Supporting Information

Facile Access to Imidazole and Imidazolium Substituted Dibenzo-Diazocines

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Figure S1: ^{1}H NMR spectrum (400 MHz, $CDCl_3$, RT) of 3

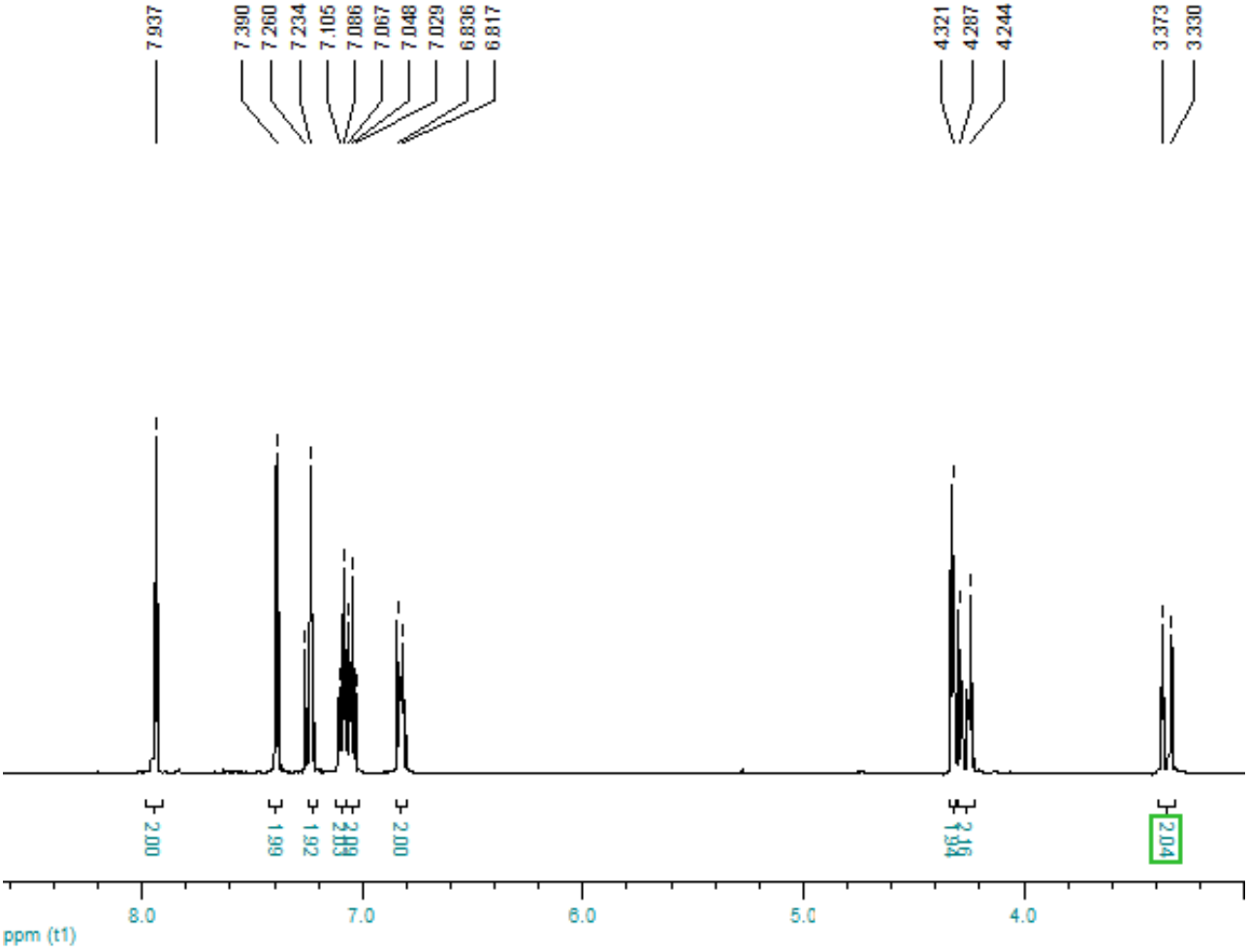


Figure S2: ^{13}C NMR spectrum (100 MHz, $CDCl_3$, RT) of 3

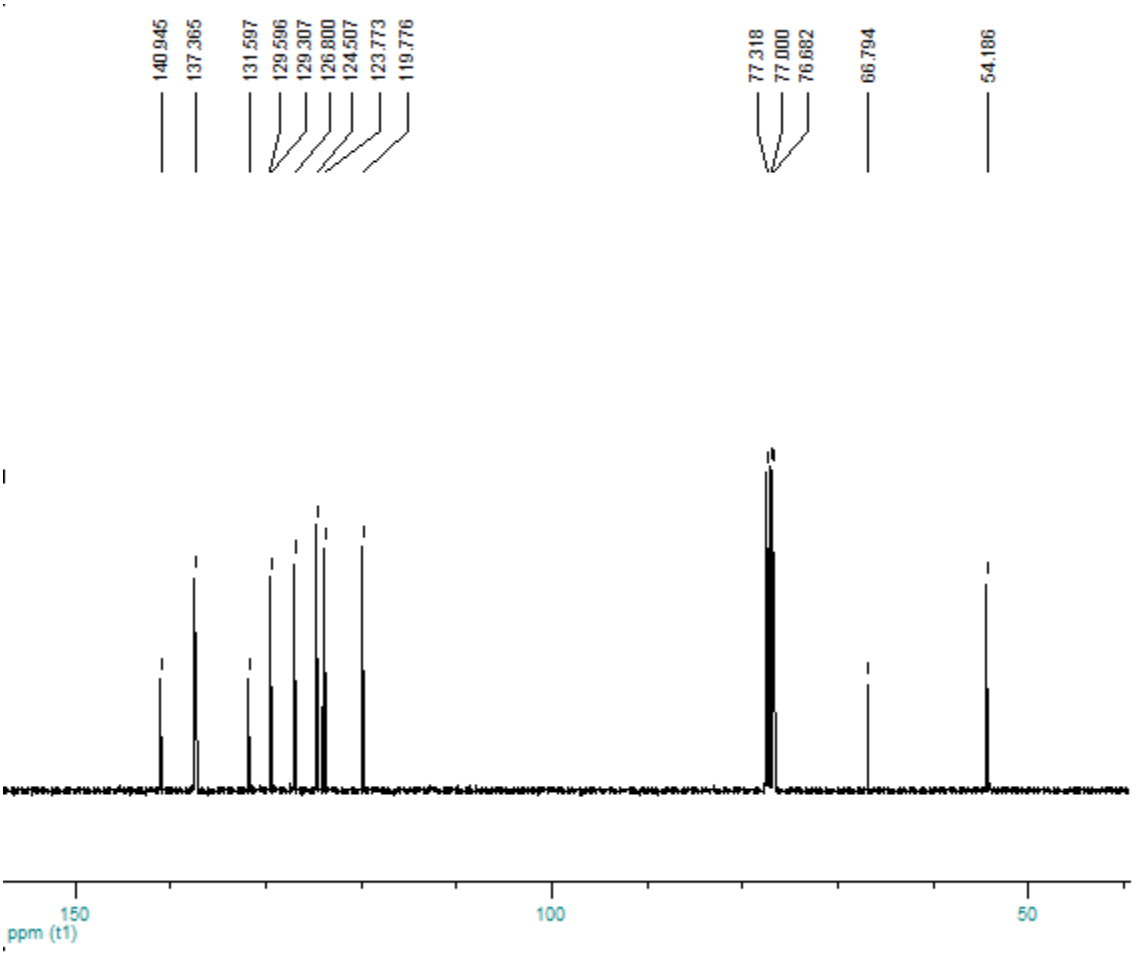


Figure S3: ^{1}H NMR spectrum (400 MHz, DMSO-d_6, RT) of 5

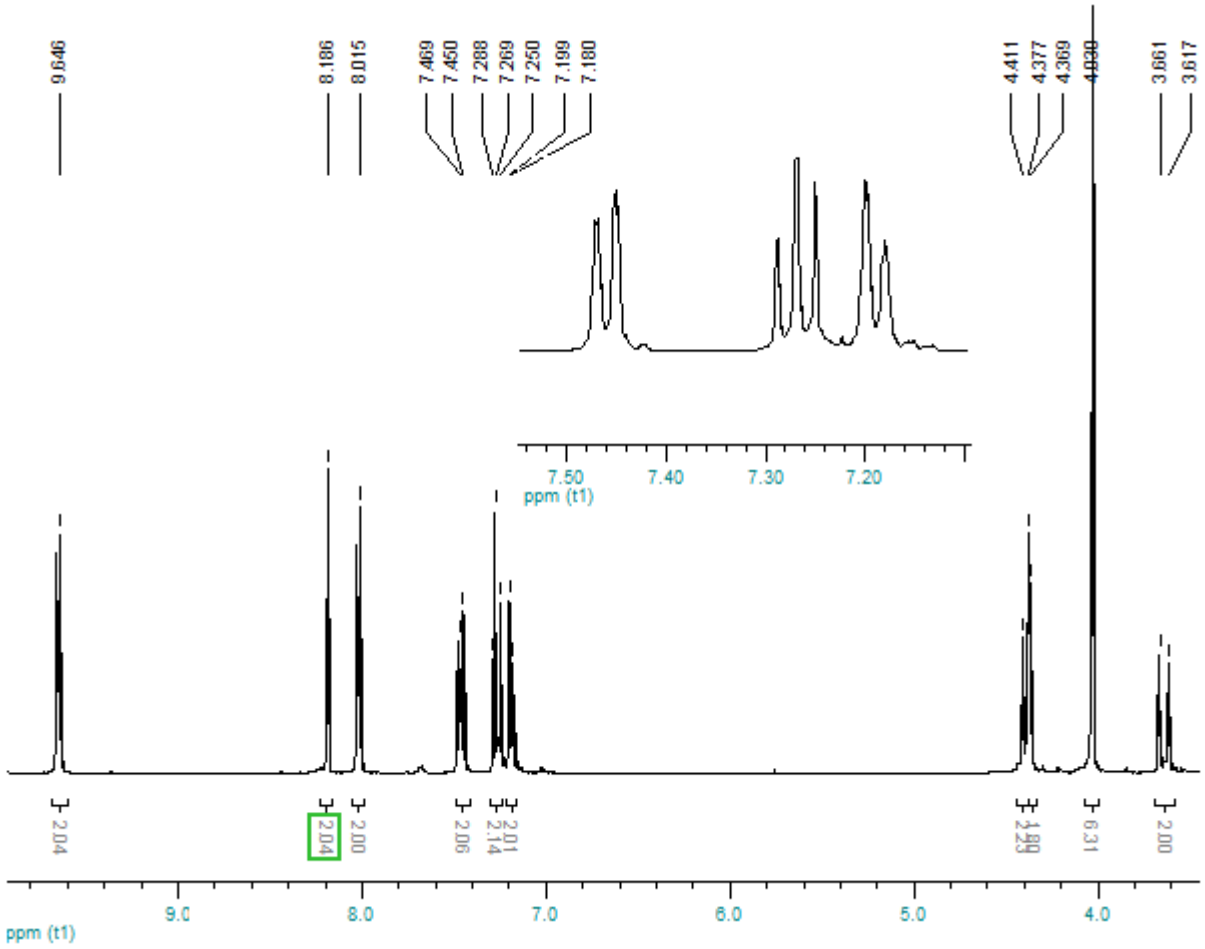


Figure S4: ^{13}C NMR spectrum (100 MHz, DMSO-d_6, RT) of 5

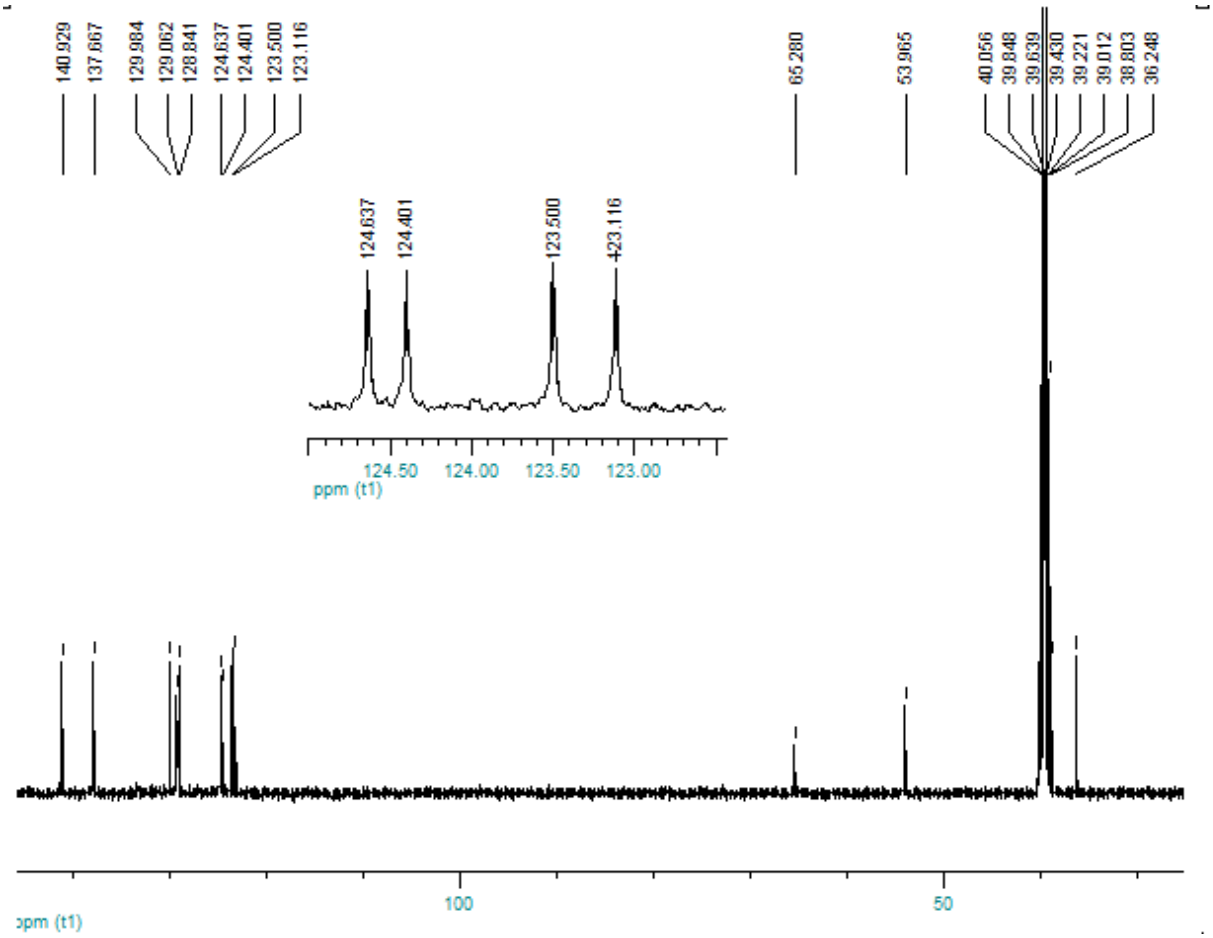


Figure S5: ^{1}H NMR spectrum (400 MHz, DMSO-d_6, RT) of 6

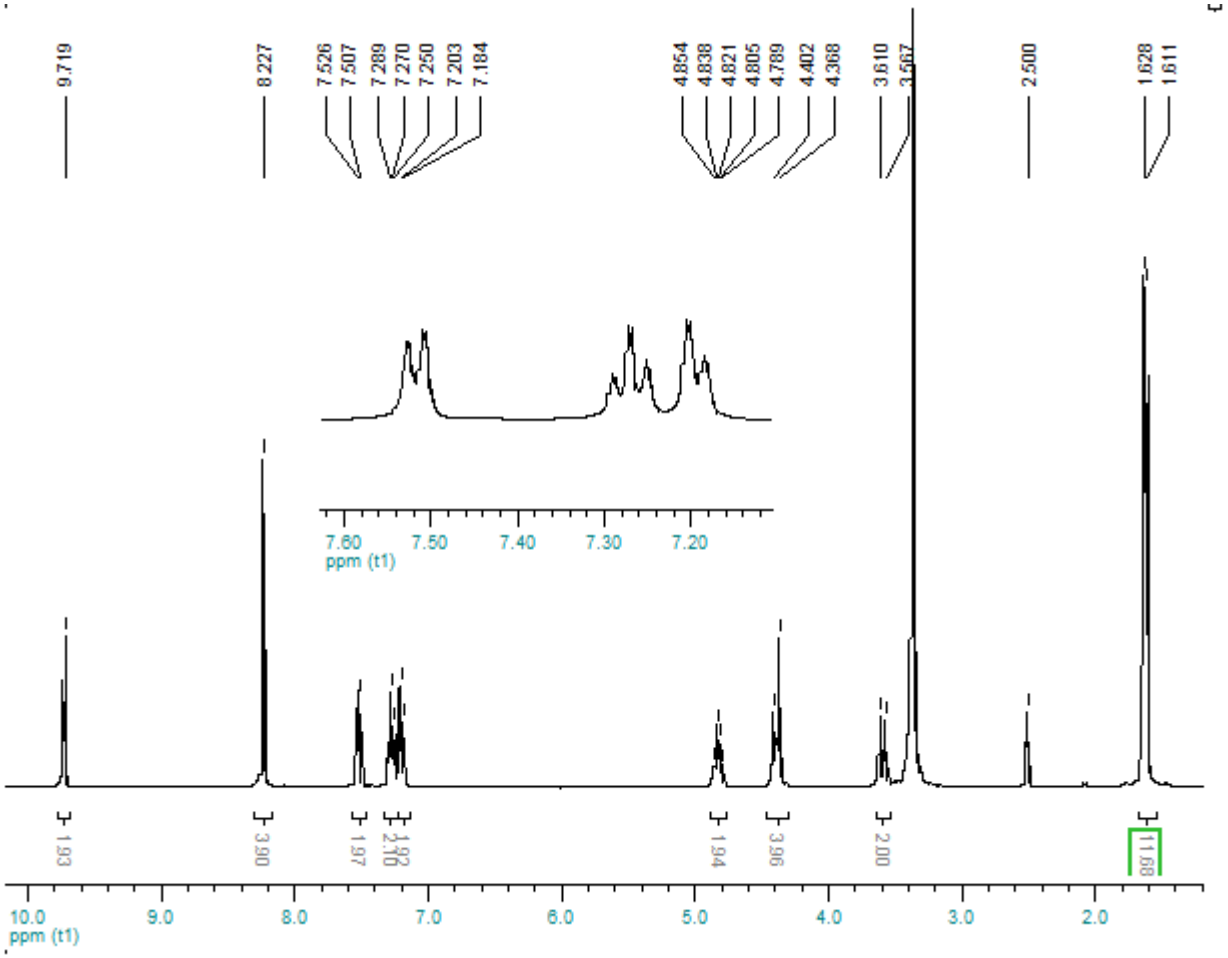


Figure S6:^{13}C NMR spectrum (100 MHz, DMSO-d_6, RT) of 6

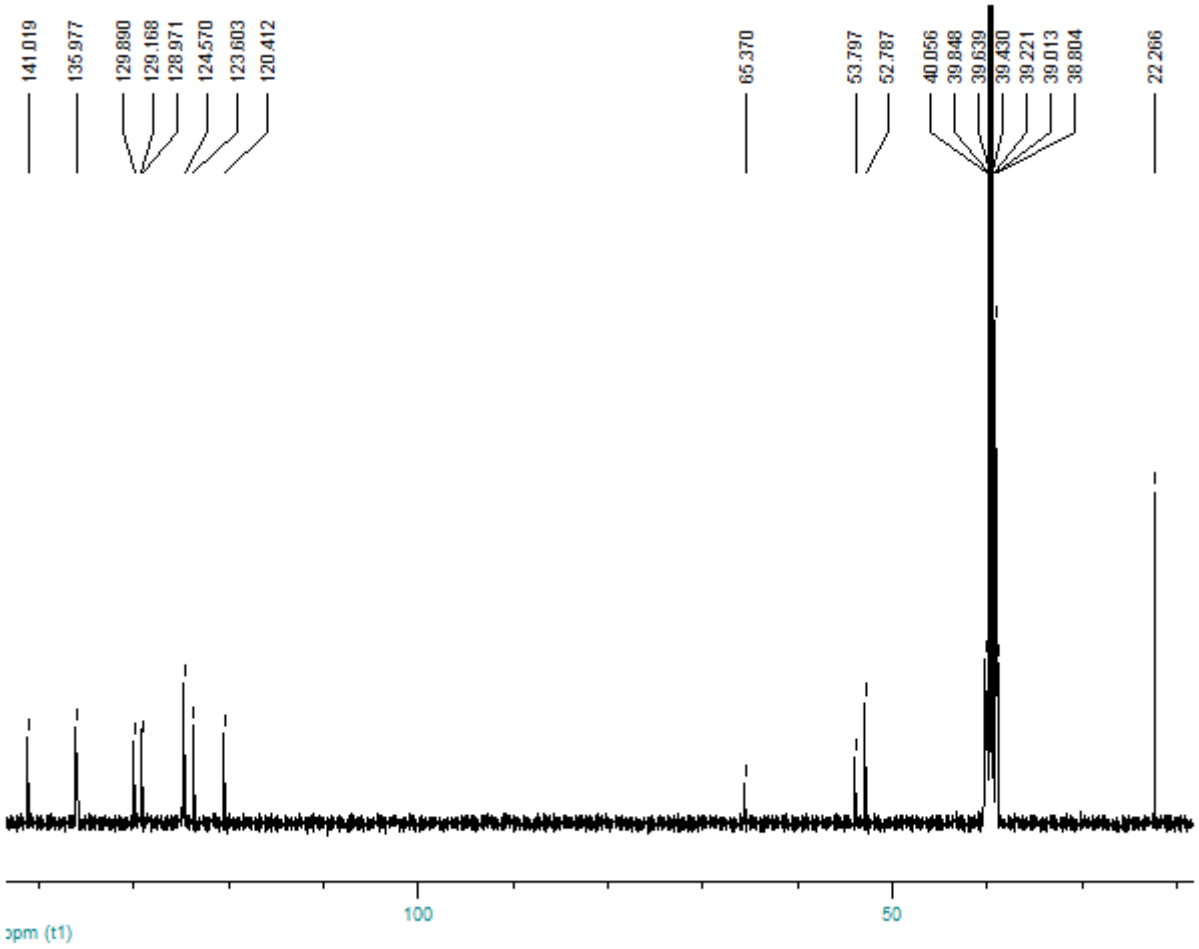


Figure S7:^{1}H NMR spectrum (400 MHz, DMSO-d_6, RT) of 7

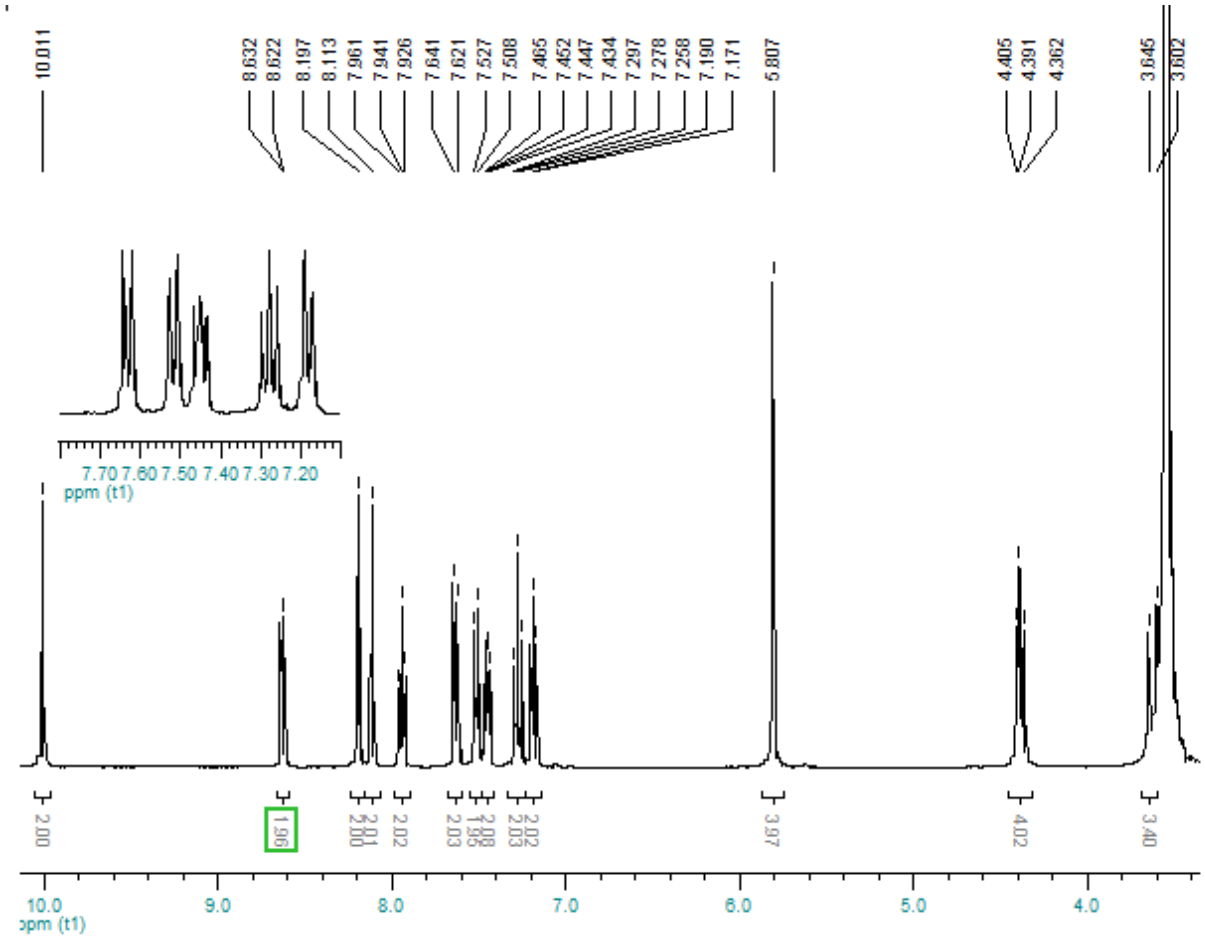


Figure S8: ^{13}**C NMR spectrum (100 MHz, DMSO-**d_6**, RT) of 7**

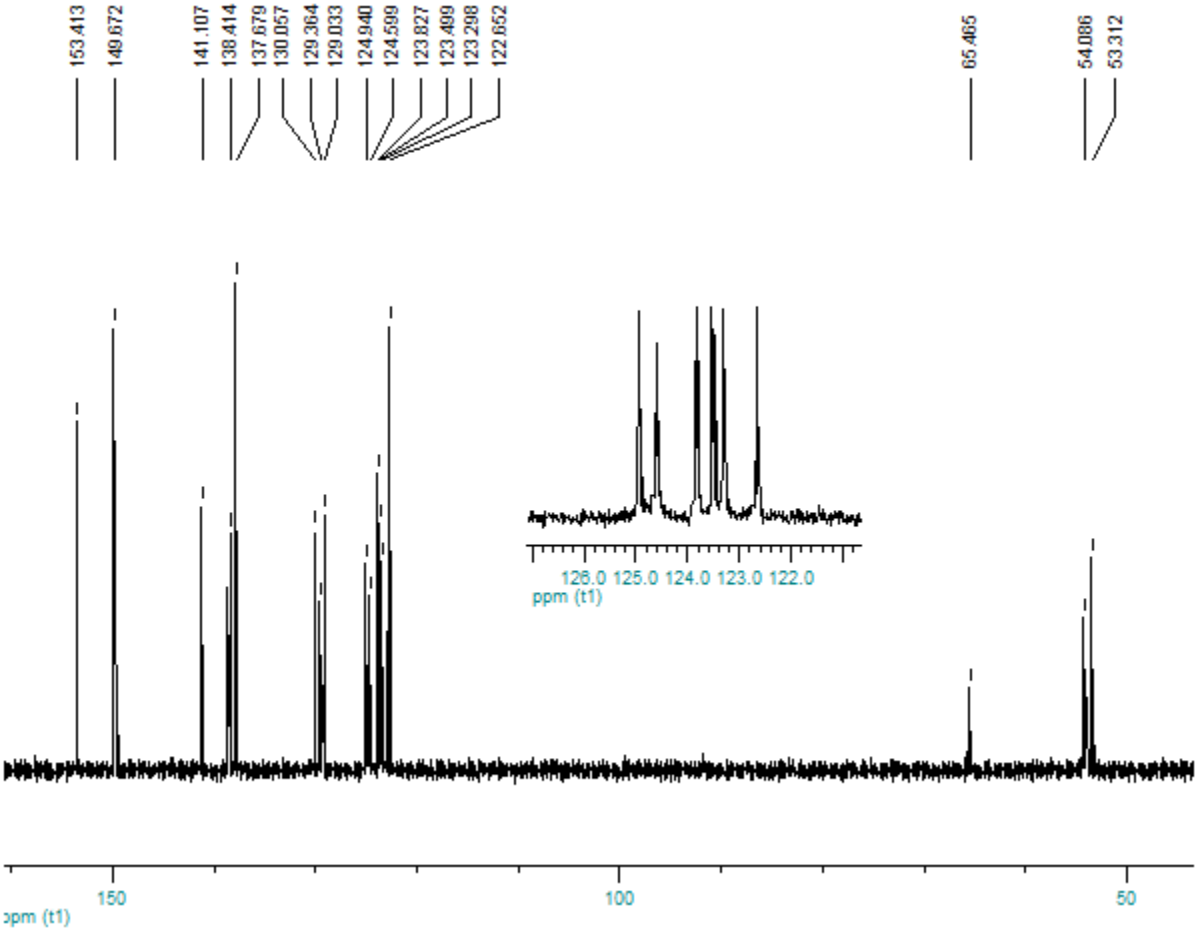


Figure S9:^{1}H NMR spectrum (400 MHz, DMSO-d_6, RT) of 8

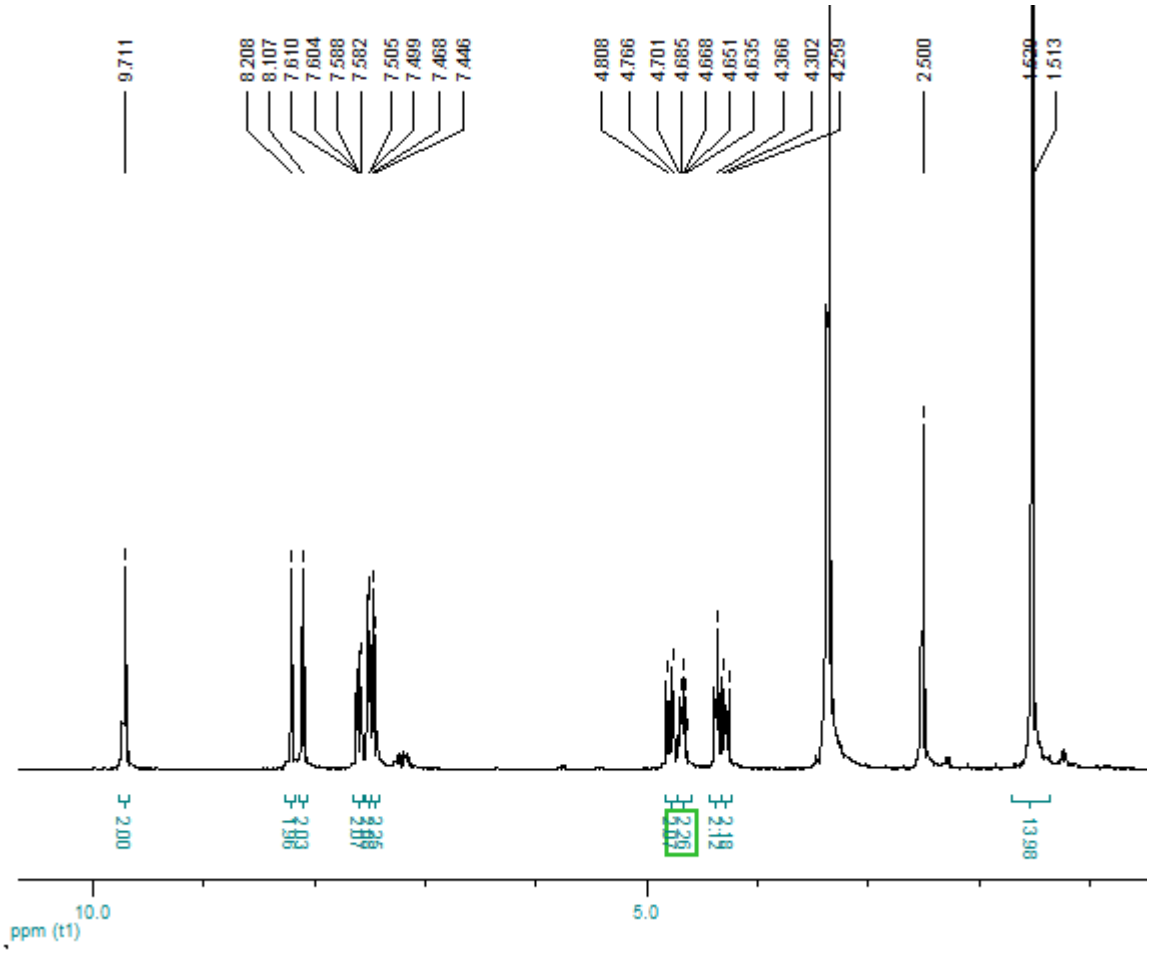


