Supporting Information
for the article

Novel [4+2] Cycloaddition Reactions of Alkyne and Enyne Key-Units: Direct Access to Bicyclic Aromatic and Heteroaromatic Products. A Mechanistic Study

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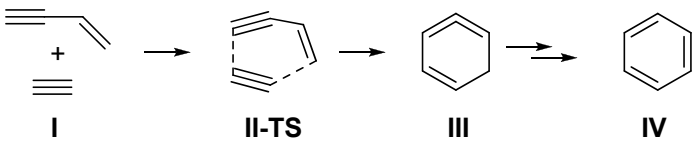
Table S1. Calculated ΔE, ΔH and ΔG energy surfaces (in kcal/mol) at B3LYP/6-311+G(d) level (see Scheme 4 for structures).

Level	1	2-TS	3	4-TS	5	6-TS	7-TS	8	9-TS	10
B3LYP (ΔE)	0.0	31.4	-16.3	33.9	4.2	17.2	8.7	-11.0	-7.6	-100.0
B3LYP (ΔH)	0.0	30.6	-14.7	32.1	5.4	17.0	8.1	-9.9	-7.9	-96.8
B3LYP (ΔG)	0.0	34.5	-9.7	37.5	9.9	21.8	13.4	-6.6	-2.8	-91.4

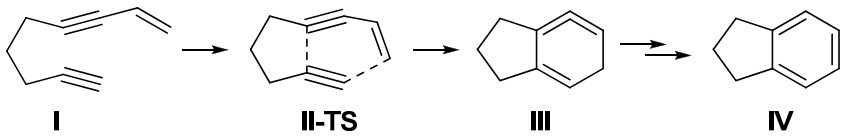
Level	11	12-TS	13	14-TS
B3LYP (ΔE)	-1.3	35.6	-13.8	2.3
B3LYP (ΔH)	-1.2	34.9	-11.9	2.5
B3LYP (ΔG)	-1.4	39.1	-7.4	7.7

Table S2. Calculated ΔE, ΔH and ΔG energy surfaces (in kcal/mol) of intermolecular [4+2] cycloaddition reaction between acetylene and vinylacetylene at B3LYP/6-311+G(d) and CCSD(T)/6-311+G(d)//B3LYP/6-311+G(d) levels.



Level	I	II-TS	III	IV
B3LYP (ΔE)	0.0	30.6	-28.3	-109.8
CCSD(T) (ΔE)	0.0	29.9	-32.7	-108.0
B3LYP (ΔH)	0.0	30.9	-24.5	-104.2
B3LYP (ΔG)	0.0	41.8	-11.6	-90.3

Table S3. Calculated ΔE, ΔH and ΔG energy surfaces (in kcal/mol) of intramolecular [4+2] cycloaddition reaction of non-1-ene-3,8-diyne at B3LYP/6-311+G(d) and CCSD(T)/6-311+G(d)//B3LYP/6-311+G(d) levels.



Level	I	II-TS	III	IV
B3LYP (ΔE)	0.0	32.5	-15.8	-97.2
CCSD(T) (ΔE)	0.0	30.4	-22.9	-99.1
B3LYP (ΔH)	0.0	31.5	-14.6	-94.5
B3LYP (ΔG)	0.0	36.7	-8.2	-87.4

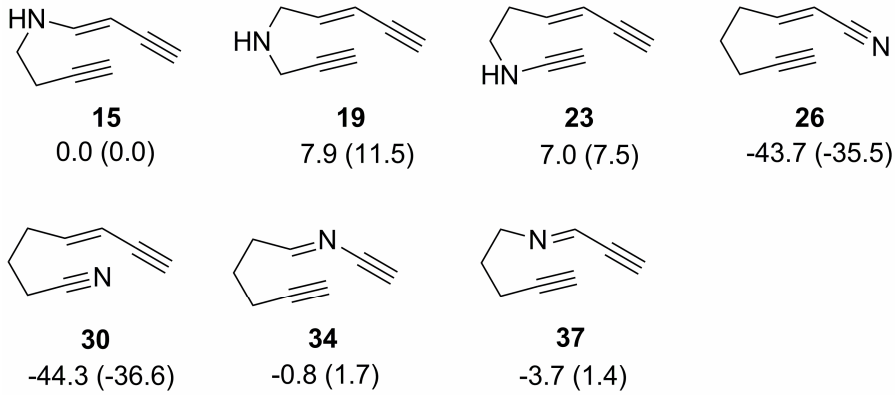


Figure S1. Relative stability (in kcal/mol) of nitrogen-containing reagents **15**, **19**, **23**, **26**, **30**, **34**, and **37**: calculated ΔE values at CCSD(T)/6-311+G(d)//B3LYP/6-311+G(d) level (without parenthesis) and ΔG values at B3LYP/6-311+G(d) level (in parenthesis); compound **15** was used as a reference point.

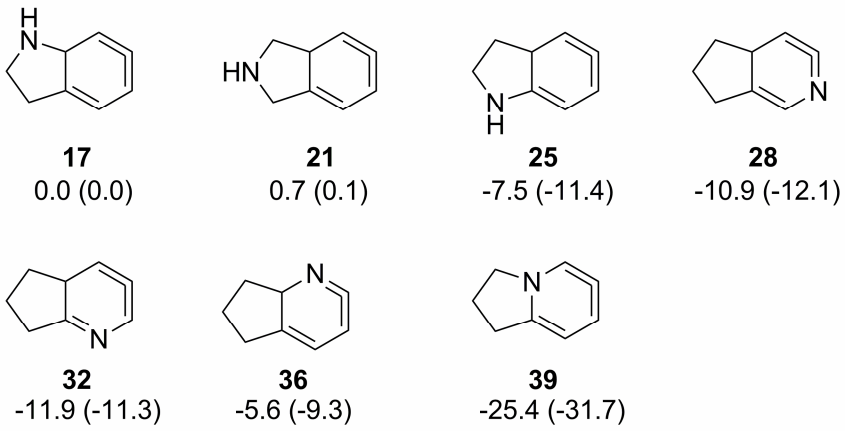


Figure S2. Relative stability (in kcal/mol) of cyclic heteroatom-substituted allenes **17**, **21**, **25**, **28**, **32**, **36**, and **39**: calculated ΔE values at CCSD(T)/6-311+G(d)//B3LYP/6-311+G(d) level (without parenthesis) and ΔG values at B3LYP/6-311+G(d) level (in parenthesis); compound **17** was used as a reference point.

