Supplementary information

A quantum chemical approach towards understanding stability and tautomerism of 2-imino-2*H*-pyran derivatives†

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Content

Table S1. Selected geometrical parameters of acyclic **Ar1** and **Alk1** conformers

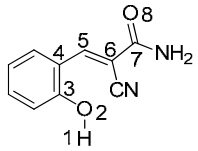
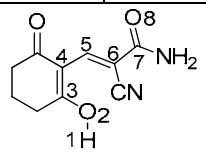
Structure	Vacuum			PCM/DMSO		
	torsion angle			torsion angle		
	1-2-3-4	***3-4-5-6***	***5-6-7-8***	***1-2-3-4***	***3-4-5-6***	***5-6-7-8***
						
Ar1_1	-20.8	19.9	0.8	ND		
Ar1_2	-175.5	33.5	2.7	178.0	33.3	2.9
Ar1_3	duplicates **Ar1_1**			ND		
Ar1_4	duplicates **Ar1_1**			ND		
Ar1_5	0.0	180.0	-0.0	4.9	-163.1	-0.8
Ar1_6	-180.0	180.0	-0.0	-180.0	-180.0	0.1
Ar1_7	duplicates **Ar1_5**			ND		
Ar1_8	179.0	-179.6	-150.7	ND		
Ar1_9	36.6	-26.5	4.3	38.3	-28.0	3.2
						
Alk1_1	125.3	41.3	6.0	6.1	44.6	2.7
Alk1_2	-172.4	40.7	4.9	-179.4	38.0	3.5
Alk1_3	-16.9	29.8	3.5	ND		
Alk1_4	-169.6	43.7	150.5	ND		
Alk1_5	4.6	-147.0	-0.3	5.6	-150.0	3.3
Alk1_6	-174.9	-148.2	2.5	-176.2	-153.8	3.3
Alk1_7	17.9	-24.1	165.8	ND		
Alk1_8	175.2	-43.0	153.0	ND		
Alk1_9	21.1	-21.1	6.2	20.7	-20.8	4.1
Alk1_10	-175.8	-70.7	-124.5	-180.0	-66.3	-132.0

Table S2. Selected geometrical parameters of acyclic **Alk1a**, **Alk1b** conformers in vacuum

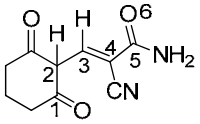
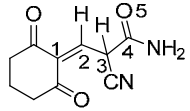
Structure	torsion angle		Structure	torsion angle	
	1-2-3-4	***3-4-5-6***		***1-2-3-4***	***2-3-4-5***
					
Alk1a_1	64.8	-0.0	**Alk1b_1**	-87.7	46.0
Alk1a_2	-118.5	0.0	**Alk1b_2**	duplicates of **Alk1b_1**	
Alk1a_3	115.5	-0.2	**Alk1b_3**	97.0	106.4
Alk1a_4	-126.8	-145.0	**Alk1b_4**	duplicates of **Alk1b_3**	
Alk1a_5	-78.2	-131.4			

Table S3. Selected geometrical parameters of the conformers of cyclic forms **Ar2**, **Alk2** and pyridones **Ar3**, **Alk3**

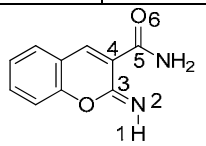
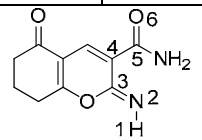
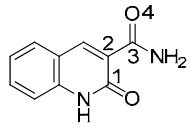
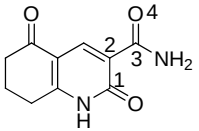
Structure	vacuum		PCM/DMSO	
	torsion angle		torsion angle	
	1-2-3-4	***3-4-5-6***	***1-2-3-4***	***3-4-5-6***
				
Ar2_1	180.0	-179.6	180.0	180.0
Ar2_2	1.3	-152.1	ND	
Ar2_3	duplicates of **Ar2_1**		ND	
Ar2_4	-1.9	26.9	ND	
				
Alk2_1	-180.0	179.7	-180.0	180.0
Alk2_2	1.0	-150.9	ND	
Alk2_3	-180.0	179.7	ND	
Alk2_4	-1.4	17.2	ND	
				
	1-2-3-4		***1-2-3-4***	
Ar3_1	180.0		180.0	
Ar3_2	duplicates **Ar3_1**		ND	
				
Alk3_1	-180.0		180.0	
Alk3_2	duplicates **Alk3_1**		ND	

Table S4. Structures and relative Gibbs energies (ΔG, kcal/mol) of the conformers of acyclic form **Ar1**

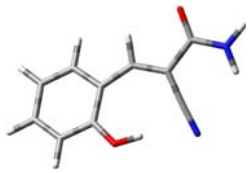
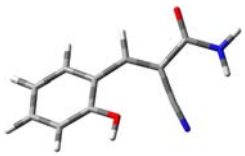
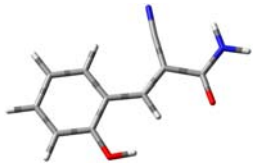
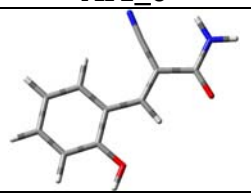
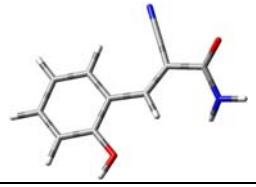
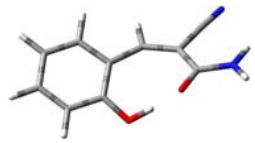
Medium	Structure					
	Ar1					
	Ar1_1	**Ar1_2**	**Ar1_5**	**Ar1_6**	**Ar1_8**	**Ar1_9**
						
Vacuum	2.18	2.62	0.80	0	5.01	1.21
PCM/DMSO	ND	2.66	2.28	0	ND	3.95

Table S5. Structures and relative Gibbs energies (ΔG, kcal/mol) of 1:1 complexes with acetone formed by hydroxyl group of acyclic form **Ar1**

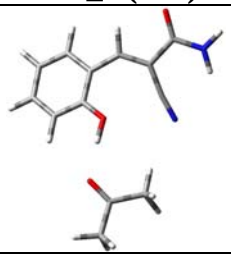
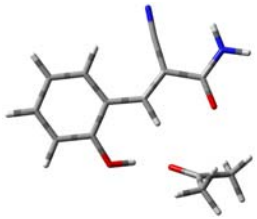
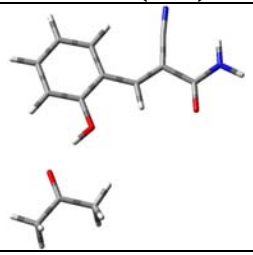
Medium	Structure					
	Ar1					
	Ar1_1 (OH)	**Ar1_2 (OH)**	**Ar1_5 (OH)**	**Ar1_6 (OH)**	**Ar1_8 (OH)**	**Ar1_9 (OH)**
	ND				ND	ND
+acetone **(OH)**, Vacuum	ND	2.4	1.37	0	ND	ND
+acetone **(OH)**, PCM/acetone	ND	ND	ND	0	ND	ND

Table S6. Structures and relative Gibbs energies (ΔG, kcal/mol) of 1:1 complexes with acetone formed by amide group of acyclic form **Ar1**.

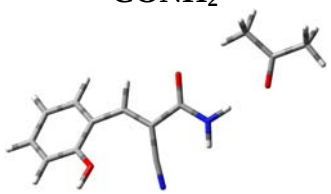
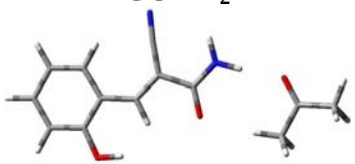
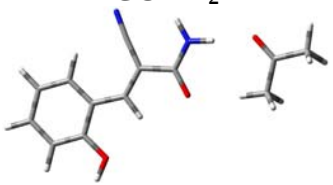
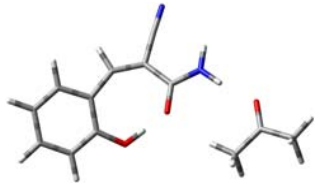
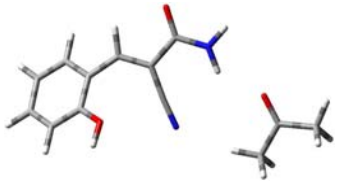
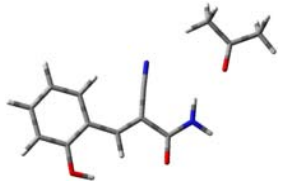
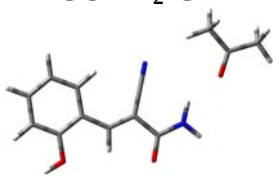
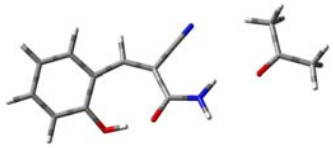
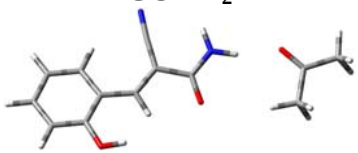
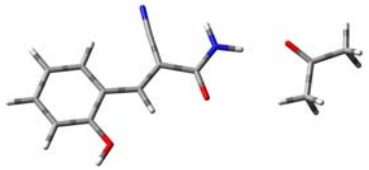
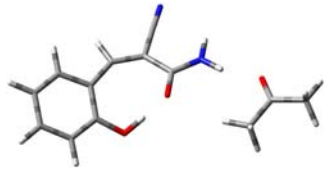
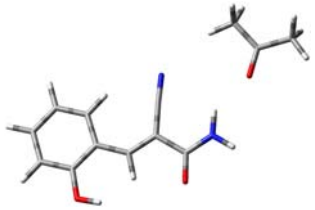
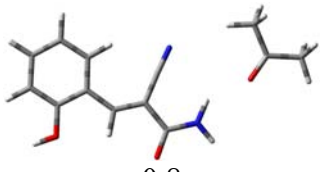
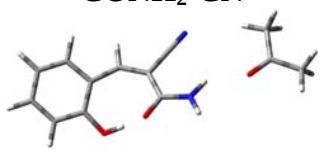
Medium	Structure					
	Ar1 ($CONH_2$)					
	Ar1_1	**Ar1_2**	**Ar1_5**	**Ar1_6**	**Ar1_8**	**Ar1_9**
+acetone **($CONH_2$)**	ND	**$CONH_2$**  2.6	**$CONH_2$**  0.6	**$CONH_2$**  0	ND	**$CONH_2$**  0.2
		$CONH_2$-CN  3.2	**$CONH_2$-CN**  1.3	**$CONH_2$-CN**  1.1		**$CONH_2$-CN**  0.3
+acetone **($CONH_2$)**, PCM/acetone	ND	ND	**$CONH_2$**  1.9	**$CONH_2$**  0	ND	**$CONH_2$**  3.6
			$CONH_2$-CN  2.9	**$CONH_2$-CN**  0.8		**$CONH_2$-CN**  3.9

Table S7. Structures and relative Gibbs energies (ΔG, kcal/mol) of 1:1 complexes with DMSO formed by hydroxyl and imino groups of acyclic form **Ar1**.

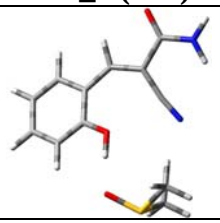
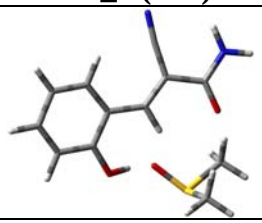
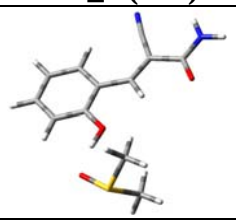
Medium	Structure					
	Ar1 (OH)					
	Ar1_1 (OH)	**Ar1_2 (OH)**	**Ar1_5 (OH)**	**Ar1_6 (OH)**	**Ar1_8 (OH)**	**Ar1_9 (OH)**
	ND				ND	ND
+DMSO **(OH)**	ND	1.7	2.7	0	ND	ND
+DMSO **(OH)**, PCM/DMSO	ND	2.3	2.6	0	ND	ND

Table S8. Structures and relative Gibbs energies (ΔG, kcal/mol) of 1:1 complexes with DMSO formed by amide group of acyclic form **Ar1**.