Figure S10:^{13}C NMR spectrum (100 MHz, DMSO-d_6, RT) of 8

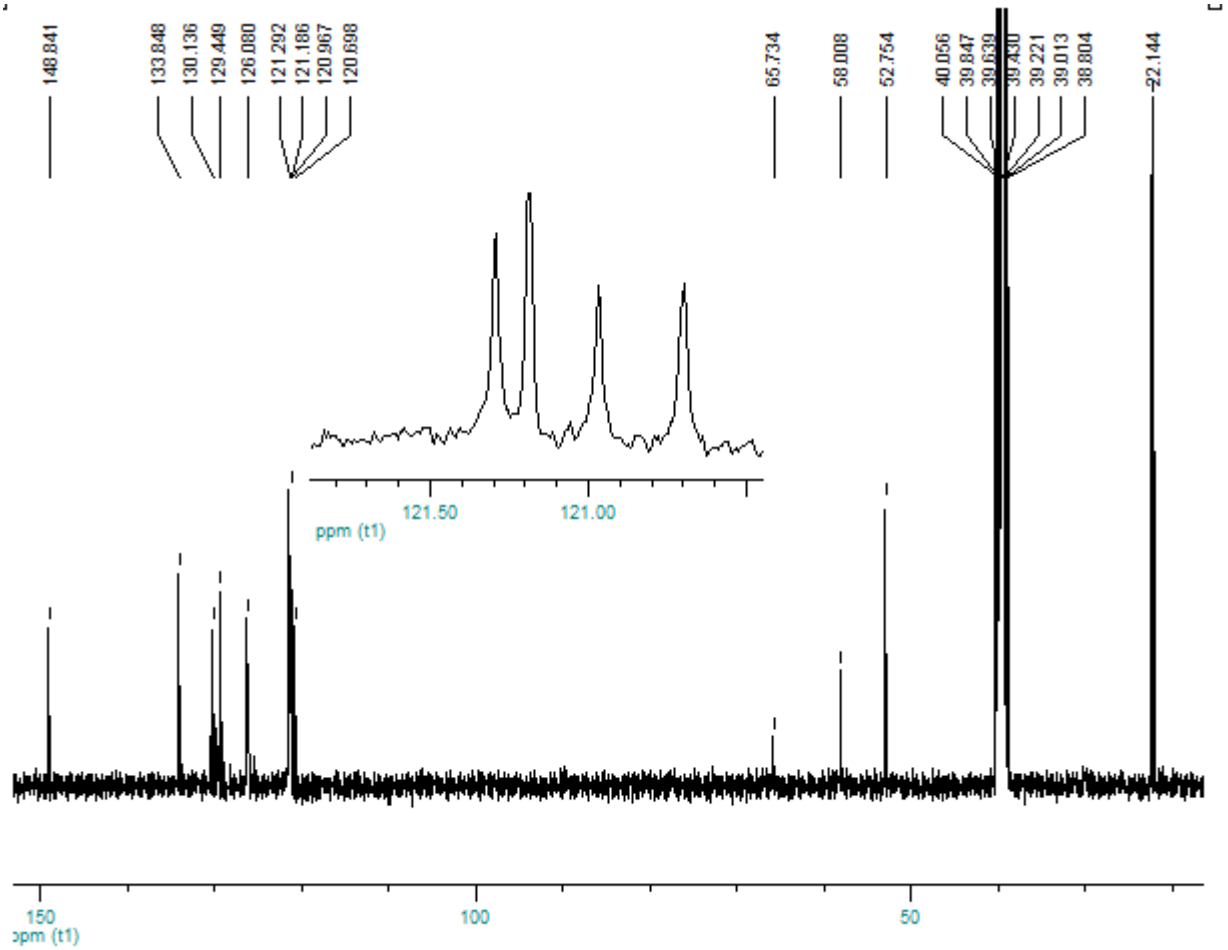


Figure S11:^{1}H NMR spectrum (400 MHz, DMSO-d_6, RT) of 9

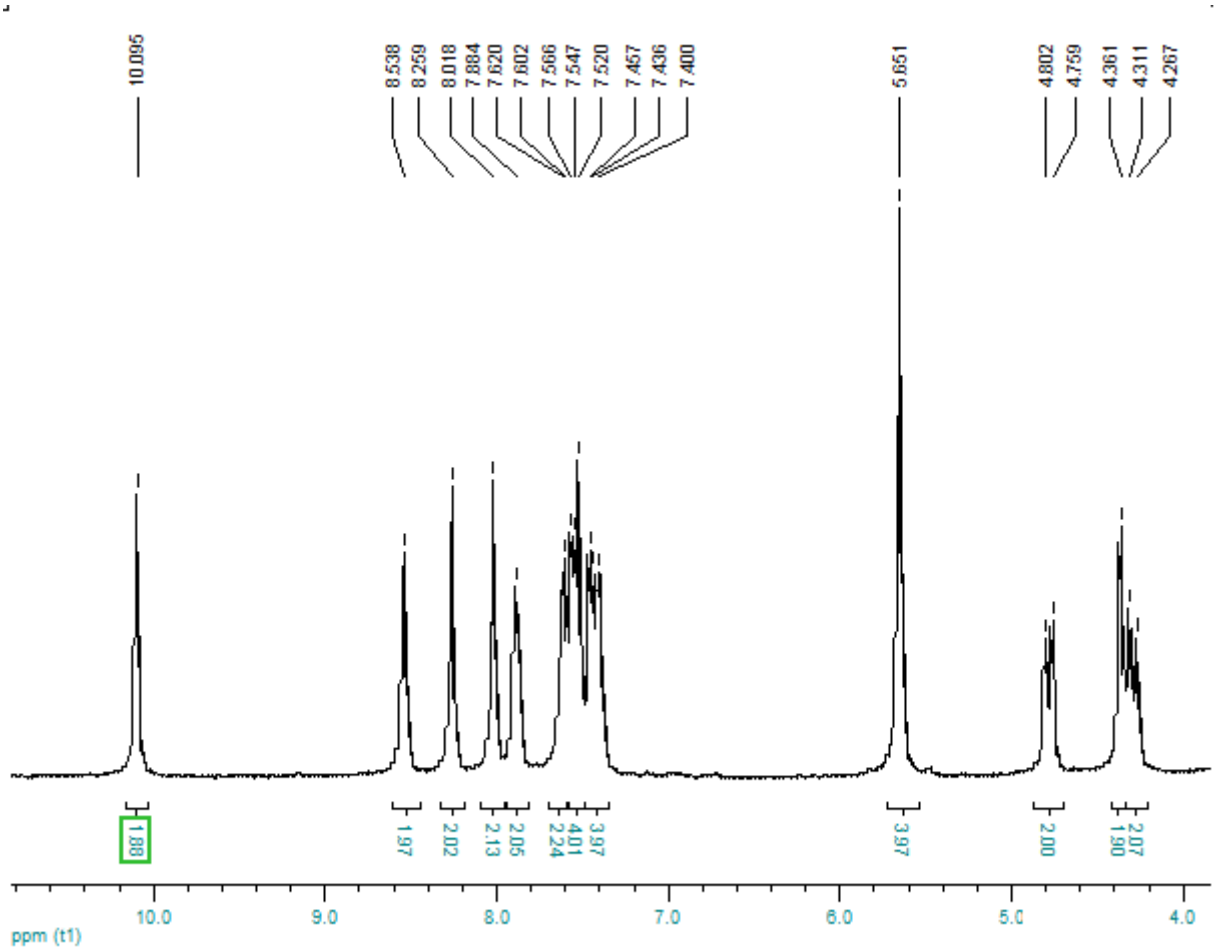
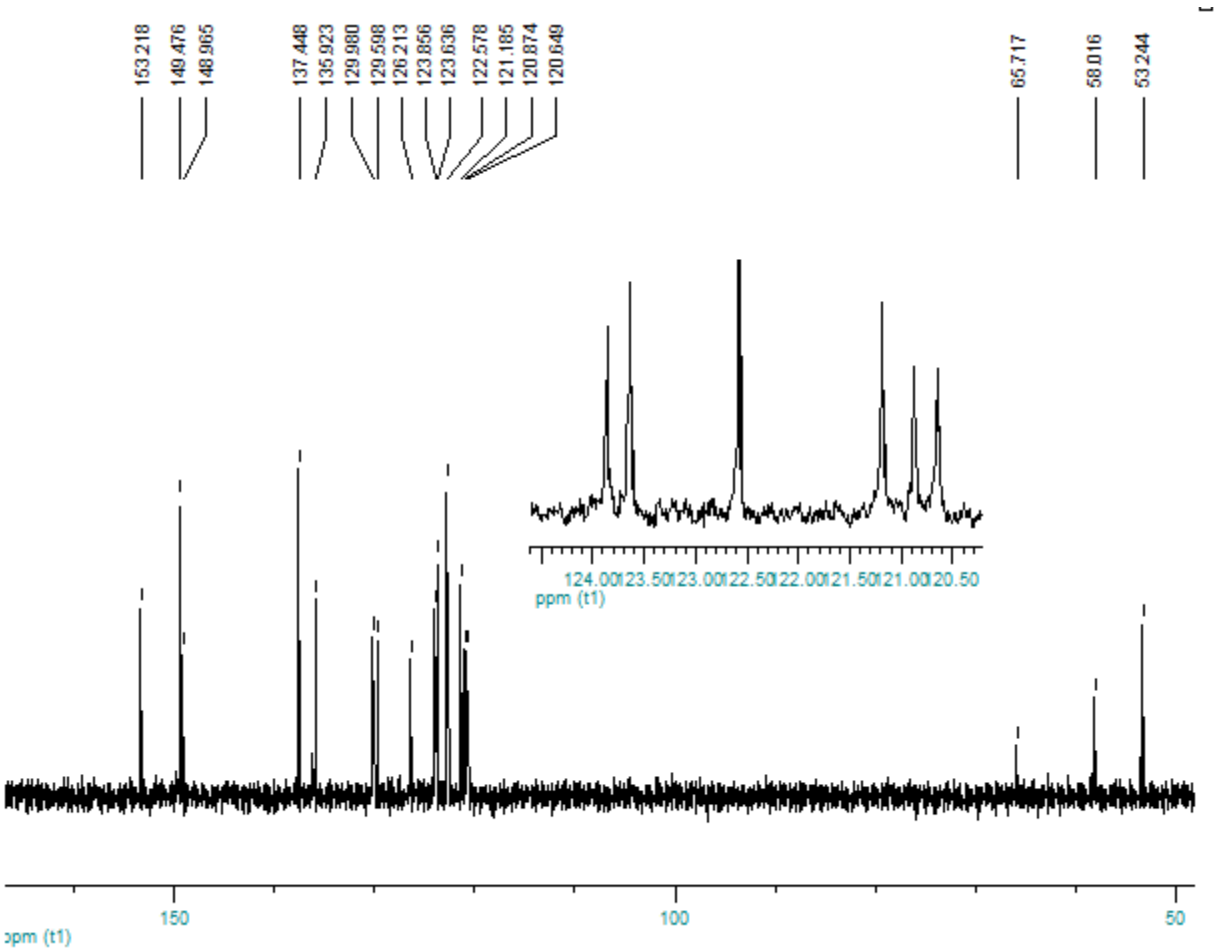
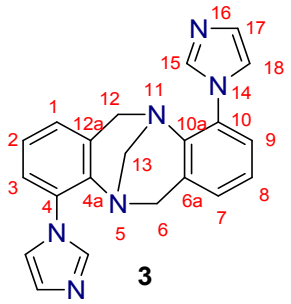


Figure S12:^{13}C NMR spectrum (100 MHz, DMSO-d_6, RT) of 9



2D NMR Spectrums

Figure S13: HSQC of 3 (400 MHz, $CDCl_3$, RT)



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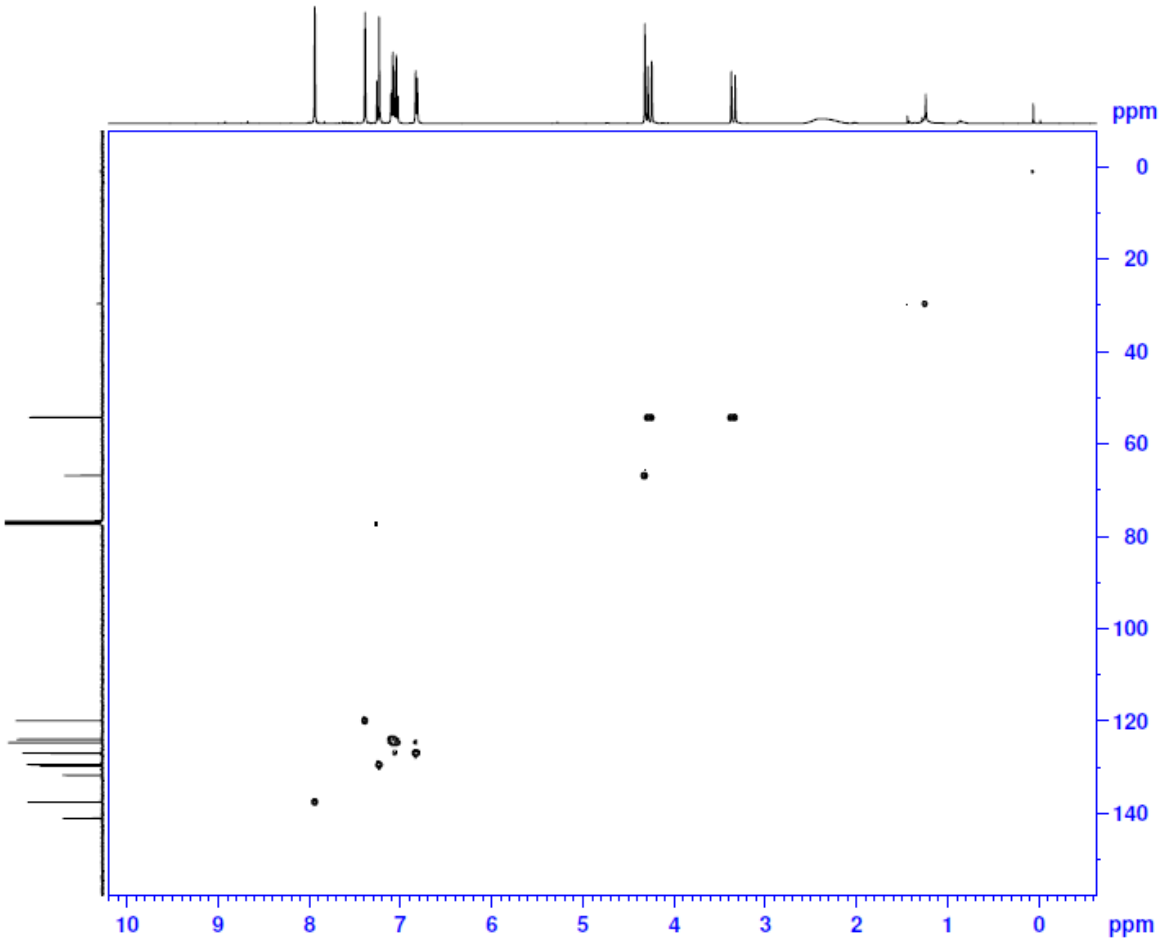


Figure S14: HSQC of 3 expansion

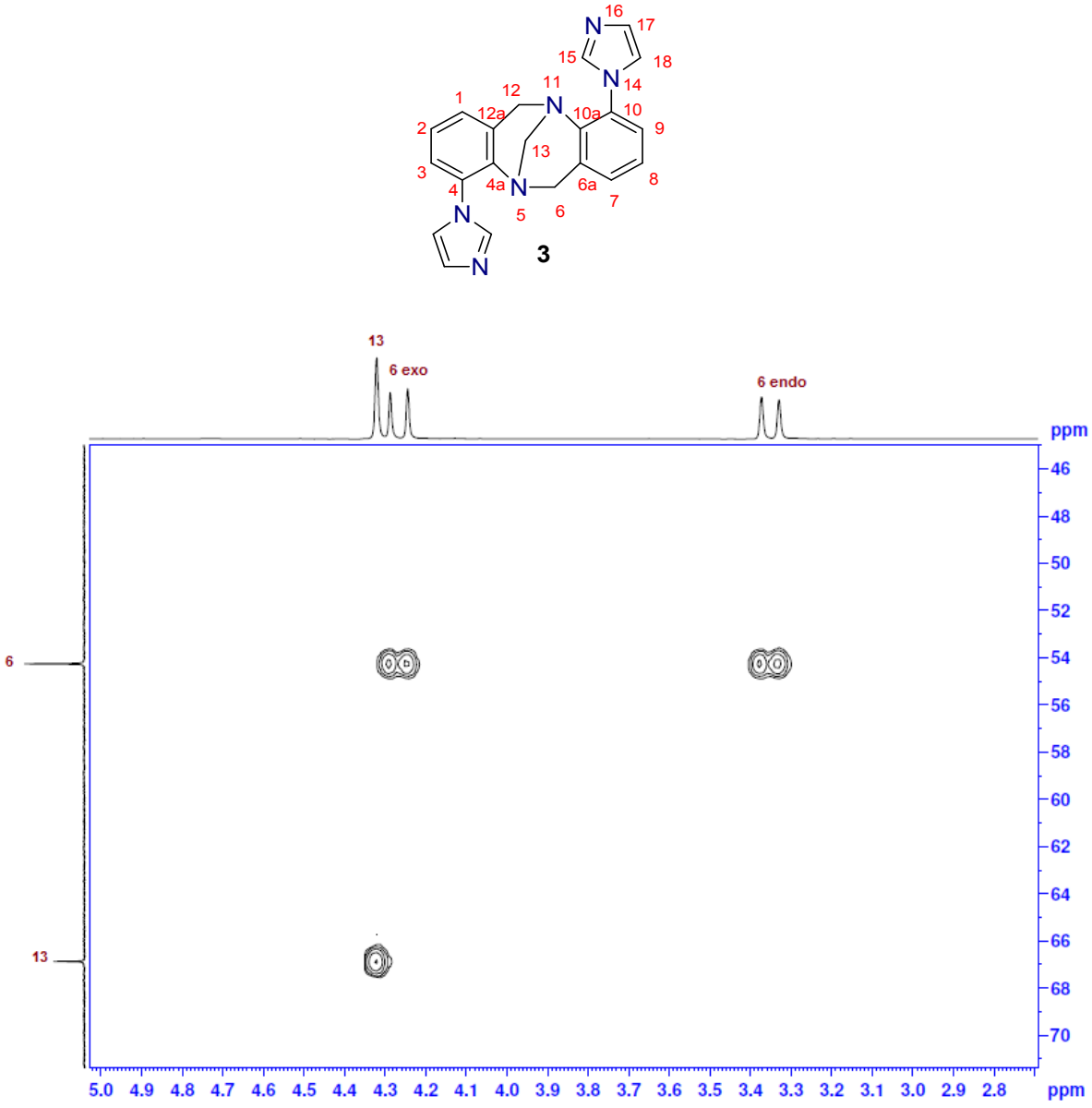
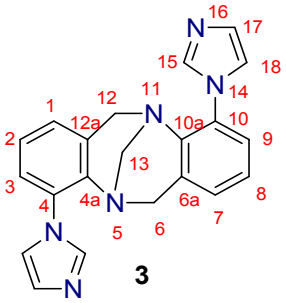


Figure S15: HSQC of 3 expansion



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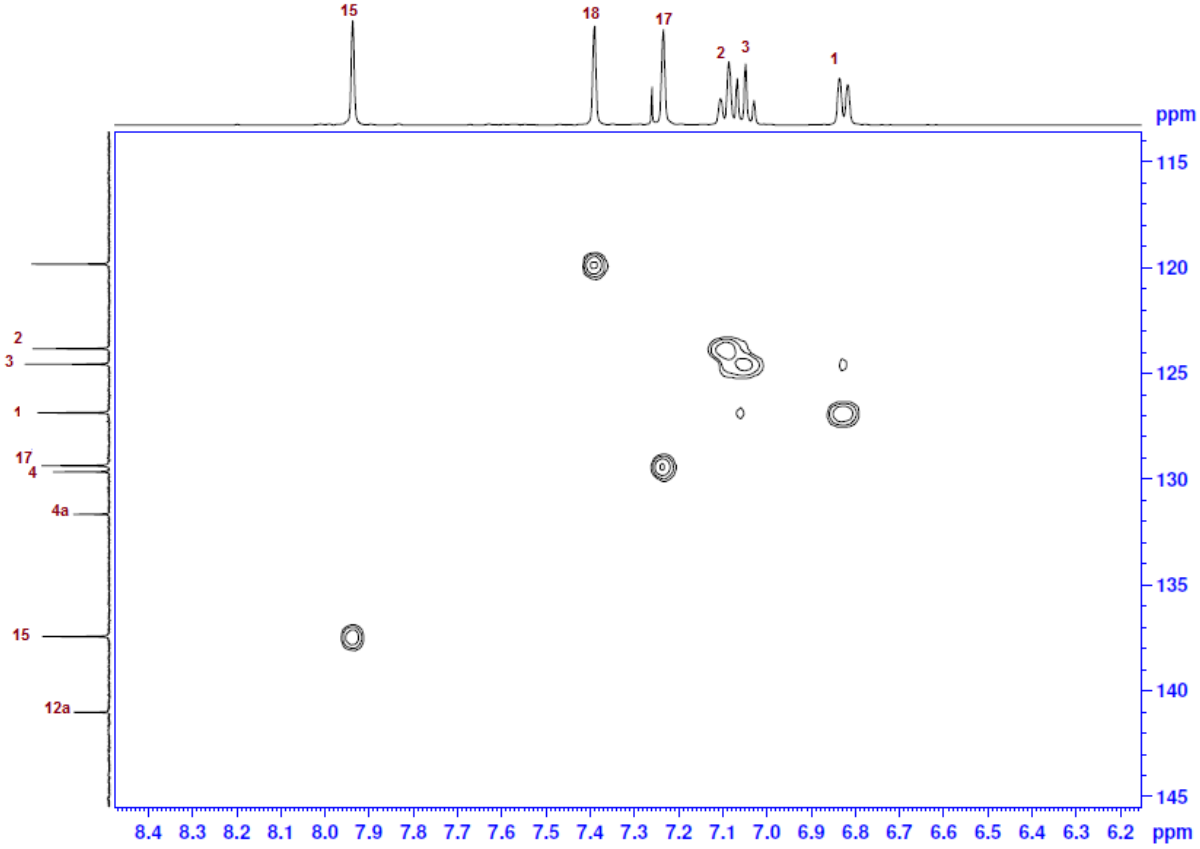


Figure S16: HMBC of 3 (400 MHz, $CDCl_3$, RT)

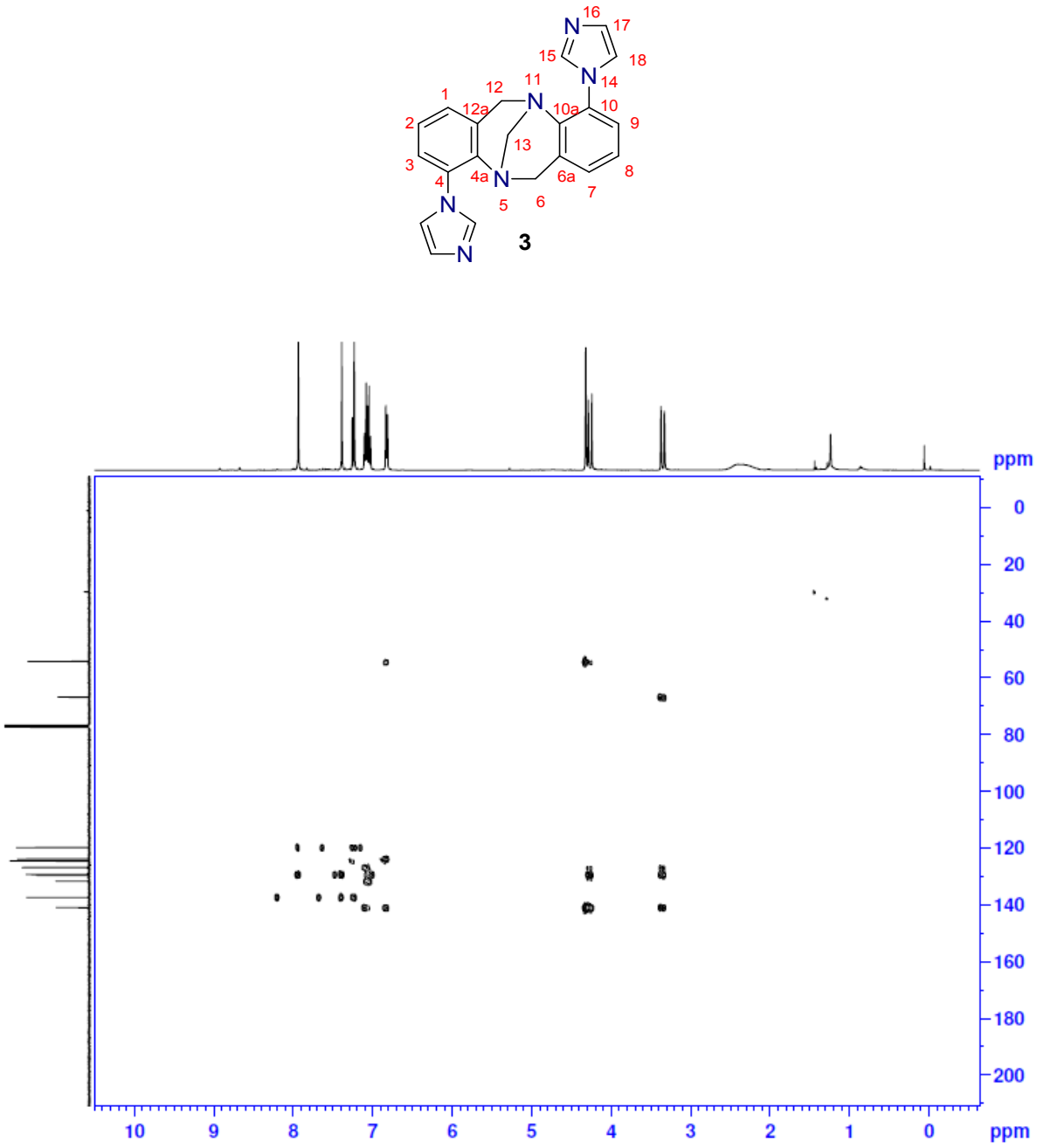
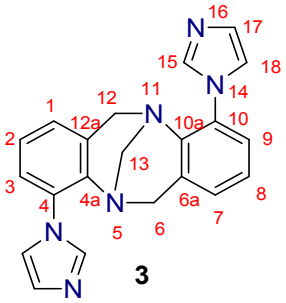


Figure S17: HMBC of 3 expansions



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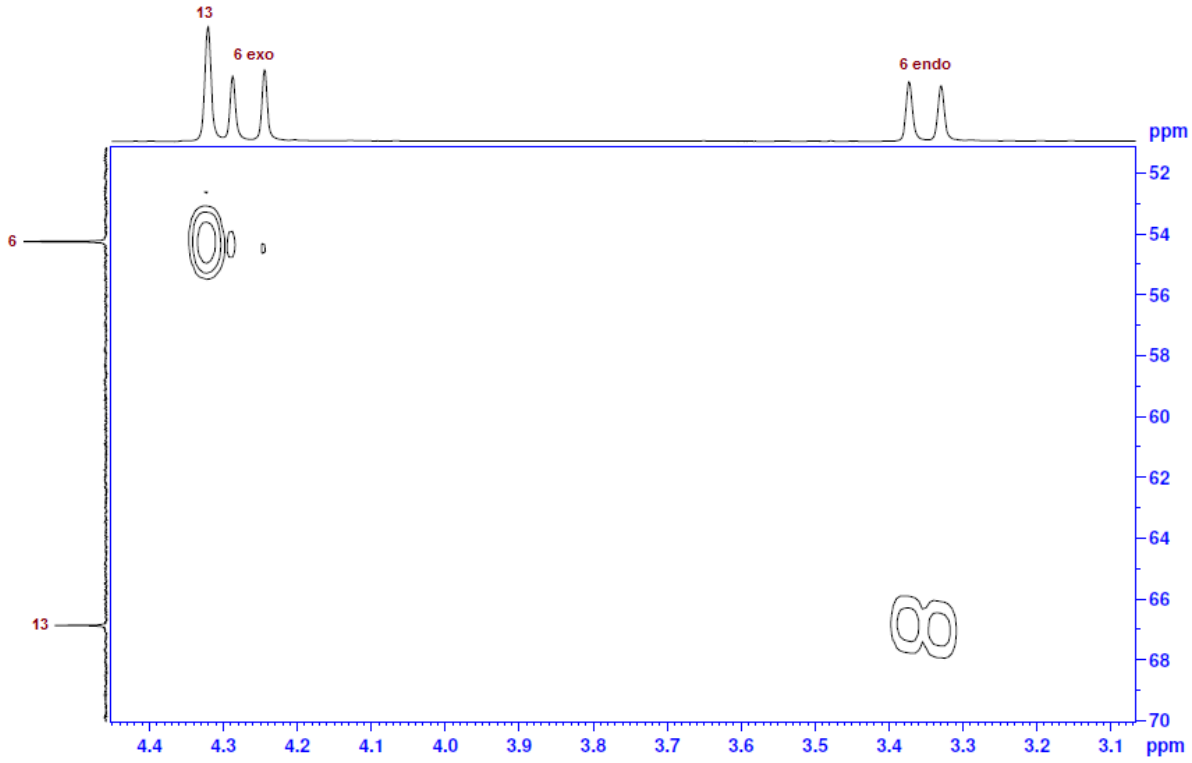


Figure S18: HMBC of 3 expansions

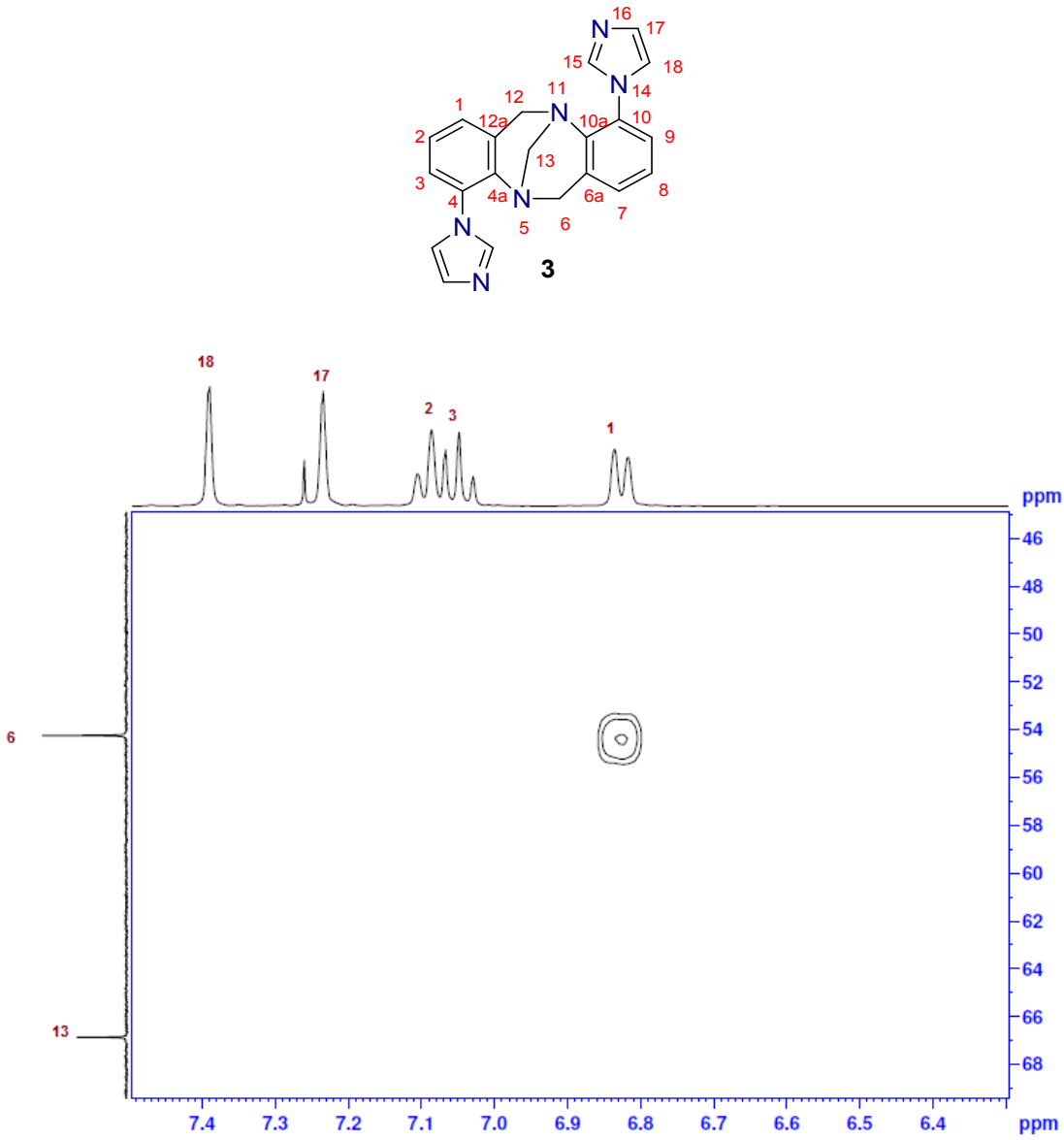
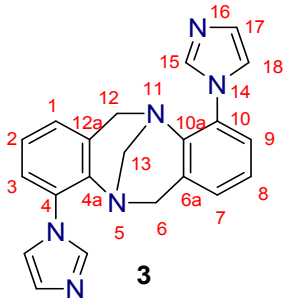