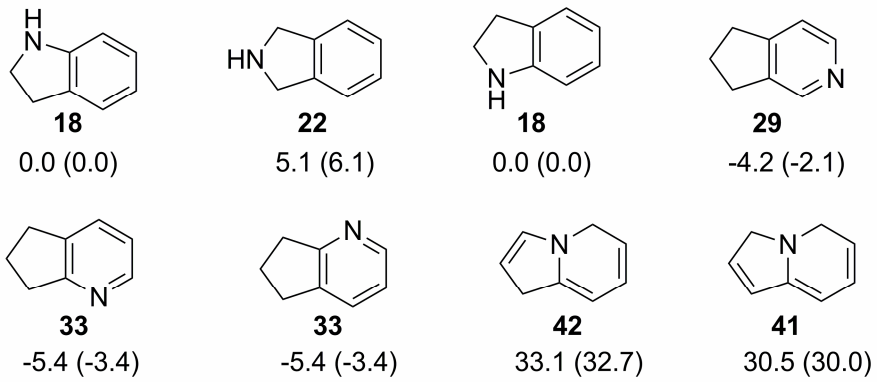
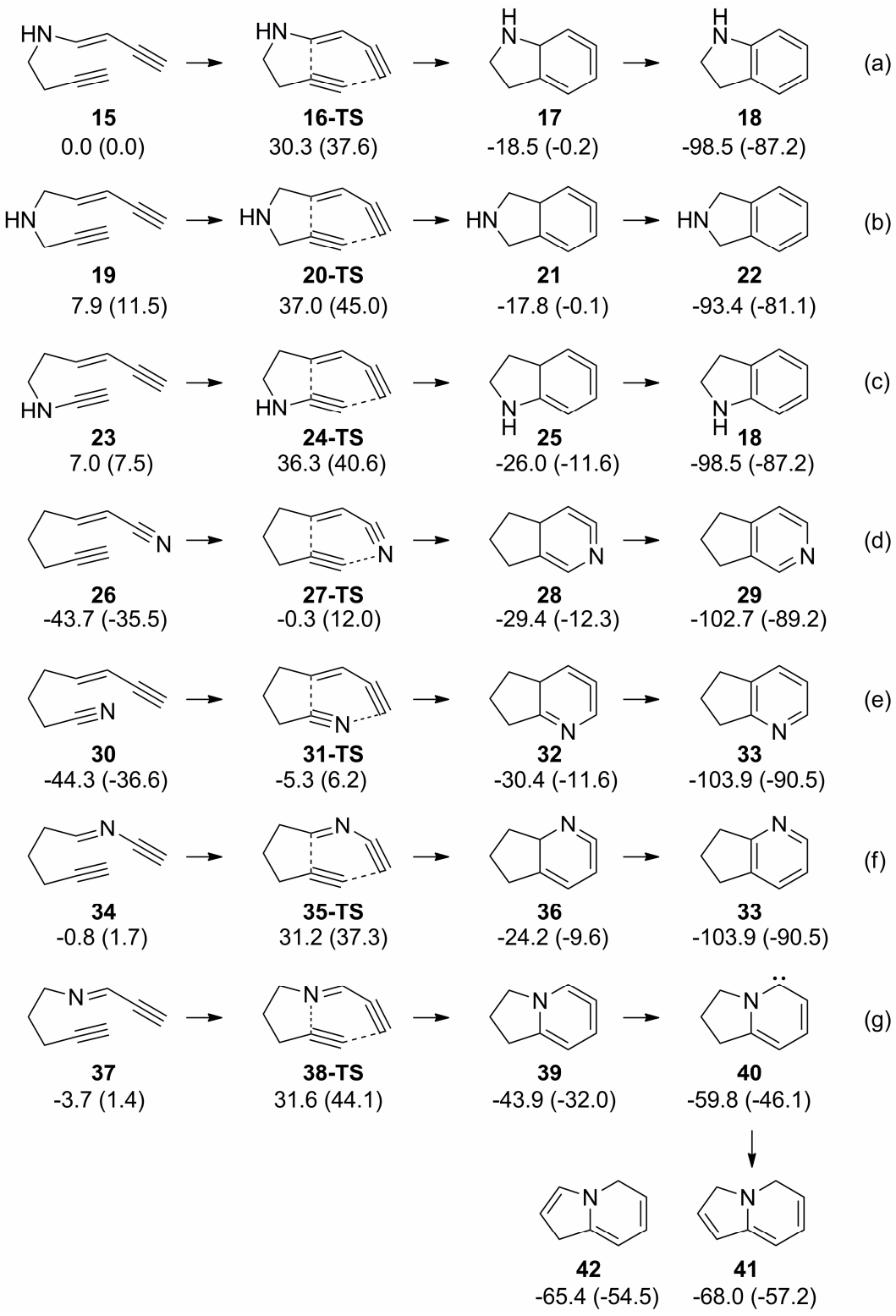


Figure S3. Relative stability (in kcal/mol) of products **18**, **22**, **29**, **33**, **41**, **42**, and **43**: calculated ΔE values at CCSD(T)/6-311+G(d)//B3LYP/6-311+G(d) level (without parenthesis) and ΔG values at B3LYP/6-311+G(d) level (in parenthesis); compound **18** was used as a reference point.

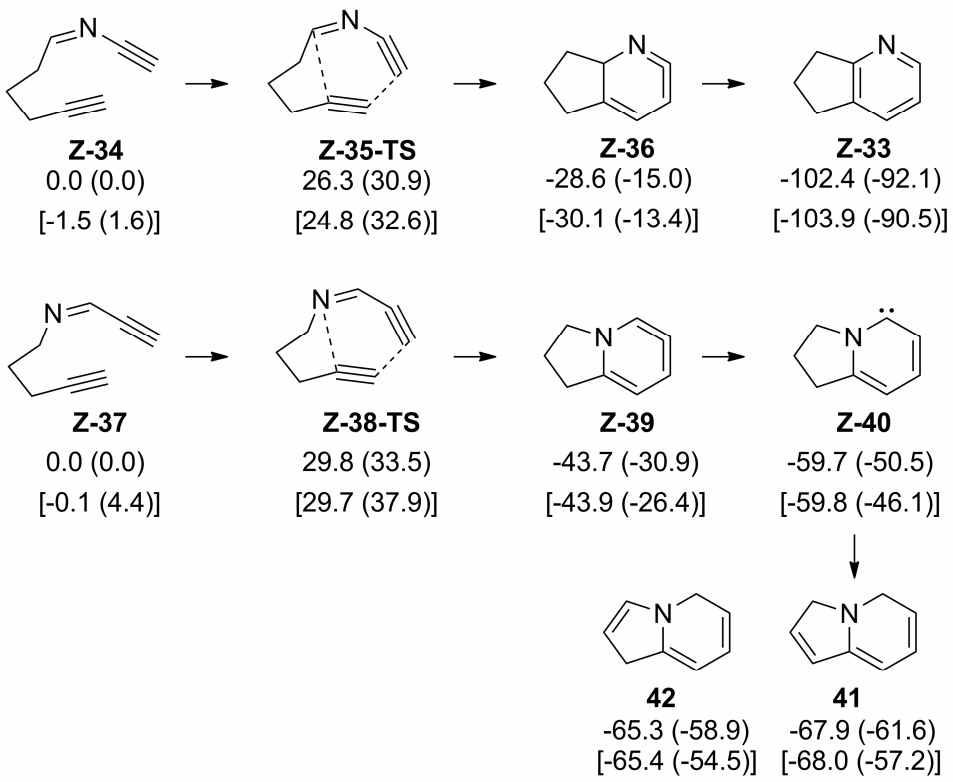
Table S4. Calculated ΔE, ΔH and ΔG energy surfaces (in kcal/mol) at B3LYP/6-311+G(d) level (see Scheme 5 for structures); compound **15** was used as a reference point.

Level	**15**	**16-TS**	**17**	**18**	**19**	**20-TS**	**21**	**22**	**23**	**24-TS**	**25**	**18**	**26**	**27-TS**	**28**	**29**
B3LYP (ΔE)	0.0	33.9	-7.2	-96.1	11.2	41.8	-7.1	-90.1	8.0	37.9	-18.6	-96.1	-36.7	8.1	-19.0	-97.9
CCSD(T) (ΔE)	0.0	30.3	-18.5	-98.5	7.9	37.0	-17.8	-93.4	7.0	36.3	-26.0	-98.5	-43.7	-0.3	-29.4	-102.7
B3LYP (ΔH)	0.0	33.3	-5.5	-92.9	11.2	40.9	-5.4	-86.7	7.7	37.0	-16.8	-92.9	-36.1	7.5	-17.6	-94.9
B3LYP (ΔG)	0.0	37.6	-0.2	-87.2	11.5	45.0	-0.1	-81.1	7.5	40.6	-11.6	-87.2	-35.5	12.0	-12.3	-89.2

Level	**30**	**31-TS**	**32**	**33**	**34**	**35-TS**	**36**	**33**	**37**	**38-TS**	**39**	**40**	**41**	**42**
B3LYP (ΔE)	-37.6	1.8	-18.2	-99.2	1.9	35.1	-15.7	-99.2	1.6	40.1	-39.9	-54.6	-64.6	-61.4
CCSD(T) (ΔE)	-44.3	-5.3	-30.4	-103.9	-0.8	31.2	-24.2	-103.9	-3.7	31.6	-43.9	-59.8	-68.0	-65.4
B3LYP (ΔH)	-37.0	1.6	-16.9	-96.2	1.6	33.7	-14.2	-96.2	1.4	39.3	-37.2	-51.8	-62.5	-59.5
B3LYP (ΔG)	-36.6	6.2	-11.6	-90.5	1.7	37.3	-9.6	-90.5	1.4	44.1	-32.0	-46.1	-57.2	-54.5



Scheme S1. Cycloaddition reactions leading to heterocyclic products with calculated ΔE values at CCSD(T)/6-311+G(d)//B3LYP/6-311+G(d) level (without parenthesis) and ΔG values at B3LYP/6-311+G(d) level (in parenthesis); compound **15** was used as a reference point (in kcal/mol). See Scheme 5 for another representation of the energy surface with individual reference points for each reaction.



