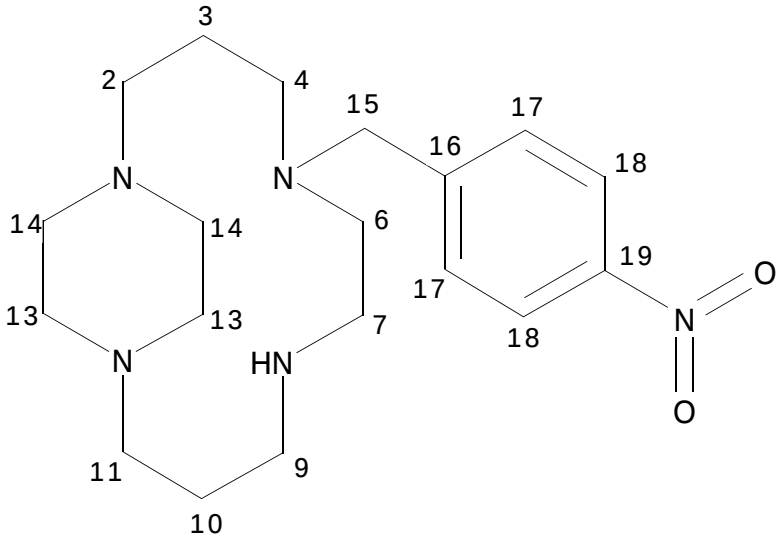
Unsymmetrically substituted side-bridged cyclam derivatives and their Cu(II) and Zn(II) complexes

Jan Plutnar, Jana Havlíčková, Jan Kotek,* Petr Hermann and Ivan Lukeš

Electronic Supplementary Information

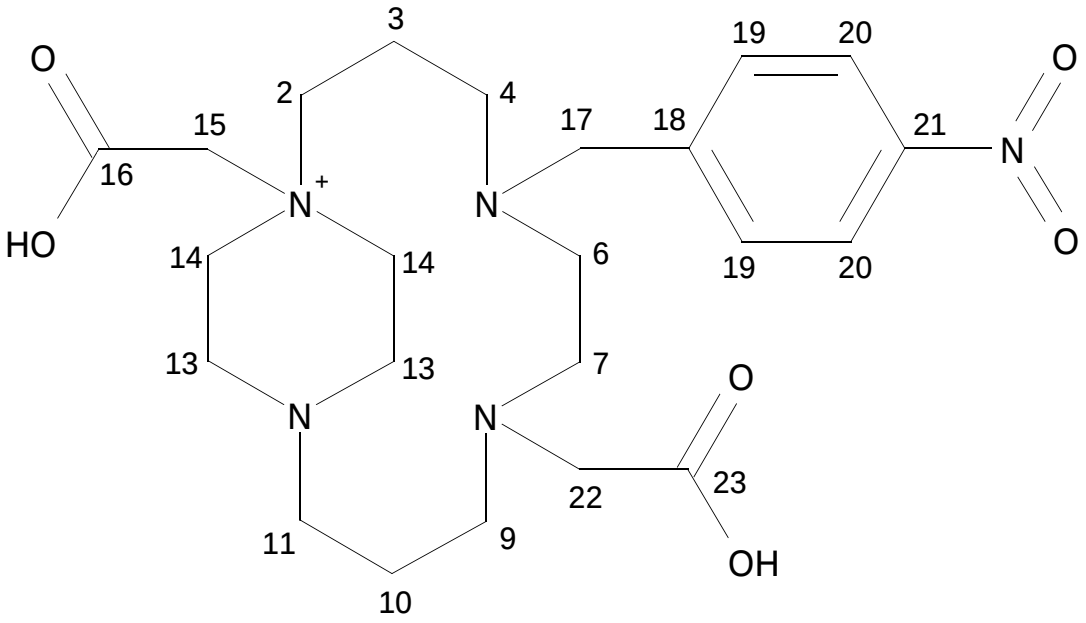
S1 – Numbering scheme of **3** for NMR signals assignment



S1a – ^{13}C and ^{1}H NMR signals assignment based on HSQC/HMBC/H-H COSY/NOESY 2D spectra

Assignment	^{13}C	^{1}H
2	54.65	2.56
3	23.63	1.69
4	54.79	2.89
6	48.33	2.53
7	55.70	2.62
9	51.22	2.66
10	26.10	1.76
11	56.95	2.64
13	50.10	2.26, 3.02
14	48.09	2.58, 3.18
15	57.58	3.71
16	147.02	---
17	129.70	7.45
18	123.29	8.18
19	146.89	---

S2 – Numbering scheme of **4**$^{+}$ for NMR signals assignment



S2a – ^{13}C and ^{1}H NMR signals assignment based on HSQC/HMBC 2D spectra

Assignment	^{13}C	^{1}H
2	56.64	4.15
3	20.04	2.40
4	52.26	3.33
6	52.74	3.38
7	54.24	3.36
9	56.14	3.25
10	22.02	2.26
11	55.13	3.63
13	45.88	3.90
14	56.34	4.27
15	63.17	4.46
16	168.46	---
17	58.86	4.44
18	139.45	---
19	134.94	7.73
20	126.60	8.33
21	150.67	---
22	57.20	3.78
23	176.50	---

