

Supporting Information

Preferential Protonation and Methylation Site of the Thiopyrimidine Derivatives in Solution. NMR Data.

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NMR spectra.

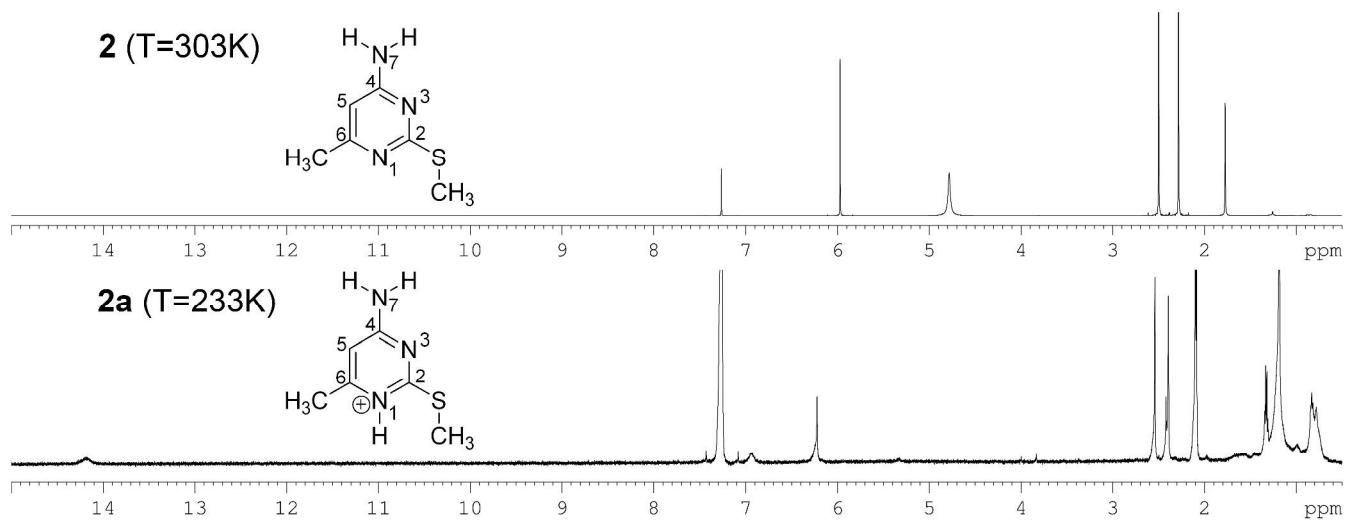


Figure S1. 1D ¹H NMR spectra in CDCl₃ of **2** (T=303K), **2a** (T=233K).

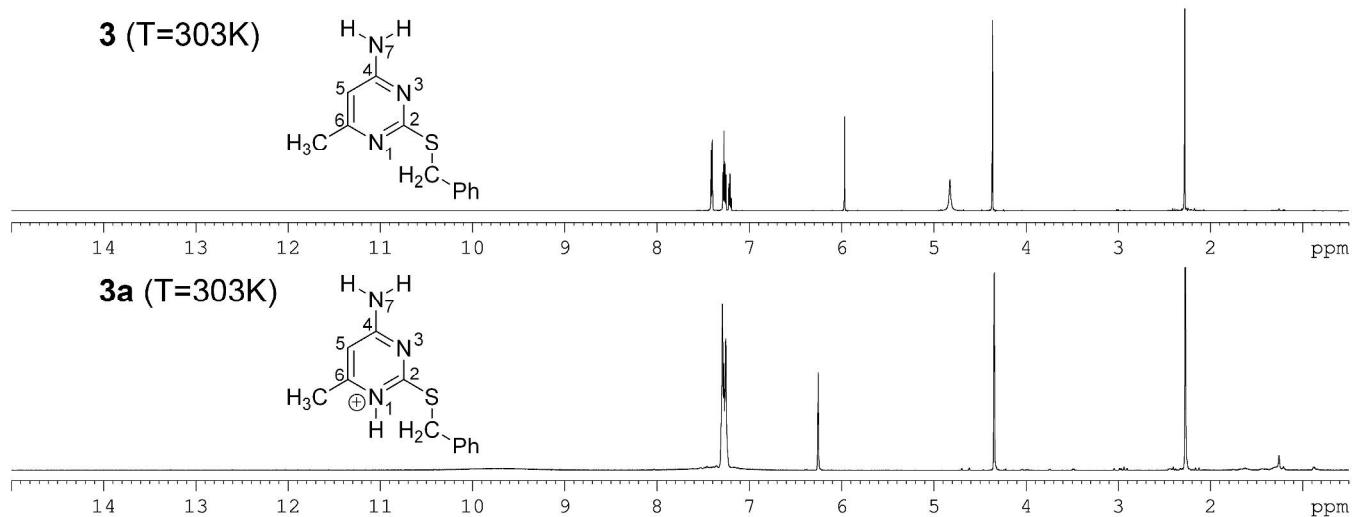


Figure S2. 1D ¹H NMR spectra in CDCl₃ of **3** (T=303K), **3a** (T=303K).

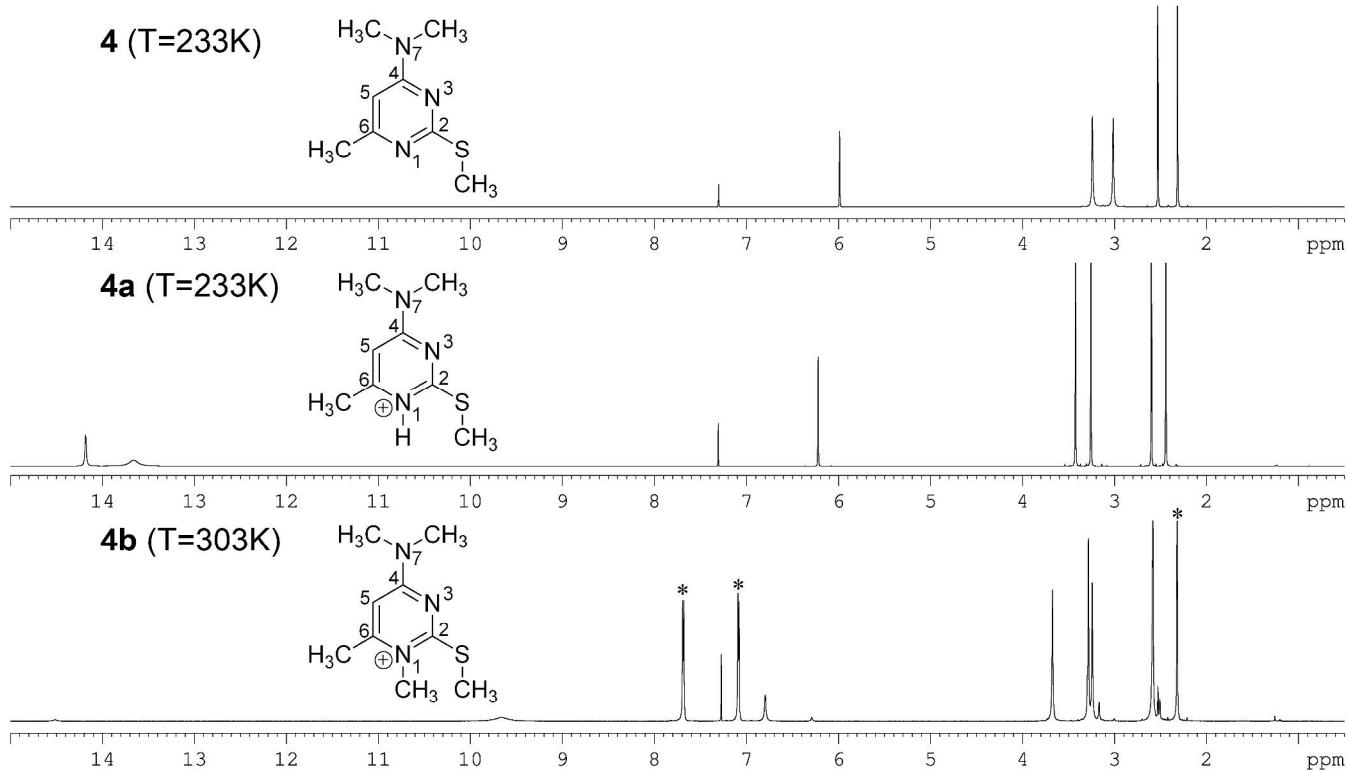


Figure S3. 1D ^1H NMR spectra in CDCl_3 of **4** (T=233K), **4a** (T=233K), **4b** (T=303K). Tosylate signals in spectrum of **4b** are indicated by asterisk.

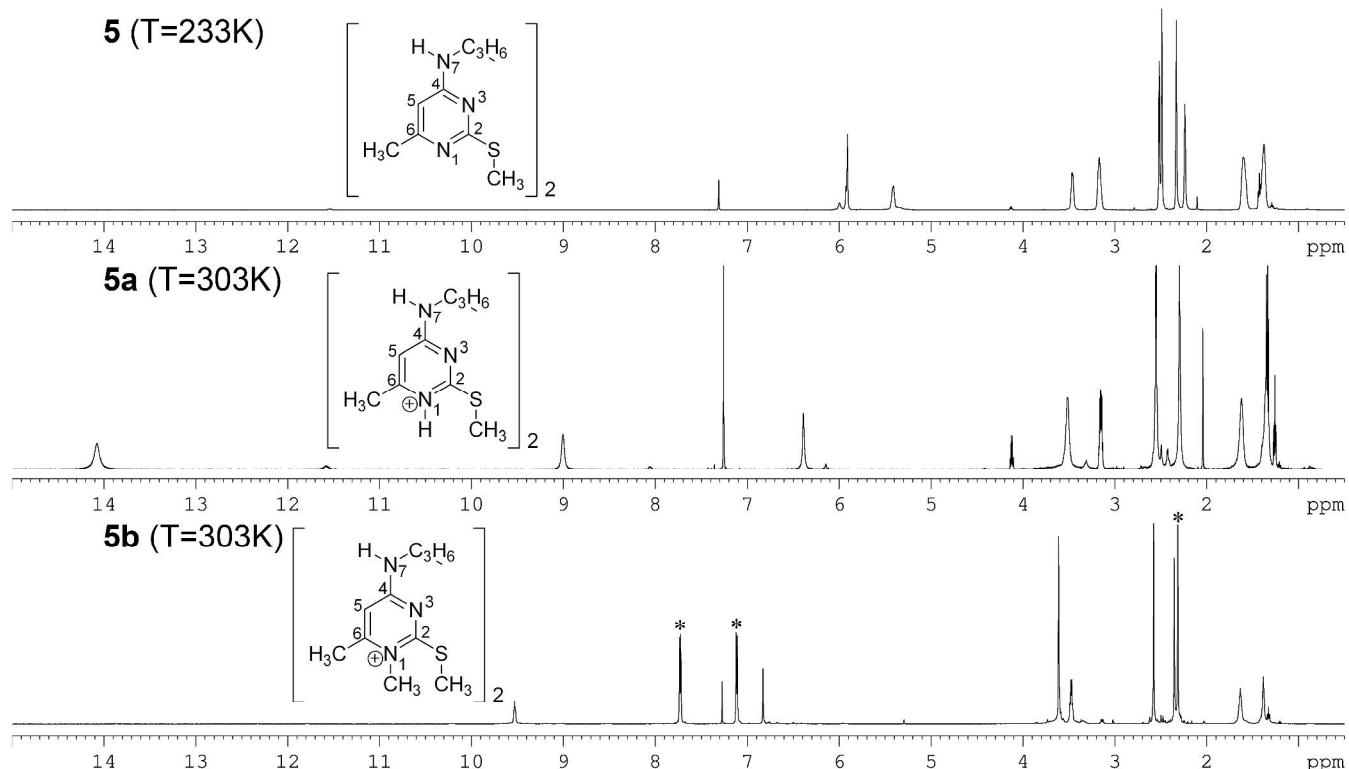


Figure S4. 1D ^1H NMR spectra in CDCl_3 of **5** (T=233K), **5a** (T=303K), **5b** (T=303K). Tosylate signals in spectrum of **5b** are indicated by asterisk.

