

Determination of nucleobase-pairing free energies from rotamer equilibria of 2-(methylamino)pyrimidines

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Electronic Supplementary Information

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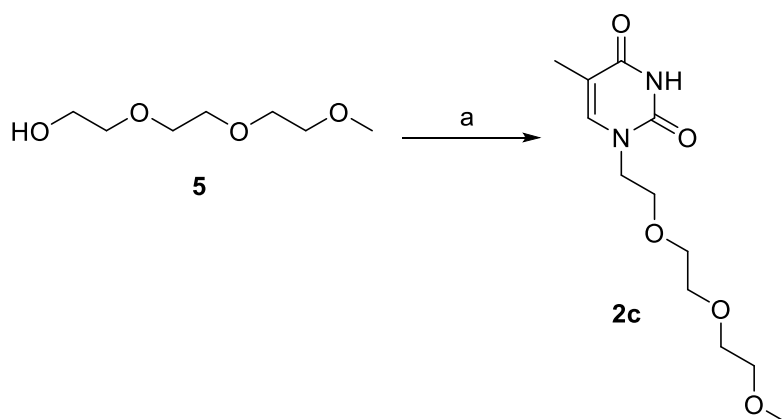
1. Methods

^1H and ^{13}C NMR spectra were recorded on a 500 MHz NMR spectrometer (^1H at 500 MHz, ^{13}C at 125.7 MHz) in $\text{DMF-}d_7$ (referenced to the solvent signal $\delta = 2.75$ (^1H) and 163.15 ppm (^{13}C), respectively) or in $\text{DMSO-}d_6$ ($\delta = 2.50$ (^1H) and 39.70 ppm (^{13}C)). Complete signal assignment is based on homo- and heteronuclear correlation experiments COSY, HSQC and HMBC.

Mass spectra were measured on LTQ Orbitrap XL (Thermo Fisher Scientific) using electrospray ionization (ESI). Column chromatography was performed on Silica gel 60 (Fluka) and thin-layer chromatography (TLC) on Silica gel 60 F254 foils (Merck). Solvents were evaporated at 2 kPa and bath temperature 30–60 °C; the compounds were dried at 13 Pa and 50 °C. UPLC samples were measured on Waters UPLC H-Class Core System, (column Waters Acquity UPLC BEH C18 1.7 μm , 2.1x100 mm), Waters Acquity UPLC PDA detector, Mass spectrometer Waters SQD2 and MassLynx Mass Spectrometry Software. For reverse-phase flash column chromatography, C-18 RediSep Rf columns Teledyne ISCO (50g) were used.

Compound **1** was prepared according to ref.¹ Compound **2a**, **2b** and **2d–2g** were purchased from Sigma Aldrich and used without purification. The preparation of compounds **2c**, **3**, and **4** is describe below.

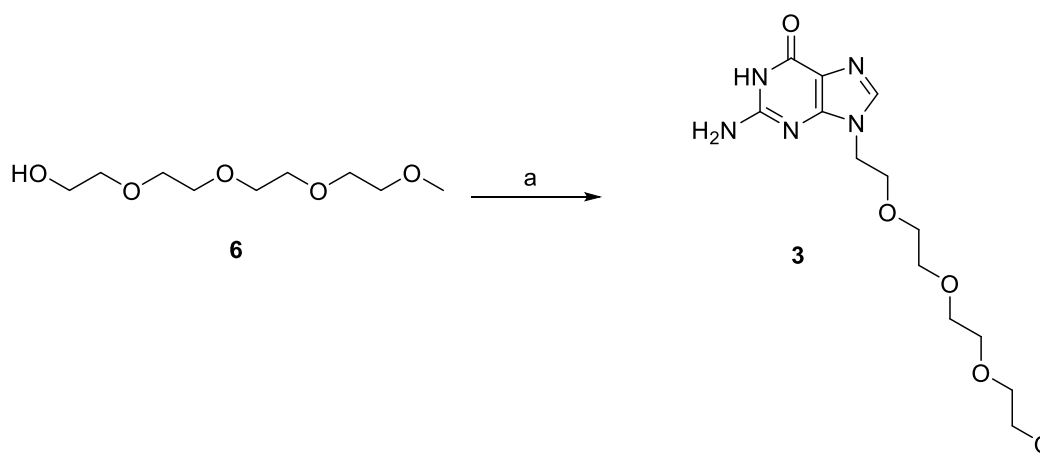
1.1. Synthesis



Scheme S1. Reagents and conditions: (a) thymine, PPh_3 , DIAD, THF, 0 °C to r.t., 18 h.

1-(2,5,8-Trioxadecan-10-yl)-5-methylpyrimidine-2,4(1*H*,3*H*)-dione (**2c**).

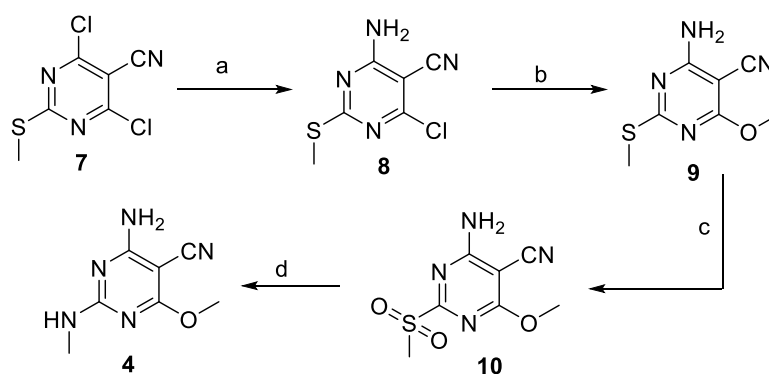
Thymine (756 mg, 6 mmol), triphenylphosphine (1.57 g, 6 mmol) and alcohol **5** (800 μL , 5 mmol) were suspended in THF (30 mL) and reaction mixture was cooled-down with ice-water bath. DIAD (1.19 mL, 6 mmol) was slowly added during 10 min and the reaction mixture was allowed to slowly warm-up to r.t. and then stirred for 16 h. Reaction mixture was filtered and filtrate was evaporated. Product was isolated by reversed-phase chromatography (100 g column, water/0.1% formic acid -acetonitrile /0.1% formic acid 0% \rightarrow 30%). Compound **2c** (250 mg, 18%) was obtained after lyophilization from dioxane. ^1H NMR ($\text{DMSO-}d_6$): 11.24 (1H, bs, NH), 7.45 (1H, q, $J_{6-\text{CH}_3} = 1.1$ Hz, H6), 3.78 (2H, t, $J_{1',2'} = 5.3$ Hz, H1'), 3.58 (2H, t, $J_{1',2'} = 5.3$ Hz, H2'), 5.36-5.46 (6H, m, H3'-H5'), 3.40 (2H, m, H6'), 3.22 (3H, s, H7'), 1.74 (3H, d, $J_{\text{CH}_3-6} = 1.1$ Hz, CH_3); ^{13}C NMR ($\text{DMSO-}d_6$): 164.54 (C4), 151.10 (C2), 142.35 (C6), 108.04 (C5), 71.49 (C6'), 70.01-69.80 (m, 3C, C3'-C5'), 68.16 (C2'), 58.26 (C7'), 47.05 (C1'), 12.13 (CH_3). ESI MS, m/z (%): 295.1 [$\text{M} + \text{Na}$] $^+$; HRMS (ESI) calcd for $\text{C}_{12}\text{H}_{20}\text{O}_5\text{N}_2\text{Na}$ [$\text{M} + \text{Na}$] $^+$ 295.1264, found 295.1262.



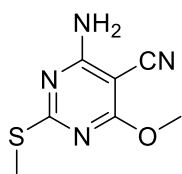
Scheme S2. Reagents and conditions: (a) 1. 2-amino-6-chloropurine, PPh₃, DIAD, THF, 0 °C to r.t., 18h; 2. DABCO, K₂CO₃, dioxane-water, reflux, 3 h.

2-Amino-9-(2,5,8,11-tetraoxatridecan-13-yl)-1,9-dihydro-6H-purin-6-one (**3**).

Suspension of 2-amino-6-chloropurine (500 mg, 2.95 mmol), triphenylphosphine (1.01 g, 3.84 mmol) and alcohol **6** (745 μ L, 3.84 mmol) in THF (15 mL) was cooled with ice-water bath. DIAD (0.75 mL, 3.84 mmol) was added dropwise during 10 min. Reaction mixture was allowed to warm to r.t. and stirred for 18 h, evaporated and crude residue was purified by reversed-phase chromatography (100 g column, water-methanol 0% \rightarrow 80%). Fractions containing product (contaminated with hydrazine byproduct) were evaporated and used in the next step. Crude material was combined with DABCO (347 mg, 3.1 mmol), potassium carbonate (567 mg, 4.1 mmol) in dioxane-water (26 mL, 1:1) and reaction mixture was heated to reflux for 3 h. Volatiles were evaporated, residue was co-evaporated with ethanol (2 x 20 mL) and solids were extracted with portions of chloroform-ethanol mixture (2 x 100 mL, 3:1). Solution was filtrated and evaporated. Product was isolated by flash chromatography (80 g column, chloroform-methanol 0% \rightarrow 40%). Final purification was then achieved by reversed-phase chromatography (100 g column, water-acetonitrile 5% \rightarrow 15%). Compound **3** (250 mg, 18%) was obtained as white foam after lyophilization from dioxane. ¹H NMR (DMSO-*d*₆): 10.55 (1H, bs, NH), 7.64 (1H, s, H8), 6.45 (2H, bs, NH₂), 4.08 (2H, t, *J*_{1',2'} = 5.4 Hz, H1'), 3.69 (2H, t, *J*_{1',2'} = 5.4 Hz, H2'), 3.53-3.43 (10H, m, H3'-H7'), 3.41 (2H, m, H8'), 3.22 (3H, s, H9'); ¹³C NMR (DMSO-*d*₆): 157.06 (C6), 153.73 (C2), 151.38 (C4), 138.01 (C8), 116.57 (C5), 71.47 (C8'), 70.0-69.73 (m, 5C, C3'-C7'), 68.61 (C2'), 58.26 (C9'), 42.69 (C1'). ESI MS, *m/z* (%): 342.2 [M + H]⁺; HRMS (ESI) calcd for C₁₄H₂₄O₅N₅ [M + H]⁺ 342.1772, found 342.1767.

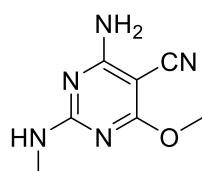


Scheme S3. Reaction conditions: a) ammonia (ethanolic solution, 2 M), r.t., 12 h; b) MeONa, MeOH, reflux, 2 h; c) *m*CPBA, CH₂Cl₂, 0 °C; d) MeNH₂ (33% ethanolic solution), *i*PrOH, 80 °C, 12 h.



4-Amino-6-methoxy-2-(methylsulfanyl)pyrimidine-5-carbonitrile (**9**)

Commercially available compound **7** (500 mg, 2.3 mmol) was treated with ammonia (ethanolic solution, 2 M, 40 mL) at r. t. for 12 h. The reaction mixture was diluted with EtOAc (60 mL) and water (100 mL). Aqueous layer was extracted by EtOAc (2 x 60 mL). Organic layers were collected, dried over MgSO₄ and filtered. The solvent was evaporated under the vacuum to give crude compound **8** in a quantitative yield. Compound **8** (400 mg, 2 mmol) was treated with MeONa (324 mg, 6 mmol) in MeOH (80 mL) under reflux for 2 h. After cooling to r. t., the solution was diluted with EtOAc (60 mL) and water (120 mL) was added. Aqueous layer was extracted with EtOAc (2 x 60 mL). Organic layers were collected, dried over MgSO₄ and filtered. The solvent was evaporated under the vacuum. Silica gel flash chromatography gave **9** (230 mg, 59%) as a white solid. ¹H NMR (DMSO-*d*₆): 7.78 (2H, bs, NH₂), 3.93 (3H, s, OCH₃), 2.46 (3H, s, SCH₃); ¹³C NMR (DMSO-*d*₆): 174.10 (C2), 169.82 (C6), 164.19 (C4), 114.57 (CN), 68.59 (C5), 54.74 (OCH₃), 13.68 (SCH₃); ESI MS, *m/z* (%): 197.0 [M + H]⁺; HRMS (ESI) calcd for C₇H₉ON₄S [M + H]⁺ 197.0492, found 197.0489.



4-Amino-6-methoxy-2-(methylamino)pyrimidine-5-carbonitrile (**4**)

Compound **9** (230 mg, 1.2 mmol) was dissolved in CH₂Cl₂ (80 mL). The solution was cooled to 0 °C and *m*PCBA (825 mg, 4.8 mmol) in CH₂Cl₂ (100 mL) was added dropwise. The reaction mixture was stirred at 0 °C for 3 h. The solution was extracted with aqueous solution of NaHCO₃ (70 mL), brine (70 mL) and water (70 mL). The organic layer was dried over MgSO₄ and filtered. The solvent was evaporated under the vacuum to give compound **10**. Compound **10** was dissolved in *i*PrOH (40 mL) and excess of MeNH₂ (33 % ethanolic solution) was added. The reaction mixture was stirred at 80 °C for 12 h. After cooling to r. t., water (50 mL) was added and the mixture was extracted by EtOAc (3 x 40 mL). Organic layers were collected, dried over MgSO₄ and filtered. The solvent was evaporated under the vacuum. Reversed-phase flash chromatography (water–MeOH, 0–100%) gave **4** (80 mg, 37%) as a white solid. ¹H NMR (DMF-*d*₇): 7.42–6.91 (4.9H, m, NH-A, NH-B, NH₂-A, NH₂-B), 3.96 (1.9H, s, OCH₃, B), 3.86 (3H, s, OCH₃, A), 2.91 (1.9, d, *J*_{CH₃,NH} = 4.8 Hz, NHCH₃, B), 2.87 (1.9, d, *J*_{CH₃,NH} = 4.8 Hz, NHCH₃, A); ¹³C NMR (DMF-*d*₇): 172.69 (C6, B), 171.86 (C6, A), 167.41 (C4, A), 166.75 (C4, B), 163.79 (C2, B), 163.49 (C2, A), 116.99 (CN, A), 116.91 (CN, B), 64.28 (C5, B), 63.84 (C5, A), 54.29 (OCH₃, B), 54.21 (OCH₃, A), 28.47 (NHCH₃, A), 28.37 (NHCH₃, B); ESI MS, *m/z* (%): 180.0 [M + H]⁺; HRMS (ESI) calcd for C₇H₁₀ON₅ [M + H]⁺ 180.0880, found 180.0878.

