Table S1 Electronic configuration for the $Ge(CN)_2$, CNGeCN, and $Ge(NC)_2$ geometries.

Electronic configuration	
The lowest-lying triplet $^3B_1$ states of $Ge(CN)_2$ and $Ge(NC)_2$ in C_{2v} point group have:	(core) $(9a_1)^2$ $(3b_1)^2$ $(6b_2)^2$ $(10a_1)^2$ $(11a_1)^2$ $(7b_2)^2$ $(12a_1)^2$ $(8b_2)^2$ $(13a_1)^2$ $(4b_1)^2$ $(2a_2)^2$ $(9b_2)^2$ $(14a_1)^1$ $(5b_1)^1$.
	core = $(1a_1)^2$ $(2a_1)^2$ $(1b_2)^2$ $(3a_1)^2$ $(1b_1)^2$ $(2b_2)^2$ $(4a_1)^2$ $(5a_1)^2$ $(3b_2)^2$ $(6a_1)^2$ $(4b_2)^2$ $(7a_1)^2$ $(2b_1)^2$ $(5b_2)^2$ $(8a_1)^2$ $(1a_2)^2$ denotes the 16 lowest-lying core (Ge: 1s, 2s, 2p, 3s, 3p, 3d-like and C: 1s-like) atomic orbitals.
For the $^3A''$ triplet excited state of CNGeCN:	(core) $(13a')^2$ $(14a')^2$ $(15a')^2$ $(16a')^2$ $(17a')^2$ $(18a')^2$ $(19a')^2$ $(5a'')^2$ $(20a')^2$ $(6a'')^2$ $(21a')^2$ $(22a')^2$ $(23a')^1$ $(7a'')^1$.
	core = $(1a')^2$ $(2a')^2$ $(1a'')^2$ $(3a')^2$ $(4a')^2$ $(5a')^2$ $(6a')^2$ $(7a')^2$ $(8a')^2$ $(9a')^2$ $(2a'')^2$ $(10a')^2$ $(11a')^2$ $(12a')^2$ $(3a'')^2$ $(4a'')^2$.

Table S2 NBO population analyses for bent geometries $Ge(CN)_2$, CNGeCN and $Ge(NC)_2$.

	NBO charge			Valence Populations		
	Ge	**C**	**N**	**Ge**	**C**	**N**
Ge$(CN)_2$	1.065	–0.231	–0.302	$4s^{1.75}\,4p^{1.18}\,5s^{0.01}\,4d^{0.01}$	$2s^{1.21}\,2p^{2.98}\,4s^{0.02}\,4p^{0.01}$	$2s^{1.61}\,2p^{3.67}\,4s^{0.01}\,3d^{0.02}$
CN**Ge**CN	1.199	–0.242	–0.301	$4s^{1.75}\,4p^{1.03}\,4d^{0.01}$	$2s^{1.22}\,2p^{2.98}\,4s^{0.02}\,4p^{0.01}$	$2s^{1.61}\,2p^{3.66}\,4s^{0.01}\,3d^{0.02}$
		0.376	–1.032		$2s^{1.58}\,2p^{2.02}\,4s^{0.01}\,3d^{0.01}\,4p^{0.01}$	$2s^{1.50}\,2p^{4.50}\,4s^{0.01}\,4p^{0.01}$
Ge$(NC)_2$	1.357	0.362	–1.040	$4s^{1.76}\,4p^{0.87}\,4d^{0.01}$	$2s^{1.58}\,2p^{2.03}\,4s^{0.01}\,3d^{0.01}\,4p^{0.01}$	$2s^{1.58}\,2p^{2.03}\,4s^{0.01}\,3d^{0.01}\,4p^{0.01}$

Table S3 Harmonic vibrational frequencies (cm^{-1}), infrared intensities (IR) (km mol^{-1}), Raman scattering activities ($Å^4$ amu^{-1}) for the $^1A_1$ ground state of $Ge(CN)_2$, $^2B_1$ ground state of the $Ge(CN)_2^-$ anion, $^2A_1$ ground state of the $Ge(CN)_2^+$ cation, and $^3B_1$ excited state of neutral $Ge(CN)_2$.

