Supplementary Material

The (*E*, *Z*) Isomerization of *C*-methoxycarbonyl-*N*-aryl chlorohydrazones

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QTAIM atomic and bond parameters.

Table S1. Atomic charges (q) and atomic dipoles (μ) of relevant atoms in the isomers and *umklapp* transition states of chlorohydrazone **1**. Data are derived from the topological analysis of the ωB97M-D4/cc-pVTZ electron density within the framework of the Quantum Theory of Atoms in Molecules. When necessary, atoms are indicated by bold, underlined symbols.

1-Eca

Atom	q (e)	$|\mu|$ (e bohr)
C_{ipso}	+0.31	0.62
N–H	-0.70	0.40
C=**N**	−0.76	0.73
N–**H**	+0.41	0.21
C=N	+0.83	0.84
Cl	−0.14	0.81
COOMe	+1.71	0.78
C=**O**	−1.14	0.81
C–**O**	−1.18	0.66

1-Ecs

Atom	q (e)	$|\mu|$ (e bohr)
C_{ipso}	+0.31	0.40
N–H	−0.70	0.50
C=**N**	−0.76	0.73
N–**H**	+0.41	0.20
C=N	+0.83	0.73
Cl	−0.26	0.25
COOMe	+1.71	0.58
C=**O**	−1.18	0.60
C–**O**	−1.15	0.41

1-Eta

Atom	q (e)	$|\mu|$ (e bohr)
C$_{ipso}$	+0.34	0.81
N–H	−0.77	0.55
C=**N**	−0.68	0.91
N–**H**	+0.49	0.19
C=N	+0.75	0.67
Cl	−0.19	0.56
COOMe	+1.64	0.78
C=**O**	−1.20	0.64
C–**O**	−1.15	0.60

1-Ets

Atom	q (e)	$|\mu|$ (e bohr)
C$_{ipso}$	+0.35	0.61
N–H	−0.76	0.62
C=**N**	−0.69	1.07
N–**H**	+0.46	0.19
C=N	+0.77	0.67
Cl	−0.14	0.66
COOMe	+1.67	0.76
C=**O**	−1.18	0.81
C–**O**	−1.15	0.44

1-Zca

Atom	q (e)	$|\mu|$ (e bohr)
C$_{ipso}$	+0.31	0.50
N–H	−0.70	0.73
C=**N**	−0.73	0.68
N–**H**	+0.41	0.20
C=N	+0.80	0.71
Cl	−0.27	0.39
COOMe	+1.72	0.78
C=**O**	−1.18	0.72
C–**O**	−1.15	0.38

1-Zcs

Atom	q (e)	$|\mu|$ (e bohr)
C_{ipso}	+0.31	0.67
N–H	−0.70	0.40
C=**N**	−0.74	0.66
N–**H**	+0.42	0.18
C=N	+0.81	0.42
Cl	−0.20	0.44
COOMe	+1.71	0.74
C=**O**	−1.19	0.63
C–**O**	−1.14	0.48

1-Zta

Atom	q (e)	$|\mu|$ (e bohr)
C_{ipso}	+0.35	0.76
N–H	−0.77	0.34
C=**N**	−0.68	0.80
N–**H**	+0.43	0.21
C=N	+0.76	0.57
Cl	−0.23	0.41
COOMe	+1.72	0.63
C=**O**	−1.18	0.49
C–**O**	−1.15	0.29

1-Zts

Atom	q (e)	$|\mu|$ (e bohr)
C_{ipso}	+0.35	0.77
N–H	−0.77	0.66
C=**N**	−0.69	0.71
N–**H**	+0.43	0.19
C=N	+0.77	0.79
Cl	−0.20	0.66
COOMe	+1.71	0.82
C=**O**	−1.19	0.65
C–**O**	−1.14	0.67

1-EcaZta

Atom	q (e)	$|\mu|$ (e bohr)
C_{ipso}	+0.29	0.51
N–H	-0.69	0.69
C=**N**	−0.89	0.90
N–**H**	+0.42	0.21
C=N	+0.95	0.91
Cl	−0.28	0.49
COOMe	+1.70	0.65
C=**O**	−1.21	0.54
C–**O**	−1.15	0.48

1-EtaZca

Atom	q (e)	$|\mu|$ (e bohr)
C_{ipso}	+0.30	0.54
N–H	-0.61	0.86
C=**N**	−0.90	0.86
N–**H**	+0.43	0.22
C=N	+0.96	0.80
Cl	−0.29	0.45
COOMe	+1.70	0.71
C=**O**	−1.20	0.50
C–**O**	−1.15	0.52

1-EtsZcs

Atom	q (e)	$|\mu|$ (e bohr)
C_{ipso}	+0.31	0.67
N–H	-0.60	0.66
C=**N**	−0.92	0.98
N–**H**	+0.42	0.18
C=N	+0.97	0.62
Cl	−0.21	0.82
COOMe	+1.69	0.84
C=**O**	−1.18	0.79
C–**O**	−1.15	0.28

1-EcsZts

Atom	q (e)	$|\mu|$ (e bohr)
C$_{ipso}$	+0.30	0.54
N–H	-0.61	0.67
C=**N**	−0.91	1.16
N–**H**	+0.41	0.19
C=N	+0.96	0.95
Cl	−0.28	0.53
COOMe	+1.69	0.71
C=**O**	−1.19	0.41
C–**O**	−1.16	0.41

Table S2. Properties of relevant bonds in the stable isomers and *umklapp* transition states of chlorohydrazone **1**. Data are derived from the topological analysis of the ωB97M-D4/cc-pVTZ electron density within the framework of the Quantum Theory of Atoms in Molecules. For each bond we report the two atoms involved (A-B), the internuclear separation (Distance), and the following properties computed at the bond critical point: the electron density (ρ), the negative of the Laplacian of the electron density ($-\nabla^2(\rho)$), and the ellipticity (ε).

1-Eca

A-B	Distance (Å)	$\rho \times 10^3$ (e/Å^3)	$-\nabla^2(\rho) \times 10^3$ (e/Å^5)	ε
C$_{ipso}$–N	1.43	281	837	0.06
N–N	1.36	356	673	0.10
C=N	1.26	399	770	0.48
C–Cl	1.74	202	303	0.09
C–C	1.50	268	746	0.14
C=O	1.20	433	238	0.14
C–O	1.33	319	580	0.05

1-Ecs

A-B	Distance (Å)	$\rho \times 10^3$ (e/Å^3)	$-\nabla^2(\rho) \times 10^3$ (e/Å^5)	ε
C_{ipso}–N	1.43	282	842	0.06
N–N	1.36	356	673	0.10
C=N	1.26	398	764	0.47
C–Cl	1.74	204	309	0.09
C–C	1.51	267	737	0.08
C=O	1.20	434	230	0.14
C–O	1.33	318	580	0.05

1-Eta

A-B	Distance (Å)	$\rho \times 10^3$ (e/Å^3)	$-\nabla^2(\rho) \times 10^3$ (e/Å^5)	ε
C_{ipso}–N	1.40	296	1202	0.01
N–N	1.31	401	934	0.13
C=N	1.28	381	707	0.51
C–Cl	1.74	203	308	0.10
C–C	1.48	279	806	0.18
C=O	1.21	418	372	0.12
C–O	1.33	323	588	0.05
O···H	1.90	31	−120	0.11

1-Ets

A-B	Distance (Å)	$\rho \times 10^3$ (e/Å^3)	$-\nabla^2(\rho) \times 10^3$ (e/Å^5)	ε
C_{ipso}–N	1.40	298	856	0.08
N–N	1.32	395	900	0.12
C=N	1.27	383	669	0.50
C–Cl	1.74	205	313	0.10
C–C	1.49	270	752	0.16
C=O	1.20	437	238	0.13
C–O	1.35	303	581	0.03
O···H	1.94	27	−115	0.04

1-Zca

A-B	Distance (Å)	$\rho \times 10^3$ (e/Å^3)	$-\nabla^2(\rho) \times 10^3$ (e/Å^5)	ε
C_{ipso}–N	1.43	279	822	0.06
N–N	1.35	366	736	0.10
C=N	1.26	394	762	0.45
C–Cl	1.74	200	281	0.07
C–C	1.50	266	734	0.15
C=O	1.19	434	248	0.13
C–O	1.33	316	585	0.05

1-Zcs

A-B	Distance (Å)	$\rho \times 10^3$ (e/Å^3)	$-\nabla^2(\rho) \times 10^3$ (e/Å^5)	ε
C_{ipso}–N	1.43	278	820	0.06
N–N	1.35	363	714	0.10
C=N	1.26	394	772	0.43
C–Cl	1.73	204	297	0.08
C–C	1.50	268	746	0.15
C=O	1.20	433	264	0.13
C–O	1.33	318	600	0.05

1-Zta

A-B	Distance (Å)	$\rho \times 10^3$ (e/Å^3)	$-\nabla^2(\rho) \times 10^3$ (e/Å^5)	ε
C_{ipso}–N	1.40	294	824	0.06
N–N	1.31	401	941	0.12
C=N	1.27	387	678	0.52
C–Cl	1.75	195	269	0.08
C–C	1.49	273	773	0.17
C=O	1.20	433	272	0.13
C–O	1.34	316	593	0.05

1-Zts

A-B	Distance (Å)	$\rho \times 10^3$ (e/Å^3)	$-\nabla^2(\rho) \times 10^3$ (e/Å^5)	ε
C_{ipso}–N	1.40	296	1205	0.04
N–N	1.32	398	923	0.12
C=N	1.27	387	680	0.51
C–Cl	1.75	199	284	0.08
C–C	1.49	274	786	0.17
C=O	1.20	432	285	0.13
C–O	1.33	317	607	0.05

1-EcaZta

A-B	Distance (Å)	$\rho \times 10^3$ (e/Å^3)	$-\nabla^2(\rho) \times 10^3$ (e/Å^5)	ε
C_{ipso}–N	1.42	284	814	0.08
N–N	1.28	417	1036	0.11
C=N	1.23	381	-54	0.48
C–Cl	1.81	175	181	0.11
C–C	1.51	264	712	0.16
C=O	1.21	427	292	0.11
C–O	1.33	321	577	0.05
O···H[a]	2.05	21	-81	0.01

(a) The hydrogen atom involved in this bond is one of the phenyl *ortho* hydrogen atoms.

1-EtsZcs

A-B	Distance (Å)	$\rho \times 10^3$ (e/Å^3)	$-\nabla^2(\rho) \times 10^3$ (e/Å^5)	ε
C_{ipso}–N	1.41	289	837	0.08
N–N	1.28	422	1066	0.10
C=N	1.22	382	-134	0.45
C–Cl	1.80	178	192	0.10
C–C	1.51	266	723	0.16
C=O	1.20	435	232	0.12
C–O	1.34	310	591	0.03
Cl⋯H[a]	2.83	7	-24	0.26

(a) The hydrogen atom involved in this bond is one of the phenyl *ortho* hydrogen atoms.

1-EcsZts

A-B	Distance (Å)	$\rho \times 10^3$ (e/Å^3)	$-\nabla^2(\rho) \times 10^3$ (e/Å^5)	ε
C_{ipso}–N	1.42	287	836	0.08
N–N	1.28	416	1030	0.10
C=N	1.22	382	-91	0.46
C–Cl	1.80	178	192	0.10
C–C	1.51	265	714	0.15
C=O	1.20	435	230	0.12
C–O	1.34	311	580	0.03
O⋯H[a]	2.33	13	-51	0.20

(a) The hydrogen atom involved in this bond is one of the phenyl *ortho* hydrogen atoms.

1-EtaZca

A-B	Distance (Å)	$\rho \times 10^3$ (e/Å^3)	$-\nabla^2(\rho) \times 10^3$ (e/Å^5)	ε
C_{ipso}–N	1.39	289	839	0.08
N–N	1.28	423	1072	0.10
C=N	1.22	382	-143	0.46
C–Cl	1.81	174	178	0.10
C–C	1.51	264	708	0.16
C=O	1.20	429	272	0.12
C–O	1.33	320	569	0.04
Cl⋯H[a]	2.80	8	-26	0.19

(a) The hydrogen atom involved in this bond is one of the phenyl *ortho* hydrogen atoms.