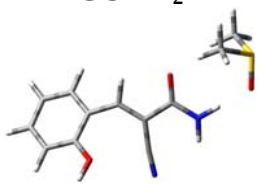
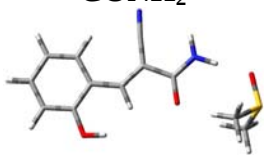
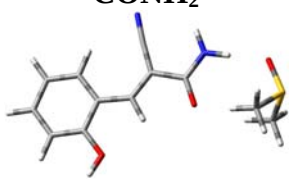
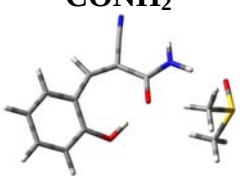
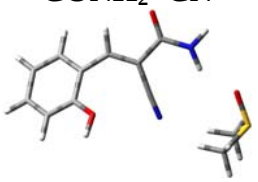
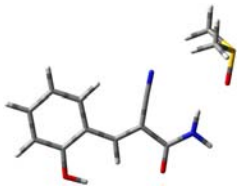
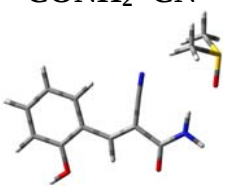
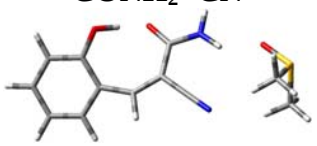
Medium	Structure					
	Ar1 ($CONH_2$)					
	Ar1_1	**Ar1_2**	**Ar1_5**	**Ar1_6**	**Ar1_8**	**Ar1_9**
+DMSO **($CONH_2$)**	ND	**$CONH_2$**  2.6	**$CONH_2$**  0.7	**$CONH_2$**  0	ND	**$CONH_2$**  4.4
		$CONH_2$+CN  4.0	**$CONH_2$+CN**  1.9	**$CONH_2$+CN**  1.6		**$CONH_2$+CN**  5.3
+DMSO **($CONH_2$)**, PCM/DMSO	ND	**$CONH_2$** 3.2	**$CONH_2$** 2.2	**$CONH_2$** 0	ND	**$CONH_2$** 7.3
		$CONH_2$+CN 3.6	**$CONH_2$+CN** 3.8	**$CONH_2$+CN** 1.5		**$CONH_2$+CN** 8.3

Table S9. Structures and relative Gibbs energies (ΔG, kcal/mol) of conformers of cyclic form **Ar2**.

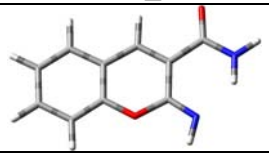
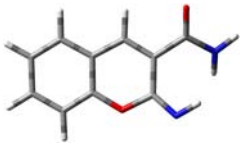
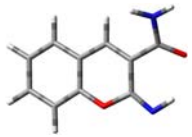
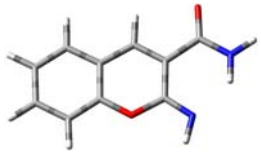
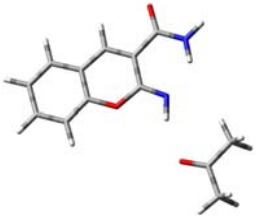
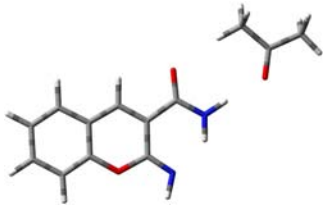
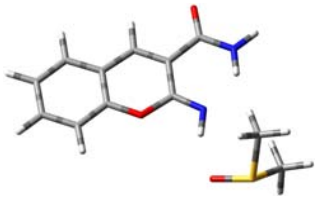
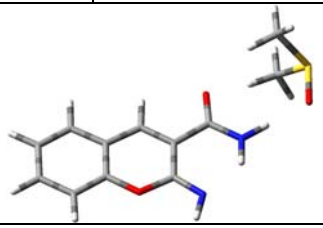
	Ar2		
	Ar2_1	**Ar2_2**	**Ar2_4**
			
Vacuum	0	8.6	8.3

Table S10.* Structures of the most stable conformer of cyclic form **Ar2** and of 1:1 complexes with DMSO and acetone formed by hydroxyl, imino and amide groups of cyclic form **Ar2**.

	PCM/DMSO	+acetone **(NH)**	+acetone **(NH)** PCM/acetone	+acetone **($CONH_2$)**	+acetone **($CONH_2$)** PCM/acetone	+DMSO **(NH)**	+DMSO **(NH)** PCM/DMSO	+DMSO **($CONH_2$)**	+DMSO **($CONH_2$)** PCM/DMSO
Ar2_1									

*Conformers **Ar2_2** and **Ar2_4** were not done in all mediums.

Table S11. Structures of the most stable conformer of pyridone **Ar3** and of 1:1 complexes with DMSO and acetone formed by NH- and amide groups of pyridone **Ar3**.

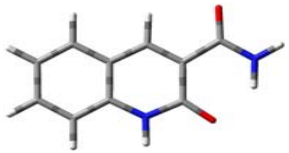
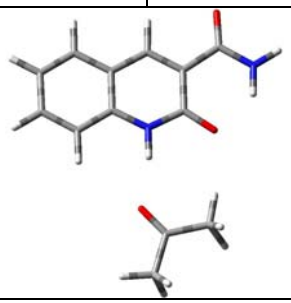
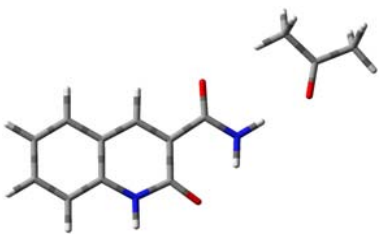
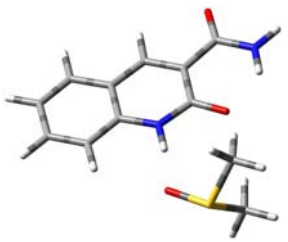
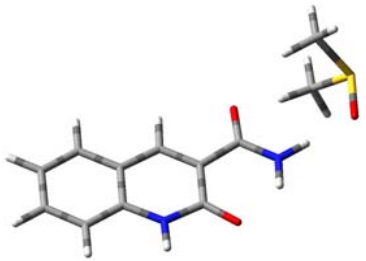
	Vacuum	PCMd	+acetone **(NH)**	+acetone **(NH)** PCM/acetone	+acetone **($CONH_2$)**	+acetone **($CONH_2$)** PCM/acetone	+DMSO **(NH)**	+DMSO **(NH)** PCM/DMSO	+DMSO **($CONH_2$)**	+DMSO **($CONH_2$)** PCM/DMSO
Ar3_1										

Table S12. Structures and relative Gibbs energies (ΔG, kcal/mol) of acyclic form **Alk1** conformers.

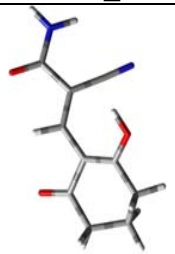
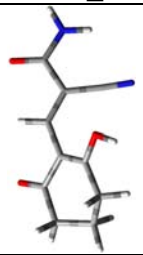
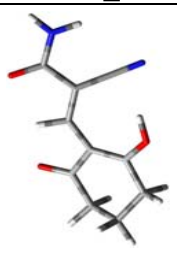
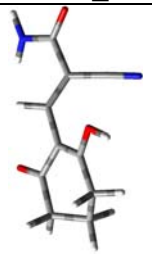
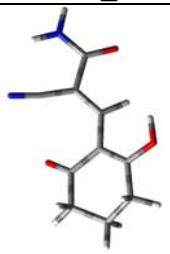
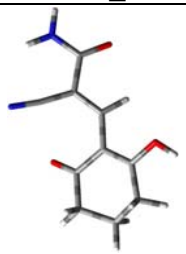
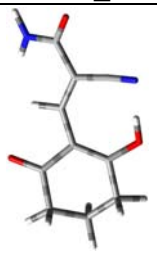
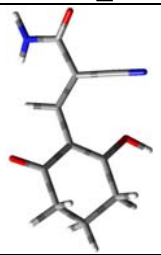
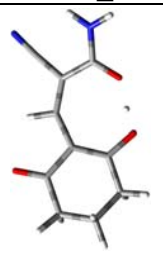
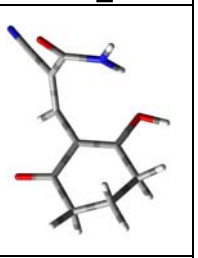
Medium	Structure									
	Alk1									
	Alk1_1	**Alk1_2**	**Alk1_3**	**Alk1_4**	**Alk1_5**	**Alk1_6**	**Alk1_7**	**Alk1_8**	**Alk1_9**	**Alk1_10**
										
Vacuum	5.2	7.3	5.4	10.9	7.2	8.9	7.6	12.1	0	17.1
PCM/DMSO	2.2	1.1	ND	ND	2.9	2.0	ND	ND	0	6.8

Table S13. Structures and relative Gibbs energies (ΔG, kcal/mol) of 1:1 complexes with acetone formed by hydroxyl group of acyclic form **Alk1**.

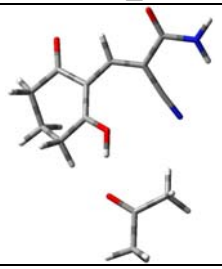
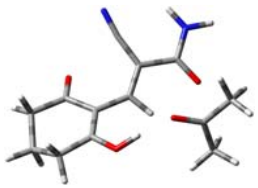
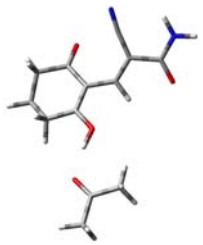
Medium	Structure									
	Alk1 (OH)									
	Alk1_1	**Alk1_2**	**Alk1_3**	**Alk1_4**	**Alk1_5**	**Alk1_6**	**Alk1_7**	**Alk1_8**	**Alk1_9**	**Alk1_10**
	ND		ND	ND			ND	ND	ND	ND
+acetone **(OH)**	ND	0	ND	ND	1.1	2.0	ND	ND	ND	ND
+acetone **(OH)** PCM/acetone	ND	0	ND	ND	ND	ND	ND	ND	ND	ND

Table S14. Structures and relative Gibbs energies (ΔG, kcal/mol) of 1:1 complexes with acetone formed by amide group of acyclic form **Alk1**.

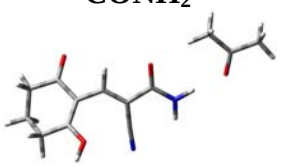
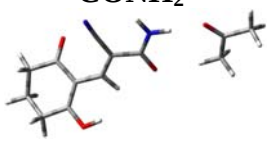
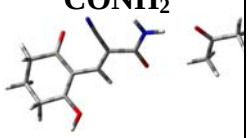
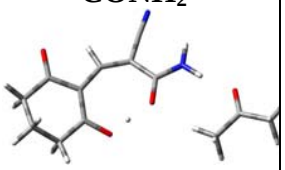
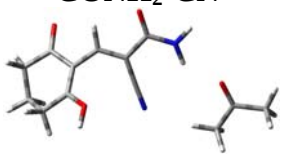
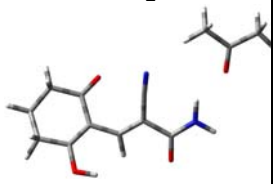
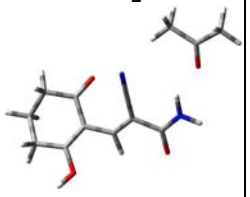
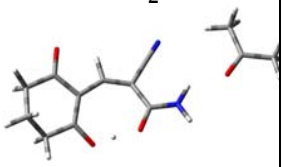
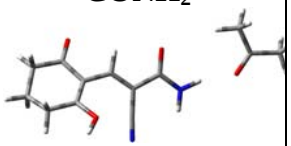
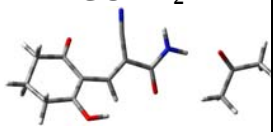
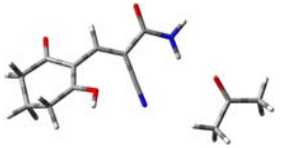
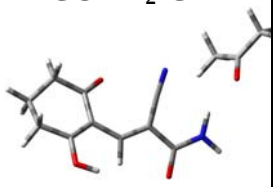
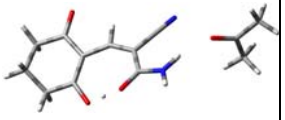
Medium	Structure									
	Alk1 ($CONH_2$)									
	Alk1_1	**Alk1_2**	**Alk1_3**	**Alk1_4**	**Alk1_5**	**Alk1_6**	**Alk1_7**	**Alk1_8**	**Alk1_9**	**Alk1_10**
+acetone **($CONH_2$)**	ND	**$CONH_2$**  8.7	ND	ND	**$CONH_2$**  8.5	**$CONH_2$**  10.4	ND	ND	**$CONH_2$**  0	ND
		$CONH_2$-CN  9.5			**$CONH_2$-CN**  8.8	**$CONH_2$-CN**  10.9			**$CONH_2$-CN**  0.7	
+acetone **($CONH_2$),** PCM/ acetone	ND	**$CONH_2$**  1.0	ND	ND	**$CONH_2$**  2.8	ND	ND	ND	ND	ND
		$CONH_2$-CN  0.6			**$CONH_2$-CN**  2.4				**$CONH_2$-CN**  0	

Table S15. Structures and relative Gibbs energies (ΔG, kcal/mol) of 1:1 complexes with DMSO formed by hydroxyl group of acyclic form **Alk1**.