$Ge(CN)_2$			**BH&HLYP**			**BLYP**			**B3LYP**		
C_{2v}		**Sym.**	**Freq**	**IR**	**Raman**	**Freq**	**IR**	**Raman**	**Freq**	**IR**	**Raman**
	ω_1	A_1	91	8	7	78	6	9	84	7	8
	ω_2	B_1	196	6	3	161	4	1	176	5	2
	ω_3	A_2	214	0	5	180	0	3	195	0	4
	ω_4	B_2	251	0	0	215	0	0	231	0	0
$^1A_1$	ω_5	A_1	393	4	3	342	2	4	366	3	3
	ω_6	B_2	463	116	6	422	88	11	443	101	8
	ω_7	A_1	492	88	11	458	68	17	475	77	13
	ω_8	B_2	2360	72	63	2115	102	71	2227	90	70
	ω_9	A_1	2362	44	199	2117	53	244	2229	50	225
	ω_1	A_1	96	7	9	83	6	13	89	7	11
	ω_2	B_1	275	3	8	236	1	11	254	2	9
	ω_3	B_2	277	1	0	240	0	0	257	0	0
	ω_4	A_2	307	0	5	275	0	3	291	0	3
$^2B_1$	ω_5	A_1	363	18	2	321	9	5	342	12	3
	ω_6	B_2	398	66	0	369	48	0	385	54	0
	ω_7	A_1	456	41	1	425	35	1	440	38	1
	ω_8	B_2	2284	45	217	2042	58	329	2154	54	281
	ω_9	A_1	2291	15	302	2050	19	444	2161	17	375
	ω_1	A_1	79	8	6	65	2	8	72	5	6
$^2A_1$	ω_2	B_1	190	1	2	177	0	1	180	0	1
	ω_3	A_2	206	0	5	179	0	3	193	0	4
	ω_4	B_2	220	0	1	195	3	6	206	1	3
	ω_5	A_1	355	4	7	326	2	9	337	3	14
	ω_6	A_1	510	20	61	405	5	194	460	10	166
	ω_7	B_2	584	79	10	476	13	40	536	38	30
	ω_8	B_2	2346	499	88	2077	303	0	2203	480	53
	ω_9	A_1	2354	82	301	2084	64	3	2211	83	131
	ω_1	A_1	87	11	7	75	7	9	81	9	8
	ω_2	B_2	261	0	1	229	2	3	244	1	2
	ω_3	B_1	286	1	2	255	0	2	268	0	2
	ω_4	A_2	308	0	3	277	0	2	292	0	2
$^3B_1$	ω_5	A_1	378	2	1	343	1	0	359	2	1
	ω_6	A_1	493	14	9	430	6	65	463	10	27
	ω_7	B_2	549	44	0	491	20	4	523	30	1
	ω_8	B_2	2301	7	148	2044	9	156	2168	8	175
	ω_9	A_1	2314	2	449	2063	1	353	2184	2	488

Table S4 Harmonic vibrational frequencies (cm^{-1}), infrared intensities (IR) (km mol^{-1}), Raman scattering activities ($Å^4$ amu^{-1}) for the $^1A'$ ground state of CNGeCN, $^2A''$ ground state of the $CNGeCN^-$ anion, $^2A'$ ground state of the $CNGeCN^+$ cation, and $^3A''$ excited state of neutral CNGeCN.