Table S3. Delocalization indexes of selected atom pairs of the four lowest-energy isomers of chlorohydrazone **1**. Data are derived from the topological analysis of the ωB97M-D4/cc-pVTZ electron density. Each atomic pair comprises the two atoms underlined in the first and second column. The first eight lines correspond to covalent bonds, the other ones to non-covalent interactions.

		1–Eta	**1**–Ets	**1**–Zta	**1**–Zts
C̲ipso	N̲–H	0.954	0.953	0.943	0.947
N̲–H	N–H̲	0.656	0.687	0.725	0.723
N̲–H	C=N̲	1.408	1.389	1.386	1.379
C̲=N	C=N̲	1.449	1.470	1.476	1.478
C̲–Cl	C–C̲l	1.061	1.060	1.030	1.039
C̲–Cl	C̲=O	0.925	0.903	0.888	0.890
C̲=O	C=O̲	1.187	1.253	1.239	1.236
C̲–O	C–O̲	0.845	0.810	0.827	0.836
N–H̲	C̲l	0.001	0.002	0.051	0.051
N–H̲	C̲l	0.041	0.041	0.084	0.083
C=N̲	C̲l	0.196	0.203	0.198	0.197
N–H̲	C–O̲	0.002	0.062	0.000	0.001
N–H̲	C–O̲	0.010	0.067	0.008	0.008
C=N̲	C–O̲	0.021	0.031	0.019	0.067
N–H̲	C=O̲	0.075	0.002	0.001	0.001
N–H̲	C=O̲	0.090	0.017	0.016	0.017
C=N̲	C=O̲	0.054	0.044	0.079	0.040

Robustness of the computational method

The Tables and Figures in the Supplementary Material allow one to compare the DFT computational results at the M08HX/cc-pVDZ, M08HX/cc-pVTZ, and ωB97M-D4/cc-pVTZ level of theory in order to assess the robustness of our computational approach. Comparison of the quantitative and graphical data shows that there are no qualitative and small quantitative differences between the above levels of theory and we can conclude that our computational approach is robust, meaning that use of other levels of theory of quality comparable to the ones we used, should not change the presented description of (*E*, *Z*) Isomerization of *C*-methoxycarbonyl-*N*-aryl chlorohydrazones. We are therefore confident that the conclusions we have drawn from the computational investigation of chlorohydrazones **1**-**7** are well founded.

As an example, we compare in some detail the results for compound **1**. The qualitative picture of the isomer energetic location (Figure S1) is the same for the employed theory levels (M08HX/cc-pVDZ and /cc-pVTZ, ωB97M-D4/cc-pVTZ). The energetics of the minimum energy structures of **1** is collected in Table SS4. The differences between M08HX/cc-pVDZ and M08HX/cc-pVTZ free energy are small, with mean unsigned difference MSD = 0.7 kJ/mol and mean absolute difference MAD = 1.3 kJ/mol. The population increase of the most stable isomer Zts from 64 to 73% is accompanied by the decrease of Zta (25 to 22%) and Eta, which is about halved from 11% to 5%. Use of the ωB97M-D4 functional brings about somewhat larger energetic differences (MSD = −2.4 and MAD = 3.5 kJ/mol), which are mainly due to the D4 dispersion term. Judging from the electronic energy, where the dispersion contribution can be distinguished, the crowded **1**-Ecγ isomers are dispersion-stabilized by more than 10 kJ/mol, whereas the dispersion contribution to Δ*G* is of at most 3 kJ/mol for the planar **1**-Φtγ isomers.

The molecular structure of the isomers of **1** can be found in Figure S2 (M08HX/cc-pVTZ only) and selected geometric parameters of **1** calculated at the three theory levels are collected in Table S5. On passing from the cc-pVDZ to the cc-pVTZ basis set with the M08HX functional, the C=N, N-N, and N-C_{ipso} bond lengths decrease by less than 0.01 Å, the Φ, θ, and ψ angles change by less than ≈1°, with the exception of ψ of unimportant Eca that increases by 2.9°. The ωB97M-D4 functional causes N-N and N-C_{ipso} bond lengths to increase by less than 0.02 Å (C=N is practically unchanged), ≈1° differences in Φ are ≈1° but somewhat larger in θ (< 4°) and ψ (< 8°). Note that, in the case of **1**, ψ is just the torsional angle of the phenyl ring with respect to the C=N-N moiety, it is not related to isomerism.

The π MOs of **1**-Zts calculated at the M08HX/cc-pVDZ and M08HX/cc-pVTZ level can be found in Figures 4 and 5, and compared with the corresponding ωB97M-D4/cc-pVTZ MOs in the main text.

The energetics of the minimum energy structures of **2**-**7** are collected in Tables 8-13. The considerations carried out above for **1** also apply to **2**-**7.** The isomerization barriers of **1** are collected in Table S14 and plotted in Figure S7. The molecular geometry and geometric parameters of selected TSs of **1** can be found in Table S15 and Figure S8. The barriers present in the shortest paths for the interconversion between **1**-Zta and **1**-Eta are plotted in Figure S9.

The π MOs of **1**-EtsZcs calculated at the M08HX/cc-pVDZ and M08HX/cc-pVTZ level can be found in Figures 11 and 12, and compared with the corresponding ωB97M-D4/cc-pVTZ MOs in the main text.

Selected isomerization barriers of **2**-**7** are collected in Tables 16-21.
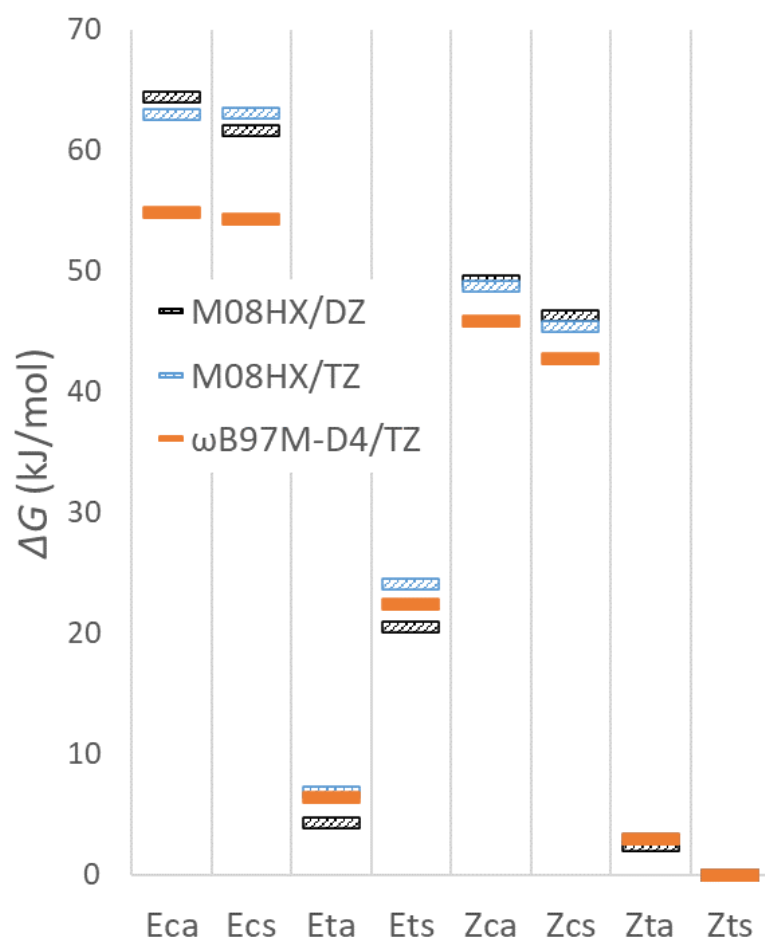
Figure S1. Relative free energy at 298 K of the minimum energy structures of **1** calculated at different levels of theory. The vertical lines are just a guide to the eye.

Table S4. Energetics of the minimum energy structures of **1**. Absolute electronic energy *E* and Gibbs free energy *G* (atomic units) are listed along with the reaction free energy *ΔG* (kJ/mol) and the relative population at 298 K.

	M08HX/cc-pVDZ				M08HX/cc-pVTZ				ωB97M-D4/cc-pVTZ			
	E (a.u.)	*G* (a.u.)	*ΔG* (kJ/mol)	Rel. pop.	*E* (a.u.)	*G* (a.u.)	*ΔG* (kJ/mol)	Rel. pop.	*E* (a.u.)	*G* (a.u.)	*ΔG* (kJ/mol)	Rel. pop.
Eca	-1068.320	-1068.188	64.5	3.3E-12	-1068.519	-1068.387	63.0	6.8E-12	-1068.940	-1068.806	54.9	1.7E-10
Ecs	-1068.322	-1068.189	61.7	1.0E-11	-1068.520	-1068.387	63.1	6.5E-12	-1068.940	-1068.806	54.3	2.2E-10
Eta	-1068.344	-1068.211	4.4	0.11	-1068.541	-1068.408	6.9	0.05	-1068.959	-1068.824	6.4	0.06
Ets	-1068.337	-1068.205	20.5	1.6E-04	-1068.534	-1068.402	24.1	4.4E-05	-1068.952	-1068.818	22.4	8.6E-05
Zca	-1068.326	-1068.194	49.1	1.6E-09	-1068.525	-1068.392	48.8	2.1E-09	-1068.943	-1068.809	45.9	6.7E-09
Zcs	-1068.327	-1068.195	46.3	5.1E-09	-1068.526	-1068.394	45.4	8.0E-09	-1068.944	-1068.810	42.8	2.3E-08
Zta	-1068.344	-1068.212	2.4	0.25	-1068.542	-1068.410	3.0	0.22	-1068.959	-1068.826	3.0	0.22
Zts	-1068.345	-1068.213	0.0	0.64	-1068.543	-1068.411	0.0	0.73	-1068.960	-1068.827	0.0	0.73

Table S5. Selected molecular geometric parameters of the minimum energy structures of **1**. Bond lengths in angstrom, planar and dihedral angles in degree.

	M08HX/cc-pVDZ						M08HX/cc-pVTZ						ωB97M-D4/cc-pVTZ					
	C=N	N-N	Φ	θ	ψ	δΣ	C=N	N-N	Φ	θ	ψ	δΣ	C=N	N-N	Φ	θ	ψ	δΣ
Eca	1.269	1.354	239.3	-39.9	-28.9	14.9	1.261	1.349	238.0	-39.3	-26.0	12.2	1.259	1.362	238.2	-38.9	-33.7	15.3
Ecs	1.271	1.351	237.7	-39.5	-25.3	13.3	1.262	1.349	236.9	-38.6	-25.3	11.8	1.260	1.362	237.3	-40.1	-29.0	14.8
Eta	1.286	1.309	237.6	179.8	0.1	0.0	1.278	1.306	236.9	179.8	0.4	0.0	1.277	1.314	237.4	178.9	0.9	0.0
Ets	1.281	1.311	235.4	179.8	0.1	0.0	1.273	1.309	234.5	179.8	0.4	0.0	1.271	1.317	235.1	178.8	1.3	0.0
Zca	1.273	1.339	123.7	-46.8	-21.9	13.2	1.264	1.337	124.1	-47.0	-20.6	12.4	1.262	1.351	123.7	-49.7	-23.8	16.1
Zcs	1.273	1.341	123.5	-47.2	-21.3	13.4	1.265	1.339	123.8	-47.6	-19.9	12.8	1.263	1.356	123.0	-51.0	-23.8	17.0
Zta	1.277	1.308	121.6	179.7	-0.7	0.0	1.269	1.307	121.6	180.0	-0.4	0.0	1.268	1.314	121.4	181.2	0.0	0.0
Zts	1.276	1.310	121.2	180.0	-0.2	0.0	1.269	1.309	121.2	180.0	-0.2	0.0	1.268	1.317	121.1	180.6	1.3	15.3

δΣ is the the difference δΣ = 360°−Σ, where Σ is the sum of the planar angles about the −NH− nitrogen atom.