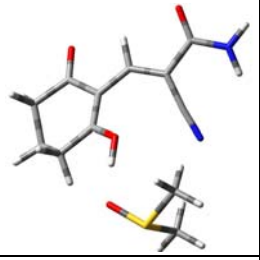
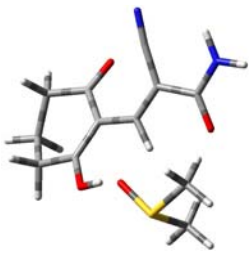
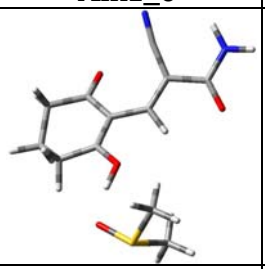
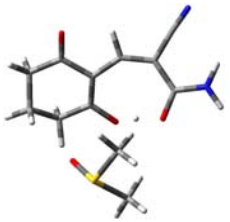
Medium	Structure									
	Alk1 (OH)									
	Alk1_1	**Alk1_2**	**Alk1_3**	**Alk1_4**	**Alk1_5**	**Alk1_6**	**Alk1_7**	**Alk1_8**	**Alk1_9**	**Alk1_10**
	ND		ND	ND			ND	ND		ND
+DMSO **(OH)**	ND	0	ND	ND	3.4	3.2	ND	ND	5.6	ND
+DMSO **(OH)**, PCM/DMSO	ND	0	ND	ND	3.7	0.3	ND	ND	ND	ND

Table S16. Structures and relative Gibbs energies (ΔG, kcal/mol) of 1:1 complexes with DMSO formed by amide group of acyclic form **Alk1**.

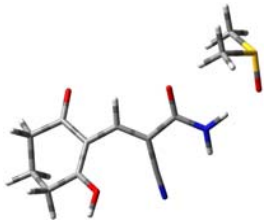
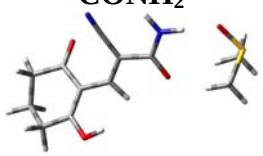
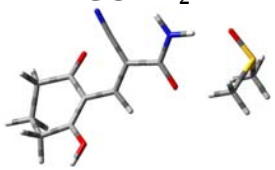
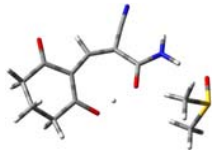
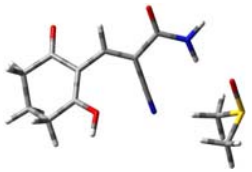
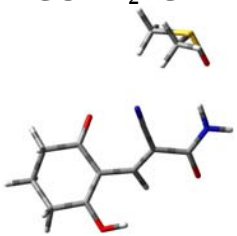
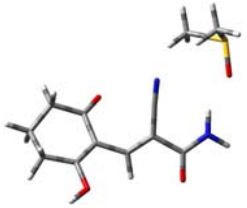
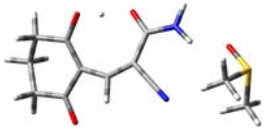
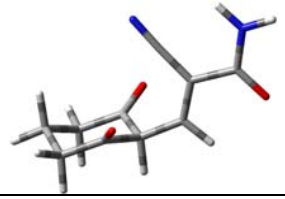
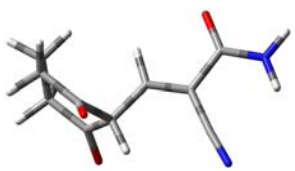
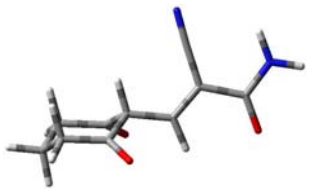
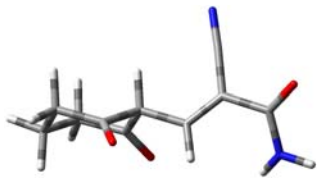
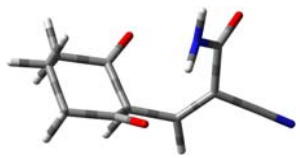
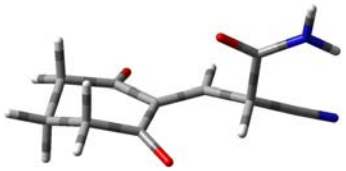
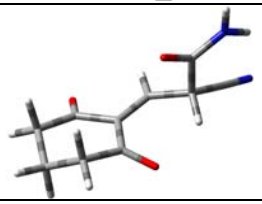
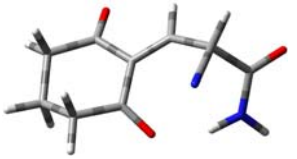
Medium	Structure									
	Alk1 ($CONH_2$)									
	Alk 1_1	**Alk1_2**	**Alk 1_3**	**Alk 1_4**	**Alk1_5**	**Alk1_6**	**Alk 1_7**	**Alk 1_8**	**Alk1_9**	**Alk 1_10**
+DMSO **($CONH_2$)**	ND	**$CONH_2$**  8.5	ND	ND	**$CONH_2$**  8.4	**$CONH_2$**  10.3	ND	ND	**$CONH_2$**  0.9	ND
		$CONH_2$+CN  10.5			**$CONH_2$+CN**  8.9	**$CONH_2$+CN**  11.3			**$CONH_2$+CN**  0	
+DMSO **($CONH_2$),** PCM/DMSO	ND	**$CONH_2$** 2.2	ND	ND	**$CONH_2$** 3.0	**$CONH_2$** 2.5	ND	ND	**$CONH_2$** 0	ND
		$CONH_2$+CN 4.3			**$CONH_2$+CN** 4.4	**$CONH_2$+CN** 3.3			**$CONH_2$+CN** 2.0	

Table S17. Structures and relative Gibbs energies (ΔG, kcal/mol) of conformers of acyclic form **Alk1a**.*

	Alk1a				
	Alk1a_1	**Alk1a_2**	**Alk1a_3**	**Alk1a_4**	**Alk1a_5**
					
Vacuum	3.5	1.6	0	3.2	10.4

*Structure and relative stability of 1:1 complexes of structure **Alk1a** with DMSO in vacuum, PCM/DMSO are shown in Tables 26, 27.

Table S18. Structures and relative Gibbs energies (ΔG, kcal/mol) of conformers of acyclic form **Alk1b**.*

	Alk1b		
	Alk1b_1	**Alk1b_2**	**Alk1b_3**
			
Vacuum	0.004	duplicates **Alk1b_1**	0

*Structure and relative stability of 1:1 complexes of structure **Alk1b** with DMSO in vacuum and in PCM/DMSO are shown in Tables 26, 27.

Table S19. Structures and relative Gibbs energies (ΔG, kcal/mol) of conformers of cyclic form **Alk2**.

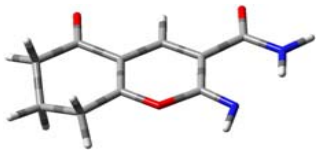
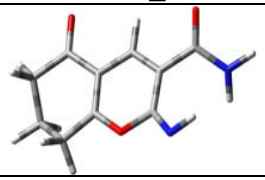
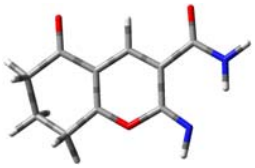
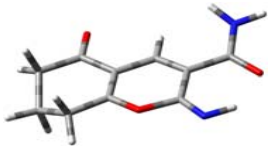
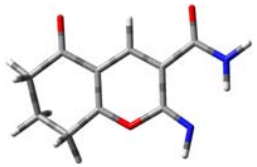
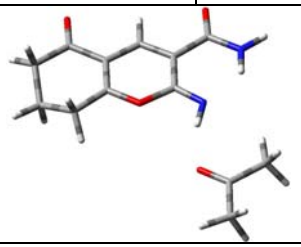
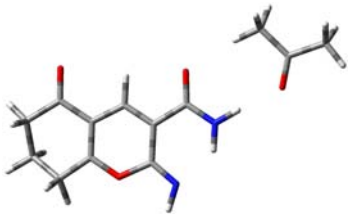
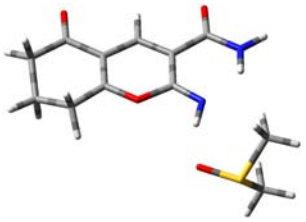
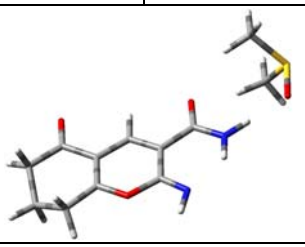
	Al2			
	Alk2_1	**Alk2_2**	**Alk2_3**	**Alk2_4**
				
Vacuum	0	7.2	duplicates **Alk2_1**	4.7

Table S20. Structures of the most stable conformer of cyclic form **Alk2** and of 1:1 complexes with DMSO and acetone formed by imino and amide groups of cyclic form **Alk2**.

	PCM/DMSO	+acetone **(NH)**	+acetone **(NH)** PCM/acetone	+acetone **($CONH_2$)**	+acetone **($CONH_2$)** PCM/acetone	+DMSO **(NH)**	+DMSO **(NH)** PCM/DMSO	+DMSO **($CONH_2$)**	+DMSO **($CONH_2$)** PCM/DMSO
Alk2_1									

*Conformers **Alk2_2**, **Alk2_3** and **Alk2_4** were not done in all mediums.

Table S21. Structures of the most stable conformer of pyridone **Alk3** and of 1:1 complex with DMSO and acetone formed by NH- and amide groups of pyridone **Alk3**.

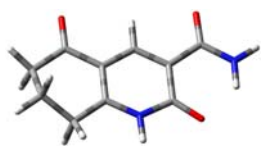
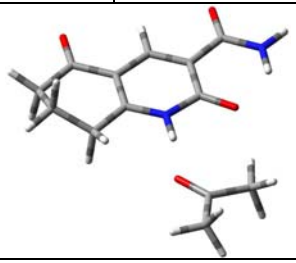
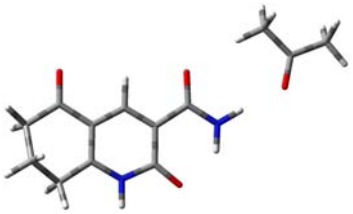
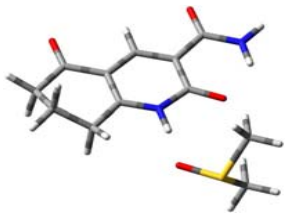
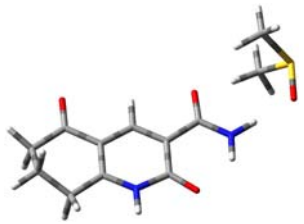
	Vacuum	PCM/DMSO	+acetone **(NH)**	+acetone **(NH)** PCM/acetone	+acetone **($CONH_2$)**	+acetone **($CONH_2$)** PCM/acetone	+DMSO **(NH)**	+DMSO **(NH)** PCM/DMSO	+DMSO **($CONH_2$)**	+DMSO **($CONH_2$)** PCM/DMSO
Alk3_1										

Table S22. Relative stability of possible conformers of cyclic **Ar2** and acyclic **Ar1** forms in vacuum (ΔG, kcal/mol).

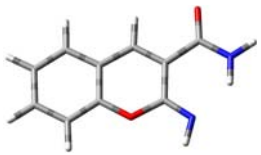
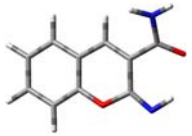
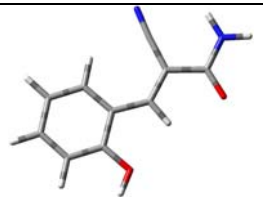
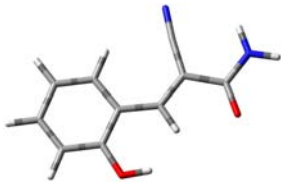
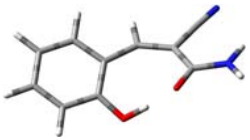
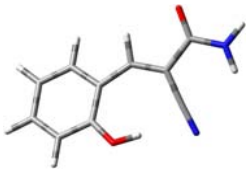
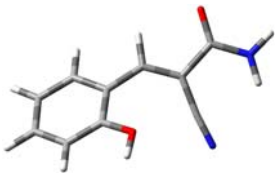
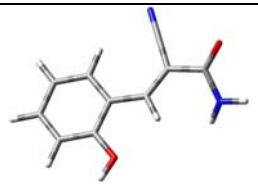
 **Ar2_1**	 **Ar2_2**	 **Ar2_4**	 **Ar1_6**	 **Ar1_5**
0	8.6	8.3	11.3	12.1
 **Ar1_9**	 **Ar1_1**	 **Ar1_2**	 **Ar1_8**	
12.5	13.4	13.9	16.3	

Table S23. Relative stability of 1:1 complexes with DMSO formed by hydroxyl, imino and amide groups of possible conformers of cyclic (**Ar2**) and acyclic (**Ar1**) forms in vacuum (ΔG, kcal/mol).