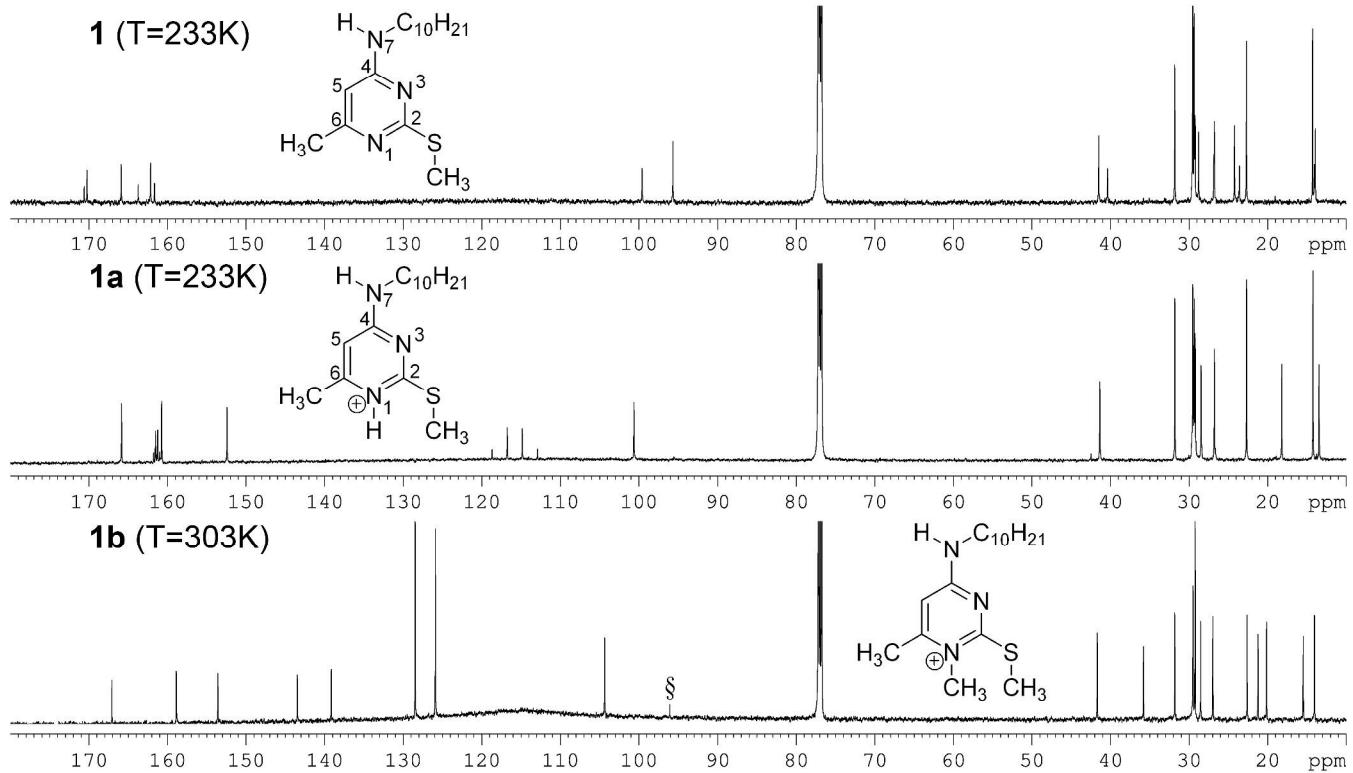


Figure S5. 1D ^{13}C NMR spectra in CDCl_3 of **1** (T=233K), **1a** (T=233K), **1b** (T=303K). § - signal of CCl_4 .

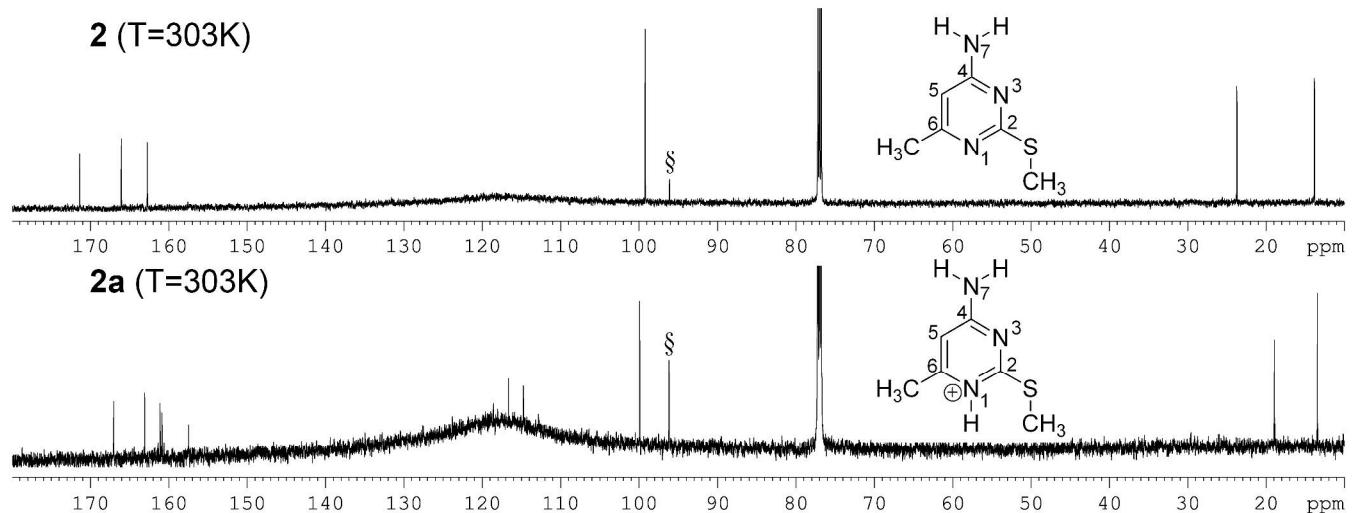


Figure S6. 1D ^{13}C NMR spectra in CDCl_3 of **2** (T=303K), **2a** (T=303K). § - signal of CCl_4 .

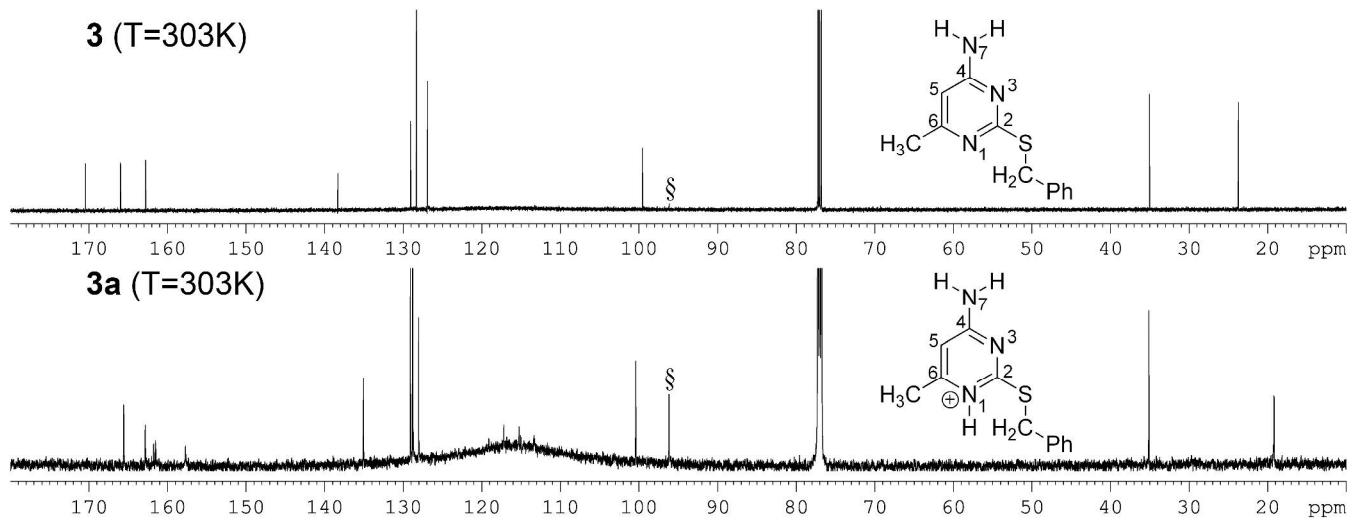


Figure S7. 1D ^{13}C NMR spectra in CDCl_3 of **3** ($T=303\text{K}$), **3a** ($T=303\text{K}$). \S - signal of CCl_4 .

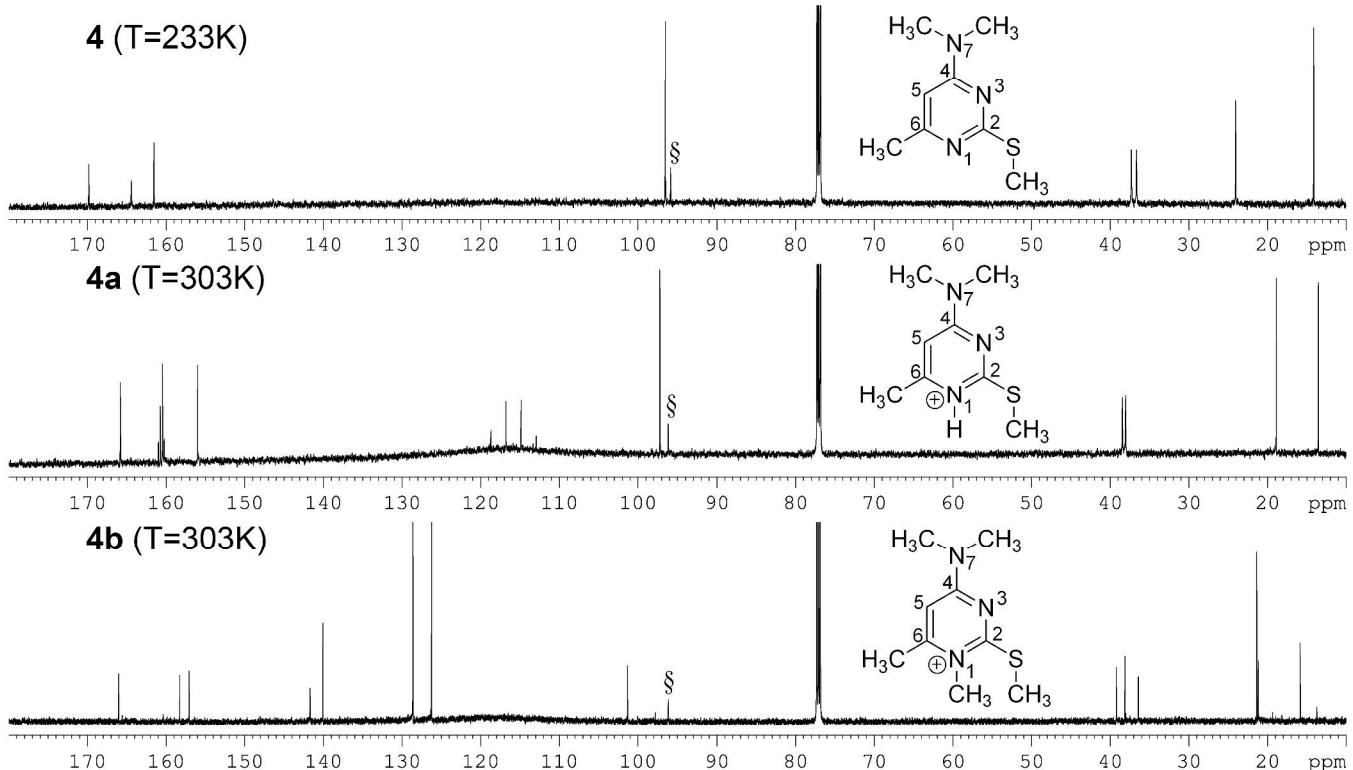


Figure S8. 1D ^{13}C NMR spectra in CDCl_3 of **4** ($T=233\text{K}$), **4a** ($T=303\text{K}$), **4b** ($T=303\text{K}$). \S - signal of CCl_4 .