S3 – ^{1}H-^{1}H-COSY spectra of **3** in $CDCl_3$

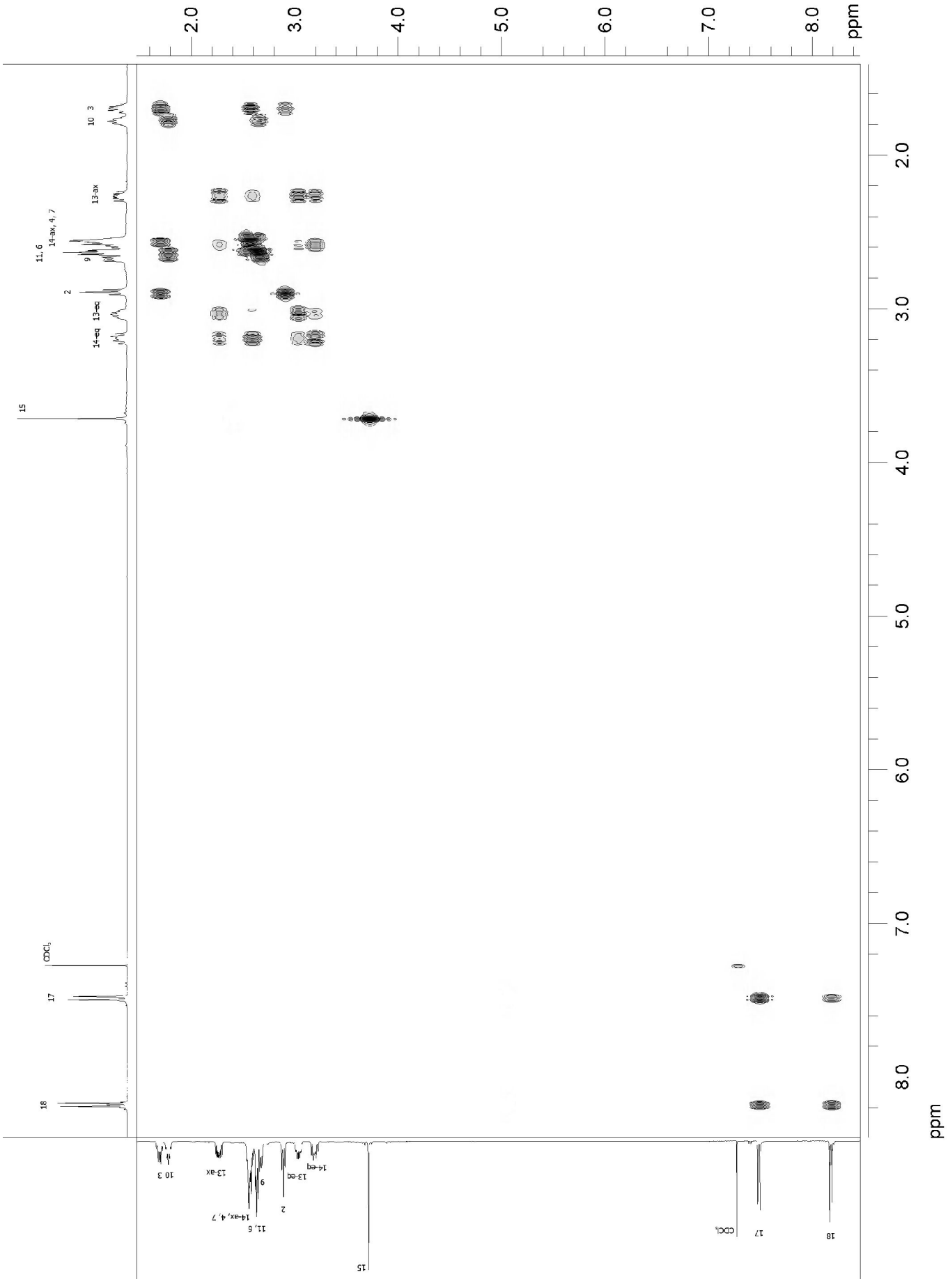
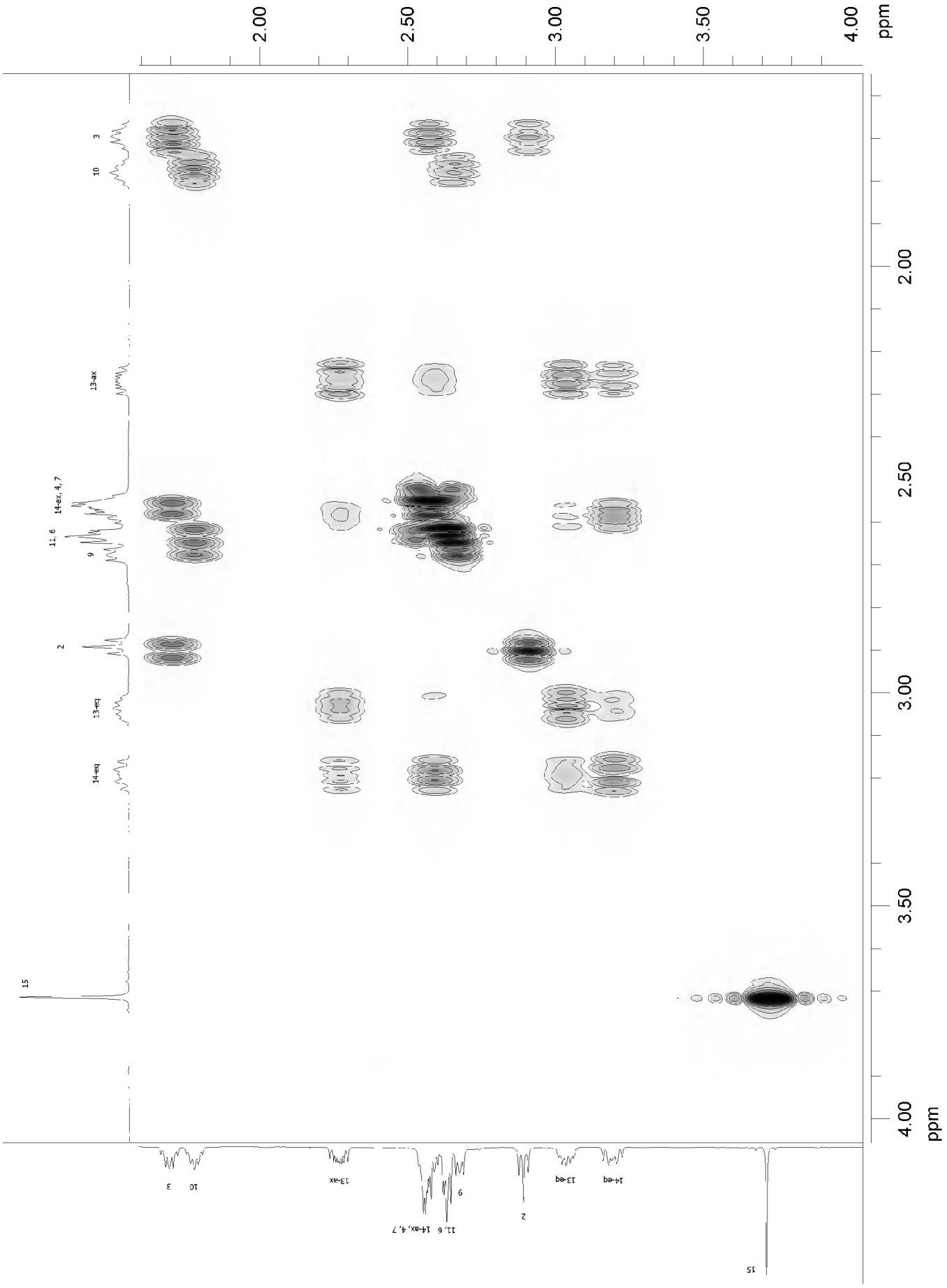
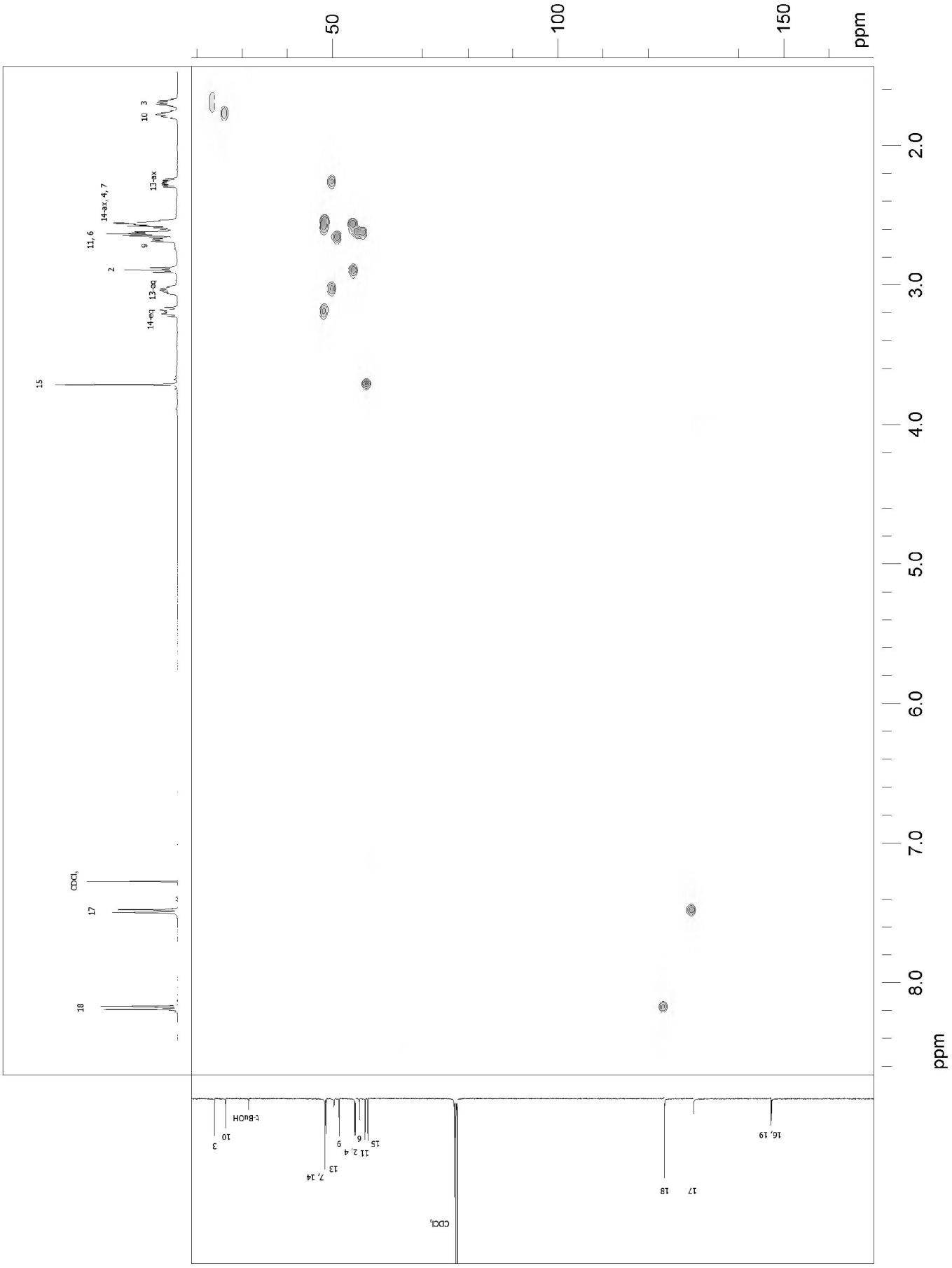