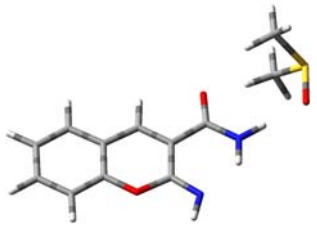
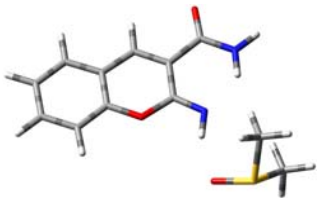
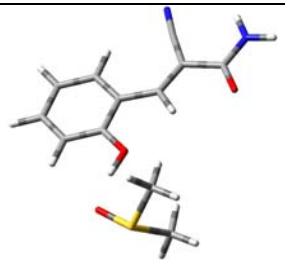
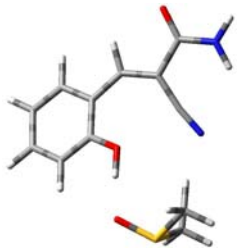
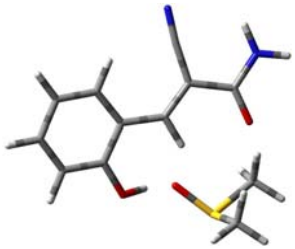
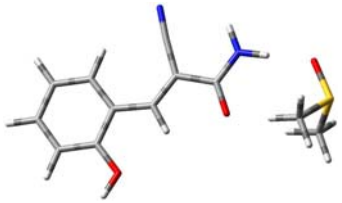
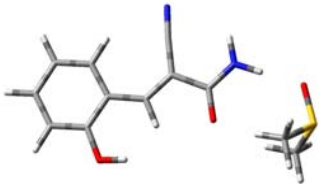
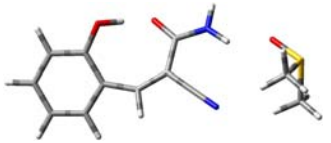
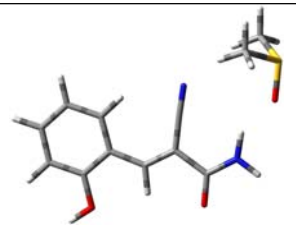
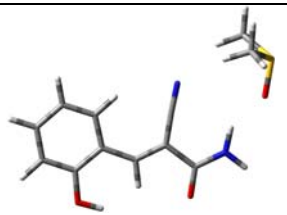
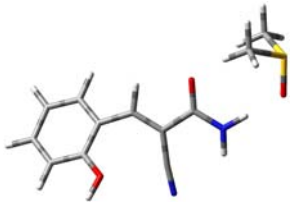
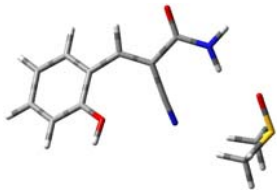
 **Ar2_1 ($CONH_2$)**	 **Ar2_1 (NH)**	 **Ar1_6 (OH)**	 **Ar1_2 (OH)**	 **Ar1_5 (OH)**
0	3.3	6.2	7.9	8.9
 **Ar1_6 ($CONH_2$)**	 **Ar1_9 ($CONH_2$)**	 **Ar1_5 ($CONH_2$)**	 **Ar1_9 ($CONH_2$-CN)**	 **Ar1_6 ($CONH_2$-CN)**
10.4	10.7	11.1	11.5	12.0
 **Ar1_5 ($CONH_2$-CN)**	 **Ar1_2 ($CONH_2$)**	 **Ar1_2 ($CONH_2$-CN)**		
12.2	12.9	14.3		

Table S24. Relative stability of 1:1 complexes with DMSO formed by hydroxyl, imino and amide groups of possible conformers of cyclic (**Ar2**) and acyclic (**Ar1**) forms in PCM/DMSO (ΔG, kcal/mol).

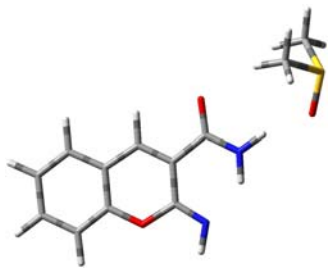
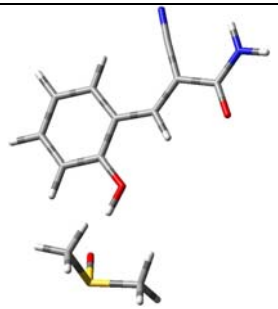
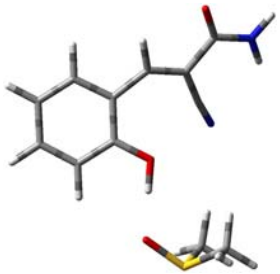
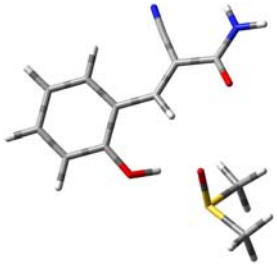
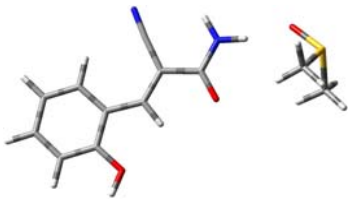
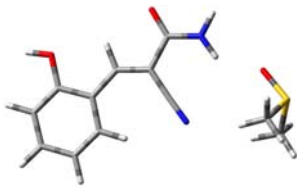
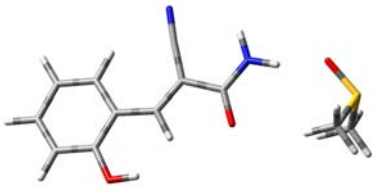
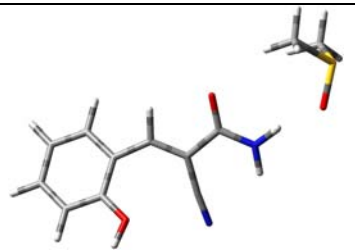
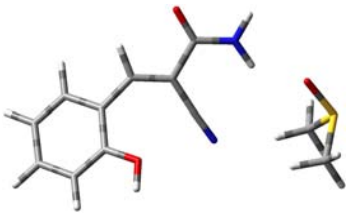
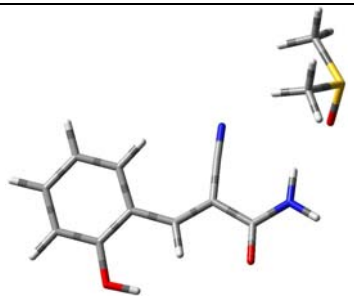
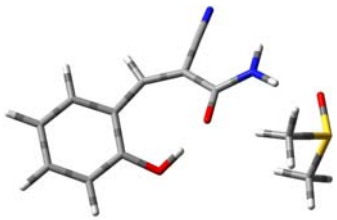
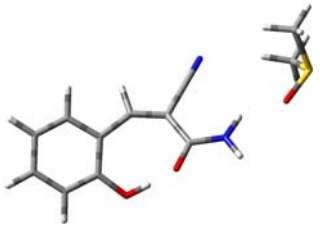
 **Ar2_1 ($CONH_2$)**	 **Ar2_1 (NH)**	 **Ar1_6 (OH)**	 **Ar1_2 (OH)**	 **Ar1_5 (OH)**
0	0.8	3.0	5.3	5.6
 **Ar1_6 ($CONH_2$)**	 **Ar1_6 ($CONH_2$-CN)**	 **Ar1_5 ($CONH_2$)**	 **Ar1_2 ($CONH_2$)**	 **Ar1_2 ($CONH_2$-CN)**
6.3	7.8	8.5	9.5	9.9
 **Ar1_5 ($CONH_2$-CN)**	 **Ar1_9 ($CONH_2$)**	 **Ar1_9 ($CONH_2$-CN)**		
10.1	10.3	11.3		

Table S25. Relative stability of possible conformers of cyclic (**Alk2**) and acyclic (**Alk1**, **Alk1a**, **Alkb**) forms in vacuum (ΔG, kcal/mol).

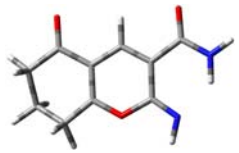
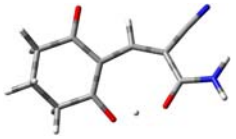
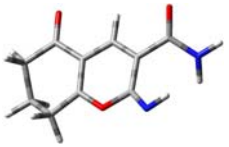
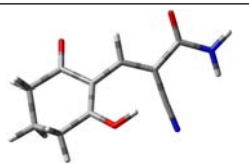
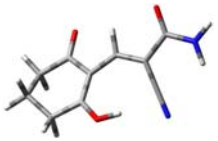
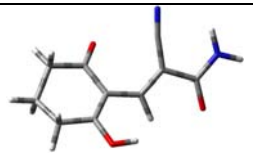
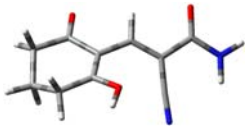
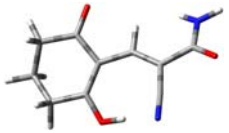
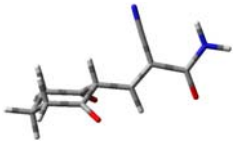
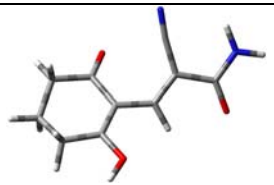
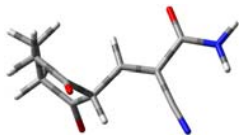
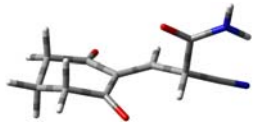
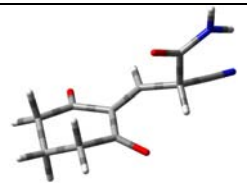
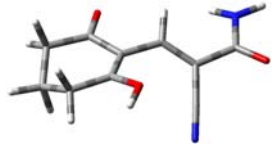
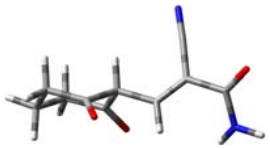
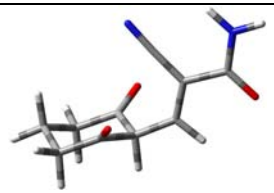
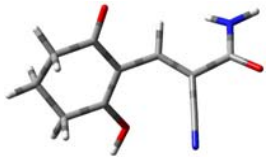
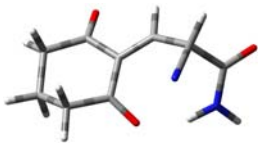
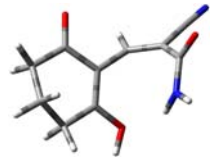
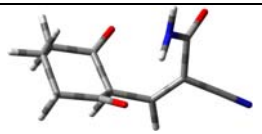
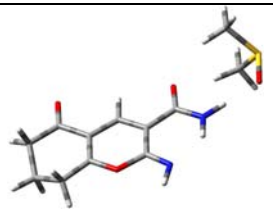
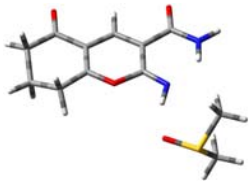
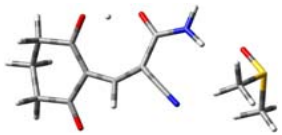
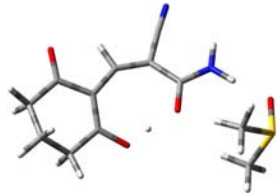
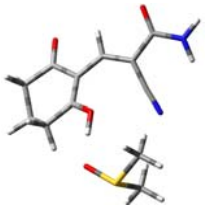
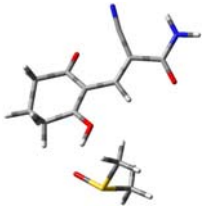
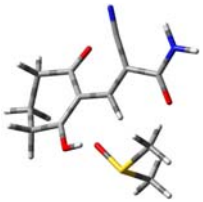
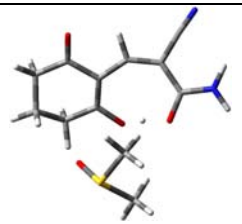
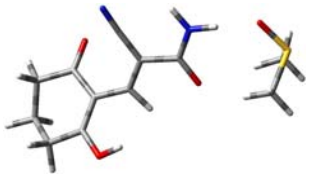
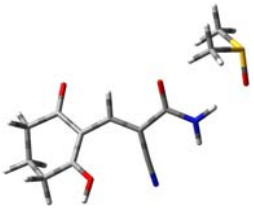
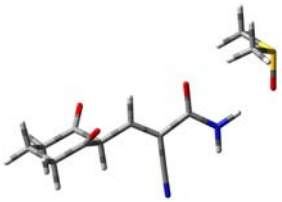
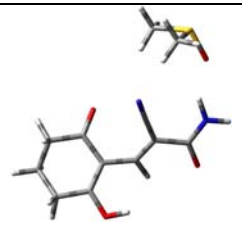
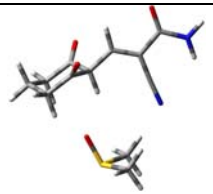
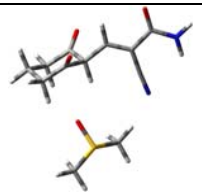
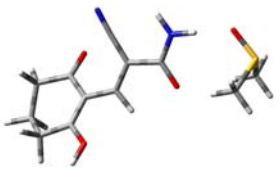
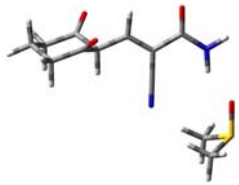
 **Alk2_1**	 **Alk2_4**	 **Alk1_9**	 **Alk2_2**	 **Alk1_1**
0	4.7	5.8	7.2	11.0
 **Alk1_3**	 **Alk1_5**	 **Alk1_2**	 **Alk1_7**	 **Alk1a_3**
11.2	13.0	13.1	13.4	13.8
 **Alk1_6**	 **Alk1a_2**	 **Alk1b_1**	 **Alk1b_2**	 **Alk1_4**
14.6	15.4	16.6	16.6	16.7
 **Alk1a_4**	 **Alk1a_1**	 **Alk1_8**	 **Alk1b_3**	 **Alk1_10**
17.0	17.3	17.9	18.6	22.9
 **Alk1a_5**				
24.2				

Table S26. Relative stability of 1:1 complexes with DMSO formed by hydroxyl, imino and amide groups of possible conformers of cyclic (**Alk2**) and acyclic (**Alk1**, **Alk1a**, **Alk1b**) forms in vacuum (ΔG, kcal/mol).

