Conformer-specific Heavy-Atom Tunneling in the Rearrangement of Benzazirines to Ketenimines

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Supporting Information

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Analysis regarding presence of conformers

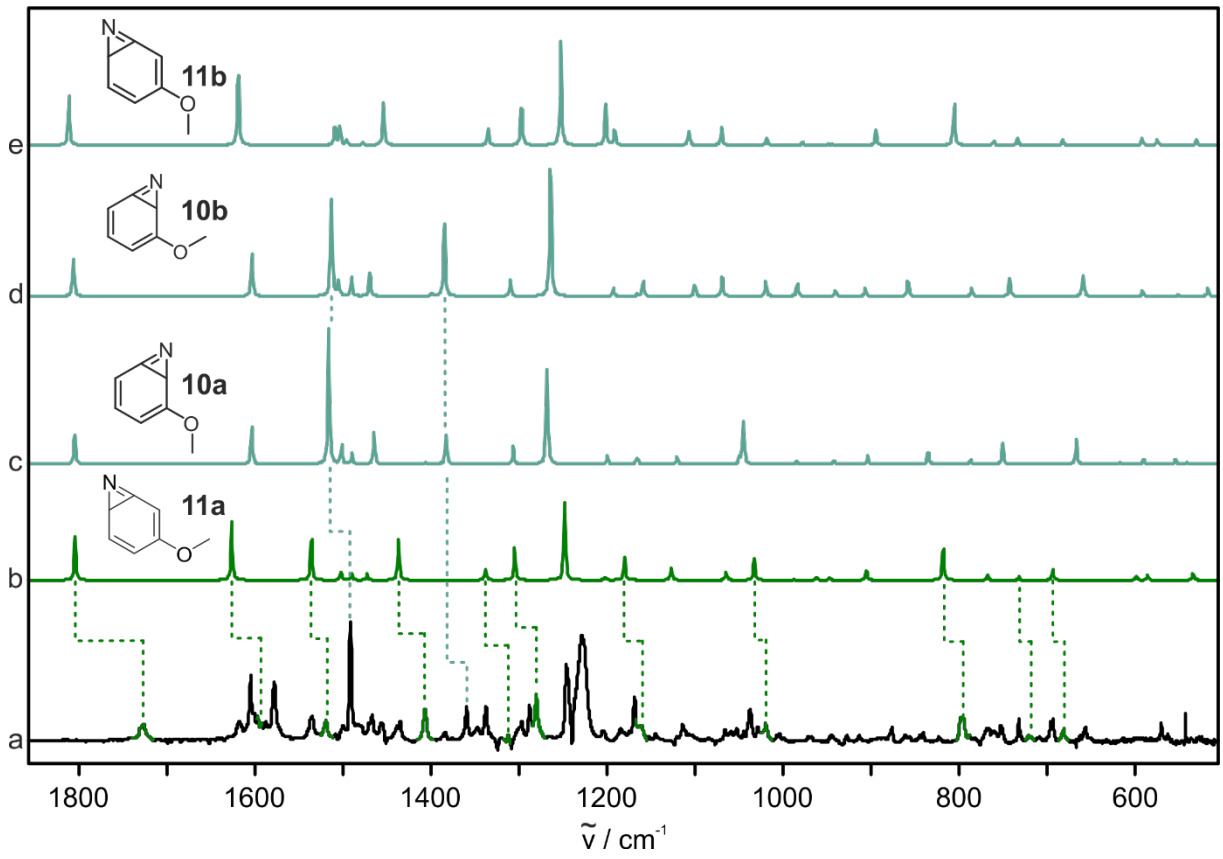


Figure S1. IR spectra highlighting the presence of different conformers of **10/11** in the matrix after initial photolysis of **8**. a) Experimental IR spectrum as recorded after photolysis of azide **8** with λ = 405 nm for 1 hr at 3 K in an argon matrix; for better comparison, residual intensities of **8** were removed from the spectrum via partial subtraction of the deposition spectrum. Peaks marked in green can be unanimously assigned to **11a** via the experimental difference spectrum recorded for the rearrangement **11a** → **13a**. b-e) Theoretical spectra of **10/11** at the B3LYP/6-311++G(d,p) level of theory. (It should be noted that H_2O residues could also contribute to the peak at ca. 1606 cm^{-1}.)