CNGeCN			BH&HLYP			BLYP			B3LYP		
C_s		Sym.	Freq	IR	Raman	Freq	IR	Raman	Freq	IR	Raman
	ω_1	A'	96	7	8	84	6	10	89	6	9
	ω_2	A″	195	3	3	162	3	2	177	3	3
	ω_3	A″	215	0	5	201	0	2	207	0	3
	ω_4	A'	229	1	0	207	0	1	216	0	0
$^1A'$	ω_5	A'	367	4	3	320	3	3	342	3	2
	ω_6	A'	470	129	8	430	104	12	451	116	9
	ω_7	A'	521	127	13	468	86	30	494	105	20
	ω_8	A'	2197	580	98	1993	453	94	2087	508	101
	ω_9	A'	2365	59	119	2121	79	153	2232	71	137
	ω_1	A'	100	8	11	90	7	15	95	7	13
	ω_2	A'	249	1	1	227	0	3	237	0	2
	ω_3	A″	258	2	11	238	0.6	15.9	249	1	13
	ω_4	A″	291	0	6	265	0	5	2761	0	5
$^2A''$	ω_5	A'	344	11	1	301	7	3	322	7	2
	ω_6	A'	391	103	2	352.6	75	2	373	87	2
	ω_7	A'	428	61	1	400	43	1	414	51	1
	ω_8	A'	2229	160	353	2002	61	601	2107	99	479
	ω_9	A'	2284	29	273	2042	39	423	2153	36	351
	ω_1	A'	86	5	6	74	0	20	74	1	26
	ω_2	A″	190	0	2	166	0	4	178	0	4
	ω_3	A″	207	2	6	212	3.9	11	214	7	55
	ω_4	A'	210	3	5	228	5	11	218	3	16
$^2A'$	ω_5	A'	328	9	12	305	14	56	313	14	298
	ω_6	A'	516	36	107	372	10	154	431	35	1003
	ω_7	A'	639	52	126	424	9	98	511	10	276
	ω_8	A'	2081	879	51	1883	61	337	1901	7	7212
	ω_9	A'	2363	223	140	2082	134	52	2213	255	36
	ω_1	A'	93	9	8	78	3	17	86	7	10
	ω_2	A'	236	1	2	228	4	15	231	1	10
	ω_3	A″	256	0	3	261	1	4	256	0	6
	ω_4	A″	302	0	3	268	1	11	284	0	2
$^3A''$	ω_5	A'	347	4	1	318	3	23	330	3	6
	ω_6	A'	502	16	15	406	7	253	462	9	134
	ω_7	A'	576	63	6	469	13	23	530	31	40
	ω_8	A'	2182	376	210	1935	8	432	2052	190	4
	ω_9	A'	2305	0	297	2046	6	166	2169	1	282

Table S5 Harmonic vibrational frequencies (cm^{-1}), infrared intensities (IR) (km mol^{-1}), Raman scattering activities ($Å^4$ amu^{-1}) for the $^1A_1$ ground state of $Ge(NC)_2$, $^2B_1$ ground state of the $Ge(NC)_2^-$ anion, $^2A_1$ ground state of the $Ge(NC)_2^+$ cation, and $^3B_1$ excited state of neutral $Ge(NC)_2$.