Figure S19: HMBC of 3 expansions



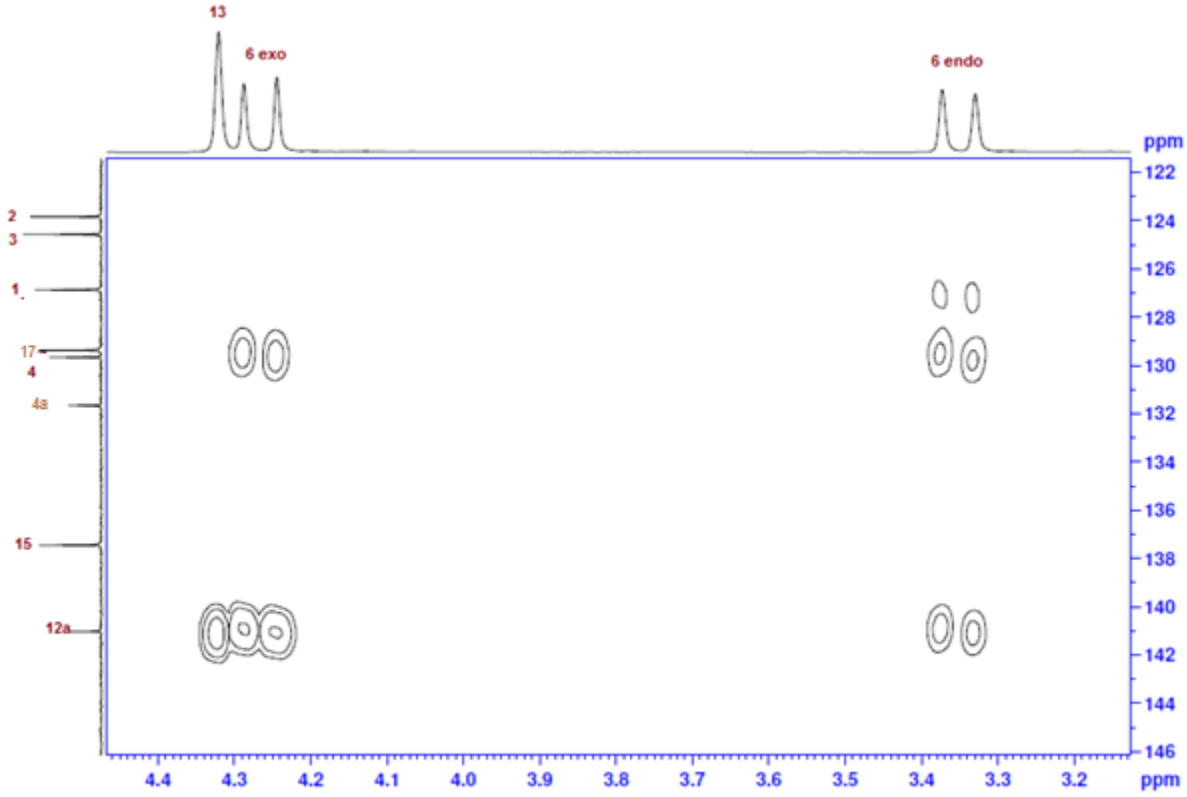


Figure S20: HMBC of 3 expansion

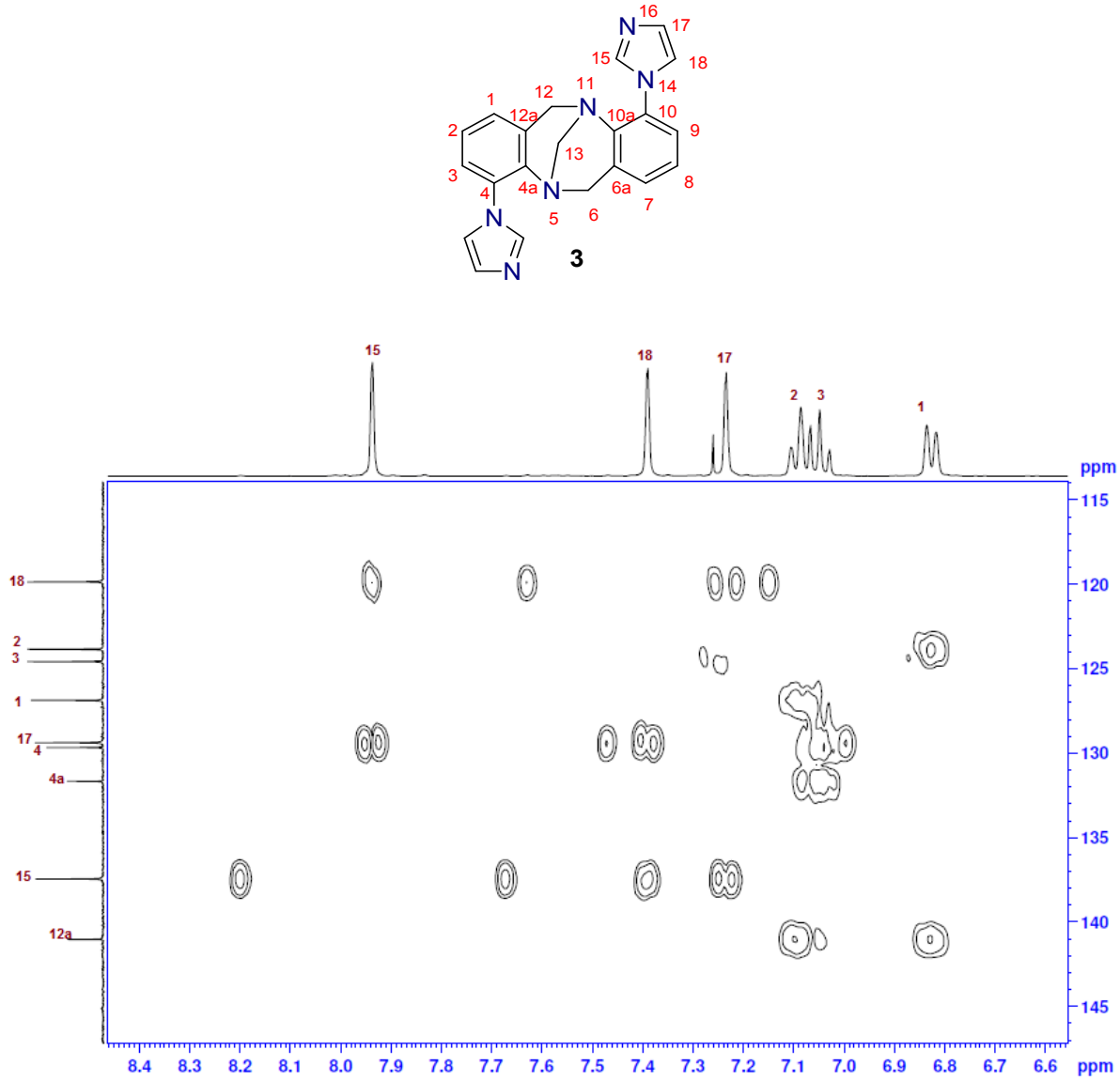


Figure S21: HSQC of 5 (400 MHz, DMSO-d_6, RT)

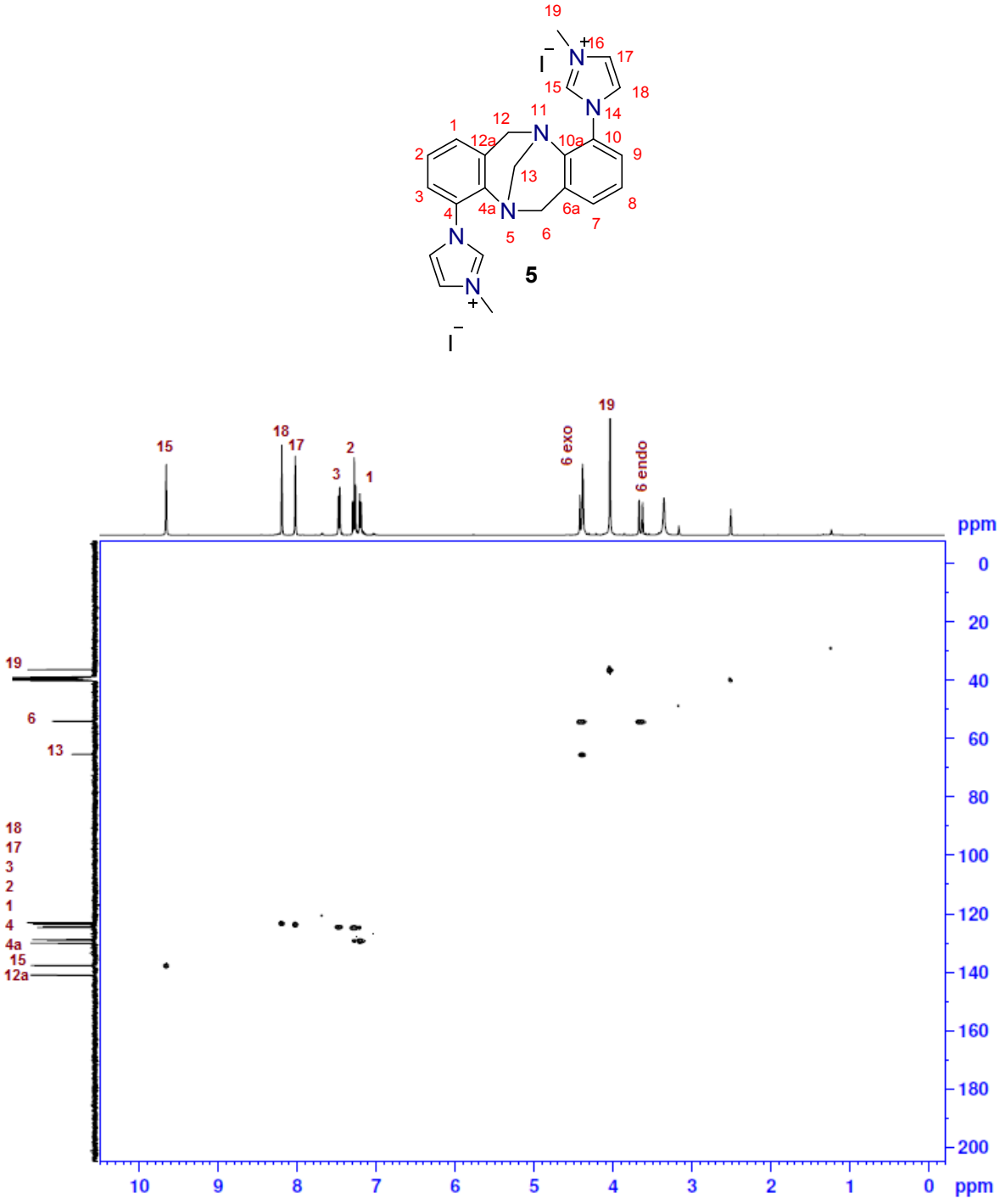


Figure S22: HSQC of 5 expansion

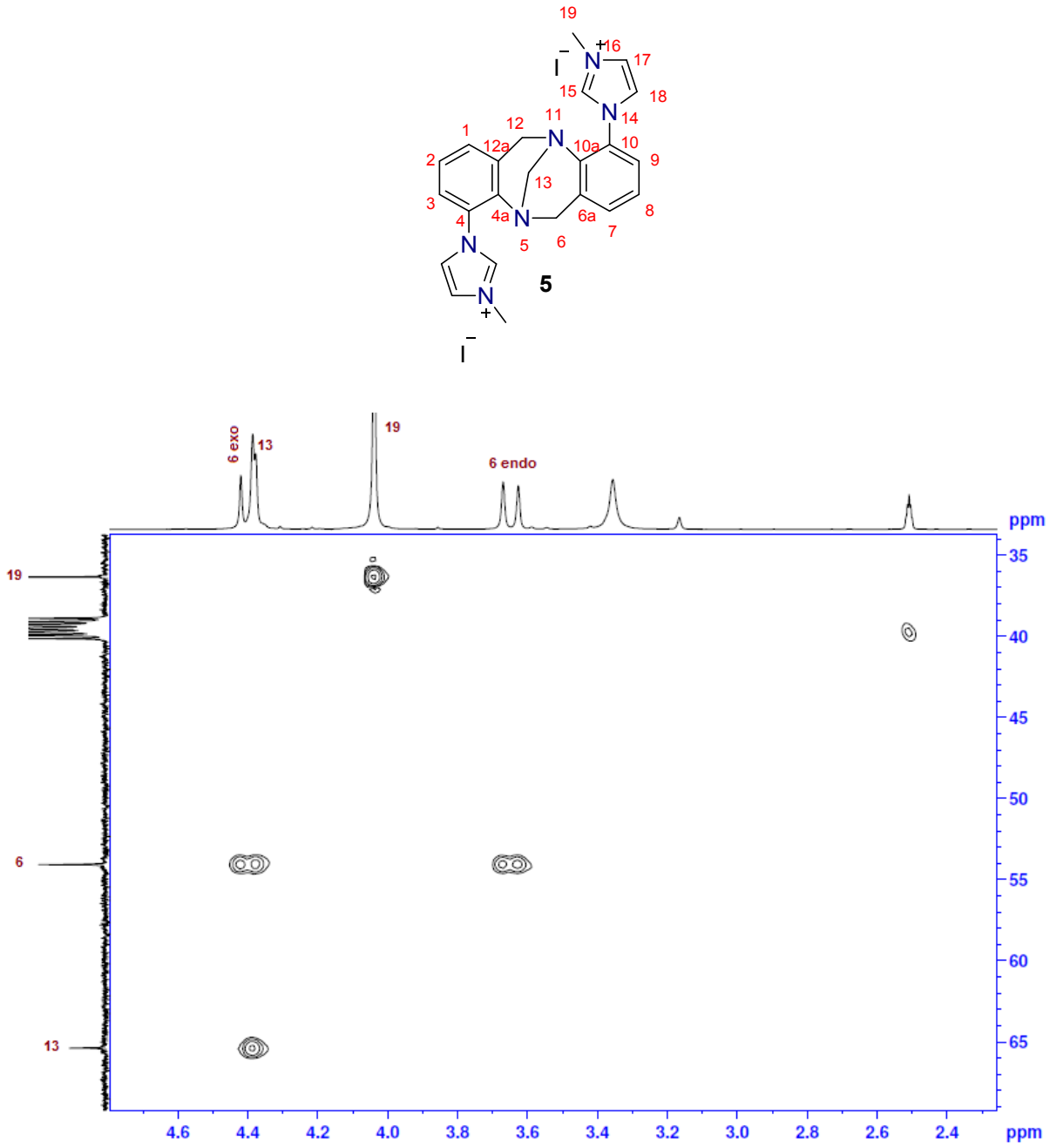


Figure S23: HSQC of 5 expansion

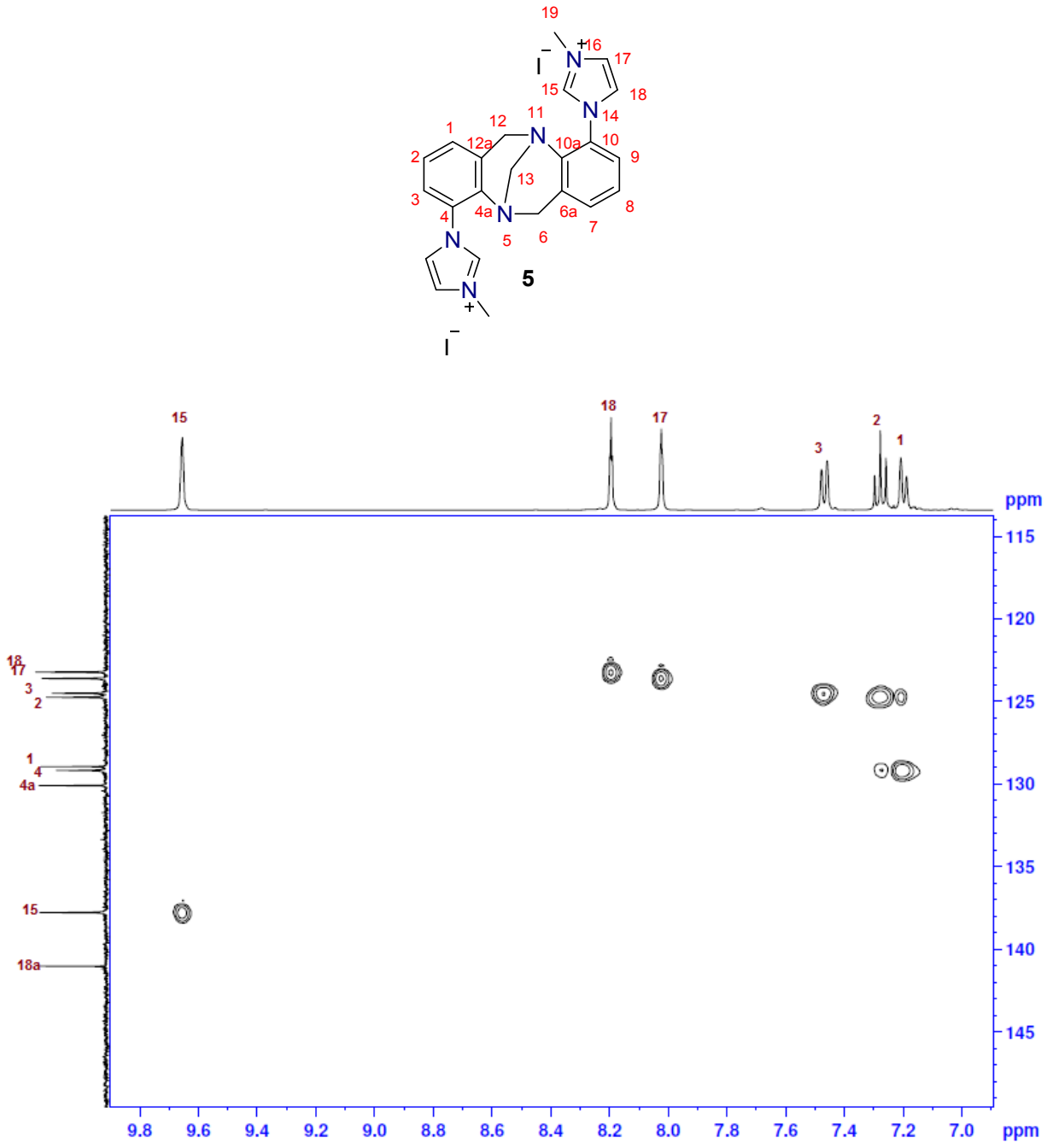


Figure S24: HMBC of 5 (400 MHz, DMSO-d_6, RT)

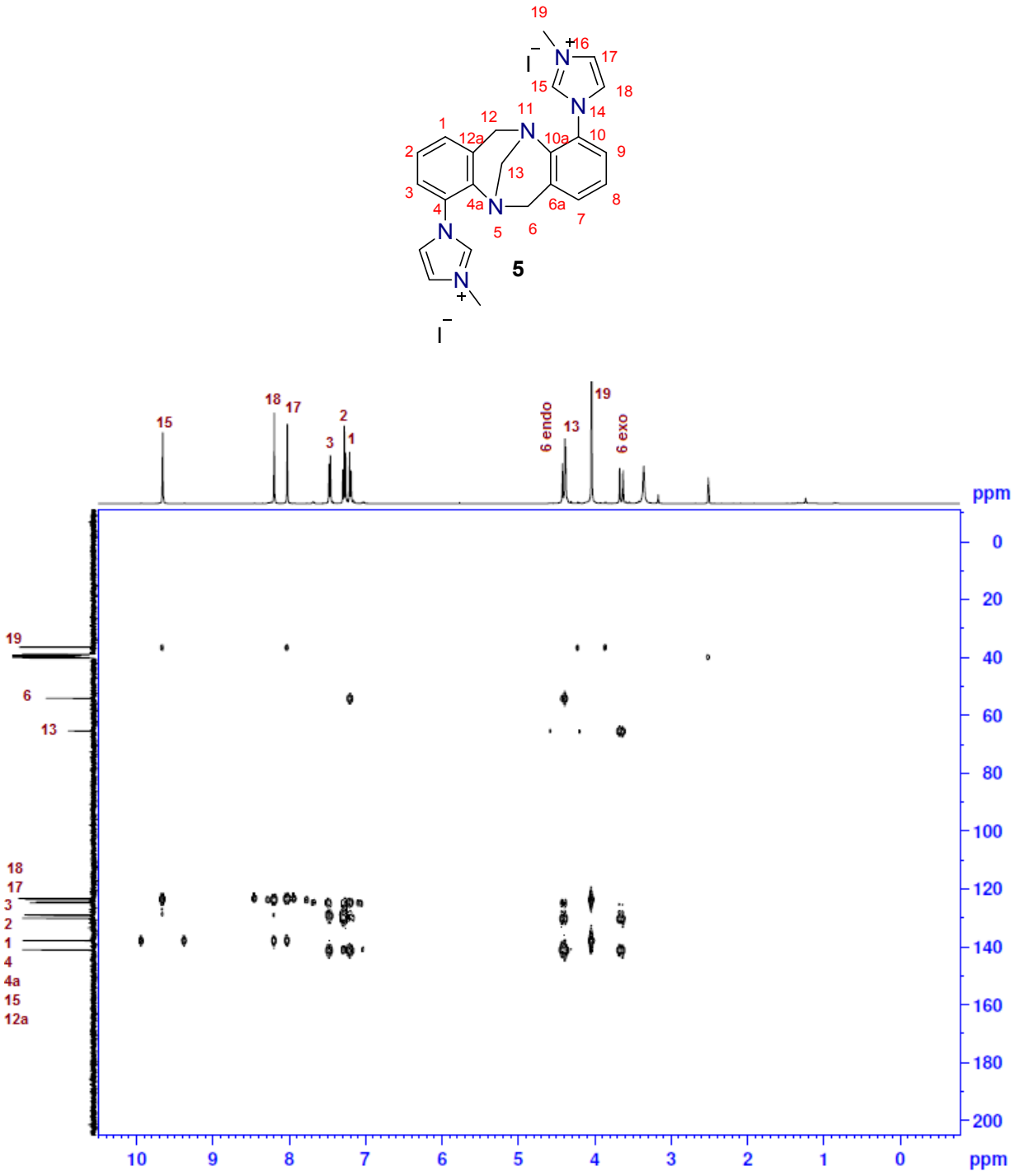


Figure S25: HMBC of 5 expansion

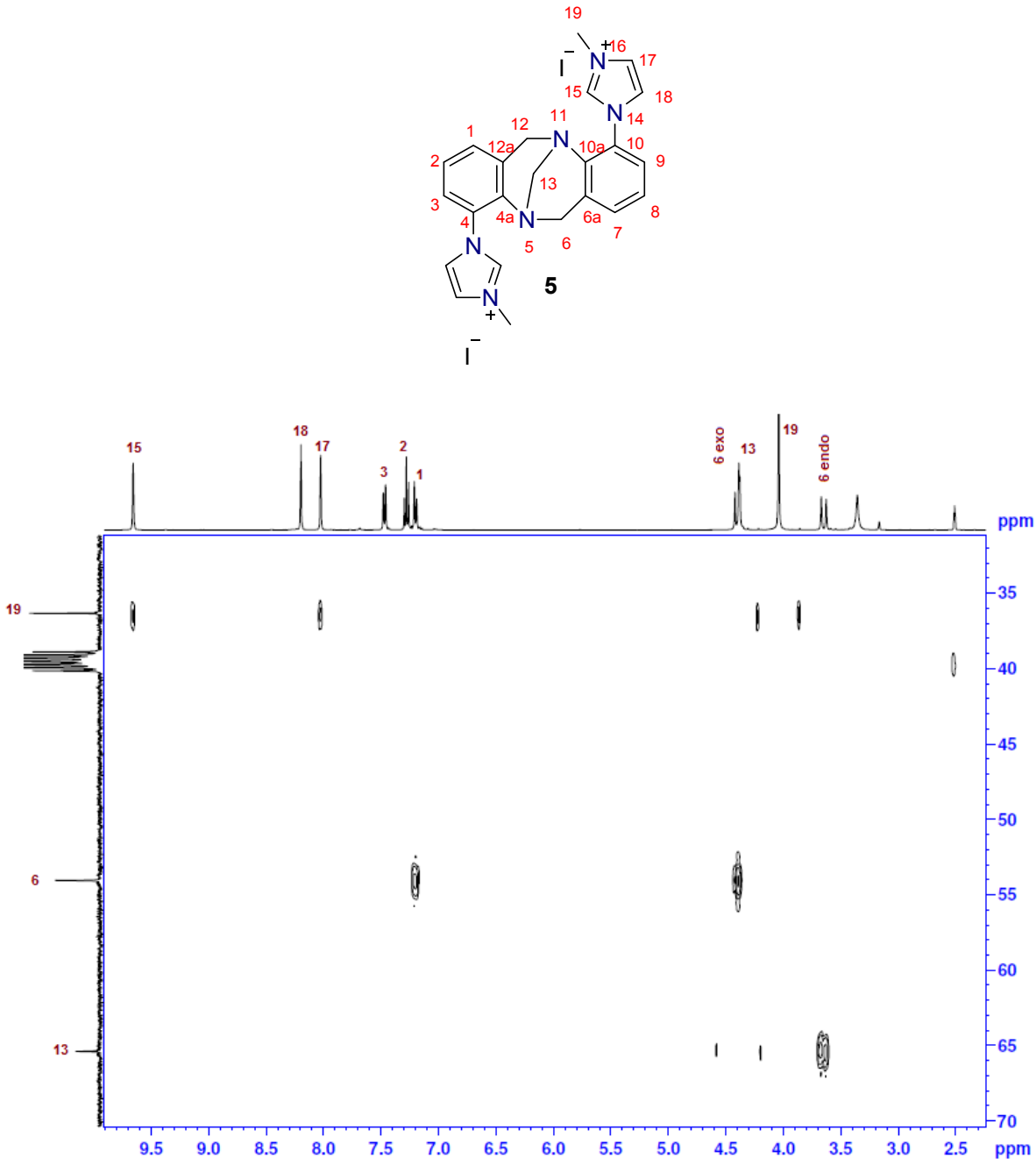


Figure S26: HMBC of 5 expansion

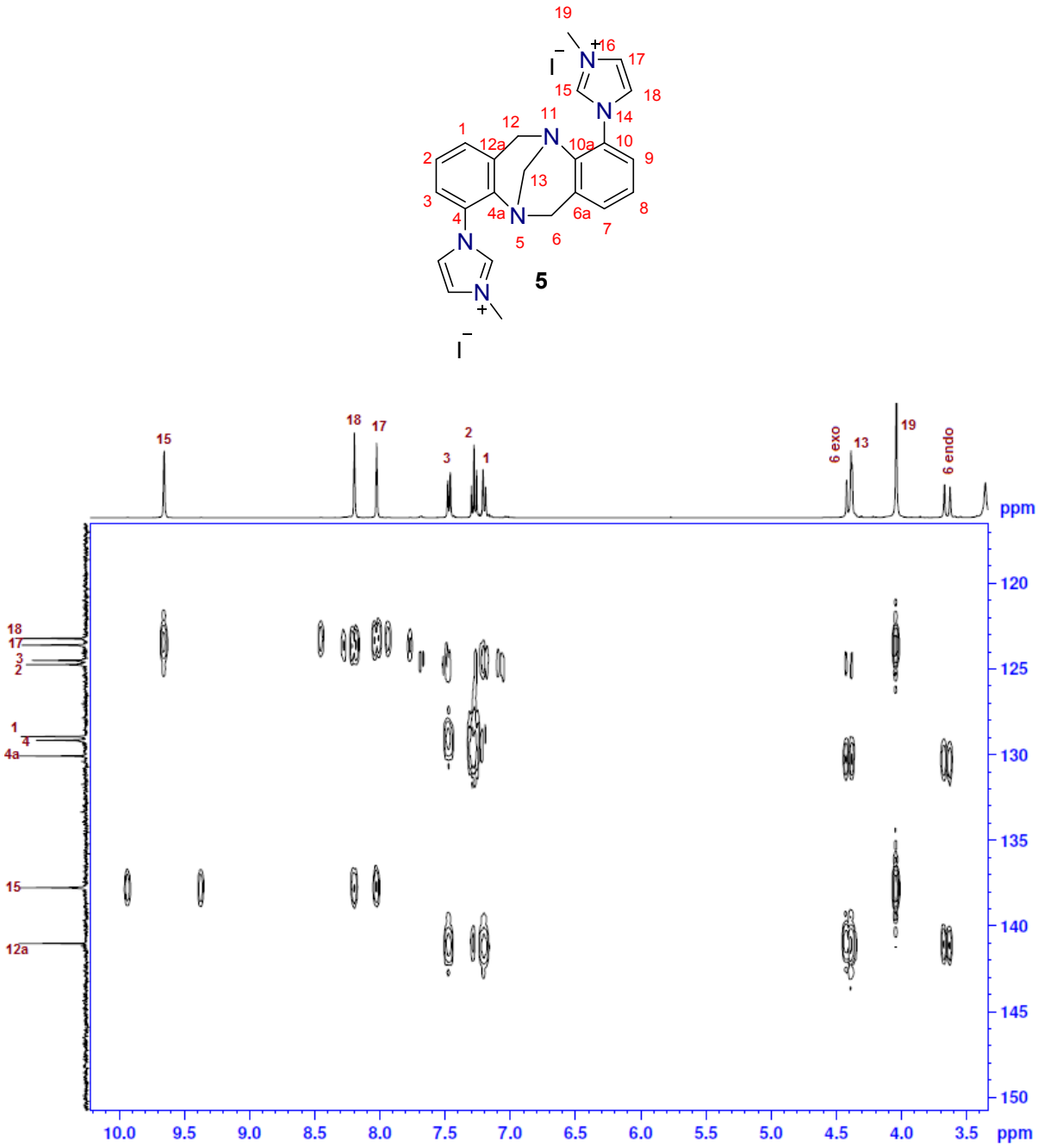


Figure S27: HMBC of 5 expansion

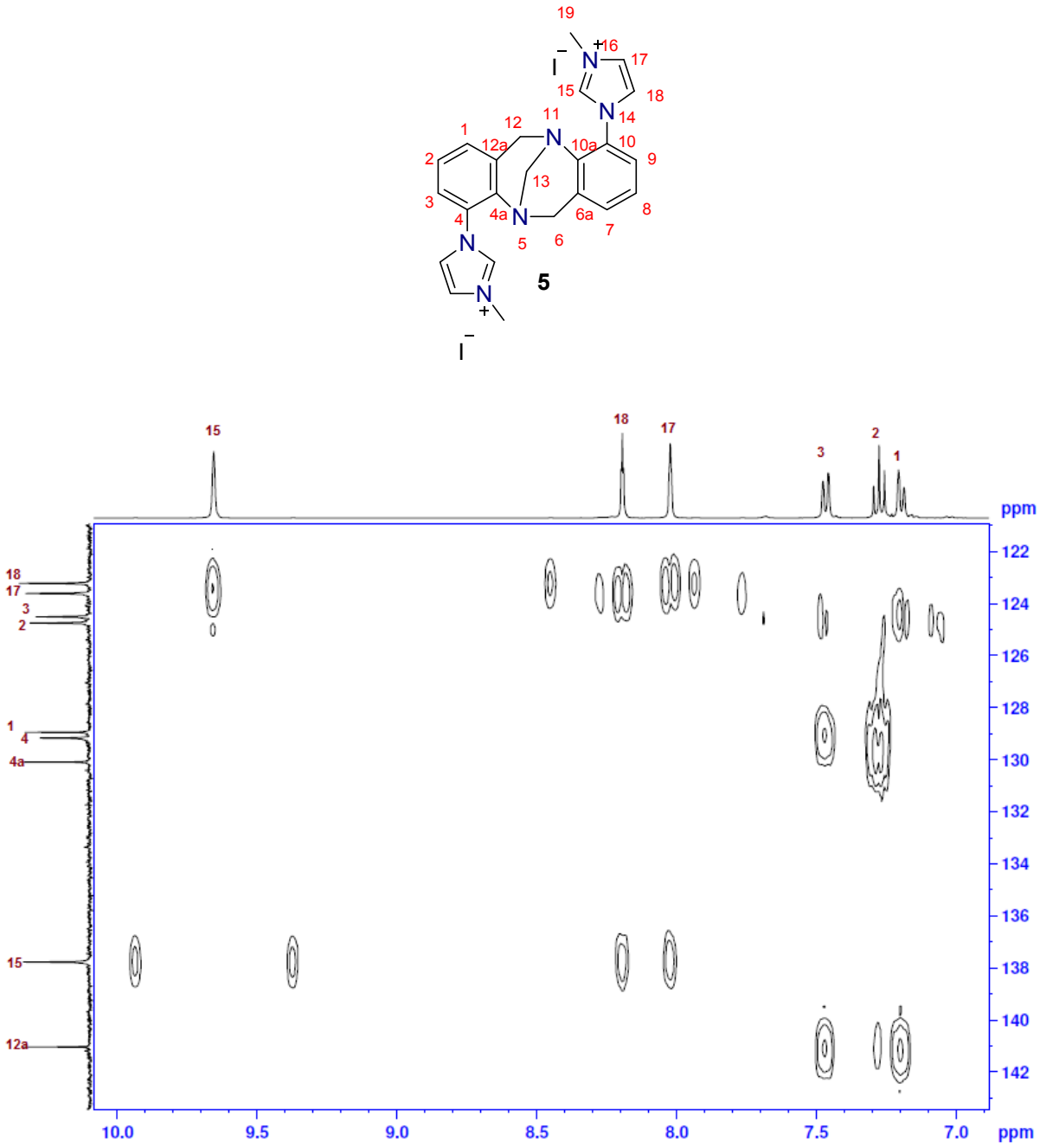


Figure S28: HMBC of 5 expansion

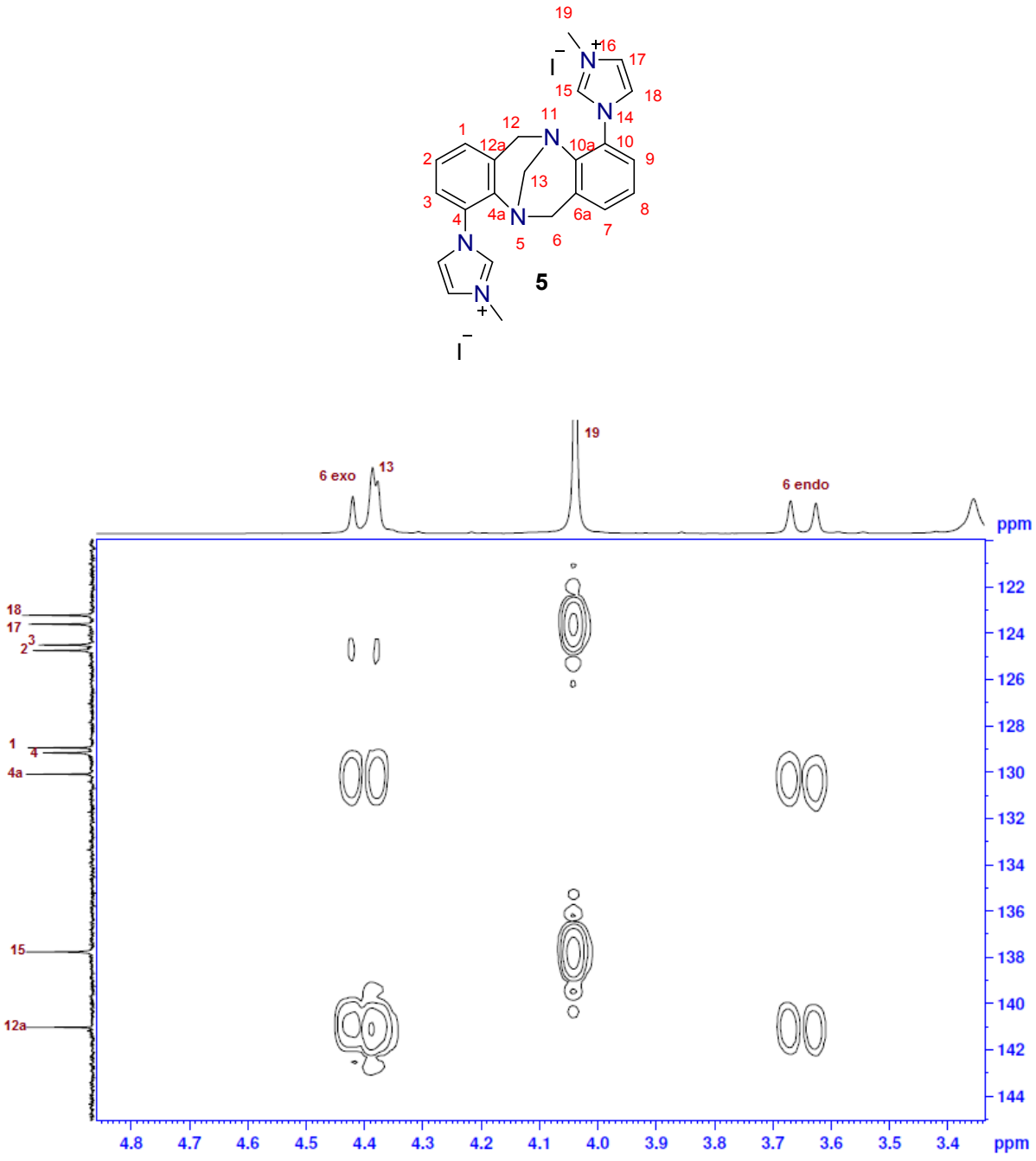
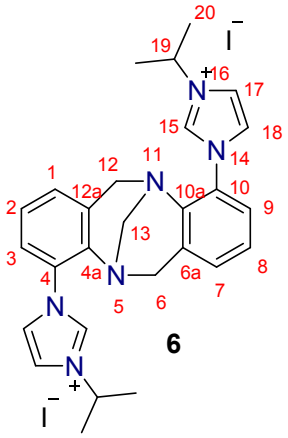