1.2. NMR spectroscopy

The NMR determination of association constants of compound **1** with compounds **2a–2h** was performed in CD₃OD or DMF-*d*₇. First, ¹H NMR spectrum of 10 mmol solution of compound **1** alone was measured and the ratio of rotamers A and B was determined by integration of signals corresponding to the individual rotamers. The binding partner was then added in five successive additions leading to the final concentration of the binding partner of 50–100 mmol, depending on the solubility of the compound. The concentration of compound **1** was calculated from the mass of the compound and the volume of the solvent used for the preparation of the solution. The concentration of the rotamers was calculated from the relative ratio and the total concentration of compound **1**. The concentration of the binding partner was also obtained from its relative signal intensity and the known concentration of compound **1**. The concentration of individual rotamers and of the binding partner was used in the calculation of the association constant according to equation (1) shown in the main text.

1.3. Computational details

The studied structures were subjected to geometry optimization at DFT level using the B3LYP functional^{2,3} with standard 6-31++g(2d,p) basis set and polarizable continuum model used for implicit DMF solvation.^{4,5} To simplify the calculations, the alkyl chain of compounds **2c** and **3** was substituted by a methyl group. Counterpoise corrections of basis set superposition error were calculated for geometry optimized complexes.⁶ The vibrational frequencies and free energies were calculated for all of the optimized structures, and the stationary-point (minimum) character was thus confirmed. The Gaussian16 program package was used throughout this study.⁷

1.4. Derivation of equation (1) in the main text

Experimentally available concentration values:

$$\begin{aligned} [L_{TOT}] &= [L] + [BL] \\ [S_{TOT}] &= [A] + [B] + [BL] \\ [A_{TOT}] &= [A] \\ [B_{TOT}] &= [B] + [BL] \end{aligned} \quad (1)$$

Equilibrium constant K_1 of reaction $B \rightarrow A$ is known from a separate measurement

$$K_1 = \frac{[A]}{[B]} \quad (2)$$

Equilibrium constant K_2 of reaction $B+L \rightarrow BL$ is defined as

$$K_2 = \frac{[BL]}{[B][L]} \quad (3)$$

Unknown concentrations are obtained from equations (1), utilizing (2)

$$\begin{aligned} [B] &= \frac{[A_{TOT}]}{[K_1]} \\ [L] &= [L_{TOT}] - [B_{TOT}] + \frac{[A_{TOT}]}{K_1} \\ [BL] &= [B_{TOT}] - \frac{[A_{TOT}]}{K_1} \end{aligned}$$

Substitution of these expressions into eq. (3) leads to

$$K_2 = \frac{K_1[B_{TOT}] - [A_{TOT}]}{[A_{TOT}] \left([L_{TOT}] - [B_{TOT}] + \frac{[A_{TOT}]}{K_1} \right)}$$

or alternatively

$$K_2 = K_1 \frac{K_1[B_{TOT}] - [A_{TOT}]}{[A_{TOT}]^2 + K_1[A_{TOT}]([L_{TOT}] - [B_{TOT}])}$$

For the purpose of ΔG calculations, the concentrations were replaced by dimensionless quotients $[X]/[X^0]$, where $[X^0]$ is 1M concentration of a given reagent (A_{TOT} , B_{TOT} , and L_{TOT}). Free energies of complex formation were then calculated using the equation: $\Delta G = -RT \ln K_2$, where R is the universal gas constant and T is temperature. Standard deviation of ΔG determined at different concentration of the ligand were used as an estimate of the ΔG error.

2. Results – additional Figures and Tables

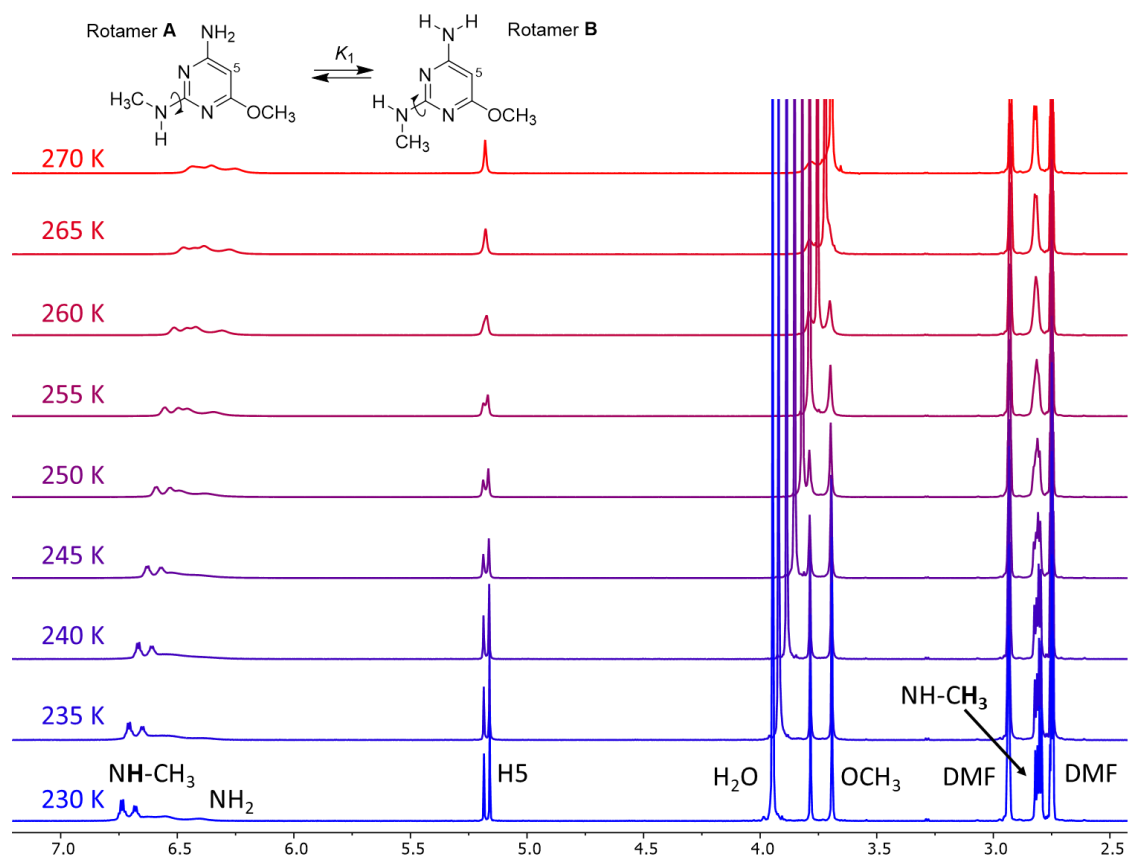


Figure S1. Variable-temperature ¹H NMR spectra of compound **1** in DMF-*d*₇.

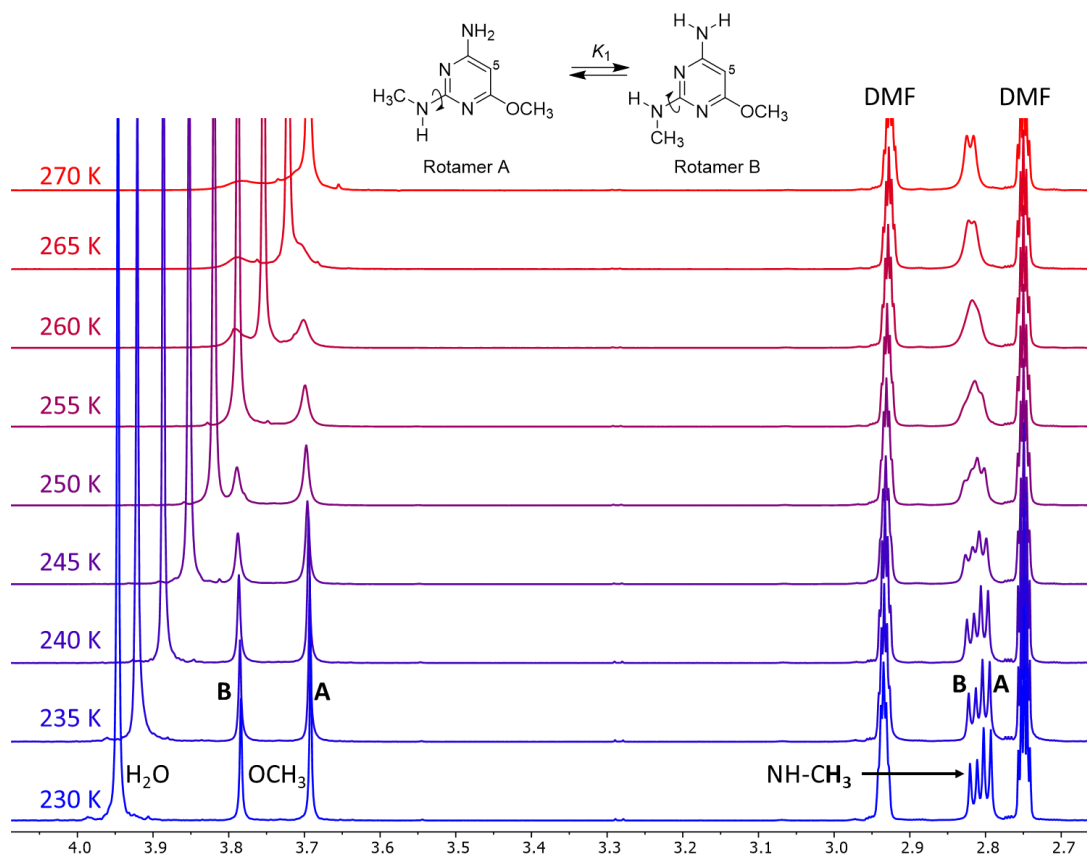


Figure S2. Aliphatic region of variable-temperature ^1H NMR spectra of compound **1** in $\text{DMF-}d_7$.

The assignment of the signals to rotamers **A** and **B** of compound **1** is based four-bond correlations between the NH hydrogen and the carbon atom C-4 or C-6 in H,C-HMBC spectra. Four-bond correlations are usually observed when the atoms in the coupling path are in a W-like arrangement (see Figure S3). The presence of the NH-C6 cross-peak (and the absence of the NH-C4 cross-peak) observed for the less abundant rotamer provides a clear evidence of the methylamino conformation with the NH hydrogen heading towards N3 and the methyl group towards N1, i.e. it is rotamer B. The C6 carbon resonance is easily identified by a strong HMBC cross-peak with hydrogen atoms of the methoxy group in position 6.

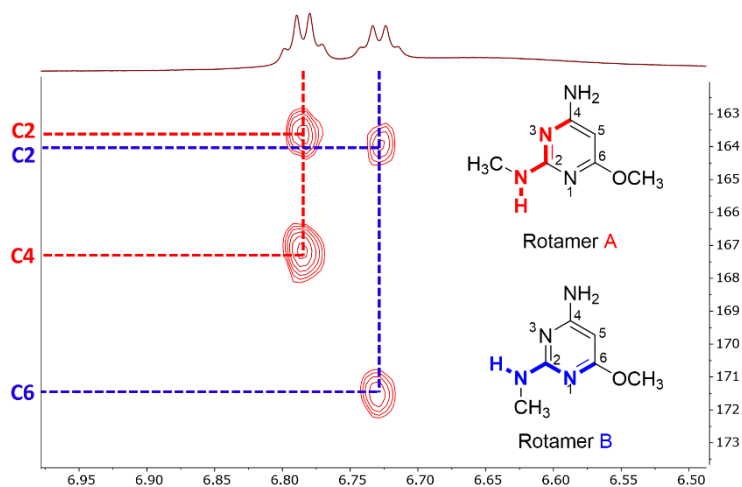


Figure S3. Part of the HMBC spectrum of compound **1** measured in $\text{DMF-}d_7$ at 243 K showing the assignment of signals corresponding to rotamer A and B.

Table S1. The dependence of the rotamer mixture composition of compound **1** on temperature and solvent. The ratio was determined by integration of the methoxy hydrogen signals in ^1H NMR spectra.

Solvent	T	A (%)	B (%)
DMF	245.0	57.33	42.67
DMF	240.0	57.83	42.17
DMF	235.0	58.70	41.30
DMF	229.9	59.00	41.00
DMF	210.0	61.51	38.49
MeOD	210.0	44.64	55.36
DMF/MeOD 1:0.5 (v/v)	210.0	55.93	44.07
DMF/MeOD 1:1 (v/v)	210.0	52.56	47.44
DMF/MeOD 1:2 (v/v)	210.0	50.64	49.36
DMF/MeOD 1:2.5 (v/v)	210.0	49.57	50.43
EtOD ^a	210.0	49.77/50.23 ^a	49.77/50.23 ^a

^aThe signals were not assigned to the individual rotamers.