Scheme S2. Cycloaddition reactions of *Z*-**34** and *Z*-**40** compounds with calculated ΔE values at CCSD(T)/6-311+G(d)//B3LYP/6-311+G(d) level (without parenthesis) and ΔG values at B3LYP/6-311+G(d) level (in parenthesis); the values shown in square brackets are relative to point **15** (in kcal/mol). See Scheme 5 and Scheme S1 for the reactions involving *E*-**34** and *E*-**37** compounds.

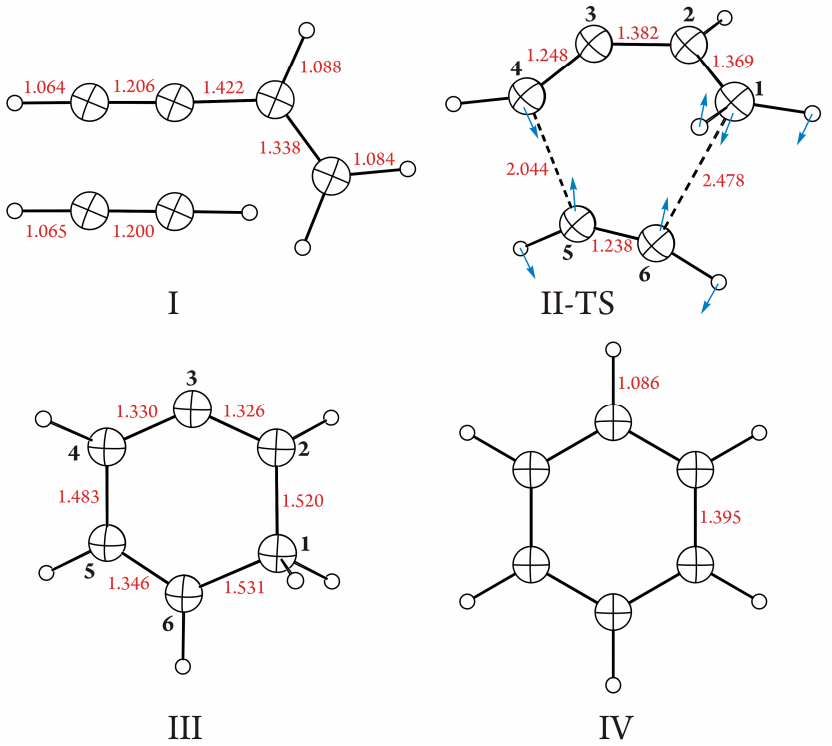


Figure S4. B3LYP/6-311+G(d) optimized molecular structures of **I-IV**. Displacement vectors corresponding to imaginary frequency are shown for transition state (see Scheme 1 for structures); imaginary frequency for the transition state: 538.3 *i* cm^{-1} (**II-TS**).

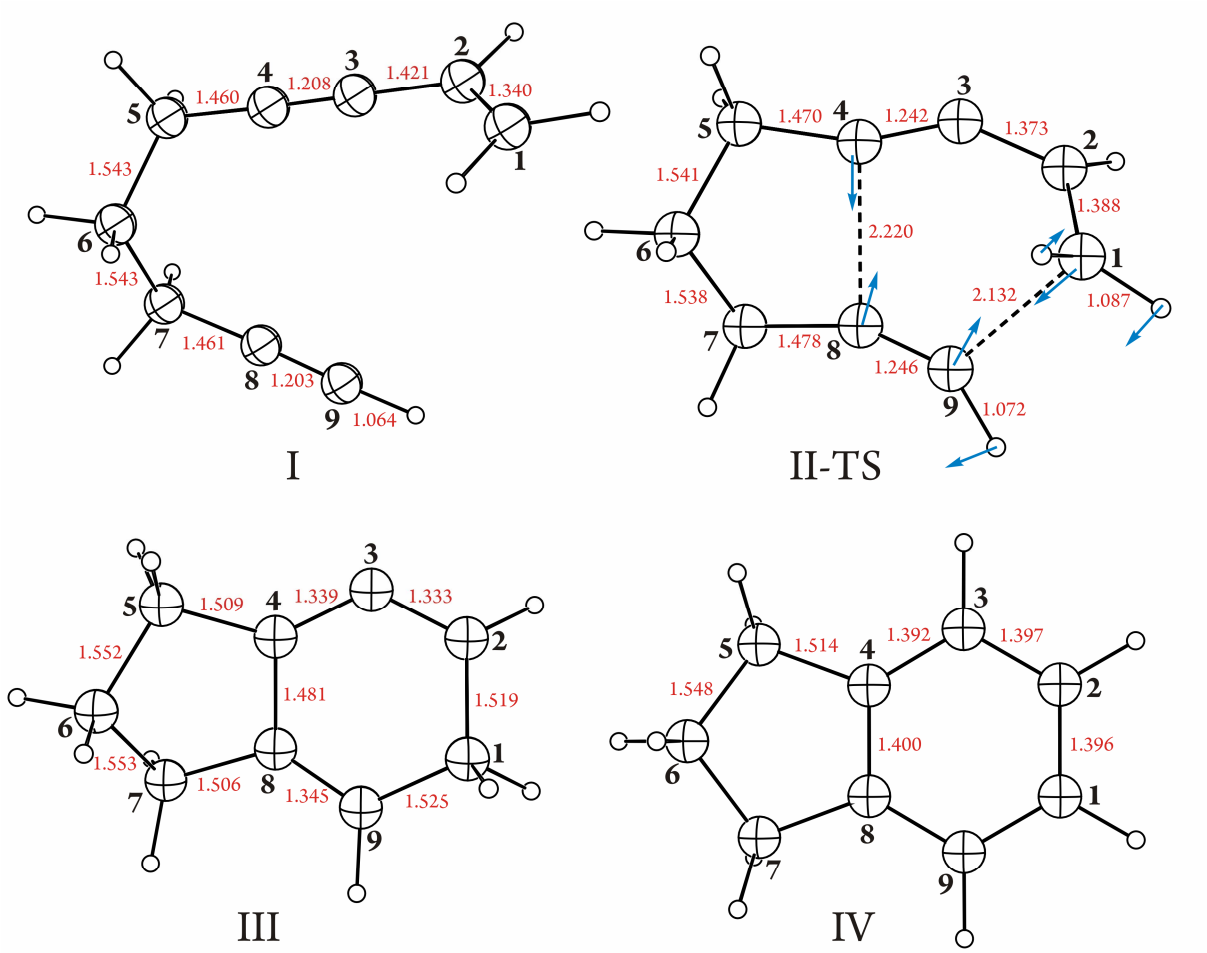


Figure S5. B3LYP/6-311+G(d) optimized molecular structures of **I-IV.** Displacement vectors corresponding to imaginary frequency are shown for transition state (see Scheme 2 for structures); imaginary frequency for the transition state: 527.2 *i* cm^{-1} (**II-TS**).