Figure S29: HSQC of 6 (400 MHz, DMSO-d_6, RT)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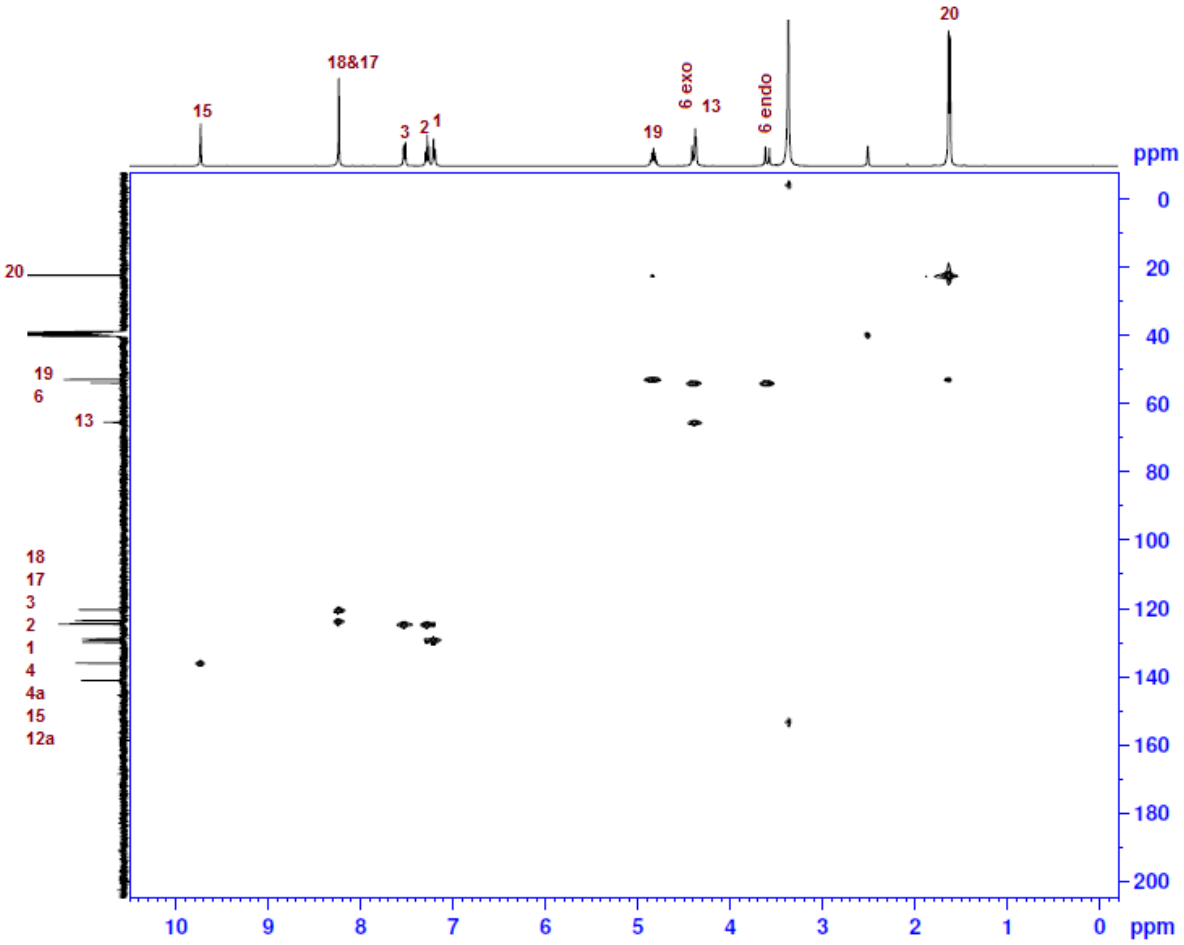
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Figure S30: HSQC of 6 expansion

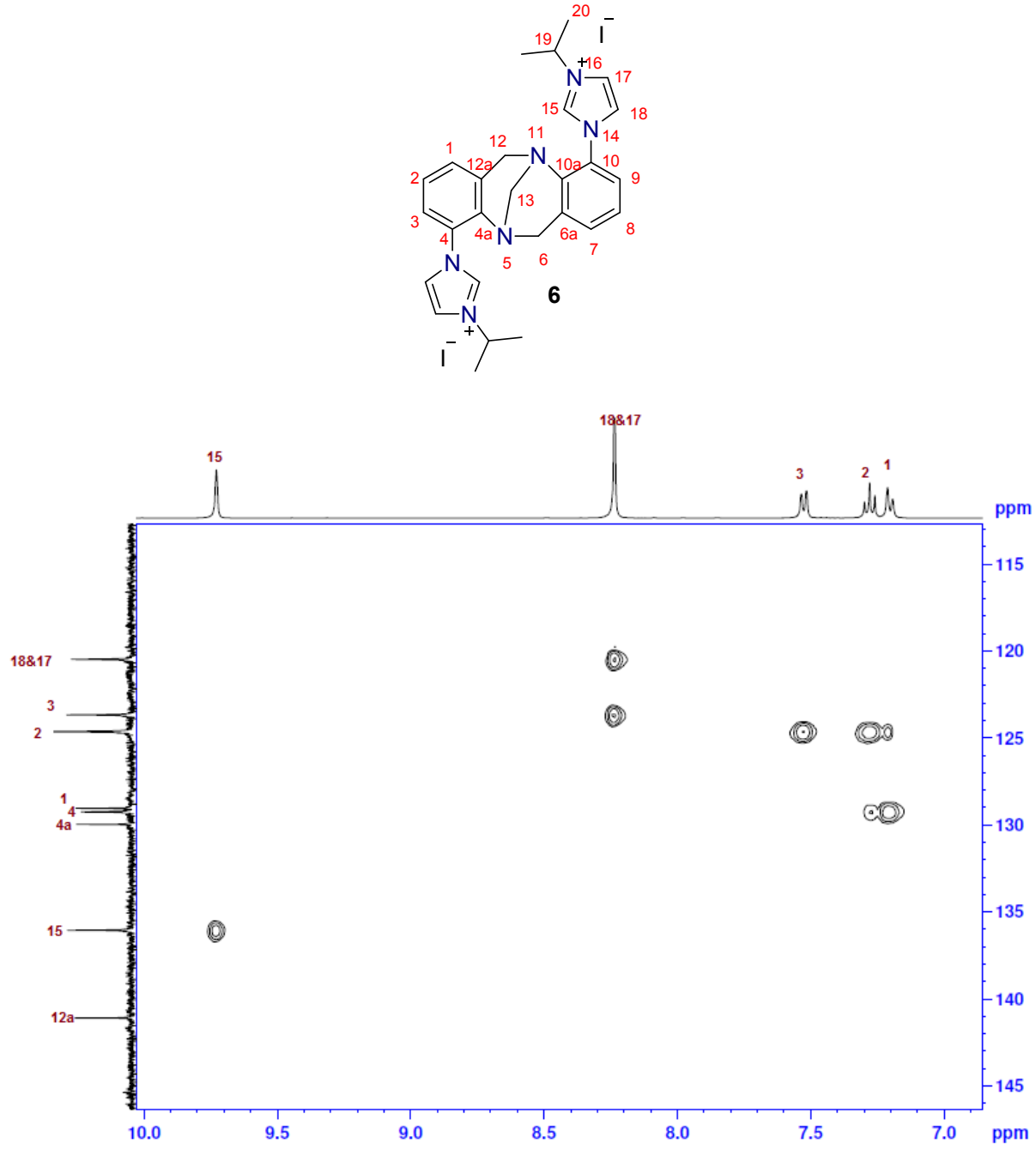


Figure S31: HSQC of 6 expansion

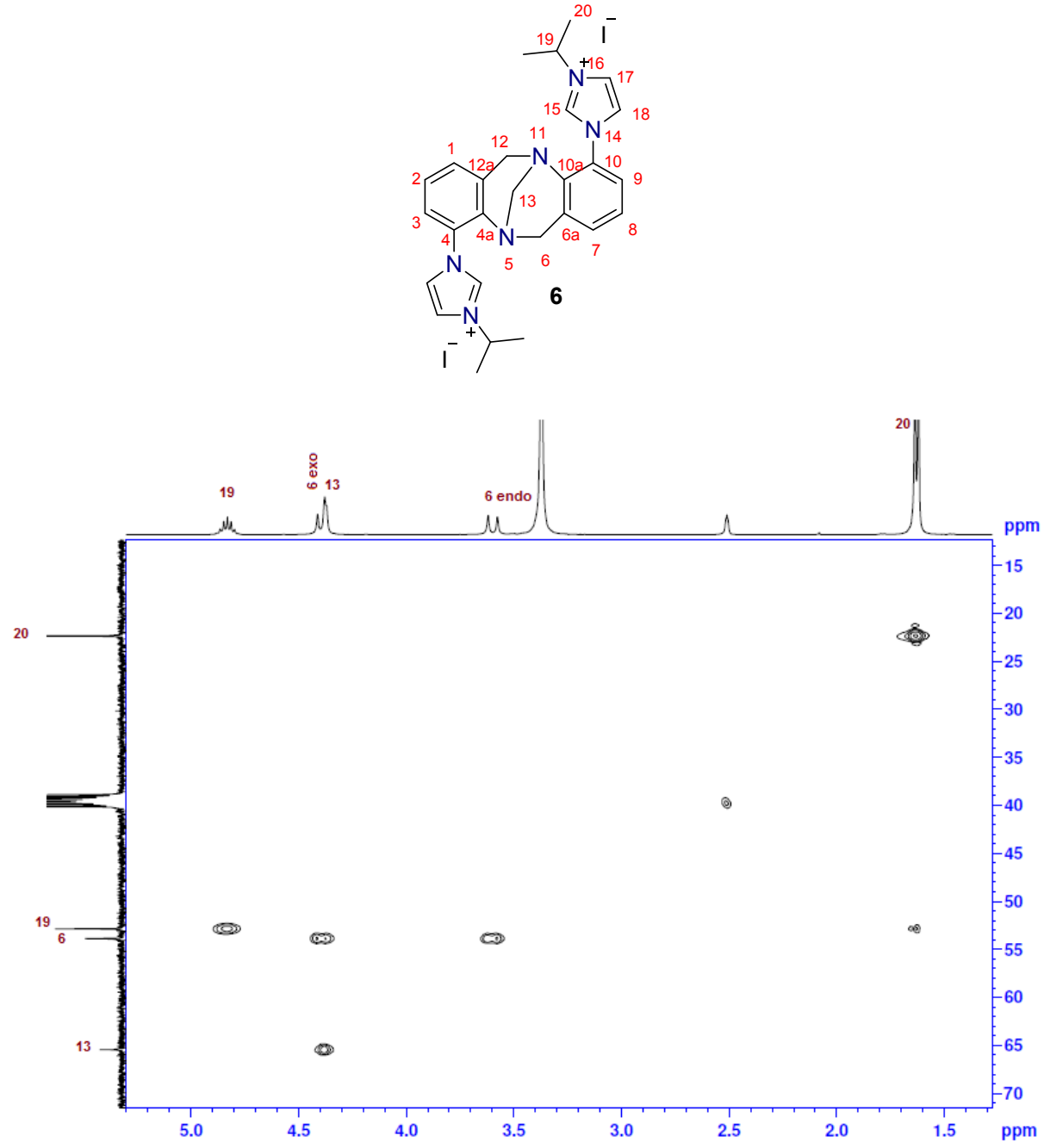


Figure S32: HMBC of 6 (400 MHz, DMSO-d_6, RT)

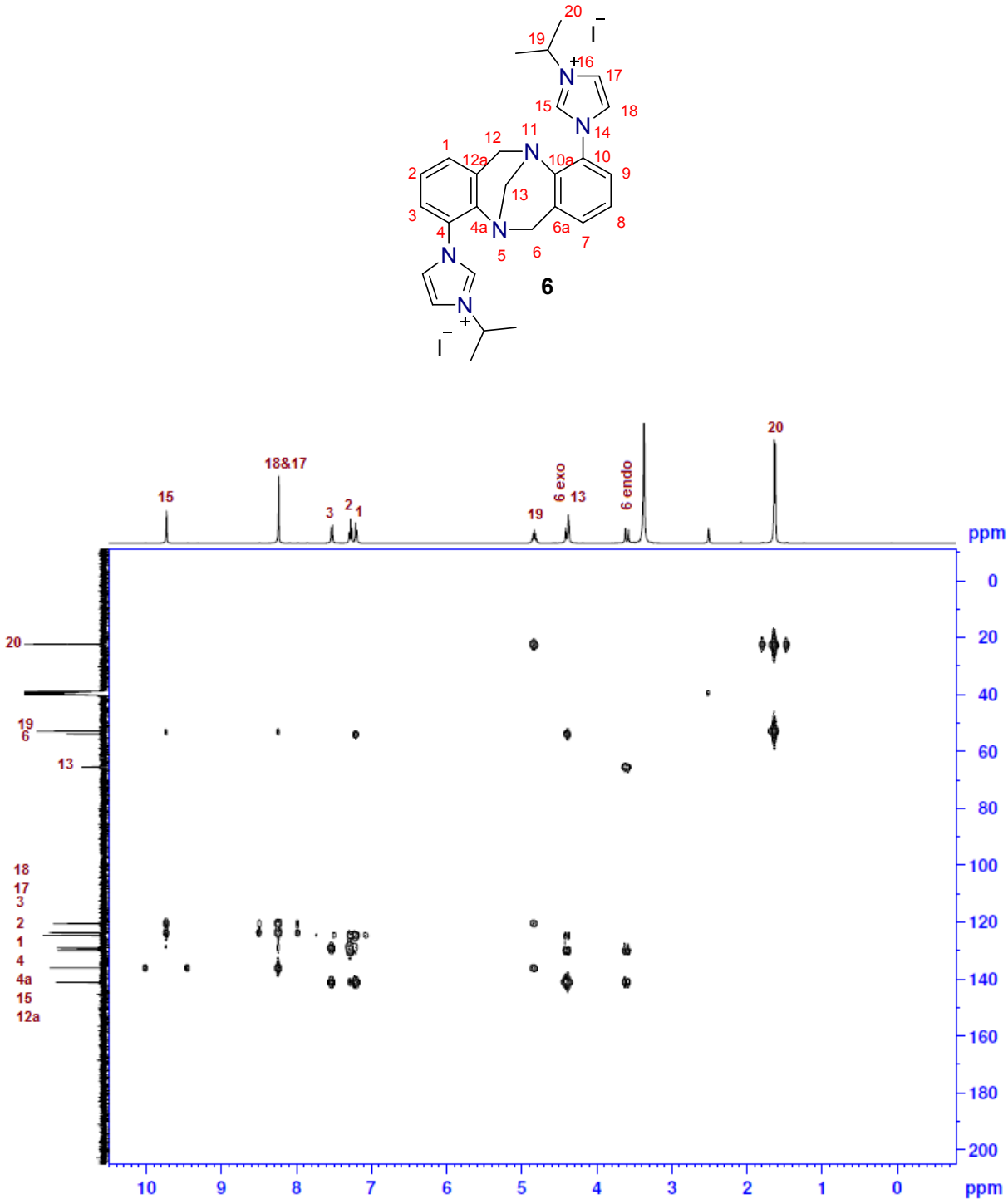


Figure S33: HMBC of 6 expansion

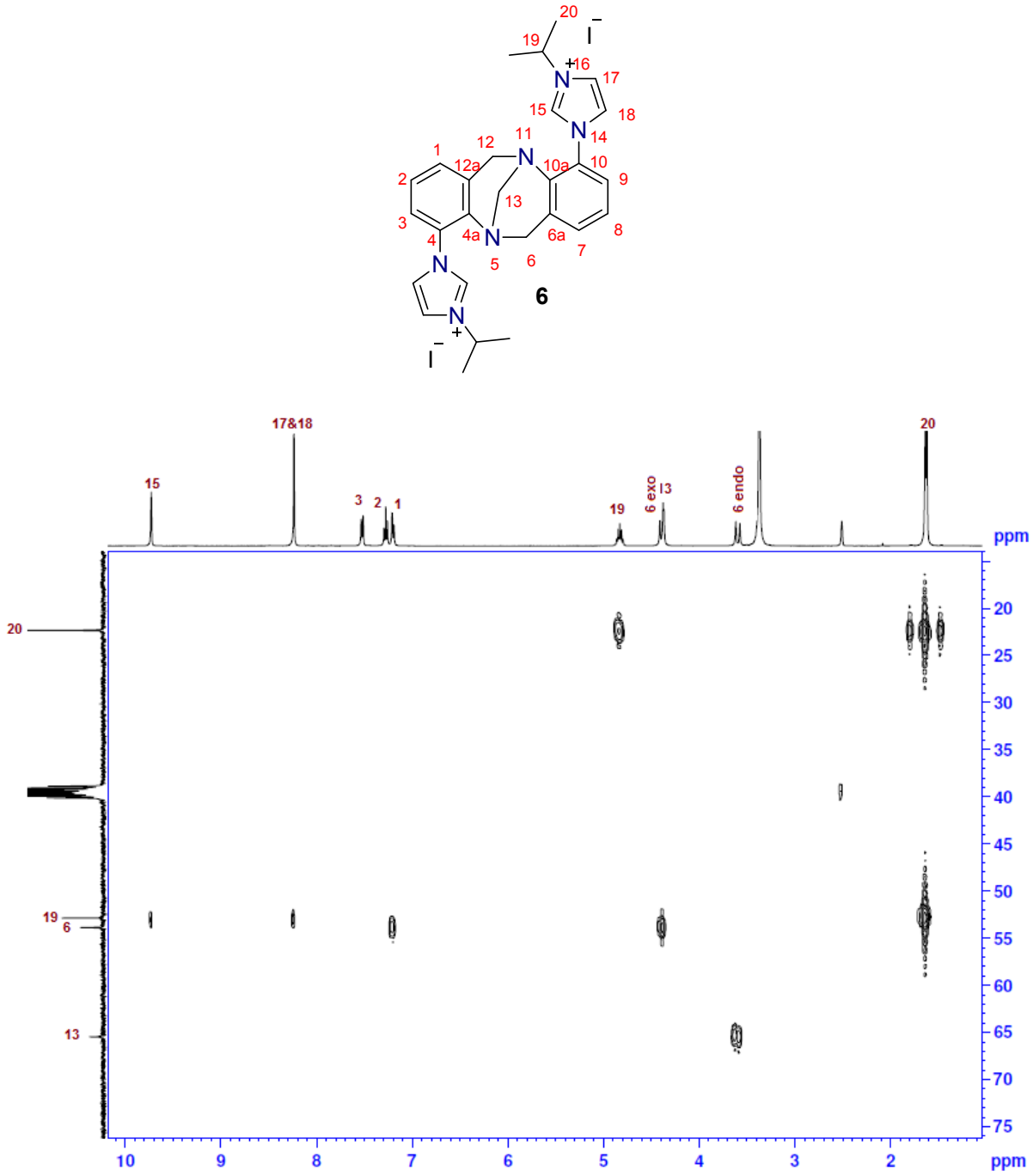
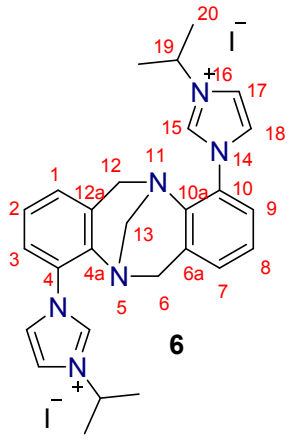


Figure S34: HMBC of 6 expansion



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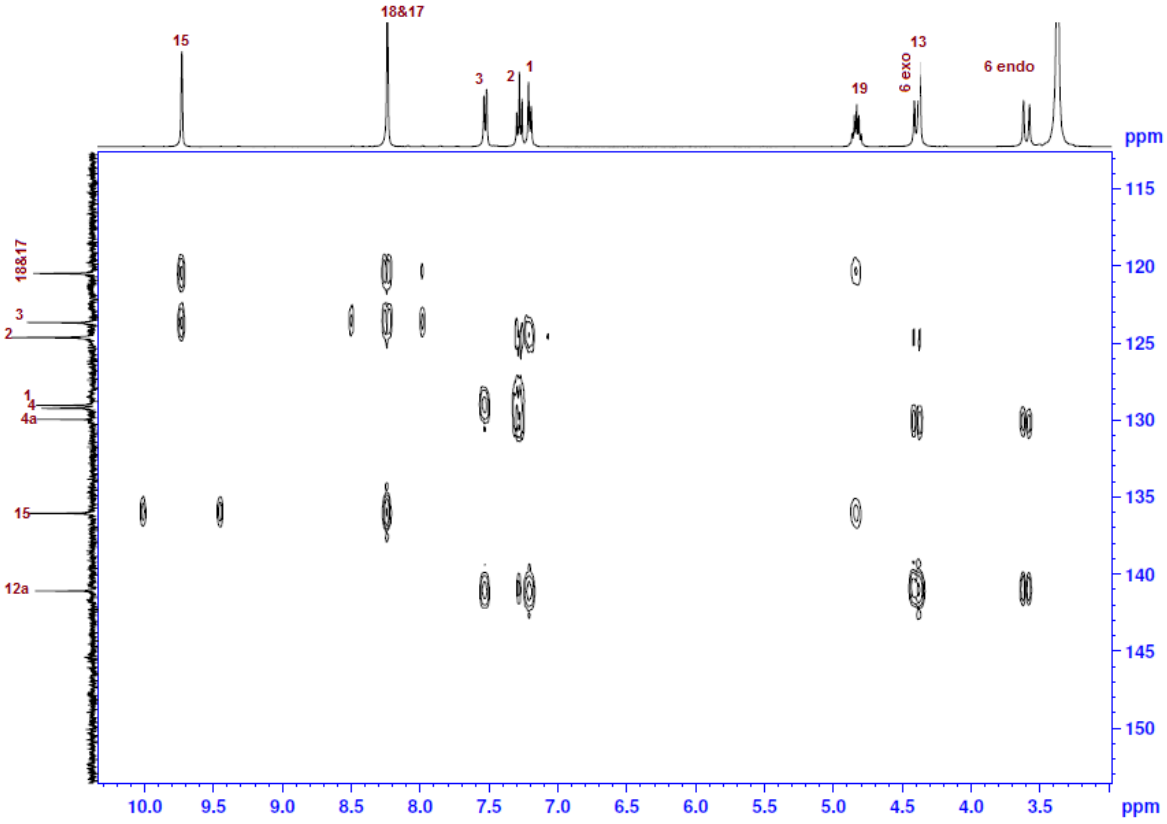
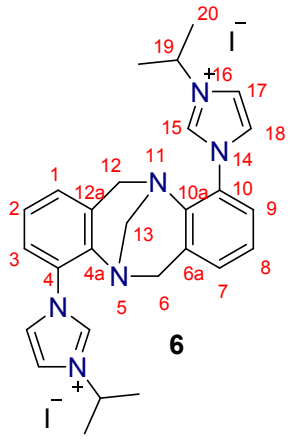


Figure S35: HMBC of 6 expansion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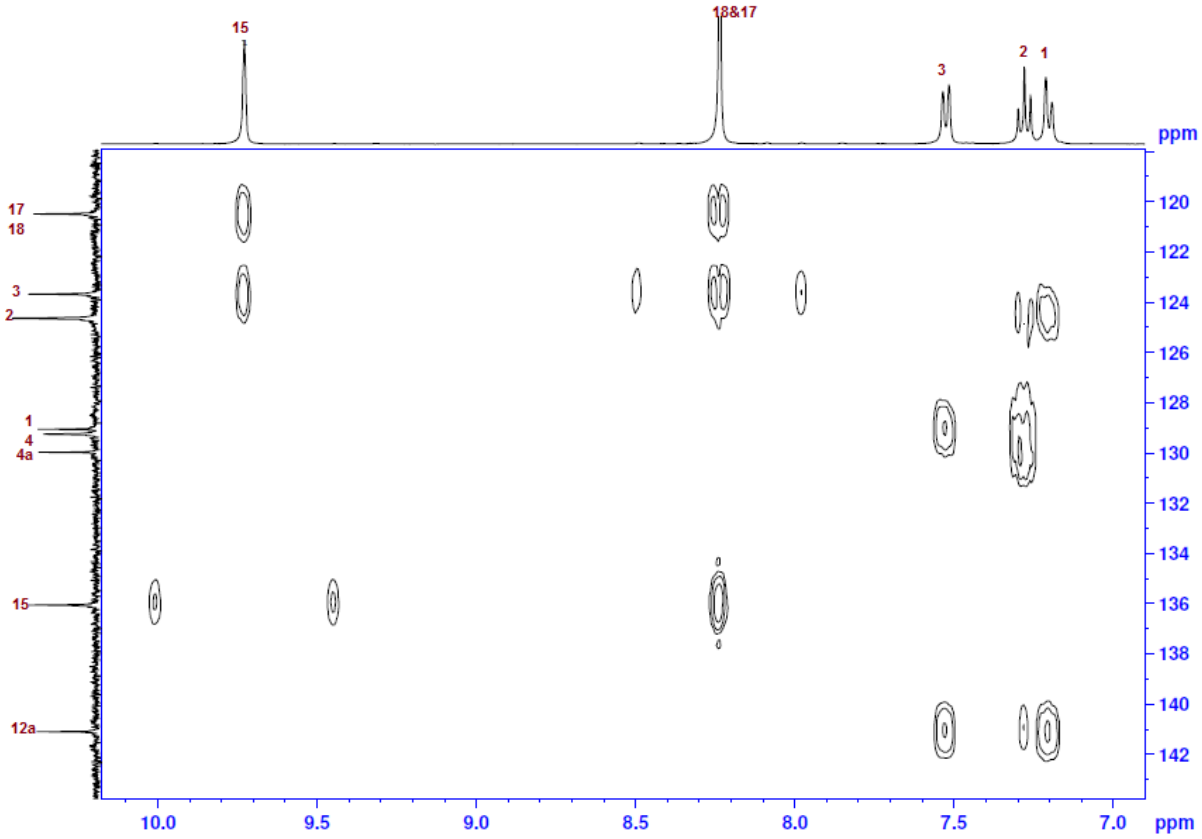
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Figure S36: HMBC of 6 expansion

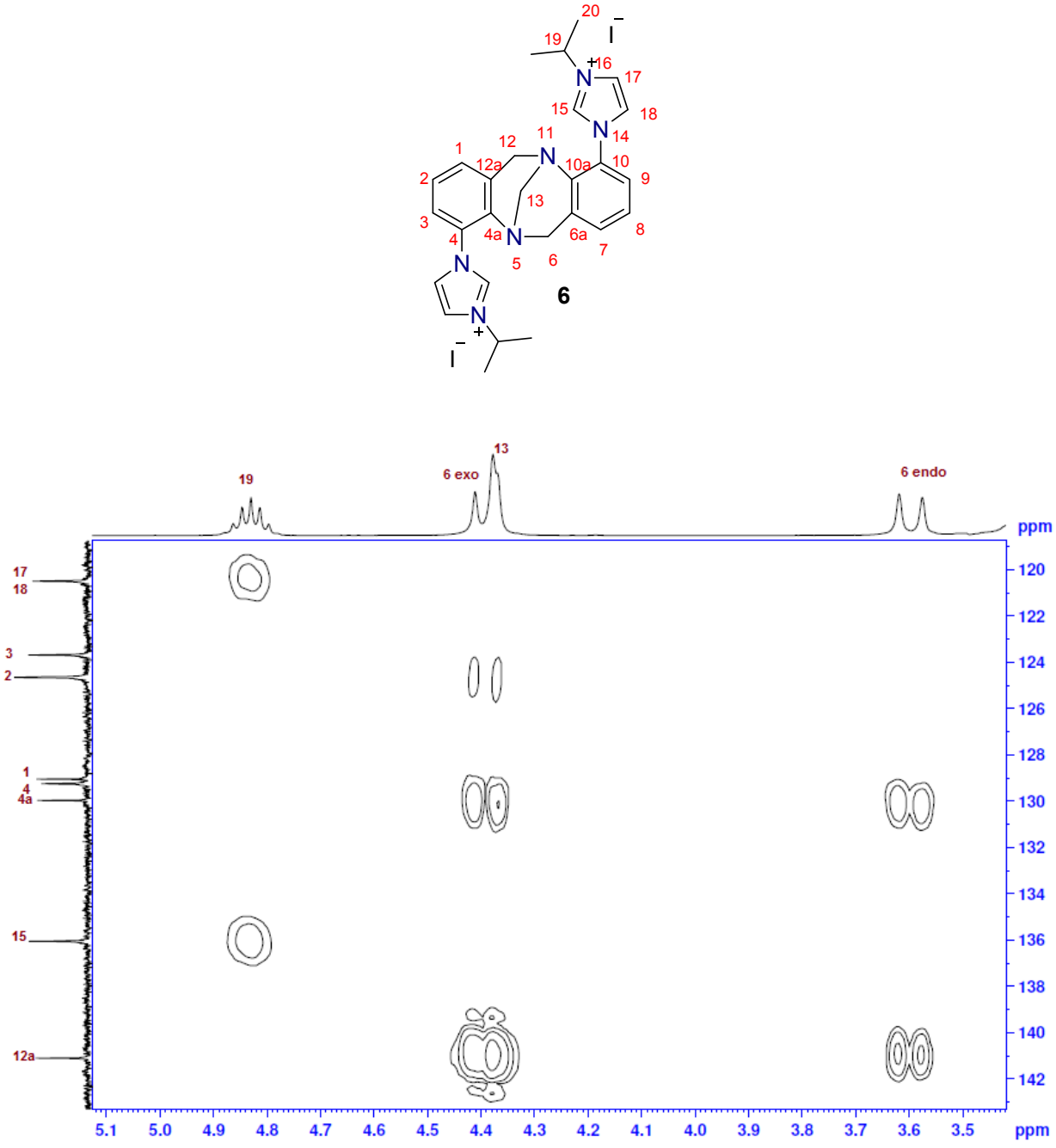


Figure S37: HSQC of 7 (400 MHz, DMSO-d_6, RT)