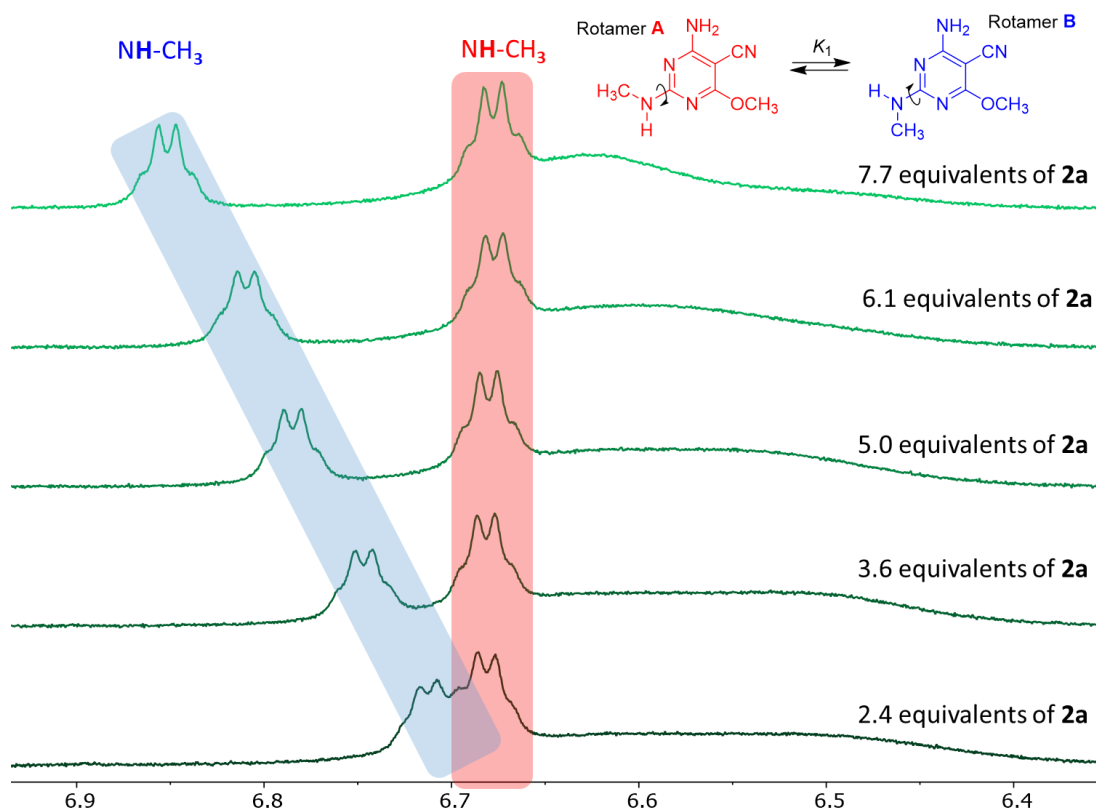


Figure S4. The amino region of ^1H NMR spectra of compound **1** (10 mM) after additions of compound **2a** measured in $\text{DMF-}d_7$ at 240 K.

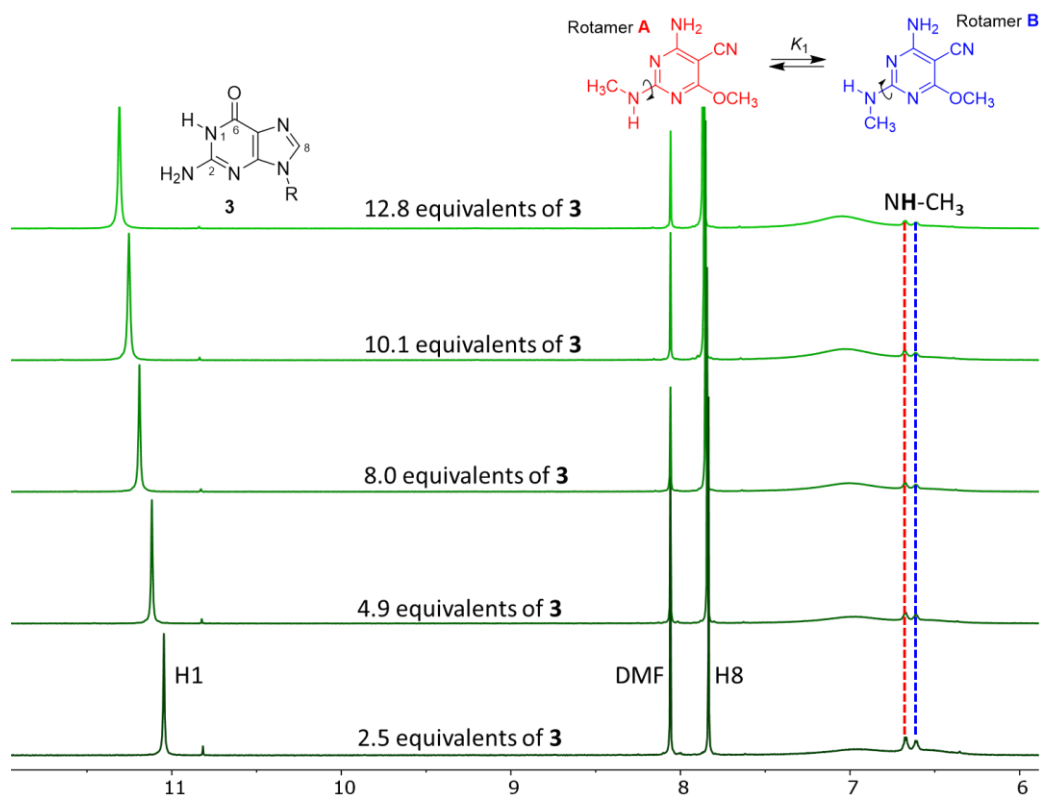


Figure S5. Downfield region of ^1H NMR spectra of compound **1** (10 mM) after successive additions of compound **3** measured in $\text{DMF-}d_7$ at 240 K.

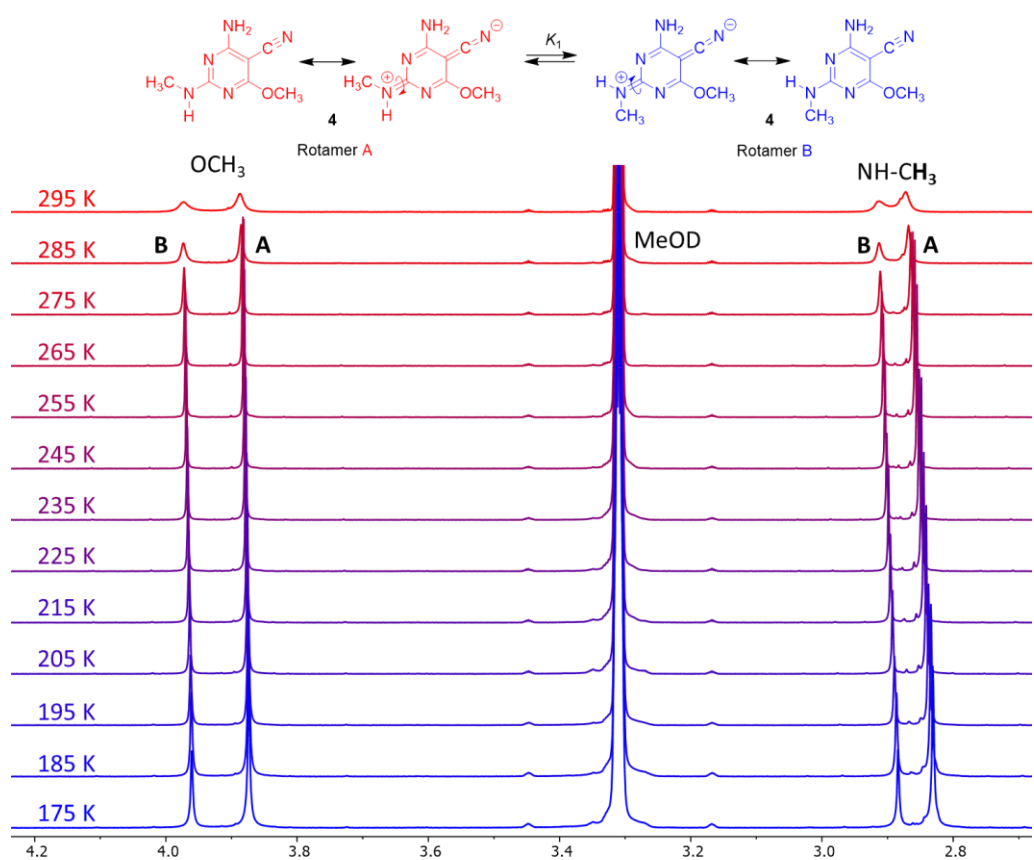


Figure S6. Aliphatic region of variable-temperature ^1H NMR spectra of compound **4** in CD_3OD .

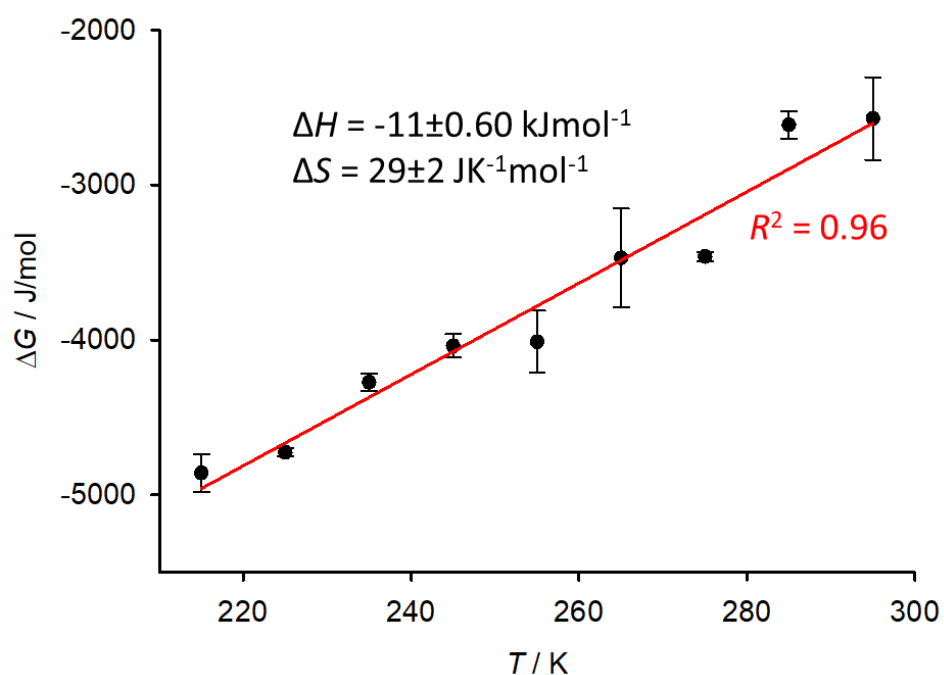


Figure S7. The temperature dependence of the free energy of formation of the intermolecular complex between compound **4** and substituted uracil **2c** in methanol.

Table S2. The calculated free energies, enthalpies and entropic terms of complex formation between compound **1** and compounds **2a–2g** calculated with implicit DMF solvation at 240 K. All data are in kJ/mol. A and B denotes two mutual orientations of the molecules in the dimer (Watson-Crick like and reverse Watson-Crick like).

	ΔG	ΔH	$-T\Delta S$
2a-A	-10.7	-50.7	40.0
2a-B	-10.4	-50.9	40.5
2b-A	-9.9	-50.5	40.6
2b-B	-10.4	-50.6	40.1
2c-A	-11.1	-51.0	39.9
2c-B	-10.9	-51.0	40.1
2d-A	-10.3	-50.9	40.6
2d-B	-11.0	-50.9	39.9
2e-A	-10.1	-50.5	40.5
2e-B	-10.5	-50.5	40.0
2f-A	-10.9	-50.6	39.7
2f-B	-9.7	-50.6	40.9

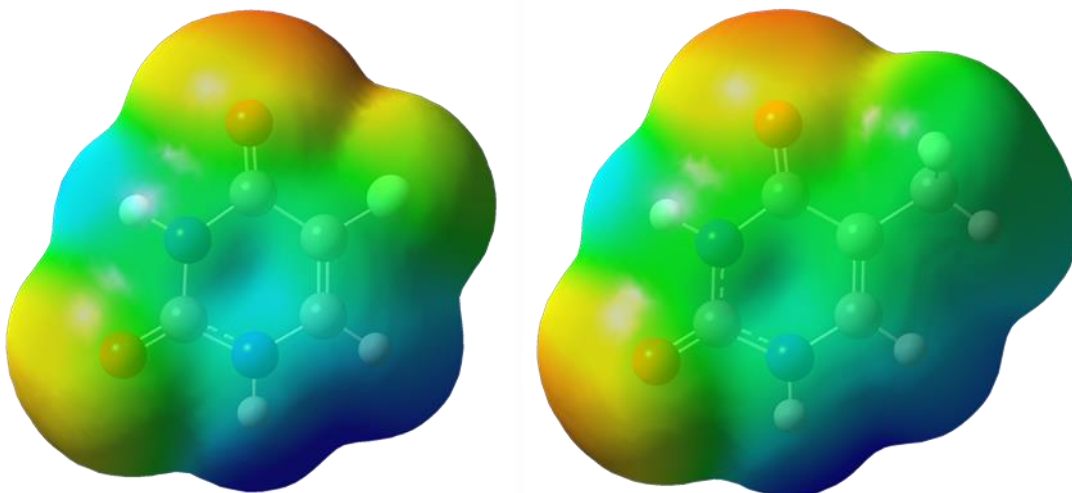


Figure S8. The calculated electrostatic potential plots of 5-fluorouracil **2d** (left) and thymine **2b** (right).

