6	20(4)	35(4)	30(4)	−16(3)	−6(3)	5(3)
N7	17(3)	29(3)	18(3)	−12(2)	1(2)	−8(2)
C8	13(3)	25(3)	15(3)	−7(3)	5(3)	−7(3)
C9	22(3)	19(3)	19(3)	−9(2)	−1(3)	−8(3)
C10	21(3)	20(3)	8(3)	0(3)	−3(3)	−1(3)
C11	19(3)	27(3)	15(3)	−15(2)	2(3)	−1(3)
C12	26(4)	27(3)	18(3)	−15(3)	7(3)	−6(3)
C13	22(4)	35(4)	21(3)	−18(3)	−5(3)	12(3)
C14	19(4)	42(4)	31(4)	−24(3)	2(3)	−2(3)
C15	24(4)	25(4)	30(4)	−13(3)	3(3)	−5(3)
C16	26(4)	22(3)	29(4)	−17(3)	3(3)	1(3)
C17	14(3)	21(3)	24(3)	−10(3)	0(3)	1(3)
C18	26(4)	23(3)	25(3)	−17(2)	−1(3)	−5(3)
C19	33(4)	51(4)	26(3)	−30(3)	−1(3)	−2(3)
C20	26(4)	29(4)	49(4)	−29(3)	−11(3)	10(3)

C21	43(5)	34(4)	27(4)	–18(3)	7(3)	–1(4)
C22	28(4)	23(4)	23(4)	–8(3)	2(3)	1(3)
C23	28(4)	24(3)	14(3)	–15(2)	2(3)	–3(3)
C24	19(3)	24(4)	19(3)	–3(3)	3(3)	–4(3)
C25	26(4)	21(3)	21(3)	–12(3)	–1(3)	–1(3)
C26	34(4)	14(3)	24(4)	–9(3)	6(3)	1(3)
C27	25(4)	27(4)	31(4)	–14(3)	–6(3)	–1(3)
C28	26(4)	23(3)	36(4)	–20(3)	–13(3)	2(3)
C29	32(4)	20(3)	16(3)	–7(3)	–3(3)	1(3)
C30	20(4)	25(3)	37(4)	–22(3)	13(3)	–9(3)
C31	29(4)	30(4)	38(4)	–15(3)	9(3)	–8(3)
C32	36(5)	31(4)	53(5)	–22(3)	10(4)	–6(3)
C33	61(6)	15(4)	82(6)	–23(4)	14(5)	–12(4)
C34	64(6)	50(5)	77(5)	–48(4)	51(4)	–24(4)
C35	46(5)	42(4)	41(4)	–23(3)	13(4)	–18(4)
S2	23(1)	22(1)	20(1)	–5(1)	–3(1)	–1(1)
O1	26(3)	31(3)	25(2)	–16(2)	6(2)	0(2)
O2	47(3)	34(3)	92(4)	–42(2)	33(3)	–20(2)
O3	41(3)	94(4)	19(3)	–16(3)	1(2)	–36(3)
C36	33(5)	43(5)	59(5)	–17(4)	–3(4)	–11(4)
C37	18(4)	33(4)	36(4)	–8(3)	–1(3)	–4(3)
C38	41(5)	41(4)	27(4)	–20(3)	–1(3)	–13(3)
C39	26(4)	25(4)	33(4)	–9(3)	7(3)	–8(3)
C40	22(4)	20(3)	25(4)	–4(3)	6(3)	–5(3)
C41	29(4)	17(3)	27(4)	–10(3)	4(3)	1(3)
C42	28(4)	34(4)	27(4)	–13(3)	14(3)	–8(3)
S1	28(1)	36(1)	23(1)	–18(1)	8(1)	–14(1)
O4	24(3)	34(3)	37(3)	–12(2)	3(2)	–7(2)
O5	28(3)	35(3)	24(2)	–10(2)	–4(2)	–1(2)
O6	22(3)	29(3)	41(3)	–16(2)	–4(2)	0(2)
C43	39(5)	31(5)	93(7)	4(5)	–29(5)	9(4)
C44	30(4)	14(3)	33(4)	3(3)	1(3)	–3(3)
C45	30(4)	35(4)	40(4)	–3(4)	–16(4)	–6(3)
C46	28(4)	22(4)	33(4)	–12(3)	–9(3)	3(3)
C47	28(4)	14(3)	19(3)	1(3)	–2(3)	–7(3)
C48	30(4)	28(4)	17(3)	–4(3)	7(3)	–5(3)
C49	34(4)	17(4)	40(4)	–5(3)	16(4)	1(3)

Table S 5: Hydrogen coordinates [× 10^4] and isotropic displacement parameters [$Å^2 \times 10^3$].