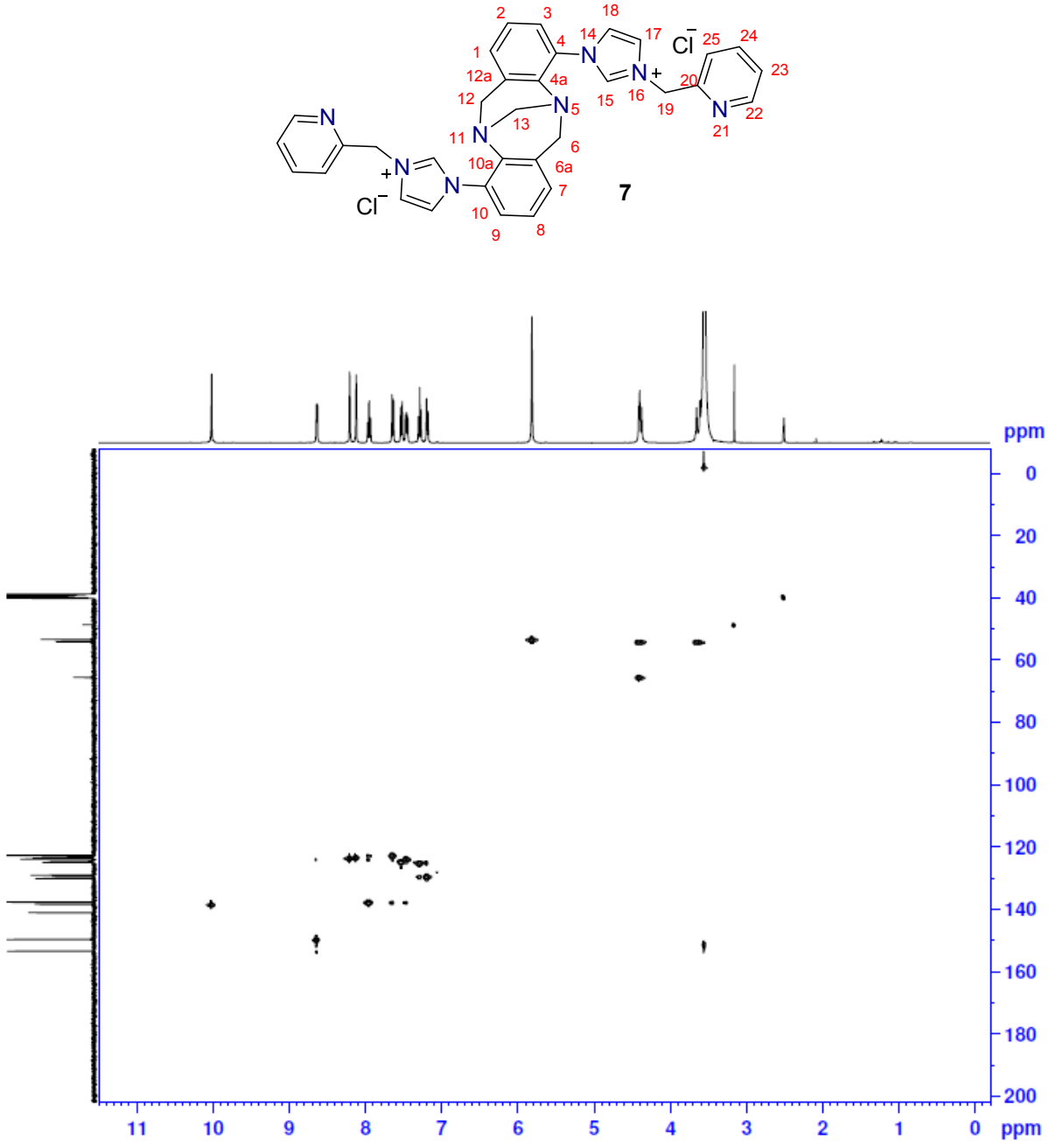


Figure S38: HSQC of 7 expansion

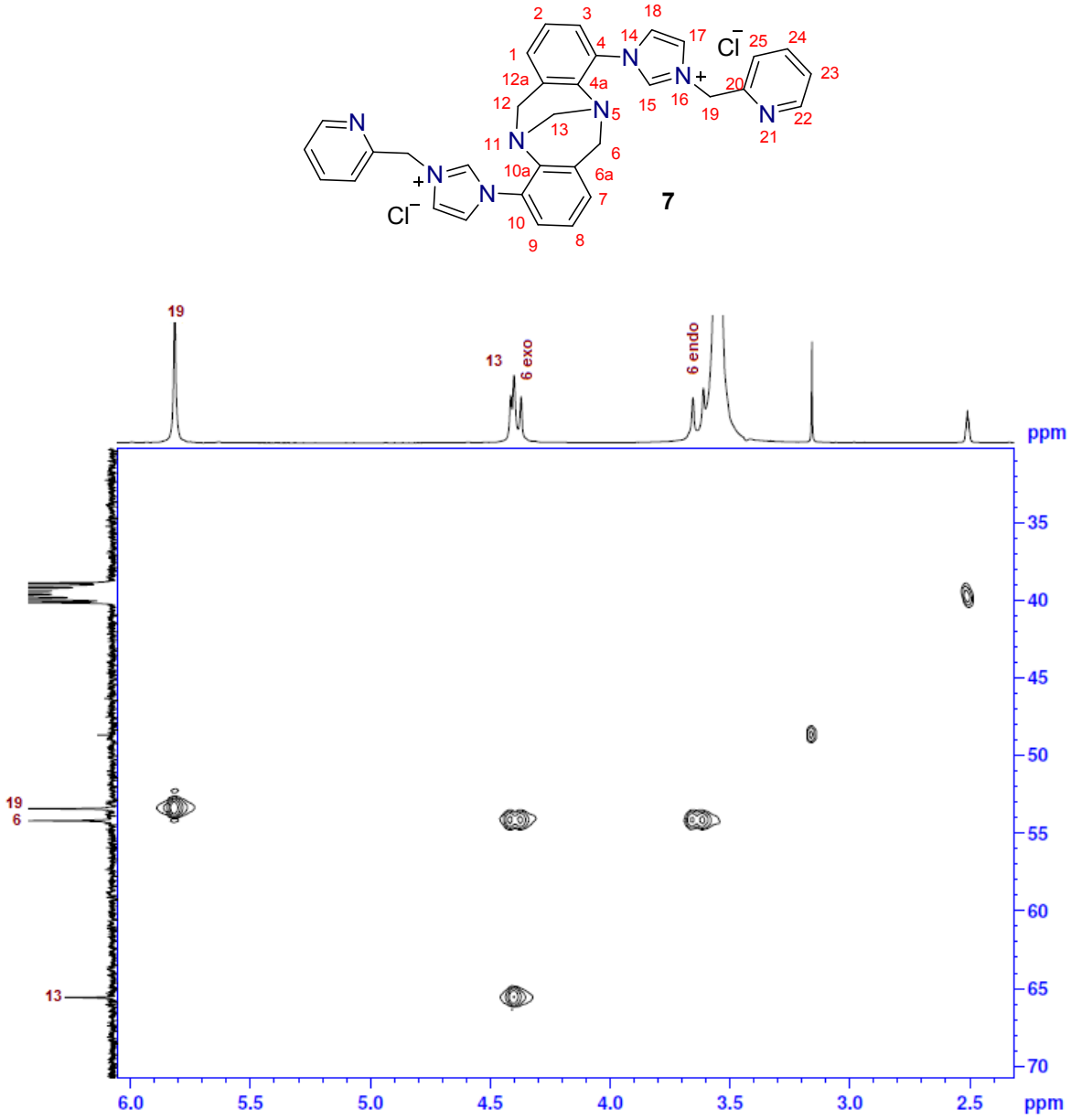


Figure S39: HSQC of 7 expansion

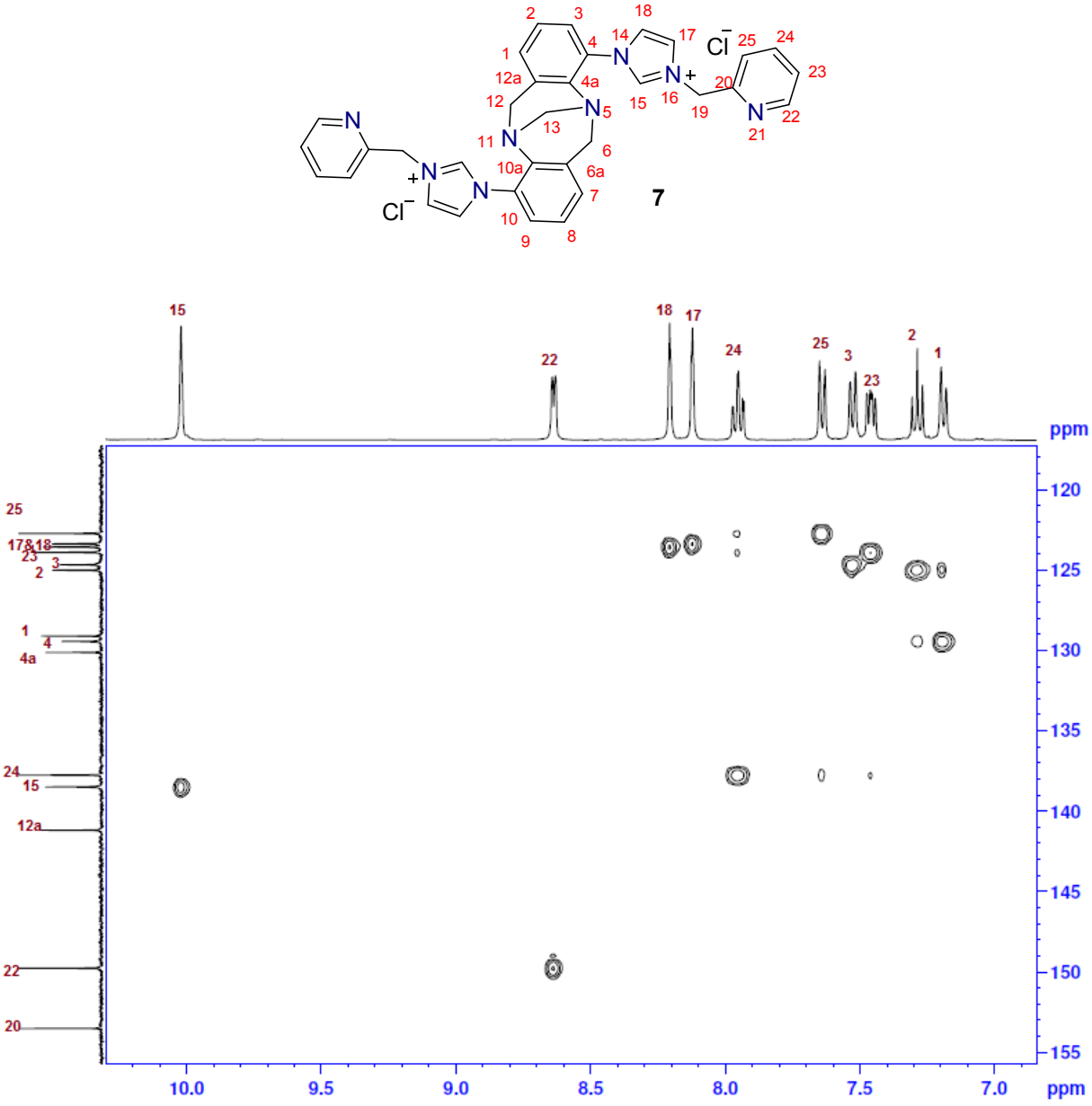


Figure S40: HMBC of 7 (400 MHz, DMSO-d_6, RT)

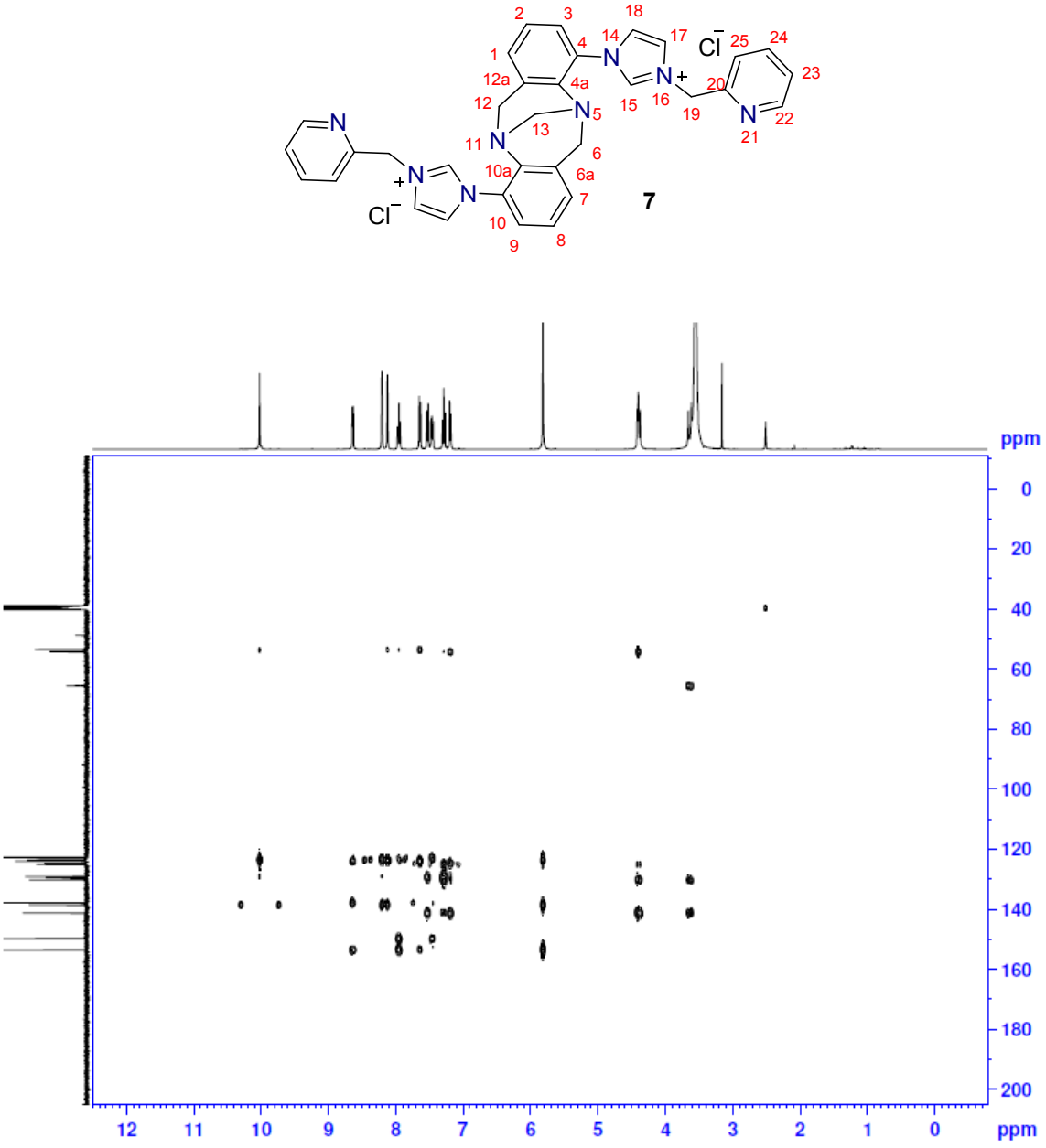


Figure S41: HMBC of 7 expansion

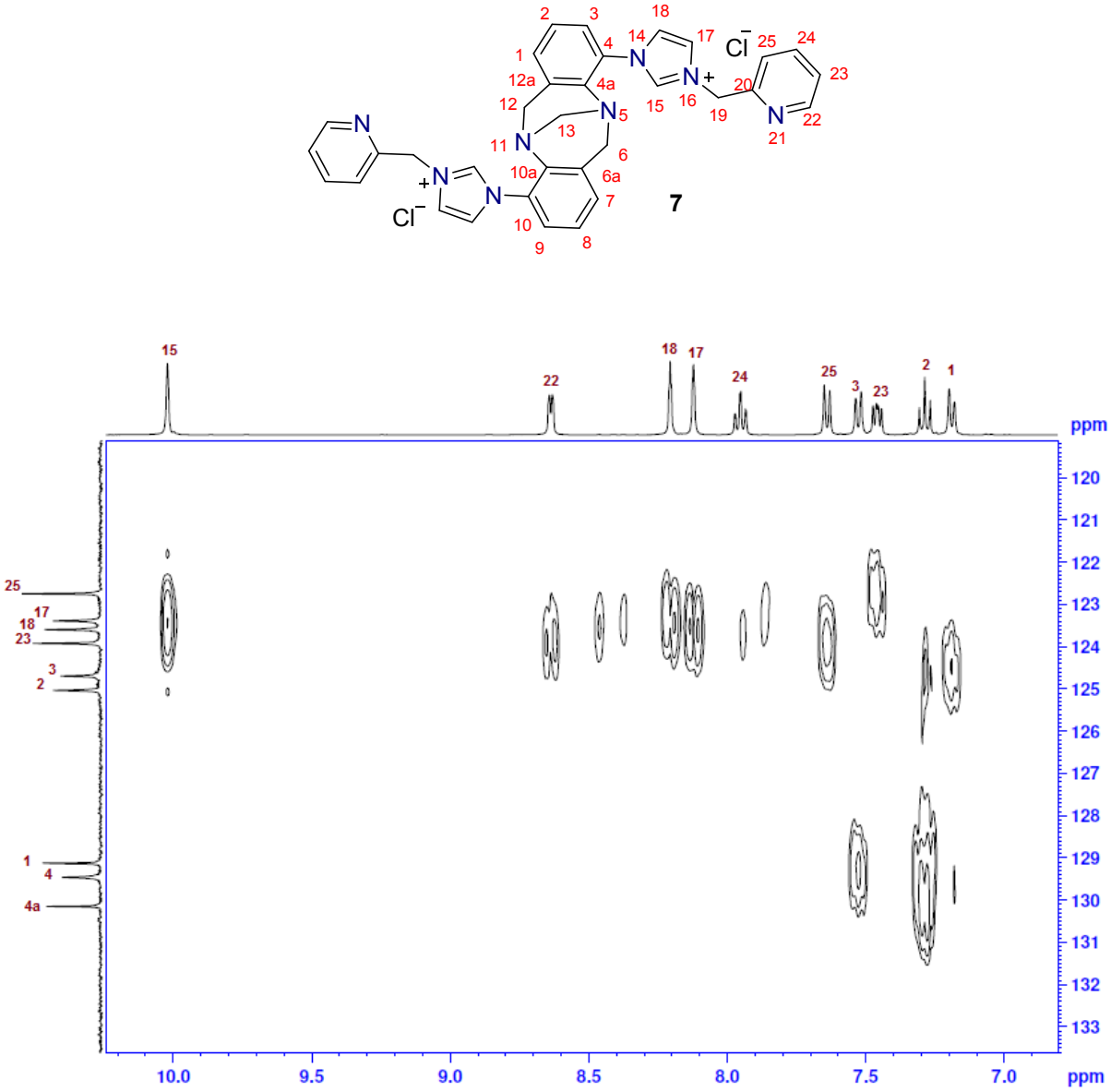


Figure S42: HMBC of 7 expansion

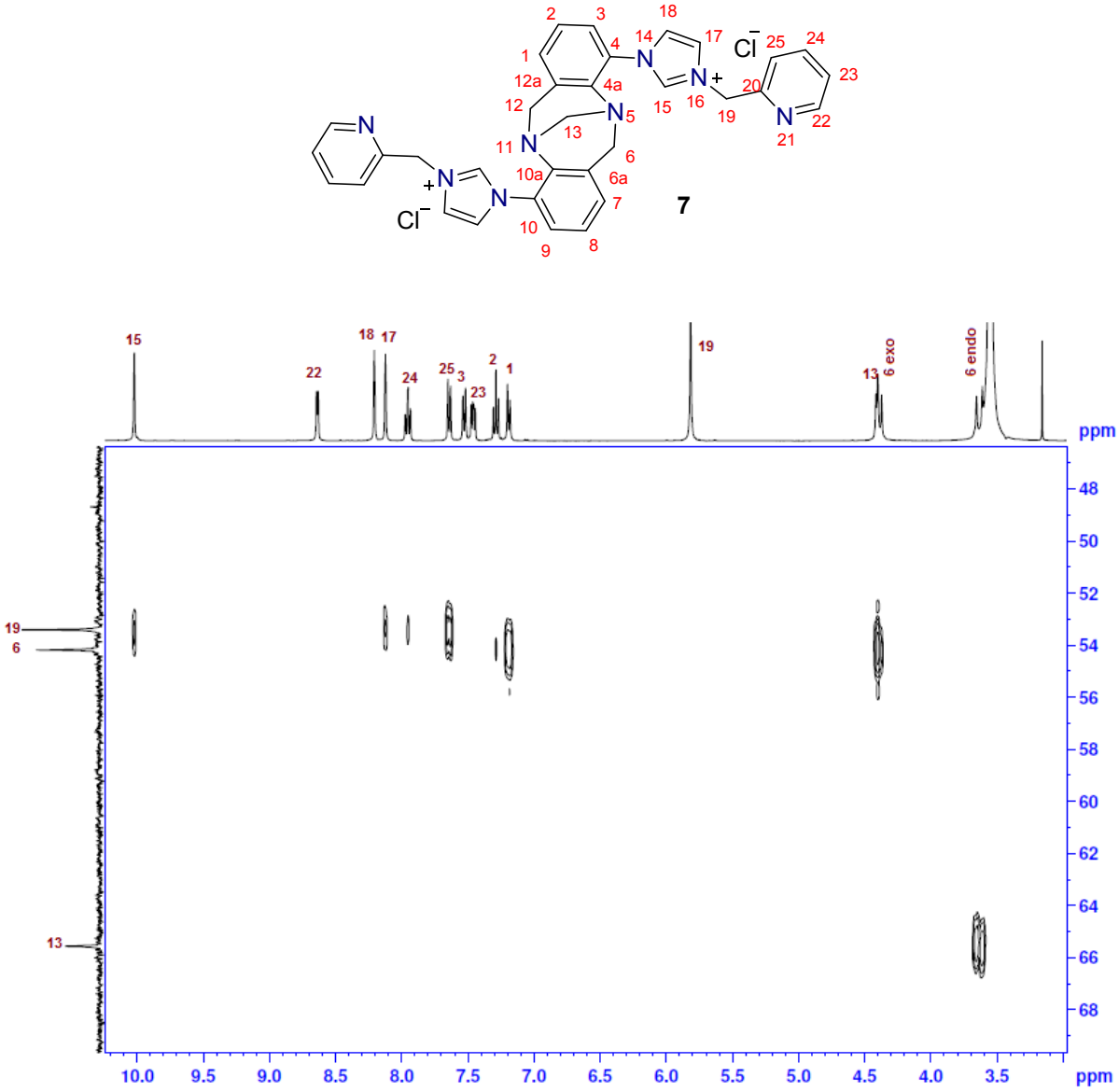


Figure S43: HMBC of 7 expansion

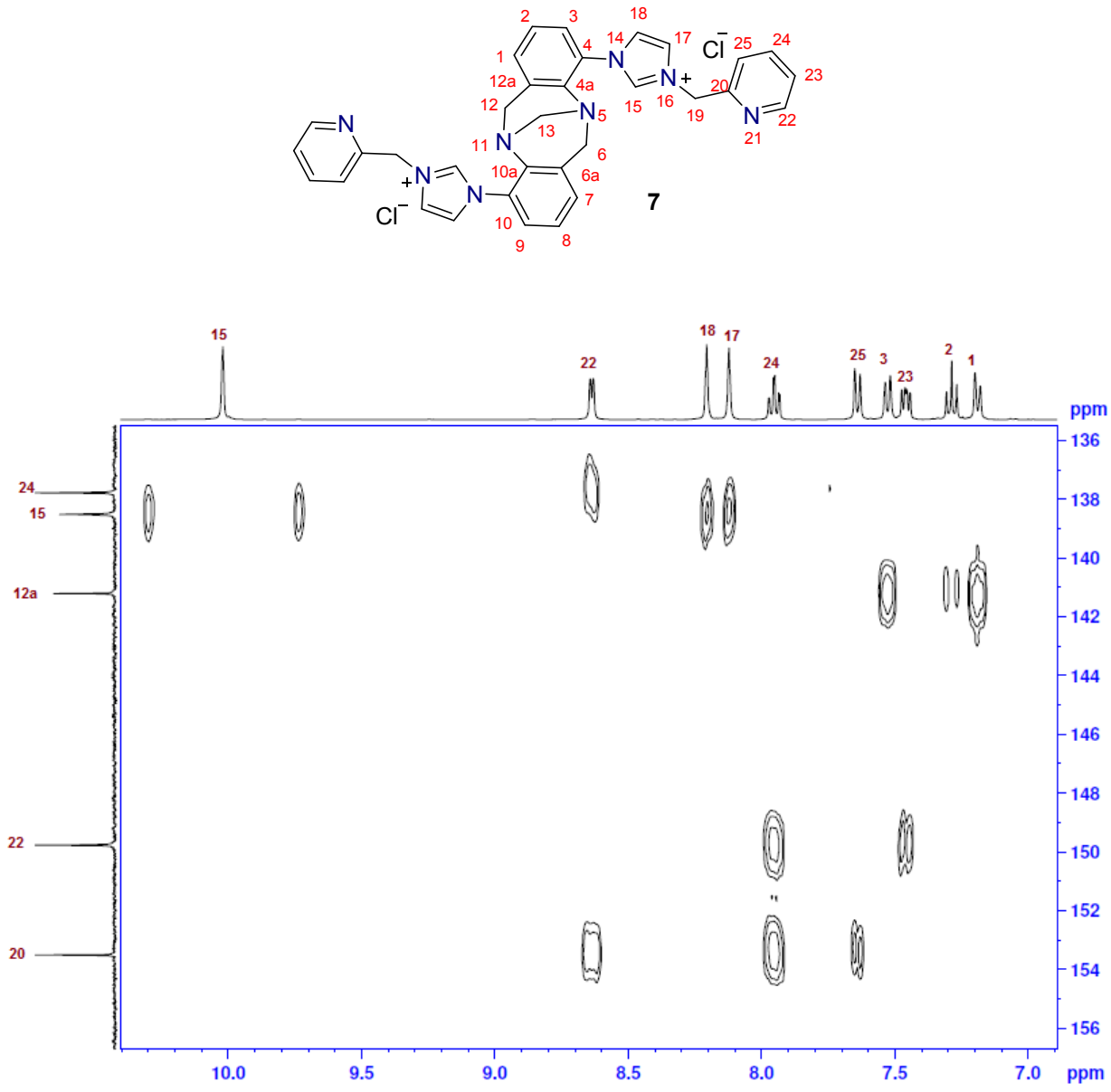


Figure S44: HMBC of 7 expansion

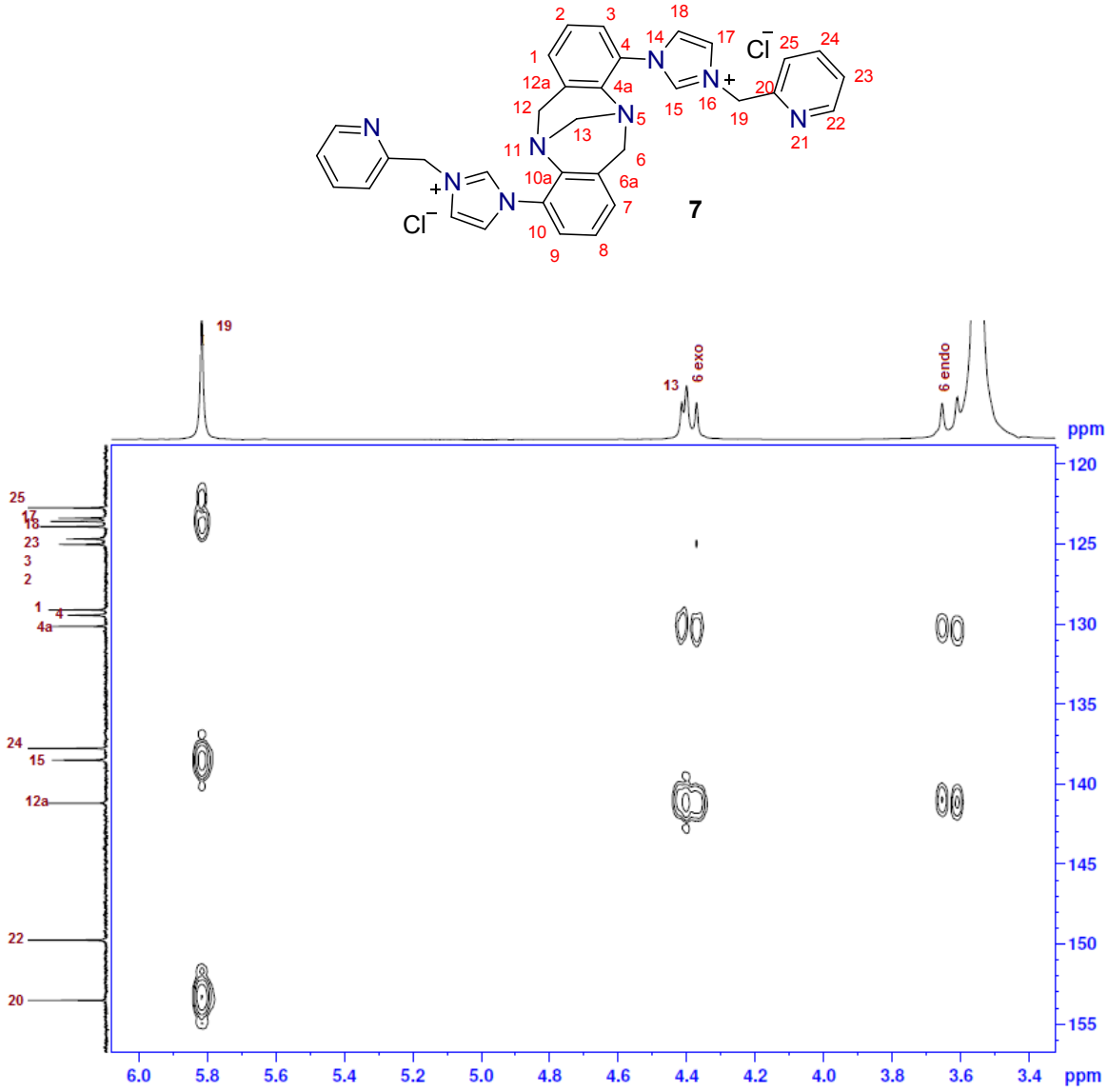


Figure S45: HSQC of 8 (400 MHz, DMSO-d_6, RT)