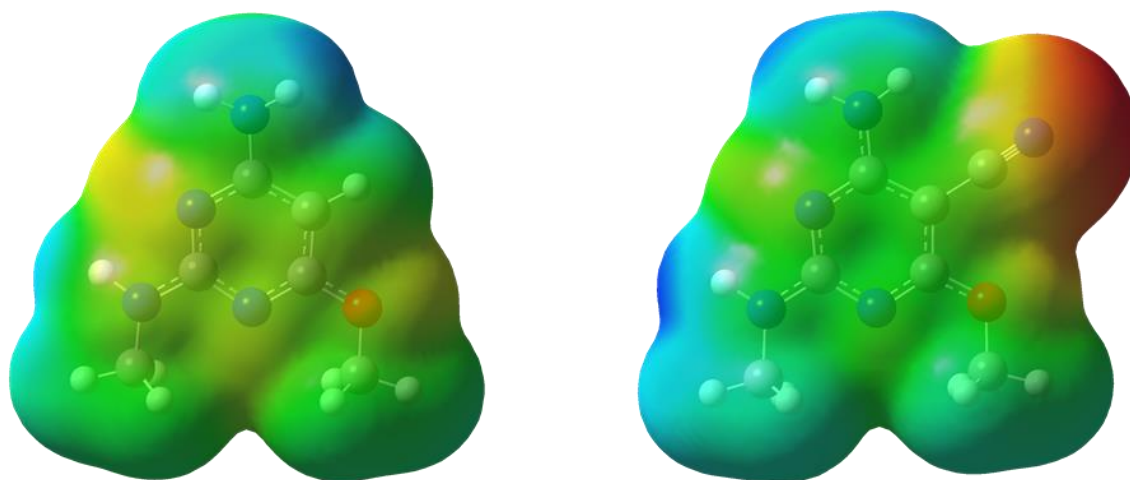
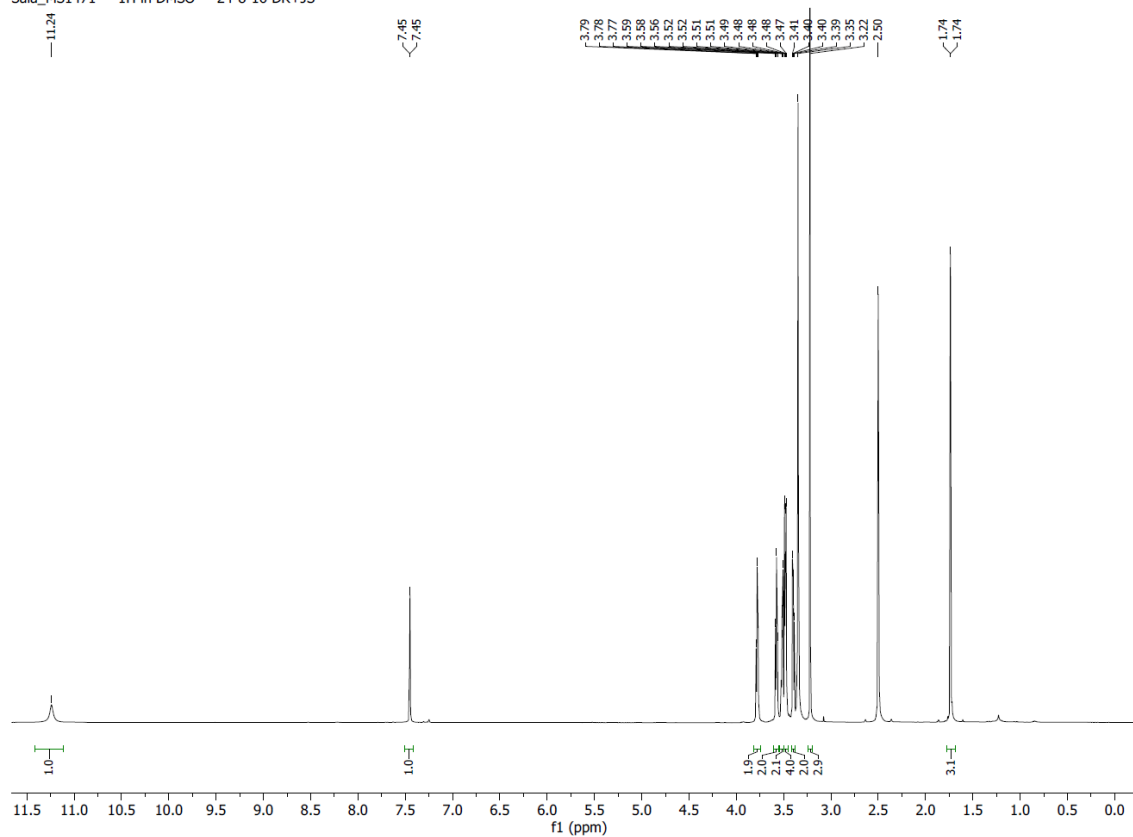


Figure S9. The calculated electrostatic potential plots of compound **1** (left) and compound **4** (right).

3. Experimental ^1H and ^{13}C NMR spectra and HRMAS spectra of newly prepared compounds

Sala_MS1471 — ^1H in DMSO — 24-8-16 DR+JS



Sala_MS1471 — APT in DMSO — 24-8-16 DR+JS

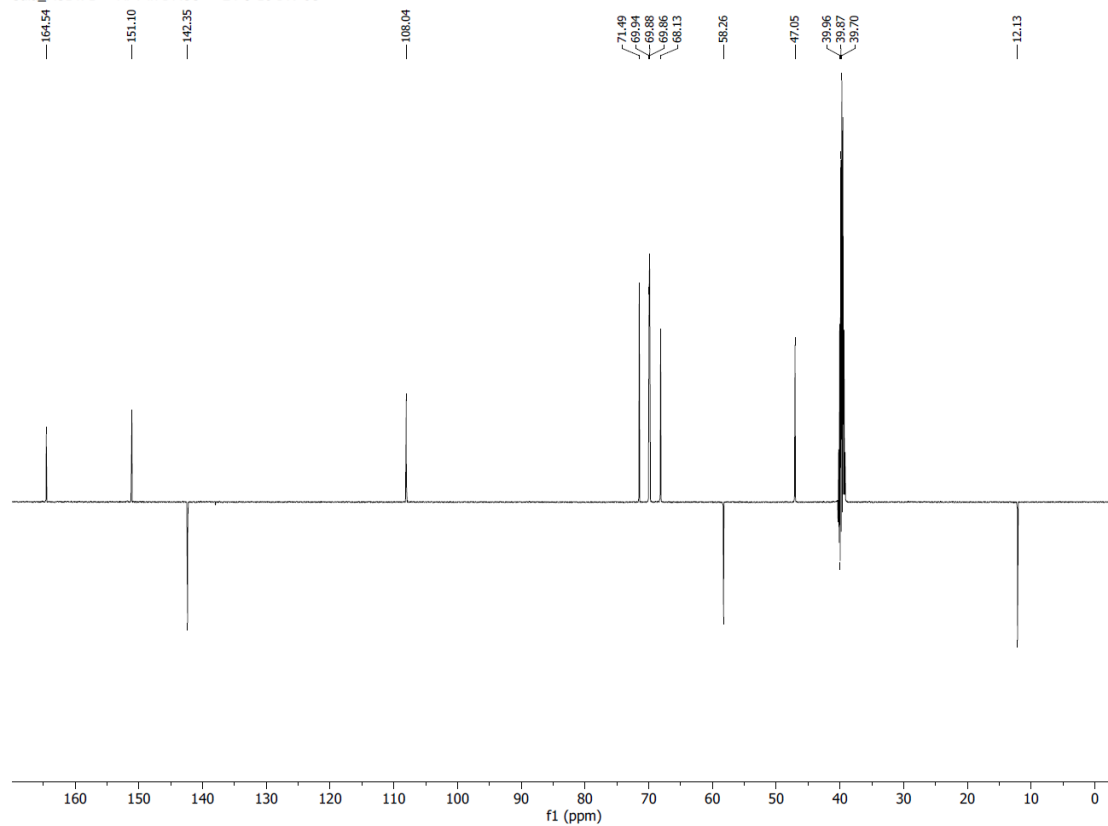


Figure S10. ^1H (top) and ^{13}C APT (bottom) spectra of compound 2c.

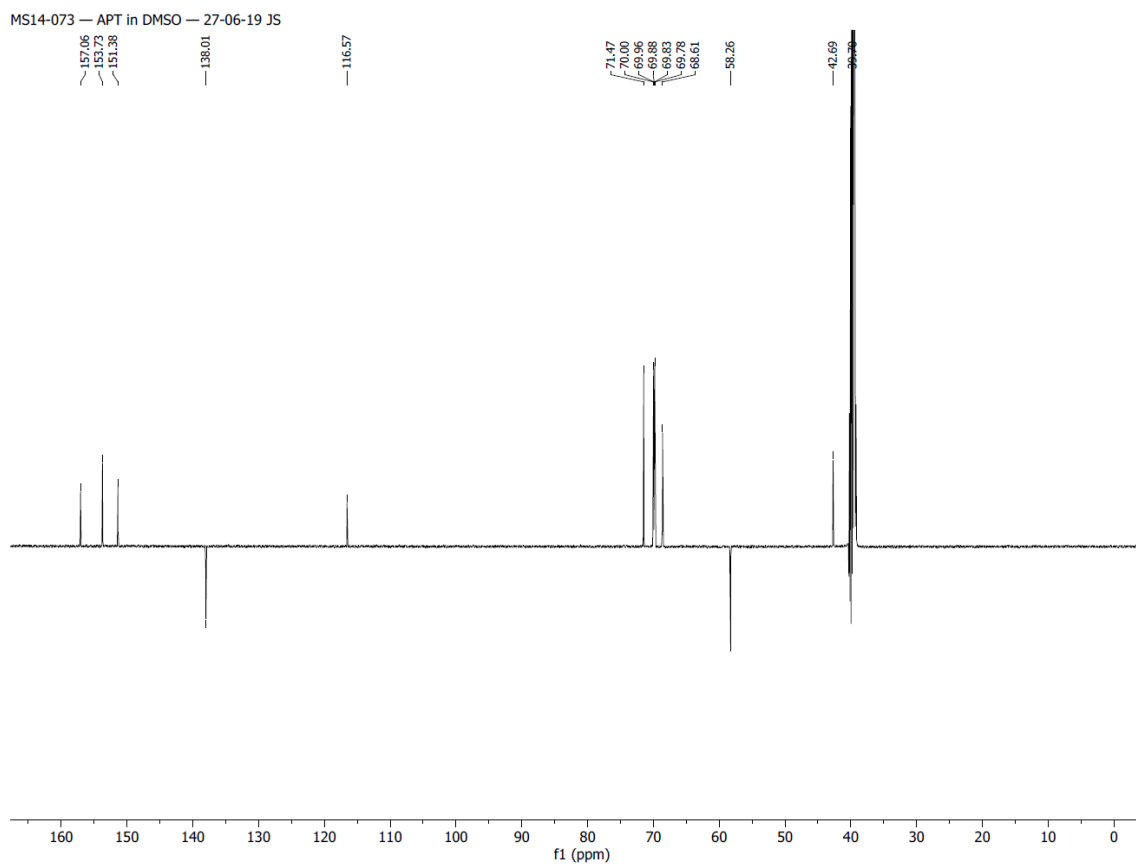
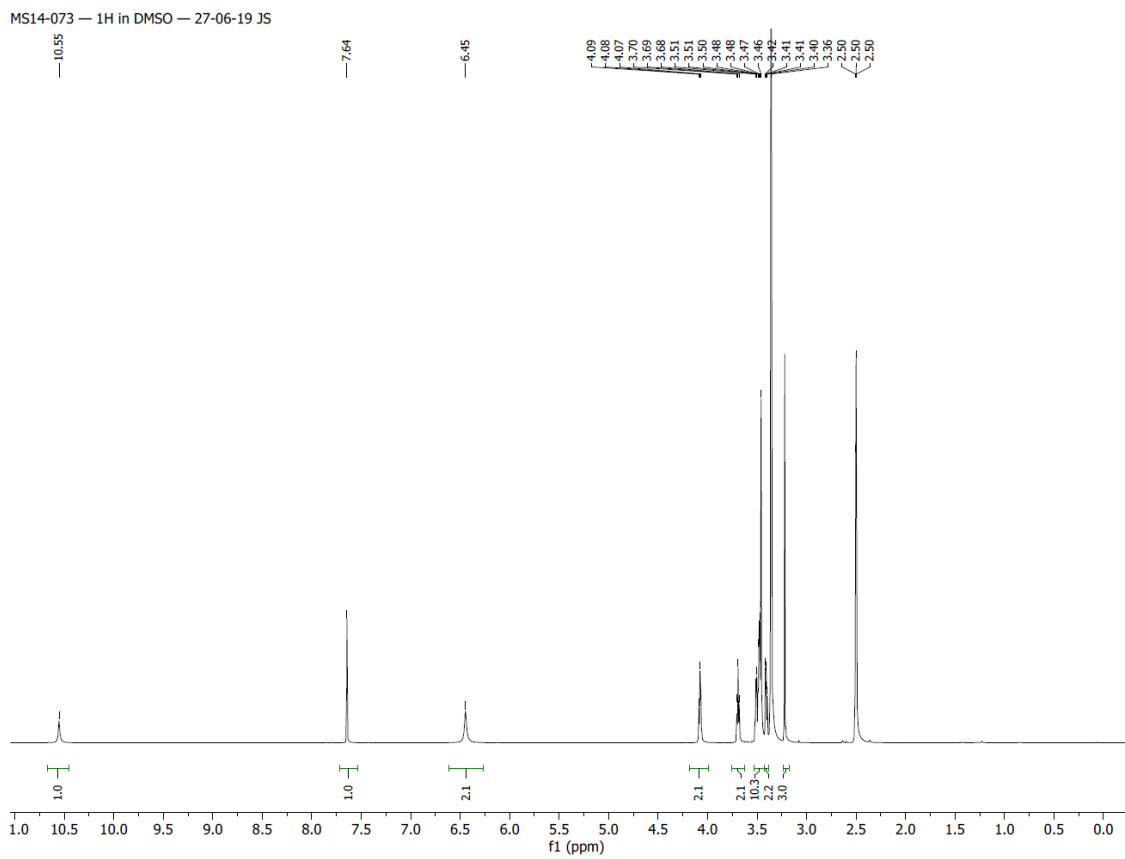


Figure S11. ¹H (top) and ¹³C APT (bottom) spectra of compound **3**.