$Ge(NC)_2$			BH&HLYP			BLYP			B3LYP		
C_{2v}		Sym.	Freq	IR	Raman	Freq	IR	Raman	Freq	IR	Raman
	ω_1	A_1	100	6	10	97	6	11	100	6	9
	ω_2	B_1	192	1	2	187	1	2	192	1	2
	ω_3	A_2	204	0	4	197	0	3	204	0	4
	ω_4	B_2	209	0	0	204	0	0	209	0	0
$^1A_1$	ω_5	A_1	320	3	1	302	2	2	320	3	1
	ω_6	B_2	469	164	13	442	140	19	469	164	13
	ω_7	A_1	501	105	24	475	89	35	501	105	24
	ω_8	B_2	2080	754	51	1985	680	48	2080	754	51
	ω_9	A_1	2104	278	146	2008	249	143	2104	278	146
	ω_1	A_1	108	8	12	99	8	19	103	8	16
	ω_2	B_2	236	1	0	222	1	1	229	1	1
	ω_3	B_1	252	1	11	241	1	19	247	1	14
	ω_4	A_2	268	0	10	258	0	9	264	0	9
$^2B_1$	ω_5	A_1	314	2	2	279	3	2	295	3	2
	ω_6	B_2	379	129	0	341	93	1	361	109	0.5
	ω_7	A_1	416	97	7	383	61	3	400	76	5
	ω_8	B_2	2219	219	291	1990	88	588	2096	139	439
	ω_9	A_1	2228	98	506	1999	33	834	2105	56	671
	ω_1	A_1	93	2	7	96	0	50	85	1	13
$^2A_1$	ω_2	B_1	187	4	1	208	0	31	215	0	66
	ω_3	B_2	194	1	11	219	0	3	223	8	2
	ω_4	A_2	201	0	10	225	7	2	225	0	26
	ω_5	A_1	293	18	47	295	5	47	297	1	1048
	ω_6	A_1	567	9	753	368	11	59	377	163	693
	ω_7	B_2	638	46	143	384	4	137	383	8	1140
	ω_8	B_2	2067	1290	100	1905	166	297	1902	846	4954
	ω_9	A_1	2104	161	777	1935	0	191	1941	62	6646
	ω_1	A_1	98	7	9	86	0	29	90	3	16
	ω_2	B_2	220	0	3	228	1	15	222	0	27
	ω_3	B_1	253	1	2	266	0	33	258	2	3
	ω_4	A_2	265	0	5	270	4	5	266	0	17
$^3B_1$	ω_5	A_1	299	8	2	293	2	85	294	4	54
	ω_6	A_1	532	18	48	370	1	327	452	1	744
	ω_7	B_2	582	74	5	423	3	46	516	20	74
	ω_8	B_2	2166	547	118	1934	0	205	2034	190	65
	ω_9	A_1	2185	97	285	1936	8.8	602	2045	18	623

Table S6 Harmonic vibrational frequencies (cm^{-1}), infrared intensities (IR) (km mol^{-1}), Raman scattering activities ($Å^4$ amu^{-1}) for the $^1A'$ ground state of Cyc_exo_CCN, $^2A''$ ground state of the Cyc_exo_CCN^- anion and $^2A'$ ground state of the Cyc_exo_CCN^+ cation.

Cyc_exo_CCN			BH&HLYP			BLYP			B3LYP		
C_s		Sym.	Freq	IR	Raman	Freq	IR	Raman	Freq	IR	Raman
	ω_1	A'	164	6	3	145	4	4	153	5	4
	ω_2	A″	215	9	1	196	8	1	205	8	1
	ω_3	A'	422	22	20	382	17	24	401	20	22
	ω_4	A'	552	30	25	479	21	16	513	25	20
$^1A'$	ω_5	A″	555	1	6	507	1	3	528	1	4
	ω_6	A'	665	15	3	601	6	13	630	9	7
	ω_7	A'	1083	8	64	964	5	58	1019	6	65
	ω_8	A'	1657	10	48	1487	4	58	1568	6	57
	ω_9	A'	2427	6	362	2161	4	455	2283	5	423
	ω_1	A'	140	5	8	100	4	46	125	4	18
	ω_2	A″	219	11	45	203	9	88	210	10	68
	ω_3	A'	358	40	47	263	43	121	319	44	98
	ω_4	A'	419	59	200	354	31	295	382	38	243
$^2A''$	ω_5	A″	548	2	0	504	2	11	523	2	2
	ω_6	A'	665	11	18	603	3	26	631	6	25
	ω_7	A'	961	9	143	827	11	42	891	9	171
	ω_8	A'	1693	63	13	1524	53	68	1610	56	13
	ω_9	A'	2362	175	538	2095	175	495	2214	203	742
	ω_1	A'	115	7	4	107	3	11	112	5	7
	ω_2	A″	217	8	0	206	7	0	212	7	0
	ω_3	A'	311	3	73	252	1	61	281	1	73
	ω_4	A'	432	12	68	389	8	12	406	9	26
$^2A'$	ω_5	A″	525	0	5	494	0	2	509	0	3
	ω_6	A'	590	58	46	523	49	34	555	55	42
	ω_7	A'	907	15	98	840	4	18	870	9	43
	ω_8	A'	1923	19	27	1778	10	23	1851	15	26
	ω_9	A'	2403	73	471	2142	77	485	2263	80	511

Table S7 Harmonic vibrational frequencies (cm^{-1}), infrared intensities (IR) (km mol^{-1}), Raman scattering activities ($Å^4$ amu^{-1}) for the $^1A'$ ground state of Cyc_exo_CNC, $^2A''$ ground state of the $Cyc\_exo\_CNC^-$ anion and $^2A'$ ground state of the $Cyc\_exo\_CNC^+$ cation.