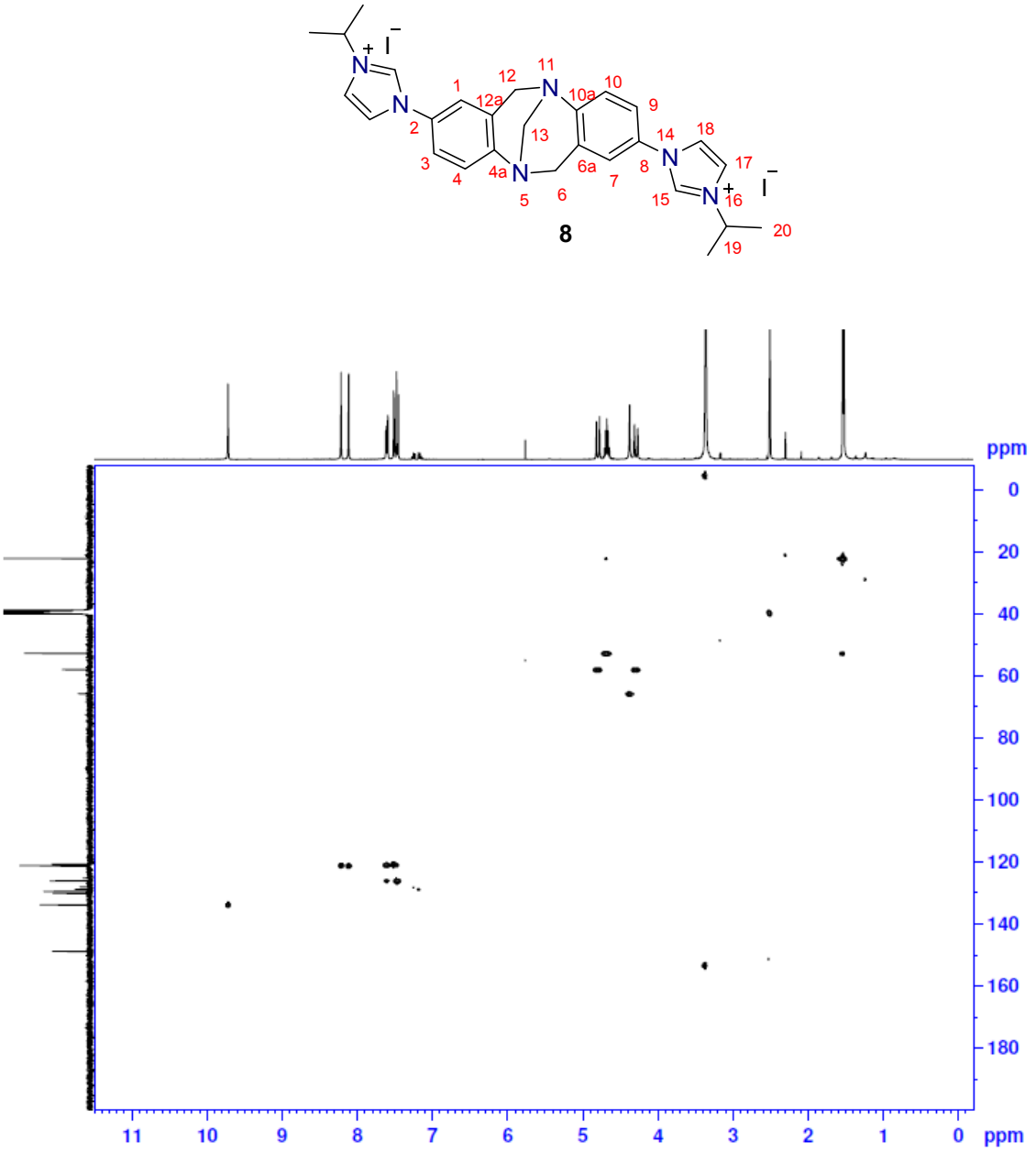


Figure S46: HSQC of 8 expansion

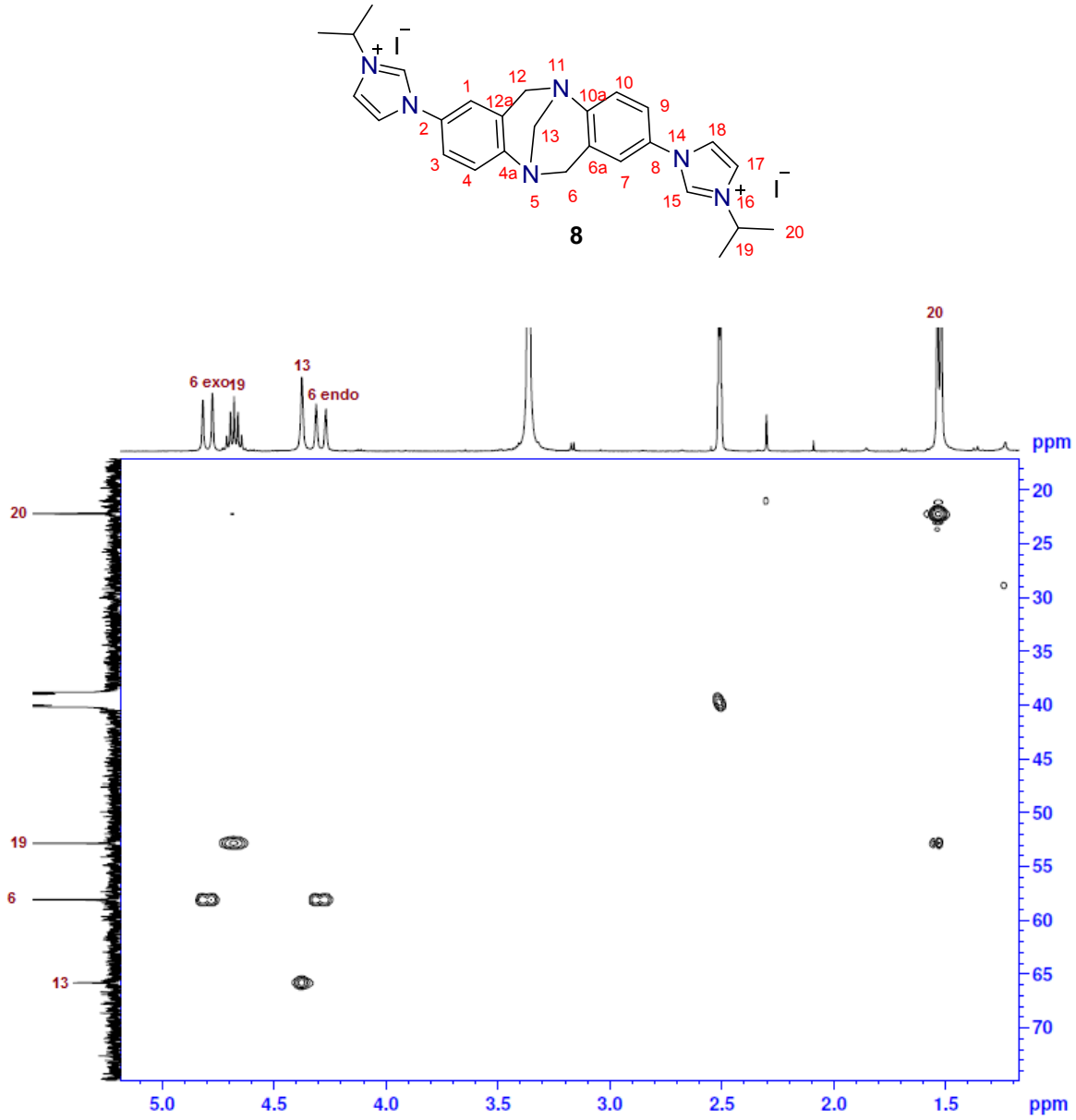


Figure S47: HSQC of 8 expansion

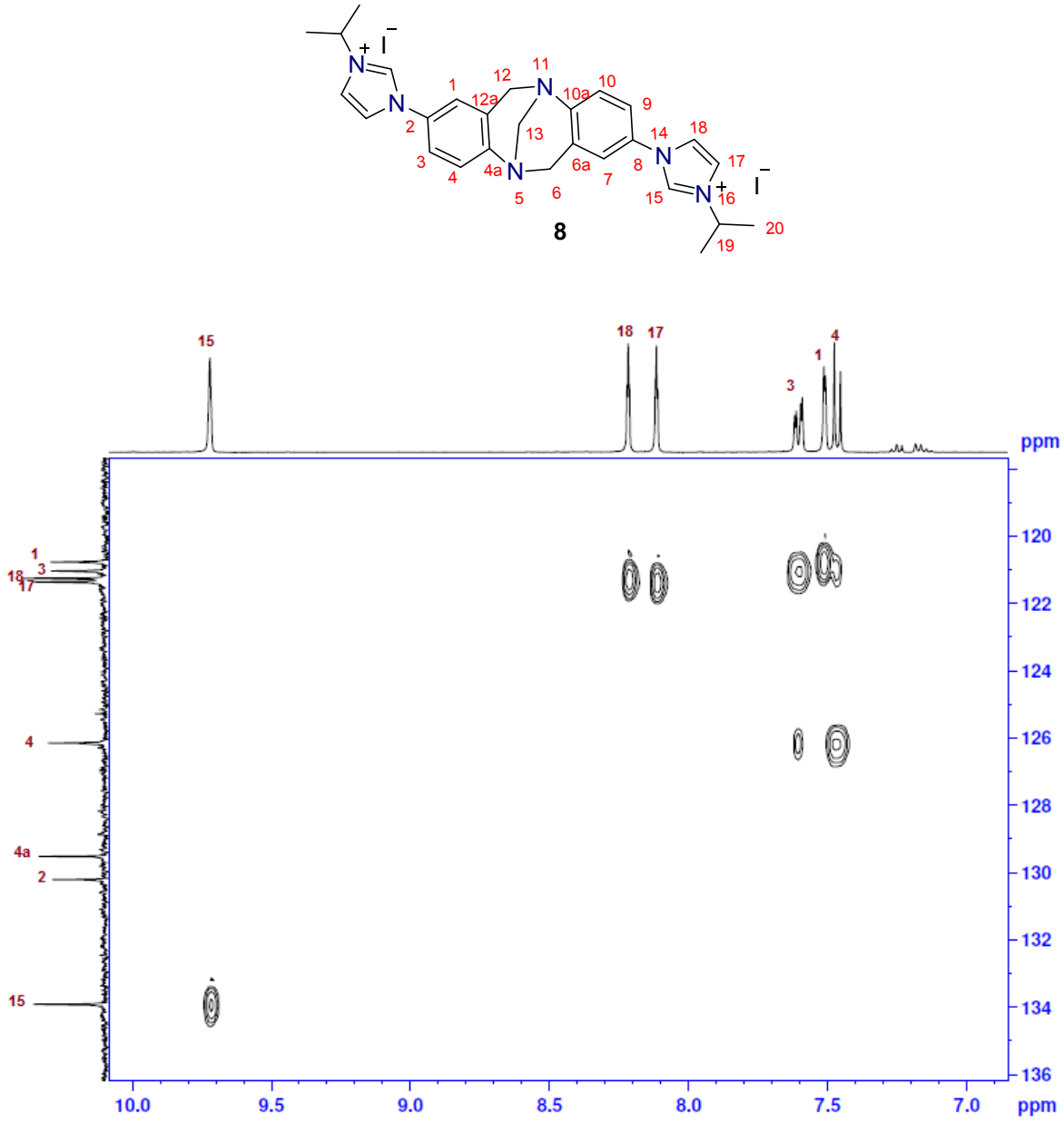


Figure S48: HMBC of 8 (400 MHz, DMSO-d_6, RT)

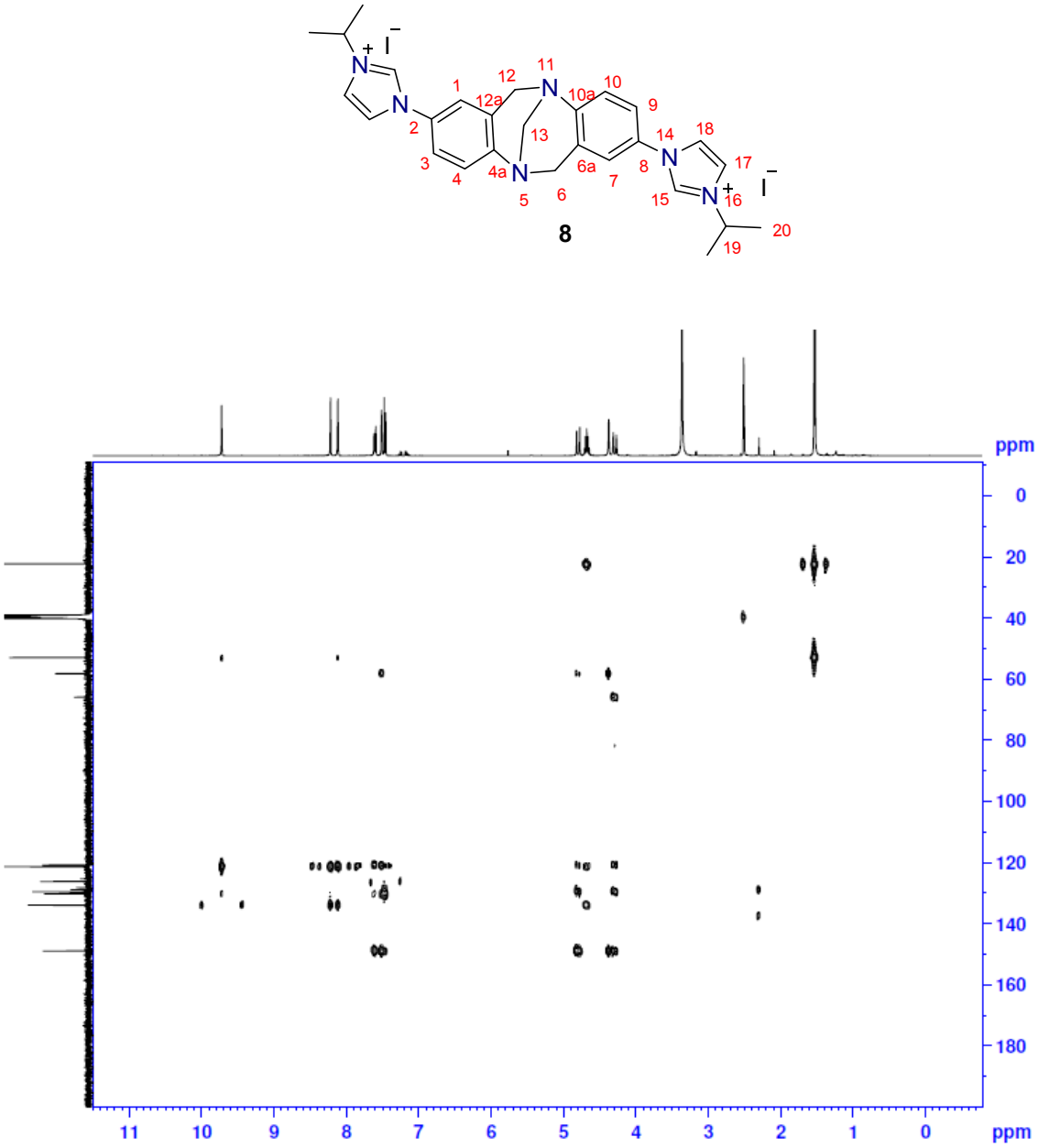


Figure S49: HMBC of 8 expansion

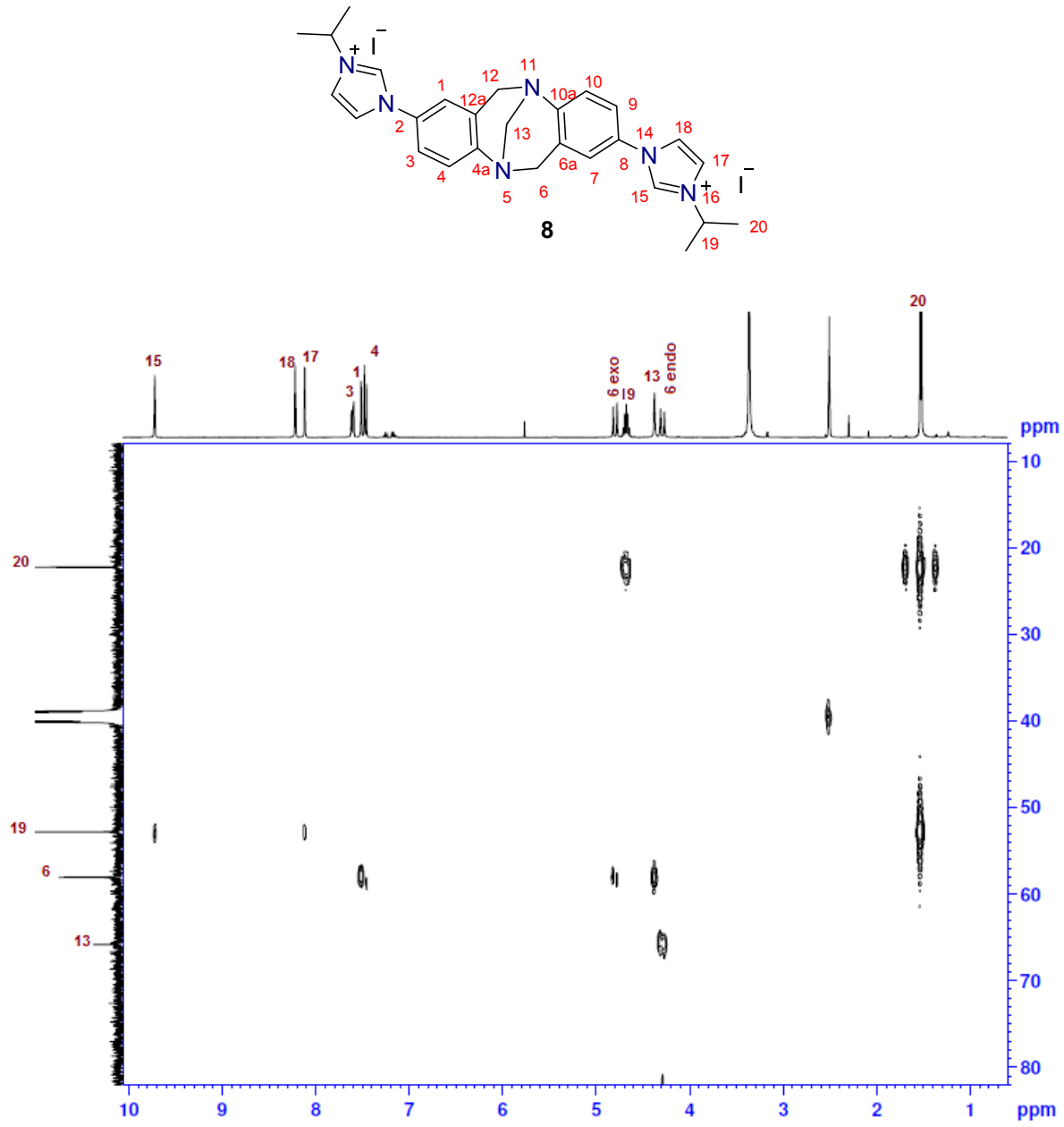


Figure S50: HMBC of 8 expansion

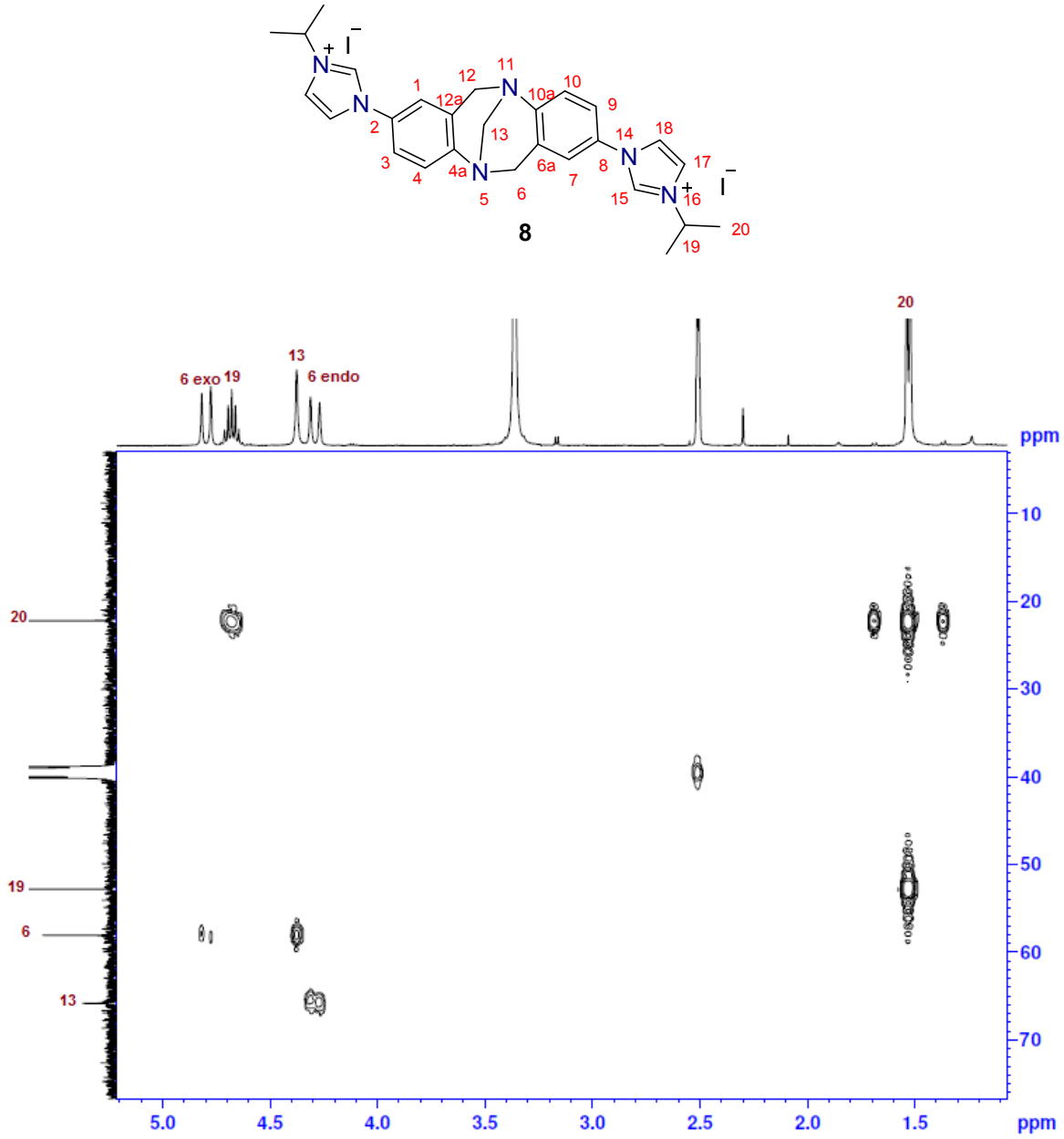
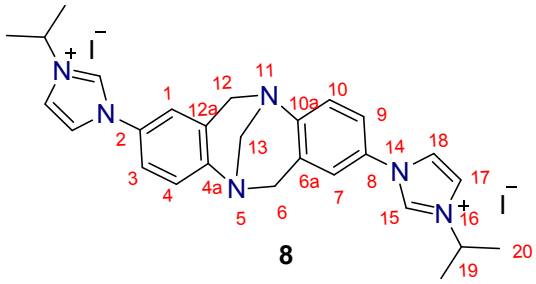


Figure S51: HMBC of 8 expansion



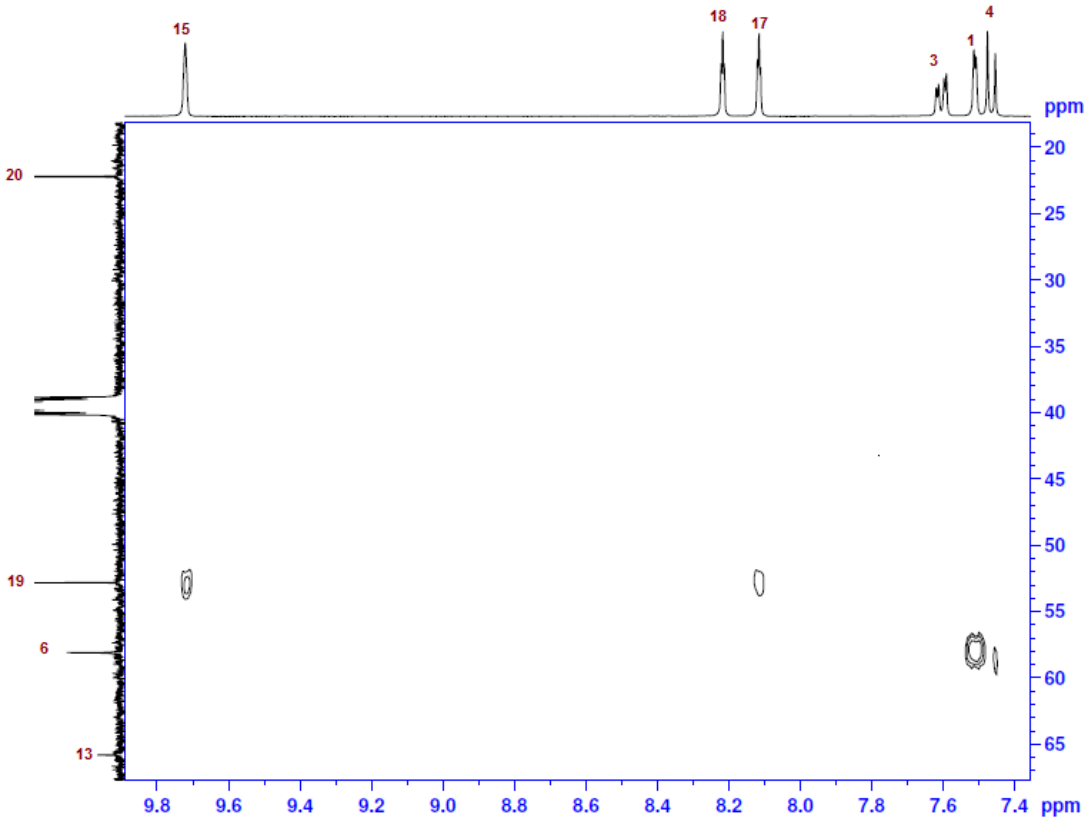


Figure S52: HMBC of 8 expansion

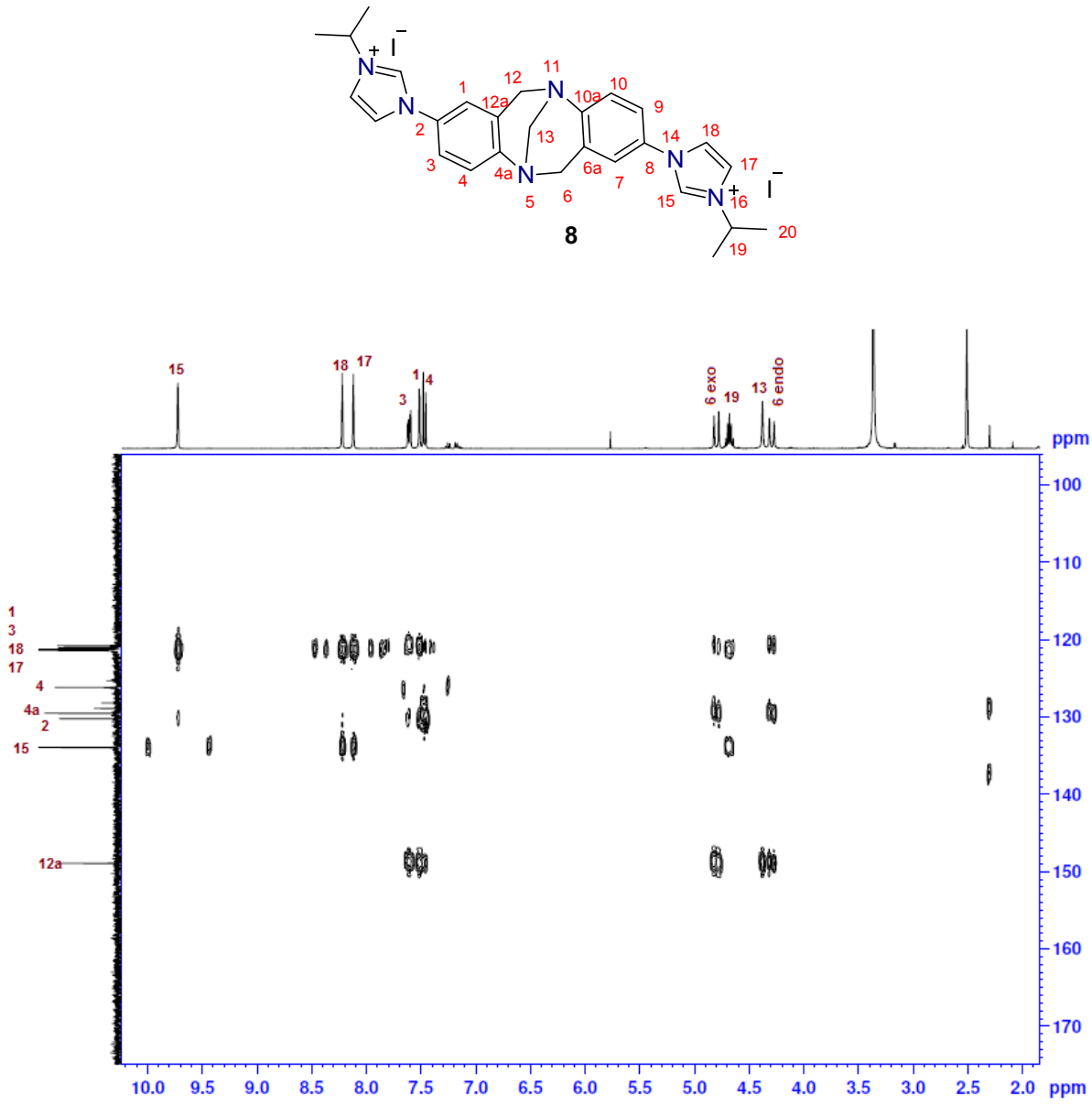


Figure S53: HSQC of 9 (400 MHz, DMSO-d_6, RT)

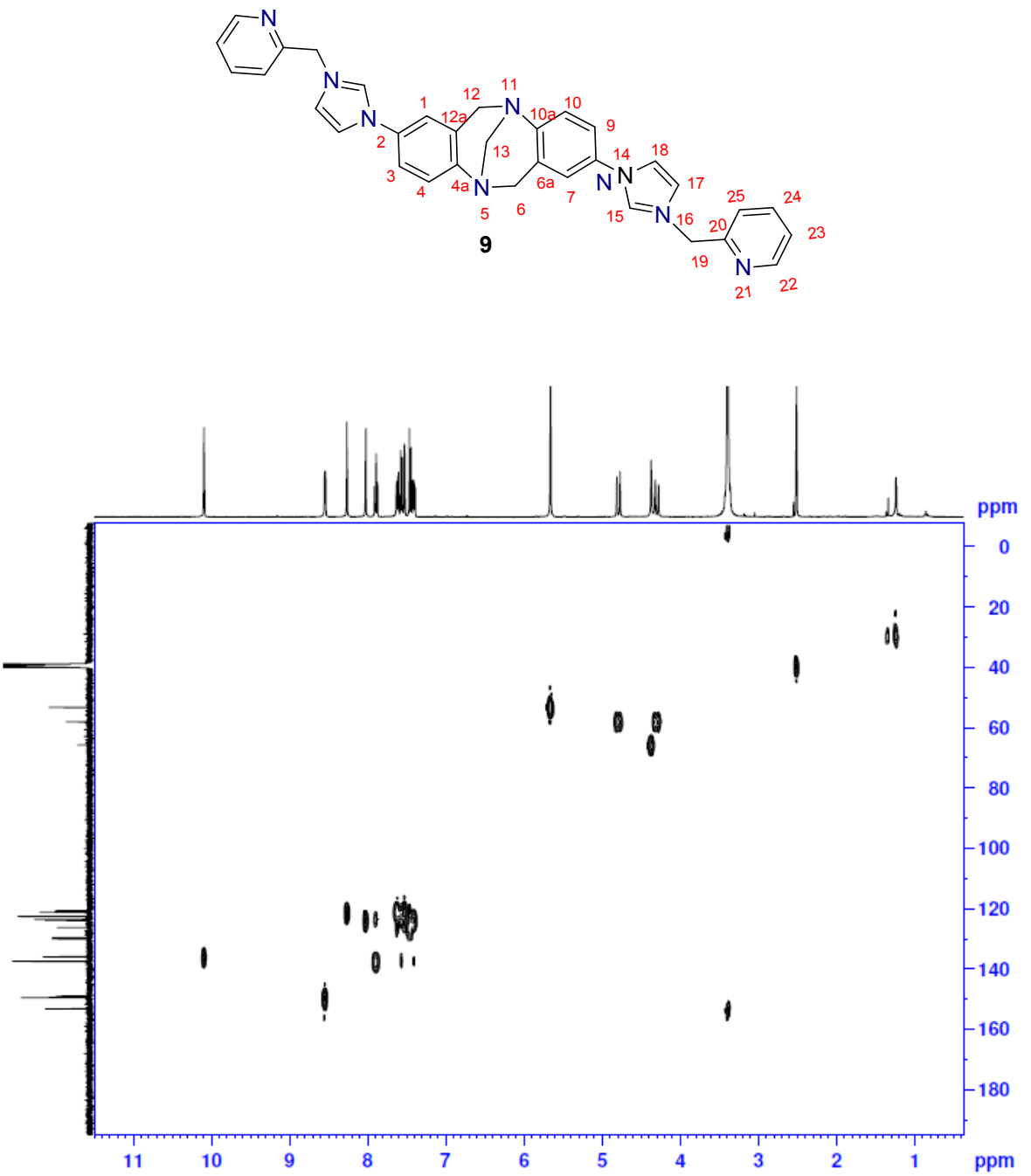
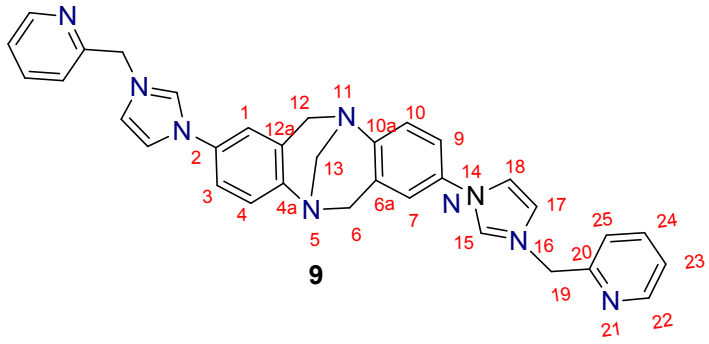