 **Alk2_1 ($CONH_2$)**	 **Alk2_3 (NH)**	 **Alk1_9 ($CONH_2$-CN)**	 **Alk1_9 ($CONH_2$)**
0	2.2	4.0	4.8
 **Alk1_2 (OH)**	 **Alk1_6 (OH)**	 **Alk1_5 (OH)**	 **Alk1_9 (OH)**
5.0	8.2	8.4	10.6
 **Alk1_5 ($CONH_2$)**	 **Alk1_2 ($CONH_2$)**	 **Alk1a_3 (NH-$CONH_2$)**	 **Alk1_5 ($CONH_2$-CN)**
12.3	12.5	12.5	12.8
 **Alk1a_3 (Ht-CN)**	 **Alk1a_2 (Ht-COc)**	 **Alk1_6 ($CONH_2$)**	 **Alk1a_3 (NH-CN)**
13.4	14.0	14.3	14.4

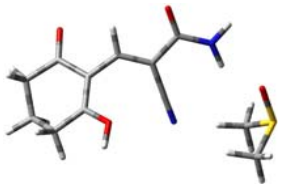
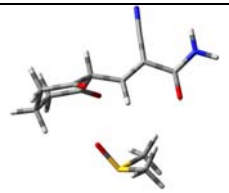
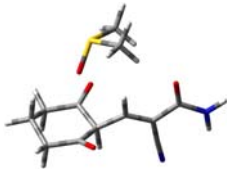
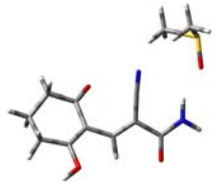
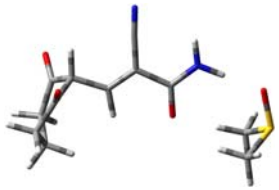
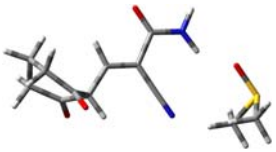
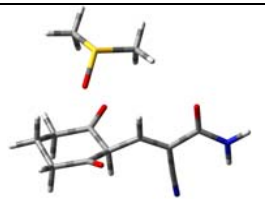
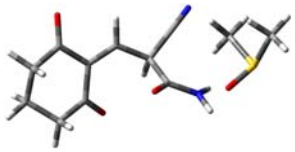
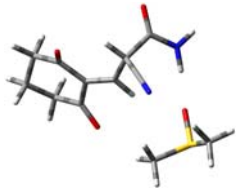
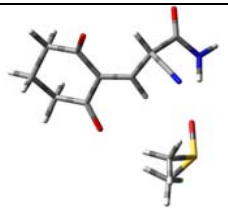
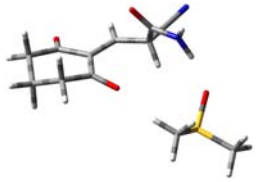
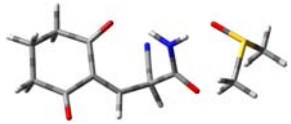
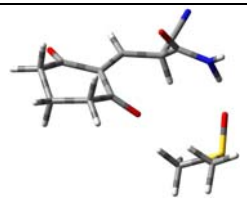
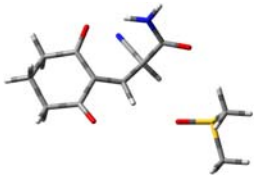
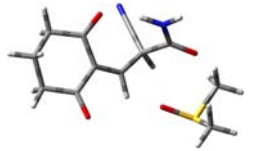
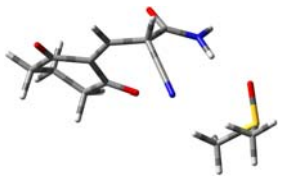
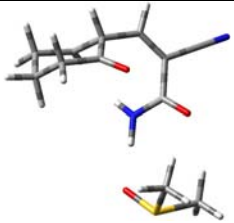
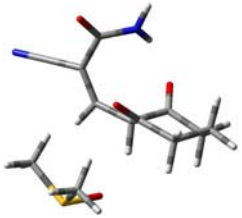
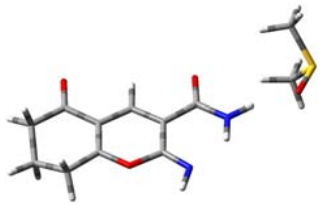
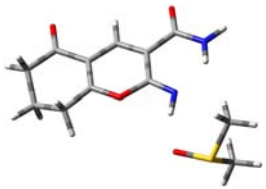
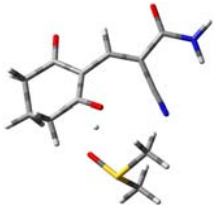
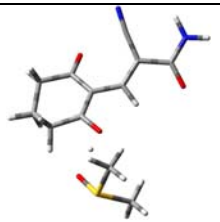
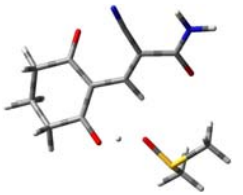
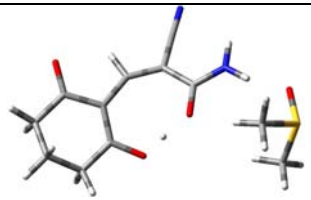
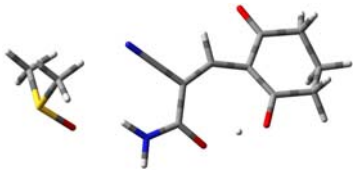
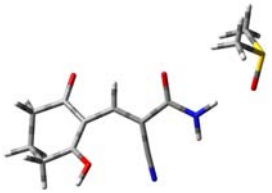
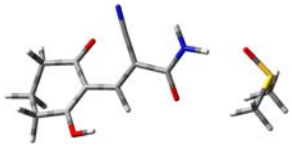
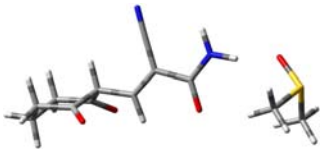
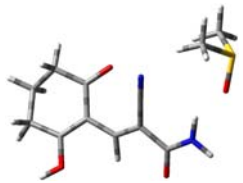
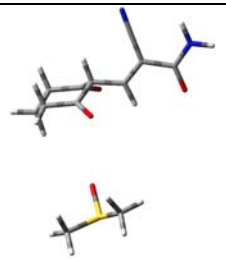
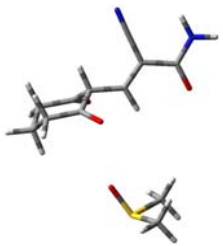
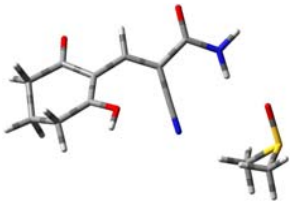
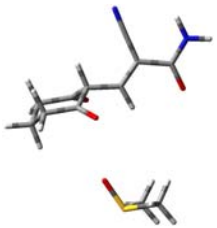
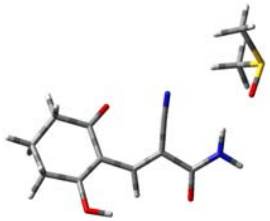
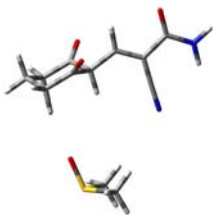
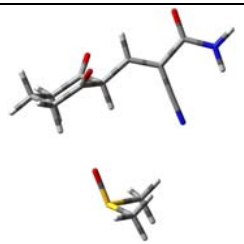
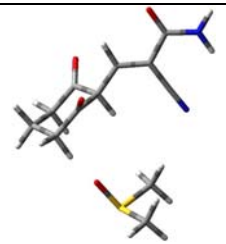
 **Alk1_2 ($CONH_2$-CN)**	 **Alk1a_2 (CH-$CONH_2$)**	 **Alk1a_3 (CH-$CONH_2$)**	 **Alk1_6 ($CONH_2$-CN)**
14.5	15.1	15.2	15.3
 **Alk1b_1 (NH-$CONH_2$)**	 **Alk1a_2 (NH-$CONH_2$)**	 **Alk1a_2 (NH-CN)**	 **Alk1a_3 (CH-COc)**
15.7	15.9	16.5	16.5
 **Alk1b_1 (NH-CN)**	 **Alk1b_1 (CH-CN)**	 **Alk1b_1 (CH-COc)**	 **Alk1b_1 (Ht-CO+N_$CONH_2$)**
16.5	17.4	17.5	17.9
 **Alk1b_3 (NH-$CONH_2$)**	 **Alk1b_1 (Ht-COc)**	 **Alk1b_3 (CH-COc)**	 **Alk1b_3 (Ht-$CONH_2$)**
17.9	18.5	19.5	19.8
 **Alk1b_3 (NH-CN)**	 **Alk1a_5 ($CONH_2$)**	 **Alk1a_5 (CO)**	
19.8	22.0	23.9	

Table S27. Relative stability of 1:1 complexes with DMSO formed by hydroxyl, imino and amide groups of possible conformers of cyclic (**Alk2**) and acyclic (**Alk1**, **Alk1a**, **Alk1b**) forms in PCM/DMSO (ΔG, kcal/mol).

 **Alk2_1 ($CONH_2$)**	 **Alk2_3 (NH)**	 **Alk1_2 (OH)**	 **Alk1_6 (OH)**	 **Alk1_5 (OH)**
0	0.5	1.3	1.6	5.0
 **Alk1_9 ($CONH_2$)**	 **Alk1_9 ($CONH_2$-CN)**	 **Alk1_2 ($CONH_2$)**	 **Alk1_6 ($CONH_2$)**	 **Alk1_5 ($CONH_2$)**
5.3	7.3	7.5	7.8	8.3
 **Alk1a_3 (NH-$CONH_2$)**	 **Alk1_6 ($CONH_2$-CN)**	 **Alk1a_3 (CH-COc)**	 **Alk1a_2 (CH-$CONH_2$)**	 **Alk1_2 ($CONH_2$-CN)**
8.3	8.6	9.5	9.5	9.5
 **Alk1a_3 (CH-$CONH_2$)**	 **Alk1_5 ($CONH_2$-CN)**	 **Alk1a_2 (Ht-CN-COc)**	 **Alk1a_3 (Ht-CN)**	 **Alk1a_2 (Ht-CN)**
9.6	9.7	9.8	9.8	10.6