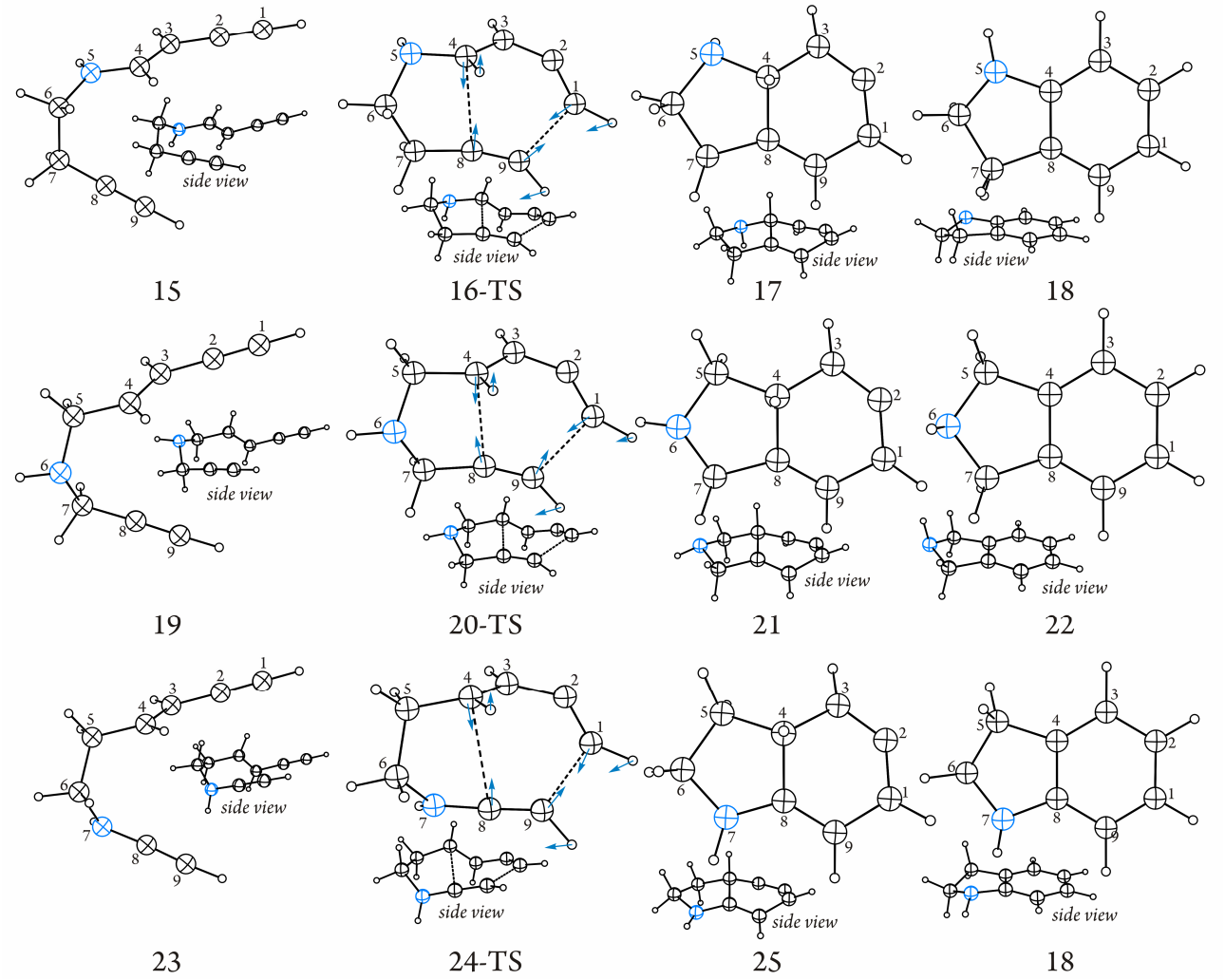


Figure S6(a). B3LYP/6-311+G(d) optimized molecular structures of **15** – **25**. Displacement vectors corresponding to imaginary frequency are shown for each transition state (see Scheme 5 for structures).

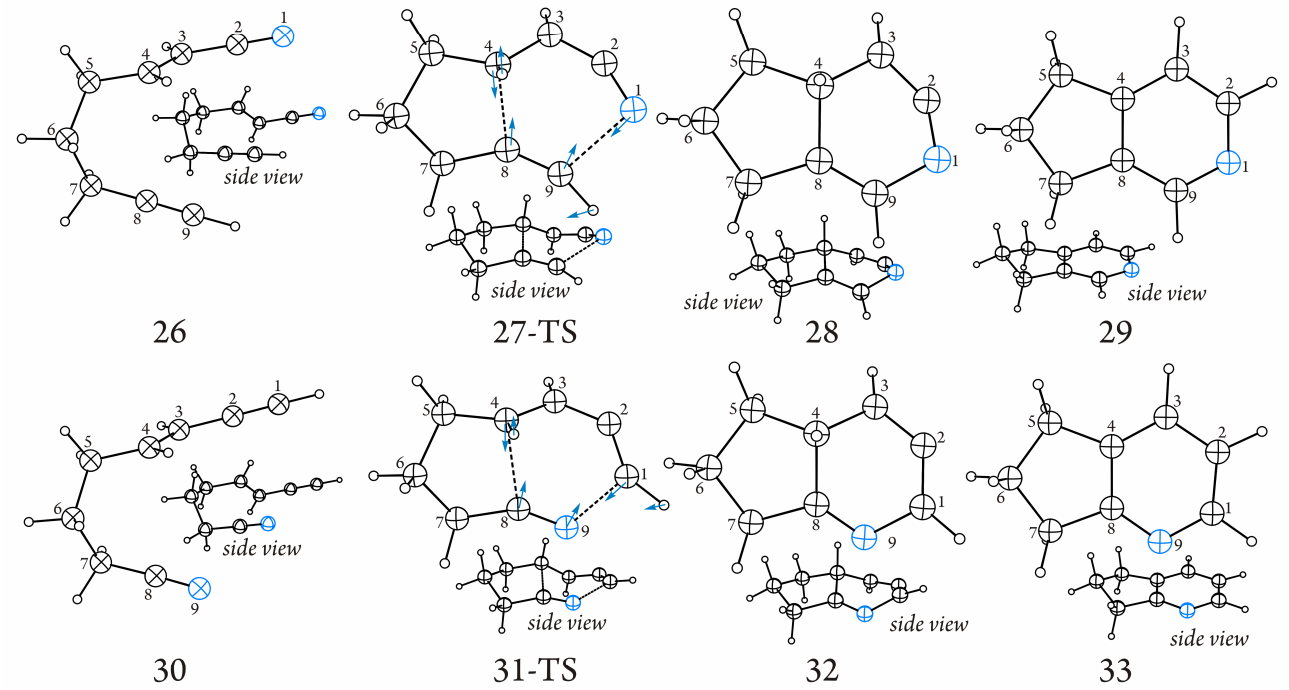


Figure S6(b). B3LYP/6-311+G(d) optimized molecular structures of **26** – **33**. Displacement vectors corresponding to imaginary frequency are shown for each transition state (see Scheme 5 for structures).