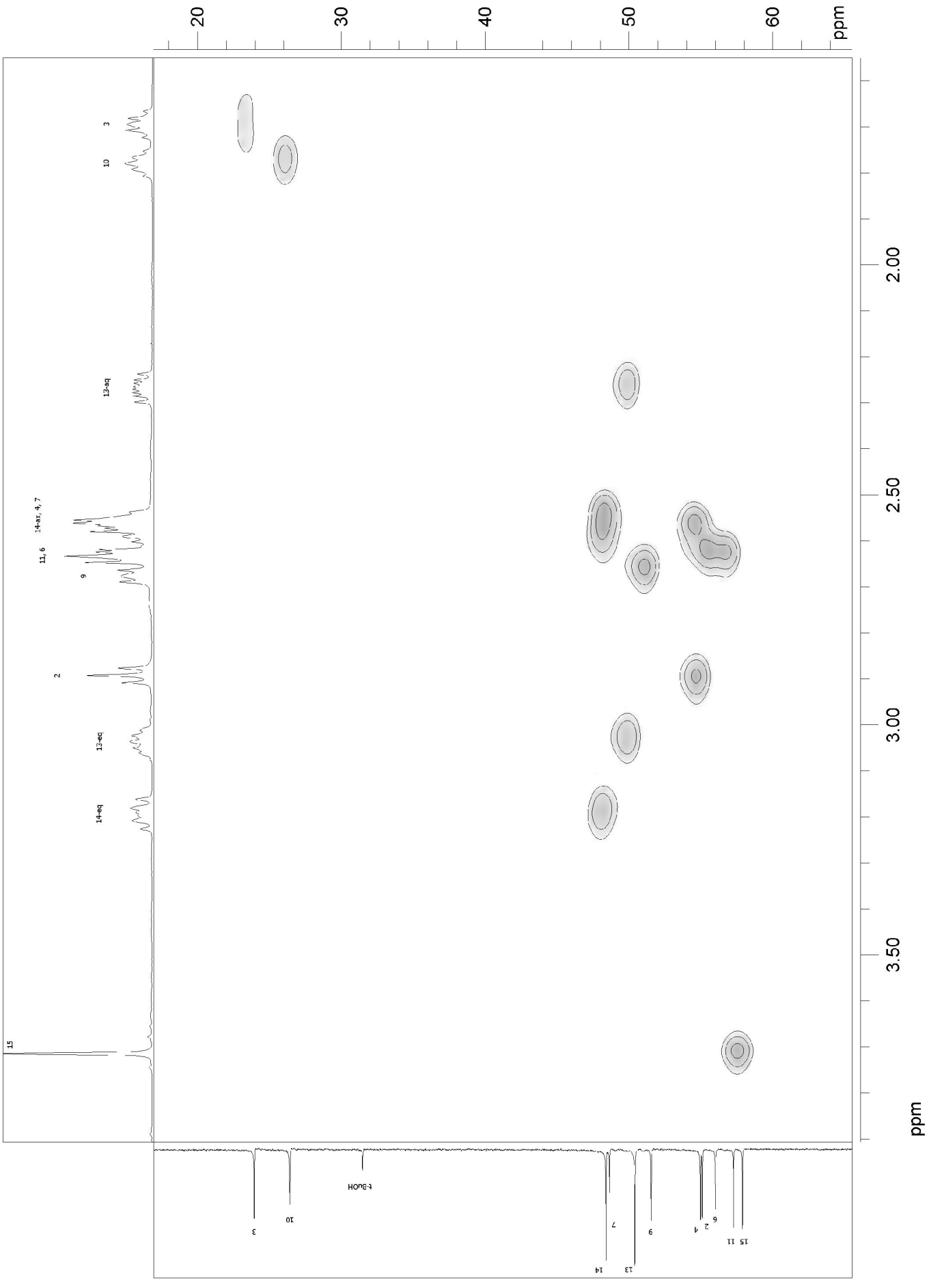
Fig.S4 – Detail of aliphatic region in ^{1}H-^{1}H COSY spectra of **3** in $CDCl_3$



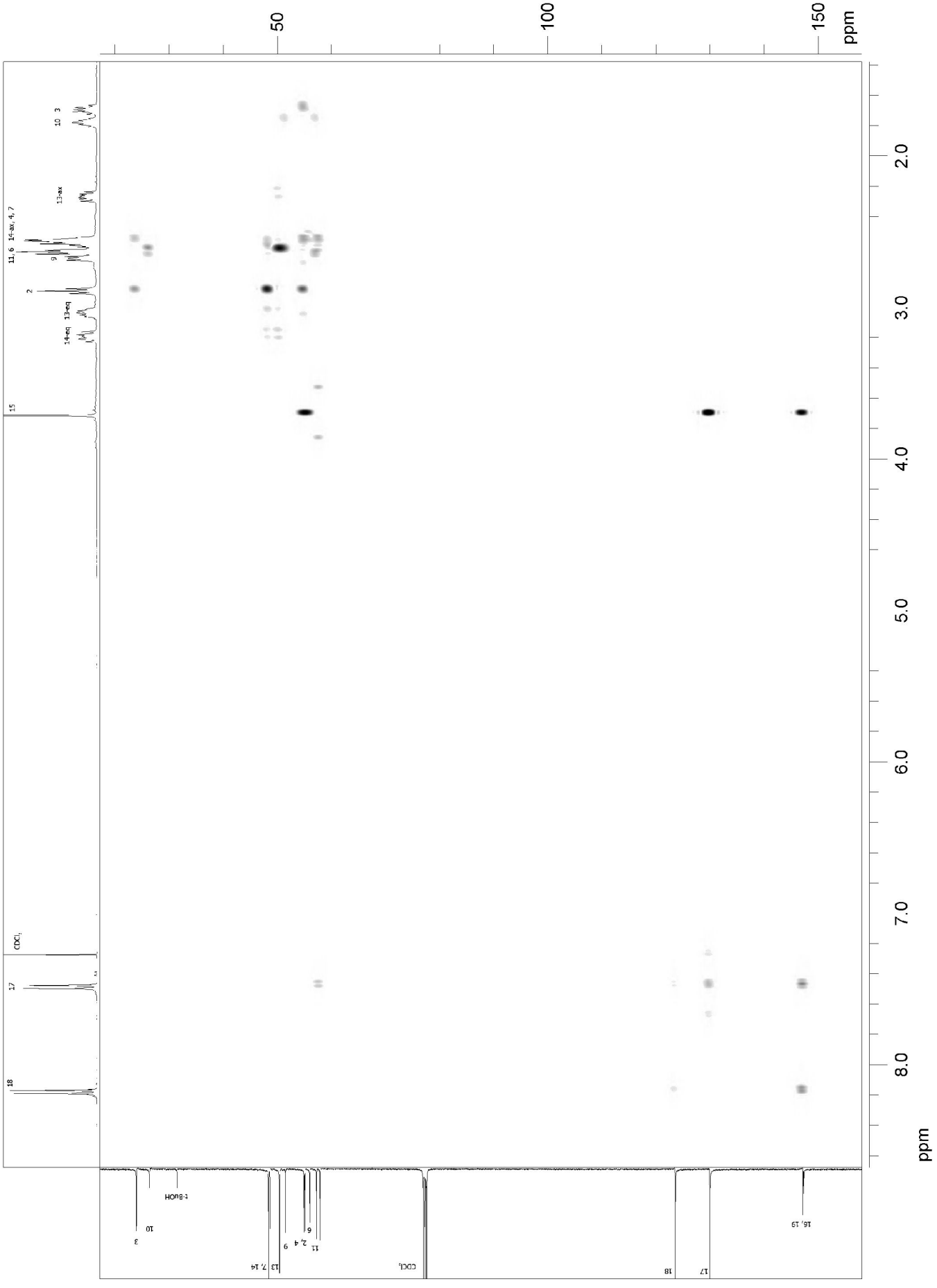
S5 – ^{1}H-^{13}C gHSQC spectra of **3** in $CDCl_3$



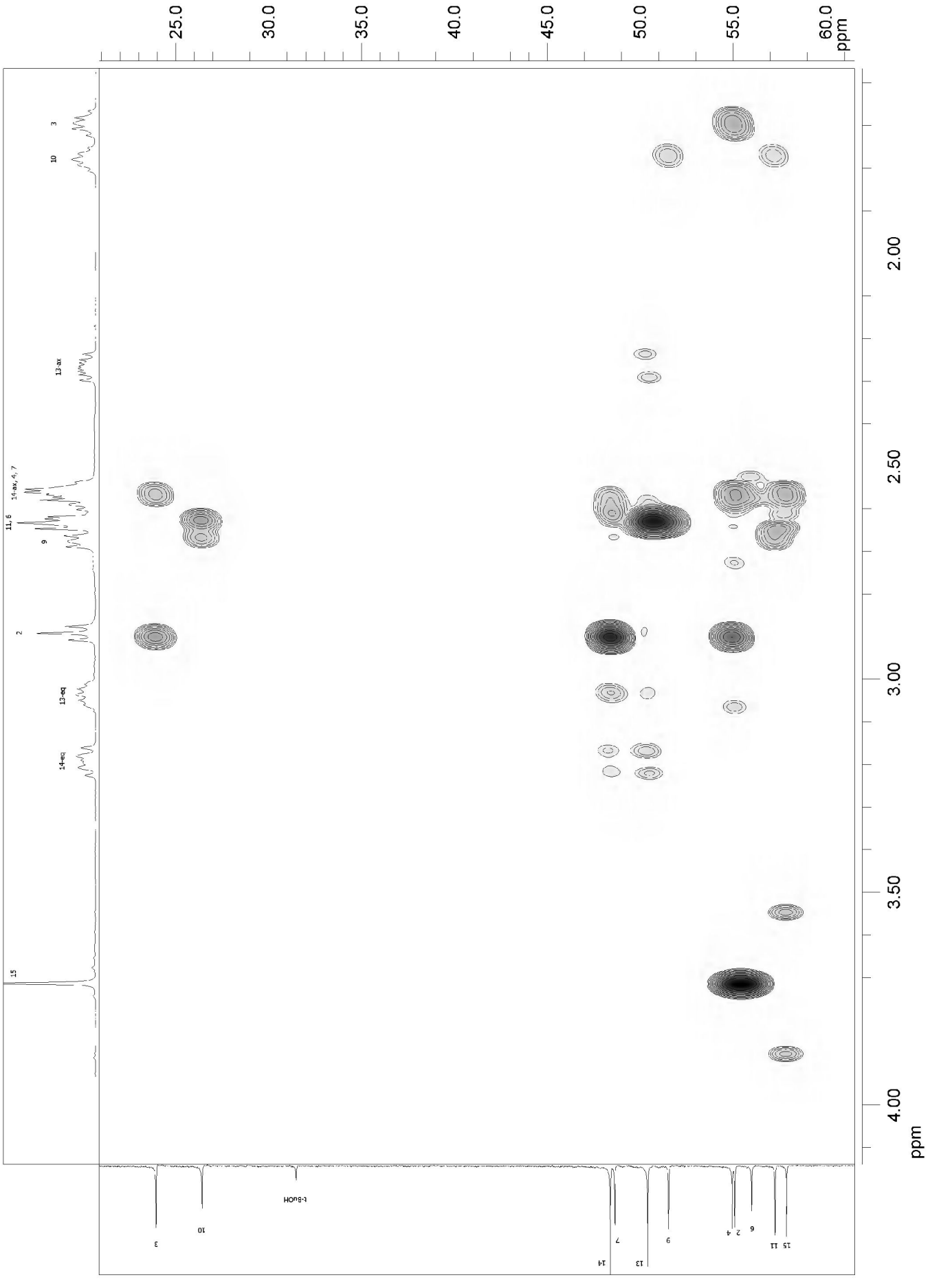
S6 – Detail of aliphatic region in ^{1}H-^{13}C gHSQC spectra of **3** in $CDCl_3$