Eca   Ecs
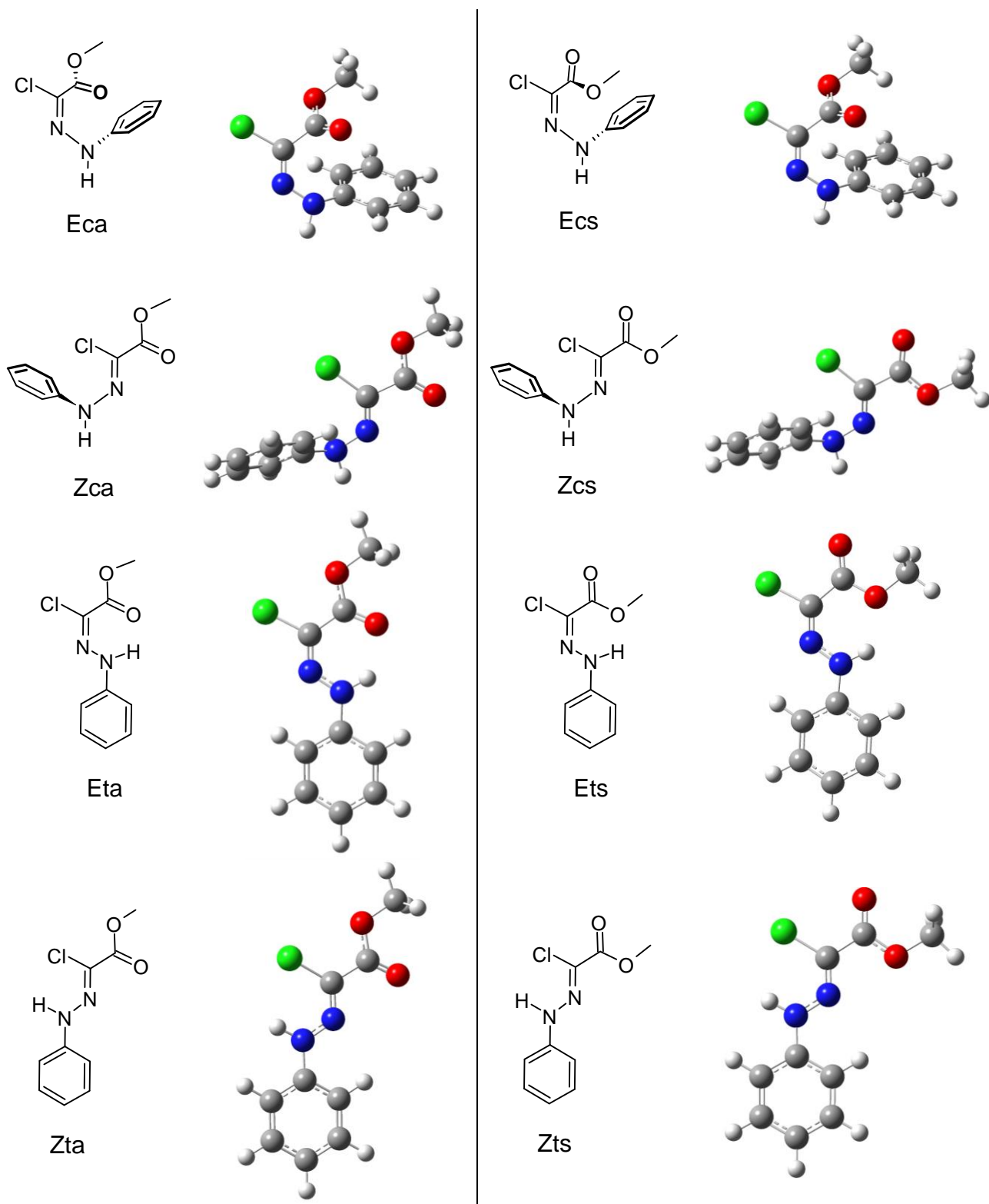
Zca   Zcs

Eta   Ets

Zta   Zts

Figure S2. Minimum energy structures of **1** calculated at the M08HX/cc-pVTZ level.

Table S6. Length of the N-N and N-C_{ipso} bonds (Å) in selected small molecules.

	M08HX /cc-pVDZ	M08HX /cc-pVTZ	ωB97M-D4 /cc-pVTZ
	N-N	N-N	N-N
$H_2N–NH_2$	1.465	1.466	1.476
$H_2N–NHPh$	1.399	1.399	1.407
HN=NH (*Z*)	1.231	1.226	1.233
HN=NH (*E*)	1.234	1.227	1.235
HN=NPh (*Z*) [a]	1.238	1.230	1.236
HN=NPh (*E*) [b]	1.234	1.227	1.232
N≡N	1.096	1.084	1.091

[a] Planar structure. [b] Non-planar structure.

Table S7. Length of the N–H ⋯ O hydrogen bond (Å) in **1**-Et(a,s) isomers.

	M08HX /cc-pVDZ	M08HX /cc-pVTZ	ωB97M-D4 /cc-pVTZ
1-Eta	1.907	1.906	1.904
1-Ets	1.944	1.958	1.951

The presence of π occupied MOs extending over the N–N and N–C$_{ipso}$ bonds, shown in the Figure below, is consistent with the extended delocalization picture and partial double bond character of the N–N bond. However, it should be borne in mind that such MOs do not represent proof additional to the structural data as the molecular geometry is dictated by the minimization of electronic energy.

HOMO (highest occ. π MO)

HOMO–1

HOMO–2

HOMO–4

HOMO–7

HOMO–11

HOMO–12

HOMO–17

HOMO – 21 (lowest occ. π MO)
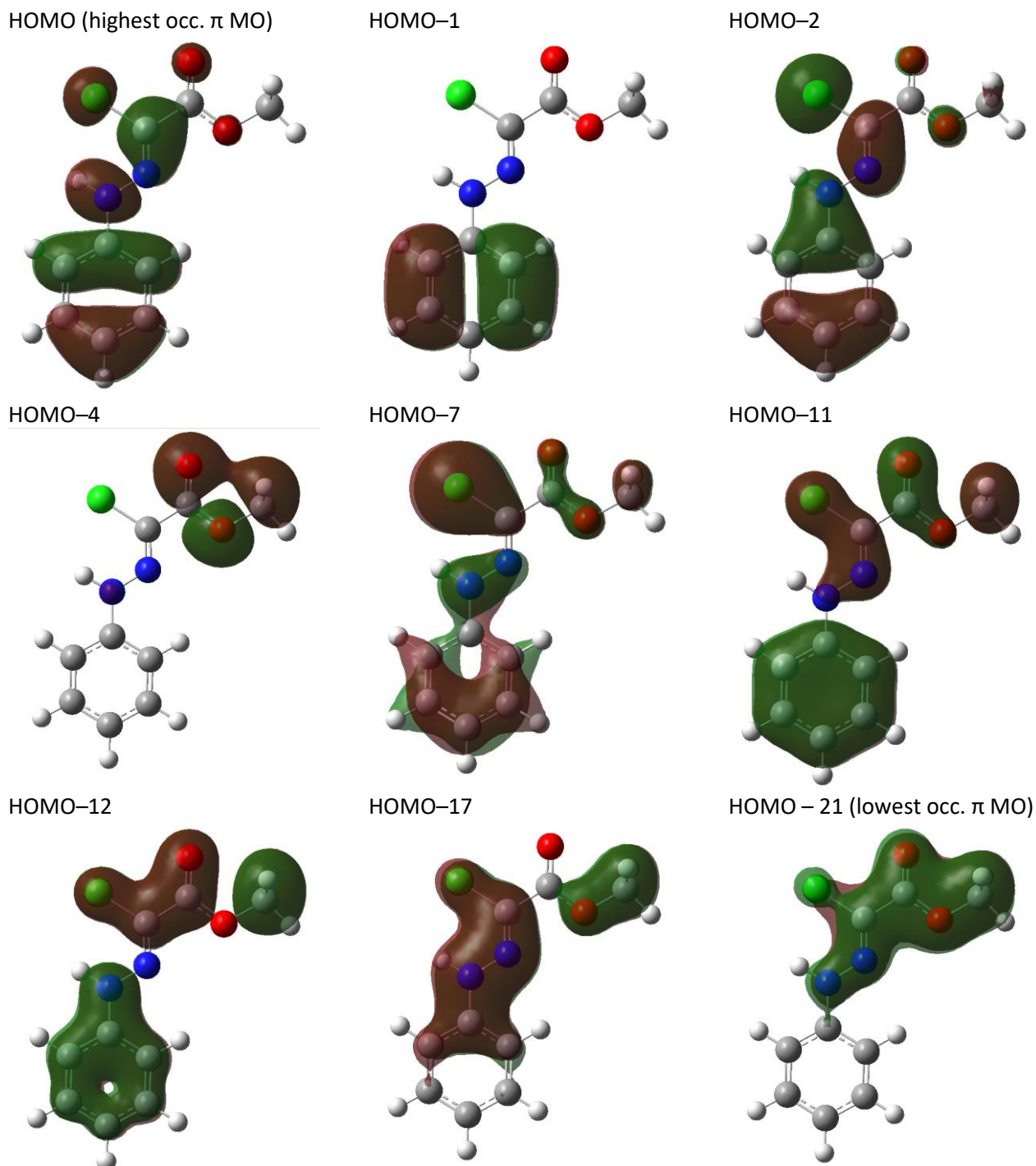
Figure S3. ωB97M-D4/cc-pVTZ π MOs of **1**-Zts.

The presence of π occupied MOs extending over the N–N and N–C$_{ipso}$ bonds is consistent with the extended delocalization picture and partial double bond character of the N–N bond. However, it should be borne in

mind that such MOs do not represent proof additional to the structural data as the molecular geometry is dictated by the minimization of electronic energy.

55 = HOMO
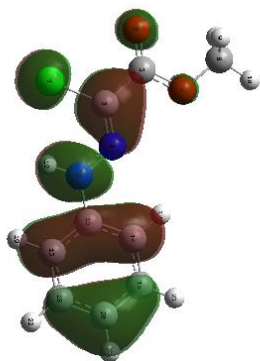
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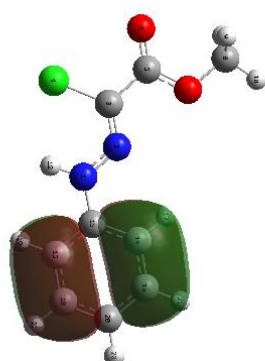
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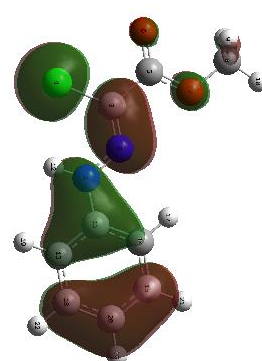
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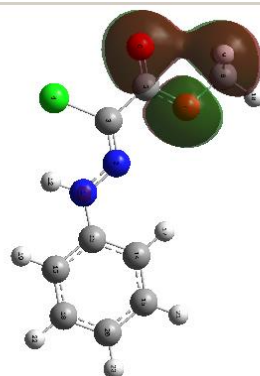
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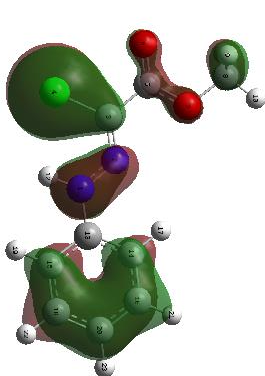
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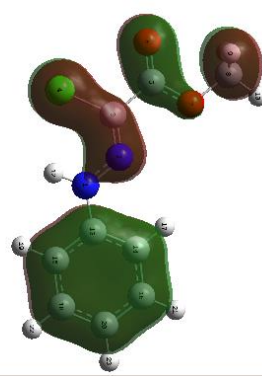
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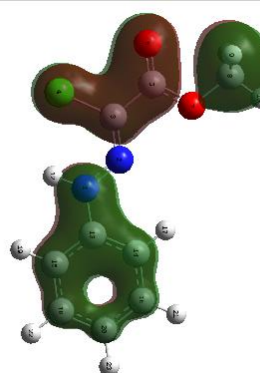
Figure S4. Selected M08HX/cc-pVDZ π MOs of 1-Zts.