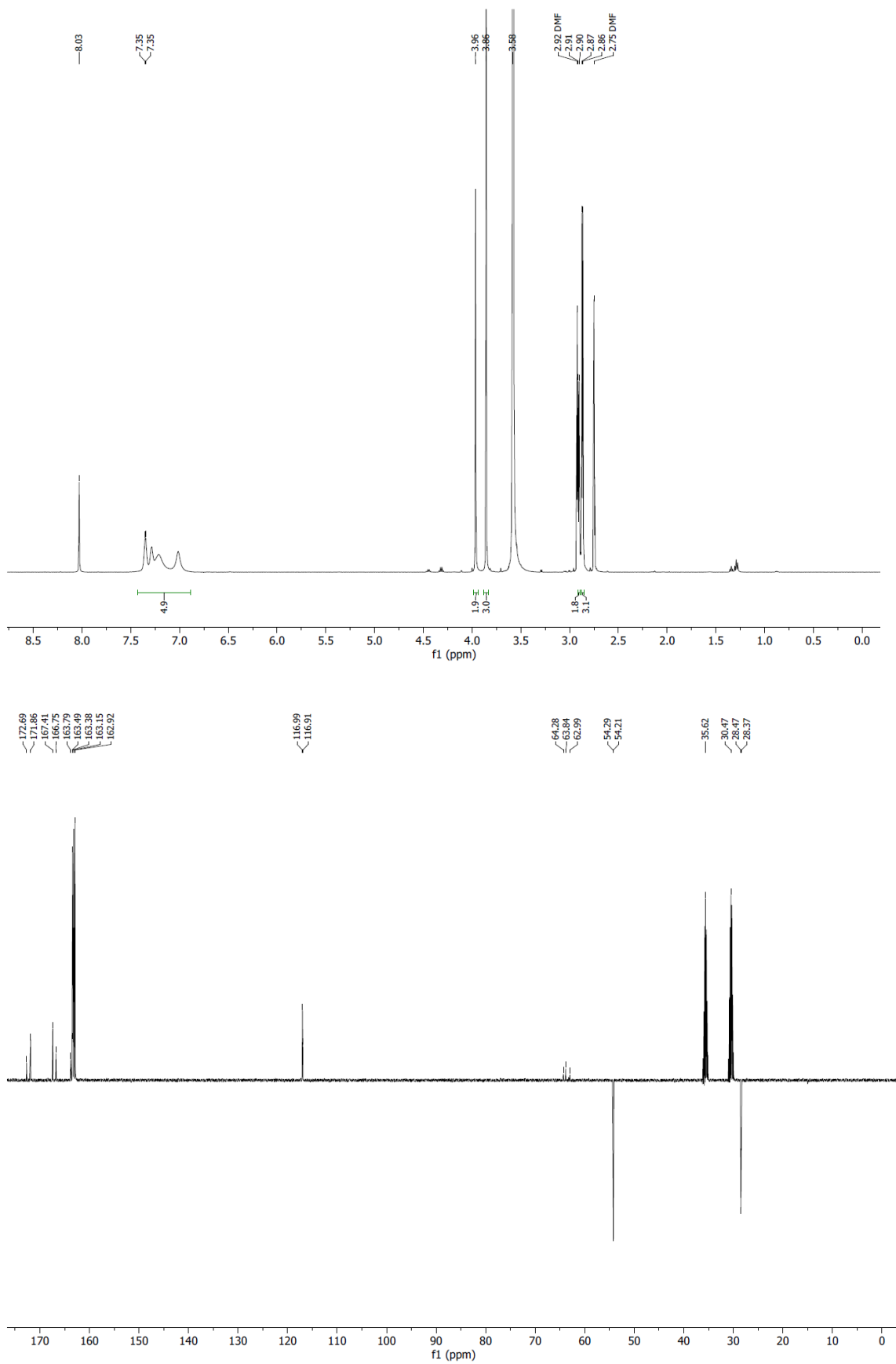


Figure S12. ^1H (top) and ^{13}C APT (bottom) spectra of compound 4.

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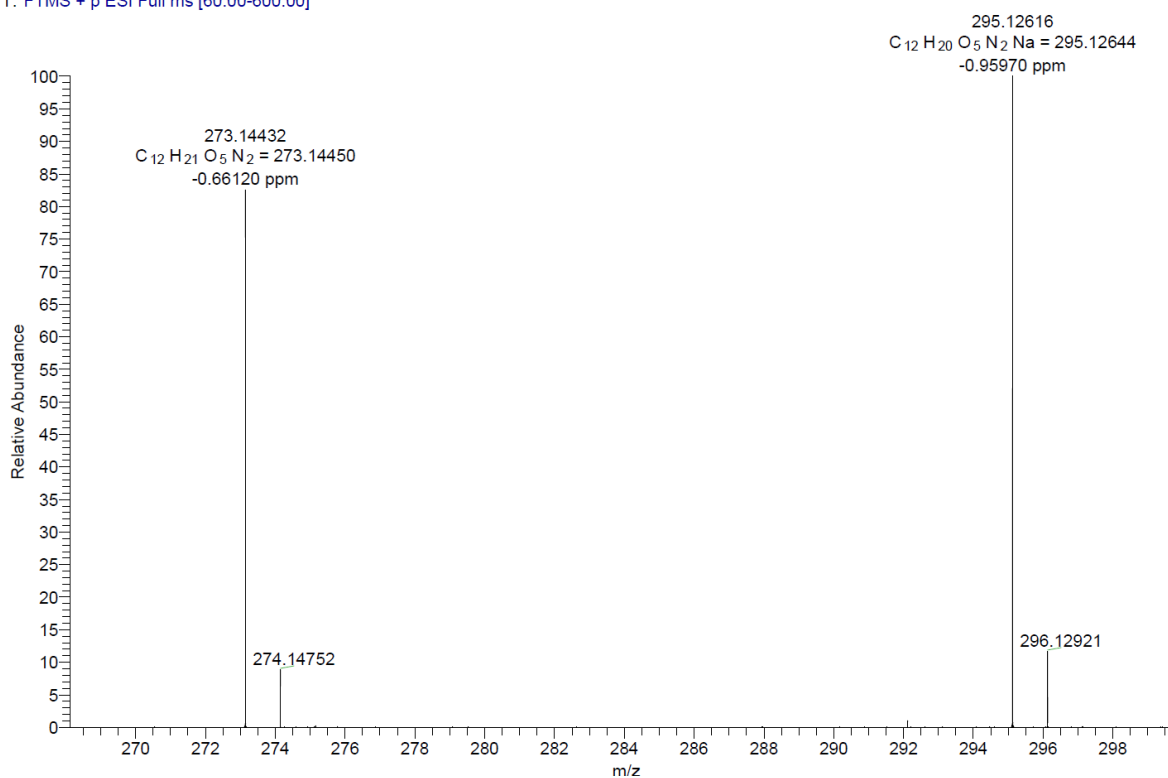


Figure S13. HRMS spectrum of compound 2c.

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T: FTMS + p ESI Full ms [200.00-2000.00]

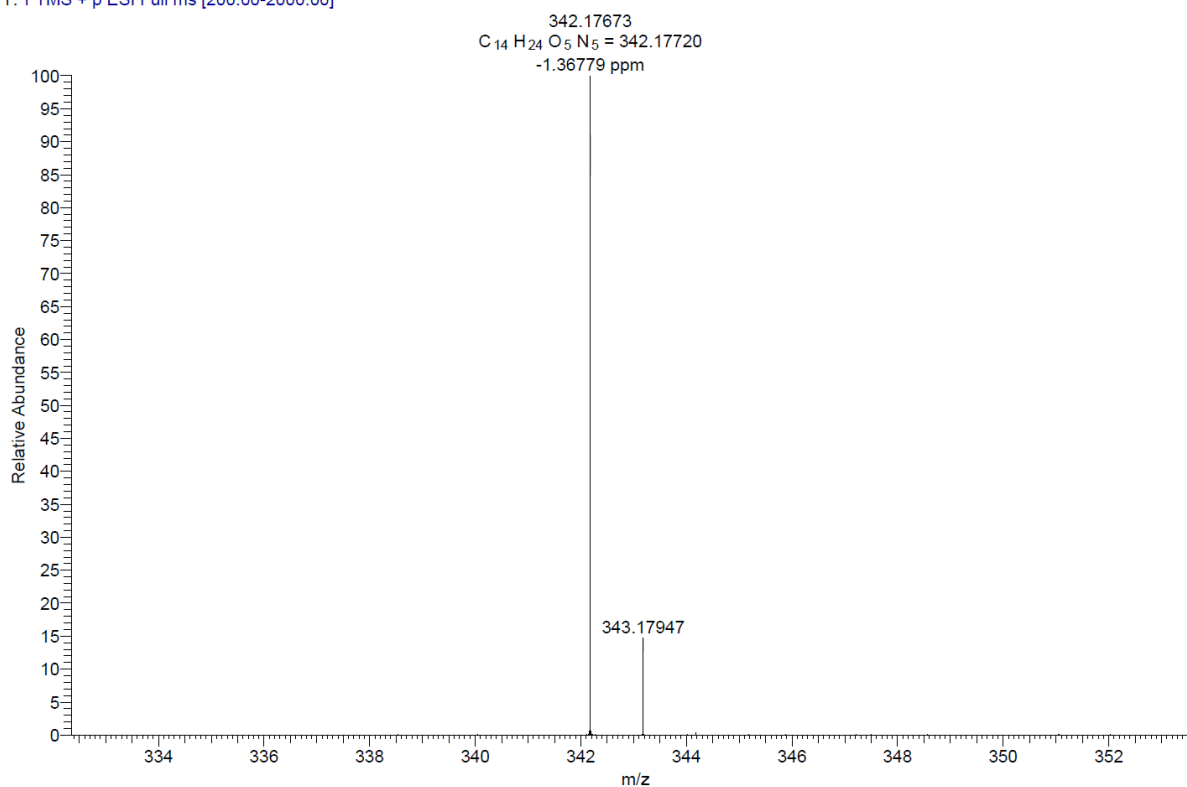


Figure S14. HRMS spectrum of compound 3.

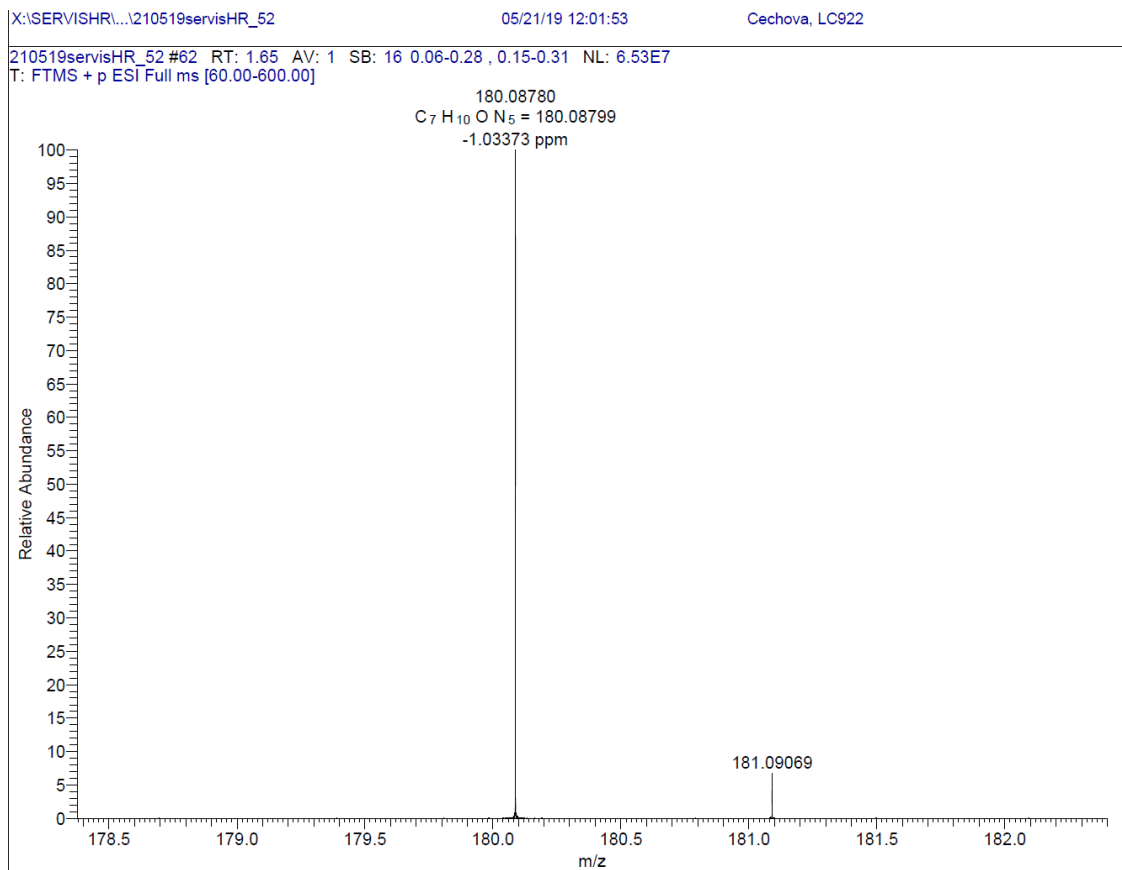


Figure S15. HRMS spectrum of compound **4**.

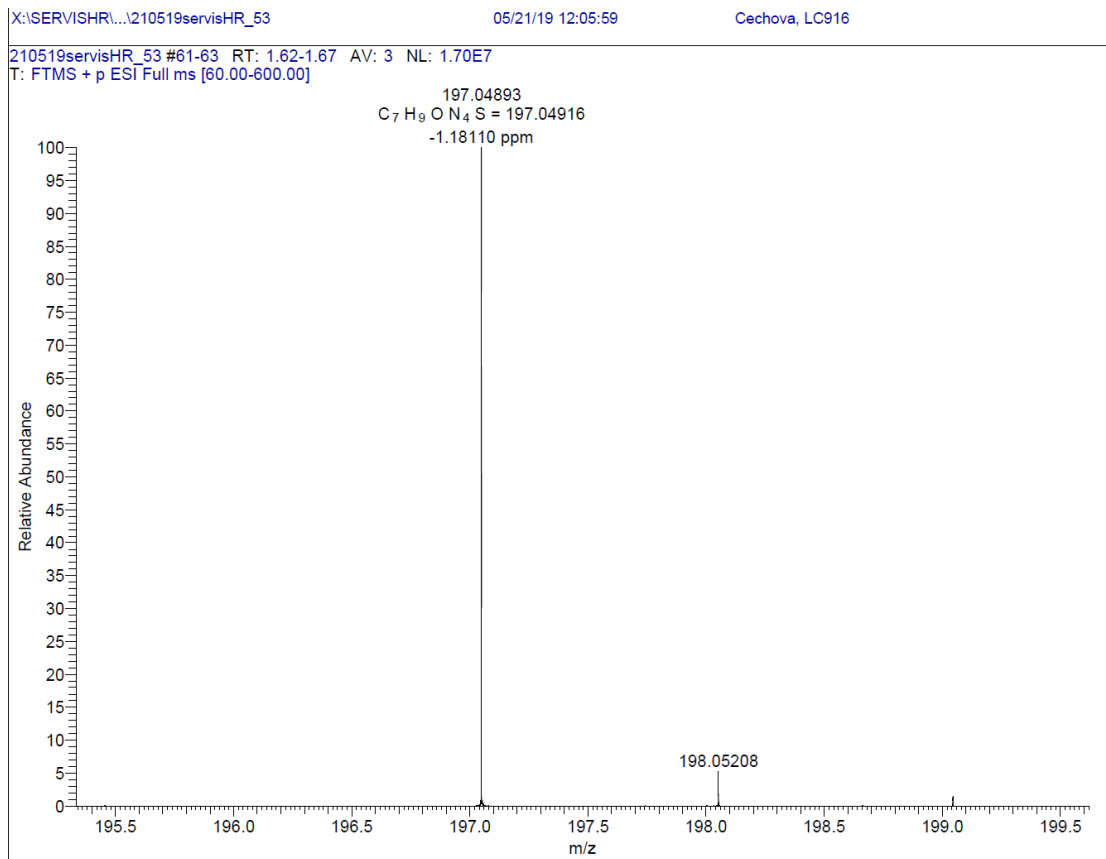


Figure S16. HRMS spectrum of compound **9**.