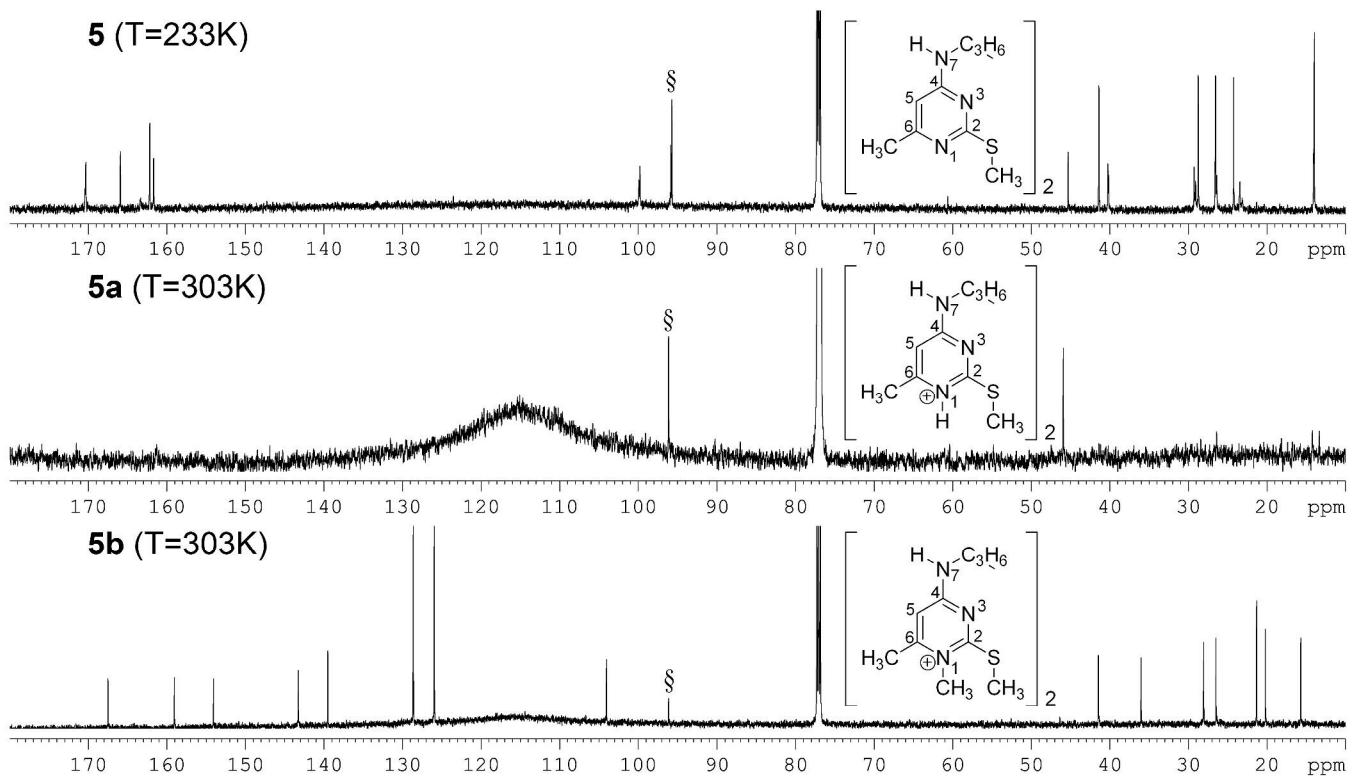


Figure S9. 1D ^{13}C NMR spectra in CDCl_3 of **5** (T=233K), **5a** (T=303K), **5b** (T=303K). § - signal of CCl_4 .

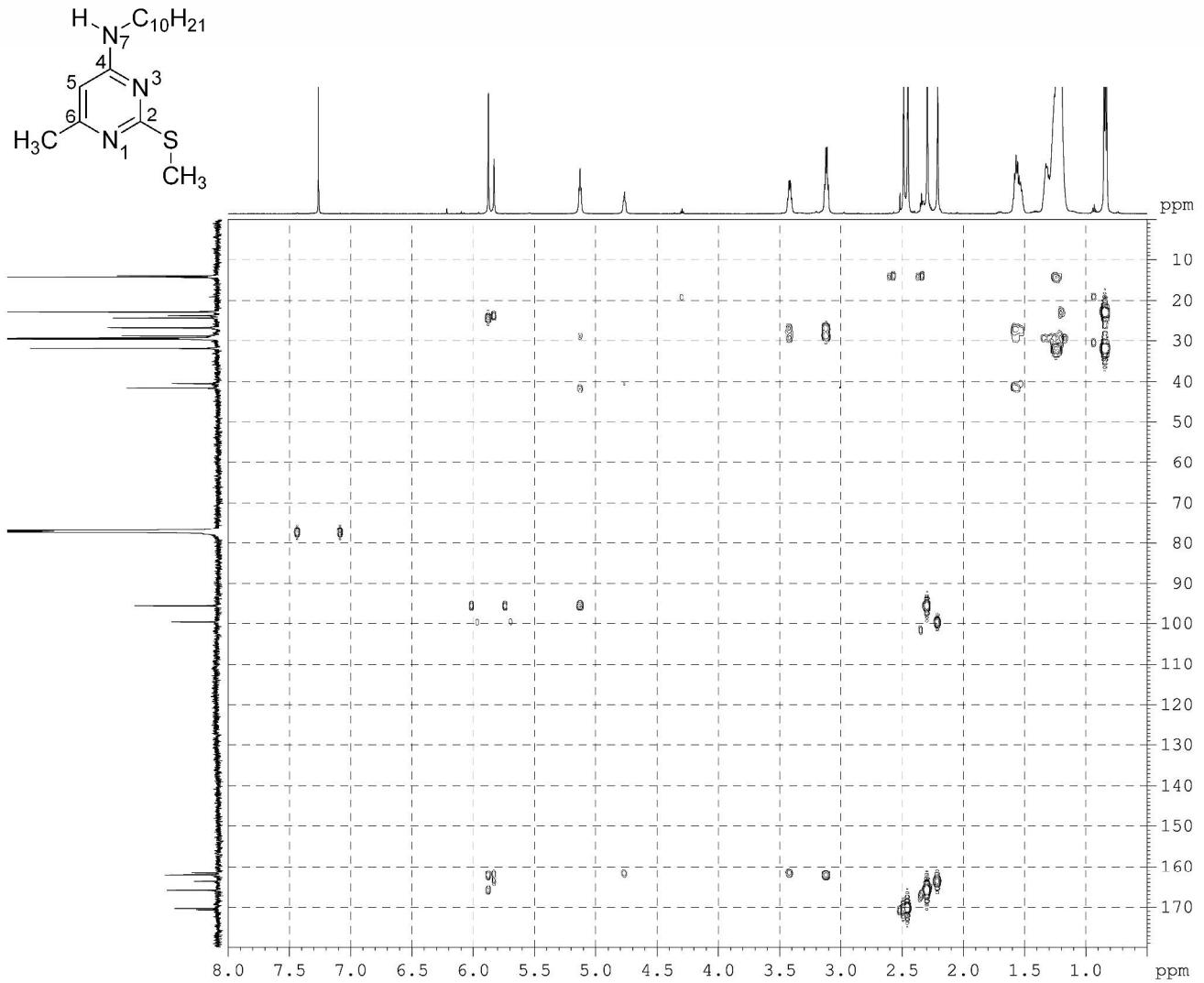


Figure S10. 2D ¹H-¹³C HMBC spectrum of **1** in CDCl₃ (T=233K).

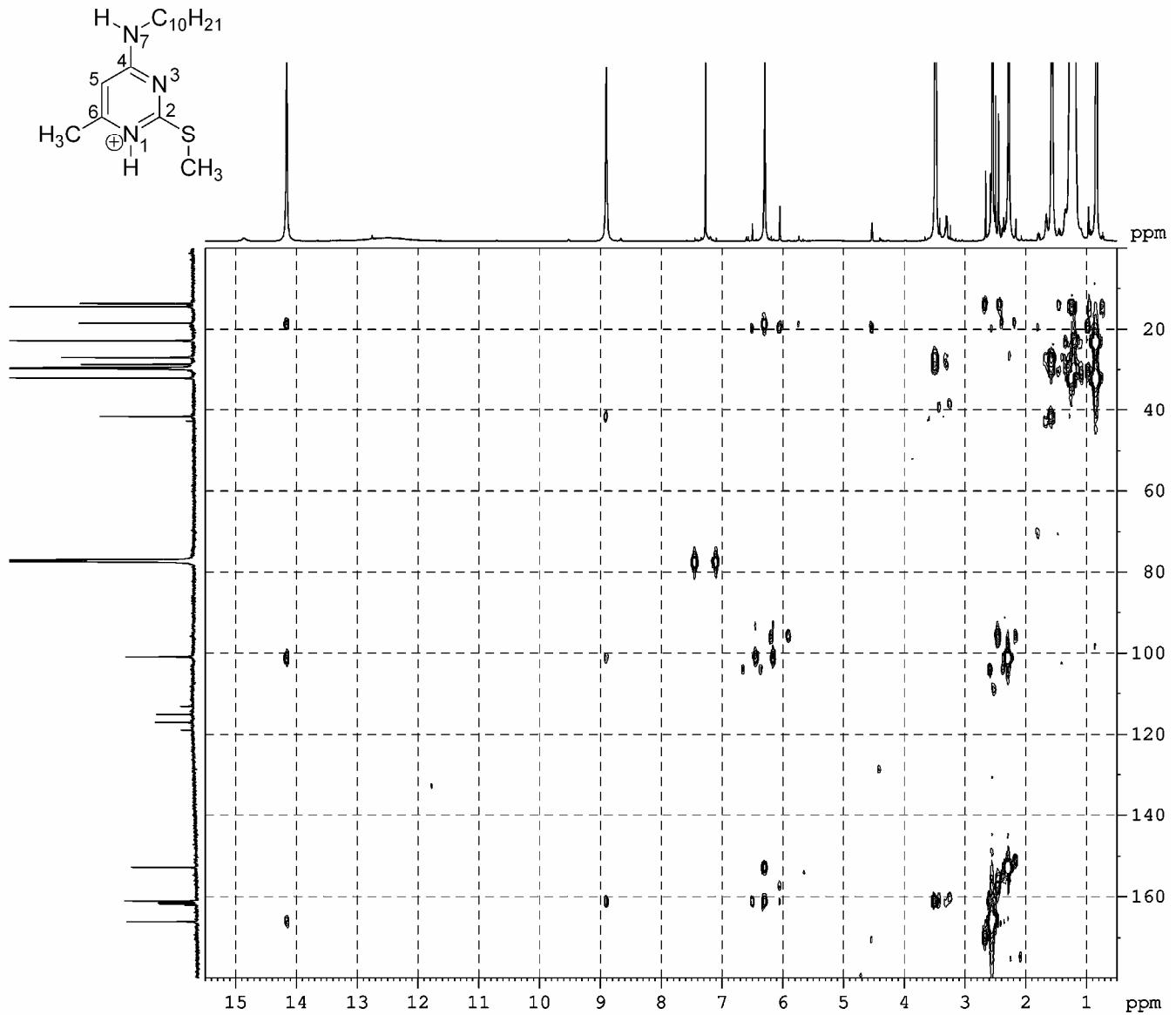


Figure S11. 2D ^1H - ^{13}C HMBC spectrum of **1a** in CDCl_3 ($T=233\text{K}$).

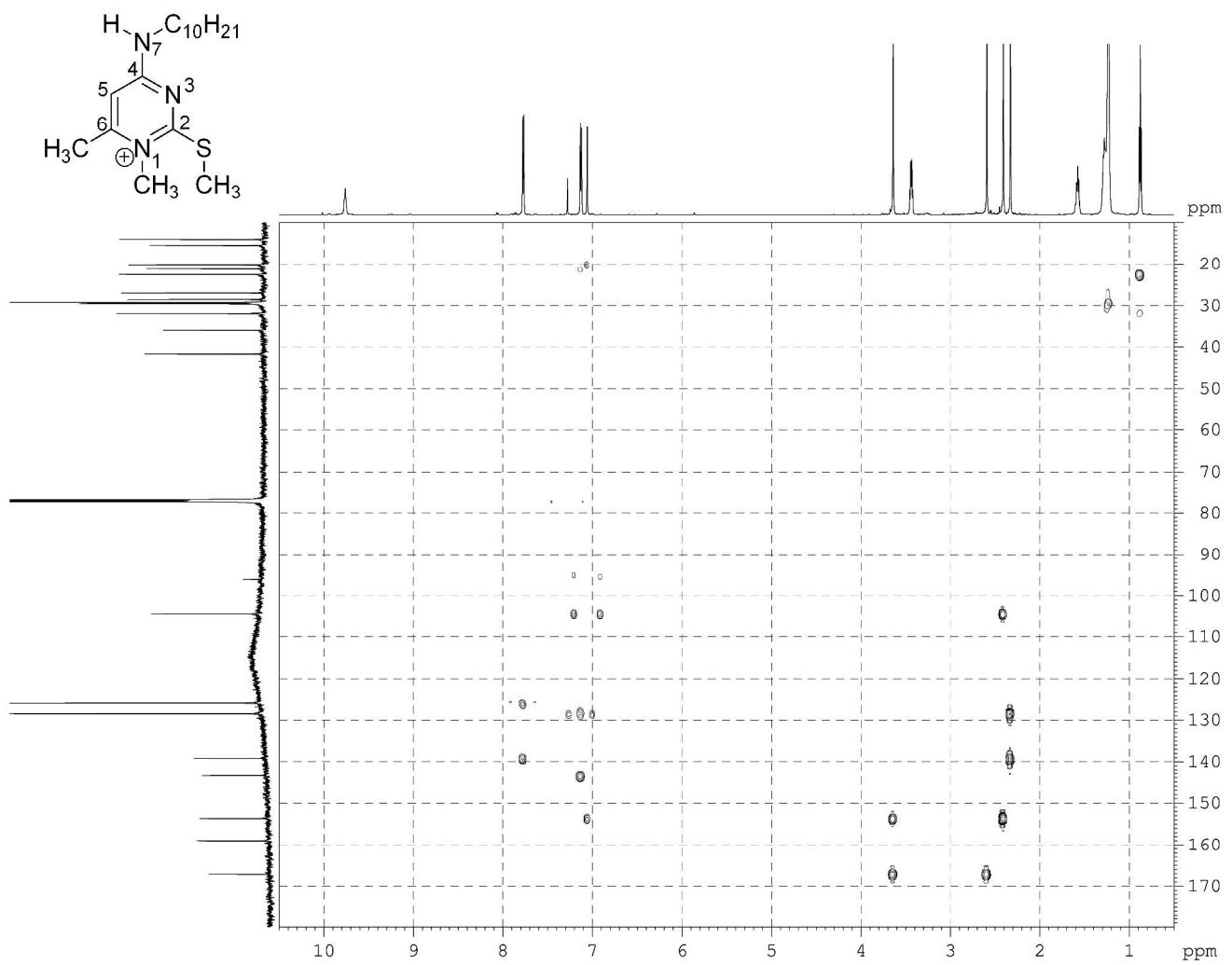


Figure S12. 2D ^1H - ^{13}C HMBC spectrum of **1b** in CDCl_3 (T=303K).