Atom	*x*	*y*	*z*	U_{eq}	*S.o.f.*
H10A	1203	4064	4268	180	0.45
H10B	1309	5023	3793	180	0.45
H10C	574	4520	3392	180	0.45
H10D	–2877	5604	3945	180	0.45
H10E	–2046	5510	3188	180	0.45
H10F	–1309	6008	3594	180	0.45
H20Z	1085	8567	1458	180	0.6
H20Y	1805	8334	755	180	0.6
H20C	2824	8164	1497	180	0.6
H20D	1745	6095	1860	180	0.6
H20E	3241	6571	1727	180	0.6
H20F	2161	6757	1003	180	0.6
H30A	3230	7648	2552	180	0.4
H30B	3258	6694	2760	180	0.4
H30C	1762	7175	2971	180	0.4
H30D	497	6979	1199	180	0.4
H30E	–24	6788	2094	180	0.4
H30F	1426	6264	1903	180	0.4
H40A	2525	7325	3294	180	0.27
H40B	3475	6525	3263	180	0.27
H40C	4154	7001	3709	180	0.27
H40D	4389	5574	4665	180	0.27
H40E	2936	5100	4696	180	0.27
H40F	3134	5417	5368	180	0.27
H50A	3219	7663	2678	180	0.33
H50B	1528	7547	2493	180	0.33
H50C	2997	7047	2283	180	0.33
H50D	1422	5492	4086	180	0.33
H50E	1853	5659	3186	180	0.33
H50F	383	6158	3396	180	0.33
H1	7952	–104	3602	20	1
H2A	7060	915	2125	24	1
H2B	7283	–60	2475	24	1
H3	4681	–148	2883	19	1
H4A	2951	997	2755	26	1
H4B	4216	1611	2294	26	1
H5	3664	963	3883	24	1
H6A	4550	2297	3185	33	1
H6B	5394	1785	4001	33	1
H7	6723	2150	2442	24	1
H8A	8856	1218	2906	21	1
H8B	8400	1034	3806	21	1

H9A	5331	–233	4037	23	1
H9B	6082	263	4447	23	1
H10	5076	1017	1275	22	1
H12	2756	1854	877	26	1
H13	165	2067	523	30	1
H14	–1299	952	908	34	1
H15	–198	–380	1688	31	1
H16	2437	–589	2028	29	1
H18	6256	560	357	26	1
H19	7684	–448	10	38	1
H20	7786	–1829	925	37	1
H21	6517	–2196	2162	40	1
H22	5070	–1183	2490	31	1
H23	7820	2348	3790	24	1
H25	8882	2710	1727	26	1
H26	11313	3082	1146	29	1
H27	13108	3433	1817	32	1
H28	12449	3390	3087	31	1
H29	10043	2988	3702	27	1
H31	6507	3835	1829	38	1
H32	4853	5029	1623	46	1
H33	3925	5327	2712	62	1
H34	4534	4398	4000	69	1
H35	6186	3169	4209	49	1
H36A	14583	2166	5712	68	1
H36B	13660	2626	6209	68	1
H36C	13647	3039	5267	68	1
H38	11193	2206	6748	40	1
H39	8937	1587	6767	35	1
H41	10532	1232	4803	29	1
H42	12751	1847	4781	36	1
H43A	–390	4447	–1032	95	1
H43B	610	5033	–1748	95	1
H43C	142	5254	–1008	95	1
H45	2129	3464	–1218	46	1
H46	4322	2672	–536	33	1
H48	4508	4283	492	32	1
H49	2284	5061	–203	41	1

Table S 6: Torsion angles [°].