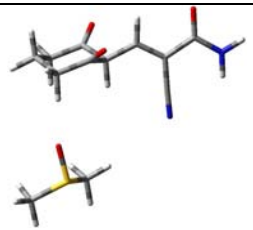
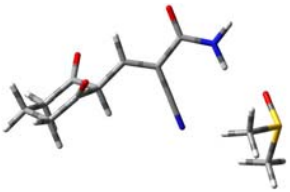
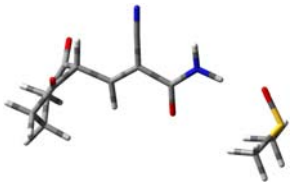
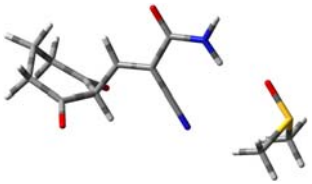
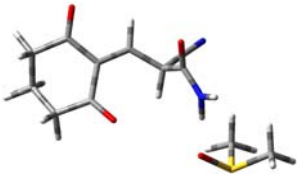
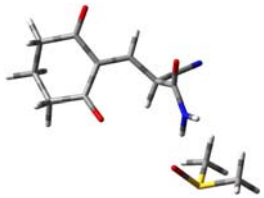
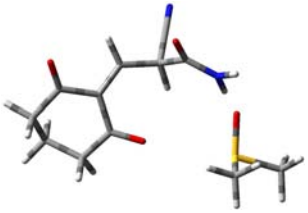
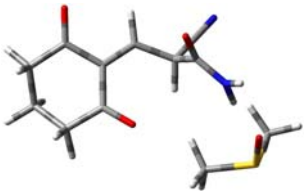
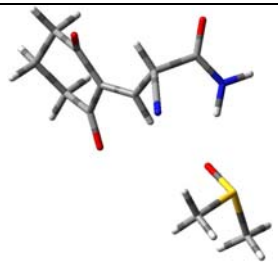
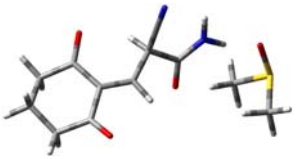
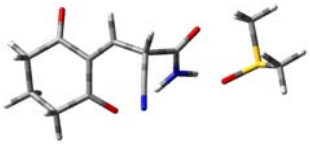
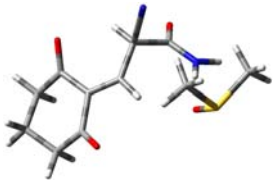
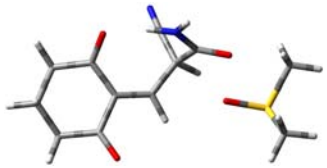
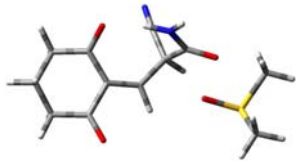
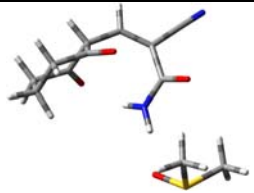
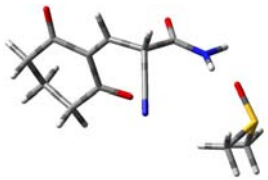
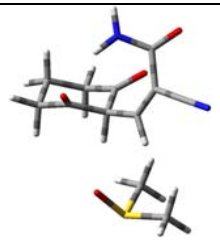
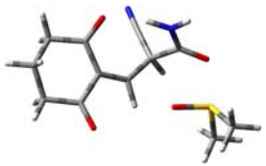
 **Alk1a_2 (Ht-COc)**	 **Alk1a_3 (NH-CN)**	 **Alk1a_2 (NH-CONH$_2$)**	 **Alk1a_2 (NH-CN)**	 **Alk1b_1 (NH-CN)**
10.6	10.7	11.7	12.1	12.4
 **Alk1b_1 (Ht_CN)**	 **Alk1b_1 (Ht-CO+N_CONH$_2$)**	 **Alk1b_1 (Ht-COc)**	 **Alk1b_1 (CH-COc)**	 **Alk1b_1 (NH-CONH$_2$)**
12.7	13.5	13.5	13.6	13.7
 **Alk1b_3 (NH-CONH$_2$)**	 **Alk1b_1 (CH-CN)**	 **Alk1b_3 (Ht-CN)**	 **Alk1b_3 (Ht-CONH$_2$)**	 **Alk1a_5 (CONH$_2$)**
14.7	14.8	16.5	16.6	16.7
 **Alk1b_3 (NH-CN)**	 **Alk1a_5 (CO)**	 **Alk1b_3 (CH-COc)**		
17.1	17.2	17.3		

Table S28. Relative stability of 1:1 complexes with acetone formed by hydroxyl, imino and amide groups of possible conformers of cyclic (**Ar2**) and acyclic (**Ar1**) forms in vacuum (ΔG, kcal/mol).

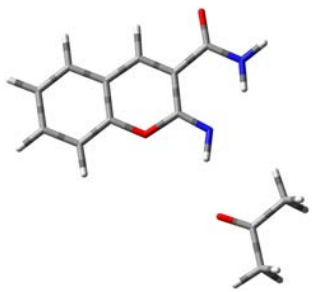
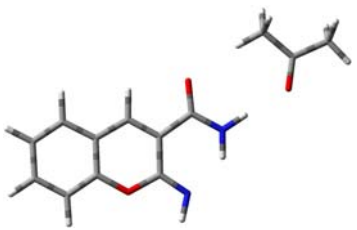
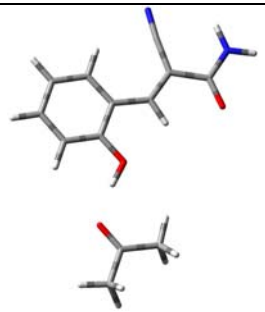
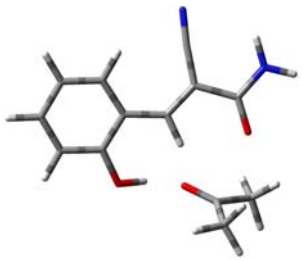
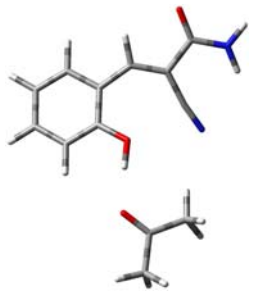
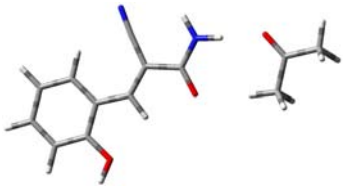
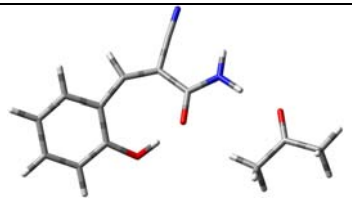
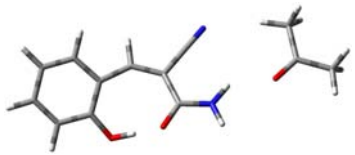
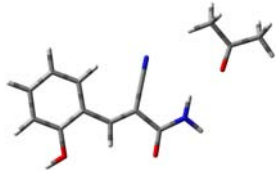
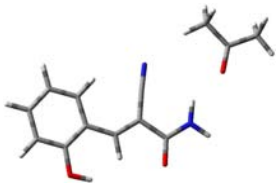
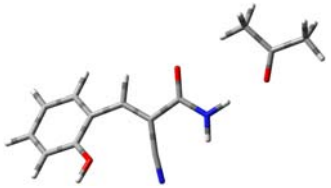
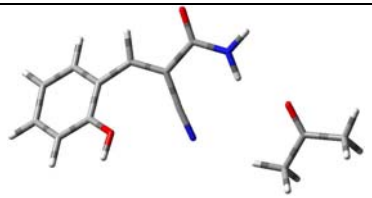
 **Ar2_1 (NH)**	 **Ar2_1 ($CONH_2$)**	 **Ar1_6 (OH)**	 **Ar1_5 (OH)**	 **Ar1_2 (OH)**
0	0.5	7.7	9.1	10.1
 **Ar1_6 ($CONH_2$)**	 **Ar1_9 ($CONH_2$)**	 **Ar1_9 ($CONH_2$-CN)**	 **Ar1_5 ($CONH_2$)**	 **Ar1_6 ($CONH_2$-CN)**
10.7	10.9	11.0	11.3	11.8
 **Ar1_5 ($CONH_2$-CN)**	 **Ar1_2 ($CONH_2$)**	 **Ar1_2 ($CONH_2$-CN)**		
11.9	13.3	13.8		

Table S29. Relative stability of 1:1 complexes with acetone formed by hydroxyl, imino and amide groups of possible conformers of cyclic (**Ar2**) and acyclic (**Ar1**) forms in PCM/acetone (ΔG, kcal/mol).

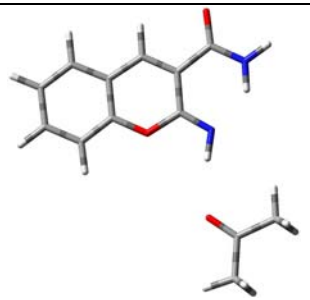
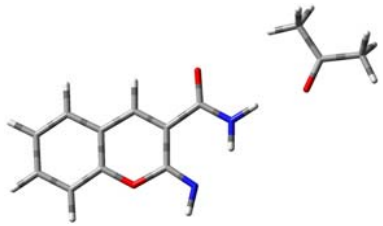
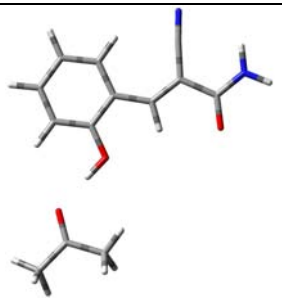
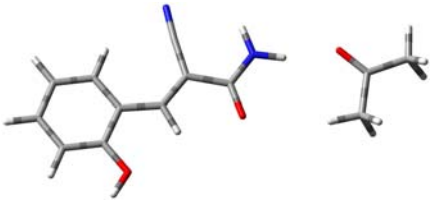
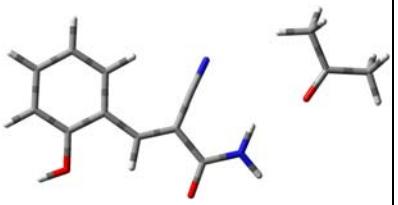
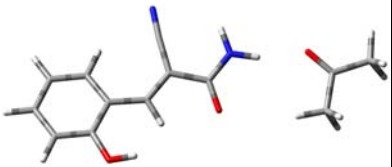
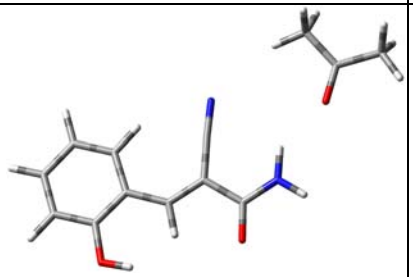
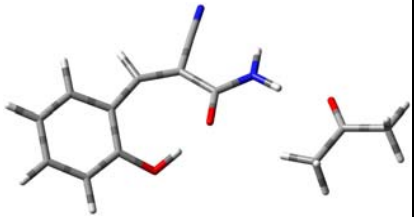
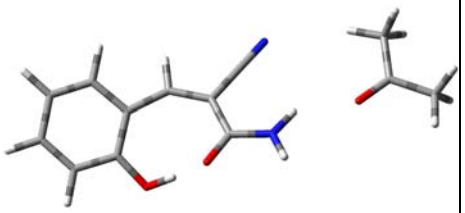
 **Ar2_1 (NH)**	 **Ar2_1 ($CONH_2$)**	 **Ar1_6 (OH)**	 **Ar1_6 ($CONH_2$)**	 **Ar1_6 ($CONH_2$-CN)**
0	0.2	4.9	6.9	7.7
 **Ar1_5 ($CONH_2$)**	 **Ar1_5 ($CONH_2$-CN)**	 **Ar1_9 ($CONH_2$)**	 **Ar1_9 ($CONH_2$-CN)**	
8.8	9.8	10.5	10.8	

Table S30. Relative stability of 1:1 complexes with acetone formed by hydroxyl, imino and amide groups of possible conformers of cyclic (**Alk2**) and acyclic (**Alk1**) forms in vacuum (ΔG, kcal/mol).