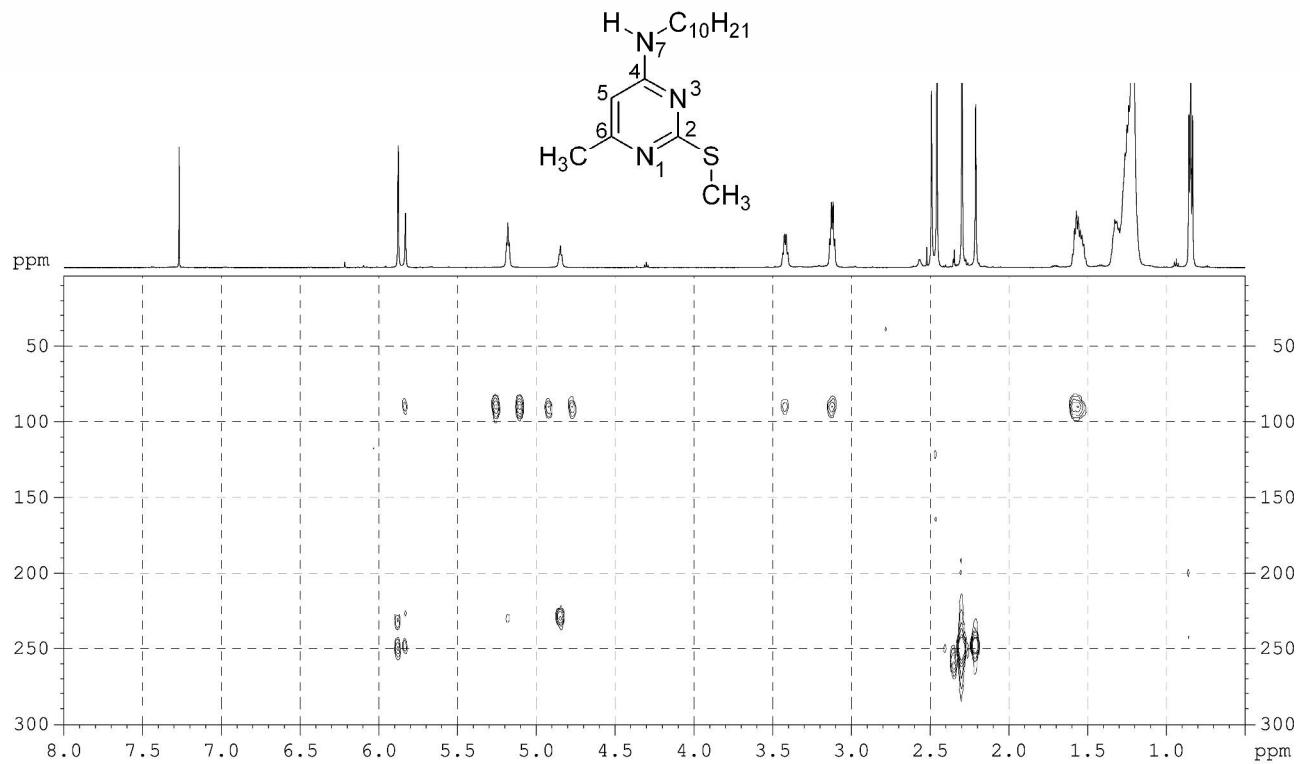


Figure S13. 2D ^1H - ^{15}N HMBC spectrum of **1** in CDCl_3 ($T=233\text{K}$).

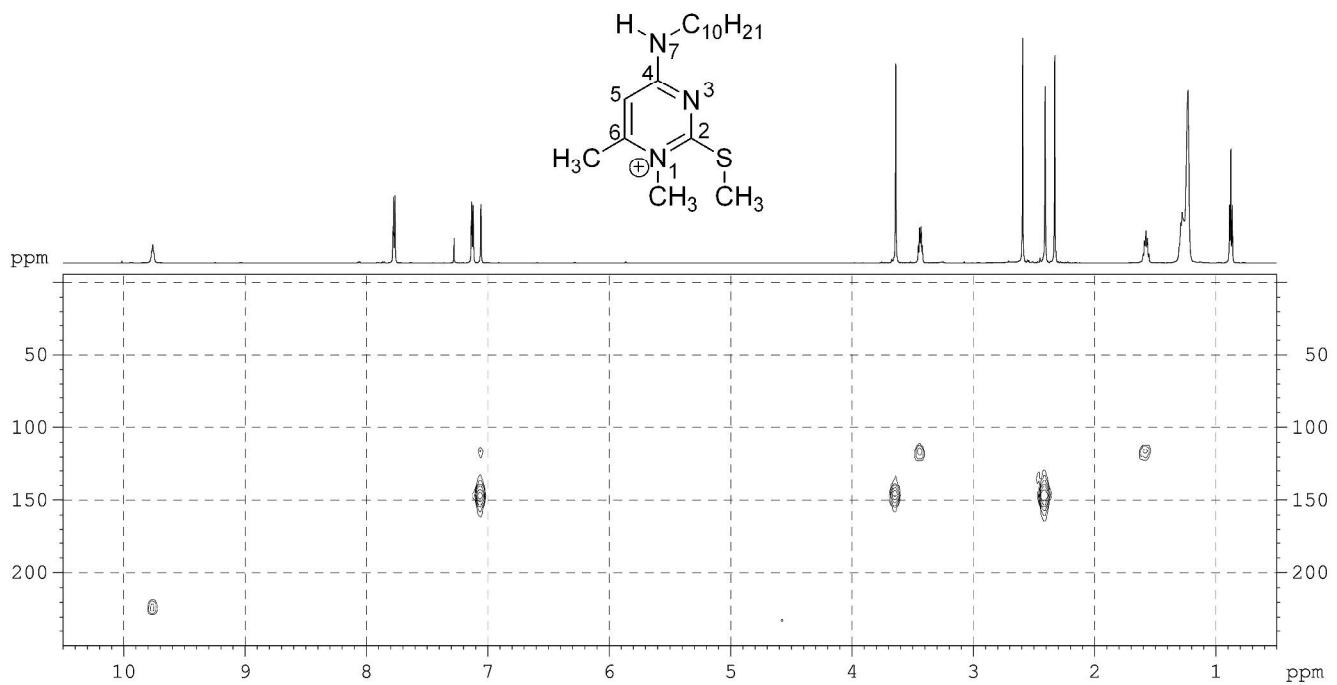


Figure S14. 2D ^1H - ^{15}N HMBC spectrum of **1b** in CDCl_3 ($T=303\text{K}$).

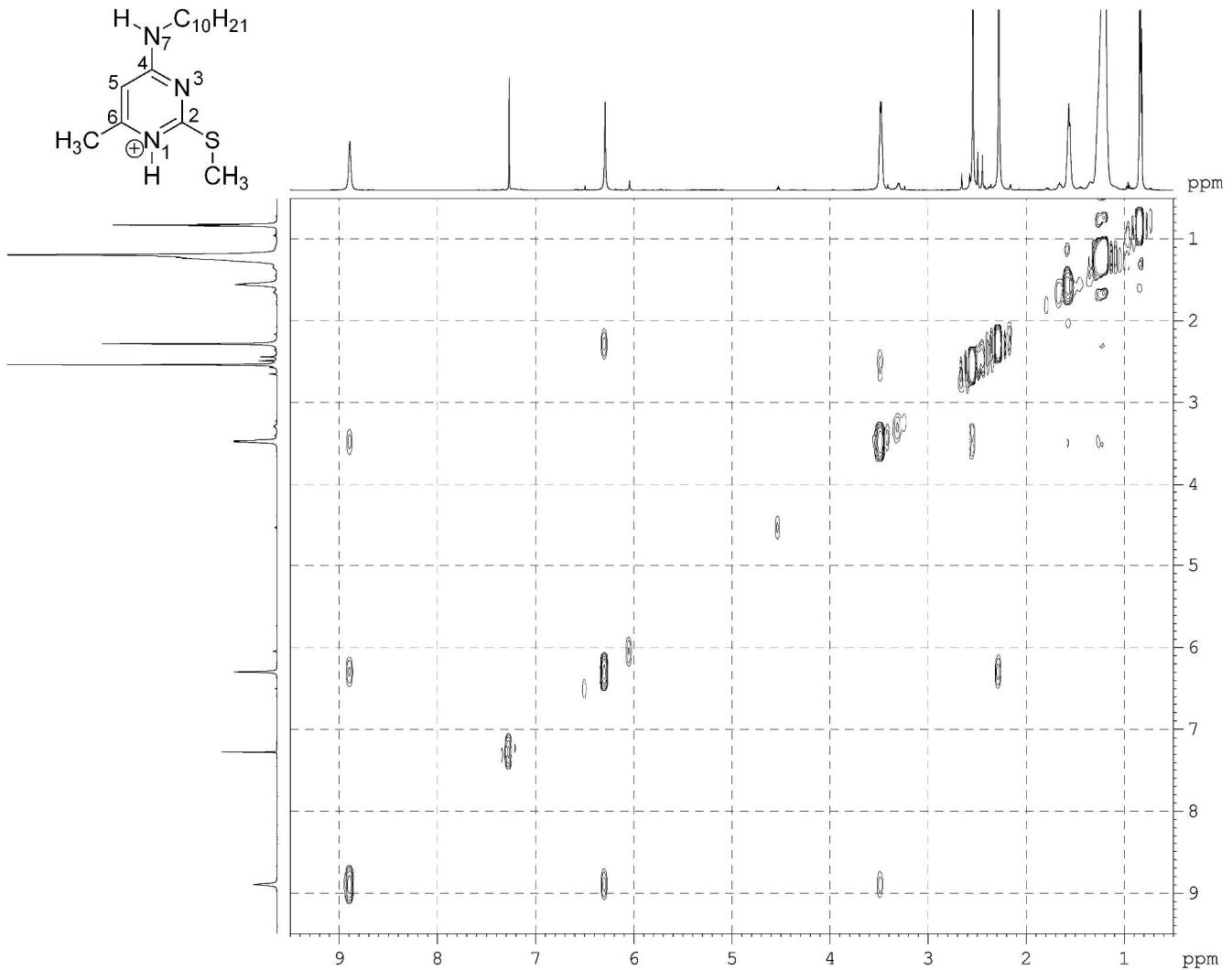


Figure S15. 2D ¹H-¹H NOESY spectrum of **1a** in CDCl₃ (T=233K).