55 HOMO highest occ. π MO
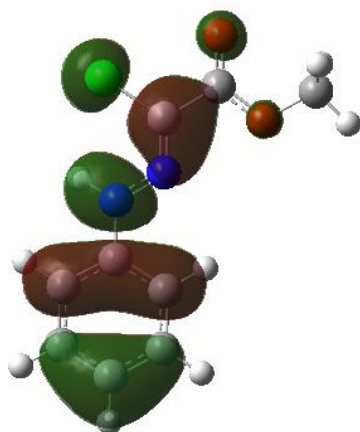
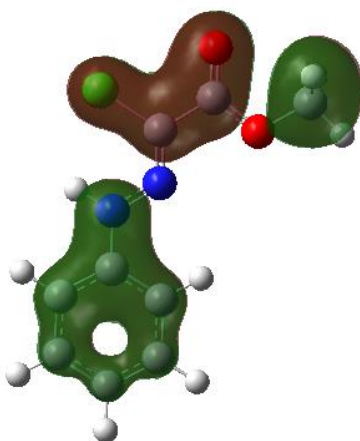47 HOMO – 8
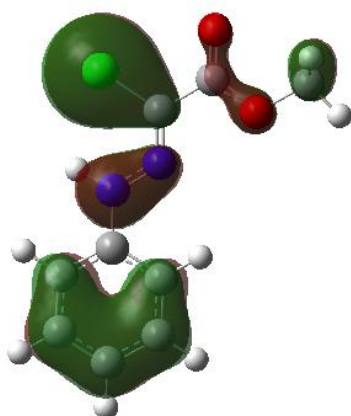
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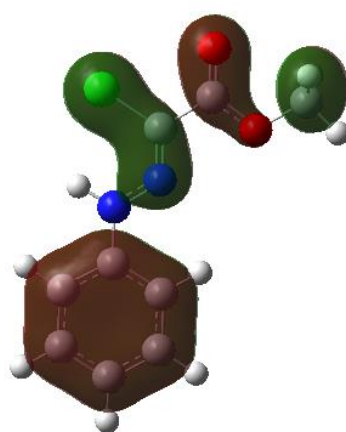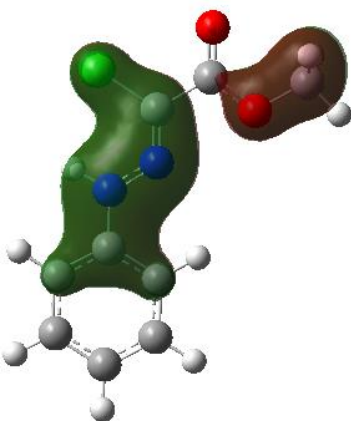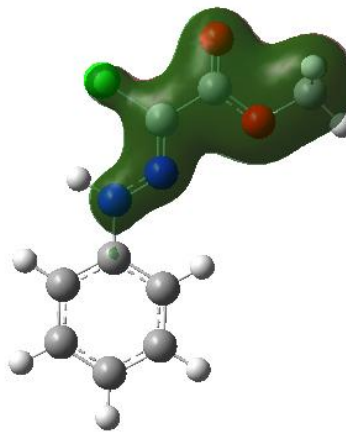
43

38

35 HOMO – 20 lowest occ. π MO

Figure S5. Selected M08HX/cc-pVTZ π MOs of **1**-Zts.

Table S8. Energetics of the minimum energy structures of **2**. Absolute electronic energy *E* and Gibbs free energy *G* (atomic units) are listed along with the reaction free energy *ΔG* (kJ/mol) and the relative population at 298 K.

| | M08HX/cc-pVDZ | | | | M08HX/cc-pVTZ | | | | ωB97M-D4/cc-pVTZ | | | |
	E (a.u.)	*G* (a.u.)	*ΔG* (kJ/mol)	Rel. pop.	*E* (a.u.)	*G* (a.u.)	*ΔG* (kJ/mol)	Rel. pop.	*E* (a.u.)	*G* (a.u.)	*ΔG* (kJ/mol)	Rel. pop.
Eca	-1527.898	-1527.778	62.4	8.1E-12	-1528.120	-1528.000	63.3	5.5E-12	-1528.613	-1528.490	53.8	2.6E-10
Ecs	-1527.899	-1527.778	61.9	9.8E-12	-1528.121	-1527.999	63.8	4.5E-12	-1528.613	-1528.490	54.8	1.7E-10
Eta	-1527.921	-1527.800	3.4	0.17	-1528.142	-1528.021	6.7	0.05	-1528.631	-1528.508	5.5	0.07
Ets	-1527.915	-1527.794	19.3	2.8E-04	-1528.135	-1528.015	24.1	4.1E-05	-1528.625	-1528.502	21.9	1.0E-04
Zca	-1527.903	-1527.783	48.3	2.4E-09	-1528.125	-1528.005	48.3	2.4E-09	-1528.616	-1528.493	46.0	5.9E-09
Zcs	-1527.904	-1527.784	45.5	7.3E-09	-1528.127	-1528.006	45.5	7.2E-09	-1528.617	-1528.494	42.6	2.4E-08
Zta	-1527.921	-1527.801	2.8	0.22	-1528.143	-1528.022	3.5	0.17	-1528.632	-1528.510	2.6	0.24
Zts	-1527.922	-1527.802	0.0	0.68	-1528.144	-1528.024	0.0	0.68	-1528.633	-1528.511	0.0	0.68

Table S9. Energetics of the minimum energy structures of **3**. Absolute electronic energy *E* and Gibbs free energy *G* (atomic units) are listed along with the reaction free energy *ΔG* (kJ/mol) and the relative population at 298 K.

| | M08HX/cc-pVDZ | | | | M08HX/cc-pVTZ | | | | ωB97M-D4/cc-pVTZ | | | |
	E (a.u.)	*G* (a.u.)	*ΔG* (kJ/mol)	Rel. pop.	*E* (a.u.)	*G* (a.u.)	*ΔG* (kJ/mol)	Rel. pop.	*E* (a.u.)	*G* (a.u.)	*ΔG* (kJ/mol)	Rel. pop.
Eca	-1484.401	-1484.282	63.5	5.2E-12	-1484.623	-1484.504	63.7	4.7E-12	-1485.092	-1484.971	54.3	2.1E-10
Ecs	-1484.402	-1484.283	61.9	9.8E-12	-1484.624	-1484.504	63.9	4.5E-12	-1485.092	-1484.970	54.9	1.6E-10
Eta	-1484.424	-1484.305	4.7	0.11	-1484.645	-1484.525	7.5	0.03	-1485.111	-1484.989	5.7	0.07
Ets	-1484.418	-1484.299	19.7	2.4E-04	-1484.638	-1484.519	24.1	4.1E-05	-1485.104	-1484.983	21.9	9.8E-05
Zca	-1484.406	-1484.288	48.3	2.4E-09	-1484.628	-1484.510	48.5	2.2E-09	-1485.095	-1484.974	46.4	5.1E-09
Zcs	-1484.407	-1484.289	45.7	6.7E-09	-1484.630	-1484.511	45.6	7.1E-09	-1485.096	-1484.975	42.7	2.3E-08
Zta	-1484.424	-1484.306	2.0	0.31	-1484.646	-1484.527	2.9	0.21	-1485.111	-1484.990	2.6	0.24
Zts	-1484.425	-1484.307	0.0	0.69	-1484.647	-1484.528	0.0	0.69	-1485.112	-1484.991	0.0	0.69

Table S10. Energetics of the minimum energy structures of **4**. Absolute electronic energy E and Gibbs free energy G (atomic units) are listed along with the reaction free energy ΔG (kJ/mol) and the relative population at 298 K.

	M08HX/cc-pVDZ				M08HX/cc-pVTZ				ωB97M-D4/cc-pVTZ			
	E (a.u.)	G (a.u.)	ΔG (kJ/mol)	Rel. pop.	E (a.u.)	G (a.u.)	ΔG (kJ/mol)	Rel. pop.	E (a.u.)	G (a.u.)	ΔG (kJ/mol)	Rel. pop.
Eca	-1363.315	-1363.198	63.1	6.2E-12	-1363.522	-1363.405	63.2	5.9E-12	-1364.129	-1364.009	54.6	1.9E-10
Ecs	-1363.317	-1363.198	62.3	8.6E-12	-1363.523	-1363.404	63.7	4.7E-12	-1364.129	-1364.008	55.3	1.5E-10
Eta	-1363.339	-1363.220	4.8	0.10	-1363.545	-1363.426	7.5	0.03	-1364.148	-1364.027	5.8	0.07
Ets	-1363.332	-1363.214	19.9	2.3E-04	-1363.537	-1363.419	24.3	3.9E-05	-1364.141	-1364.021	22.0	9.8E-05
Zca	-1363.320	-1363.203	48.8	1.9E-09	-1363.527	-1363.410	48.9	1.9E-09	-1364.132	-1364.012	46.9	4.2E-09
Zcs	-1363.322	-1363.204	46.2	5.6E-09	-1363.529	-1363.411	45.9	6.4E-09	-1364.133	-1364.013	43.0	2.1E-08
Zta	-1363.338	-1363.221	2.0	0.31	-1363.545	-1363.427	2.9	0.22	-1364.148	-1364.028	2.7	0.24
Zts	-1363.339	-1363.222	0.0	0.70	-1363.546	-1363.429	0.0	0.70	-1364.149	-1364.029	0.0	0.70

Table S11. Energetics of the minimum energy structures of **5**. Absolute electronic energy *E* and Gibbs free energy *G* (atomic units) are listed along with the reaction free energy *ΔG* (kJ/mol) and the relative population at 298 K.

	M08HX/cc-pVDZ				M08HX/cc-pVTZ				ωB97M-D4/cc-pVTZ			
	E (a.u.)	*G* (a.u.)	*ΔG* (kJ/mol)	Rel. pop.	*E* (a.u.)	*G* (a.u.)	*ΔG* (kJ/mol)	Rel. pop.	*E* (a.u.)	*G* (a.u.)	*ΔG* (kJ/mol)	Rel. pop.
Ecca	-1527.896	-1527.776	70.3	3.6E-13	-1528.118	-1527.997	72.0	1.8E-13	-1528.612	-1528.488	59.5	2.8E-11
Eccs	-1527.896	-1527.775	72.8	1.3E-13	-1528.117	-1527.996	75.8	3.9E-14	-1528.611	-1528.488	61.2	1.4E-11
Ecta	-1527.897	-1527.777	66.8	1.5E-12	-1528.120	-1527.999	67.2	1.2E-12	-1528.611	-1528.489	59.1	3.3E-11
Ects	-1527.899	-1527.778	63.6	5.2E-12	-1528.121	-1527.999	65.9	2.1E-12	-1528.612	-1528.489	57.7	5.8E-11
Etca	-1527.911	-1527.790	31.5	2.2E-06	-1528.132	-1528.011	34.8	5.8E-07	-1528.622	-1528.499	31.4	2.3E-06
Etcs	-1527.904	-1527.785	47.0	4.3E-09	-1528.125	-1528.005	51.2	8.0E-10	-1528.615	-1528.493	47.8	3.1E-09
Etta	-1527.922	-1527.800	5.5	0.08	-1528.143	-1528.021	9.2	0.02	-1528.631	-1528.508	7.4	0.04
Etts	-1527.917	-1527.796	17.2	7.0E-04	-1528.137	-1528.016	22.3	9.0E-05	-1528.626	-1528.504	19.9	2.4E-04
Zcca	-1527.902	-1527.782	53.4	3.3E-10	-1528.124	-1528.003	55.8	1.2E-10	-1528.614	-1528.492	51.5	7.1E-10
Zccs	-1527.903	-1527.783	50.0	1.3E-09	-1528.125	-1528.005	52.1	5.4E-10	-1528.616	-1528.493	48.0	2.9E-09
Zcta	-1527.903	-1527.783	51.4	7.2E-10	-1528.126	-1528.005	52.2	5.3E-10	-1528.615	-1528.492	49.3	1.7E-09
Zcts	-1527.905	-1527.784	48.5	2.3E-09	-1528.127	-1528.006	48.7	2.2E-09	-1528.616	-1528.494	46.1	6.1E-09
Ztca	-1527.910	-1527.791	30.0	4.2E-06	-1528.132	-1528.012	32.1	1.8E-06	-1528.623	-1528.500	28.9	6.4E-06
Ztcs	-1527.912	-1527.793	25.7	2.3E-05	-1528.134	-1528.014	27.2	1.3E-05	-1528.624	-1528.502	24.4	3.9E-05
Ztta	-1527.922	-1527.802	1.8	0.35	-1528.144	-1528.023	2.7	0.25	-1528.633	-1528.510	2.2	0.30
Ztts	-1527.923	-1527.802	0.0	0.73	-1528.145	-1528.024	0.0	0.73	-1528.634	-1528.511	0.0	0.73

Table S12. Energetics of the minimum energy structures of **6**. Absolute electronic energy *E* and Gibbs free energy *G* (atomic units) are listed along with the reaction free energy *ΔG* (kJ/mol) and the relative population at 298 K.