Figure S54: HSQC of 9 expansion



9

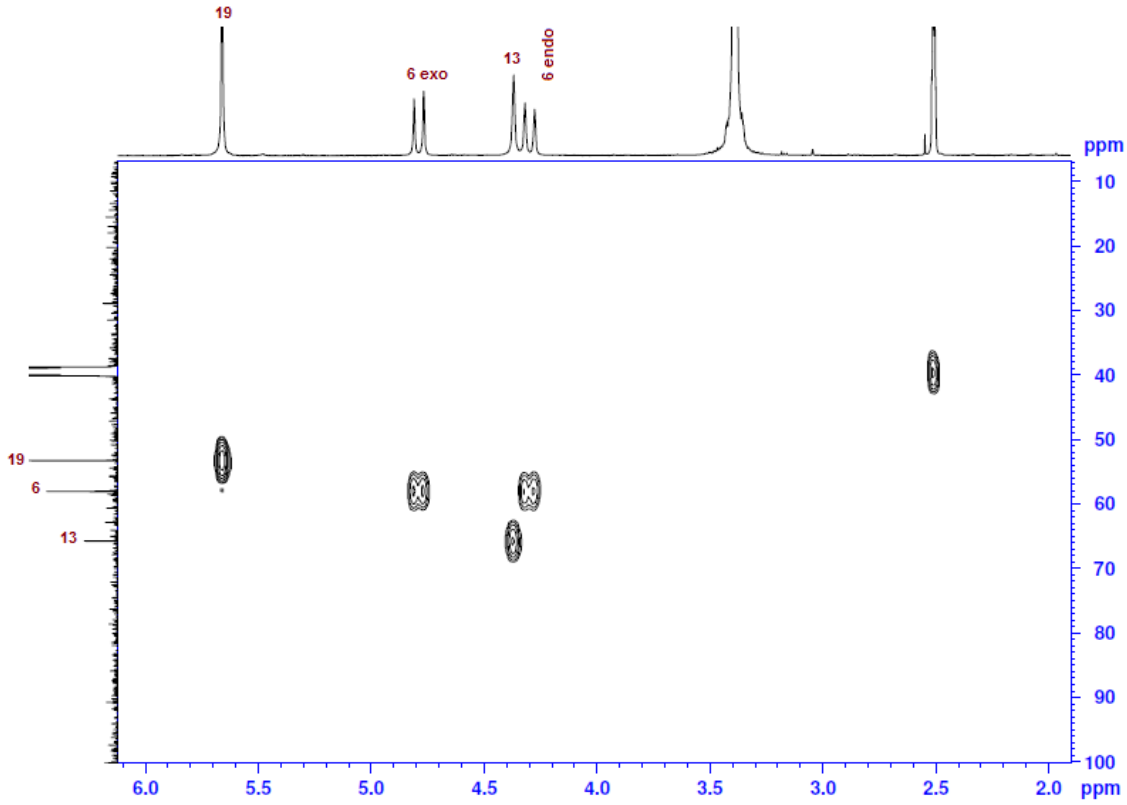


Figure S55: HSQC of 9 expansion

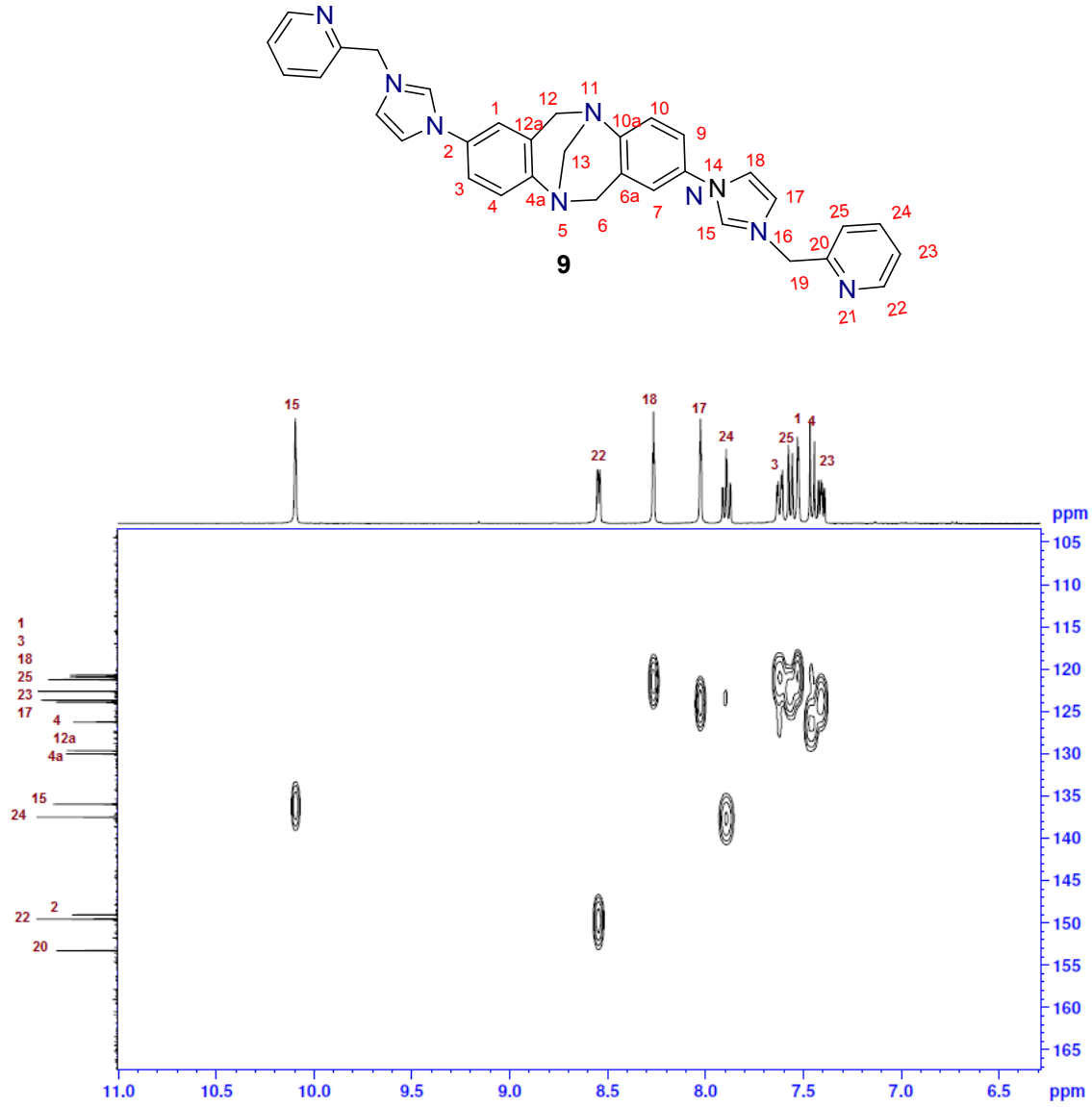


Figure S56: HSQC of 9 expansion

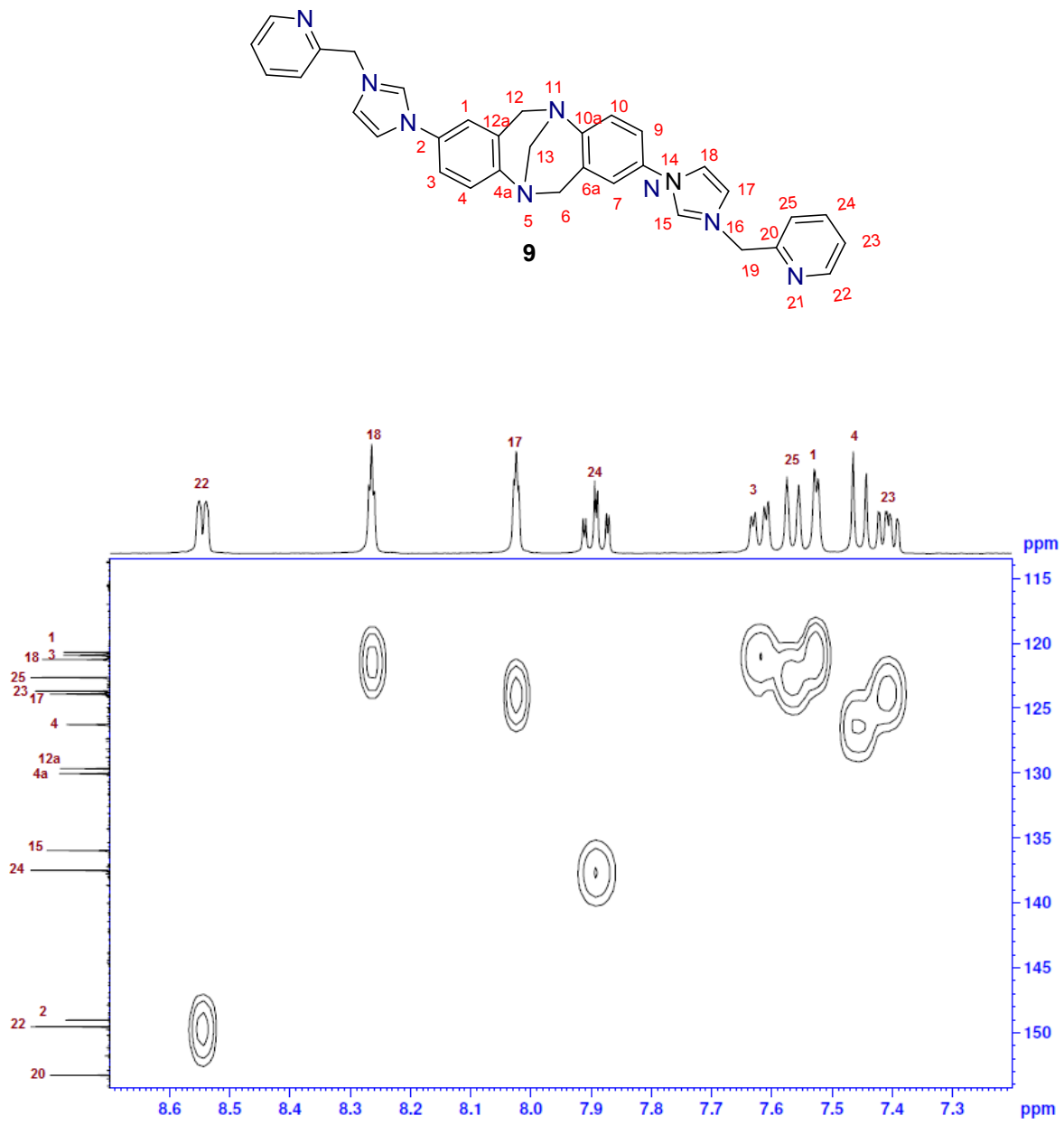


Figure S57: HMBC of 9 (400 MHz, DMSO-d_6, RT)

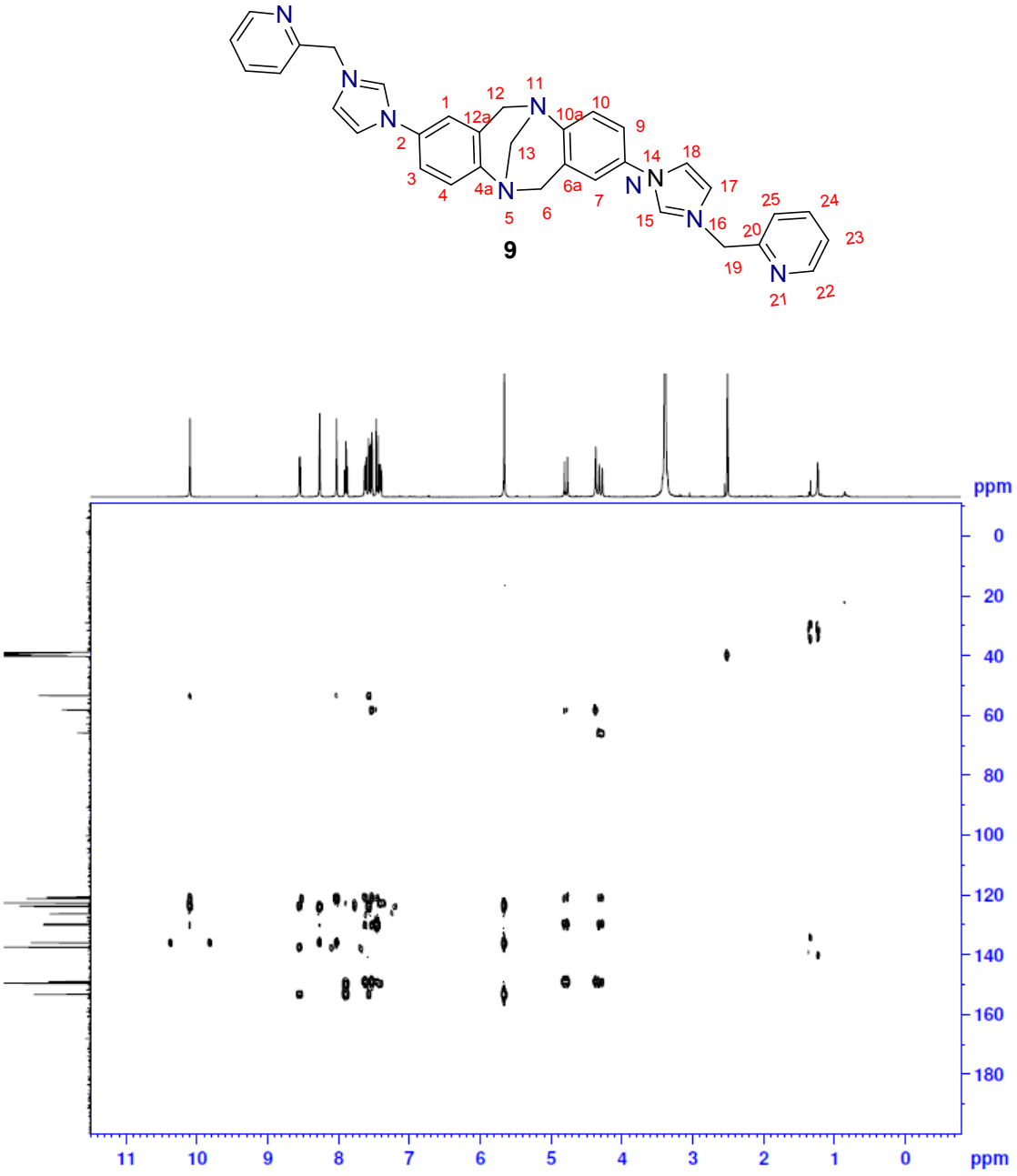


Figure S58: HMBC of 9 expansion

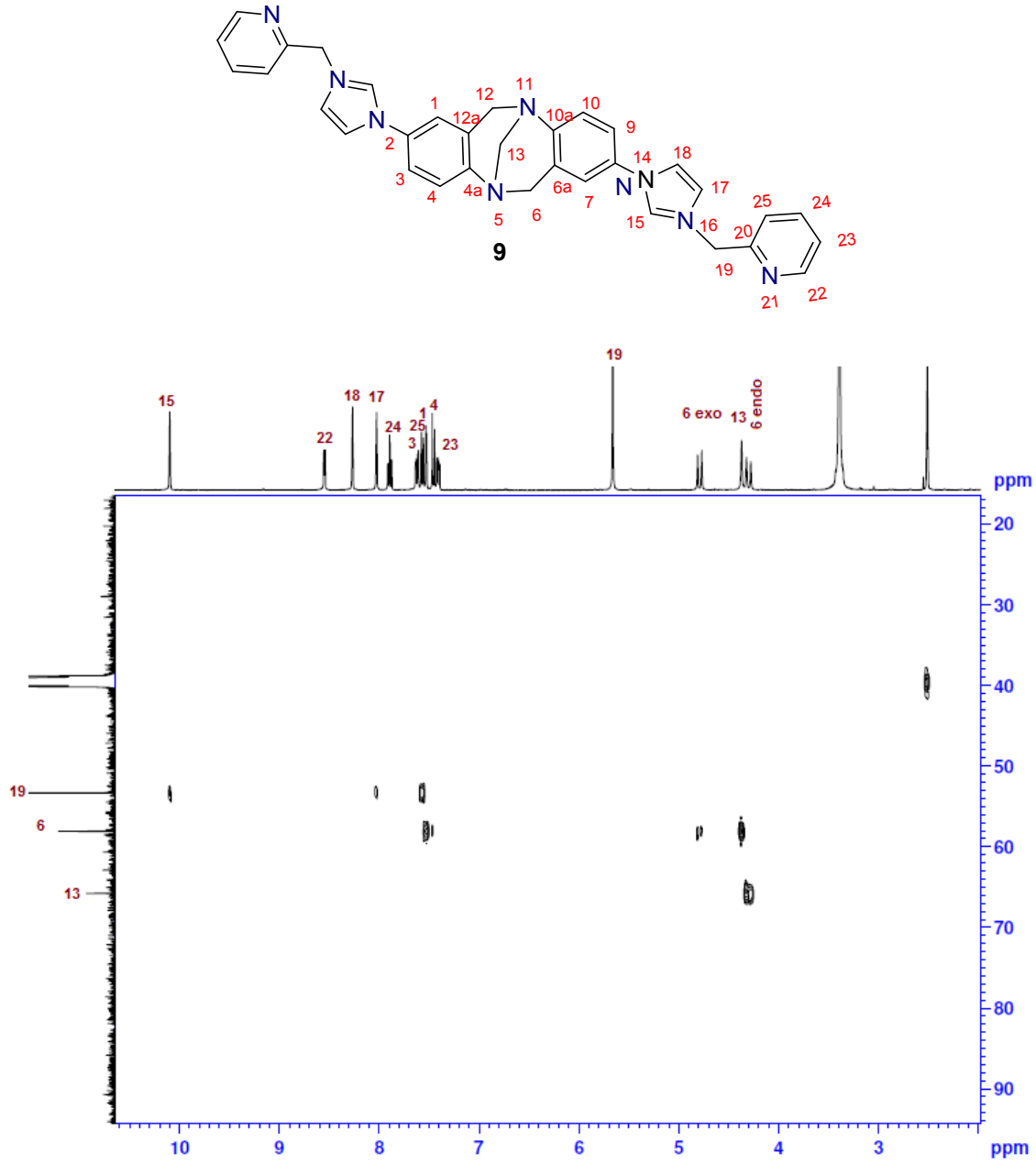


Figure S59: HMBC of 9 expansion

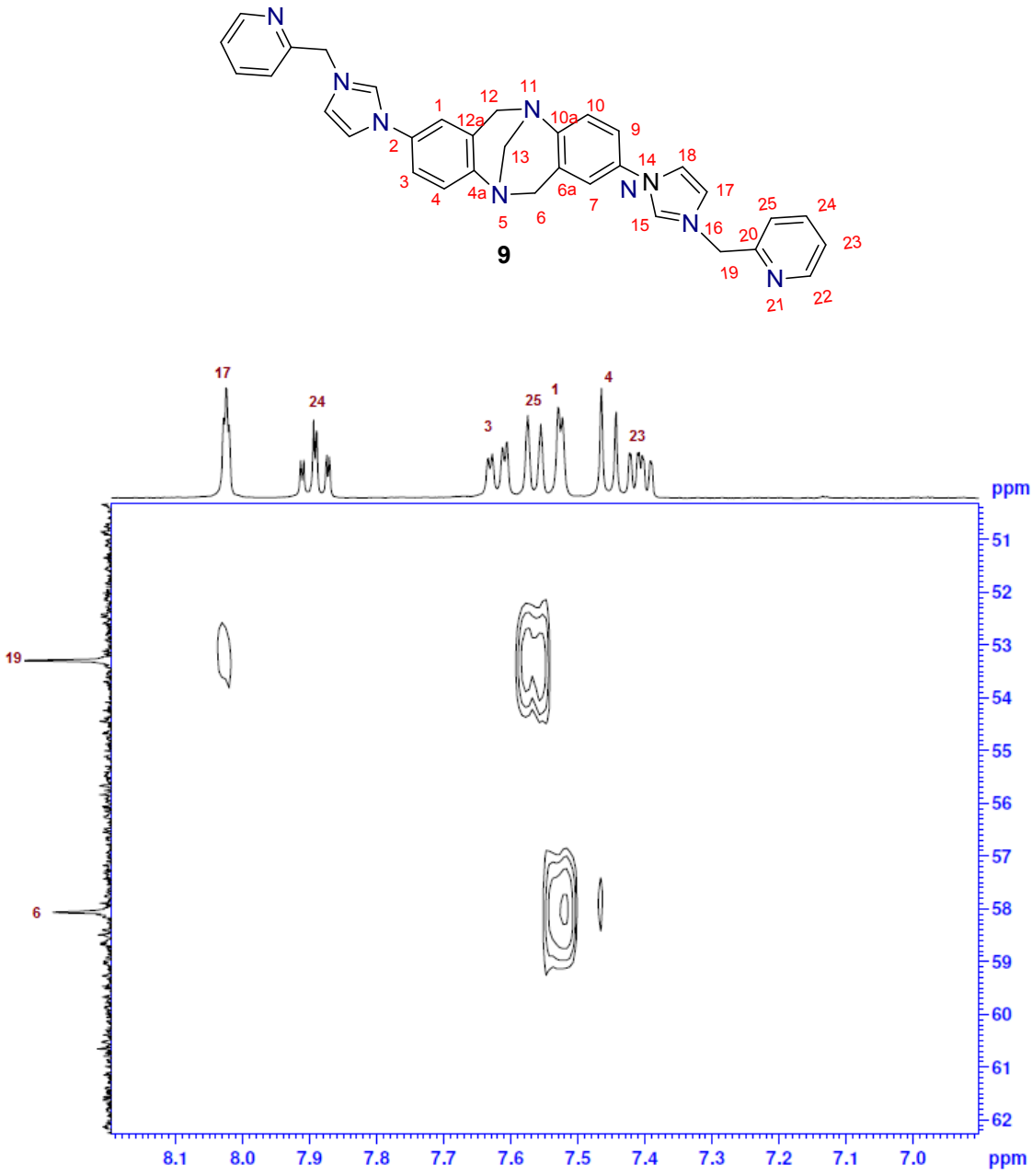


Figure S60: HMBC of 9 expansion

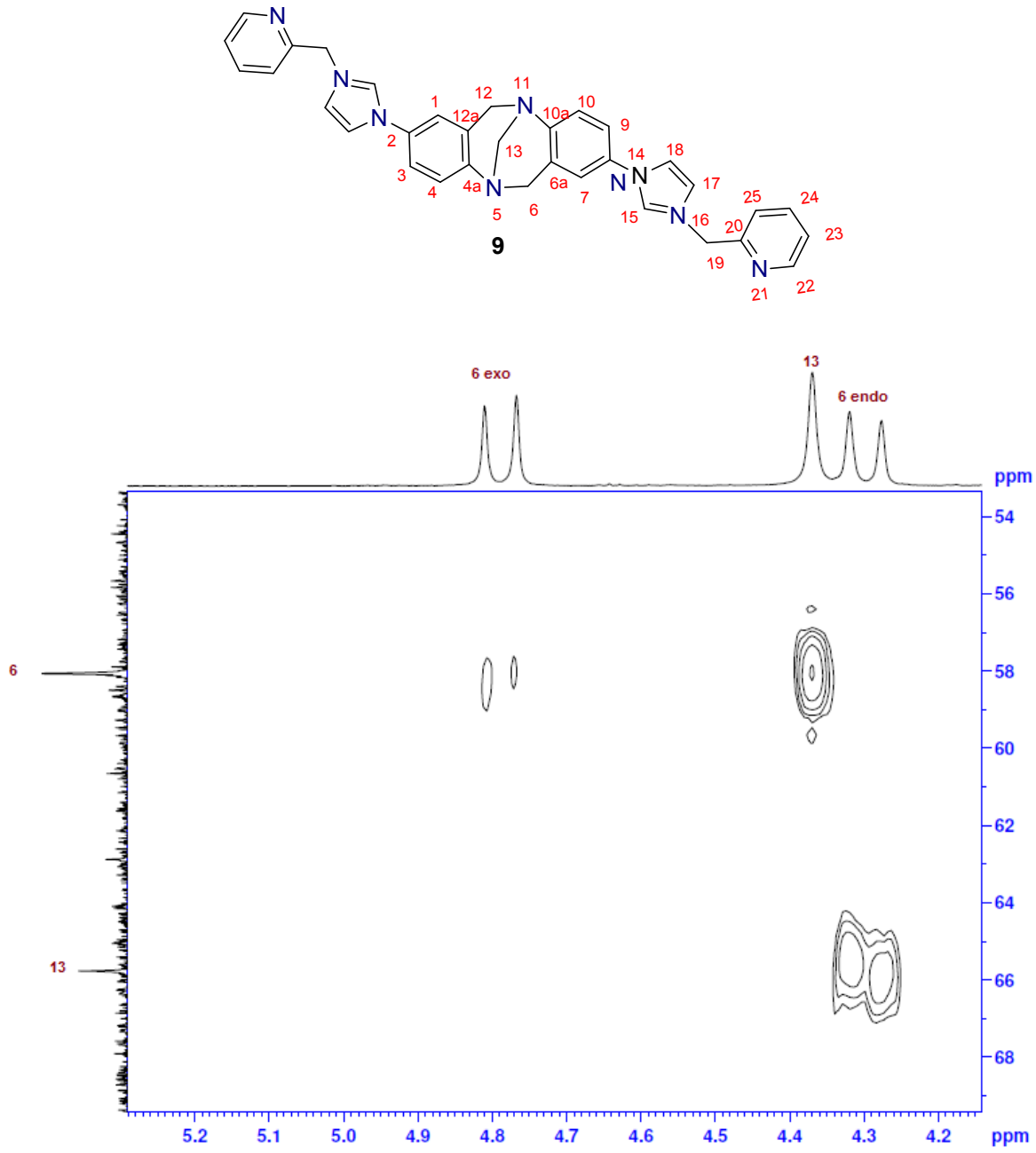


Figure S61: HMBC of 9 expansion

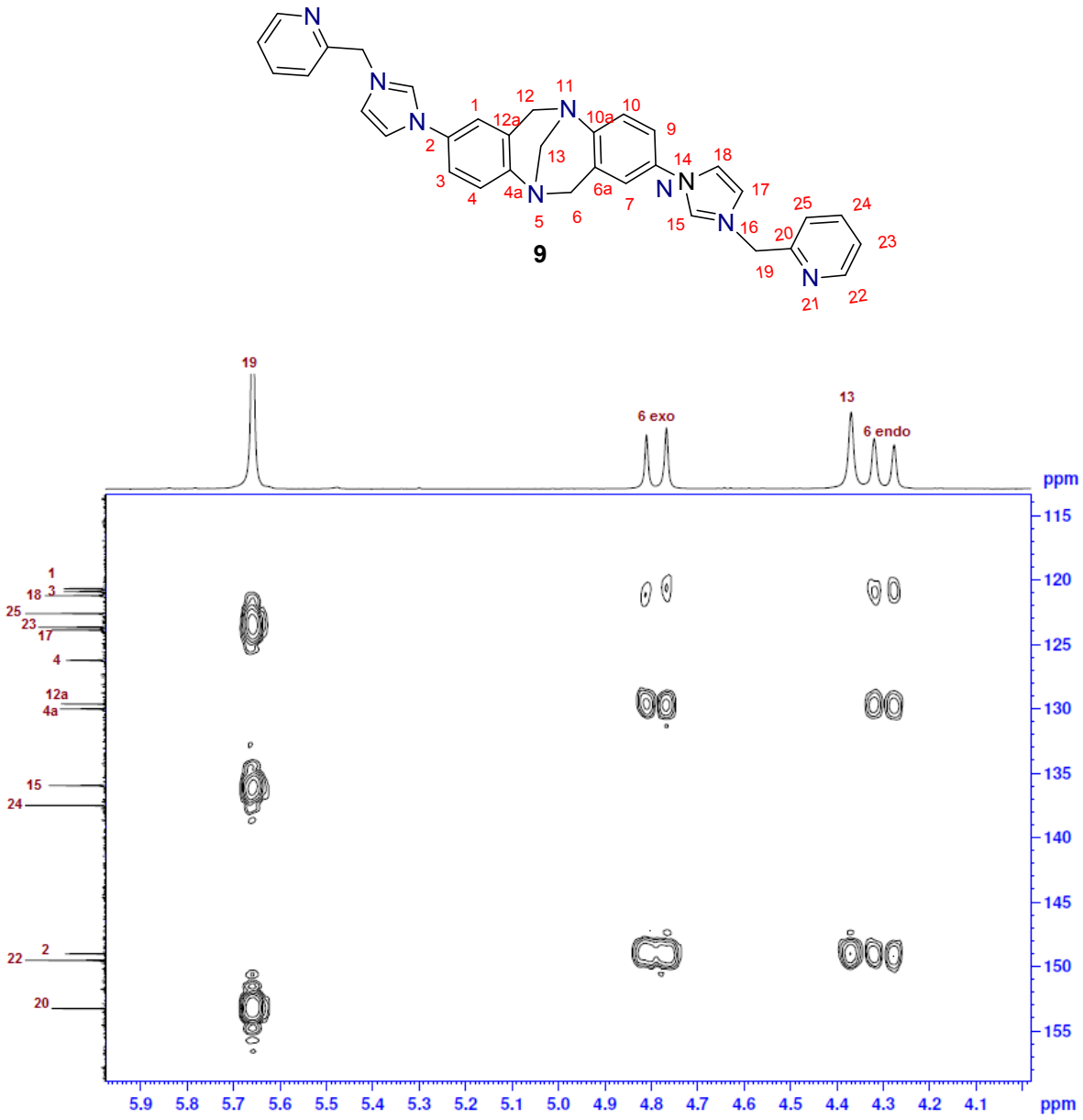


Figure S62: HMBC of 9 expansion

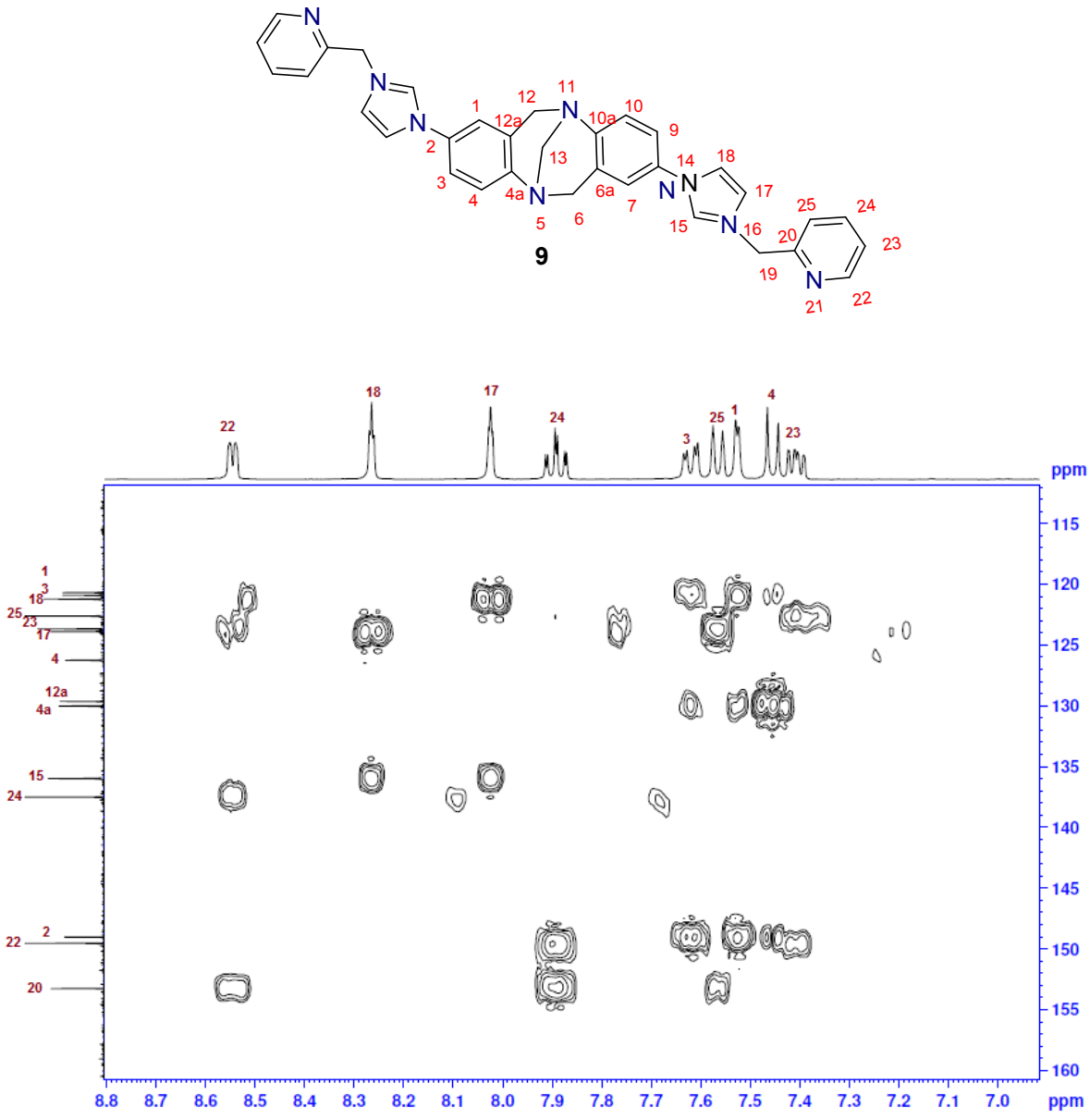


Figure S63: HMBC of 9 expansion

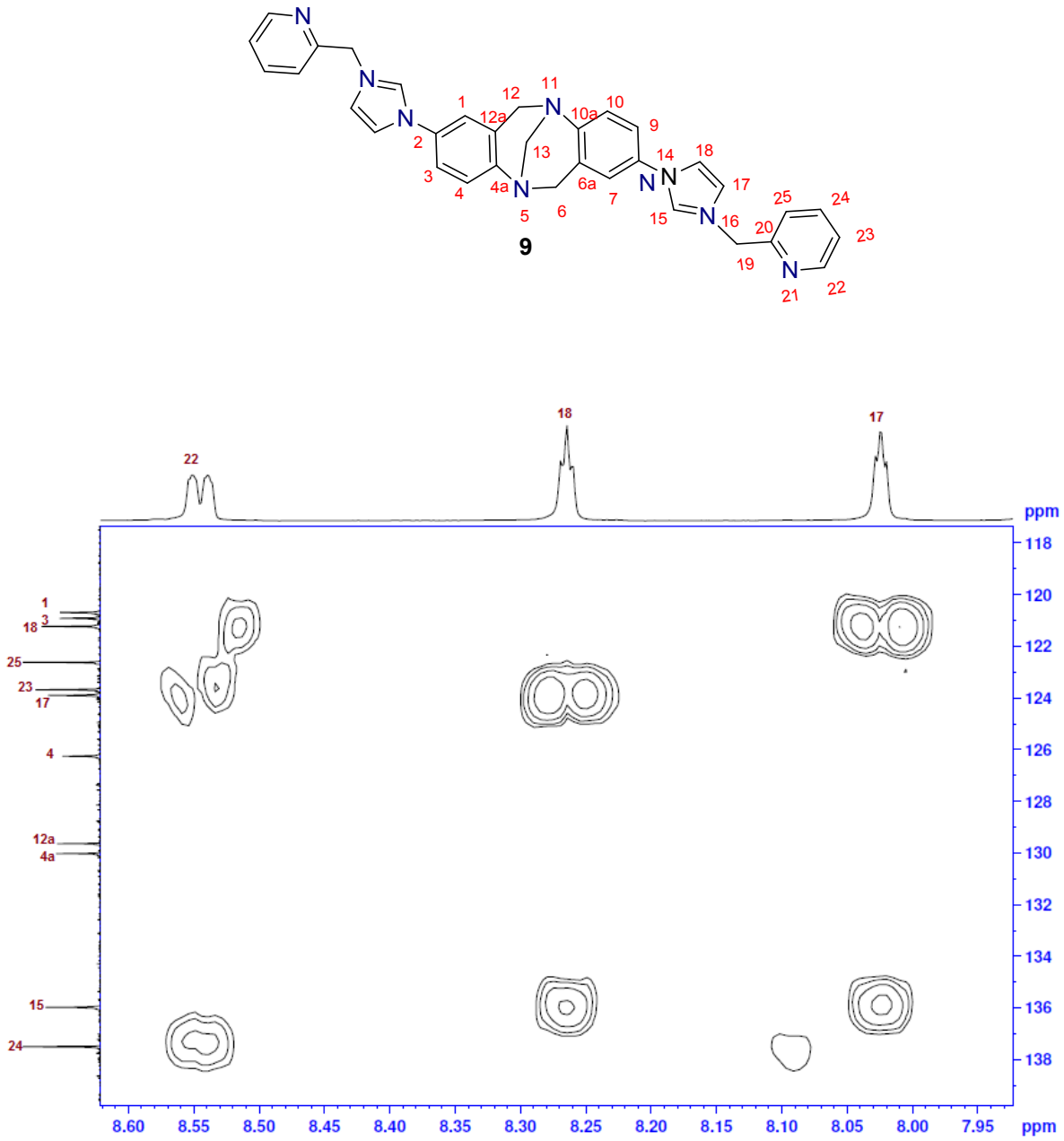


Figure S64: ^{1}H NMR spectrum (400 MHz, DMSO-d_6, RT) of 10 (type II)