4. Cartesian coordinates and calculated energies of all studied compounds and complexes

Table S3. Cartesian coordinates (Å) and electronic and free energies (240 K, a.u.) of geometry optimized structures of compound 1.

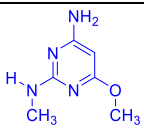
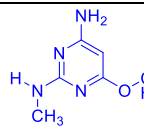
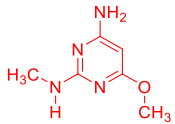

							
Z	x	y	z	Z	x	y	z
6	0.02484	1.098203	-0.023511	6	1.264185	0.115128	-0.027109
6	0.174443	-1.162539	-0.000196	6	-0.873749	-0.647861	-0.007354
6	-1.212004	-1.288657	0.010568	6	-1.37097	0.649673	0.008437
6	-1.929559	-0.082866	0.009833	6	-0.39987	1.673533	0.010333
7	-1.320009	1.114007	-0.010095	7	0.912516	1.418433	-0.010374
7	0.814262	0.00601	-0.013717	7	0.432972	-0.937365	-0.0204
7	-3.300051	-0.068403	0.077183	7	-0.771144	2.989554	0.079086
1	-3.746186	0.796665	-0.194129	1	-0.064396	3.667829	-0.167822
1	-3.791438	-0.906278	-0.197801	1	-1.715111	3.23266	-0.182434
7	0.641646	2.30714	-0.066168	7	2.59835	-0.138399	-0.072294
1	0.040566	3.109131	0.040721	1	3.197596	0.662258	0.053971
8	0.894357	-2.301648	0.004329	8	-1.648925	-1.752423	-0.010064
6	2.327539	-2.196226	-0.009097	6	-3.071633	-1.590779	0.005465
1	2.688058	-3.225095	-0.003722	1	-3.481865	-2.600417	-0.001225
1	2.672	-1.678748	-0.908221	1	-3.397326	-1.067774	0.910835
1	2.687568	-1.664023	0.875185	1	-3.414611	-1.048878	-0.882238
6	2.077612	2.483654	0.04642	6	3.16892	-1.466636	0.052514
1	2.598857	1.956643	-0.75797	1	2.796949	-2.124079	-0.73832
1	2.298558	3.54969	-0.032667	1	4.253213	-1.384076	-0.042379
1	2.462697	2.11148	1.003559	1	2.931227	-1.927451	1.019316
1	-1.693692	-2.256974	0.025883	1	-2.424434	0.885404	0.024966
E	-528.988090			E	-528.986791		
G	-528.845399			G	-528.843355		
							
Z	x	y	z	Z	x	y	z
6	-0.780952	-0.645141	-0.027788	6	-1.092043	-0.546031	-0.031007
6	1.328874	0.184658	-0.001476	6	1.179449	-0.520258	-0.00581
6	0.846078	1.494824	0.00078	6	1.191818	0.873413	-0.004848
6	-0.546636	1.625225	-0.009526	6	-0.072038	1.491329	-0.013409
7	-1.370034	0.55719	-0.018262	7	-1.217666	0.791672	-0.020925
7	0.55078	-0.890923	-0.016434	7	0.060026	-1.244918	-0.019628
7	-1.153855	2.854123	-0.054943	7	-0.191259	2.853522	-0.05559
1	-2.129955	2.873926	0.205337	1	-1.09752	3.232377	0.179738
1	-0.615577	3.6562	0.238559	1	0.60113	3.414047	0.220635
7	-1.581377	-1.741353	-0.06192	7	-2.234591	-1.280577	-0.066802
1	-1.114852	-2.627843	0.049242	1	-2.116756	-2.274429	0.052793
8	2.667712	0.029966	0.015222	8	2.294824	-1.2807	0.009754
6	3.193077	-1.307192	0.015759	6	3.570003	-0.629445	0.027737
1	4.27659	-1.187357	0.029547	1	4.308351	-1.431019	0.038201
1	2.861326	-1.8558	0.90119	1	3.709549	-0.013741	-0.86706
1	2.883088	-1.84796	-0.882264	1	3.684115	-0.013614	0.92606
6	-3.026624	-1.686606	0.049656	6	-3.562842	-0.711432	0.064975
1	-3.456553	-1.0888	-0.759293	1	-3.761621	0.003726	-0.738435
1	-3.415202	-2.704005	-0.022191	1	-4.290498	-1.522391	-0.001112
1	-3.347481	-1.250211	1.003455	1	-3.694506	-0.193531	1.022918
1	1.515418	2.344263	0.011119	1	2.097521	1.460823	0.003026
E	-528.988139			E	-528.986658		
G	-528.845389			G	-528.843241		

Table S4. Cartesian coordinates (\AA) and electronic and free energies (240 K, a.u.) of geometry optimized structure of compound **2a**.

Z	x	y	z
7	-0.737459	-1.005612	0.000257
6	-1.703641	0.005536	-0.000101
6	-1.144125	1.336526	-0.000073
6	0.200491	1.498783	0.000028
7	1.083257	0.450102	0.000294
6	0.635444	-0.861964	0.000091
8	-2.898522	-0.284569	-0.000095
1	-1.073577	-1.961986	0.000129
8	1.397719	-1.819154	-0.000192
6	2.534113	0.663772	-0.000111
1	2.728048	1.735503	0.001482
1	2.976911	0.212094	-0.889807
1	2.977687	0.209356	0.88778
1	0.654809	2.481826	-0.00001
1	-1.811738	2.185647	-0.000144
E	-454.200541		
G	-454.110584		

Table S5. Cartesian coordinates (\AA) and electronic and free energies (240 K, a.u.) of geometry optimized structure of compound **2b**.

Z	x	y	z
7	0.726005	1.027784	-0.00007
6	-0.666169	0.891205	0.000138
6	-1.154212	-0.481977	0.000019
6	-0.237601	-1.478455	0.000004
7	1.116694	-1.240378	-0.000046
6	1.667505	0.019583	0.000003
8	-1.376428	1.893558	-0.000069
1	1.09059	1.97357	0.000073
8	2.874149	0.227991	0.000049
6	-2.635794	-0.71799	0.00001
1	-3.103037	-0.264133	-0.880581
1	-3.103102	-0.263568	0.880269
1	-2.86104	-1.787313	0.000336
1	-0.516412	-2.52535	0.000037
1	1.769964	-2.011643	-0.000206
E	-454.212191		
G	-454.122059		

Table S6. Cartesian coordinates (Å) and electronic and free energies (240 K, a.u.) of geometry optimized structure of compound **2c**.

Z	x	y	z
7	-0.015732	-1.383558	-0.000231
6	1.249731	-0.795428	0.000108
6	1.239531	0.657025	0.00005
6	0.037106	1.283101	-0.000121
7	-1.17331	0.62874	-0.00039
6	-1.241692	-0.750098	-0.000026
8	2.256292	-1.502757	-0.000011
1	-0.048657	-2.396633	-0.000063
8	-2.301859	-1.365529	0.000251
6	2.549241	1.389881	0.000136
6	-2.441306	1.364309	0.000114
1	3.144561	1.125444	-0.880581
1	3.144889	1.12454	0.88035
1	2.39302	2.47165	0.000708
1	-2.225349	2.431837	-0.001559
1	-3.020558	1.109302	0.8898
1	-3.02248	1.106954	-0.887615
1	-0.033259	2.364181	-0.000173
E	-493.525786		
G	-493.409508		

Table S7. Cartesian coordinates (Å) and electronic and free energies (240 K, a.u.) of geometry optimized structure of compound **2d**.

Z	x	y	z
7	0.636782	1.050902	0.000115
6	-0.748558	0.877157	0.000221
6	-1.134557	-0.522903	0.000068
6	-0.218723	-1.509883	0.00002
7	1.120801	-1.211264	0.000046
6	1.618244	0.074116	0.000164
8	-1.515072	1.829802	-0.000146
1	0.970766	2.008271	-0.000002
8	2.812289	0.330468	-0.000202
1	-0.48984	-2.557371	-0.000114
1	1.80515	-1.955529	-0.000206
9	-2.451702	-0.796214	-0.000096
E	-514.118287		
G	-514.063697		

Table S8. Cartesian coordinates (Å) and electronic and free energies (240 K, a.u.) of geometry optimized structure of compound **2e**.

Z	x	y	z
7	1.146814	1.005575	0.000077
6	-0.250984	1.031118	0.000176
6	-0.847341	-0.300653	0.000087
6	-0.060297	-1.401264	0.000037
7	1.303078	-1.298938	0.000052
6	1.980471	-0.095934	0.000176
8	-0.853797	2.093836	-0.00009
1	1.609825	1.90771	-0.000049
8	3.198103	-0.015385	-0.000213
1	-0.463786	-2.4052	-0.000081
1	1.873872	-2.133964	-0.000154
17	-2.579688	-0.431895	-0.000062
E	-874.475546		
G	-874.422924		

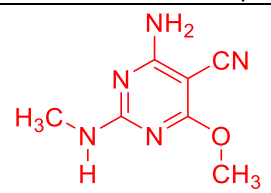
Table S9. Cartesian coordinates (Å) and electronic and free energies (240 K, a.u.) of geometry optimized structure of compound **2f**.

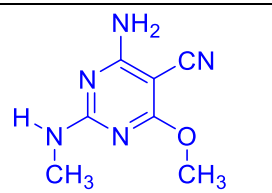
Z	x	y	z
7	1.775503	0.977451	0.000093
6	0.382337	1.094119	0.000131
6	-0.305227	-0.191959	0.000072
6	0.411052	-1.339742	0.000009
7	1.778028	-1.330429	-0.000007
6	2.534815	-0.17578	0.000131
8	-0.14409	2.197221	-0.000128
1	2.29623	1.847522	0.000058
8	3.755084	-0.176259	-0.000131
1	-0.051994	-2.31804	-0.000085
1	2.290113	-2.202942	-0.000186
35	-2.183854	-0.209806	-0.000011
E	-2986.159198		
G	-2986.107611		

Table S10. Cartesian coordinates (Å) and electronic and free energies (240 K, a.u.) of geometry optimized structure of compound **3**.

Z	x	y	z
7	-1.966398	0.242044	0.002737
6	-1.133721	1.387929	-0.000823
6	0.242899	1.010703	-0.002123
6	0.562675	-0.348495	-0.000176
7	-0.274702	-1.409634	-0.005131
6	-1.546143	-1.064819	0.001132
8	-1.64197	2.50955	0.000266
7	-2.506725	-2.02917	0.060072
1	-2.959052	0.445197	0.028906
7	1.392863	1.778998	-0.003091
7	1.929725	-0.405394	-0.000592
1	-2.186715	-2.967119	-0.135615
1	-3.439797	-1.81892	-0.264501
6	2.369814	0.90138	-0.001932
6	2.741578	-1.613463	0.001689
1	3.425286	1.132909	-0.002217
1	2.526551	-2.211571	-0.886727
1	2.529708	-2.206214	0.894465
1	3.793826	-1.328003	-0.001005
E	-581.958559		
G	-581.840927		

Table S11. Cartesian coordinates (Å) and electronic and free energies (240 K, a.u.) of geometry optimized structures of compound **4**.





Z	x	y	z		Z	x	y	z
7	1.273754	-1.048556	0.001389	a	7	-0.478738	-1.780213	-0.000547
6	1.46044	0.278743	-0.000529		6	-1.339748	-0.744903	0.000979
7	0.49187	1.234206	-0.00028		7	-1.019152	0.570434	0.001493
6	-0.749098	0.797344	-0.000189		6	0.27003	0.85252	0.000647
6	-1.089508	-0.577574	-0.001051		6	1.280029	-0.134904	0.000837
6	0.006257	-1.48395	0.000206		6	0.823486	-1.485698	0.001656
7	2.726102	0.733849	-0.001258		7	-2.649509	-1.051299	0.000404
7	-0.181477	-2.819563	-0.019289		7	1.693044	-2.519207	0.028741
8	-1.766918	1.660714	0.001329		8	0.67418	2.123479	-0.000894
6	-1.462856	3.07006	0.004118		6	-0.332329	3.156805	-0.001485
6	3.900634	-0.120492	-0.001905		6	-3.720119	-0.068887	-0.001875
1	2.83954	1.735787	-0.001249		1	-2.87731	-2.033704	-0.000147
1	-1.097131	-3.22513	0.093974		1	2.681083	-2.373991	-0.107844
1	0.622308	-3.420207	0.080731		1	1.33117	-3.452894	-0.091338
1	-2.432751	3.565896	0.005211		1	0.226866	4.091558	-0.002436
1	-0.894469	3.336921	0.897858		1	-0.95678	3.081589	-0.894315
1	-0.894544	3.340564	-0.888556		1	-0.956255	3.083089	0.891833
1	4.785827	0.51671	-0.003382		1	-4.671095	-0.60291	-0.002298
1	3.923225	-0.760111	0.885938		1	-3.671472	0.570366	0.884948
1	3.921215	-0.761365	-0.888873		1	-3.669562	0.568438	-0.890011
6	-2.42772	-1.020257	-0.003647		6	2.651448	0.191369	0.000766
7	-3.519788	-1.425368	-0.005465		7	3.793374	0.420688	-0.000146
E	-621.249184				E	-621.248928		
G	-621.109375				G	-621.109426		

Table S12. Cartesian coordinates (Å) and electronic and free energies (240 K, a.u.) of geometry optimized structure of intermolecular complex **1–2a**. **A** and **B** corresponds to Watson-Crick and reversed Watson-Crick geometry, respectively.