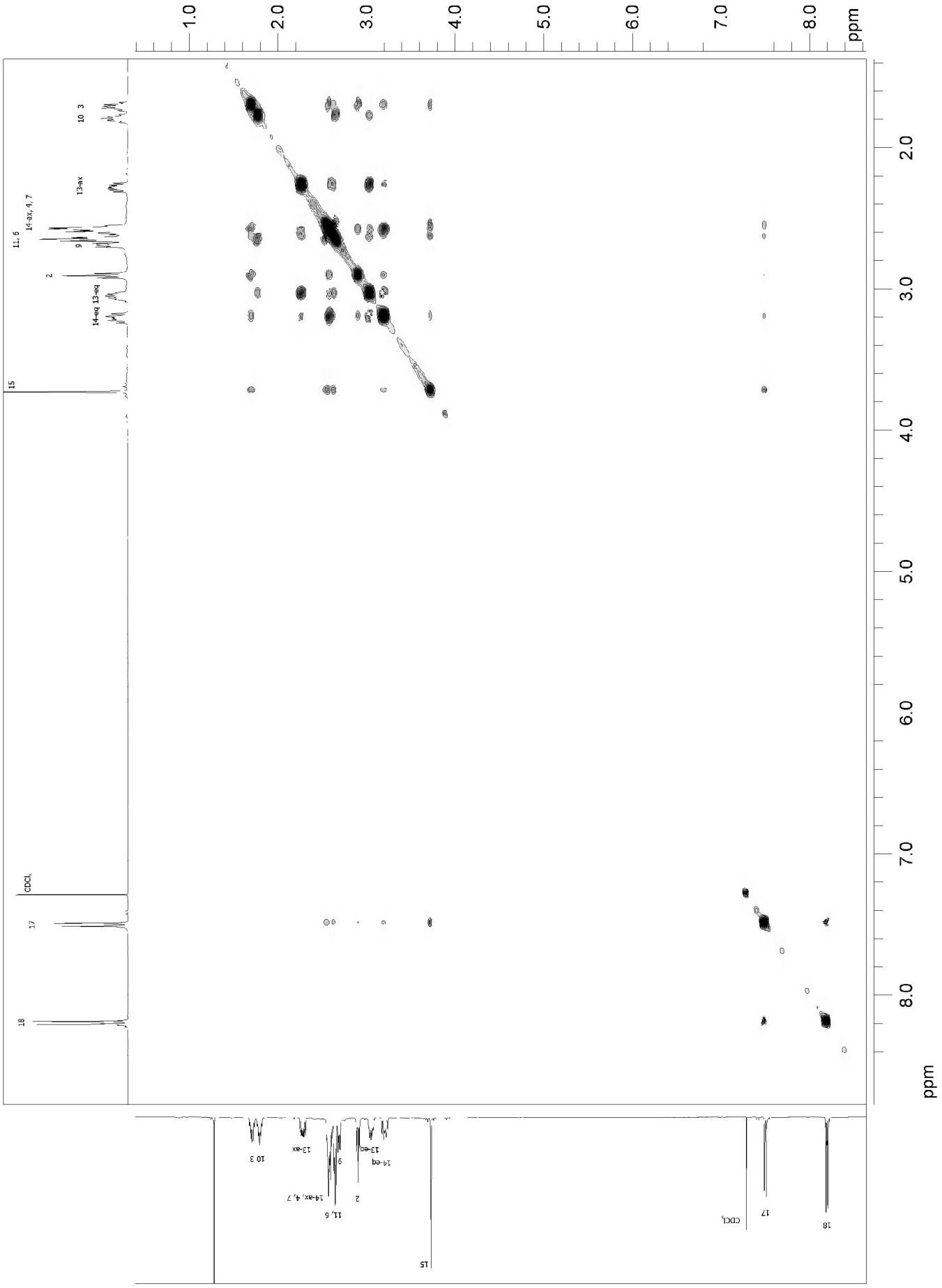
S7 – gHMBC spectra of **3** in $CDCl_3$



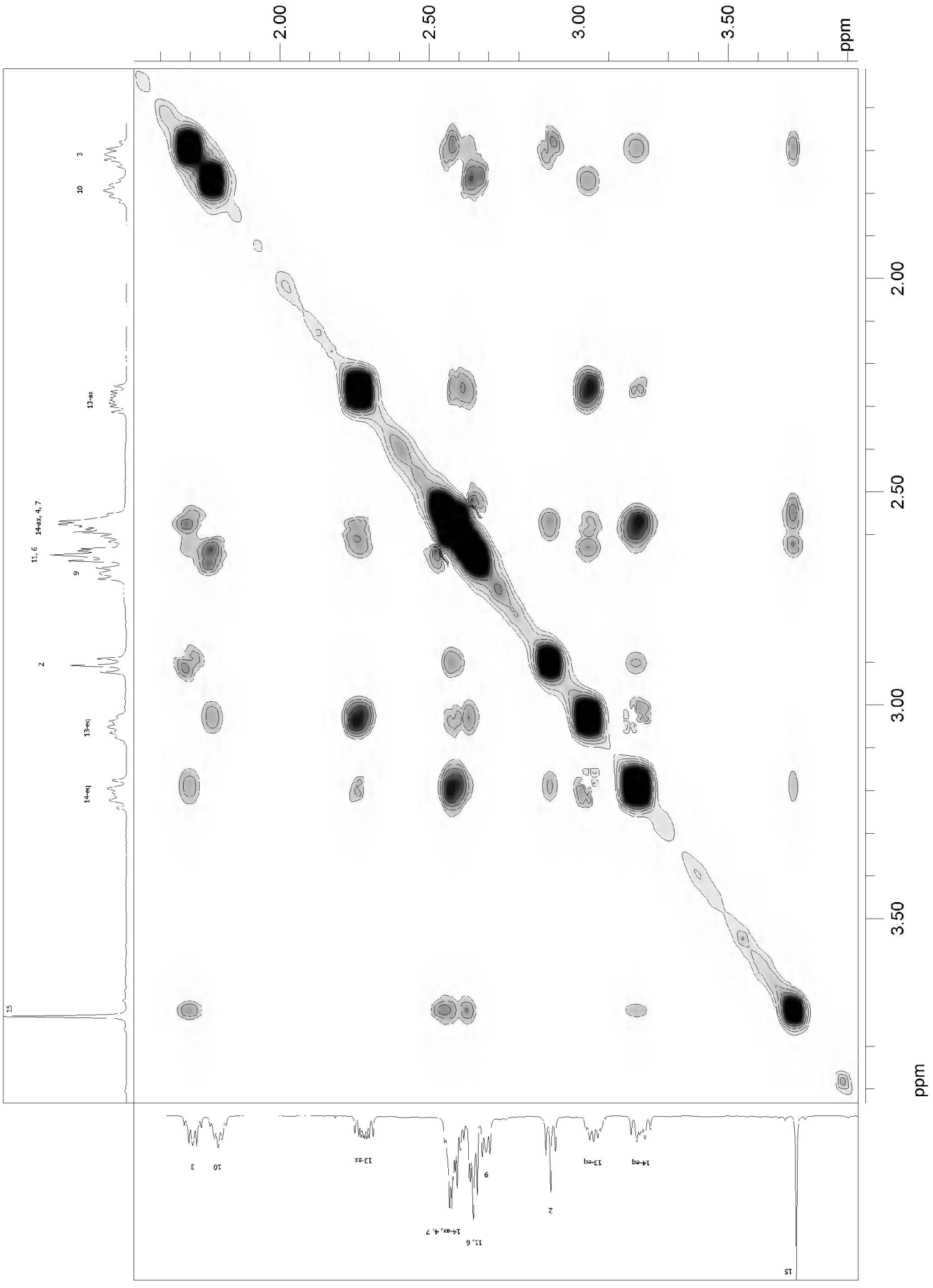
S8 – Detail of aliphatic region in gHMBC of **3** in $CDCl_3$