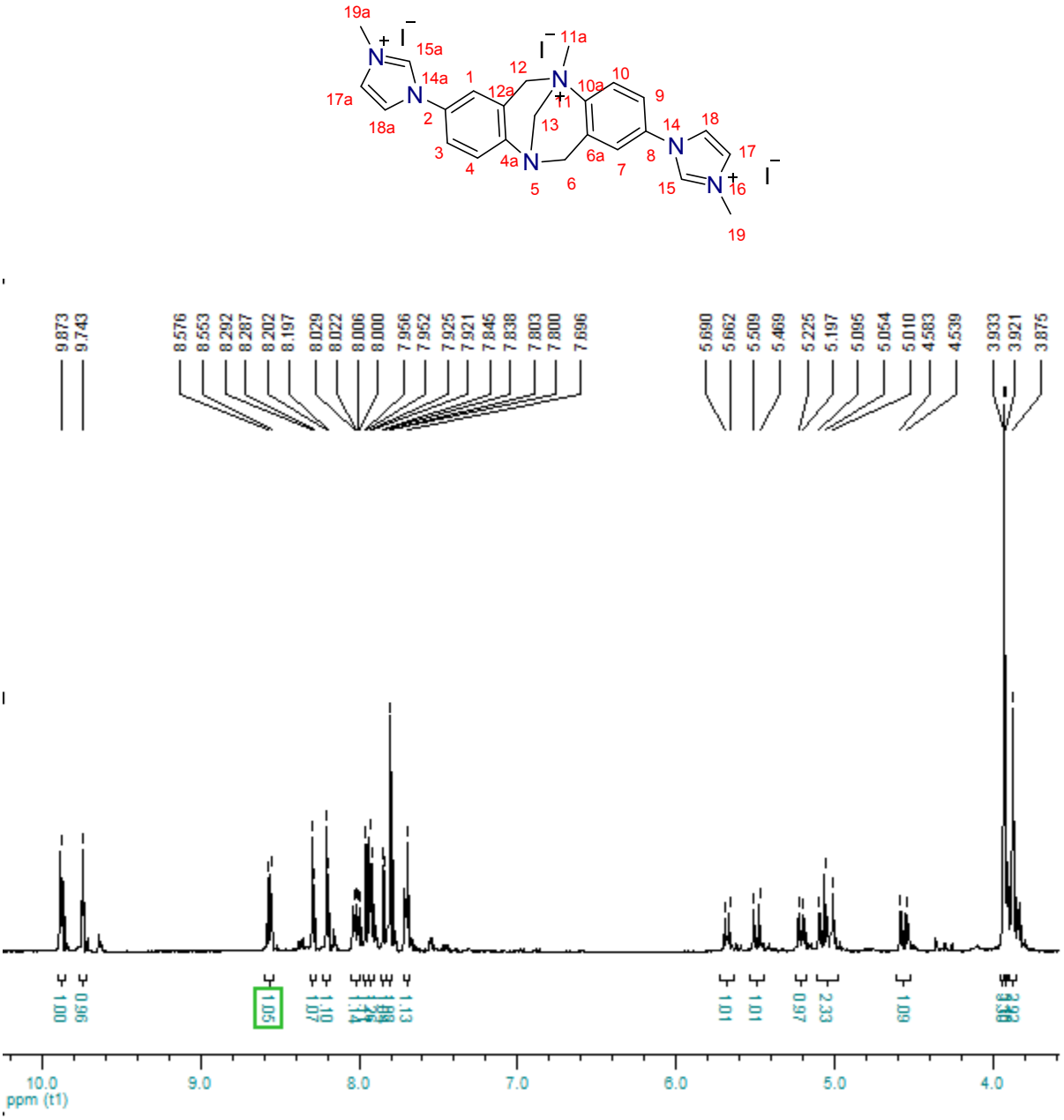


Figure S65: ^{13}C NMR spectrum (100 MHz, DMSO-d_6, RT) of 10 (type II)

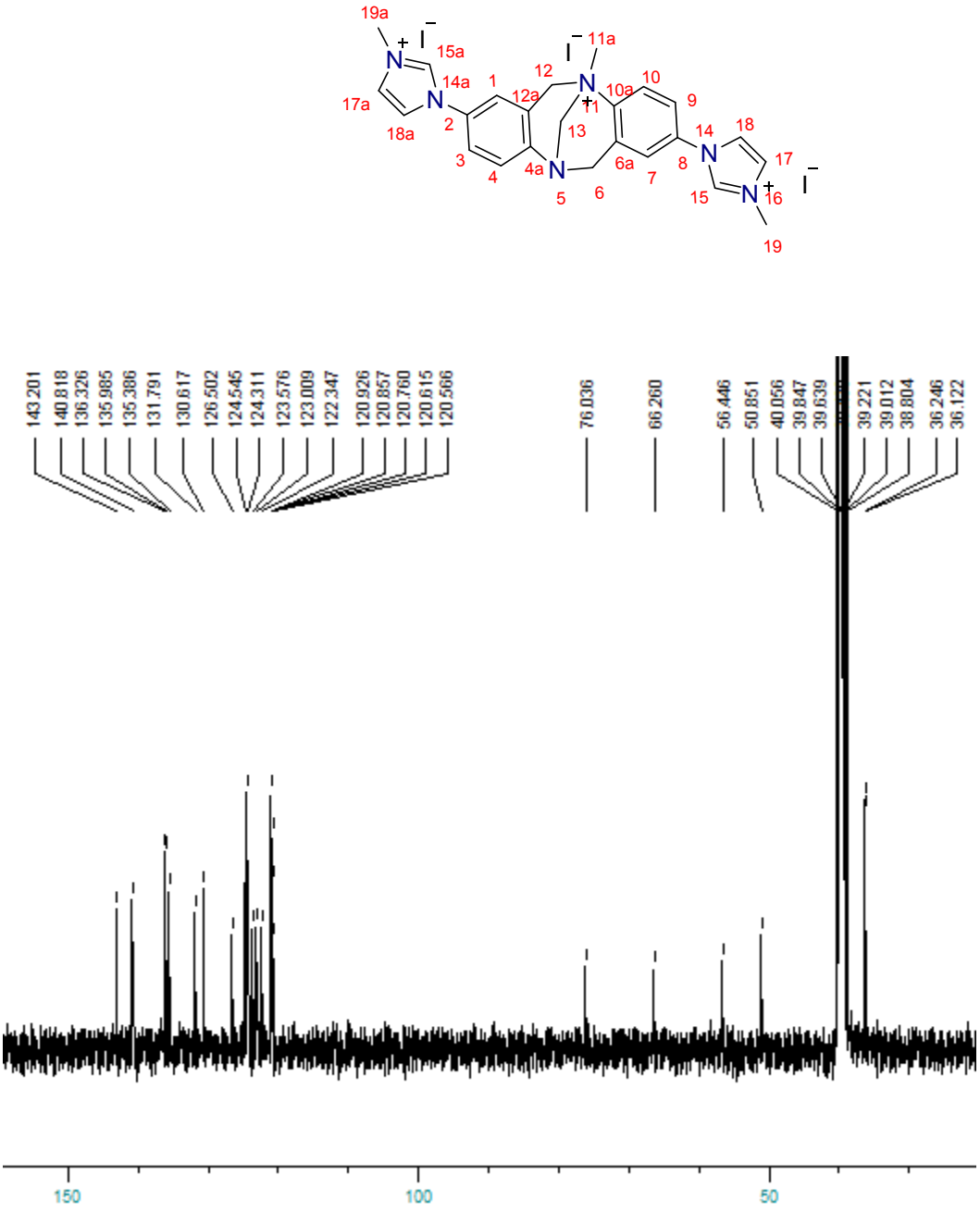


Figure S66: HRM spectrum of 3

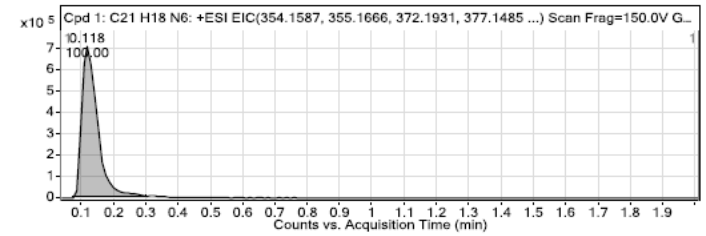
Compound Table

Compound Label	RT	Mass	Abund	Formula	Tgt Mass	Diff (ppm)	MFG Formula	DB Formula
Cpd 1: C21 H18 N6	0.118	354.1579	5098	C21 H18 N6	354.1593	-3.82	C21 H18 N6	C21 H18 N6

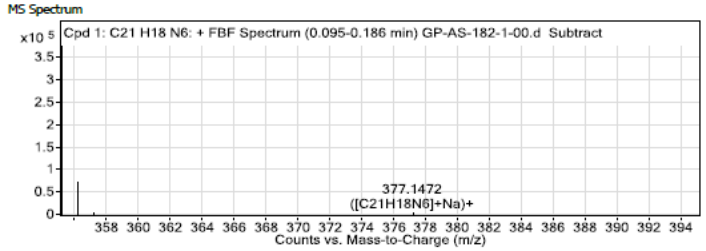
Compound Label	*m/z*	RT	Algorithm	Mass
Cpd 1: C21 H18 N6	377.1472	0.118	Find By Formula	354.1579

MS Spectrum Peak List

m/z	z	Abund	Formula	Ion
355.1651	1	375616.09	C21H18N6	(M+H)+
356.1686	1	75762.84	C21H18N6	(M+H)+
357.1716	1	8268.2	C21H18N6	(M+H)+



MS Spectrum



MS Zoomed Spectrum

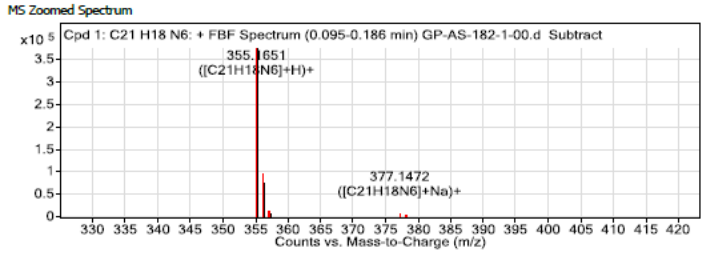
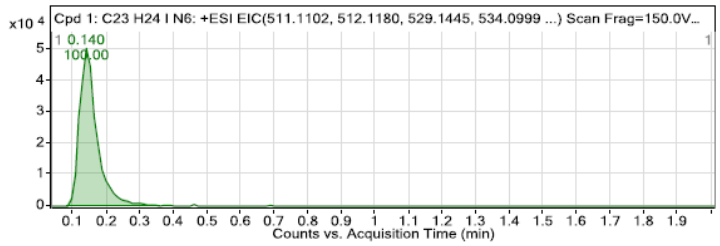


Figure S67: HRM spectrum of 5

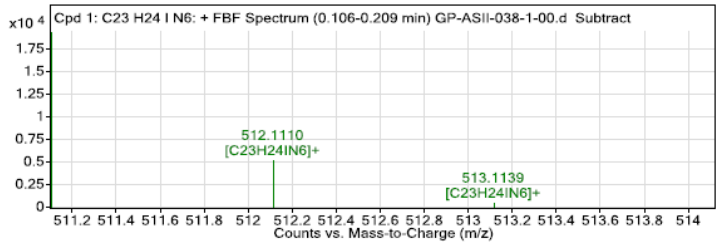
Compound Table

Compound Label	RT	Mass	Abund	Formula	Tgt Mass	Diff (ppm)	MFG Formula	DB Formula
Cpd 1: C23 H24 I N6	0.14	511.1086	19428	C23 H24 I N6	511.1107	-4.14	C23 H24 I N6	C23 H24 I N6

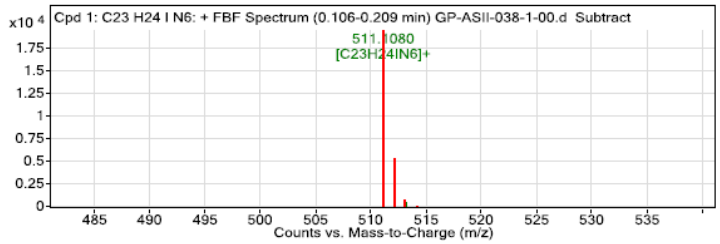
Compound Label	*m/z*	RT	Algorithm	Mass
Cpd 1: C23 H24 I N6	511.108	0.14	Find By Formula	511.1086



MS Spectrum



MS Zoomed Spectrum



MS Spectrum Peak List

m/z	z	Abund	Formula	Ion
511.108	1	19428.18	C23H24IN6	M+
512.111	1	5272.98	C23H24IN6	M+
513.1139	1	559.64	C23H24IN6	M+
514.1218	1	22.27	C23H24IN6	M+

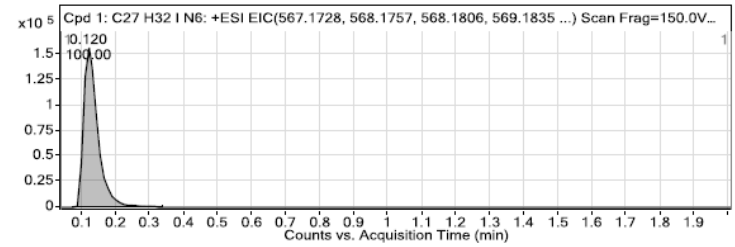
--- End Of Report ---

Figure S68: HRM spectrum of 6

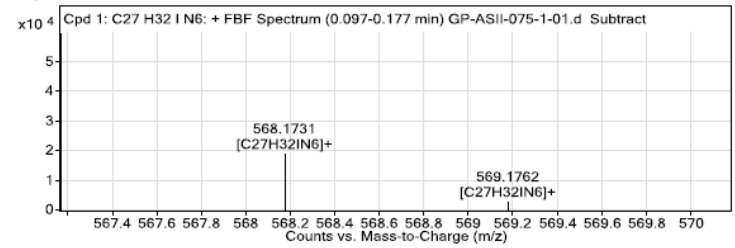
Compound Table

Compound Label	RT	Mass	Abund	Formula	Tgt Mass	Diff (ppm)	MFG Formula	DB Formula
Cpd 1: C27 H32 I N6	0.12	567.1708	59875	C27 H32 I N6	567.1733	-4.35	C27 H32 I N6	C27 H32 I N6

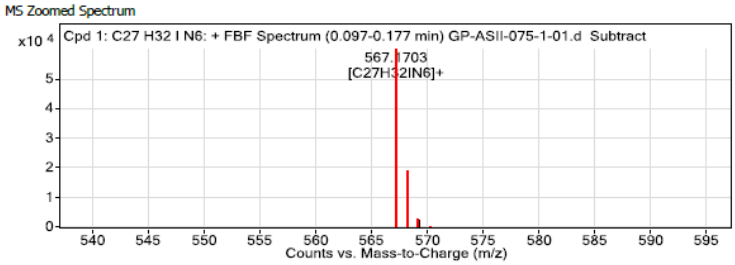
Compound Label	*m/z*	RT	Algorithm	Mass
Cpd 1: C27 H32 I N6	567.1703	0.12	Find By Formula	567.1708



MS Spectrum



MS Zoomed Spectrum



MS Spectrum Peak List

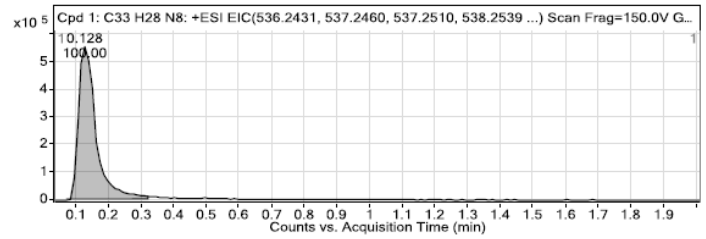
m/z	z	Abund	Formula	Ion
567.1703	1	59875.1	C27H32IN6	M+
568.1731	1	19133.39	C27H32IN6	M+
569.1762	1	2904.67	C27H32IN6	M+
570.1784	1	202.14	C27H32IN6	M+

Figure S69: HRM spectrum of 7

Compound Table

Compound Label	RT	Mass	Abund	Formula	Tgt Mass	Diff (ppm)	MFG Formula	DB Formula
Cpd 1: C33 H28 N8	0.128	536.2413	207118	C33 H28 N8	536.2437	-4.45	C33 H28 N8	C33 H28 N8

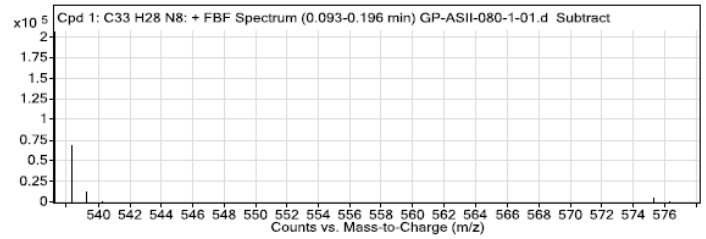
Compound Label	*m/z*	RT	Algorithm	Mass
Cpd 1: C33 H28 N8	537.2479	0.128	Find By Formula	536.2413



MS Spectrum Peak List

m/z	z	Abund	Formula	Ion
537.2479	1	207117.88	C33H28N8	(M+H)+
538.2514	1	69668.34	C33H28N8	(M+H)+
539.2543	1	12869.21	C33H28N8	(M+H)+
540.2571	1	1610.24	C33H28N8	(M+H)+
575.2236	1	5224.53	C33H28N8	(M+K)+
576.2249	1	1874.42	C33H28N8	(M+K)+
577.229	1	291.32	C33H28N8	(M+K)+
578.241	1	36.66	C33H28N8	(M+K)+

MS Spectrum



MS Zoomed Spectrum

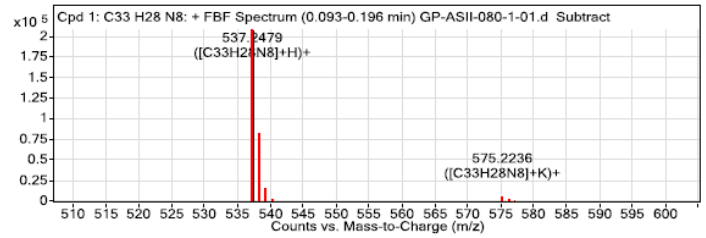
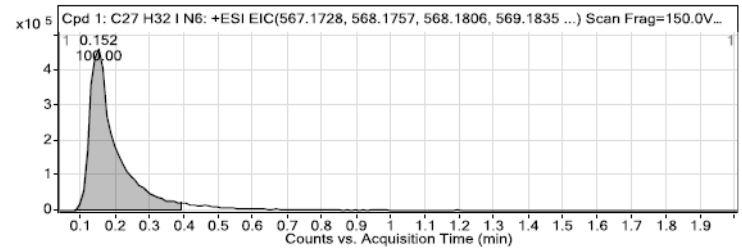


Figure S70: HRM spectrum of 8

Compound Table

Compound Label	RT	Mass	Abund	Formula	Tgt Mass	Diff (ppm)	MFG Formula	DB Formula
Cpd 1: C27 H32 I N6	0.152	567.1708	140445	C27 H32 I N6	567.1733	-4.49	C27 H32 I N6	C27 H32 I N6

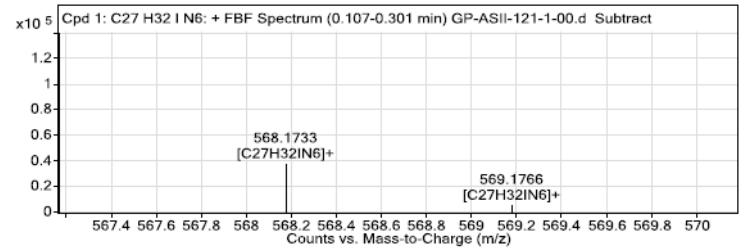
Compound Label	*m/z*	RT	Algorithm	Mass
Cpd 1: C27 H32 I N6	567.1702	0.152	Find By Formula	567.1708



MS Spectrum Peak List

m/z	z	Abund	Formula	Ion
567.1702	1	140444.5	C27H32IN6	M+
568.1733	1	38573.97	C27H32IN6	M+
569.1766	1	6100.02	C27H32IN6	M+
570.1791	1	623.26	C27H32IN6	M+

MS Spectrum



MS Zoomed Spectrum

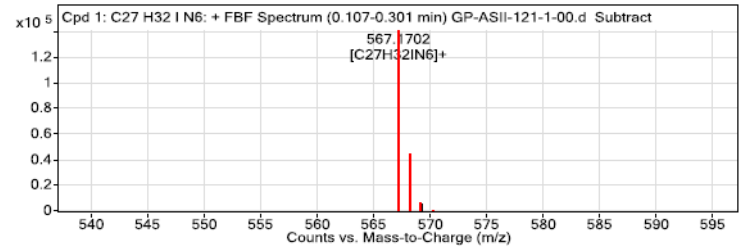
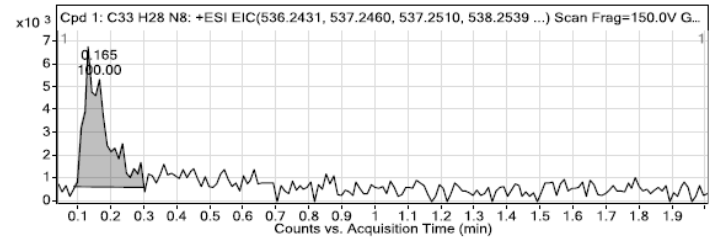


Figure S71: HRM spectrum of 9

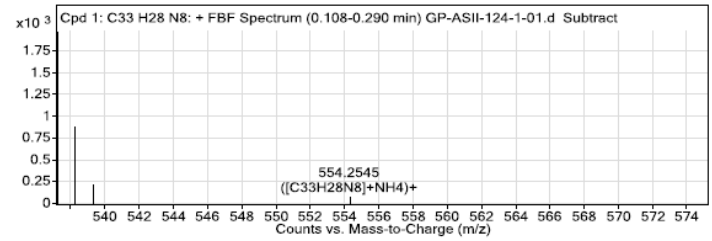
Compound Table

Compound Label	RT	Mass	Abund	Formula	Tgt Mass	Diff (ppm)	MFG Formula	DB Formula
Cpd 1: C33 H28 N8	0.165	536.2411	1975	C33 H28 N8	536.2437	-4.88	C33 H28 N8	C33 H28 N8

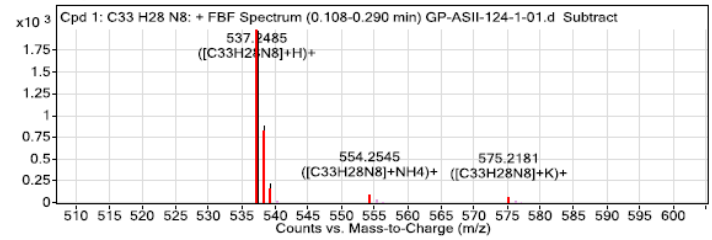
Compound Label	*m/z*	RT	Algorithm	Mass
Cpd 1: C33 H28 N8	537.2485	0.165	Find By Formula	536.2411



MS Spectrum



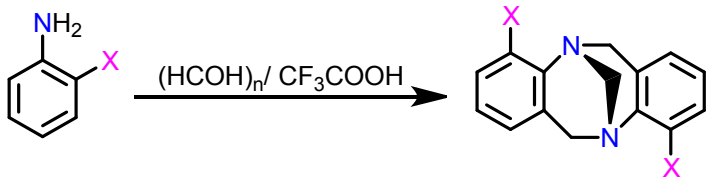
MS Zoomed Spectrum



MS Spectrum Peak List

m/z	z	Abund	Formula	Ion
537.2485	1	1975.08	C33H28N8	(M+H)+
538.252	1	884.58	C33H28N8	(M+H)+
539.2535	1	221.35	C33H28N8	(M+H)+
554.2545	1	81.82	C33H28N8	(M+NH4)+
575.2181	1	64.73	C33H28N8	(M+K)+

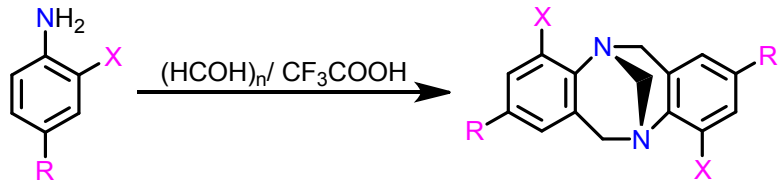
Table S1: Known 4,10-dihalogen and imidazole substituted methano dibenzo-diazocines.



Entry	X	Yield%	Reference
1	F	27	[1]
2	Cl	19	[1]
3	Br	9,10	[1]
4	I	6[a]	[3]
5	Imidazole	79%	**This work**

a) Isolated an impure product

Table S2: Known 4,10-di substituted methano dibenzo-diazocines with substituents at 2,8-positions.



Entry	R	X	Yield%	Reference
1	Me	Br	85, 98	[1] [5]
2	Me	Cl	77	[1]
3	Me	F	75	[1]
4	Me	I	30	[1]
5	Bu^t	Br	30	[6]
6	Me	NO_2	36	[2]
7	OMe	CO_2Hexyl	16	[7]
8	Me	CO_2Hexyl	16	[7]
9	Br	Br	33, 60, 72	[8] [9], [4]
10	Br	Cl	86	[4]
11	CF_3	CF_3	5	[6]
12	CO_2Et	Br	48	[7]
13	CO_2Hexyl	Br	88	[7]
14	NO_2	Br	28	[2]

Table S3: NMR comparison of 4,10-dihalo Träger's base analogues with 3.

	No.	*1/7*	*2/8*	*3/9*	*4/10*	*4a/10a*	*6/12*	*6/12*	*13*	*6a/12a*
	X						*endo*	*exo*		
^{1}H NMR	Br[(a)]	6.91-6.96 (m)	6.91-6.96 (m)	7.46 (d,d) J=6.7, 2.6 Hz	-	-	4.379(d) J=17.3 Hz	4.62 (d) J=17.3 Hz	4.39 (s)	-
	Cl[(a)]	6.90 (d,d) J=7.7, 0.8 Hz	6.99 (t) J=7.7 Hz	7.27 (d,d) J=7.7, 0.8 Hz	-	-	4.35 (d) J=17.6 Hz	4.63 (d) J=17.6 Hz	4.38 (s)	-
	F[(a)]	6.76 (d) J=7.3 Hz	6.90-7.00 (m)	6.90-7.00	-	-	4.23 (d) J=17.1 Hz	4.63 (d) J=17.1 Hz	4.32 (s)	-
	Im[(b)]	6.82 (d) J=7.6 Hz	7.09 (d) J=7.6 Hz	7.04 (t) J=7.6 Hz	-	-	3.33 (d) J=17.2 Hz	4.26 (d) J=17.2	4.32 (s)	-
^{13}C NMR	Br[(a)]	126.47	125.76	131.69	120.27	144.92	55.6		67.72	131.06
	Cl[(a)]	125.79	125.10	128.49	129.45	143.67	54.97		67.69	130.59
	F[(a)]	122.54	124.54	114.06	156.32	145.23	55.38		67.42	130.30
	Im[(b)]	126.80	123.77	124.50	129.59	131.59	54.18		66.79	140.94

a) Listed spectral values are taken from: A. Hansson, J. Jensen, O. F. Wendt and K. Wärnmark, Eur. J. Org. Chem., 2003, 3179.

b) Present work.

Table S4. Crystallographic data, details of data collection and structure refinement parameters for compounds 3-7.

parameters	**3a**	**3b**	**4**	**5**	**6**	**7**
Empirical formula	$C_{5.25}H_5N_{1.5}O_{0.25}$	$C_{5.25}H_{4.5}N_{1.5}$	$C_{21}HN_6$	$C_{23}H_{24}I_2N_6$	$C_{6.75}H_8N_{1.5}I_{0.5}$	$C_{16.5}H_{15}N_4ClO_{0.5}$
Formula weight	372.43	372.43	354.42	638.30	694.40	625.56
Temperature/K	150	150	150	298	150	150
Crystal system	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic	triclinic
Space group	$P2_1/c$	$P2_1/c$	C2/c	$P2_1/c$	C2/c	$P\bar{1}$
a/Å	12.8104(4)	12.9360(5)	25.140(4)	10.9300(2)	10.1807(5)	8.3442(10)
b/Å	9.7998(2)	9.8962(3)	5.5409(5)	16.8443(3)	13.9648(7)	12.5633(12)
c/Å	15.3326(4)	15.4643(5)	13.9897(17)	14.0472(3)	20.5397(9)	15.0779(16)
α/°	90	90	90	90	90	84.154(8)
β/°	113.436(3)	113.922(4)	122.157(19)	107.695(3)	101.629(5)	79.178(10)
γ/°	90	90	90	90	90	87.113(9)
Volume/Å^3	1766.04(9)	1809.63(12)	1649.8(5)	2463.83(10)	2860.2(2)	1543.7(3)
Z	4	4	4	4	4	2
ρ_{calc}mg/mm^3	1.4006	1.3669	1.4268	1.7206	1.6125	1.3458
μ/mm^{-1}	0.734	0.717	0.712	20.220	17.468	2.223
F(000)	786.4	786.4	746.2	1242.1	1370.3	655.2
2Θ range for data collection	6.28 to 141.42°	7.48 to 141.58°	8.3 to 140.76°	6.6 to 141.54°	8.8 to 141.38°	7.08 to 142.48°
Reflections collected	6629	7054	2878	10257	5536	8560
Independent reflections	3321[R(int) = 0.0257]	3405[R(int) = 0.0225]	1547[R(int) = 0.0269]	4654[R(int) = 0.0464]	2707[R(int) = 0.0341]	5183[R(int) = 0.0338]
Data/restraints/parameters	3321/0/263	3405/0/253	1547/0/122	4654/0/282	2707/0/162	5183/0/401
Goodness-of-fit on F^2	1.053	1.044	1.040	1.045	1.021	1.090
Largest diff. peak/hole / e Å^{-3}	0.26/-0.27	0.70/-0.65	0.23/-0.30	1.40/-2.08	0.71/-0.76	0.54/-0.51

Final R indexes [I>=2σ (I)]	R_1 = 0.0400, wR_2 = 0.1079	R_1 = 0.0578, wR_2 = 0.1571	R_1 = 0.0410, wR_2 = 0.1152	R_1 = 0.0520, wR_2 = 0.1422	R_1 = 0.0325, wR_2 = 0.0838	R_1 = 0.0723, wR_2 = 0.2241

Table S5. The bond distances and angles comparison of 3-7.

	3a	**3b**	**4**	**5**	**6**	**7**
			Bond lengths (Å)			
N_a–C_a	1.471(17)	1.471(2)	1.467(18)	1.461(7)	1.473(4)	1.471(6)
N_b–C_a	1.464(17)	1.463(3)	1.467(18)	1.469(7)	1.473(4)	1.461(7)
			Bond angles (^{o})			
N_a–C_a–N_b	111.90(11)	112.00(16)	111.45(18)	111.6(4)	111.1(5)	111.4(5)
N_c–C_h–N_d	111.79(13)	112.4(2)	112.26(15)	108.4(4)	109.2(4)	109.2(6)
N_e–C_i–N_f	112.01(12)	112.2(2)	112.26(15)	108.7(5)	109.2(4)	107.8(5)

Table S6: Single Crystal X-Ray Parameters of 10.

Crystal system	monoclinic
Space group	$P2_1/b11$
a/Å	18.3095(7)
b/Å	9.4486(2)
c/Å	36.0558(11)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	6237.6(3)
Reflections collected	10885
Independent reflections	6946[R(int) = 0.1001]
Data/restraints/parameters	6946/0/597
Largest diff. peak/hole / e Å^{-3}	4.35/-5.34

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