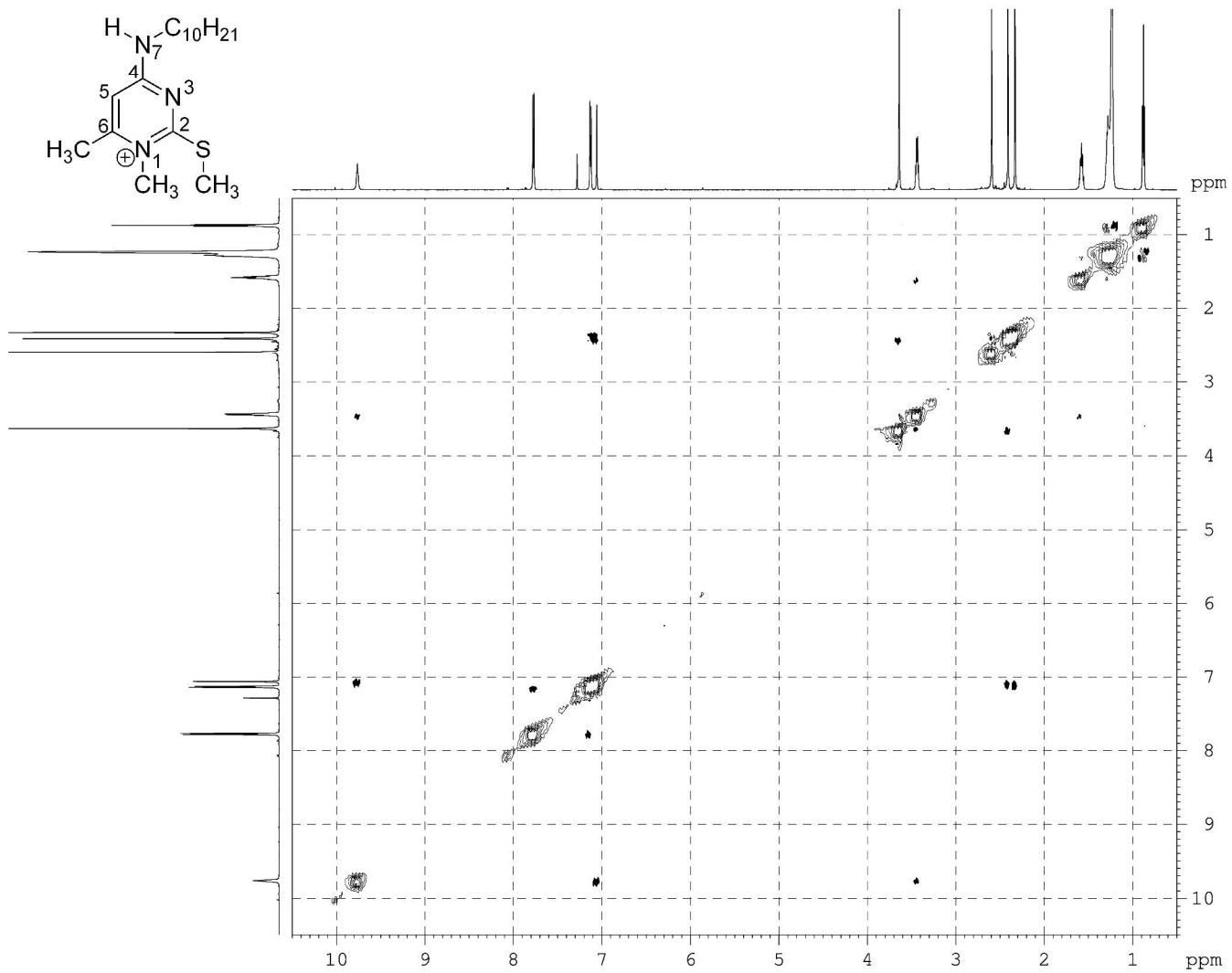


Figure S16. 2D ^1H - ^1H ROESY spectrum of **1b** in CDCl_3 ($T=303\text{K}$). *

* 2D spectra of **2-5 a/b** or something not quoted here can be obtain by request to authors.

NMR experimental chemical shifts (CS).

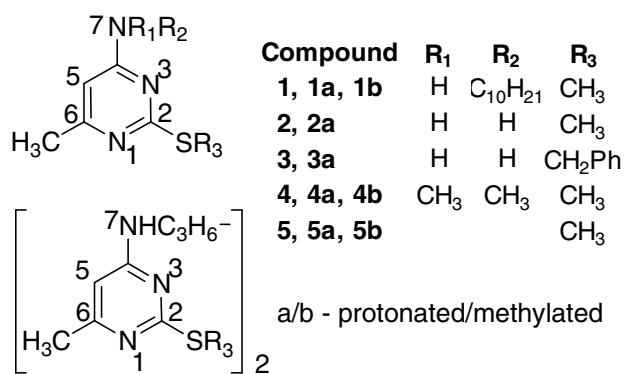


Table S1. ^1H , ^{13}C and ^{15}N experimental CSs for **1-5** in CDCl_3 ^{*}

nucleus	1 (233K)	1a (233K)	1b (303K)	2 (303K)	2a (303K)	3 (303K)	3a (303K)
N1	241.50 (243.70)	154.50 (159.50)	146.67	249.98	166.33	248.76	170.85
N3	223.30	218.20	223.32	228.24	na [†]	227.27	na
N7	84.00	112.20	116.14	68.20	na	68.76	94.40
C2	170.63 (170.27)	165.87 (165.24)	167.06	171.37	167.06	170.45	165.61
C4	161.67 (162.20)	160.81	158.91	162.73	163.11	162.81	162.87
C5	99.64 (95.71)	100.67 (95.59)	104.37	99.22	99.92	99.58	100.41
C6	163.76 (165.91)	152.48 (156.80)	153.63	166.05	157.50	166.02	157.73
<u>CH₃</u> (C6)	23.65 (24.25)	18.23	20.12	23.75	18.94	23.71	19.19
<u>CH₃</u> (S)/ <u>CH₂</u> (S)	14.09 (13.96)	13.48	15.47	13.84	13.46	35.04	35.11
<u>CH₂</u> (8)/ <u>CH₃</u> (8)	40.43 (41.55)	41.39 (42.51)	41.68				
<u>CH₃'(8)</u>							
<u>CH₂</u> (9)	29.27 (28.82)	25.50	28.51				
<u>CH₂</u> (10)	26.88 (26.82)	26.81	26.97				
<u>CH₂</u> (11-14)	29.39-29.57	29.26-29.57	29.23-29.52				
<u>CH₂</u> (15)	31.87	31.84	31.82				
<u>CH₂</u> (16)	22.73	22.71	22.60				
<u>CH₃</u> (17)	14.32	14.26	14.02				
<u>CH₃</u> (⁺ N1)			35.81				
<i>ipso</i> -C (Ph)						138.35	135.07
<i>o</i> -C (Ph)						129.09	129.09
<i>m</i> -C (Ph)						128.35	128.79
<i>p</i> -C (Ph)						126.93	128.03
H(C5)	5.83 (5.88)	6.28 (6.03)	7.06	5.97	6.27 ^a	5.97	6.26
H(N7)/ <u>CH₃</u> (8)	4.77 (5.13)	8.89 (7.24)	9.76	4.79	6.98 ^a	4.83	na
H'(N7)/ <u>CH₃'(8)</u>				4.79	na	4.83	na
<u>CH₃</u> (C6)	2.22 (2.30)	2.27 (2.44)	2.41	2.28	2.44 ^a	2.28	2.27
<u>CH₃</u> (S)/ <u>CH₂</u> (S)	2.49 (2.46)	2.53 (2.48)	2.59	2.50	2.58 ^a	4.37	4.35
<u>CH₂</u> (8)	3.42 (3.12)	3.47 (3.29)	3.44				
<u>CH₂</u> (9)	1.54-1.56	1.55	1.58				
<u>CH₂</u> (10-16)/ <u>CH₂</u> (10)	1.21-1.33	1.18-1.23	1.20-1.35				
<u>CH₃</u> (17)	0.85	0.82	0.88				
H(⁺ N1)/ <u>CH₃</u> (⁺ N1)		14.15	3.64		14.23 ^a		na
<i>o</i> -H (Ph)						7.41	7.30
<i>m</i> -H (Ph)						7.27	7.30
<i>p</i> -H (Ph)						7.21	7.28

^{*} In the case if two conformers are presented in the spectra CSs are given as in Z (E) form; ^a - T=233K;[†] Due to low solubility of protonated forms S/N in NMR spectra are essentially worse in these cases and no signals for some nuclei were obtained.

Table S1. ^1H , ^{13}C and ^{15}N experimental CSs for **1-5** (continued)*

nucleus	4 (233K)	4a (233K)	4b (303K)	5 (233K)	5a (303K)	5b (303K)
N1	238.00	155.98	149.44	243.74	155.46	147.64
N3	226.12	224.00	na [†]	225.91	na	223.36
N7	67.39	93.74	94.65	84.20	na	113.94
C2	169.81	165.82 ^b	166.06	170.40 (170.32)	166.55	167.47
C4	161.57	160.45 ^b	158.26	161.72 (162.21)	na	159.08
C5	96.54	97.20 ^b	101.35	99.79 (95.73)	101.25	104.05
C6	164.46	155.98 ^b	157.10	163.38 (165.94)	152.95	154.09
<u>CH</u> ₃ (C6)	24.06	18.85 ^b	21.18	23.45 (24.23)	18.12	20.21
<u>CH</u> ₃ (S)/ <u>CH</u> ₂ (S)	14.12	13.49 ^b	15.85	14.06 (13.96)	na	15.70
<u>CH</u> ₂ (8)/ <u>CH</u> ₃ (8)	36.65	38.00 ^b	38.12	40.25 (41.40)	40.63	41.44
<u>CH</u> ₃ '(8)	37.30	38.41 ^b	39.23			
<u>CH</u> ₂ (9)				29.27 (28.75)	na	28.05
<u>CH</u> ₂ (10)				26.39 (26.55)	na	26.49
<u>CH</u> ₂ (11-14)						
<u>CH</u> ₂ (15)						
<u>CH</u> ₂ (16)						
<u>CH</u> ₃ (17)						
<u>CH</u> ₃ (⁺ N1)			36.45			36.02
<i>ipso</i> -C (Ph)						
<i>o</i> -C (Ph)						
<i>m</i> -C (Ph)						
<i>p</i> -C (Ph)						
H(C5)	5.99	6.22	6.80	5.93 (5.91)	6.39 (6.15)	6.83
H(N7)/ <u>CH</u> ₃ (8)	3.02	3.26	3.24	5.41	9.01 (8.06)	9.53
H'(N7)/ <u>CH</u> ₃ '(8)	3.24	3.42	3.28			
<u>CH</u> ₃ (C6)	2.32	2.44	2.58	2.24 (2.33)	2.30 (2.43)	2.35
<u>CH</u> ₃ (S)/ <u>CH</u> ₂ (S)	2.53	2.60	2.58	2.52 (2.49)	2.55 (2.49)	2.58
<u>CH</u> ₂ (8)				3.46 (3.17)	3.52 (3.31)	3.47
<u>CH</u> ₂ (9)				1.60	1.62	1.63
<u>CH</u> ₂ (10-16)/ <u>CH</u> ₂ (10)				1.38	1.35	1.38
<u>CH</u> ₃ (17)						
H(⁺ N1)/ <u>CH</u> ₃ (⁺ N1)		14.18	3.67		14.08	3.61
<i>o</i> -H (Ph)						
<i>m</i> -H (Ph)						
<i>p</i> -H (Ph)						

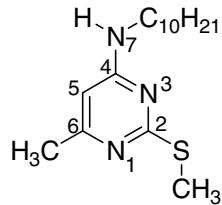
* In the case if two conformers are presented in the spectra CSs are given as in Z (E) form; ^b - T=303K;

† Due to low solubility of protonated forms S/N in NMR spectra are essentially worse in these cases and no signals for some nuclei were obtained.

Chemical shifts calculations.

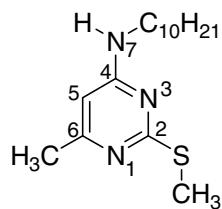
DFT GIAO CSs (RB3LYP/6-31G(d)//RHF/6-31G).

Table S2. Principal ^1H , ^{13}C and ^{15}N DFT GIAO and experimental CSs for protonation of **1**^{*}



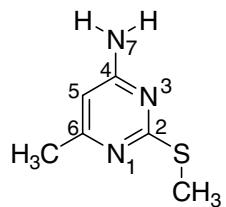
nucleus	experimental CS	proton position			
		N1	N3	C5	N7
N1	154.50	133.92 (97.95)	242.67 (227.08)	280.86 (263.72)	289.67 (281.66)
N3	218.20	215.12 (196.41)	121.27 (88.60)	213.00 (189.62)	237.67 (234.20)
N7	112.20	108.10 (60.27)	85.29 (37.93)	134.12 (92.04)	69.04 (11.38)
C2	165.84	167.22 (186.19)	161.91 (177.94)	196.09 (219.61)	180.37 (191.69)
C4	160.78	148.93 (169.02)	142.59 (163.15)	154.03 (176.30)	143.09 (158.58)
C5	100.64	95.15 (99.64)	95.56 (99.85)	28.83 (32.55)	96.91 (107.09)
C6	152.45	146.75 (164.78)	167.14 (184.30)	178.87 (195.82)	169.63 (183.94)
<u>CH</u> ₃ (C6)	18.20	17.76 (19.39)	24.10 (25.37)	26.06 (27.37)	24.04 (25.20)
<u>CH</u> ₃ (S)	13.46	24.89 (26.66)	11.78 (12.85)	26.83 (26.68)	23.85 (23.90)
<u>CH</u> ₂ (8)	41.37	40.25 (37.81)	36.85 (34.52)	42.26 (40.57)	55.89 (54.54)
H(C5)	6.28	5.57 (6.50)	5.85 (6.74)	2.90 (3.39)	6.17 (7.21)
<u>CH</u> ₃ (C6)	2.27	2.20 (2.75)	2.46 (3.03)	2.41 (3.00)	2.62 (3.19)
<u>CH</u> ₃ (S)	2.53	2.73 (3.23)	2.78 (3.27)	2.80 (3.16)	2.59 (2.94)
<u>CH</u> ₂ (8)	3.47	3.52 (3.77)	3.14 (3.26)	3.78 (4.15)	3.73 (4.13)
H(N7)	8.89	4.46 (4.56)	3.98 (4.23)	5.15 (5.38)	4.71 (4.47)
H(⁺ N1)	14.15	7.14 (7.97)	7.00 (7.92)	2.90 (3.39)	4.89 (5.12)

* in brackets data for HF/6-31G//HF/6-31G GIAO CSs.