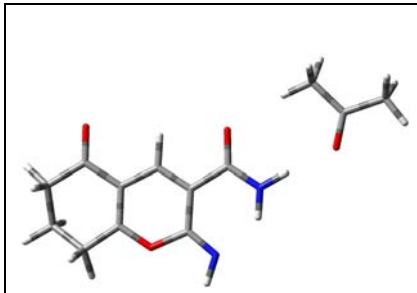
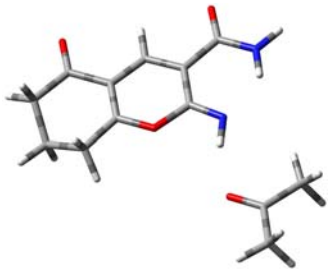
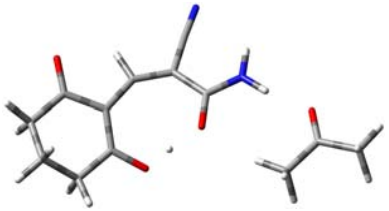
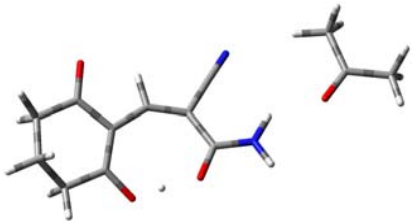
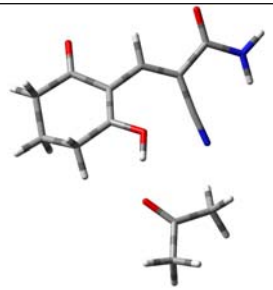
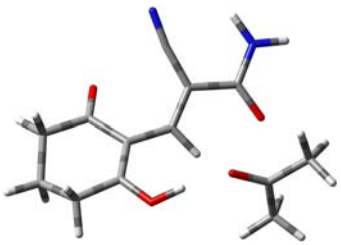
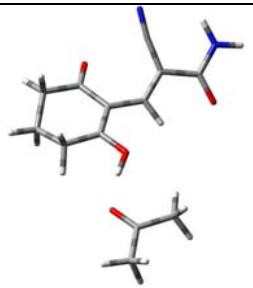
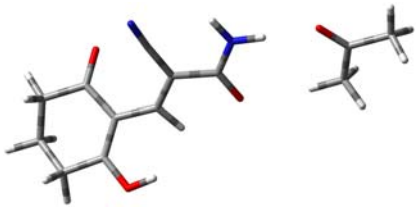
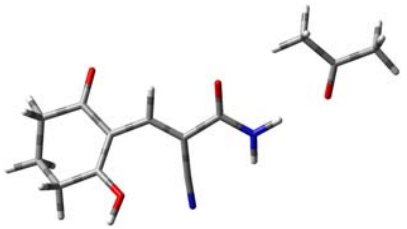
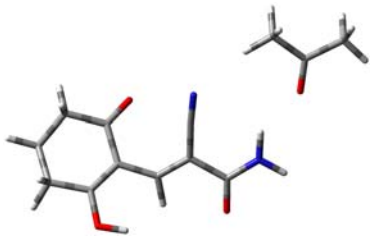
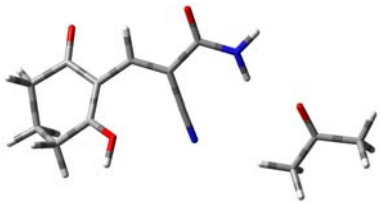
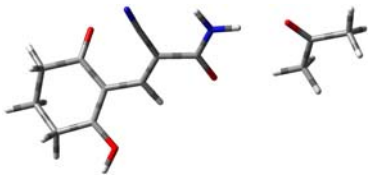
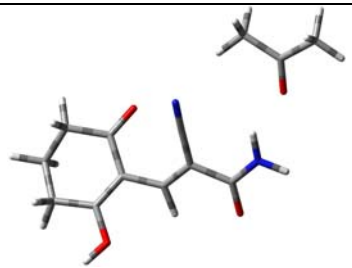
 **Alk2_1 ($CONH_2$)**	 **Alk2_1 (NH)**	 **Alk1_9 ($CONH_2$)**	 **Alk1_9 ($CONH_2$-CN)**	 **Alk1_2 (OH)**
0	0.6	3.7	4.4	7.8
 **Alk1_5 (OH)**	 **Alk1_6(OH)**	 **Alk1_5 ($CONH_2$)**	 **Alk1_2 ($CONH_2$)**	 **Alk1_5 ($CONH_2$-CN)**
8.9	9.4	12.2	12.4	12.6
 **Alk1_2 ($CONH_2$-CN)**	 **Alk1_6 ($CONH_2$)**	 **Alk1_6 ($CONH_2$-CN)**		
13.2	14.2	14.6		

Table S31. Relative stability of 1:1 complexes with acetone formed by hydroxyl, imino and amide groups of possible conformers of cyclic (**Alk2**) and acyclic (**Alk1**) forms in PCM/acetone (ΔG, kcal/mol).

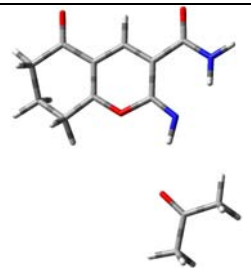
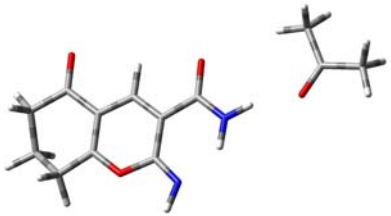
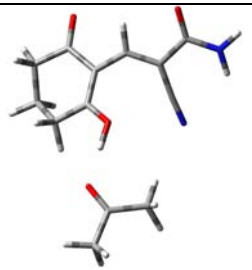
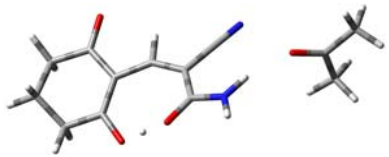
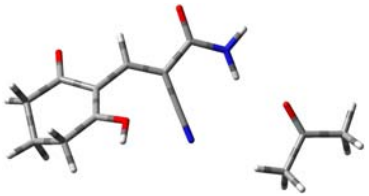
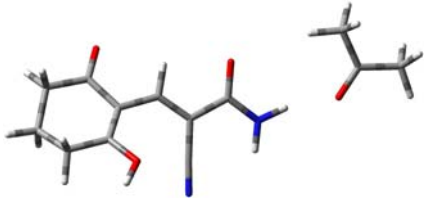
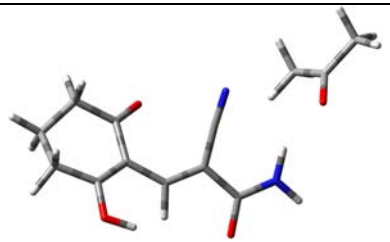
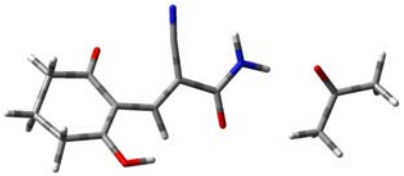
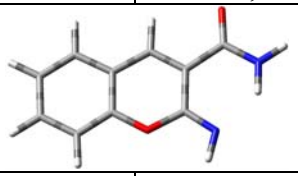
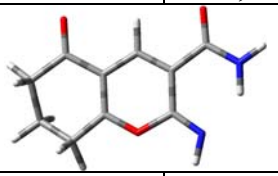
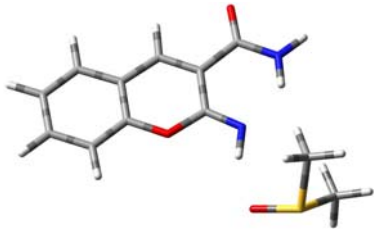
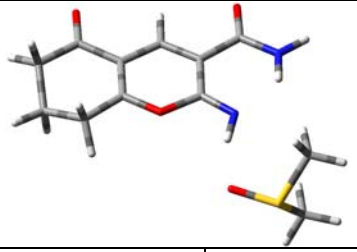
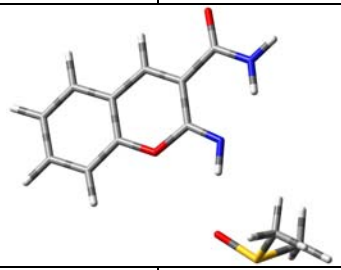
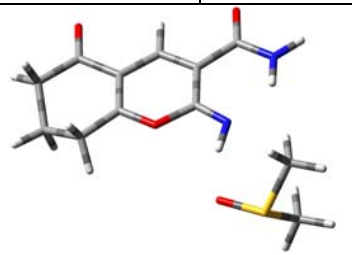
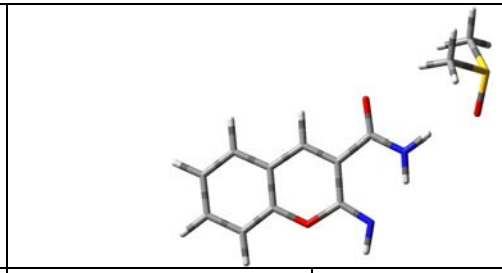
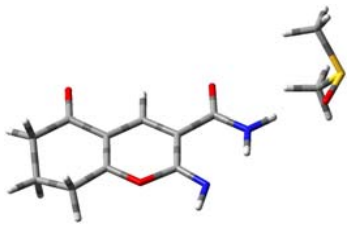
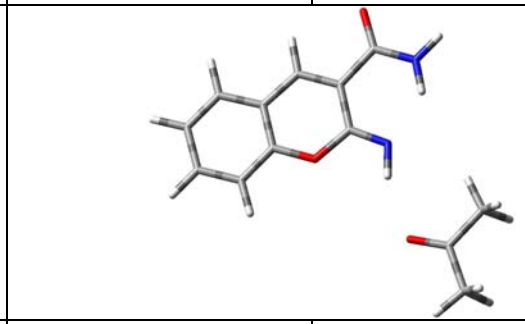
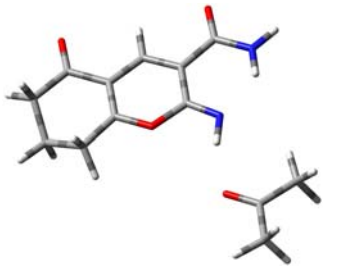
 **Alk2_1 (NH)**	 **Alk2_3 ($CONH_2$)**	 **Alk1_2 (OH)**	 **Alk1_9 ($CONH_2$-CN)**
0	0.4	3.6	6.9
 **Alk1_2 ($CONH_2$-CN)**	 **Alk1_2 ($CONH_2$)**	 **Alk1_5 ($CONH_2$-CN)**	 **Alk1_5 ($CONH_2$)**
7.5	7.9	9.4	9.7

Table S32. Intra- and intermolecular bond lengths and estimation of the bond energies for the most stable conformers of cyclic structures **Ar2**, **Alk2** and their 1:1 complexes with DMSO and acetone formed by imino and amide groups of substrate in vacuum, PCM/DMSO and PCM/acetone.

Medium	Bond	**Ar2_1**		**Alk2_1**	
		l, Å	E, kcal/mol	*l*, Å	E, kcal/mol
					
Vacuum	N–H…N (intramol)	1.931	-6.8	1.955	-6.4
PCM/DMSO	N–H…N (intramol)	1.914	-7.7	1.940	-7.2
					
+DMSO **(NH)**	N–H…N(=C) (intramol) N–H…O(=S) (intermol) C–H…N(intermol) C–H…N(intermol) **All** **intermol**	1.918 2.043 2.944 2.773	-7.2 -4.7 -0.7 -1.0 **-13.6** **-6.4**	1.945 2.000 2.833 2.976	-6.6 -5.2 -0.9 -0.6 **-13.3** **-6.6**
					
+DMSO **(NH)** PCM/DMSO	N–H…O(=S) (intermol) N–H…N(=C) (intramol) **All** **intermol**	2.040 1.903	-4.6 -7.5 **-12.0** **-4.6**	1.994 1.929	-5.0 -6.9 **-11.9** **-5.0**

					
+DMSO **($CONH_2$)** PCM/DMSO	N–H…O(=S) (intermol) (C=)O...H (intermol) (C=)O...H (intermol) N–H…N(=C) (intramol) **All** **intermol**	1.911 3.160 3.193 1.923	-5.9 -0.3 -0.3 -7.0 **-13.6** **-6.6**	1.910 3.167 3.150 1.950	-5.9 -0.3 -0.3 -6.6 **-13.1** **-6.6**
					
+acetone **(NH)**	N–H…N (intramol) N–H…O (intermol) C–H…N (intermol) **All** **intermol**	1.916 2.152 2.782	-7.2 -3.7 -0.9 **-11.7** **-4.6**	1.943 2.109 2.873	-6.6 -4.0 -0.8 **-11.3** **-4.7**
+acetone **(NH)** PCM/acetone	N–H…O(=C) (intermol) N–H…N(=C) (intramol) **All** **intermol**	2.139 1.903	-3.7 -7.4 **-11.1** **-3.7**	2.105 1.930	-4.0 -6.9 **-10.9** **-4.0**