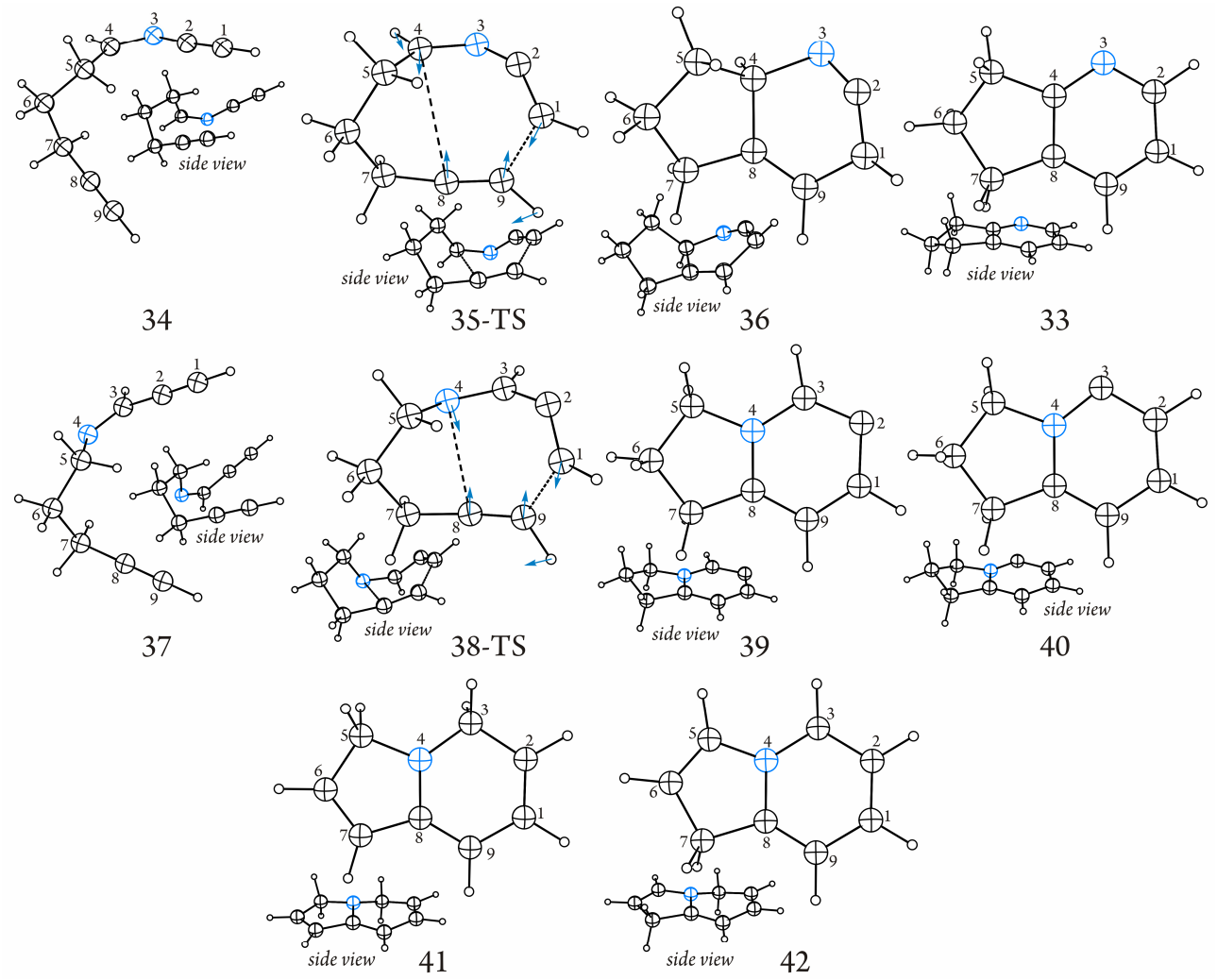


Figure S6(c). B3LYP/6-311+G(d) optimized molecular structures of **34** – **42**. Displacement vectors corresponding to imaginary frequency are shown for each transition state (see Scheme 5 for structures).

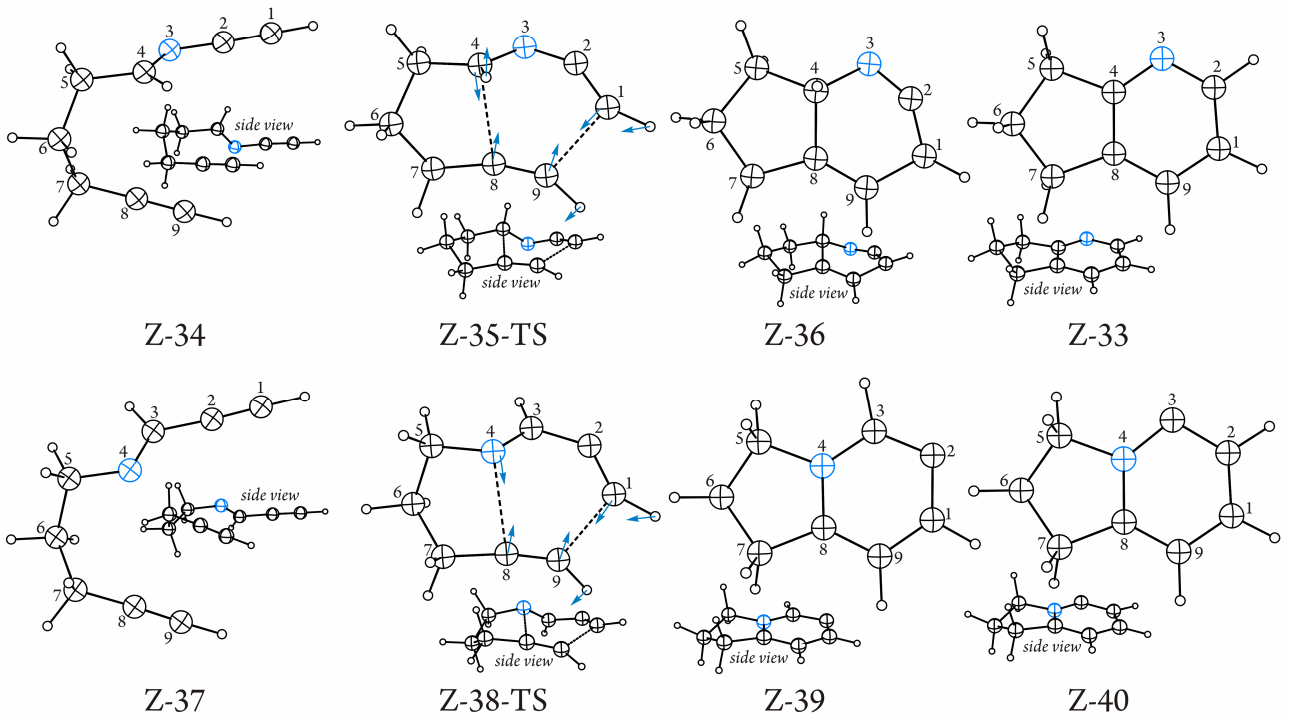


Figure S6(d). B3LYP/6-311+G(d) optimized molecular structures of **Z-34** – **Z-40**. Displacement vectors corresponding to imaginary frequency are shown for each transition state (see Scheme S2 for structures).

Table S5(a). Optimized geometry parameters of molecular structures **15** – **25** at B3LYP/6-311+G(d) level (bond length in Å, angles in deg); see Sheme 5; for atoms numbering see Figure S6(a).[a]

(a)					(b)					(c)				
	15	**16-TS**	**17**	**18**		**19**	**20-TS**	**21**	**22**		**23**	**24-TS**	**25**	**18**
C1-C2	1.209	1.255	1.329	1.395	C1-C2	1.206	1.248	1.330	1.396	C1-C2	1.206	1.263	1.352	1.395
C2-C3	1.414	1.381	1.327	1.398	C2-C3	1.421	1.383	1.328	1.398	C2-C3	1.421	1.404	1.332	1.401
C3-C4	1.353	1.376	1.507	1.393	C3-C4	1.340	1.371	1.509	1.391	C3-C4	1.341	1.357	1.512	1.385
C4-N5	1.372	1.386	1.468	1.402	C4-C5	1.501	1.495	1.533	1.517	C4-C5	1.498	1.484	1.536	1.514
N5-C6	1.448	1.462	1.475	1.477	C5-N6	1.465	1.468	1.470	1.481	C5-C6	1.542	1.566	1.541	1.546
C6-C7	1.549	1.564	1.557	1.546	N6-C7	1.468	1.471	1.477	1.481	C6-N7	1.464	1.463	1.464	1.477
C7-C8	1.458	1.464	1.509	1.514	C7-C8	1.465	1.473	1.509	1.517	N7-C8	1.342	1.323	1.361	1.402
C8-C9	1.203	1.244	1.341	1.385	C8-C9	1.202	1.241	1.342	1.391	C8-C9	1.207	1.252	1.364	1.393
C4-C8	3.372	2.457	1.569	1.404	C4-C8	3.210	2.368	1.553	1.396	C4-C8	3.343	2.873	1.550	1.404
C1-C9	5.842	2.041	1.494	1.401	C1-C9	5.296	2.104	1.490	1.398	C1-C9	5.512	1.972	1.459	1.398
C1-H	1.063	1.074	1.087	1.085	C1-H	1.064	1.072	1.086	1.086	C1-H	1.064	1.075	1.088	1.086
C3-H	1.089	1.088	1.087	1.086	C3-H	1.089	1.088	1.087	1.086	C3-H	1.089	1.091	1.088	1.087
C4-H	1.085	1.083	1.101	–	C4-H	1.086	1.084	1.100	–	C4-H	1.088	1.088	1.102	–
C2-H	–	–	–	1.086	C2-H	–	–	–	1.086	C2-H	–	–	–	1.085
C9-H	1.064	1.074	1.086	1.087	C9-H	1.064	1.072	1.086	1.086	C9-H	1.063	1.077	1.086	1.086
C1-C2-C3	178.5	139.9	131.0	121.2	C1-C2-C3	178.2	139.8	130.9	120.5	C1-C2-C3	178.2	131.9	128.2	119.9
C2-C3-C4	123.1	114.4	111.1	118.3	C2-C3-C4	124.5	115.5	111.4	118.9	C2-C3-C4	124.6	121.7	112.7	119.4
C9-C8-C7	178.8	166.0	131.5	131.4	C9-C8-C7	177.8	160.4	130.2	130.5	C9-C8-N7	176.3	176.5	130.8	128.5

[a] Imaginary frequencies for the transition states: 456.8 *i* cm^{-1} (**16-TS**), 478.0 *i* cm^{-1} (**20-TS**), 415.3 *i* cm^{-1} (**24-TS**).