	M08HX/cc-pVDZ				M08HX/cc-pVTZ				ωB97M-D4/cc-pVTZ			
	E (a.u.)	*G* (a.u.)	*ΔG* (kJ/mol)	Rel. pop.	*E* (a.u.)	*G* (a.u.)	*ΔG* (kJ/mol)	Rel. pop.	*E* (a.u.)	*G* (a.u.)	*ΔG* (kJ/mol)	Rel. pop.
Ecca	-1484.399	-1484.280	70.9	2.7E-13	-1484.621	-1484.502	72.1	1.7E-13	-1485.091	-1484.969	59.5	2.8E-11
Eccs	-1484.399	-1484.279	74.2	7.4E-14	-1484.620	-1484.500	75.9	3.7E-14	-1485.090	-1484.968	61.2	1.4E-11
Ecta	-1484.401	-1484.282	67.5	1.1E-12	-1484.623	-1484.503	67.3	1.2E-12	-1485.091	-1484.970	58.6	4.0E-11
Ects	-1484.403	-1484.284	62.8	7.2E-12	-1484.624	-1484.504	65.1	2.8E-12	-1485.092	-1484.970	57.0	7.5E-11
Etca	-1484.414	-1484.295	33.1	1.2E-06	-1484.635	-1484.515	35.7	4.0E-07	-1485.101	-1484.980	31.4	2.3E-06
Etcs	-1484.407	-1484.289	48.5	2.4E-09	-1484.628	-1484.509	52.1	5.5E-10	-1485.095	-1484.974	47.8	3.1E-09
Etta	-1484.425	-1484.305	6.1	0.06	-1484.646	-1484.526	8.8	0.02	-1485.111	-1484.989	7.5	0.04
Etts	-1484.420	-1484.301	17.9	5.3E-04	-1484.640	-1484.521	21.8	1.1E-04	-1485.105	-1484.984	19.8	2.4E-04
Zcca	-1484.405	-1484.287	53.7	2.8E-10	-1484.626	-1484.508	55.7	1.3E-10	-1485.093	-1484.972	51.6	6.6E-10
Zccs	-1484.406	-1484.288	50.2	1.2E-09	-1484.628	-1484.509	52.1	5.4E-10	-1485.095	-1484.973	48.3	2.5E-09
Zcta	-1484.407	-1484.288	51.6	6.6E-10	-1484.629	-1484.509	51.8	6.2E-10	-1485.094	-1484.973	49.3	1.7E-09
Zcts	-1484.408	-1484.289	48.9	2.0E-09	-1484.630	-1484.511	48.4	2.4E-09	-1485.096	-1484.974	45.7	7.2E-09
Ztca	-1484.413	-1484.295	31.9	1.8E-06	-1484.635	-1484.517	32.8	1.3E-06	-1485.102	-1484.981	28.8	6.5E-06
Ztcs	-1484.415	-1484.297	28.0	9.0E-06	-1484.637	-1484.518	28.0	9.2E-06	-1485.103	-1484.982	24.5	3.7E-05
Ztta	-1484.425	-1484.307	1.8	0.35	-1484.647	-1484.528	2.6	0.25	-1485.112	-1484.991	2.2	0.30
Ztts	-1484.426	-1484.307	0.0	0.73	-1484.648	-1484.529	0.0	0.73	-1485.113	-1484.992	0.0	0.73

Table S13. Energetics of the minimum energy structures of **7**. Absolute electronic energy *E* and Gibbs free energy *G* (atomic units) are listed along with the reaction free energy *ΔG* (kJ/mol) and the relative population at 298 K.

	M08HX/cc-pVDZ				M08HX/cc-pVTZ				ωB97M-D4/cc-pVTZ			
	E (a.u.)	*G* (a.u.)	*ΔG* (kJ/mol)	Rel. pop.	*E* (a.u.)	*G* (a.u.)	*ΔG* (kJ/mol)	Rel. pop.	*E* (a.u.)	*G* (a.u.)	*ΔG* (kJ/mol)	Rel. pop.
Ecca	-1363.314	-1363.196	70.4	3.4E-13	-1363.520	-1363.402	72.2	1.6E-13	-1364.128	-1364.007	58.8	3.7E-11
Eccs	-1363.314	-1363.195	73.0	1.2E-13	-1363.519	-1363.401	75.7	4.0E-14	-1364.127	-1364.007	60.6	1.8E-11
Ecta	-1363.315	-1363.198	66.8	1.5E-12	-1363.522	-1363.404	67.4	1.2E-12	-1364.128	-1364.008	57.0	7.6E-11
Ects	-1363.318	-1363.199	62.4	8.5E-12	-1363.524	-1363.405	64.5	3.8E-12	-1364.129	-1364.009	55.0	1.7E-10
Etca	-1363.329	-1363.211	30.9	2.8E-06	-1363.535	-1363.417	34.6	6.5E-07	-1364.139	-1364.018	30.0	4.1E-06
Etcs	-1363.322	-1363.205	46.5	5.2E-09	-1363.528	-1363.410	51.1	8.2E-10	-1364.132	-1364.012	46.2	6.0E-09
Etta	-1363.339	-1363.220	6.6	0.05	-1363.545	-1363.426	9.9	0.01	-1364.147	-1364.027	7.7	0.03
Etts	-1363.334	-1363.216	17.5	6.3E-04	-1363.539	-1363.421	22.4	8.8E-05	-1364.142	-1364.022	19.7	2.6E-04
Zcca	-1363.320	-1363.203	53.3	3.4E-10	-1363.526	-1363.408	56.0	1.1E-10	-1364.130	-1364.010	50.9	8.8E-10
Zccs	-1363.321	-1363.204	49.9	1.4E-09	-1363.527	-1363.410	52.8	4.2E-10	-1364.132	-1364.011	47.9	3.0E-09
Zcta	-1363.321	-1363.204	50.0	1.3E-09	-1363.528	-1363.410	51.4	7.5E-10	-1364.132	-1364.012	47.1	4.2E-09
Zcts	-1363.323	-1363.205	47.2	4.1E-09	-1363.530	-1363.411	48.1	2.8E-09	-1364.133	-1364.013	43.9	1.5E-08
Ztca	-1363.328	-1363.212	29.2	5.7E-06	-1363.535	-1363.418	32.0	1.8E-06	-1364.139	-1364.019	27.2	1.3E-05
Ztcs	-1363.330	-1363.213	26.3	1.9E-05	-1363.537	-1363.419	27.8	1.0E-05	-1364.141	-1364.021	22.9	7.2E-05
Ztta	-1363.340	-1363.222	1.7	0.38	-1363.546	-1363.429	2.8	0.24	-1364.149	-1364.029	2.1	0.31
Ztts	-1363.340	-1363.223	0.0	0.74	-1363.547	-1363.430	0.0	0.74	-1364.150	-1364.030	0.0	0.74
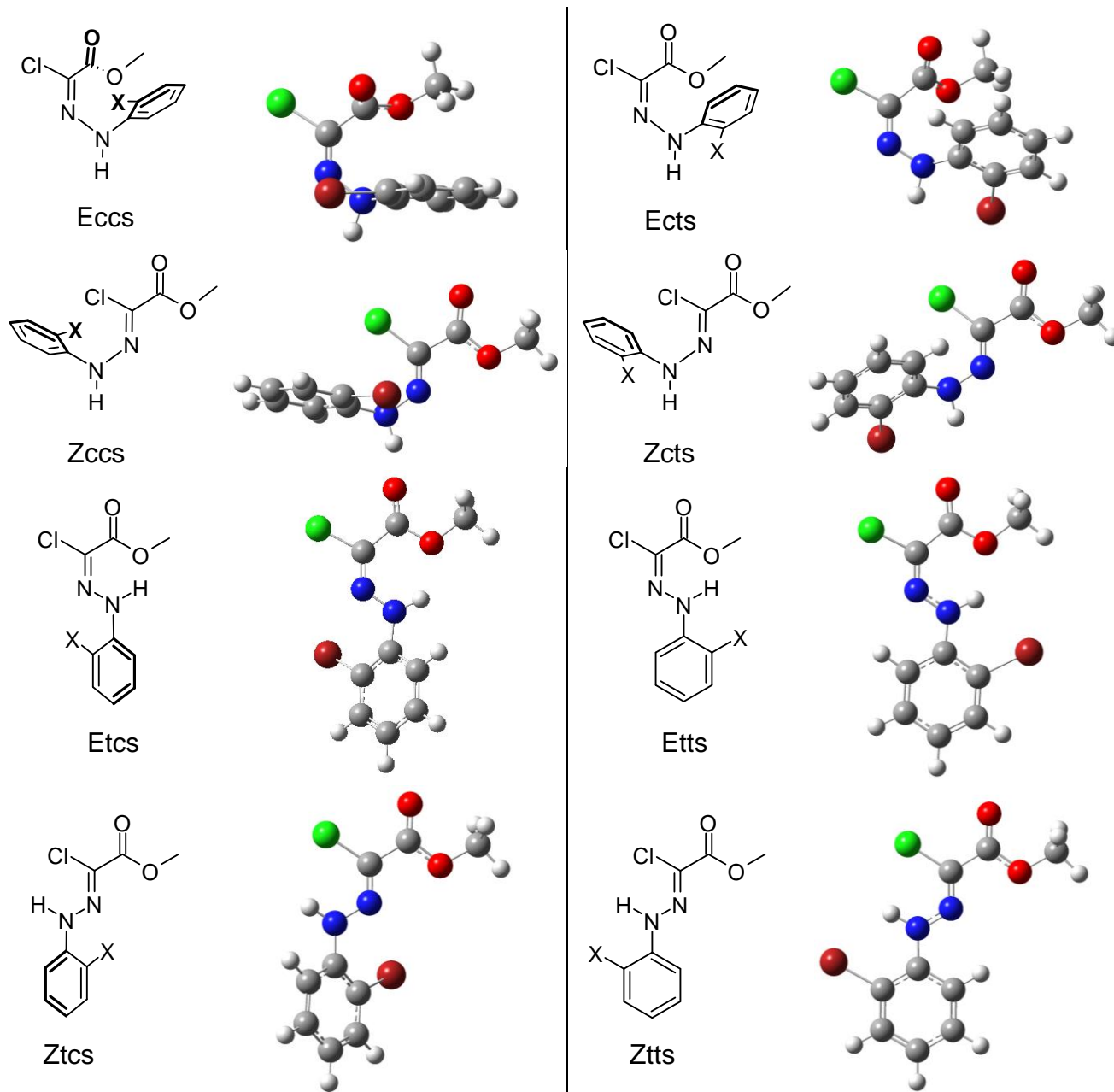
Figure S6. Selected (γ = s) M08-HX/cc-pVTZ minimum energy structures of **6** (X = Br).