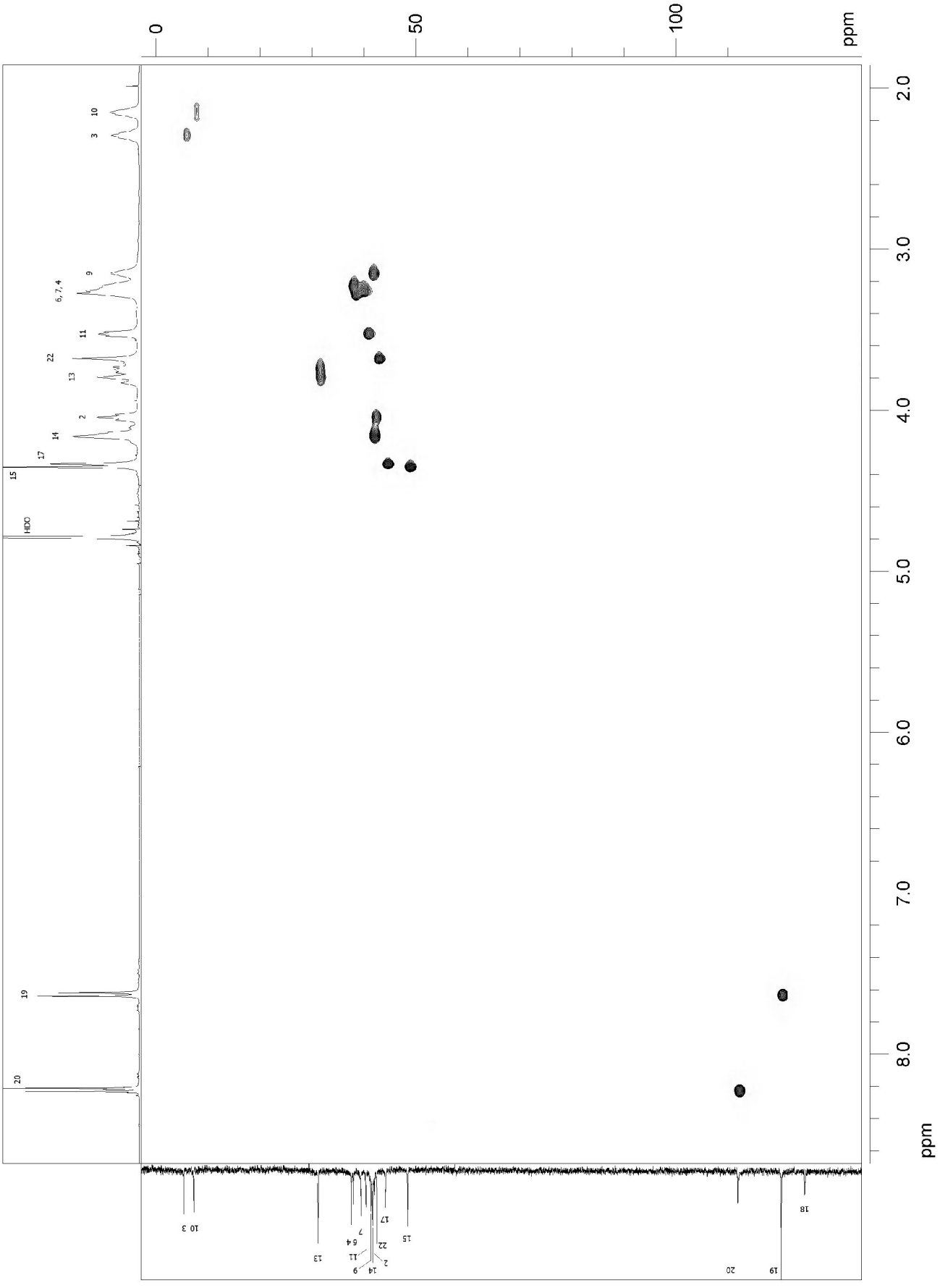
S9 – ^{1}H-^{1}H NOESY spectra of **3** in $CDCl_3$



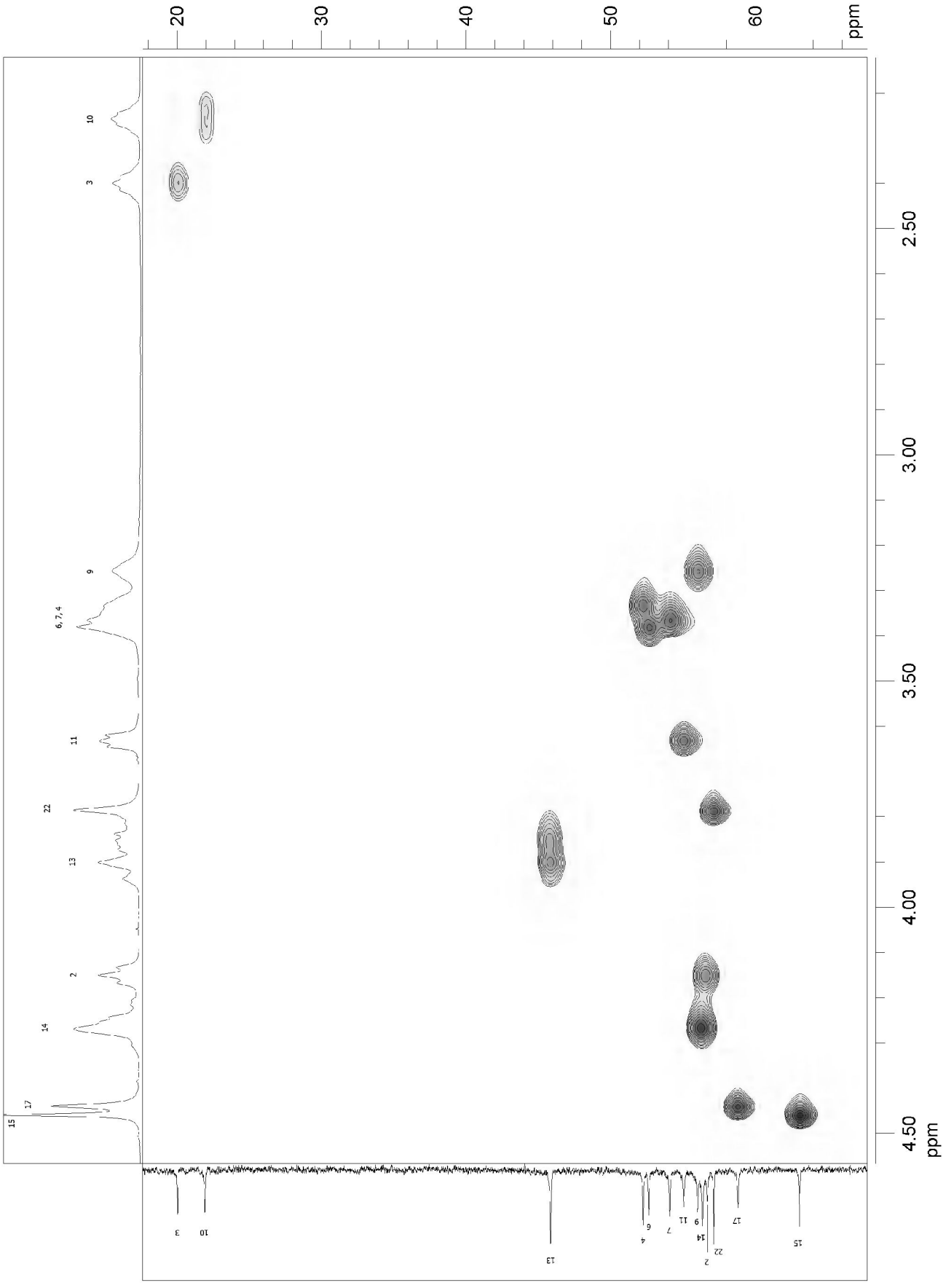
S10 – Detail of aliphatic region in ^{1}H-^{1}H NOESY spectra of **3** in $CDCl_3$