Table S3. Principal ^1H , ^{13}C and ^{15}N DFT GIAO and experimental CSs for methylation of **1**^{*}

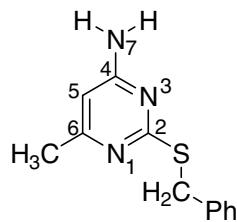
nucleus	experimental CS	Me position			
		N1	N3	C5	N7
N1	146.67	145.07 (105.20)	251.20 (234.97)	283.16 (267.67)	289.67 (280.76)
N3	223.32	221.01 (201.26)	136.82 (101.02)	207.35 (181.79)	237.16 (233.07)
N7	116.14	102.58 (53.88)	86.77 (36.82)	134.85 (92.26)	76.03 (10.72)
C2	167.06	170.14 (189.75)	167.17 (184.22)	193.97 (218.09)	179.62 (190.77)
C4	158.91	146.55 (166.72)	149.44 (171.78)	160.95 (183.99)	149.81 (165.33)
C5	104.37	97.51 (101.83)	100.22 (104.60)	38.27 (39.14)	95.56 (105.55)
C6	153.63	150.10 (168.84)	163.64 (181.43)	183.94 (200.06)	169.17 (183.69)
<u>CH</u> ₃ (C6)	20.12	20.10 (21.53)	23.19 (24.59)	24.87 (26.13)	24.10 (25.28)
<u>CH</u> ₃ (S)	15.47	25.97 (27.20)	26.82 (28.09)	25.78 (25.29)	23.75 (23.73)
<u>CH</u> ₂ (8)	41.68	39.71 (37.13)	45.22 (41.81)	41.86 (39.93)	57.34 (54.90)
<u>CH</u> ₃ (⁺ N1)	35.81	34.22 (35.55)	38.91 (39.73)	21.13 (18.85)	38.89 (39.76)
H(C5)	7.06	5.68 (6.54)	5.87 (6.69)	2.86 (2.98)	6.08 (7.10)
<u>CH</u> ₃ (C6)	2.41	2.24 (2.73)	2.40 (2.97)	2.43 (2.97)	2.59 (3.15)
<u>CH</u> ₃ (S)	2.59	2.68 (3.16)	2.72 (3.19)	2.65 (3.06)	2.57 (2.91)
<u>CH</u> ₂ (8)	3.44	3.46 (3.69)	3.48 (3.54)	3.70 (4.01)	3.46 (3.65)
H(N7)	9.76	4.24 (4.31)	5.87 (6.69)	5.23 (5.41)	4.57 (4.42)
<u>CH</u> ₃ (⁺ N1)	3.64	3.38 (3.98)	3.51 (4.08)	1.49 (1.74)	3.11 (3.54)

* in brackets data for HF/6-31G//HF/6-31G GIAO CSs.

Table S4. Principal ^1H , ^{13}C and ^{15}N DFT GIAO and experimental CSs for protonation of **2**

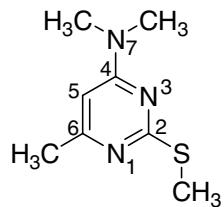
nucleus	experimental CS	proton position			
		N1	N3	C5	N7
N1	166.33	134.93	246.28	280.22	292.81
N3	na [†]	222.11	123.18	214.92	235.08
N7	na	80.26	59.33	99.46	40.32
C2	167.06	167.55	163.27	198.90	181.08
C4	163.11	150.14	142.13	157.66	137.64
C5	99.92	94.45	94.33	28.19	97.44
C6	157.50	149.25	170.58	179.63	170.39
<u>CH</u> ₃ (C6)	18.94	17.87	24.48	26.15	24.17
<u>CH</u> ₃ (S)	13.46	19.32	26.32	27.41	24.23
H(C5)	6.27	5.80	6.00	3.02	6.23
H(N7)	6.98	5.07	3.92	5.84	5.51
H'(N7)	6.98	4.65	4.17	5.27	4.68
<u>CH</u> ₃ (C6)	2.44	2.27	2.54	2.50	2.68
<u>CH</u> ₃ (S)	2.58	2.46	2.83	2.87	2.64
H(⁺ N1)	14.23	7.03	7.00	3.02	5.41

[†] Due to low solubility of protonated forms S/N in NMR spectra are essentially worse in these cases and no signals for some nuclei were obtained.

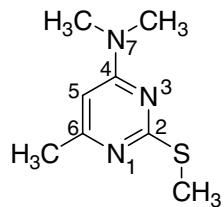
Table S5. Principal ^1H , ^{13}C and ^{15}N DFT GIAO and experimental CSs for protonation of **3**

nucleus	experimental CS	proton position			
		N1	N3	C5	N7
N1	170.85	135.61	251.88	285.17	300.44
N3	na [†]	217.83	123.16	212.08	227.78
N7	94.40	78.43	57.21	97.92	40.32
C2	165.61	168.74	163.38	197.15	181.92
C4	162.87	150.55	142.10	157.62	137.83
C5	100.41	93.38	93.31	28.02	97.50
C6	157.73	168.74	163.38	197.15	181.92
<u>CH</u> ₃ (C6)	19.19	18.10	24.65	25.70	24.23
<u>CH</u> ₂ (S)	35.11	55.46	45.92	56.60	48.93
<i>ipso</i> -C (Ph)	135.07	117.18	115.47	117.11	119.27
<i>o</i> -C (Ph)	129.09	123.51	122.99	123.10	122.77
<i>m</i> -C (Ph)	128.79	122.93	123.38	123.22	122.56
<i>p</i> -C (Ph)	128.03	125.26	125.51	125.29	123.88
H(C5)	6.26	5.72	5.98	2.98	6.18
H(N7)	na	4.55	4.07	5.20	5.45
H'(N7)	na	4.94	3.77	5.74	4.68
<u>CH</u> ₃ (C6)	2.27	2.23	2.51	2.44	2.64
<u>CH</u> ₂ (S)	4.35	4.76	4.16	4.68	4.20
H(⁺ N1)	na	7.19	6.85	2.98	5.45
<i>o</i> -H (Ph)	7.30	7.47	7.45	7.45	7.41
<i>m</i> -H (Ph)	7.30	7.58	7.64	7.62	7.55
<i>p</i> -H (Ph)	7.28	7.66	7.73	7.70	7.60

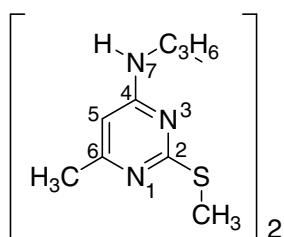
[†] Due to low solubility of protonated forms S/N in NMR spectra are essentially worse in these cases and no signals for some nuclei were obtained.

Table S6. Principal ^1H , ^{13}C and ^{15}N DFT GIAO and experimental CSs for protonation of **4**

nucleus	experimental CS	proton position			
		N1	N3	C5	N7
N1	155.98	130.84	240.31	280.20	290.72
N3	224.00	223.53	123.71	214.27	232.25
N7	93.74	99.62	73.37	133.12	55.64
C2	165.82	164.04	162.49	193.00	180.26
C4	160.45	148.16	142.85	155.56	148.16
C5	97.20	94.12	94.70	29.24	96.71
C6	155.98	145.84	166.81	177.65	169.73
<u>CH₃(C6)</u>	18.85	17.98	24.44	25.88	24.00
<u>CH₃(S)</u>	13.49	19.22	25.75	26.27	23.90
<u>CH₃(8)</u>	38.00	38.66	40.01	37.22	45.98
<u>CH₃'(8)</u>	38.41	41.90	36.58	37.95	45.98
H(C5)	6.22	5.81	5.98	2.77	6.02
<u>CH₃(8)</u>	3.26	3.13	3.18	3.04	3.33
<u>CH₃'(8)</u>	3.42	3.26	3.07	3.58	3.33
<u>CH₃(C6)</u>	2.44	2.22	2.49	2.45	2.60
<u>CH₃(S)</u>	2.60	2.42	2.77	2.76	2.60
H(⁺ N1)	14.18	6.86	6.97	2.77	4.40

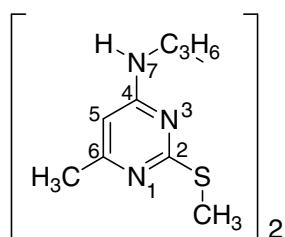
Table S7. Principal ^1H , ^{13}C and ^{15}N DFT GIAO and experimental CSs for methylation of **4**

nucleus	experimental CS	Me position			
		N1	N3	C5	N7
N1	149.44	143.96	253.03	278.13	289.48
N3	-	226.21	143.08	209.95	236.61
N7	94.65	92.34	66.46	135.46	60.08
C2	166.06	167.94	168.51	190.45	179.24
C4	158.26	146.62	153.69	160.80	153.08
C5	101.35	96.09	100.67	35.80	95.57
C6	157.10	149.91	164.79	182.89	169.35
<u>CH₃(C6)</u>	21.18	20.48	23.70	24.26	24.32
<u>CH₃(S)</u>	15.85	25.69	26.81	25.90	23.79
<u>CH₃(8)</u>	38.12	38.68	38.56	36.36	55.35
<u>CH₃'(8)</u>	39.23	40.80	41.46	37.55	55.35
<u>CH₃(⁺N1)</u>	36.45	34.08	39.71	19.07	47.33
H(C5)	6.80	5.85	6.22	3.09	6.24
<u>CH₃(8)</u>	3.24	3.10	2.97	3.12	3.33
<u>CH₃'(8)</u>	3.28	3.20	2.99	3.47	3.33
<u>CH₃(C6)</u>	2.58	2.28	2.48	2.42	2.61
<u>CH₃(S)</u>	2.58	2.66	2.74	2.73	2.58
<u>CH₃(⁺N1)</u>	3.67	3.39	3.48	1.38	3.17

Table S8. Principal ^1H , ^{13}C and ^{15}N DFT GIAO and experimental CSs for protonation of **5**

nucleus	experimental CS	proton position			
		N1	N3	C5	N7
N1	155.46	134.90	249.19	282.38	296.81
N3	na [†]	216.05	117.83	209.13	229.90
N7	na	101.85	79.72	127.15	58.42
C2	166.55	167.81	161.08	197.62	181.33
C4	na	148.76	142.56	155.46	140.76
C5	101.25	95.34	95.45	29.31	99.66
C6	152.95	148.04	169.65	179.45	170.07
<u>CH₃(C6)</u>	18.12	17.66	24.44	26.05	24.09
<u>CH₃(S)</u>	na	22.09	22.75	26.82	23.52
<u>CH₂(8)</u>	40.63	44.29	42.33	45.20	52.20
H(C5)	6.39	5.60	5.84	2.92	6.11
H(N7)	9.01	4.31	4.26	5.27	4.86
<u>CH₃(C6)</u>	2.30	2.26	2.55	2.49	2.68
<u>CH₃(S)</u>	2.55	2.62	2.65	2.78	2.53
<u>CH₂(8)</u>	3.52	3.42	3.19	3.67	3.90
H(¹⁵ N1)	14.08	7.16	6.87	2.92	4.84

[†] Due to low solubility of protonated forms S/N in NMR spectra are essentially worse in these cases and no signals for some nuclei were obtained.