Table S5(b). Optimized geometry parameters of molecular structures **26** – **33** at B3LYP/6-311+G(d) level (bond length in Å, angles in deg); see Sheme 5; for atoms numbering see Figure S6(b).[a]

(d)					**(e)**				
	26	**27-TS**	**28**	**29**		**30**	**31-TS**	**32**	**33**
N1-C2	1.157	1.186	1.237	1.337	C1-C2	1.206	1.265	1.324	1.394
C2-C3	1.425	1.363	1.322	1.397	C2-C3	1.420	1.381	1.333	1.397
C3-C4	1.339	1.424	1.532	1.390	C3-C4	1.341	1.384	1.498	1.388
C4-C5	1.498	1.514	1.539	1.512	C4-C5	1.500	1.501	1.534	1.510
C5-C6	1.540	1.535	1.542	1.550	C5-C6	1.540	1.544	1.544	1.553
C6-C7	1.544	1.538	1.550	1.550	C6-C7	1.545	1.539	1.544	1.547
C7-C8	1.461	1.505	1.514	1.513	C7-C8	1.462	1.487	1.510	1.511
C8-C9	1.203	1.258	1.340	1.391	C8-N9	1.153	1.194	1.272	1.331
C4-C8	3.181	1.893	1.557	1.398	C4-C8	3.203	2.159	1.581	1.402
N1-C9	4.979	2.137	1.458	1.339	C1-N9	5.141	1.856	1.461	1.341
C3-H	1.087	1.083	1.080	1.086	C1-H	1.064	1.071	1.083	1.087
C4-H	1.088	1.089	1.101	–	C3-H	1.090	1.089	1.088	1.087
C2-H	–	–	–	1.087	C4-H	1.088	1.089	1.101	–
C9-H	1.064	1.067	1.082	1.088	C2-H	–	–	–	1.085
N1-C2-C3	178.9	151.1	142.7	124.1	C1-C2-C3	178.2	131.7	128.2	119.1
C2-C3-C4	123.0	108.5	104.2	117.6	C2-C3-C4	124.6	117.1	110.4	117.8
C9-C8-C7	178.5	141.2	129.8	130.4	N9-C8-C7	177.7	147.5	126.4	124.7

[a] Imaginary frequencies for the transition states: 506.1 *i* cm^{-1} (**27-TS**), 471.0 *i* cm^{-1} (**31-TS**).

Table S5(c). Optimized geometry parameters of molecular structures **34** – **42** at B3LYP/6-311+G(d) level (bond length in Å, angles in deg); see Sheme 5; for atoms numbering see Figure S6(c).[a]

(f)					**(g)**						
	34	**35-TS**	**36**	**33**		**37**	**38-TS**	**39**	**40**	**41**	**42**
C1-C2	1.208	1.275	1.332	1.394	C1-C2	1.205	1.297	1.418	1.385	1.348	1.345
C2-N3	1.335	1.302	1.222	1.341	C2-C3	1.436	1.392	1.392	1.422	1.510	1.512
N3-C4	1.281	1.301	1.524	1.331	C3-N4	1.274	1.312	1.370	1.365	1.457	1.462
C4-C5	1.502	1.499	1.535	1.511	N4-C5	1.458	1.449	1.482	1.485	1.455	1.400
C5-C6	1.536	1.546	1.557	1.547	C5-C6	1.529	1.540	1.535	1.533	1.503	1.339
C6-C7	1.544	1.562	1.571	1.553	C6-C7	1.542	1.565	1.545	1.544	1.343	1.515
C7-C8	1.461	1.450	1.505	1.510	C7-C8	1.461	1.446	1.506	1.505	1.456	1.518
C8-C9	1.203	1.252	1.347	1.388	C8-C9	1.204	1.272	1.382	1.372	1.361	1.353
C4-C8	3.892	3.074	1.530	1.402	N4-C8	3.771	2.599	1.354	1.371	1.390	1.394
C1-C9	5.295	1.776	1.486	1.397	C1-C9	5.402	1.613	1.403	1.406	1.447	1.453
C1-H	1.063	1.075	1.079	1.085	C1-H	1.065	1.083	1.091	1.087	1.086	1.086
C4-H	1.093	1.091	1.094	–	C2-H	–	–	–	1.087	1.085	1.085
C2-H	–	–	–	1.087	C3-H	1.092	1.093	1.090	–	1.097	1.095
C9-H	1.064	1.080	1.087	1.087	C9-H	1.064	1.086	1.087	1.084	1.082	1.083
C1-C2-N3	173.5	141.6	143.6	123.8	C1-C2-C3	177.6	127.4	111.8	124.0	121.2	120.7
C2-N3-C4	122.8	124.0	110.0	116.3	C2-C3-N4	127.4	126.1	124.2	111.0	109.4	109.1
C9-C8-C7	179.1	170.1	128.6	131.1	C9-C8-C7	179.2	168.4	131.6	130.5	131.4	131.7

[a] Imaginary frequencies for the transition states: 343.5 *i* cm^{-1} (**35-TS**), 217.0 *i* cm^{-1} (**38-TS**).

Table S5(d). Optimized geometry parameters of molecular structures **Z-33** – **Z-40** at B3LYP/6-311+G(d) level (bond length in Å, angles in deg); see Sheme S2; for atoms numbering see Figure S6(d).[a]

Z-33 – Z-36					**Z-37 – Z-40**				
	Z-34	**Z-35-TS**	**Z-36**	**Z-33**		**Z-37**	**Z-38-TS**	**Z-39**	**Z-40**
C1-C2	1.208	1.249	1.323	1.394	C1-C2	1.204	1.254	1.391	1.385
C2-N3	1.335	1.299	1.234	1.341	C2-C3	1.429	1.411	1.374	1.423
N3-C4	1.280	1.318	1.489	1.331	C3-N4	1.271	1.287	1.365	1.365
C4-C5	1.496	1.492	1.528	1.511	N4-C5	1.450	1.447	1.471	1.485
C5-C6	1.539	1.540	1.542	1.547	C5-C6	1.535	1.544	1.532	1.533
C6-C7	1.543	1.541	1.552	1.553	C6-C7	1.546	1.541	1.544	1.544
C7-C8	1.461	1.476	1.512	1.510	C7-C8	1.460	1.462	1.507	1.505
C8-C9	1.203	1.239	1.340	1.388	C8-C9	1.203	1.240	1.374	1.372
C4-C8	3.131	2.347	1.567	1.402	N4-C8	3.200	2.404	1.372	1.371
C1-C9	4.885	2.125	1.509	1.397	C1-C9	5.462	2.004	1.422	1.406
C1-H	1.063	1.069	1.080	1.085	C1-H	1.064	1.073	1.090	1.087
C4-H	1.096	1.093	1.102	–	C2-H	–	–	–	1.087
C2-H	–	–	–	1.087	C3-H	1.101	1.098	1.087	–
C9-H	1.064	1.071	1.086	1.087	C9-H	1.064	1.073	1.087	1.087
C1-C2-N3	174.6	144.6	143.6	123.8	C1-C2-C3	176.3	134.0	116.0	124.0
C2-N3-C4	121.4	113.4	105.2	116.3	C2-C3-N4	122.6	116.5	121.0	111.1
C9-C8-C7	178.9	160.5	131.3	131.1	C9-C8-C7	177.5	170.1	132.6	130.5

[a] Imaginary frequencies for the transition states: 483.6 *i* cm^{-1} (**Z-35-TS**), 465.1 *i* cm^{-1} (**Z-38-TS**).

Table S6. Calculated ΔE, ΔH and ΔG energy surfaces (in kcal/mol) at B3LYP/6-311+G(d) and CCSD(T)/6-311+G(d)//B3LYP/6-311+G(d) levels (see Scheme 6 for structures).