Table S14. Free energy activation barrier $\Delta G^{\ddagger}$ and corresponding rate constant at 298 K for the isomer interconversion processes of **1**. The barriers are grouped with respect to the interconversion mechanism.

Isomerization	From	To	M08HX /cc-pVDZ $\Delta G^{\ddagger}$ (kJ/mol)	k (s^{-1}) [a]	M08HX /cc-pVTZ $\Delta G^{\ddagger}$ (kJ/mol)	k (s^{-1}) [a]	ωB97M-D4 /cc-pVTZ $\Delta G^{\ddagger}$ (kJ/mol)	k (s^{-1}) [a]
Rotation, γ	Eca	Ecs	14.9	1.5E+10	15.0	1.4E+10	7.4	3.2E+11
	Ecs	Eca	17.6	5.1E+09	15.0	1.5E+10	7.9	2.6E+11
	Eta	Ets	50.3	9.5E+03	43.1	1.8E+05	37.4	1.7E+06
	Ets	Eta	34.2	6.4E+06	25.9	1.8E+08	21.4	1.1E+09
	Zca	Zcs	20.0	2.0E+09	16.0	9.6E+09	9.6	1.3E+11
	Zcs	Zca	22.8	6.2E+08	19.4	2.5E+09	12.7	3.7E+10
	Zta	Zts	30.4	3.0E+07	26.1	1.7E+08	19.5	2.4E+09
	Zts	Zta	32.7	1.1E+07	29.0	5.2E+07	22.5	7.1E+08
Rotation, θ	Eca	Eta	14.2	2.0E+10	29.4	4.4E+07	27.3	1.0E+08
	Eta	Eca	74.3	5.9E-01	85.5	6.6E-03	75.8	3.3E-01
	Ecs	Ets	32.2	1.4E+07	32.0	1.5E+07	27.8	8.4E+07
	Ets	Ecs	73.4	8.6E-01	71.0	2.2E+00	59.7	2.2E+02
	Zca	Zta	24.4	3.4E+08	23.6	4.5E+08	20.8	1.4E+09
	Zta	Zca	71.1	2.1E+00	69.4	4.2E+00	63.7	4.3E+01
	Zcs	Zts	24.3	3.5E+08	23.5	4.8E+08	18.8	3.2E+09
	Zts	Zcs	70.5	2.7E+00	68.9	5.2E+00	61.6	1.0E+02
Umklapp, Φ (θ)	Eca	Zta	51.7	5.4E+03	50.8	7.7E+03	59.8	2.1E+02
	Zta	Eca	113.8	7.1E-08	110.9	2.3E-07	111.7	1.6E-07
	Ecs	Zts	63.8	4.1E+01	63.0	5.7E+01	68.1	7.2E+00
	Zts	Ecs	125.5	6.5E-10	126.1	5.1E-10	122.5	2.2E-09
	Eta	Zca	110.2	3.1E-07	105.7	1.9E-06	104.5	3.1E-06
	Zca	Eta	65.4	2.2E+01	63.8	4.1E+01	65.0	2.5E+01
	Ets	Zcs	94.9	1.5E-04	89.9	1.1E-03	89.9	1.1E-03
	Zcs	Ets	69.2	4.7E+00	68.5	6.2E+00	69.6	4.0E+00

[a] The rate constants were calculated using Eyring formula $k = \kappa \, (k_{B}T/h) \exp(-\Delta G^{\ddagger}/RT)$ with $\kappa = 1$ and $T = 298$ K.
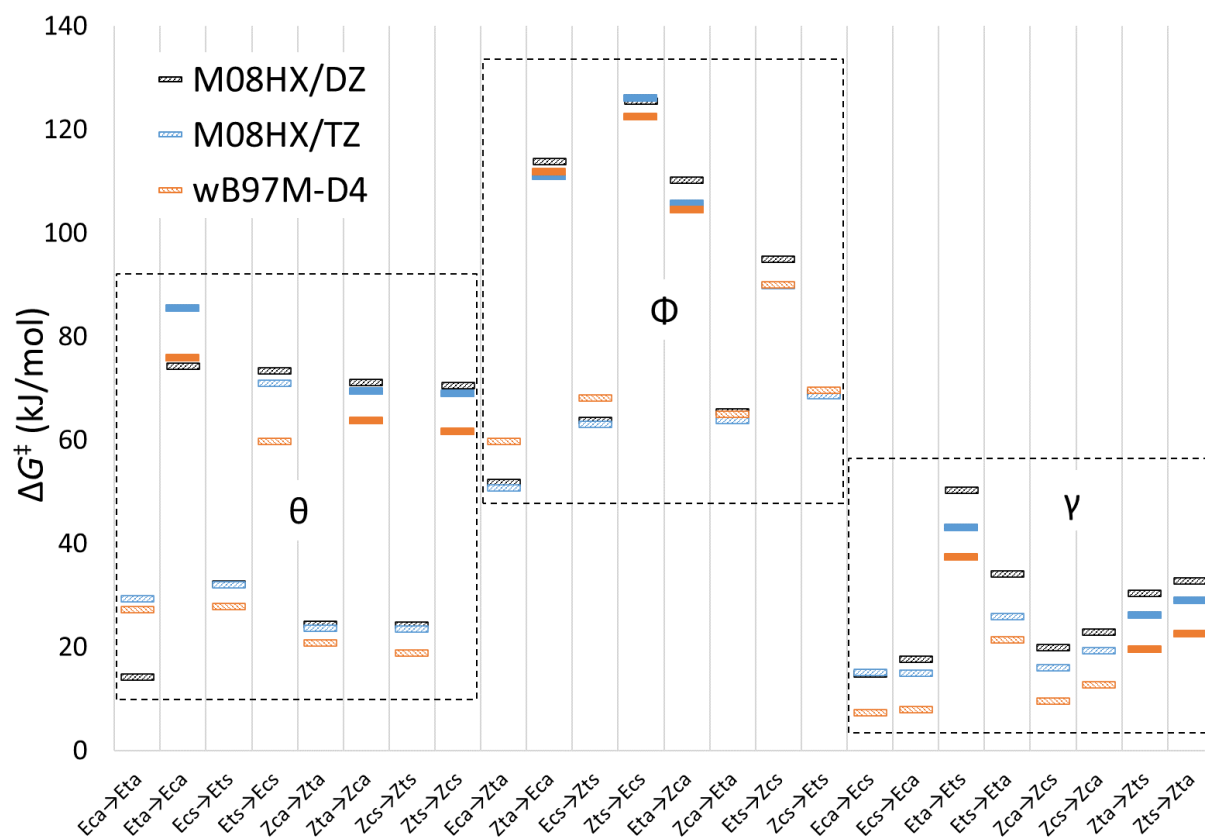
Figure S7. Activation barriers $\Delta G^{\ddagger}$ at 298 K of the isomerization processes of **1** calculated at the M08HX/DZ, M08HX/TZ, and ωB97M-D4/TZ level of theory. The barriers are grouped as to the isomerization type. The vertical lines are just a guide to the eye.

EcaEcs

EtaEts

ZtaZts

EcaEta

ZcaZts

ZcsZts

EtaZca

EcaZta

EcsZts
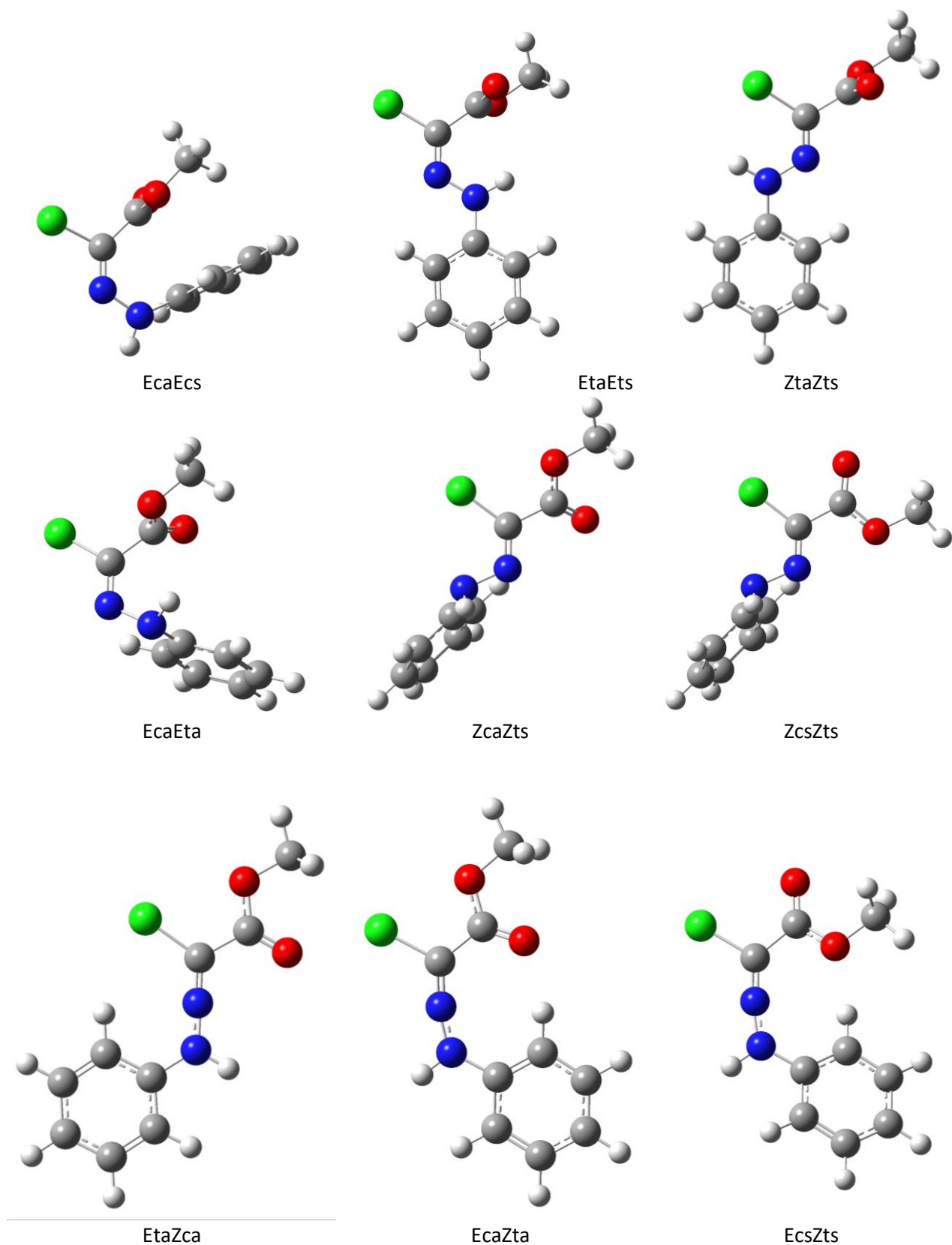
Figure S8. Selected transition state structures of **1** calculated at the M08HX/cc-pVTZ level.

Table S15. Selected molecular geometric parameters of the TS structures of **1**. Bond lengths in angstrom, planar and dihedral angles in degree. When Φ ≈ 180°, θ is of limited structural meaning, as the C=N–N moiety is nearly linear.