Cyc_exo_CNC C_s		Sym.	BH&HLYP Freq	BH&HLYP IR	BH&HLYP Raman	BLYP Freq	BLYP IR	BLYP Raman	B3LYP Freq	B3LYP IR	B3LYP Raman
	ω_1	A'	175	6	4	159	4	5	167	5	5
	ω_2	A″	219	4	1	207	5	1	213	5	1
	ω_3	A'	387	22	14	355	17	17	371	19	15
	ω_4	A″	504	1	4	475	23	20	490	0	3
$^1A'$	ω_5	A'	547	31	27	477	0	2	510	27	23
	ω_6	A'	690	28	5	624	15	15	654	19	9
	ω_7	A'	1145	47	81	1014	27	91	1076	35	90
	ω_8	A'	1661	42	60	1481	24	76	1567	31	72
	ω_9	A'	2269	446	418	2024	248	559	2139	330	505
	ω_1	A'	150	5	12	129	3	53	139	4	26
	ω_2	A″	220	9	49	209	8	88	215	9	69
	ω_3	A'	334	24	39	286	29	203	312	25	95
	ω_4	A'	415	89	277	346	52	353	378	67	344
$^2A''$	ω_5	A″	491	0	4	470	0	7	481	0	5
	ω_6	A'	660	12	14	606	5	11	632	7.8	15
	ω_7	A'	976	63	347	823	52	578	896	47	499
	ω_8	A'	1705	28	65	1521	18	118	1614	20	85
	ω_9	A'	2268	144	938	2006	31	1298	2126	64	1239
	ω_1	A'	131	6	4	125	2	14	130	4	9
	ω_2	A″	228	2	0	221	2	0	226	2	0
	ω_3	A'	290	4	41	249	0	51	273	1	57
	ω_4	A'	438	3	128	390	4	36	406	4	63
$^2A'$	ω_5	A″	490	3	3	477	1	2	485	2	2
	ω_6	A'	656	123	62	578	103	54	615	116	63
	ω_7	A'	1014	42	127	914	11	23	959	25	54
	ω_8	A'	1889	5	20	1743	15	10	1818	8	9
	ω_9	A'	2191	1107	584	1968	626	546	2076	845	608

Table S8 Dipole moment (Debye) for the ground state $Ge(CN)_2$, CNGeCN, $Ge(NC)_2$ Cyclic_exo_CCN and Cyclic_exo_CNC isomers.

	Neutral	**Anion**	**Cation**	**Triplet**
		$Ge(CN)_2$		
B3LYP	4.54	4.16	3.35	3.45
BLYP	4.49	4.27	3.26	3.39
BHLYP	4.61	4.05	3.55	3.61
MP2	4.30	4.19	3.60	4.41
		CNGeCN		
B3LYP	4.19	4.00	3.13	3.27
BLYP	4.20	4.15	2.97	3.19
BHLYP	4.17	3.82	3.26	3.38
MP2	4.17	3.75	3.20	3.95
		$Ge(NC)_2$		
B3LYP	4.40	4.65	2.16	3.41
BLYP	4.52	4.90	1.78	3.09
BHLYP	4.22	4.34	2.96	3.49
MP2	4.64	4.69	2.93	3.31
		Cyc_exo_CCN		
B3LYP	4.57	2.17	3.76	-
BLYP	4.47	2.18	3.49	-
BHLYP	4.73	2.11	4.17	-
MP2	3.99	8.31	-	-
		Cyc_exo_CNC		
B3LYP	4.24	2.30	2.68	-
BLYP	4.26	2.45	2.57	-
BHLYP	4.23	2.16	2.87	-
MP2	4.10	8.01	2.36	-

Table S9 Rotational constants (MHz) for the ground state $Ge(CN)_2$, CNGeCN, $Ge(NC)_2$, Cyc_exo_CCN and Cyc_exo_CNC.