A				B			
Z	x	y	z	Z	x	y	z
7	-0.920837	-0.468982	-0.095042	7	0.88135	-0.334513	-0.135046
6	-1.659121	0.660643	-0.006095	6	1.804457	0.646776	-0.011059
7	-3.004796	0.725274	0.039277	7	3.139242	0.471387	0.063699
6	-3.642656	-0.443074	-0.008267	6	3.56236	-0.789906	0.005814
6	-3.003713	-1.673733	-0.104354	6	2.71899	-1.887042	-0.129017
6	-1.600045	-1.63496	-0.150418	6	1.346165	-1.600079	-0.200204
7	-0.983467	1.828906	0.046384	7	1.34383	1.914375	0.04762
7	-0.865005	-2.772185	-0.288783	7	0.424725	-2.588904	-0.375937
8	-4.990087	-0.452394	0.03771	8	4.885215	-1.038343	0.080265
6	-5.672903	0.808237	0.133811	6	5.776987	0.079398	0.222189
6	-1.634201	3.122726	0.113641	6	2.212354	3.070977	0.148557
1	0.028783	1.796959	-0.04124	1	0.343845	2.065693	-0.072477
1	-1.328856	-3.653639	-0.131409	1	0.723001	-3.539152	-0.21631
1	0.135416	-2.741305	-0.091607	1	-0.552356	-2.384746	-0.174118
1	-6.73322	0.55569	0.158492	1	6.775451	-0.356814	0.259801
1	-5.388444	1.337789	1.046766	1	5.691666	0.75714	-0.631105
1	-5.453788	1.437451	-0.732798	1	5.569256	0.629555	1.143631
1	-0.858373	3.890097	0.151783	1	1.58459	3.96395	0.176052
1	-2.268272	3.305728	-0.761575	1	2.818089	3.039166	1.060454
1	-2.25987	3.210642	1.008136	1	2.893789	3.144854	-0.706928
1	-3.559674	-2.600606	-0.144734	1	3.103675	-2.896769	-0.175535
7	2.0023	-0.426933	0.012306	7	-1.977234	0.260528	-0.055938
6	2.662086	-1.643316	0.145329	6	-2.355731	1.593969	-0.158513
6	4.099537	-1.547651	0.187318	6	-3.777771	1.822507	-0.109818
6	4.688296	-0.331245	0.098431	6	-4.616163	0.768417	0.032721
7	3.973774	0.829952	-0.029122	7	-4.172368	-0.523182	0.13208
6	2.589932	0.810063	-0.076319	6	-2.818855	-0.814117	0.087413
8	2.015943	-2.695564	0.216429	8	-1.496241	2.475648	-0.279255
1	0.958552	-0.442016	-0.029001	1	-0.956012	0.041813	-0.090984
8	1.936423	1.846787	-0.190595	8	-2.406982	-1.970684	0.171925
6	4.634081	2.136365	-0.120033	6	-5.10067	-1.648215	0.285916
1	5.710573	1.987278	-0.04904	1	-6.117895	-1.259499	0.305321
1	4.297704	2.779724	0.69496	1	-4.892004	-2.17787	1.217213
1	4.390607	2.611654	-1.072106	1	-4.987913	-2.340711	-0.550237
1	5.7644	-0.212626	0.123986	1	-5.690876	0.893448	0.076907
1	4.684689	-2.450002	0.287614	1	-4.151799	2.833028	-0.184499
E	-983.211065			E	-983.211072		
G	-982.961178			G	-982.961051		

Table S13. Cartesian coordinates (Å) and electronic and free energies (240 K, a.u.) of geometry optimized structure of intermolecular complex **1–2b**. **A** and **B** corresponds to Watson-Crick and reversed Watson-Crick geometry, respectively.

A				B			
Z	x	y	z	Z	x	y	z
7	-0.889705	-0.338952	-0.141384	7	0.929252	-0.46431	-0.106575
6	-1.810999	0.642832	-0.014333	6	1.666108	0.666037	-0.008573
7	-3.145577	0.469773	0.064727	7	3.011798	0.730353	0.04308
6	-3.570377	-0.791353	0.009742	6	3.650333	-0.437106	-0.009182
6	-2.728871	-1.889561	-0.126058	6	3.012329	-1.667788	-0.116157
6	-1.355696	-1.604836	-0.202908	6	1.609281	-1.628813	-0.166499
7	-1.349054	1.910734	0.043257	7	0.989216	1.832803	0.046991
7	-0.435712	-2.593759	-0.379073	7	0.874973	-2.766871	-0.31555
8	-4.893283	-1.038124	0.088964	8	4.99739	-0.446421	0.043002
6	-5.783351	0.080489	0.233869	6	5.679281	0.813737	0.152052
6	-2.215682	3.068751	0.1459	6	1.639622	3.126274	0.12425
1	-0.350529	2.059968	-0.07675	1	-0.023808	1.802533	-0.050438
1	-0.735683	-3.544093	-0.223341	1	1.338448	-3.647626	-0.152331
1	0.544285	-2.391357	-0.181833	1	-0.121993	-2.736826	-0.109289
1	-6.782077	-0.35475	0.275751	1	6.739572	0.56141	0.179694
1	-5.571431	0.630915	1.154206	1	5.46383	1.449592	-0.71059
1	-5.700909	0.757728	-0.620113	1	5.3903	1.335985	1.06779
1	-1.586686	3.960813	0.173333	1	0.863401	3.893168	0.164535
1	-2.897779	3.143899	-0.708883	1	2.262166	3.208866	1.021425
1	-2.820342	3.036864	1.058427	1	2.276778	3.315056	-0.747561
1	-3.115017	-2.898878	-0.169341	1	3.568893	-2.594122	-0.159975
7	1.972874	0.216842	-0.061574	7	-1.987066	-0.388196	0.005231
6	2.839905	-0.86039	0.084485	6	-2.602604	0.855009	-0.088569
6	4.258953	-0.543349	0.142463	6	-4.056393	0.861282	-0.031606
6	4.614535	0.759545	0.046718	6	-4.683018	-0.330248	0.11222
7	3.687667	1.762852	-0.098759	7	-3.993455	-1.51465	0.201541
6	2.334548	1.536379	-0.156488	6	-2.623283	-1.594822	0.150573
8	2.386807	-2.007624	0.156374	8	-1.913547	1.873519	-0.21184
1	0.948806	0.012098	-0.101275	1	-0.943467	-0.415396	-0.039714
8	1.51927	2.451253	-0.282348	8	-2.023864	-2.667729	0.229453
6	5.244712	-1.662993	0.300775	6	-4.780129	2.171495	-0.130795
1	5.163148	-2.374276	-0.528179	1	-4.547918	2.674815	-1.07551
1	5.053765	-2.222912	1.222575	1	-4.475084	2.847312	0.675341
1	6.26812	-1.280894	0.331695	1	-5.861563	2.025473	-0.071457
1	5.646228	1.088096	0.078302	1	-5.761054	-0.420733	0.165681
1	3.984249	2.727218	-0.163844	1	-4.490499	-2.388707	0.308164
E	-983.222685			E	-983.222742		
G	-982.972352			G	-982.972588		

Table S14. Cartesian coordinates (Å) and electronic and free energies (240 K, a.u.) of geometry optimized structure of intermolecular complex **1–2c**. **A** and **B** corresponds to Watson-Crick and reversed Watson-Crick geometry, respectively.

A				B			
Z	x	y	z	Z	x	y	z
7	-1.1441360	-0.4187580	-0.1147130	7	1.1462510	-0.4110270	-0.1158810
6	-1.9792170	0.6376390	0.0089450	6	1.9774380	0.6493410	0.0046790
7	-3.3249990	0.5803760	0.0647730	7	3.3236140	0.5964600	0.0613620
6	-3.8558530	-0.6390060	-0.0087510	6	3.8588000	-0.6209800	-0.0092400
6	-3.1103170	-1.8048010	-0.1414960	6	3.1174950	-1.7898180	-0.1401840
6	-1.7162450	-1.6391550	-0.1956180	6	1.7231160	-1.6288600	-0.1946480
7	-1.4093230	1.8595880	0.0899740	7	1.4029860	1.8688890	0.0807410
7	-0.8819160	-2.7014180	-0.3676500	7	0.8931090	-2.6953820	-0.3662640
8	-5.1965930	-0.7699840	0.0467440	8	5.1999210	-0.7473310	0.0475590
6	-5.9868020	0.4219520	0.1877790	6	5.9859630	0.4476290	0.1860370
6	-2.1738910	3.0881960	0.1785300	6	2.1634870	3.0999050	0.1698190
1	-0.4005150	1.9218420	-0.0237540	1	0.3922140	1.9286320	-0.0303310
1	-1.2629510	-3.6248570	-0.2290190	1	1.2763250	-3.6168510	-0.2207280
1	0.1116160	-2.5841790	-0.1671110	1	-0.0992160	-2.5802970	-0.1659810
1	-7.0205120	0.0762560	0.2117780	1	7.0208270	0.1055110	0.2116210
1	-5.7406670	0.9456670	1.1151400	1	5.8292570	1.1180350	-0.6629800
1	-5.8318380	1.0951290	-0.6593640	1	5.7374030	0.9728970	1.1118650
1	-1.4706770	3.9210430	0.2420520	1	1.4573640	3.9305850	0.2296920
1	-2.8153910	3.2339160	-0.6985940	1	2.7992430	3.1136100	1.0612900
1	-2.8122210	3.0980710	1.0681100	1	2.8072010	3.2463380	-0.7055770
1	-3.5819080	-2.7762180	-0.2015060	1	3.5925120	-2.7596640	-0.1984910
7	1.7630180	-0.1110580	-0.0305130	7	-1.7585370	-0.0772180	-0.0287190
6	2.5296390	-1.2604300	0.0955580	6	-2.2554490	1.2152120	-0.1108710
6	3.9647200	-1.0561570	0.1431040	6	-3.6995850	1.3376370	-0.0651930
6	4.4226420	0.2168620	0.0570890	6	-4.4243240	0.1983860	0.0563250
7	3.6043460	1.3140700	-0.0689580	7	-3.8657340	-1.0549230	0.1364300
6	2.2333830	1.1752640	-0.1142150	6	-2.4980690	-1.2266960	0.0936880
8	1.9802340	-2.3674580	0.1587330	8	-1.4777460	2.1724350	-0.2146100
1	0.7256740	-0.2231480	-0.0672550	1	-0.7223840	-0.1999800	-0.0646710
8	1.4844150	2.1487930	-0.2221940	8	-1.9802200	-2.3433480	0.1613560
6	4.8663530	-2.2476330	0.2815520	6	-4.3178900	2.7022430	-0.1504820
6	4.1510020	2.6718650	-0.1550740	6	-4.6954080	-2.2568990	0.2657010
1	4.7251780	-2.9429470	-0.5529770	1	-4.0371540	3.1997350	-1.0850940
1	4.6430870	-2.8007620	1.2002700	1	-3.9691230	3.3404440	0.6686390
1	5.9159370	-1.9438370	0.3061430	1	-5.4081240	2.6419750	-0.1034260
1	5.2374480	2.6134980	-0.1045510	1	-5.7417770	-1.9560630	0.2938260
1	3.7773700	3.2774770	0.6728710	1	-4.4416310	-2.7878250	1.1851500
1	3.8520010	3.1354610	-1.0971380	1	-4.5270660	-2.9200580	-0.5850720
1	5.4825100	0.4396040	0.0838260	1	-5.5067720	0.2187450	0.0983670
<i>E</i>	-1022.536452			<i>E</i>	-1022.536469		
<i>G</i>	-1022.260281			<i>G</i>	-1022.260197		

Table S15. Cartesian coordinates (Å) and electronic and free energies (240 K, a.u.) of geometry optimized structure of intermolecular complex **1–2d**. **A** and **B** corresponds to Watson-Crick and reversed Watson-Crick geometry, respectively.

A				B			
Z	x	y	z	Z	x	y	z
7	-0.872741	-0.345177	-0.142512	7	0.903559	-0.453499	-0.111349
6	-1.780501	0.649572	-0.007156	6	1.659985	0.662673	0.006577
7	-3.11675	0.49489	0.071508	7	3.005694	0.703231	0.05786
6	-3.561292	-0.758604	0.004763	6	3.625863	-0.472642	-0.018872
6	-2.736049	-1.867497	-0.143135	6	2.967363	-1.689868	-0.151901
6	-1.359342	-1.603253	-0.216222	6	1.565603	-1.627776	-0.19671
7	-1.302512	1.910762	0.06081	7	1.004566	1.840797	0.087387
7	-0.45694	-2.607597	-0.402443	7	0.813792	-2.752083	-0.366474
8	-4.887008	-0.986049	0.083258	8	4.971822	-0.504188	0.03317
6	-5.760193	0.144406	0.241332	6	5.672865	0.74272	0.173753
6	-2.156211	3.078757	0.163889	6	1.680977	3.121527	0.163759
1	-0.305518	2.05025	-0.076516	1	-0.002861	1.834593	-0.047316
1	-0.776476	-3.552529	-0.251354	1	1.26795	-3.640921	-0.220346
1	0.522035	-2.429158	-0.185963	1	-0.176142	-2.714443	-0.132142
1	-6.765134	-0.276412	0.280479	1	6.729014	0.473431	0.19714
1	-5.538326	0.681784	1.166969	1	5.468559	1.402145	-0.673665
1	-5.66874	0.828958	-0.605815	1	5.389528	1.246752	1.10132
1	-1.516883	3.963197	0.196932	1	0.920464	3.902166	0.229285
1	-2.834485	3.164451	-0.69294	1	2.322361	3.18033	1.048861
1	-2.763989	3.049868	1.074184	1	2.304056	3.308278	-0.718814
1	-3.136734	-2.870612	-0.195509	1	3.508399	-2.624241	-0.214562
7	1.978246	0.168926	-0.063777	7	-1.989327	-0.337143	0.001659
6	2.816828	-0.923144	0.107258	6	-2.575357	0.913506	-0.127788
6	4.224227	-0.577979	0.162561	6	-4.023079	0.892758	-0.052905
6	4.639816	0.697664	0.048957	6	-4.700303	-0.256296	0.131217
7	3.721054	1.70105	-0.120436	7	-4.017379	-1.439052	0.249062
6	2.363119	1.484935	-0.180642	6	-2.645221	-1.532683	0.188293
8	2.376803	-2.067917	0.198441	8	-1.901029	1.929962	-0.287518
1	0.945943	-0.019903	-0.104692	1	-0.941194	-0.382747	-0.046846
8	1.562859	2.405851	-0.327089	8	-2.059977	-2.607726	0.293409
1	5.683208	0.981806	0.083975	1	-5.779555	-0.298864	0.19336
1	4.028024	2.661244	-0.201051	1	-4.522757	-2.30475	0.383998
9	5.101216	-1.584128	0.329193	9	-4.665874	2.068291	-0.170258
<i>E</i>	-1043.128832			<i>E</i>	-1043.128861		
<i>G</i>	-1042.914173			<i>G</i>	-1042.914454		

Table S16. Cartesian coordinates (Å) and electronic and free energies (240 K, a.u.) of geometry optimized structure of intermolecular complex **1–2e**. **A** and **B** corresponds to Watson-Crick and reversed Watson-Crick geometry, respectively.