Isomerization	TS	M08HX /cc-pVDZ						M08HX /cc-pVTZ						ωB97M-D4 /cc-pVTZ					
		C=N	N-N	Φ	θ	ψ	δΣ	C=N	N-N	Φ	θ	ψ	δΣ	C=N	N-N	Φ	θ	ψ	δΣ
Rotation, γ	EcaEcs	1.265	1.354	236.2	12.7	-95.4	11.3	1.256	1.353	235.4	15.8	-92.8	12.0	1.259	1.346	235.5	0.0	-113.4	2.6
	EtaEts	1.269	1.330	240.2	-177.8	4.4	0.4	1.260	1.332	239.7	-176.4	5.8	1.0	1.259	1.347	240.3	170.4	16.3	5.5
	ZcaZcs	1.263	1.372	119.8	63.0	-6.5	22.7	1.255	1.369	120.8	61.3	-7.3	20.4	1.254	1.382	120.1	-64.7	-7.9	23.4
	ZtaZts	1.267	1.322	121.4	179.8	0.1	0.0	1.258	1.322	121.5	179.5	0.2	0.0	1.257	1.332	121.2	175.3	9.5	1.1
Rotation, θ	EcaEta	1.268	1.401	241.0	91.8	-16.2	27.3	1.255	1.412	244.4	91.8	-15.8	22.6	1.257	1.436	243.6	-54.1	-34.6	18.4
	EcsEts	1.265	1.430	243.6	54.4	-29.8	20.4	1.257	1.432	243.9	60.1	-29.2	21.1	1.258	1.436	243.6	-54.8	-33.0	18.5
	ZcaZta	1.263	1.419	115.0	-117.8	-22.1	32.5	1.254	1.418	115.6	-117.3	-23.4	31.0	1.252	1.428	115.6	121.0	-31.4	31.4
	ZcsZts	1.264	1.420	115.0	-117.9	-24.2	32.2	1.256	1.419	115.6	-118.3	-26.9	30.6	1.256	1.427	115.3	118.8	-25.5	31.1
Umklapp, Φ (θ)	EcaZta	1.236	1.274	192.5	-0.3	0.0	0.0	1.228	1.272	191.7	-1.2	-1.3	0.0	1.225	1.281	191.0	0.9	-1.9	0.1
	EcsZts	1.233	1.275	189.6	-14.8	-16.4	0.3	1.224	1.273	188.4	-16.9	-19.2	0.3	1.222	1.282	187.5	-17.5	-19.1	0.4
	EtaZca	1.228	1.269	179.5	178.0	-179.8	0.0	1.220	1.267	180.0	-35.4	0.2	0.0	1.220	1.276	179.8	-30.7	1.1	0.0
	EtsZcs	1.228	1.270	178.7	179.1	-179.7	0.0	1.221	1.268	178.9	-178.7	0.3	0.0	1.220	1.276	179.1	163.2	1.1	0.0

δΣ is the difference δΣ = 360°–Σ, where Σ is the sum of the planar angles about the –NH– atom.
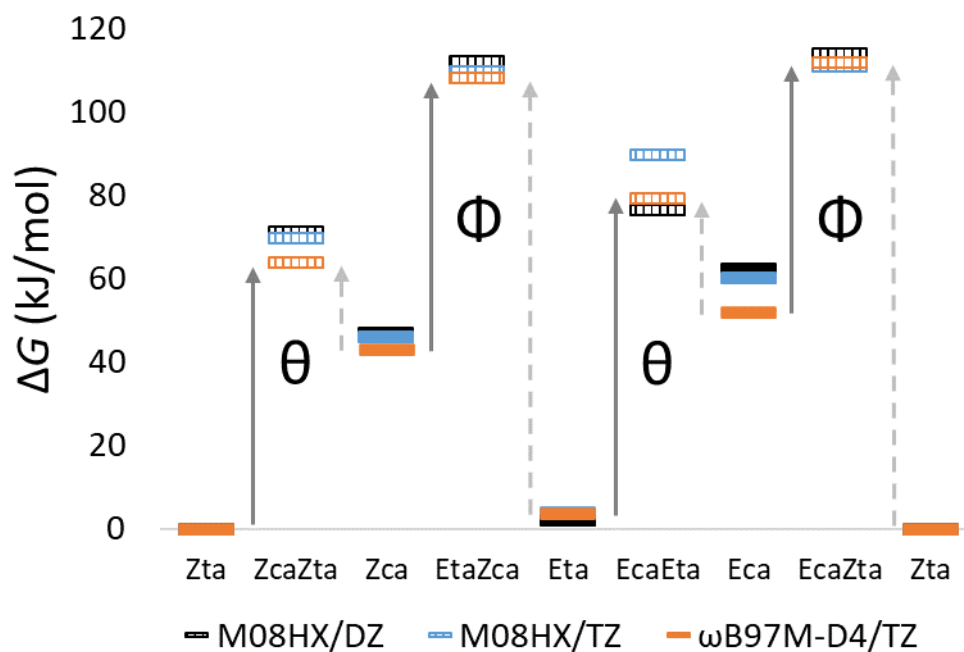
Figure S9. Energetics of the shortest paths for the interconversion between **1**-Zta and **1**-Eta involving an umklapp and a θ isomerization step. Solid bars indicate minimum energy isomers and hatched bars indicate transition states. The fast (slow) pathways are indicated by full (dashed) arrows.
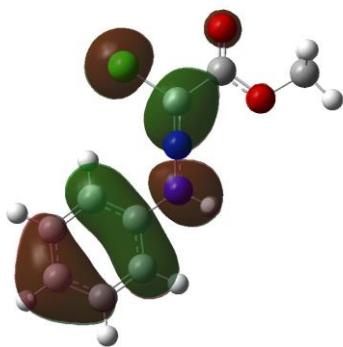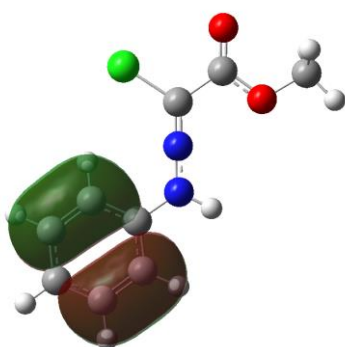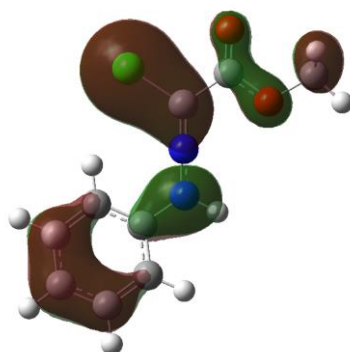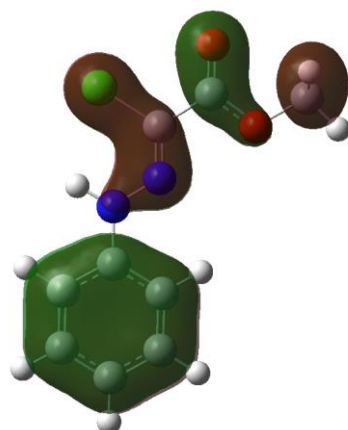
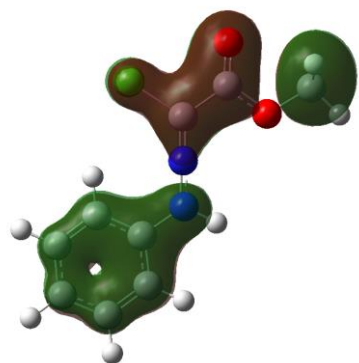HOMO (highest occ. π MO)   HOMO–2   HOMO–3
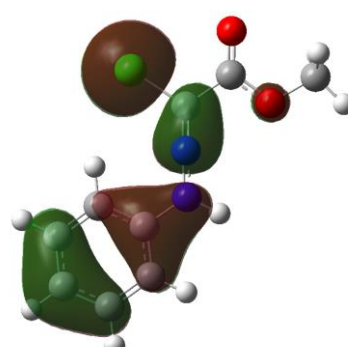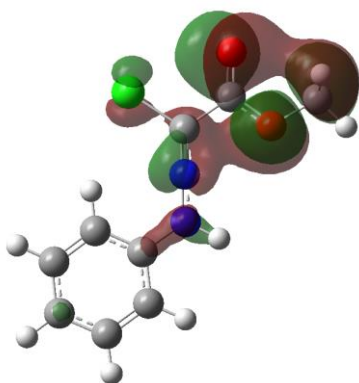
HOMO–6   HOMO–7   HOMO–11

HOMO–12   HOMO–18   HOMO–20 (lowest occ. π MO)
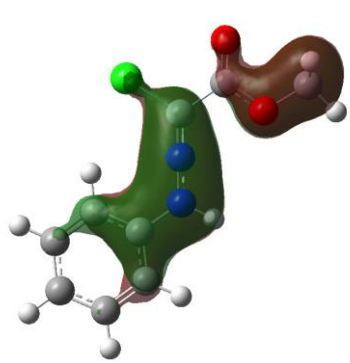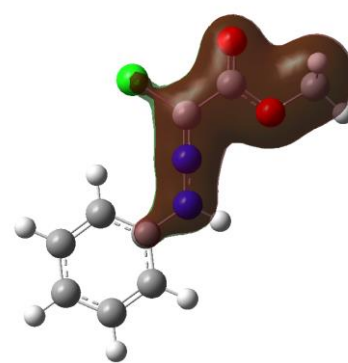
Figure S10. ωB97M-D4/cc-pVTZ π MOs of **1**-EtsZcs. Comparison with Figure S3 shows that TS MOs can be viewed as a merely "straightened" version of the MOs of the minimum energy isomer.

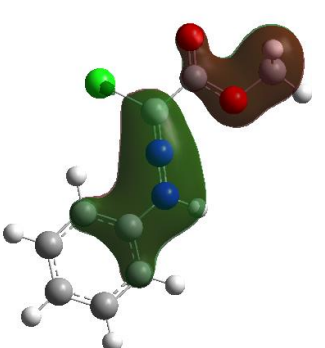55 HOMO highest occ. π

53 HOMO – 2

52

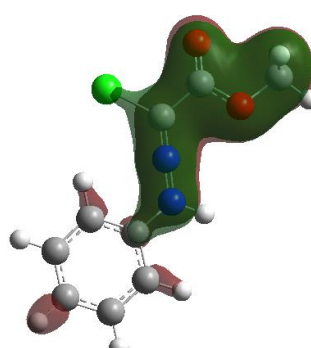50

48 HOMO – 7

44

43

37
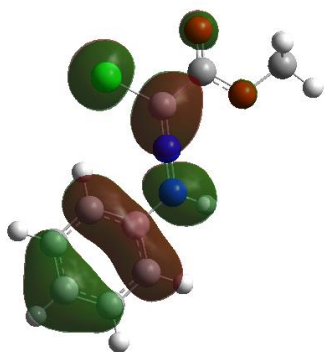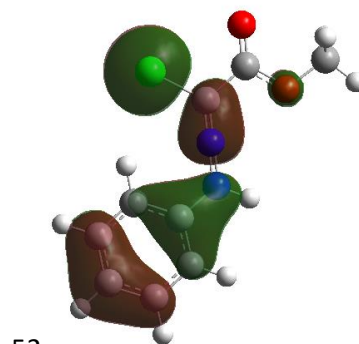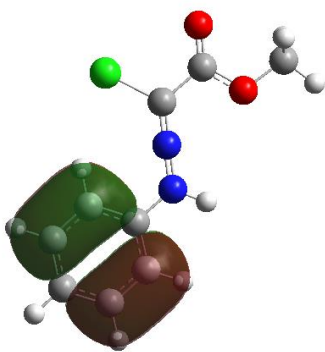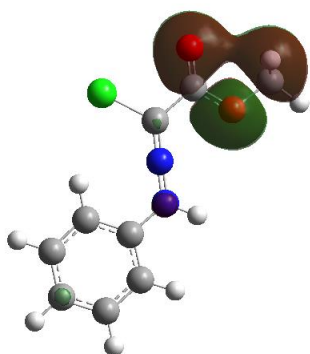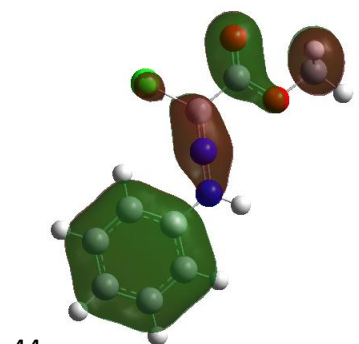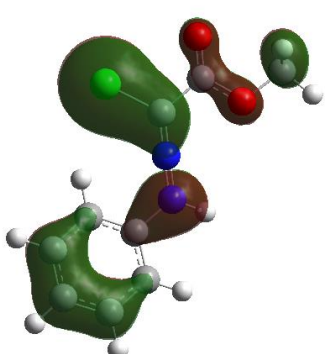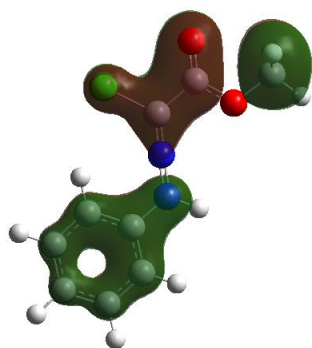
34 HOMO – 21 lowest occ. π