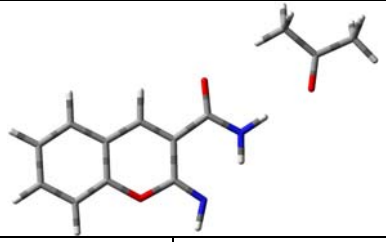
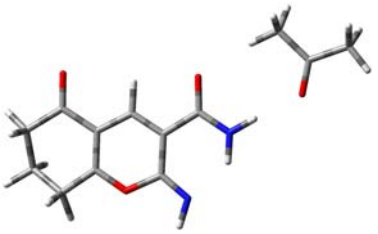
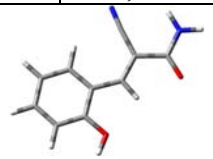
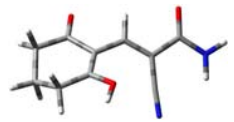
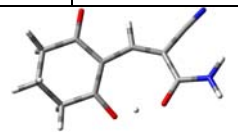
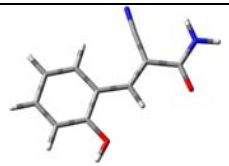
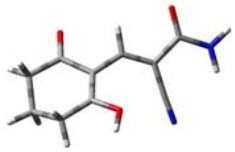
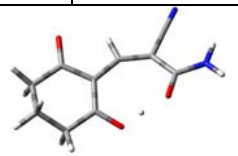
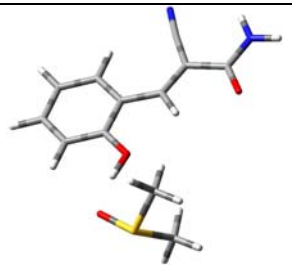
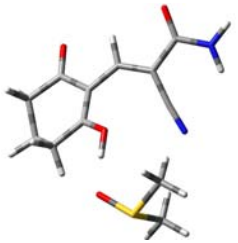
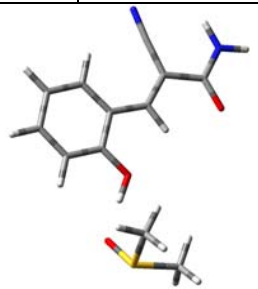
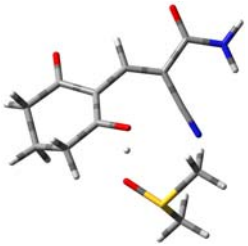
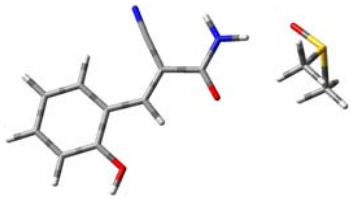
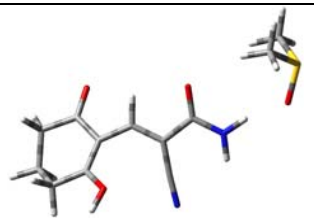
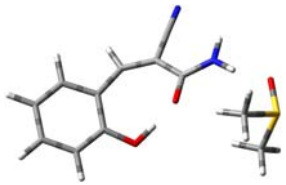
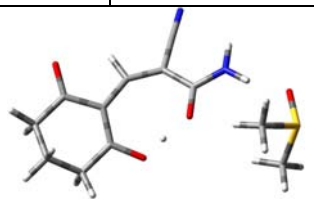
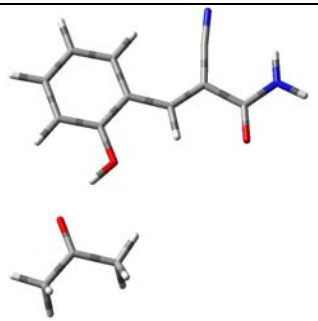
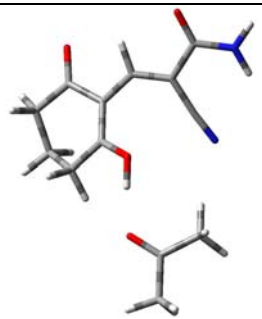
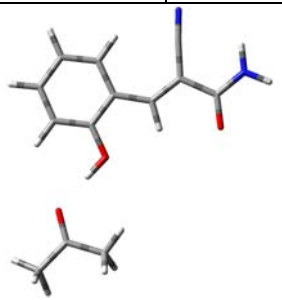
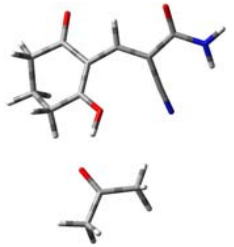
					
+acetone **($CONH_2$)**	N–H…O(=C) (intermol) (C=)O...H (intermol) N–H…N(=C) (intramol) **All** **intermol**	1.982 2.342 1.944	-5.0 -2.6 -6.6 **-14.2** **-7.6**	1.978 2.338 1.970	-5.0 -2.6 -6.2 **-13.8** **-7.6**
+acetone **($CONH_2$)** PCM/acetone	(C=)O...H (intermol) N–H…O(=C) (intermol) N–H…N(=C) (intramol) **All** **intermol**	3.040 2.009 1.923	-0.5 -4.7 -7.0 **-12.2** **-5.2**	3.058 2.003 1.949	-0.5 -4.8 -6.6 **-11.9** **-5.3**

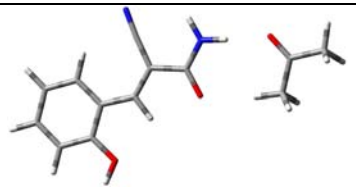
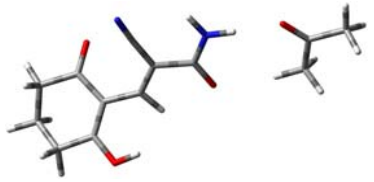
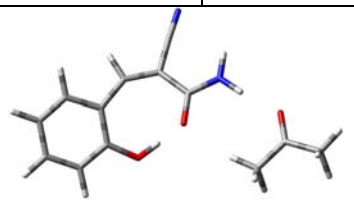
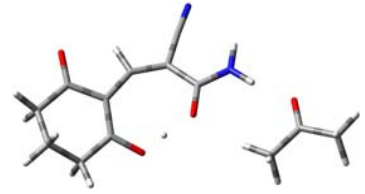
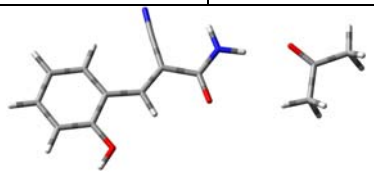
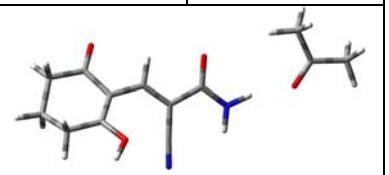
Table S33. Intra- and intermolecular bond lengths and estimation of the bond energies for the most stable conformers of cyclic structures **Ar1**, **Alk1** and their 1:1 complexes with DMSO and acetone formed by imino and amide groups of substrate in vacuum, PCM/DMSO, and PCM/acetone.

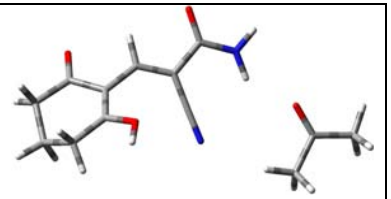
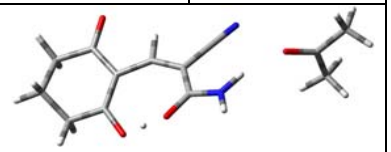
Medium	Bond	**Ar1**		Bond	**Alk1**	
		l, Å	E, kcal/mol		*l*, Å	E, kcal/mol
Vacuum		 **Ar1_6**			 **Alk1_2**	
	PhH…C(≡N)	2.378	-2.5	H–O…C(≡N)	2.799	-2.5
					 **Alk1_9**	
				C–H...O(=C) O(–H)... O(=CNH_2) **All**	2.106 1.418	-6.5 -38.7 **-45.2**
PCM/DMSO		 **Ar1_6**			 **Alk1_2**	
	H–O…H(–C) PhH…C(≡N) **All**	2.289 2.401	-4.3 -2.5 **-6.8**	H–O…C(≡N) **All**	2.795	-2.7
					 **Alk1_9**	
				C–H...O(=C) O(–H)... O(=CNH_2) **All**	2.127 1.406	-6.2 -40.8 **-47.0**

+DMSO **(OH)**		 **Ar1_6 (OH)**			 **Alk1_2 (OH)**	
	PhH…C(≡N) PhO…HC (intramol) O–H…O(=S) C–H…OPh C–H…OPh **All** **intermol**	2.404 2.287 1.644 2.722 2.723	-2.3 -4.2 -14.3 -1.1 -1.1 **-22.9** **-16.4**	O…C(≡N) O–H…O(=S) (intermol) CH…O CH…O **All** **intermol**	2.725 1.563 2.607 2.441	-3.0 -19.2 -1.3 -1.9 **-25.4** **-22.4**
+DMSO **(OH),** PCM/DMSO		 **Ar1_6 (OH)**			 **Alk1_2 (OH)**	
	(S=)O…HPh O–H…O(=S) H–O…HC (intramol) (N≡)C…HPh (intramol) **All** **intermol**	2.648 1.606 2.289 2.401	-1.4 -16.1 -4.1 -2.3 **-24.0** **-17.6**	(C≡)N…H(CH_2S) O–H…O(=S) (intermol) H-O…C(≡N) (intramol) **All** **intermol**	2.766 1.505 2.774	-0.9 -24.4 -2.7 **-27.9** **-25.3**

+DMSO **($CONH_2$),** PCM/DMSO		 **Ar1_6 ($CONH_2$)**			 **Alk1_2 ($CONH_2$)**	
	N–H…O(=S) (intermol) (C=)O...H (intermol) (C=)O...H (intermol) (H)O…H (intramol) (N≡)C…H(Ar) (intramol) **All** **intermol**	1.859 3.109 3.128 2.290 2.403	6.8 0.4 0.4 4.0 2.3 **-13.8** **-7.5**	N–H…O(=S) (intermol) (C=)O...H (intermol) (C=)O...H (intermol) (H)O…C(≡N) (intramol) **All** **intermol**	1.864 3.020 3.184 2.805	-6.7 -0.5 -0.3 -2.4 **-9.9** **-7.5**
		 **Ar1_9 ($CONH_2$)**			 **Alk1_9 ($CONH_2$)**	
	(C=)O...H(O) (intramol) N–H…O(=S) (intermol) (C=)O...H (intermol) (C=)O...H (intermol) **All** **intermol**	1.505 1.814 3.096 2.839	-25.4 -7.8 -0.4 -0.8 **-34.3** **-9.0**	N–H…O(=S) (intermol) (C=)O...H (intermol) (C=)O...H (intermol) (C=)O...H(O) (intramol) (C=)O...H (intramol) **All** **intermol**	1.808 2.958 2.922 1.386 2.162	7.9 0.6 0.6 41.6 5.5 **-56.1** **-7.1**

+acetone **(OH)**		 **Ar1_6 (OH)**			 **Alk1_2 (OH)**	
	PhH…C(≡N) (intramol) PhO…HC (intramol) O–H…O(=C) (intermol) **All** **intermol**	2.389 2.293 1.756	-2.4 -4.1 -9.3 **-15.8** **-9.3**	(H)O…C(≡N) O–H…O (intermol) C–H…N (intermol) **All** **intermol**	2.751 1.695 2.490	-2.8 -11.5 -1.6 **-15.9** **-13.1**
+acetone **(OH),** PCM/acetone		 **Ar1_6 (OH)**			 **Alk1_2 (OH)**	
	O–H…O(=C) (intermol) PhH… O(=C) (intermol) PhO…HC (intramol) PhH…C(≡N) (intramol) **All** **intermol**	1.706 2.667 2.288 2.403	-11.0 -1.3 -4.1 -2.3 **-18.7** **-12.3**	O–H…O(=C) (intermol) (C≡)N...H(intermol) (H)O…C(≡N) (intramol) **All** **intermol**	1.633 3.000 2.779	-14.5 -0.5 -2.6 **-17.6** **-15.0**

+acetone **($CONH_2$)**		 **Ar1_6 ($CONH_2$)**			 **Alk1_5 ($CONH_2$)**	
	(CONH)H…O(=C) (intermol) (C=)O…H(CH_2) (intermol) PhH…C(≡N) (intramol) **All** **intermol**	1.932 2.365 2.375	-5.6 -2.4 -2.5 **-10.5** **-8.0**	(CONH)H…O(=C) (intermol) (C=)O…H(CH_2) (intermol) (C=)O…H(C) (intramol) (cycleC=)O…C(≡N) (intramol) **All** **intermol**	1.923 2.388 2.279 2.833	-5.8 -2.3 -4.5 -2.3 **-14.9** **-8.1**
		 **Ar1_9 ($CONH_2$)**			 **Alk1_9 ($CONH_2$)**	
	(CONH)H…O(=C) (intermol) (C=)O…H(CH_2) (intermol) (C=)O…H(O) (intramol) **All** **intermol**	1.891 2.461 1.511	-6.2 -1.9 -24.5 **-32.6** **-8.1**	(CONH)H…O(=C) (intermol) (C=)O…H(CH_2) (intermol) (C=)O…H(O) (intramol) (cycleC=)O…H(C) (intramol) **All** **intermol**	1.889 2.508 1.397 2.122	-6.3 -1.7 -39.7 -5.9 **-53.6** **-8.0**
+acetone **($CONH_2$),** PCM/acetone		 **Ar1_6 ($CONH_2$)**			 **Alk1_2 ($CONH_2$)**	
	(CONH)H…O(=C) (intermol) (C=)O…H(CH_2) (intermol) (H)O…H(C) (intramol) PhH…C(≡N) (intramol) **All** **intermol**	1.958 3.034 2.290 2.399	-5.3 -0.5 -4.0 -2.3 **-12.1** **-5.8**	(CONH)H…O(=C) (intermol) (C=)O…H(CH_2) (intermol) (H)O… C(≡N) (intramol) **All** **intermol**	1.934 2.356 2.810	-6.0 -2.8 -2.6 **-11.4** **-8.8**

			 **Alk1_2 ($CONH_2$-CN)**	
		(CONH)H…O(=C) (intermol) (C≡)N...H(CH_2) (intermol) (H)O…C(≡N) (intramol) **All** **intermol**	2.130 2.719 2.821	-3.8 -1.0 -2.4 **-7.2** **-4.8**
			 **Alk1_9 ($CONH_2$-CN)**	
		(CONH)H…O(=C) (intermol) (C≡)N…O(=C) (intermol) (cycleC=)O...H(C) (intramol) (C=)O…H(O) (intramol) **All** **intermol**	1.984 3.394 2.142 1.394	-5.1 -0.8 -5.7 -40.2 **-51.8** **-5.9**