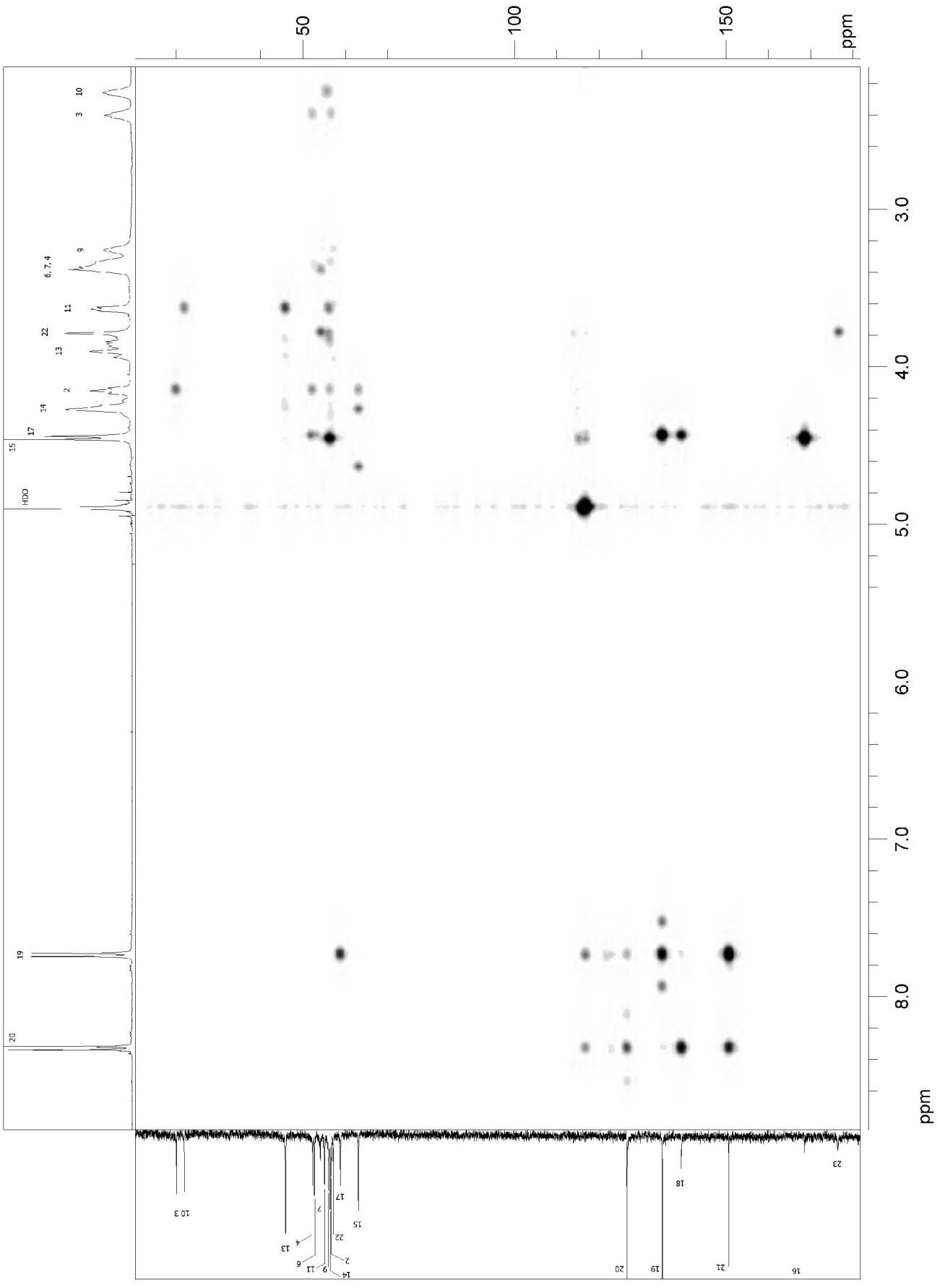
S11 - ^{1}H-^{13}C gHSQC spectra of **4** in D_2O



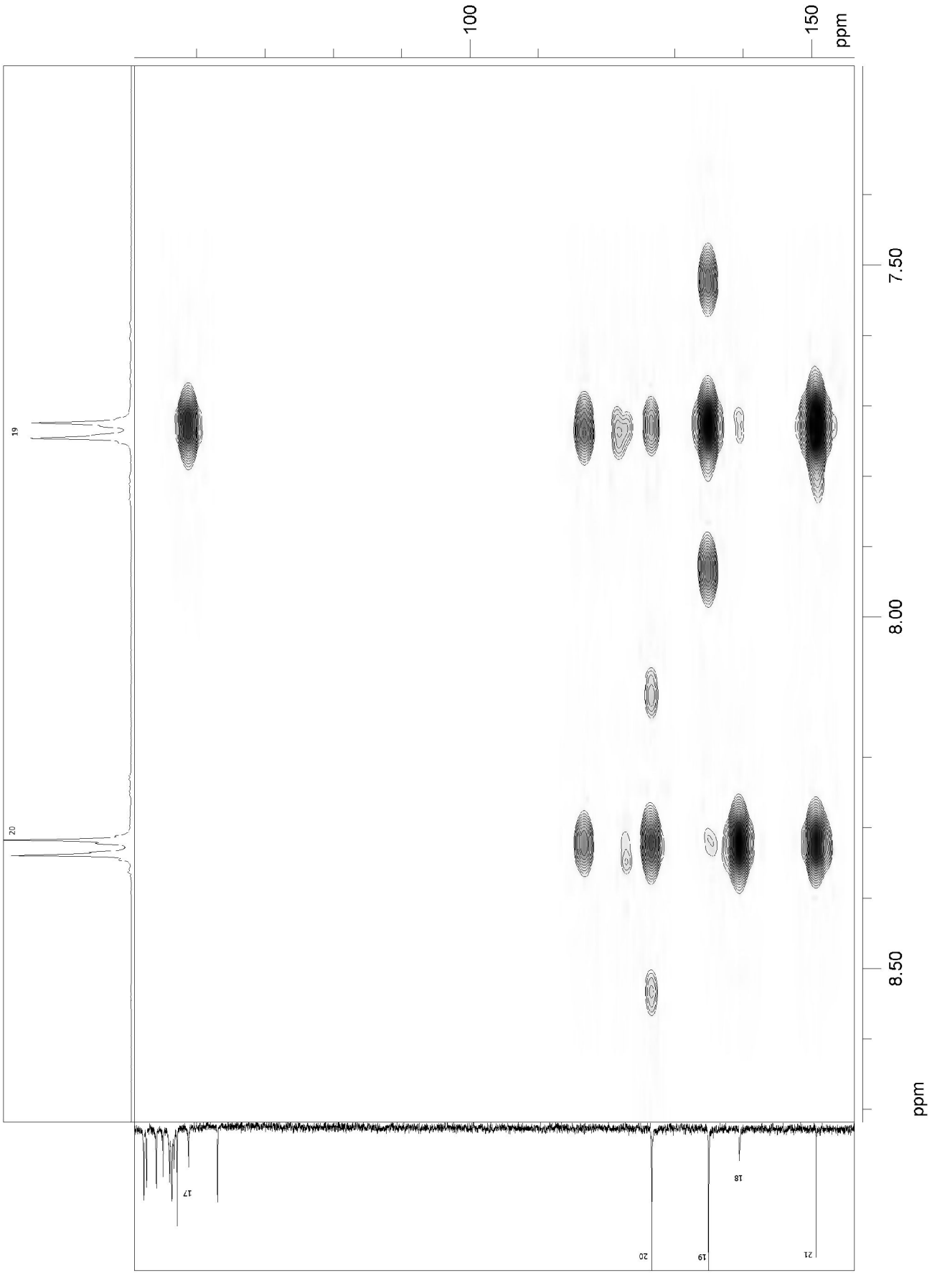
S12 – Detail of aliphatic region in ^{1}H-^{13}C gHSQC spectra of **4** in D_2O