Level	**43**	**44-TS**	**45**	**46**	**47**	**48-TS**	**49**	**50**	**51**	**52-TS**	**53**	**54**
B3LYP (ΔE)	0.0	33.3	-16.9	-102.5	0.0	29.7	-18.9	-102.2	0.0	31.1	-18.7	-102.6
CCSD(T) (ΔE)	0.0	31.3	-25.8	-103.9	0.0	28.1	-26.4	-101.2	0.0	29.3	-27.4	-103.1
B3LYP (ΔH)	0.0	32.4	-14.9	-99.2	0.0	28.8	-17.2	-99.0	0.0	30.3	-16.7	-99.2
B3LYP (ΔG)	0.0	36.4	-9.9	-93.4	0.0	32.7	-12.3	-94.0	0.0	34.3	-11.8	-93.9

Level	**55**	**56-TS**	**57**	**58**
B3LYP (ΔE)	0.0	31.7	-17.4	-101.7
CCSD(T) (ΔE)	0.0	30.2	-26.4	-102.8
B3LYP (ΔH)	0.0	30.8	-15.4	-98.3
B3LYP (ΔG)	0.0	34.9	-10.5	-93.4

Table S7. Optimized geometry parameters of molecular structures **43** – **58** at B3LYP/6-311+G(d) level (bond length in Å, angles in deg); for atoms numbering see Figure S7.[a]

	43	**44-TS**	**45**	**46**	**47**	**48-TS**	**49**	**50**	**51**	**52-TS**	**53**	**54**	**55**	**56-TS**	**57**	**58**
C1-C2	1.206	1.255	1.328	1.395	1.206	1.247	1.329	1.397	1.206	1.251	1.329	1.396	1.206	1.253	1.329	1.396
C2-C3	1.420	1.388	1.326	1.394	1.420	1.382	1.328	1.397	1.420	1.386	1.326	1.393	1.419	1.387	1.325	1.392
C3-C4	1.342	1.367	1.519	1.396	1.340	1.372	1.510	1.391	1.342	1.369	1.516	1.396	1.344	1.368	1.521	1.398
C4-C5	1.493	1.489	1.554	1.513	1.500	1.495	1.533	1.506	1.491	1.487	1.531	1.509	1.483	1.480	1.533	1.509
C5-P(O/S/Se)6	1.891	1.891	1.894	1.885	1.427	1.429	1.429	1.434	1.847	1.844	1.839	1.847	2.003	1.995	1.984	1.988
P(O/S/Se)6-C7	1.894	1.895	1.884	1.885	1.423	1.429	1.436	1.434	1.850	1.852	1.852	1.847	2.003	2.007	1.999	1.988
C7-C8	1.453	1.457	1.498	1.513	1.466	1.474	1.507	1.506	1.453	1.458	1.511	1.509	1.446	1.449	1.507	1.509
C8-C9	1.203	1.243	1.345	1.396	1.202	1.241	1.341	1.391	1.202	1.242	1.344	1.396	1.203	1.243	1.347	1.398
C4-C8	3.660	2.615	1.560	1.402	3.169	2.337	1.550	1.393	3.423	2.524	1.555	1.396	3.616	2.627	1.552	1.398
C1-C9	5.236	1.991	1.488	1.394	5.351	2.123	1.492	1.397	5.058	2.034	1.487	1.393	5.199	1.997	1.483	1.392
C1-H	1.064	1.074	1.087	1.085	1.064	1.071	1.086	1.085	1.064	1.073	1.086	1.085	1.064	1.073	1.087	1.085
C3-H	1.089	1.088	1.087	1.086	1.090	1.088	1.087	1.086	1.089	1.088	1.087	1.086	1.089	1.088	1.087	1.086
C4-H	1.088	1.087	1.100	–	1.086	1.085	1.100	–	1.086	1.085	1.100	–	1.086	1.085	1.101	–
C2-H	–	–	–	1.085	–	–	–	1.085	–	–	–	1.085	–	–	–	1.085
C9-H	1.064	1.075	1.086	1.086	1.064	1.071	1.086	1.086	1.064	1.074	1.0868	1.086	1.064	1.075	1.087	1.086
C1-C2-C3	178.2	137.8	130.6	120.1	178.3	140.3	131.2	120.5	178.2	139.3	130.8	120.1	178.1	139.1	130.5	119.9
C2-C3-C4	124.4	116.8	113.2	120.0	124.6	115.3	111.2	118.7	124.4	116.1	112.2	119.8	124.5	116.6	113.3	120.3
C9-C8-C7	179.2	165.3	126.7	125.0	177.4	160.0	131.0	130.6	178.5	161.5	125.6	124.3	178.7	163.0	123.9	122.3

[a] Imaginary frequencies for the transition states: 468.8 *i* cm^{-1} (**44-TS**), 475.0 *i* cm^{-1} (**48-TS**), 473.0 *i* cm^{-1} (**52-TS**), 467.5 *i* cm^{-1} (**56-TS**).

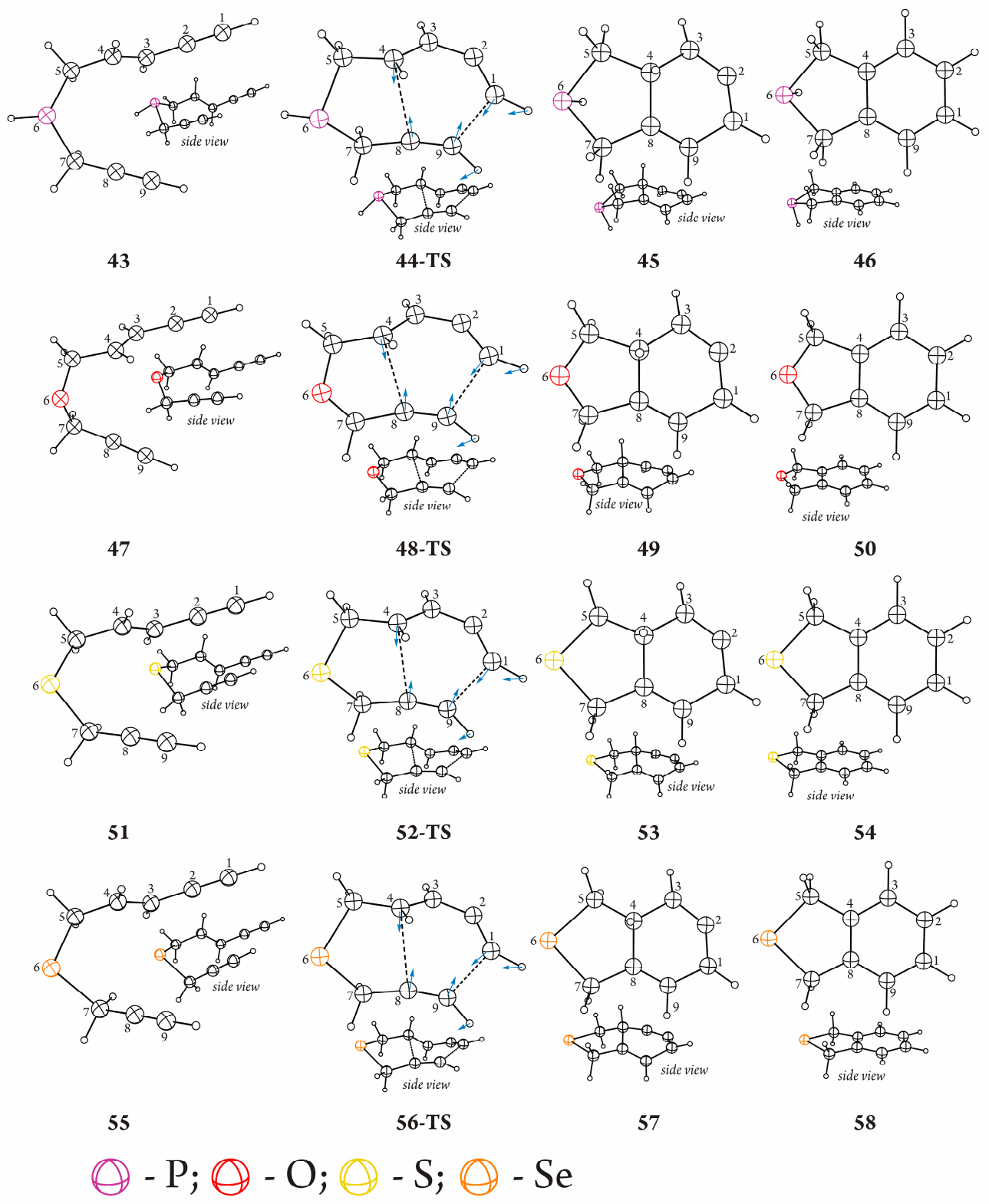


Figure S7. B3LYP/6-311+G(d) optimized molecular structures of **43** – **58.** Displacement vectors corresponding to imaginary frequency are shown for each transition state (see Scheme 6 for structures).