	B3LYP											
	Neutral			**Anion**			**Cation**			**Triplet**		
	A	**B**	**C**	**A**	**B**	**C**	**A**	**B**	**C**	**A**	**B**	**C**
Ge$(CN)_2$	5.274	2.372	1.636	5.177	2.292	1.589	9.028	1.975	1.620	9.698	1.926	1.607
CN**Ge**CN	5.711	2.481	1.730	5.366	2.399	1.658	7.941	2.214	1.731	9.333	2.084	1.704
Ge$(NC)_2$	6.041	2.669	1.851	5.475	2.565	1.747	6.291	2.612	1.846	8.865	2.272	1.808
Cyc_exo_CCN	16.734	1.637	1.491	14.867	1.585	1.432	15.299	1.525	1.387	-	-	-
Cyc_exo_CNC	17.504	1.744	1.586	14.940	1.692	1.520	17.178	1.599	1.463	-	-	-
	BLYP											
Ge$(CN)_2$	5.247	2.304	1.601	5.212	2.216	1.555	7.377	2.029	1.591	9.138	1.906	1.577
CN**Ge**CN	5.635	2.412	1.689	5.354	2.322	1.620	6.038	2.348	1.690	7.991	2.108	1.668
Ge$(NC)_2$	5.898	2.600	1.804	5.422	2.483	1.703	5.599	2.626	1.788	6.829	2.374	1.762
Cyc_exo_CCN	15.818	1.616	1.466	13.432	1.583	1.416	14.799	1.488	1.352	-	-	-
Cyc_exo_CNC	16.692	1.713	1.554	13.763	1.677	1.495	16.711	1.554	1.422	-	-	-
	BH&HLYP											
Ge$(CN)_2$	5.292	2.438	1.669	5.121	2.365	1.618	10.077	1.976	1.652	9.776	1.965	1.636
CN**Ge**CN	5.764	2.552	1.769	5.347	2.476	1.692	10.353	2.130	1.767	9.828	2.113	1.739
Ge$(NC)_2$	6.165	2.740	1.897	5.501	2.646	1.787	11.070	2.287	1.895	9.996	2.274	1.852
Cyc_exo_CCN	17.830	1.657	1.516	16.193	1.597	1.453	16.295	1.549	1.415	-	-	-
Cyc_exo_CNC	18.465	1.772	1.617	16.158	1.709	1.545	18.198	1.632	1.497	-	-	-
	MP2											
Ge$(CN)_2$	5.196	2.394	1.639	4.806	2.368	1.586	8.467	2.030	1.638	6.998	2.101	1.616
CN**Ge**CN	5.580	2.525	1.738	5.005	2.480	1.658	10.229	2.089	1.735	7.937	2.179	1.710
Ge$(NC)_2$	5.867	2.731	1.863	5.152	2.650	1.750	11.162	2.229	1.858	9.181	2.266	1.818
Cyc_exo_CCN	16.625	1.623	1.4789	17.603	1.572	1.443	-	-	-	-	-	-
Cyc_exo_CNC	17.060	1.740	1.500	17.856	1.681	1.536	15.376	1.623	1.468	-	-	-

Table S10 Theoretical harmonic vibrational frequencies (cm^{-1}) for the transition state structures, and zero-point vibrational energy (ZPVE in kcal mol^{-1}) at the B3LYP functional.

