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SUPPLEMENTARY MATERIALS

A DFT study on the molecular mechanism of additions of electrophilic and nucleophilic carbenes to non-enolizable cycloaliphatic thioketones

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Table S1. Kinetic and thermodynamic parameters of reaction between carbene **1a** and thione **2a** in chloroform solution, according to wb97xd/6-311g(d,p)(PCM) calculations (ΔH and ΔG values are giving in kcal/mol^{-1}; ΔS values are giving in cal/mol^{-1} K^{-1}).

Transition	ΔH	ΔG	ΔS
1a + 2a → TS1A	-2.0	9.9	-39.8
1a + 2a → 7aa	-15.9	-3.4	-41.9
7aa → TS2A	10.3	12.1	-6.0
7aa → 8aa	-51.6	-49.0	-8.7
8aa + 1a → TS1A2	-2.1	9.8	-39.7
8aa + 1a → 9aa	-14.3	-1.8	-42.0
9aa → TS2A2*cis*	8.9	10.5	-5.2
9aa → *cis*-3aa	-51.0	-48.9	-7.3
9aa → TS2A2*trans*	10.5	12.1	-5.4
9aa → *trans*-3aa	-48.7	-45.7	-9.8

Table S2. Kinetic and thermodynamic parameters of reaction between carbene **1a** and thione **2b** in chloroform solution, according to wb97xd/6-311g(d,p) (PCM) calculations (ΔH and ΔG values are giving in kcal/mol^{-1}; ΔS values are giving in cal/mol^{-1} K^{-1}).

Transition	ΔH	ΔG	ΔS
1a + 2b → TS1A	-2.2	9.9	-40.5
1a + 2b → 7ab	-16.8	-4.3	-41.7
7ab → TS2A	11.2	13.4	-7.3

7ab → 8ab	-51.2	-48.8	-8.1
1a + 2b → TSC	5.1	18.1	-43.5
1a + 2b → 10ab	-52.7	-38.2	-48.8

Table S3. Kinetic and thermodynamic parameters of reaction between carbene **1a** and thione **2c** in chloroform solution, according to wb97xd/6-311g(d,p)(PCM) calculations (ΔH and ΔG values are giving in kcal/mol^{-1}; ΔS values are giving in cal/mol^{-1} K^{-1}).

Transition	ΔH	ΔG	ΔS
1a + 2c → TS1A	-3.1	8.7	-39.4
1a + 2c → 7ac	-15.1	-3.4	-39.1
7ac → TS2A	9.1	11.8	-9.1
7ac → 8ac	-51.4	-47.7	-12.4

Table S4. Kinetic and thermodynamic parameters of reaction between carbene **1a** and thione **2d** in chloroform solution, according to wb97xd/6-311g(d,p) (PCM) calculations (ΔH and ΔG values are giving in kcal/mol^{-1}; ΔS values are giving in cal/mol^{-1} K^{-1}).

Transition	ΔH	ΔG	ΔS
1a + 2d → TS1A	-3.2	8.8	-40.4
1a + 2d → 7ad	-11.7	0.1	-39.6
7ad → TS2A	6.6	9.1	-8.4
7ad → 8ad	-47.3	-43.8	-11.6

Table S5. Kinetic and thermodynamic parameters of reaction between thione **2a** and carbenes **1b-d** in chloroform solution, according to wb97xd/6-311g(d,p) (PCM) calculations (ΔH and ΔG values are giving in kcal/mol^{-1}; ΔS values are giving in cal/mol^{-1} K^{-1}).

Transition	ΔH	ΔG	ΔS
1b + 2a → TS1A	-2.3	8.9	-37.4
1b + 2a → 7ba	-18.6	-6.7	-39.8
7ba → TS2A	10.5	12.6	-7.0
7ba → 8ba	-48.7	-45.7	-10.2
1c + 2a → TSB	10.2	23.1	-43.2
1c + 2a → 8ca	-53.6	-38.9	-49.5
1d + 2a → TSB	3.0	16.5	-45.2
1d + 2a → 8da	-53.8	-39.4	-48.6

Table S6. Selected parameters of carbenes **1a-d** (wb97xd/6-311g(d,p)(PCM), chloroform).