Table S9. Principal ^1H , ^{13}C and ^{15}N DFT GIAO and experimental CSs for methylation of **5**

nucleus	experimental CS	Me position			
		N1	N3	C5	N7
N1	147.64	147.92	254.95	280.87	295.07
N3	223.36	220.08	137.67	203.41	230.61
N7	113.94	96.00	79.41	128.91	64.33
C2	167.47	170.79	168.14	194.63	180.30
C4	159.08	146.68	149.27	162.38	146.72
C5	104.05	97.47	99.96	38.92	98.65
C6	154.09	151.43	165.54	186.25	170.32
<u>CH₃(C6)</u>	20.21	20.00	23.40	25.27	24.06
<u>CH₃(S)</u>	15.70	25.47	27.62	26.22	23.05
<u>CH₂(8)</u>	41.44	43.58	48.93	44.49	60.52
<u>CH₃(⁺N1)</u>	36.02	34.56	39.09	21.17	43.53
H(C5)	6.83	5.68	5.88	2.86	6.03
H(N7)	9.53	4.07	3.41	5.50	4.51
<u>CH₃(C6)</u>	2.35	2.30	2.47	2.51	2.64
<u>CH₃(S)</u>	2.58	2.66	2.82	2.75	2.50
<u>CH₂(8)</u>	3.47	3.36	3.35	3.76	3.54
<u>CH₃(⁺N1)</u>	3.61	3.44	3.51	1.50	3.32

Tautomerization.

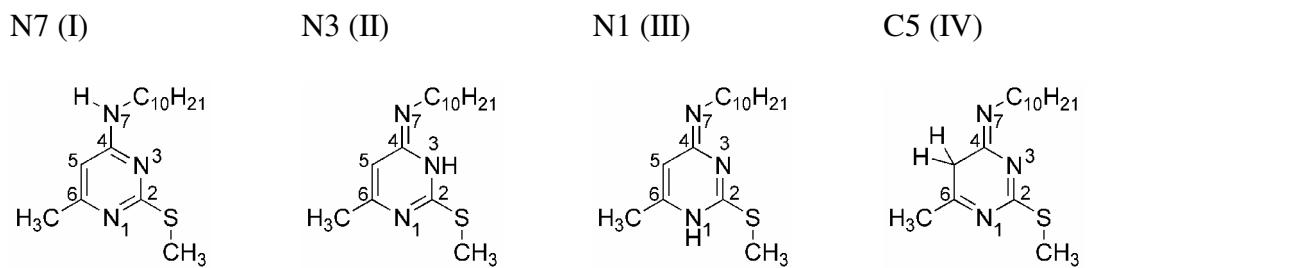
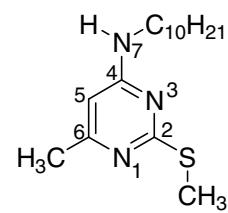


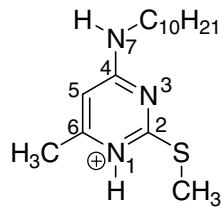
Table S10. Principal ^1H , ^{13}C and ^{15}N DFT GIAO and experimental CSs for tautomerization of **1**^{*}



nucleus	experimental CS	proton position			
		N7 (I)	N3 (II)	N1 (III)	C5 (IV)
N1	241.50	268.21 (221.47)	229.55 (184.40)	133.15 (64.72)	308.42 (273.93)
N3	223.30	242.61 (204.28)	155.49 (89.01)	260.90 (227.65)	271.83 (245.50)
N7	84.00	94.70 (22.91)	225.96 (190.30)	275.32 (252.13)	340.09 (332.83)
C2	170.59	171.80 (184.83)	155.34 (171.87)	149.19 (161.07)	169.55 (175.42)
C4	161.64	150.58 (167.47)	137.07 (152.28)	142.01 (154.17)	144.34 (155.38)
C5	99.60	88.35 (100.21)	96.50 (101.41)	95.20 (99.39)	27.95 (29.59)
C6	163.72	158.51 (172.90)	149.68 (161.70)	131.61 (145.28)	172.13 (184.76)
<u>CH₃(C6)</u>	23.61	23.37 (24.36)	23.01 (24.11)	17.82 (19.24)	25.34 (26.82)
<u>CH₃(S)</u>	13.92	20.81 (20.35)	21.44 (22.02)	22.12 (22.69)	21.54 (20.58)
<u>CH₂(8)</u>	40.39	36.23 (33.33)	42.06 (38.01)	42.89 (39.52)	45.75 (41.83)
H(C5)	5.82	5.38 (6.15)	5.49 (6.13)	5.03 (5.69)	2.27 (2.72)
<u>CH₃(C6)</u>	2.20	2.01 (2.48)	1.76 (2.22)	1.56 (2.00)	1.88 (2.40)
<u>CH₃(S)</u>	2.48	2.01 (2.33)	2.14 (2.51)	2.22 (2.60)	2.11 (2.28)
<u>CH₂(8)</u>	3.41	3.11 (3.44)	3.23 (3.25)	2.93 (2.95)	2.92 (3.01)
H(X)	4.84	3.71 (2.61)	5.87 (6.74)	4.96 (5.38)	2.27 (2.72)

* in brackets data for HF/6-31G//HF/6-31G GIAO CSs.

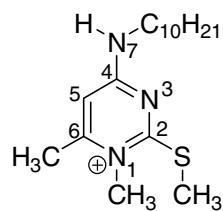
Table S11. Principal ^1H , ^{13}C and ^{15}N DFT GIAO and experimental CSs for tautomerization of **1a** (protonated at N1)^{*}



nucleus	experimental CS	proton position			
		N7 (I)	N3 (II)	N1 (III)	C5 (IV)
N1	154.50	133.92 (97.95)	114.39 (72.92)	59.56 (7.16)	179.91 (143.35)
N3	218.20	215.12 (196.41)	143.50 (105.19)	275.24 (302.43)	262.95 (269.79)
N7	112.20	108.10 (60.27)	268.40 (273.92)	389.58 (432.65)	375.28 (403.25)
C2	165.84	167.22 (186.19)	162.13 (186.63)	138.68 (140.18)	147.43 (153.27)
C4	160.78	148.93 (169.02)	126.35 (136.71)	128.31 (134.85)	124.80 (132.30)
C5	100.64	95.15 (99.64)	100.44 (105.50)	107.68 (118.45)	30.77 (30.51)
C6	152.45	146.75 (164.78)	135.32 (144.02)	126.01 (129.42)	191.38 (214.27)
<u>CH</u> ₃ (C6)	18.20	17.76 (19.39)	17.21 (18.22)	17.87 (18.55)	24.72 (26.81)
<u>CH</u> ₃ (S)	13.46	24.89 (26.66)	20.78 (21.61)	27.95 (29.40)	27.57 (28.24)
<u>CH</u> ₂ (8)	41.37	40.25 (37.81)	45.60 (41.89)	50.44 (46.59)	49.49 (45.29)
H(C5)	6.28	5.57 (6.50)	5.90 (6.64)	6.67 (7.70)	3.11 (3.43)
<u>CH</u> ₃ (C6)	2.27	2.20 (2.75)	1.98 (2.45)	2.01 (2.51)	2.49 (3.11)
<u>CH</u> ₃ (S)	2.53	2.73 (3.23)	2.58 (3.02)	2.91 (3.35)	2.85 (3.27)
<u>CH</u> ₂ (8)	3.47	3.52 (3.77)	3.49 (3.68)	3.98 (4.30)	3.76 (3.99)
H(X)	8.89	4.46 (4.56)	6.69 (7.93)	4.74 (4.50)	3.98 (4.27)
H(⁺ N1)	14.15	7.14 (7.97)	5.38 (6.08)	4.72 (4.49)	8.02 (8.91)

* in brackets data for HF/6-31G//HF/6-31G GIAO CSs.

Table S12. Principal ^1H , ^{13}C and ^{15}N DFT GIAO and experimental CSs for tautomerization of **1b** (methylated at N1)^{*}



nucleus	experimental CS	proton position			
		N7 (I)	N3 (II)	N1 (III)	C5 (IV)
N1	146.67	145.07 (105.20)	124.01 (79.44)	70.79 (11.95)	194.85 (153.60)
N3	223.32	221.01 (201.26)	143.88 (102.89)	273.24 (295.13)	272.60 (281.12)
N7	116.14	102.58 (53.88)	257.70 (258.18)	377.22 (415.93)	371.77 (395.01)
C2	167.06	170.14 (189.75)	164.36 (189.35)	147.48 (149.68)	153.31 (158.83)
C4	158.91	146.55 (166.72)	126.55 (137.84)	130.31 (137.21)	124.79 (133.20)
C5	104.37	97.51 (101.83)	102.21 (106.79)	108.67 (118.76)	34.46 (33.92)
C6	153.63	150.10 (168.84)	140.25 (150.28)	133.10 (137.55)	190.35 (213.00)
<u>CH</u> ₃ (C6)	20.12	20.10 (21.53)	19.54 (20.56)	16.80 (17.32)	23.76 (25.74)
<u>CH</u> ₃ (S)	15.47	25.97 (27.20)	22.35 (22.88)	27.97 (29.08)	27.83 (28.47)
<u>CH</u> ₂ (8)	41.68	39.71 (37.13)	45.00 (41.24)	50.32 (46.41)	49.27 (44.96)
<u>CH</u> ₃ ⁺ (N1)	35.81	34.22 (35.55)	33.82 (34.81)	47.31 (47.33)	37.43 (38.79)
H(C5)	7.06	5.68 (6.54)	5.92 (6.60)	6.58 (7.47)	3.19 (3.42)
<u>CH</u> ₃ (C6)	2.41	2.24 (2.73)	2.04 (2.48)	2.05 (2.45)	2.41 (2.94)
<u>CH</u> ₃ (S)	2.59	2.68 (3.16)	2.62 (3.08)	2.85 (3.26)	2.74 (3.17)
<u>CH</u> ₂ (8)	3.44	3.46 (3.69)	3.43 (3.60)	3.96 (4.22)	3.75 (3.94)
H(X)	9.76	4.24 (4.31)	6.39 (7.44)	4.43 (3.71)	3.99 (4.18)
<u>CH</u> ₃ ⁺ (N1)	3.64	3.38 (3.98)	3.17 (3.76)	3.28 (3.74)	3.55 (4.12)

* in brackets data for HF/6-31G//HF/6-31G GIAO CSs.

Chemical shifts correlation analysis.

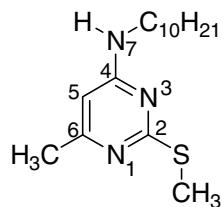
R^2 , R- correlation coefficient;

$$RMS = \sqrt{\frac{\sum (\delta_{\text{calc}} - \delta_{\text{exp}})^2}{n}} ;$$

$$MAD = \frac{\sum |\delta_{\text{calc}} - \delta_{\text{exp}}|}{n} ;$$

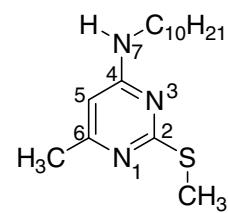
$$a, \delta_{\text{calc}} = \delta_{\text{exp}} \cdot a + b ;$$

Table S13. Statistical parameters of CSs correlation analysis for protonation of **1***



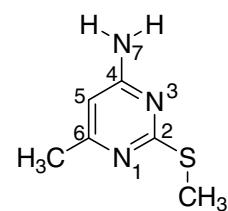
nucleus type	proton position	R^2	RMS	MAD	a
¹⁵ N	N1	0.970 (0.982)	12.2 (46.1)	9.3 (43.4)	1.031 (1.305)
	N3	0.011 (0.021)	77.2 (95.9)	70.7 (92.2)	0.160 (0.266)
	C5	0.190 (0.218)	74.1 (66.2)	51.2 (52.7)	0.600 (0.754)
	N7	0.419 (0.481)	82.7 (94.1)	65.9 (81.3)	1.399 (1.875)
¹³ C	N1	0.992 (0.989)	6.9 (10.8)	5.3 (8.6)	0.932 (1.064)
	N3	0.978 (0.980)	9.6 (13.4)	7.7 (8.8)	0.973 (1.099)
	C5	0.812 (0.828)	31.7 (37.6)	22.5 (29.1)	1.038 (1.189)
	N7	0.966 (0.977)	13.0 (17.1)	12.0 (13.8)	0.958 (1.057)
¹ H	N1	0.988 (0.994)	0.4 (0.5)	0.3 (0.4)	0.803 (0.910)
	N3	0.985 (0.938)	0.3 (0.6)	0.3 (0.5)	0.840 (0.939)
	C5	0.039 (0.057)	1.7 (1.6)	1.0 (1.2)	0.062 (0.066)
	N7	0.994 (0.987)	0.2 (0.8)	0.2 (0.7)	0.913 (1.062)

* in brackets data for HF/6-31G//HF/6-31G GIAO CSs.