Species	state	ω_1	ω_2	ω_3	ω_4	ω_5	ω_6	ω_7	ω_8	ω_9	ZPVE
TS_1a_S	^{1}A	***309i***	66	110	177	306	386	452	2078	2229	8.296
TS_1b_S	^{1}A	***285i***	144	244	438	494	570	701	1698	2025	9.026
TS_1c_S	^{1}A	***225i***	205	309	442	494	521	795	1590	2049	9.156
TS_2a_S	^{1}A	***298i***	96	125	201	276	382	488	2078	2086	8.194
TS_2b_S	^{1}A	***482i***	132	173	191	254	409	762	1788	1976	8.127
TS_2c_S	^{1}A	***335i***	124	183	349	445	575	695	1295	1986	8.080
TS_1a_T	^{3}A	***246i***	101	132	287	303	464	538	1980	2166	8.536
TS_1a_□	^{3}A	***202i***	76	126	287	310	465	552	1897	2166	8.403
TS_2a_T	^{3}A	***275i***	107	132	261	267	463	527	1979	2035	8.251
TS_2a_□	^{3}A	***232i***	74	136	266	272	468	537	1899	2033	8.126

Table S11 Theoretical activation energies + ZPVE, the Gibbs free energy ΔG (in parentheses) and enthalpies of the reactions, ΔH (kcal mol^{-1}) at 298 K.

	Activation energies, E_a			
	B3LYP	**BLYP**	**BHLYP**	**MP2**
R1a_S	17.5 (17.1)	17.7 (17.2)	17.3 (16.9)	19.8 (19.6)
R1b_S	67.6 (68.3)	60.5 (61.4)	77.6 (78.1)	77.9 (78.8)
R1c_S	32.5 (32.8)	28.5 (28.7)	38.5 (38.8)	36.7 (37.0)
R2a_S	15.6 (15.9)	15.9 (16.1)	15.5 (15.7)	17.7 (18.0)
R2b_S	79.3 (79.8)	72.1 (72.6)	89.3 (89.5)	85.2 (85.7)
R2c_S	42.5 (42.3)	38.9 (38.7)	44.5 (44.2)	48.0 (47.7)
R1a_T	22.5 (22.2)	20.9 (20.6)	24.3 (23.9)	18.2 (18.2)
R1a_□	20.9 (20.5)	21.0 (20.5)	19.9 (19.6)	16.3 (15.9)
R2a_T	22.2 (22.3)	19.9 (20.0)	24.4 (24.4)	19.5 (19.9)
R2a_□	20.6 (20.6)	19.6 (19.4)	19.7 (19.8)	17.9 (17.9)
	Enthalpies of reaction, ΔH			
R1a_S	2.3	3.3	0.3	7.0
R1b_S	14.5	13.7	17.2	18.6
R1c_S	–12.2	–10.4	–16.9	–11.5
R2a_S	1.0	2.1	–1.1	5.2
R2b_S	27.5	26.5	30.9	32.0
R2c_S	–26.5	–24.4	–32.0	–26.7
R1a_T	10.5	9.9	9.2	6.8
R1a_□	10.5	9.9	9.2	6.8
R2a_T	10.6	8.4	9.8	8.8
R2a_□	10.6	8.4	9.8	8.8

Table S12 The theoretical rate constants k (s^{-1}) in the temperature range of 220 – 2500 K including zero-point vibrational corrections using equation [14].