A				B			
Z	x	y	z	Z	x	y	z
7	-1.151605	-0.310675	-0.136761	7	-1.217809	0.496886	-0.109481
6	-2.123329	0.619368	0.012287	6	-1.879285	-0.679907	-0.007501
7	-3.446421	0.375652	0.086876	7	-3.21715	-0.833428	0.044354
6	-3.806945	-0.903579	0.003471	6	-3.933035	0.287855	-0.013887
6	-2.910144	-1.953436	-0.157803	6	-3.37839	1.557324	-0.128107
6	-1.553893	-1.59723	-0.227938	6	-1.976177	1.612738	-0.177254
7	-1.7286	1.908139	0.101206	7	-1.129064	-1.800588	0.051726
7	-0.586752	-2.535616	-0.428715	7	-1.323405	2.798191	-0.333306
8	-5.115051	-1.217873	0.077133	8	-5.277099	0.206891	0.038869
6	-6.058861	-0.147552	0.248641	6	-5.872435	-1.095586	0.159598
6	-2.656339	3.018099	0.204703	6	-1.695042	-3.133203	0.132354
1	-0.744661	2.113998	-0.04462	1	-0.121765	-1.706046	-0.045016
1	-0.840369	-3.502435	-0.29325	1	-1.848299	3.645089	-0.176947
1	0.379108	-2.292467	-0.216596	1	-0.328742	2.841002	-0.122514
1	-7.034834	-0.632247	0.281279	1	-6.947301	-0.915087	0.185065
1	-5.871682	0.391119	1.181127	1	-5.613958	-1.723332	-0.697071
1	-6.010837	0.552364	-0.589485	1	-5.549098	-1.588207	1.080206
1	-2.074902	3.940354	0.263502	1	-0.871298	-3.849152	0.163841
1	-3.323094	3.075517	-0.663696	1	-2.302828	-3.256196	1.034966
1	-3.276961	2.936086	1.102754	1	-2.326938	-3.359456	-0.734128
1	-3.243644	-2.980134	-0.224275	1	-3.995196	2.444367	-0.177213
7	1.666663	0.395478	-0.081186	7	1.688654	0.622743	0.011741
6	2.581711	-0.640702	0.060323	6	2.380764	-0.579074	-0.074701
6	3.974013	-0.211711	0.087893	6	3.829767	-0.44392	-0.004839
6	4.281378	1.101119	-0.023038	6	4.390938	0.779121	0.136081
7	3.298628	2.040025	-0.157984	7	3.613352	1.899147	0.213325
6	1.95501	1.733476	-0.191242	6	2.236102	1.874044	0.155674
8	2.201372	-1.805634	0.14946	8	1.778134	-1.642897	-0.198373
1	0.650163	0.135111	-0.107168	1	0.64176	0.575978	-0.038612
8	1.094207	2.60092	-0.309377	8	1.565487	2.899505	0.228242
1	5.298758	1.469192	-0.010635	1	5.46054	0.931518	0.19408
1	3.538667	3.019881	-0.235243	1	4.041994	2.809838	0.3149
17	5.214769	-1.415516	0.260632	17	4.806333	-1.877372	-0.102617
E	-1403.486122			E	-1403.486143		
G	-1403.273350			G	-1403.273522		

Table S17. Cartesian coordinates (Å) and electronic and free energies (240 K, a.u.) of geometry optimized structure of intermolecular complex **1–2f**. **A** and **B** corresponds to Watson-Crick and reversed Watson-Crick geometry, respectively.

A				B			
Z	x	y	z	Z	x	y	z
7	-1.697434	-0.272256	-0.130268	7	-1.791194	0.53232	-0.117463
6	-2.737516	0.57963	0.024318	6	-2.32747	-0.704424	0.007535
7	-4.038099	0.235139	0.095863	7	-3.642536	-0.994421	0.056298
6	-4.300014	-1.067157	0.002429	6	-4.47026	0.044687	-0.0323
6	-3.325715	-2.044202	-0.165752	6	-4.049295	1.361905	-0.175329
6	-2.000392	-1.585206	-0.231231	6	-2.660248	1.561686	-0.215825
7	-2.443794	1.89444	0.122618	7	-1.46554	-1.739619	0.096997
7	-0.964759	-2.445928	-0.435757	7	-2.1312	2.805277	-0.394176
8	-5.580448	-1.481023	0.0722	8	-5.798945	-0.173909	0.016994
6	-6.603596	-0.487341	0.249202	6	-6.256722	-1.52779	0.169248
6	-3.456076	2.926941	0.236099	6	-1.892855	-3.122101	0.193197
1	-1.478707	2.177551	-0.019621	1	-0.474277	-1.545378	-0.018474
1	-1.143079	-3.430199	-0.306432	1	-2.743273	3.595508	-0.257947
1	-0.018905	-2.129589	-0.2293	1	-1.152342	2.955275	-0.159563
1	-7.539325	-1.045887	0.280653	1	-7.344591	-1.459173	0.188157
1	-6.457466	0.060408	1.18375	1	-5.9306	-2.146245	-0.670923
1	-6.610836	0.217557	-0.586158	1	-5.887929	-1.961208	1.10246
1	-2.949278	3.891776	0.301691	1	-1.000819	-3.747991	0.26087
1	-4.126906	2.937973	-0.630939	1	-2.507792	-3.288359	1.083705
1	-4.066989	2.788716	1.133929	1	-2.475656	-3.43076	-0.682524
1	-3.580073	-3.092632	-0.241685	1	-4.755006	2.178212	-0.247868
7	1.059388	0.647211	-0.095729	7	1.078176	0.958816	0.02739
6	2.053867	-0.317246	0.013769	6	1.891592	-0.163705	-0.064524
6	3.411095	0.20993	0.01845	6	3.318171	0.112019	0.024051
6	3.611925	1.544104	-0.079885	6	3.745158	1.385569	0.185603
7	2.560593	2.409098	-0.183472	7	2.858667	2.420692	0.268382
6	1.243132	2.003908	-0.193888	6	1.49188	2.257527	0.190757
8	1.760648	-1.508089	0.09675	8	1.398216	-1.280843	-0.207449
1	0.065762	0.309937	-0.108834	1	0.041927	0.803974	-0.034363
8	0.317771	2.805753	-0.283441	8	0.719026	3.208314	0.263338
1	4.596637	1.99299	-0.082615	1	4.791675	1.651746	0.258898
1	2.725894	3.404577	-0.254578	1	3.192675	3.368119	0.387938
35	4.853942	-0.984868	0.160635	35	4.531866	-1.317598	-0.08714
<i>E</i>	-3515.170360			<i>E</i>	-3515.170521		
<i>G</i>	-3514.958986			<i>G</i>	-3514.958594		

Table S18. Cartesian coordinates (Å) and electronic and free energies (240 K, a.u.) of geometry optimized structure of the dimer of compound **3**.

Z	x	y	z
7	3.256551	-1.878624	-0.432495
6	4.541627	-1.537892	-0.079509
7	4.895492	-0.310492	0.24794
6	3.875661	0.570526	0.189209
6	2.546036	0.325349	-0.152718
6	2.160838	-0.998364	-0.495373
7	1.809599	1.492428	-0.093725
6	2.674302	2.410155	0.275674
7	3.943492	1.910696	0.462509
8	1.04659	-1.42595	-0.820741
7	5.479273	-2.519694	-0.124954
6	5.132309	2.646563	0.871313
1	3.04695	-2.837556	-0.686806
1	2.454684	3.456886	0.425863
1	5.197197	-3.487431	-0.067898
1	6.363915	-2.298524	0.309178
1	5.490368	2.274783	1.833923
1	5.918138	2.526738	0.122638
1	4.87671	3.702395	0.962182
7	-1.579661	-0.420411	-0.19886
6	-1.963074	0.846446	-0.565191
7	-3.214599	1.273069	-0.504071
6	-4.070695	0.334521	-0.048018
6	-3.787569	-0.967475	0.366088
7	-0.993359	1.666447	-1.048415
7	-4.943982	-1.607499	0.77796
6	-5.888919	-0.71031	0.613761
7	-5.422381	0.488081	0.115468
6	-6.19429	1.685248	-0.179347
1	-0.024805	1.554661	-0.723826
1	-1.291506	2.624113	-1.172068
1	-6.937659	-0.851885	0.832622
1	-6.093268	1.947177	-1.235182
6	-2.435352	-1.424776	0.299822
8	-1.980084	-2.530497	0.607435
1	-0.604143	-0.708705	-0.354544
1	-5.843155	2.520023	0.431984
1	-7.243684	1.490959	0.044613
E	-1163.935706		
G	-1163.684657		

Table S19. Cartesian coordinates (Å) and electronic and free energies (240 K, a.u.) of geometry optimized structure of intermolecular complex **4–2c**. **A** and **B** corresponds to Watson-Crick and reversed Watson-Crick geometry, respectively.

A				B			
Z	x	y	z	Z	x	y	z
7	-0.87232	-0.053343	0.000292	7	0.872422	-0.047276	-0.000517
6	-1.568693	1.106321	0.000047	6	1.564627	1.115571	-0.000512
7	-2.918422	1.222558	-0.000208	7	2.914214	1.23586	-0.000187
6	-3.603672	0.095799	-0.000208	6	3.603313	0.111683	0.000161
6	-3.000849	-1.180208	0.000081	6	3.004922	-1.166594	0.000252
6	-1.573169	-1.198012	0.000324	6	1.57748	-1.188726	-0.000101
7	-0.859499	2.243045	0.000014	7	0.851325	2.249025	-0.000905
7	-0.888629	-2.352742	0.000598	7	0.897415	-2.346717	-0.000029
8	-4.937669	0.127655	-0.000337	8	4.937171	0.148112	0.000528
6	-5.587654	1.415053	-0.000545	6	5.582522	1.437846	0.000474
6	-1.461761	3.564902	-0.000284	6	1.449734	3.572592	-0.000762
1	0.15777	2.172563	0.000201	1	-0.167596	2.176407	-0.000799
1	-1.376364	-3.234625	0.000268	1	1.387309	-3.227319	0.000278
1	0.134031	-2.355283	0.000346	1	-0.123271	-2.352131	-0.000398
1	-6.653451	1.189993	-0.000627	1	6.64913	1.216655	0.000872
1	-5.314986	1.981454	0.892556	1	5.307966	2.002984	-0.892849
1	-5.314803	1.981249	-0.893719	1	5.307376	2.003363	0.893375
1	-0.656081	4.300893	0.000004	1	0.641793	4.306125	-0.000627
1	-2.083963	3.71981	-0.887411	1	2.071969	3.729485	0.886034
1	-2.084667	3.719879	0.886331	1	2.071859	3.72972	-0.887598
7	2.058589	-0.102866	0.000289	7	-2.058705	-0.072202	-0.000713
6	2.678837	-1.342766	0.000002	6	-2.7036	1.155269	-0.000032
6	4.127791	-1.318492	-0.000424	6	-4.151887	1.101983	0.000758
6	4.735809	-0.106343	-0.000394	6	-4.735659	-0.122061	0.00068
7	4.056361	1.088839	0.000008	7	-4.032304	-1.303407	-0.000178
6	2.679061	1.120592	0.000362	6	-2.654677	-1.307526	-0.000725
8	1.995801	-2.375438	0.000139	8	-2.040821	2.200906	-0.000126
1	1.018877	-0.085817	0.000416	1	-1.018825	-0.067048	-0.000877
8	2.048978	2.180914	0.000715	8	-2.004078	-2.355515	-0.001219
6	4.879051	-2.617543	-0.000868	6	-4.928739	2.385915	0.001556
6	4.76426	2.373259	0.00024	6	-4.714042	-2.601913	-0.000036
1	4.622003	-3.216201	-0.881403	1	-4.684355	2.989903	-0.878949
1	4.6225	-3.216519	0.879595	1	-4.683299	2.989458	0.882072
1	5.958354	-2.44574	-0.001143	1	-6.004434	2.192873	0.002147
1	5.836061	2.18018	-0.000414	1	-5.789445	-2.430394	-0.002457
1	4.495308	2.94648	0.889504	1	-4.434947	-3.169075	0.88999
1	4.494359	2.947308	-0.888193	1	-4.431294	-3.170941	-0.88767
1	5.815302	-0.016053	-0.000699	1	-5.813198	-0.23401	0.001286
6	-3.757392	-2.36887	0.000193	6	3.765365	-2.352743	0.000651
7	-4.347058	-3.373601	0.000306	7	4.358339	-3.355549	0.000888
E	-1114.798383			E	-1114.798424		
G	-1114.524670			G	-1114.524730		

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