C8–C1–C2–N3	–119.4
C9–C1–C2–N3	4.5
C1–C2–N3–C4	52.2
C1–C2–N3–C10	175.2
C2–N3–C4–C5	–50.8
C10–N3–C4–C5	–171.5
N3–C4–C5–C9	–5.8
N3–C4–C5–C6	118.5
C9–C5–C6–N7	56.4
C4–C5–C6–N7	–69.5
C5–C6–N7–C8	–44.8
C5–C6–N7–C23	–164.4
C9–C1–C8–N7	–56.4
C2–C1–C8–N7	68.4
C6–N7–C8–C1	44.7
C23–N7–C8–C1	163.2
C6–C5–C9–C1	–66.2
C4–C5–C9–C1	61.2
C8–C1–C9–C5	66.4
C2–C1–C9–C5	–60.2
C2–N3–C10–C17	60.1
C4–N3–C10–C17	–177.7
C2–N3–C10–C11	–172.0
C4–N3–C10–C11	–49.8
C17–C10–C11–C12	–130.2
N3–C10–C11–C12	103.6
C17–C10–C11–C16	43.3
N3–C10–C11–C16	–82.9
C16–C11–C12–C13	0.5
C10–C11–C12–C13	174.2
C11–C12–C13–C14	–0.5
C12–C13–C14–C15	0.9
C13–C14–C15–C16	–1.3
C12–C11–C16–C15	–0.9
C10–C11–C16–C15	–174.4
C14–C15–C16–C11	1.3
N3–C10–C17–C18	–135.4
C11–C10–C17–C18	97.6
N3–C10–C17–C22	44.9
C11–C10–C17–C22	–82.0
C22–C17–C18–C19	–1.1
C10–C17–C18–C19	179.2
C17–C18–C19–C20	0.4
C18–C19–C20–C21	–0.1

C19–C20–C21–C22	0.6
C20–C21–C22–C17	–1.4
C18–C17–C22–C21	1.6
C10–C17–C22–C21	–178.7
C8–N7–C23–C30	–174.4
C6–N7–C23–C30	–52.3
C8–N7–C23–C24	60.3
C6–N7–C23–C24	–177.6
C30–C23–C24–C25	–89.8
N7–C23–C24–C25	35.8
C30–C23–C24–C29	85.7
N7–C23–C24–C29	–148.7
C29–C24–C25–C26	1.5
C23–C24–C25–C26	176.7
C24–C25–C26–C27	–1.4
C25–C26–C27–C28	0.4
C26–C27–C28–C29	0.5
C27–C28–C29–C24	–0.3
C25–C24–C29–C28	–0.7
C23–C24–C29–C28	–176.5
C24–C23–C30–C35	–122.2
N7–C23–C30–C35	112.1
C24–C23–C30–C31	55.3
N7–C23–C30–C31	–70.3
C35–C30–C31–C32	–0.4
C23–C30–C31–C32	–177.9
C30–C31–C32–C33	1.4
C31–C32–C33–C34	–1.8
C32–C33–C34–C35	1.2
C31–C30–C35–C34	–0.2
C23–C30–C35–C34	177.5
C33–C34–C35–C30	–0.2
C42–C37–C38–C39	–0.8(11)
C36–C37–C38–C39	179.2(6)
C37–C38–C39–C40	1.4(11)
C38–C39–C40–C41	–1.8(10)
C38–C39–C40–S1	178.2(5)
C39–C40–C41–C42	1.7(10)
S1–C40–C41–C42	–178.3(5)
C40–C41–C42–C37	–1.1(10)
C38–C37–C42–C41	0.7(11)
C36–C37–C42–C41	–179.3(6)
C39–C40–S1–O3	123.1(5)
C41–C40–S1–O3	–56.9(6)
C39–C40–S1–O2	–116.1(6)
C41–C40–S1–O2	64.0(5)
C39–C40–S1–O1	4.1(6)

C41–C40–S1–O1	–175.9(5)
C49–C44–C45–C46	3.1(11)
C43–C44–C45–C46	–177.2(7)
C44–C45–C46–C47	–2.0(11)
C45–C46–C47–C48	0.6(10)
C45–C46–C47–S2	179.7(5)
O4–S2–C47–C46	117.4(6)
O6–S2–C47–C46	–4.6(6)
O5–S2–C47–C46	–122.4(6)
O4–S2–C47–C48	–63.5(6)
O6–S2–C47–C48	174.4(5)
O5–S2–C47–C48	56.7(6)
C46–C47–C48–C49	–0.5(10)
S2–C47–C48–C49	–179.6(5)
C47–C48–C49–C44	1.7(10)
C45–C44–C49–C48	–2.9(11)
C43–C44–C49–C48	177.4(7)

Table S 7: Hydrogen bonds [Å and °].

D–H···*A*	*d*(*D*–H)	*d*(H···*A*)	*d*(*D*···*A*)	∠(*D*H*A*)
C4–H4B···O5	0.97	2.38	3.255(5)	149.9
C6–H6B···O3	0.97	2.32	3.140	141.6
N7–H7···O5	0.98	1.82	2.776(5)	165.7
C8–H8B···O3	0.97	2.62	3.342	131.7
C10–H10···O6	0.98	2.37	3.333(5)	168.0
C23–H23···O3	0.98	2.39	3.235	144.0