	Rate constant k (s^{-1})									
T	**R1a_S**	**R1b_S**	**R1c_S**	**R2a_S**	**R2b_S**	**R2c_S**	**R1a_T**	**R1a_□**	**R2a_T**	**R2a_□**
(K)	**TS1a_S**	**TS1b_S**	**TS1c_S**	**TS2a_S**	**TS2b_S**	**TS2c_S**	**TS1a_T**	**TS1a_□**	**TS2a_T**	**TS2a_□**
220	4.7×10^{-5}	9.5×10^{-56}	5.5×10^{-20}	1.1×10^{-3}	7.5×10^{-67}	6.6×10^{-29}	4.1×10^{-10}	2.4×10^{-8}	4.4×10^{-10}	2.5×10^{-8}
250	6.6×10^{-3}	1.3×10^{-47}	4.0×10^{-16}	9.6×10^{-2}	2.3×10^{-57}	6.2×10^{-24}	2.3×10^{-7}	8.4×10^{-6}	2.3×10^{-7}	8.1×10^{-6}
300	2.9	1.2×10^{-37}	2.2×10^{-11}	2.2×10	9.1×10^{-46}	7.7×10^{-18}	5.4×10^{-4}	1.1×10^{-2}	4.7×10^{-4}	9.8×10^{-3}
400	6.2×10^{3}	2.9×10^{-25}	1.9×10^{-5}	2.1×10^{4}	2.9×10^{-31}	3.5×10^{-10}	9.2	9.8×10	7.0	7.3×10
700	1.3×10^{8}	2.0×10^{-9}	9.6×10^{2}	1.5×10^{8}	1.3×10^{-12}	3.13	2.7×10^{6}	1.2×10^{7}	1.7×10^{6}	7.4×10^{6}
1000	7.2×10^{9}	4.1×10^{-3}	1.2×10^{6}	5.5×10^{9}	3.7×10^{-5}	3.4×10^{4}	4.3×10^{8}	1.3×10^{9}	2.6×10^{8}	7.6×10^{8}
2100	1.0×10^{12}	2.1×10^{5}	8.8×10^{9}	4.6×10^{11}	5.2×10^{4}	3.6×10^{9}	2.2×10^{11}	4.3×10^{11}	1.2×10^{11}	2.3×10^{11}
2500	2.1×10^{12}	2.9×10^{6}	3.2×10^{10}	8.9×10^{11}	1.1×10^{6}	2.0×10^{10}	5.5×10^{11}	1.0×10^{12}	3.0×10^{11}	5.4×10^{11}

Table S13 The theoretical rate constants k (s^{-1}) in the temperature range of 220 – 2500 K derived from Gibbs free energies using equation [15].

	Rate constant k (s^{-1})									
T	**R1a_S**	**R1b_S**	**R1c_S**	**R2a_S**	**R2b_S**	**R2c_S**	**R1a_T**	**R1a_□**	**R2a_T**	**R2a_□**
(K)	**TS1a_S**	**TS1b_S**	**TS1c_S**	**TS2a_S**	**TS2b_S**	**TS2c_S**	**TS1a_T**	**TS1a_□**	**TS2a_T**	**TS2a_□**
220	4.4×10^{-5}	2.7×10^{-56}	3.9×10^{-20}	9.4×10^{-4}	5.0×10^{-67}	7.7×10^{-29}	3.6×10^{-10}	2.2×10^{-8}	3.9×10^{-10}	2.3×10^{-8}
250	6.0×10^{-3}	3.6×10^{-48}	2.9×10^{-16}	7.6×10^{-2}	1.4×10^{-57}	7.1×10^{-24}	1.9×10^{-7}	7.4×10^{-6}	1.9×10^{-7}	7.1×10^{-6}
300	2.4	2.9×10^{-38}	1.5×10^{-11}	1.6×10	5.3×10^{-46}	8.6×10^{-18}	4.1×10^{-4}	9.2×10^{-3}	3.7×10^{-4}	7.9×10^{-3}
400	4.5×10^{3}	7.1×10^{-26}	1.3×10^{-5}	1.4×10^{4}	1.5×10^{-31}	3.7×10^{-10}	6.2	6.8×10	4.8	5.1×10
700	7.5×10^{7}	5.6×10^{-10}	5.8×10^{2}	8.4×10^{7}	6.1×10^{-13}	2.7	1.5×10^{6}	6.7×10^{6}	9.8×10^{5}	4.2×10^{6}
1000	3.8×10^{9}	1.3×10^{-3}	7.0×10^{5}	2.8×10^{9}	1.7×10^{-5}	2.6×10^{4}	2.2×10^{8}	6.7×10^{8}	1.3×10^{8}	4.0×10^{8}
2100	4.6×10^{11}	7.8×10^{4}	4.3×10^{9}	2.1×10^{11}	2.3×10^{4}	2.1×10^{9}	9.9×10^{10}	2.0×10^{11}	5.5×10^{10}	1.1×10^{11}
2500	9.2×10^{11}	1.1×10^{6}	1.5×10^{10}	3.9×10^{11}	5.0×10^{5}	1.1×10^{10}	2.4×10^{11}	4.5×10^{11}	1.3×10^{11}	2.4×10^{11}