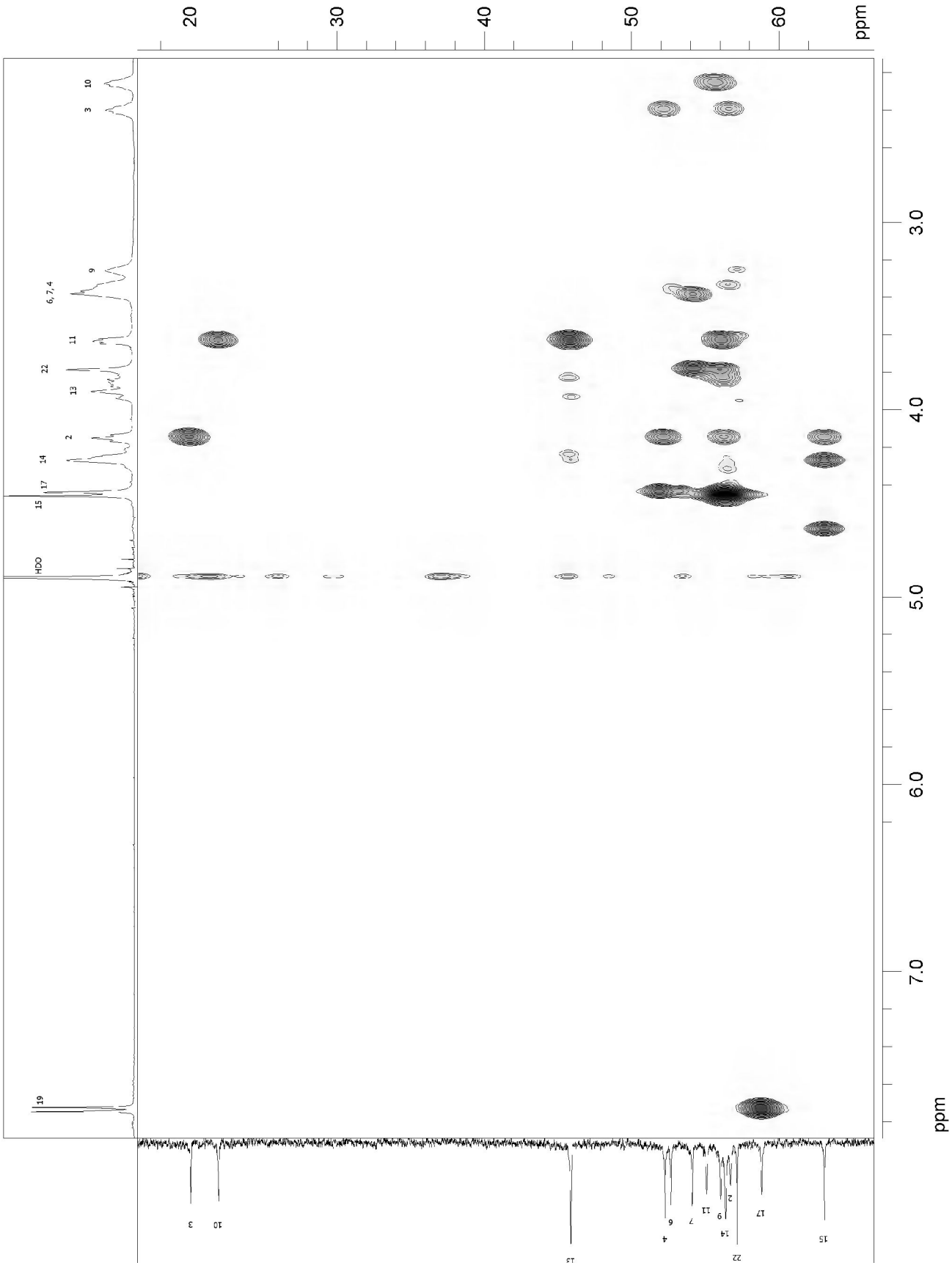
S13 – gHMBC spectra of **4** in D_2O



S14 – Detail of aromatic region in gHMBC spectra of **4** in D_2O



S15 – Detail of aliphatic region in gHMBC spectra of **4** in D_2O

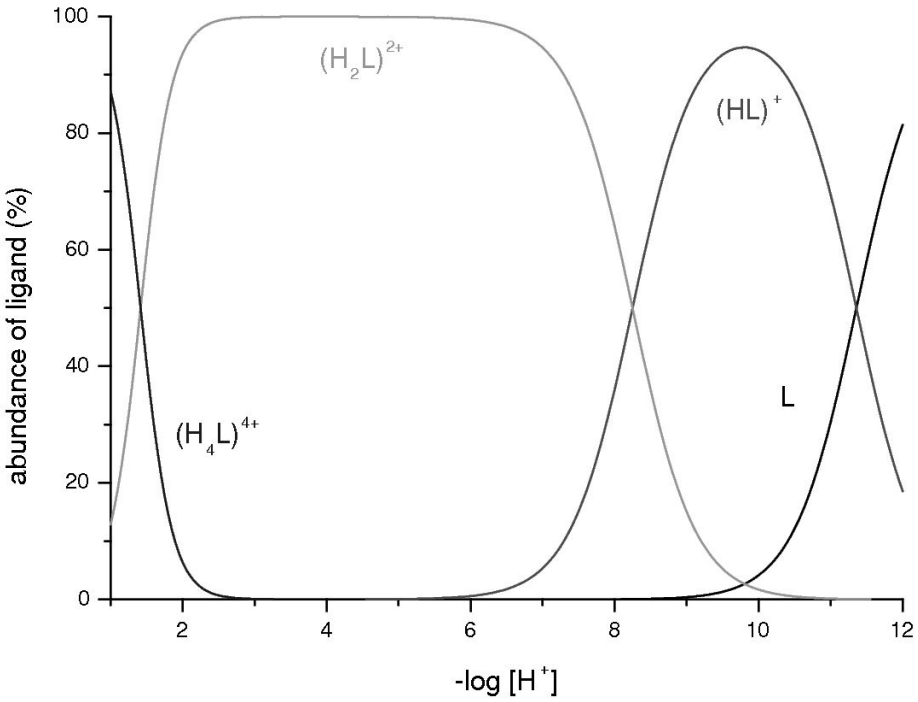


S16 X-ray crystal data collection and refinement details for [Cu(**3**)Br]PF_6 and $\mathbf{4}^{Br}\cdot 2.5H_2O$

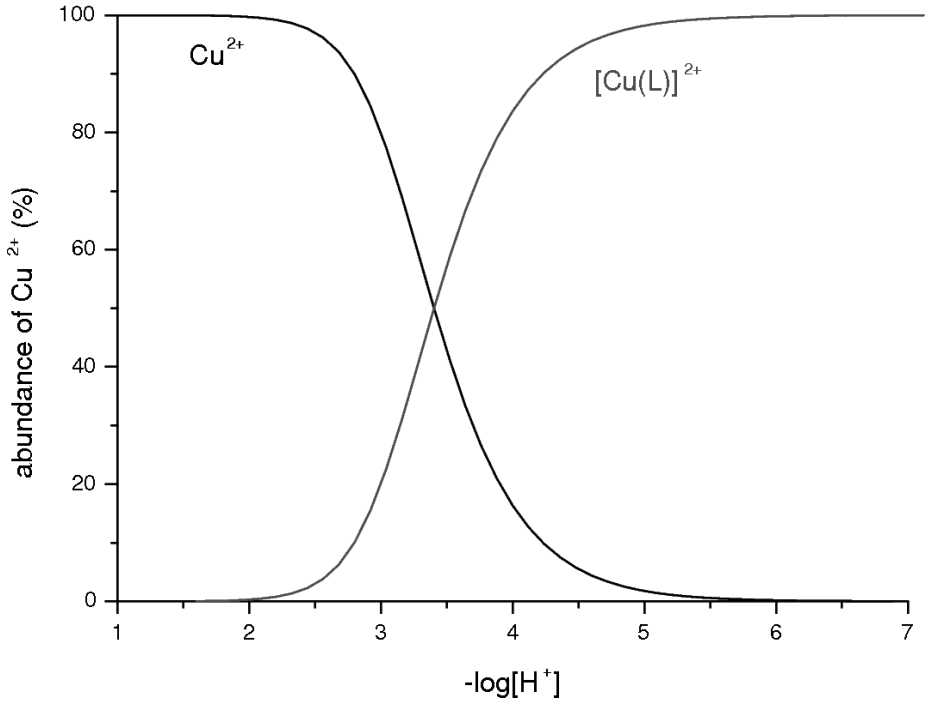
	[Cu(**3**)Br][PF_6]	$\mathbf{4}^{Br}\cdot 2.5H_2O$
Empirical formula	$C_{19}H_{31}CuN_5O_2BrF_6P$	$C_{21}H_{39}N_5O_{6.5}Br$
fw	649.91	545.48
Crystal shape	plate	prism
Color	blue	colourless
Crystal system	triclinic	monoclinic
Space group	$P\bar{1}$ (No. 2)	*C*2/c (No. 15)
a (Å)	6.9960(4)	19.4788(4)
b (Å)	10.2570(8)	19.7272(4)
c (Å)	17.8780(15)	13.7214(3)
α (deg)	73.592(3)	90
β (deg)	84.539(5)	97.7160(11)
γ (deg)	80.636(4)	90
V (Å^3)	1212.60(16)	5224.88(19)
Z	2	8
ρ_{calc} (g·cm^{-3})	1.780	1.387
T (K)	150(1)	150(1)
μ (mm^{-1})	2.688	1.619
F (000)	658	2296
θ range of data collection (deg)	2.09–27.47	3.44–27.50
Index ranges, *hkl*	–8 to 7, –13 to 13, –23 to 23	–25 to 25, –25 to 25, –17 to 17
Reflections measured	5090	5978
Reflections observed [$I > 2\sigma(I)$]	3452	4839
Data, restraints, parameters	5090, 0, 327	5978, 0, 311
Goodness-of-fit on F^2	1.993	1.045
Wavelength (Å)	0.71073	0.71073
R, *R'* [$I > 2\sigma(I)$]†	0.2134, 0.1759	0.0736, 0.0590
wR, *wR'* [$I \geq 2\sigma(I)$]†	0.5043, 0.4889	0.1828, 0.1680
Maximum shift/esd	0.004	0.000
$\Delta\rho_{max,\ min}$ (e·Å^{-3})	2.415, –2.128	0.907, –0.935