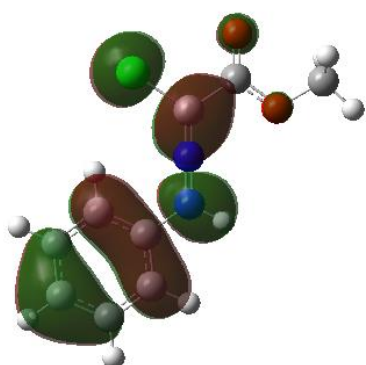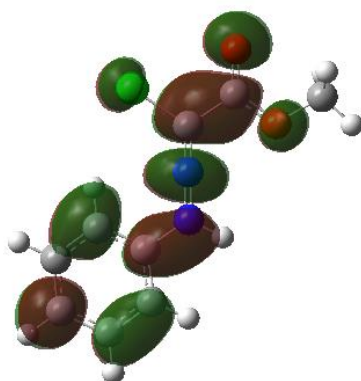**Figure S11**. M08HX/cc-pVDZ π MOs of **1**-EtsZcs.
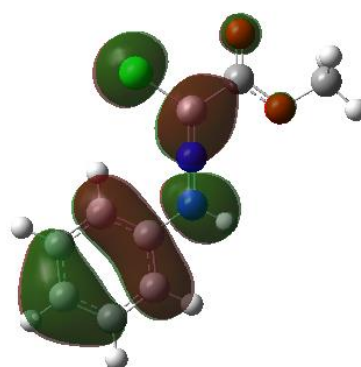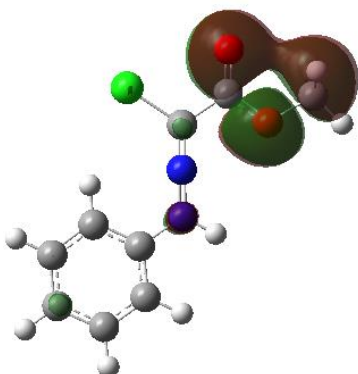
55 HOMO highest occ. π
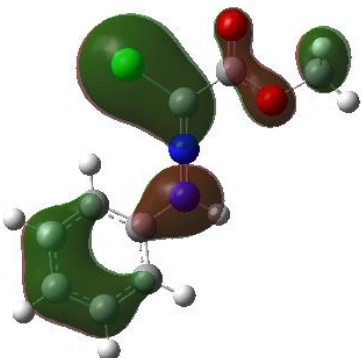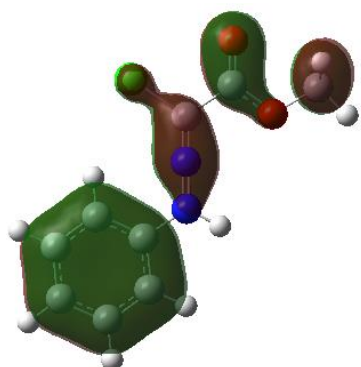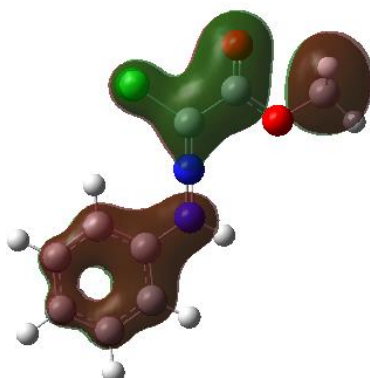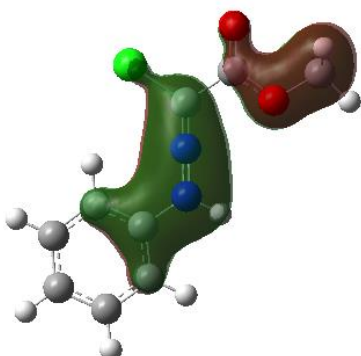
53 HOMO – 2

52

50

48 HOMO – 7

44

43

37

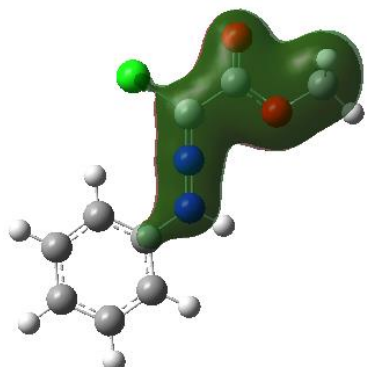34 HOMO – 21 lowest occ. π

Figure S12. M08HX/cc-pVTZ π MOs of **1**-EtsZcs.

Table S16. Free energy activation barrier $\Delta G^{\ddagger}$ for selected isomer interconversion processes of **2**. The barriers are grouped with respect to the interconversion mechanism.

Isomerization	From	To	$\Delta G^{\ddagger}$ (kJ/mol)		
			M08HX /cc-pVDZ	M08HX /cc-pVDZ	ωB97M-D4 /cc-pVTZ
Rotation,	Zta	Zts	28.6	25.0	19.4
γ	Zts	Zta	31.4	28.4	22.0
	Eca	Eta	28.2	26.4	22.7
Rotation,	Eta	Eca	87.1	83.0	70.9
θ	Zca	Zta	23.6	24.1	16.2
	Zta	Zca	69.1	68.9	59.7
	Eca	Zta	53.8	52.2	60.8
Umklapp, Φ	Zta	Eca	113.3	112.0	112.0
(θ)	Eta	Zca	111.5	106.6	105.9
	Zca	Eta	66.6	65.0	65.4

Table S17. Free energy activation barrier $\Delta G^{\ddagger}$ for selected isomer interconversion processes of **3**. The barriers are grouped with respect to the interconversion mechanism.

Isomerization	From	To	$\Delta G^{\ddagger}$ (kJ/mol)		
			M08HX /cc-pVDZ	M08HX /cc-pVDZ	ωB97M-D4 /cc-pVTZ
Rotation,	Zta	Zts	29.7	25.6	18.9
γ	Zts	Zta	31.7	28.5	21.5
	Eca	Eta	27.3	25.6	22.0
Rotation,	Eta	Eca	86.1	81.8	70.7
θ	Zca	Zta	23.7	23.9	16.1
	Zta	Zca	70.1	69.5	59.9
	Eca	Zta	52.2	58.7	60.6
Umklapp, Φ	Zta	Eca	113.7	119.5	112.4
(θ)	Eta	Zca	110.7	106.5	106.0
	Zca	Eta	67.1	65.4	65.3

Table S18. Free energy activation barrier $\Delta G^{\ddagger}$ for selected isomer interconversion processes of **4**. The barriers are grouped with respect to the interconversion mechanism.

Isomerization	From	To	$\Delta G^{\ddagger}$ (kJ/mol)		
			M08HX /cc-pVDZ	M08HX /cc-pVDZ	ωB97M-D4 /cc-pVTZ
Rotation, γ	Zta	Zts	29.9	25.9	18.8
	Zts	Zta	31.9	28.8	21.4
Rotation, θ	Eca	Eta	27.1	26.2	21.5
	Eta	Eca	85.4	81.9	70.2
	Zca	Zta	23.1	23.0	18.6
	Zta	Zca	69.9	69.0	62.9
Umklapp, Φ (θ)	Eca	Zta	53.0	51.5	61.0
	Zta	Eca	114.0	111.8	112.9
	Eta	Zca	110.4	105.8	106.1
	Zca	Eta	66.3	64.5	65.0

Table S19. Free energy activation barrier $\Delta G^{\ddagger}$ for selected isomer interconversion processes of **5**. The barriers are grouped with respect to the interconversion mechanism.

Isomerization	From	To	$\Delta G^{\ddagger}$ (kJ/mol)		
			M08HX /cc-pVDZ	M08HX /cc-pVDZ	ωB97M-D4 /cc-pVTZ
Rotation, γ	Ztta	Ztts	28.8	25.5	18.9
	Ztts	Ztta	30.7	28.2	21.2
Rotation, θ	Ecta	Etta	25.7	24.3	17.3
	Etta	Ecta	87.0	82.3	68.9
	Zcta	Ztta	20.4	18.1	10.4
	Ztta	Zcta	69.9	67.6	57.4
Rotation, ψ	Etca	Etta	13.5	12.7	6.1
	Etta	Etca	39.5	38.3	30.1
	Ztca	Ztta	12.1	10.6	5.0
	Ztta	Ztca	40.2	40.0	31.7
	Ztcs	Ztts	13.2	11.7	-16.3
	Ztts	Ztcs	38.9	38.8	29.9
Umklapp, Φ (θ)	Ecta	Ztta	50.0	51.1	57.8
	Ztta	Ecta	115.0	115.6	114.6
	Etta	Zcta	110.3	105.7	104.9
	Zcta	Etta	64.4	62.7	63.0

Table S20. Free energy activation barrier $\Delta G^{\ddagger}$ for selected isomer interconversion processes of **6**. The barriers are grouped with respect to the interconversion mechanism.

Isomerization	From	To	$\Delta G^{\ddagger}$ (kJ/mol)		
			M08HX /cc-pVDZ	M08HX /cc-pVDZ	ωB97M-D4 /cc-pVTZ
Rotation, γ	Ztta	Ztts	29.7	25.4	18.8
	Ztts	Ztta	31.5	28.1	21.0
Rotation, θ	Ecta	Etta	25.0	23.9	17.6
	Etta	Ecta	86.4	82.5	68.7
	Zcta	Ztta	20.6	18.2	10.4
	Ztta	Zcta	70.4	67.3	57.6
Rotation, ψ	Etca	Etta	12.1	11.5	5.9
	Etta	Etca	39.0	38.4	29.8
	Ztca	Ztta	10.9	10.2	5.2
	Ztta	Ztca	41.0	40.3	31.8
	Ztcs	Ztts	12.0	11.1	-15.7
	Ztts	Ztcs	40.0	39.0	29.9
Umklapp, Φ (θ)	Ecta	Ztta	49.4	52.0	58.7
	Ztta	Ecta	115.2	116.7	115.1
	Etta	Zcta	110.1	105.7	104.6
	Zcta	Etta	64.6	62.7	62.8

Table S21. Free energy activation barrier $\Delta G^{\ddagger}$ for selected isomer interconversion processes of **7**. The barriers are grouped with respect to the interconversion mechanism.

Isomerization	From	To	$\Delta G^{\ddagger}$ (kJ/mol)		
			M08HX /cc-pVDZ	M08HX /cc-pVDZ	ωB97M-D4 /cc-pVTZ
Rotation, γ	Ztta	Ztts	29.3	25.8	18.5
	Ztts	Ztta	31.0	28.5	20.6
Rotation, θ	Ecta	Etta	25.5	23.7	19.0
	Etta	Ecta	85.6	81.2	68.3
	Zcta	Ztta	22.4	19.2	16.9
	Ztta	Zcta	70.7	67.8	61.8
Rotation, ψ	Etca	Etta	12.7	12.1	5.8
	Etta	Etca	37.0	36.8	28.1
	Ztca	Ztta	12.0	10.1	5.5
	Ztta	Ztca	39.5	39.4	30.6
	Ztcs	Ztts	12.4	10.9	-14.8
	Ztts	Ztcs	38.7	38.7	29.2
Umklapp, Φ (θ)	Ecta	Ztta	50.1	53.0	59.8
	Ztta	Ecta	115.2	117.6	114.7
	Etta	Zcta	109.5	105.1	104.2
	Zcta	Etta	66.2	63.7	64.8