Table S8(a). Calculated ΔH and ΔG energy surfaces (in kcal/mol) constructed from the CCSD(T)/6-311+G(d)//B3LYP/6-311+G(d) single point energies and B3LYP/6-311+G(d) frequencies (see Schemes 4 for structures).

	1	**2-TS**	**3**	**4-TS**	**5**	**6-TS**	**7-TS**	**8**	**9-TS**	**10**	**11**	**12-TS**	**13**	**14-TS**
CCSD(T) (ΔH)	0.0	29.1	-22.2	26.2	-3.5	15.0	8.7	-9.4	-8.4	-96.7	-1.4	31.9	-18.0	2.0
CCSD(T) (ΔG)	0.0	32.9	-17.2	31.7	1.0	19.8	14.0	-6.2	-3.3	-91.2	-1.6	36.0	-13.4	7.2

Table S8(b). Calculated ΔH and ΔG energy surfaces (in kcal/mol) constructed from the CCSD(T)/6-311+G(d)//B3LYP/6-311+G(d) single point energies and B3LYP/6-311+G(d) frequencies (see Schemes 5 for structures); compound 15 was used as a reference point.

	15	**16-TS**	**17**	**18**	**19**	**20-TS**	**21**	**22**	**23**	**24-TS**	**25**	**18**	**26**	**27-TS**	**28**
CCSD(T) (ΔH)	0.0	29.7	-16.8	-95.3	7.9	36.1	-16.2	-90.0	6.7	35.4	-24.2	-95.3	-43.1	-0.9	-28.0
CCSD(T) (ΔG)	0.0	34.0	-11.5	-89.5	8.2	40.2	-10.9	-84.4	6.5	39.0	-19.0	-89.5	-42.6	3.6	-22.7
	29	**30**	**31-TS**	**32**	**33**	**34**	**35-TS**	**36**	**33**	**37**	**38-TS**	**39**	**40**	**41**	**42**
CCSD(T) (ΔH)	-99.6	-43.7	-5.6	-29.0	-100.9	-1.2	29.8	-22.7	-100.9	-3.8	30.7	-41.2	-56.9	-66.0	-63.5
CCSD(T) (ΔG)	-94.0	-43.3	-0.9	-23.7	-95.2	-1.1	33.3	-18.1	-95.2	-3.9	35.5	-35.9	-51.3	-60.7	-58.4

Table S8(c). Calculated ΔH and ΔG energy surfaces (in kcal/mol) constructed from the CCSD(T)/6-311+G(d)//B3LYP/6-311+G(d) single point energies and B3LYP/6-311+G(d) frequencies (see Schemes S2 for structures); compound 15 was used as a reference point.

	15	**Z-34**	**Z-35-TS**	**Z-36**	**Z-33**	**Z-37**	**Z-38-TS**	**Z-39**	**Z-40**	**41**	**42**
CCSD(T) (ΔH)	0.0	-1.9	23.5	-28.9	-100.9	-0.4	28.5	-41.3	-56.9	-66.0	-63.5
CCSD(T) (ΔG)	0.0	-1.4	27.4	-23.6	-95.2	-0.1	32.6	-35.8	-51.3	-60.7	-58.4

Table S8(d). Calculated ΔH and ΔG energy surfaces (in kcal/mol) constructed from the CCSD(T)/6-311+G(d)//B3LYP/6-311+G(d) single point energies and B3LYP/6-311+G(d) frequencies (see Schemes 6 for structures).

	43	**44-TS**	**45**	**46**		**47**	**48-TS**	**49**	**50**
CCSD(T) (ΔH)	0.0	30.5	-23.8	-100.5		0.0	27.2	-24.7	-98.1
CCSD(T) (ΔG)	0.0	34.4	-18.8	-94.7		0.0	31.1	-19.8	-93.0
	51	**52-TS**	**53**	**54**		**55**	**56-TS**	**57**	**58**
CCSD(T) (ΔH)	0.0	28.5	-25.5	-99.7		0.0	29.4	-24.4	-99.4
CCSD(T) (ΔG)	0.0	32.5	-20.5	-94.4		0.0	33.5	-19.5	-94.5

Details of QTAIM calculations

Nucleus of nitrogen atom in these molecules is most powerful attractor of electrons, and localization of electrons in nitrogen atom basin should result in decrease of total energy. In molecule **36** the nitrogen atom is surrounded by two carbon atoms, and Bader atomic charges (a.u.) at MP2(full)/6-311++G(d,p) level of theory are: q(N) = -1.101, q(C2) = +0.609, q(C4) = +0.283 (see Figure S6(c) for structures). However, nitrogen atom is able to more electronic charge accumulation, which become evident in molecule **39**, where nitrogen atom is surrounded by three carbon atoms with an additional source of electrons. For compound **39** Bader atomic charges (a.u.) at MP2(full)/6-311++G(d,p) level of theory are: q(N) = -1.206, q(C3) = +0.330, q(C5) = +0.310, q(C8) = +0.405. Thus, lowering of total energy of compound **39** resulted from more effective accumulation of electrons in the nitrogen atom basin. Analysis of atomic energies ($E_e(\Omega)$) changes shown, that electronic energy of the nitrogen atom was decreased to the highest degree when transition from **36** to **39** did occur.

Compounds **36** and **39** have different distribution of delocalization indices (δ(A,B)) in six-membered heterocycle, which may be interpreted in terms of bonds orders.[1] In molecule **36** chemical bonds have different values of δ(A,B) (MP2(full)/6-311++G(d,p)): δ(C1,C2) = 1.306, δ(C2,N3) = 1.425, δ(N3,C4) = 0.770, δ(C4,C8) = 0.809, δ(C8,C9) = 1.354, δ(C9,C1) = 0.934 (see Scheme 5 for atoms numbering). In molecule **39** delocalization indices are distributed more uniformly: δ(C1,C2) = 1.145, δ(C2,N3) = 1.171, δ(N3,C4) = 0.956, δ(C4,C8) = 0.953, δ(C8,C9) = 1.145, δ(C9,C1) = 1.159. At the same level of theory δ(A,B) values of heterocycle **39** are similar to δ(A,B) values of pyridine molecule: δ(N1,C2) = 1.101, δ(C2,C3) = 1.142, δ(C3,C4) = 1.172. The δ(A,B) values are known to depend on theory level,[2] however, the calculated relative changes of δ(A,B) values were conserved at different levels of theory.

QTAIM calculations (Quantum Theory of Atoms in Molecules) were carried out for fully optimized molecular geometries at MP2(full)/6-311++G(d,p) and B3LYP/6-311++G(d,p) levels of theory. Topological parameters of electron density function were calculated by AIMAll Standard software.[3] For all atoms and parameters "Proaim" basin integration method with "Very High" basin quadrature option were used.

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[1] C.F. Matta, R.J. Boyd, *The quantum theory of atoms in molecules: from solid state to DNA and drug design*, Wiley-VCH Verlag GmbH & Co. KGaA, 2007.

[2] For example, at B3LYP/6-311++G(d,p) level the values for molecule **36** are: δ(C1,C2) = 1.580, δ(C2,N3) = 1.740, δ(N3,C4) = 0.889, δ(C4,C8) = 0.961, δ(C8,C9) = 1.666, δ(C9,C1) = 1.079; for molecule **39**: δ(C1,C2) = 1.346, δ(C2,N3) = 1.403, δ(N3,C4) = 1.109, δ(C4,C8) = 1.124, δ(C8,C9)

= 1.360, δ(C9,C1) = 1.373; and for pyridine molecule: δ(N1,C2) = 1.318, δ(C2,C3) = 1.350, δ(C3,C4) = 1.391.

[3] *Keith T.A., AIMAll 10.05.04 Standard,* http://aim.tkgristmill.com