Structure	Fragment	Interatomic distances [Å]
1a	C—Cl	1.725
1b	C—Br	1.883
1c	C—F	1.299
1d	C—OMe	1.317

Table S7. Selected parameters of key structures of the reaction between carbene **1a** and thione **2a** to create **8aa** (wb97xd/6-311g(d,p)(PCM), chloroform).

Structure	Interatomic distances [Å]			GEDT
	C1-S2	S2-C3	C1-C3	[e]
2a		1.611		
TS1A	2.501	1.615	3.638	0.287
7aa	1.646	1.623	2.808	
TS2A	1.685	1.679	2.447	0.000
8aa	1.785	1.844	1.478	

Table S8. Selected parameters of key structures of the reaction between thione **8aa** and carbene **1a** to create *cis*-**3aa** and *trans*-**3aa** (wb97xd/6-311g(d,p)(PCM), chloroform).

Structure	Interatomic distances [Å]			GEDT
	C4-S5	S5-C6	C4-C6	[e]
8aa		1.612		
TS1A2	2.461	1.617	3.631	0.309
9aa	1.650	1.626	2.824	
TS2A2*cis*	1.684	1.681	2.468	0.000
cis-**3aa**	1.783	1.849	1.479	
TS2A2*trans*	1.685	1.679	2.455	0.000
trans-**3aa**	1.781	1.849	1.482	

Table S9. Selected parameters of key structures of the reaction between carbene **1a** and thione **2b** to create **7ab** (wb97xd/6-311g(d,p)(PCM), chloroform).

Structure	Interatomic distances [Å]			GEDT
	C1-S2	S2-C3	C1-C3	[e]
2b		1.612		
TS1A	2.545	1.615	3.678	0.265
7ab	1.647	1.622	2.805	
TS2A	1.685	1.679	2.443	0.000
8ab	1.786	1.846	1.476	

Table S10. Selected parameters of key structures of the reaction between thione **8ab** and carbene **1a** to create **10ab** (wb97xd/6-311g(d,p)(PCM), chloroform).

Structure	Interatomic distances [Å]			GEDT
	C4-O5	O5-C6	C4-C6	[e]
8ab		1.196		
TSB	2.336	1.231	2.056	0.024
10ab	1.365	1.447	1.454	

Table S11. Selected parameters of key structures of the reaction between carbene **1a** and thiones **2c-d** and (wb97xd/6-311g(d,p)(PCM), chloroform).

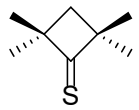
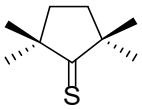
Thioketone	Structure	Interatomic distances [Å]			GEDT
		C1-S2	S2-C3	C1-C3	[e]
 **2c**	**2c**		1.618		
	TS1A	2.706	1.619	3.853	0.191
	7ac	1.649	1.626	2.824	
	TS2A	1.682	1.690	2.460	0.000
	8ac	1.781	1.857	1.478	
 **2d**	**2d**		1.628		
	TS1A	2.599	1.633	3.881	0.230
	7ad	1.652	1.632	2.892	
	TS2A	1.678	1.703	2.457	0.000
	8ad	1.774	1.878	1.493	

Table S12. Selected parameters of key structures of the reaction between carbenes **1b-d** and thione **2a** and (wb97xd/6-311g(d,p)(PCM), chloroform).

Carbene	Structure	Interatomic distances [Å]			GEDT
		C1-S2	S2-C3	C1-C3	[e]
$\ddot{C}Br_2$ **1b**	**2a**		1.611		
	TS1A	2.645	1.613	3.786	0.187
	7ba	1.648	1.622	2.829	
	TS2A	1.688	1.679	2.446	0.000

	8ba	2.446	1.843	1.480	
$\ddot{C}F_2$ **1c**	**2a**		1.611		
	TSB	2.795	1.659	2.152	0.107
	7ca	1.783	1.861	1.460	
$\ddot{C}(OMe)_2$ **1d**	**2a**		1.611		
	TSB	3.011	1.649	2.404	0.188
	8da	1.867	1.842	1.469	

The global electron density transfer (GEDT) values were designated based on the formula:

GEDT = + ΣqA

where qA is the net Mulliken charge, and the sum is performed over all the atoms of carbenes **1a-d**.