Table S14. Statistical parameters of CSs correlation analysis for methylation of **1**^{*}

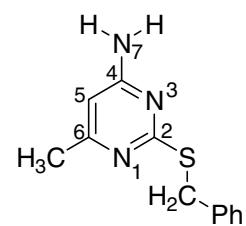
nucleus type	Me position	R ²	RMS	MAD	a
¹⁵ N	N1	0.993 (0.995)	8.0 (45.0)	5.8 (41.9)	1.083 (1.352)
	N3	0.003 (0.006)	80.1 (98.4)	73.5 (96.6)	0.088 (0.146)
	C5	0.070 (0.083)	80.1 (75.1)	57.1 (62.1)	0.355 (0.458)
	N7	0.287 (0.354)	86.1 (98.6)	65.6 (83.1)	1.081 (1.554)
¹³ C	N1	0.991 (0.987)	6.9 (11.8)	5.5 (9.4)	0.943 (1.081)
	N3	0.990 (0.988)	7.2 (14.2)	6.0 (10.8)	0.951 (1.087)
	C5	0.842 (0.845)	29.6 (37.4)	20.1 (29.3)	1.074 (1.228)
	N7	0.975 (0.985)	11.3 (15.9)	10.6 (12.6)	0.978 (1.080)
¹ H	N1	0.981 (0.995)	0.7 (0.4)	0.4 (0.4)	0.698 (0.791)
	N3	0.992 (0.993)	0.6 (0.5)	0.3 (0.4)	0.720 (0.801)
	C5	0.022 (0.027)	2.1 (2.1)	1.1 (1.4)	0.038 (-0.038)
	N7	0.996 (0.990)	0.5 (0.4)	0.3 (0.3)	0.762 (0.896)

* in brackets data for HF/6-31G//HF/6-31G GIAO CSs.

Table S15. Statistical parameters of CSs correlation analysis for protonation of **2**

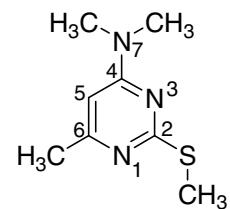
nucleus type	proton position	R ²	RMS	MAD	a
¹⁵ N	N1	na [†]	31.4	31.4	na
	N3	na	80.0	80.0	na
	C5	na	113.9	113.9	na
	N7	na	126.5	126.5	na
¹³ C	N1	0.995	7.1	5.7	0.938
	N3	0.971	11.9	10.3	0.907
	C5	0.806	34.0	25.4	1.050
	N7	0.956	13.9	11.8	0.948
¹ H	N1	1.000	0.3	0.3	1.094
	N3	0.998	0.2	0.2	1.132
	C5	0.558	1.9	1.2	6.040
	N7	0.998	0.1	0.1	1.053

[†] Due to low solubility no full set of experimental data were available to calculate the value.

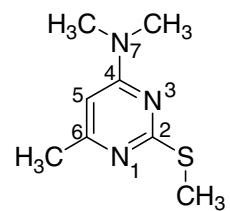
Table S16. Statistical parameters of CSs correlation analysis for protonation of **3**

nucleus type	proton position	R^2	RMS	MAD	a
^{15}N	N1	na [†]	27.4	25.6	0.748
	N3	na	63.0	59.1	2.547
	C5	na	80.9	58.9	2.449
	N7	na	99.3	91.8	3.403
^{13}C	N1	0.954	10.7	8.7	0.943
	N3	0.966	10.6	8.6	0.900
	C5	0.750	29.5	20.9	1.087
	N7	0.913	14.3	12.0	0.972
^1H	N1	0.973	0.3	0.3	0.949
	N3	0.983	0.3	0.3	0.951
	C5	0.644	1.4	0.8	0.684
	N7	0.989	0.2	0.2	0.994

[†]Due to low solubility no full set of experimental data were available to calculate the value.

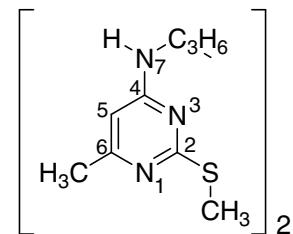
Table S17. Statistical parameters of CSs correlation analysis for protonation of **4**

nucleus type	proton position	R^2	RMS	MAD	a
^{15}N	N1	0.937	14.9	10.5	0.958
	N3	0.073	76.6	68.3	0.354
	C5	0.280	75.4	57.8	0.598
	N7	0.495	81.0	60.4	1.322
^{13}C	N1	0.997	6.3	4.8	0.928
	N3	0.982	8.9	7.0	0.913
	C5	0.849	27.5	17.8	1.049
	N7	0.983	10.0	9.0	0.984
^1H	N1	0.998	0.2	0.2	1.064
	N3	0.986	0.2	0.2	1.074
	C5	0.003	1.5	0.8	0.214
	N7	0.997	0.1	0.1	1.080

Table S18. Statistical parameters of CSs correlation analysis for methylation of **4**

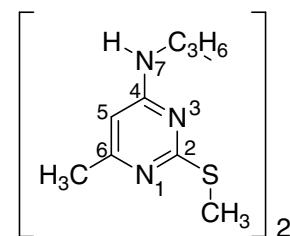
nucleus type	Me position	R ²	RMS	MAD	a
¹⁵ N	N1	na [†]	4.2	3.9	0.942
	N3	na	75.9	65.9	3.405
	C5	na	95.5	84.8	2.604
	N7	na	102.0	87.3	4.187
¹³ C	N1	0.994	6.0	4.6	0.930
	N3	0.995	5.0	3.9	0.965
	C5	0.873	25.8	16.9	1.085
	N7	0.982	11.2	10.2	1.011
¹ H	N1	0.988	0.4	0.3	1.249
	N3	0.991	0.3	0.3	1.137
	C5	0.030	1.8	1.1	0.372
	N7	0.981	0.3	0.2	1.149

[†] Due to low solubility no full set of experimental data were available to calculate the value.

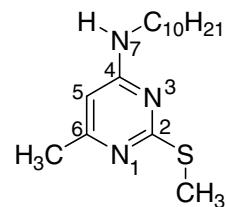
Table S19. Statistical parameters of CSs correlation analysis for protonation of **5**

nucleus type	proton position	R ²	RMS	MAD	a
¹⁵ N	N1	na [†]	20.6	20.6	na
	N3	na	93.7	93.7	na
	C5	na	126.9	126.9	na
	N7	na	141.3	141.3	na
¹³ C	N1	0.997	3.9	3.2	0.996
	N3	0.980	8.8	7.2	0.991
	C5	0.775	37.2	28.4	1.206
	N7	0.991	11.7	10.2	1.077
¹ H	N1	0.998	0.3	0.2	1.246
	N3	0.992	0.3	0.2	1.169
	C5	0.387	1.4	0.7	1.483
	N7	0.982	0.3	0.2	1.048

[†] Due to low solubility no full set of experimental data were available to calculate the value.

Table S20. Statistical parameters of CSs correlation analysis for methylation of **5**

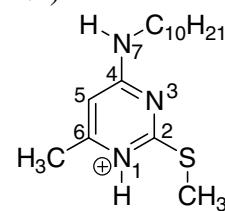
nucleus type	proton position	R ²	RMS	MAD	a
¹⁵ N	N1	0.985	10.5	7.2	1.103
	N3	0.013	81.8	75.8	0.181
	C5	0.084	78.3	56.1	0.393
	N7	0.278	89.9	68.1	1.119
¹³ C	N1	0.993	5.7	4.1	0.940
	N3	0.990	6.9	5.7	0.949
	C5	0.873	25.3	16.5	1.089
	N7	0.976	10.5	8.9	0.999
¹ H	N1	0.995	0.5	0.3	1.322
	N3	0.992	0.4	0.3	1.256
	C5	0.190	1.7	1.0	0.949
	N7	0.986	0.3	0.2	1.172

Table S21. Statistical parameters of CSs correlation analysis for tautomerization of **1**^{*}

nucleus type	proton position	R ²	RMS	MAD	a
¹⁵ N	N7 (I)	0.999 (0.999)	20.0 (38.7)	18.9 (33.4)	1.087 (1.276)
	N3 (II)	0.134 (0.205)	91.1 (104.2)	73.9 (99.2)	-0.177 (-0.299)
	N1 (III)	0.436 (0.464)	128.8 (140.9)	112.4 (116.4)	-0.600 (-0.806)
	C5 (IV)	0.613 (0.826)	155.4 (145.4)	16.2 (16.2)	-0.311 (-0.470)
¹³ C	N7 (I)	0.993 (0.995)	7.0 (7.7)	5.7 (6.3)	0.955 (1.063)
	N3 (II)	0.994 (0.996)	12.6 (4.9)	9.5 (3.6)	0.852 (0.959)
	N1 (III)	0.988 (0.993)	16.9 (9.1)	13.4 (7.1)	0.815 (0.905)
	C5 (IV)	0.842 (0.852)	28.3 (27.9)	16.2 (16.2)	0.934 (1.009)
¹ H	N7 (I)	0.995 (0.989)	0.4 (0.2)	0.4 (0.2)	0.962 (1.071)
	N3 (II)	0.996 (0.994)	0.3 (0.2)	0.3 (0.1)	1.018 (1.081)
	N1 (III)	0.987 (0.979)	0.6 (0.3)	0.5 (0.2)	0.909 (0.983)
	C5 (IV)	0.075 (0.257)	1.8 (1.6)	1.2 (1.0)	0.074 (0.102)

* in brackets data for HF/6-31G//HF/6-31G GIAO CSs.

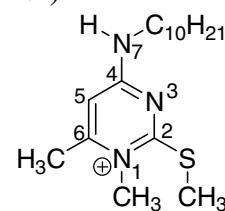
Table S22. Statistical parameters of CSs correlation analysis for tautomerization of **1a** (protonated at N1)^{*}



nucleus type	proton position	R ²	RMS	MAD	a
¹⁵ N	N7 (I)	0.970 (0.982)	12.2 (46.1)	9.3 (43.4)	1.031 (1.305)
	N3 (II)	0.467 (0.496)	102.6 (123.3)	90.3 (118.8)	-1.048 (-1.424)
	N1 (III)	0.053 (0.035)	172.4 (209.4)	143.1 (184.0)	-0.722 (-0.761)
	C5 (IV)	0.225 (0.169)	154.8 (170.8)	27.4 (28.6)	-0.871 (-1.000)
¹³ C	N7 (I)	0.992 (0.989)	6.9 (10.8)	5.3 (8.6)	0.932 (1.064)
	N3 (II)	0.971 (0.958)	15.0 (12.9)	9.7 (9.5)	0.845 (0.955)
	N1 (III)	0.969 (0.953)	20.1 (18.7)	16.7 (16.3)	0.741 (0.772)
	C5 (IV)	0.738 (0.715)	34.5 (37.8)	27.4 (28.6)	0.857 (0.939)
¹ H	N7 (I)	0.988 (0.994)	0.4 (0.5)	0.3 (0.4)	0.803 (0.910)
	N3 (II)	0.989 (0.994)	0.2 (0.3)	0.2 (0.3)	0.933 (1.012)
	N1 (III)	0.977 (0.992)	0.4 (0.9)	0.4 (0.8)	1.086 (1.234)
	C5 (IV)	0.124 (0.062)	1.6 (1.6)	1.0 (1.2)	0.103 (0.052)

* in brackets data for HF/6-31G//HF/6-31G GIAO CSs.

Table S23. Statistical parameters of CSs correlation analysis for tautomerization of **1b** (methylated at N1)^{*}



nucleus type	proton position	R ²	RMS	MAD	a
¹⁵ N	N7 (I)	0.993 (0.995)	8.0 (45.0)	5.8 (41.9)	1.083 (1.352)
	N3 (II)	0.381 (0.398)	94.6 (114.3)	81.2 (109.9)	-0.807 (-1.110)
	N1 (III)	0.009 (0.003)	159.6 (194.2)	129.0 (168.8)	-0.273 (-0.196)
	C5 (IV)	0.118 (0.060)	152.9 (164.5)	25.4 (26.5)	-0.551 (-0.536)
¹³ C	N7 (I)	0.991 (0.987)	6.9 (11.8)	5.5 (9.4)	0.943 (1.081)
	N3 (II)	0.974 (0.964)	13.6 (12.0)	8.8 (8.2)	0.863 (0.982)
	N1 (III)	0.976 (0.970)	16.4 (14.4)	13.9 (13.0)	0.796 (0.834)
	C5 (IV)	0.754 (0.733)	33.4 (36.7)	25.4 (26.5)	0.878 (0.962)
¹ H	N7 (I)	0.981 (0.995)	0.7 (0.4)	0.4 (0.4)	0.698 (0.791)
	N3 (II)	0.978 (0.990)	0.6 (0.3)	0.4 (0.3)	0.779 (0.841)
	N1 (III)	0.956 (0.978)	0.4 (0.6)	0.4 (0.5)	0.891 (1.004)
	C5 (IV)	0.149 (0.084)	1.9 (1.9)	1.1 (1.3)	0.103 (0.058)

* in brackets data for HF/6-31G//HF/6-31G GIAO CSs.