$w = 1/[\sigma^2(F_o^2) + (AP)^2 + BP]$, $P = (F_o^2 + 2F_c^2)/3$; R, $R' = \Sigma|F_o - F_c|/\Sigma|F_c|$, wR, $wR' = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$

S17 Distribution of species in solutions† of **3**

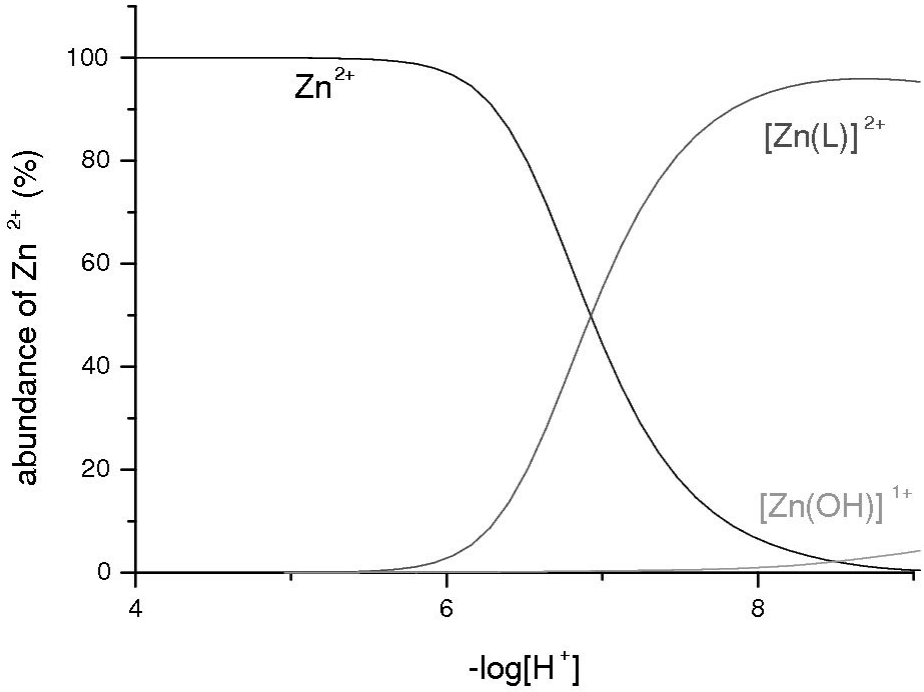


S18 Distribution of species in system Cu^{II} / **3**†

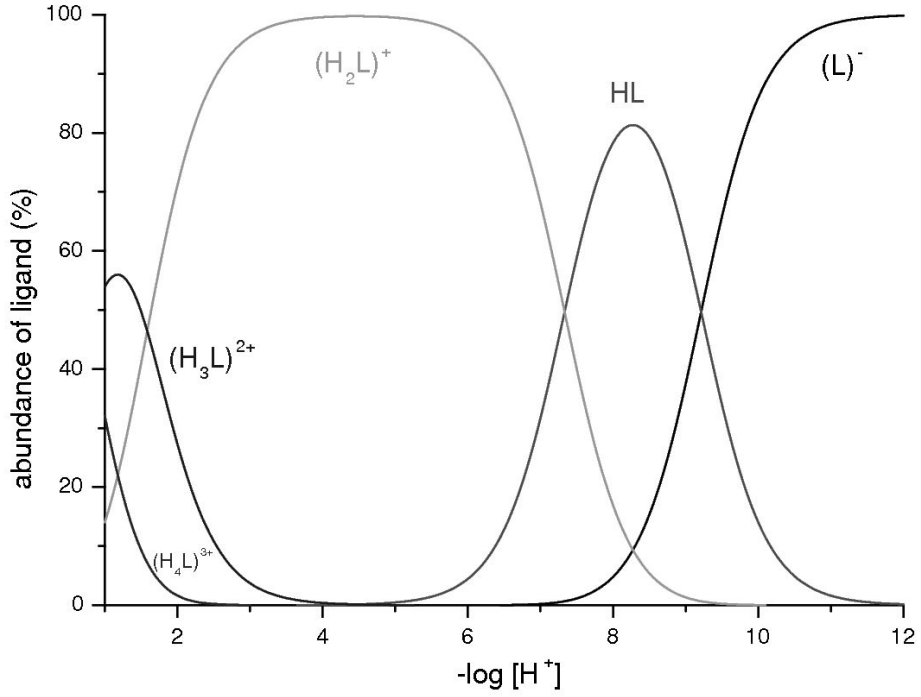


† 0.1 M aq. KNO_3, 25 °C

S19 Distribution of species in system Zn^{II} / **3**†

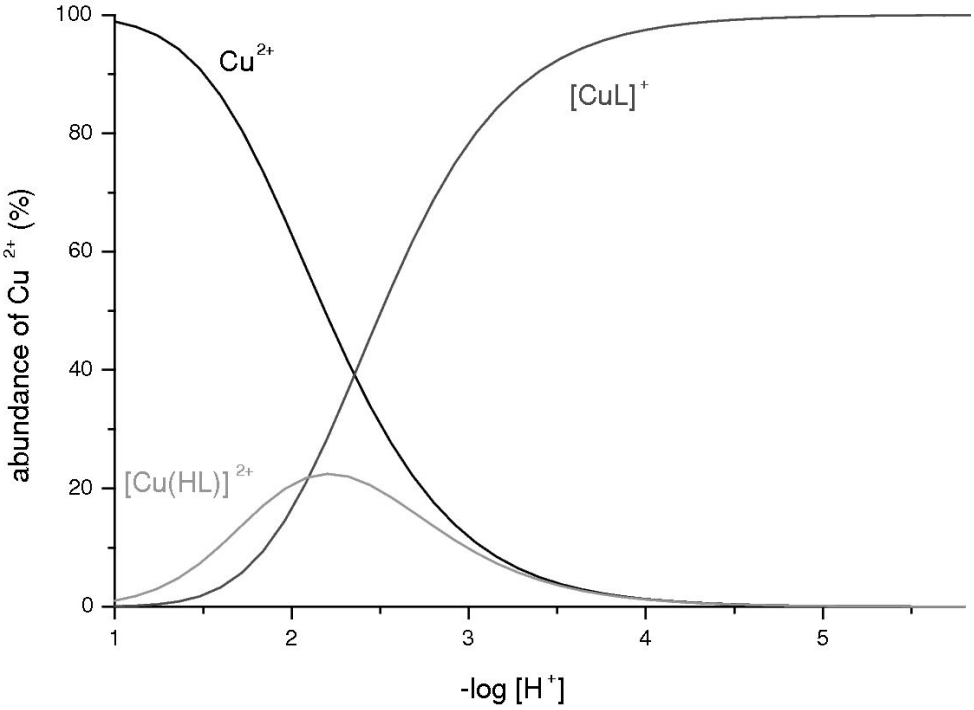


S20 Distribution of species in solutions† of **6**

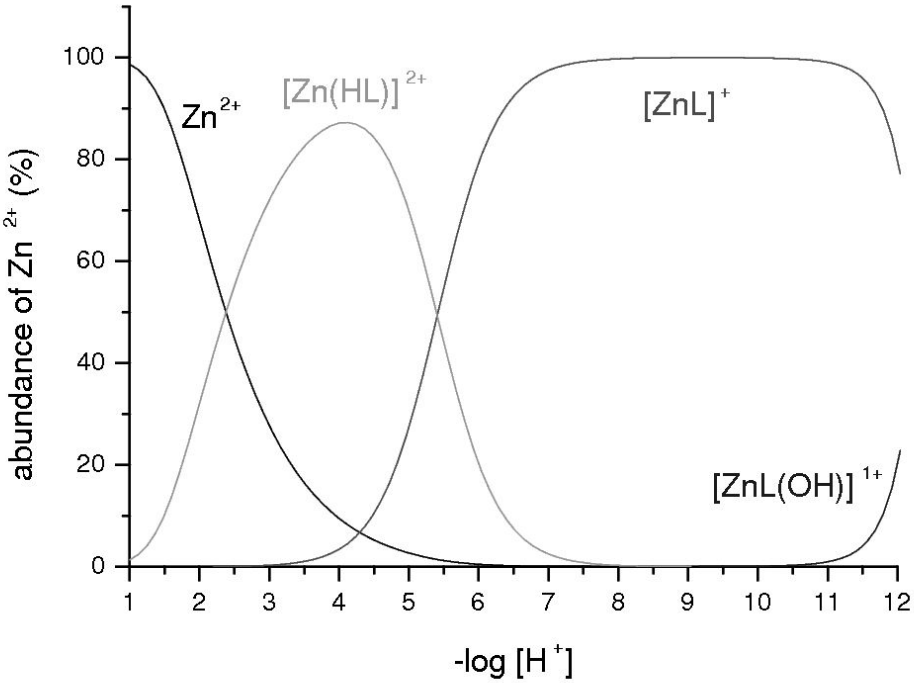


† 0.1 M aq. KNO_3, 25 °C

S21 Distribution of species in system Cu^{II} / **6**†



S22 Distribution of species in system Zn^{II} / **6**†



† 0.1 M aq. KNO_3, 25 °C