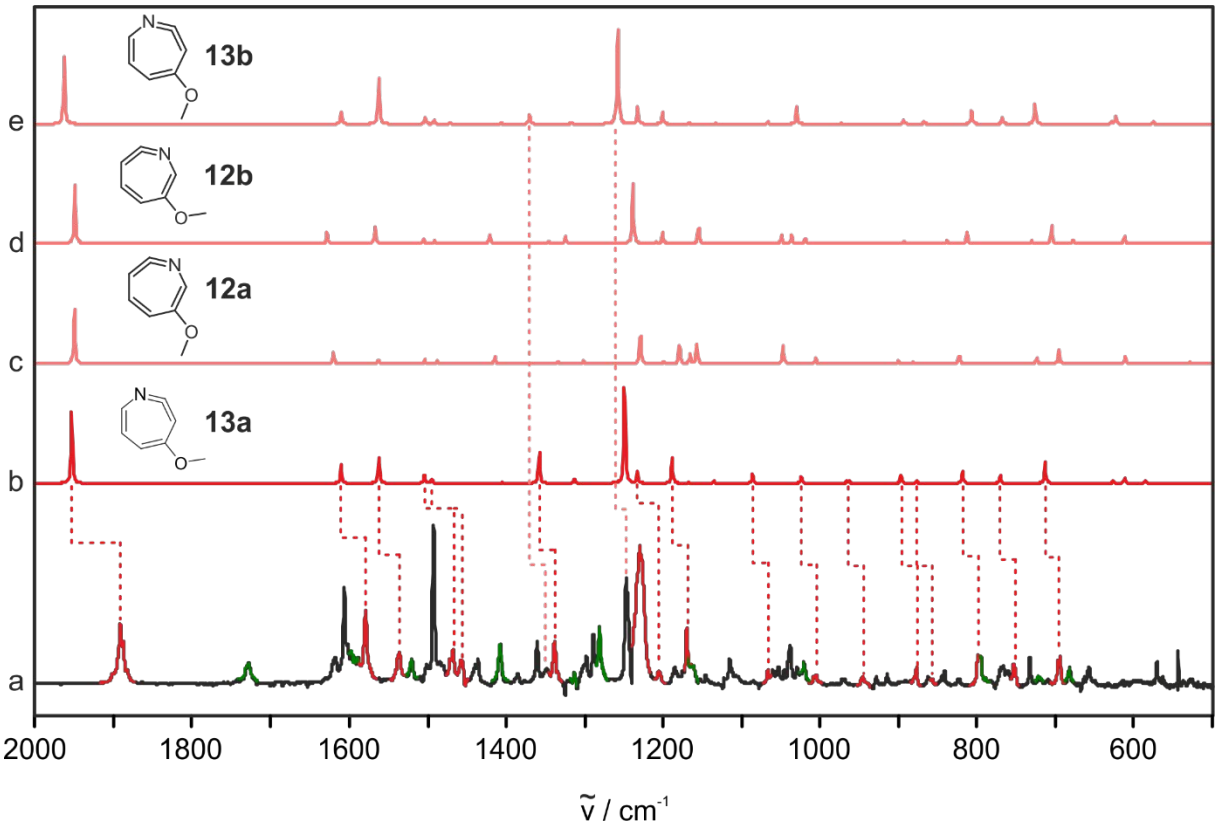
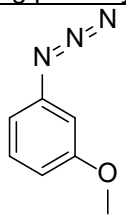
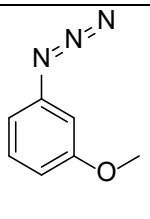
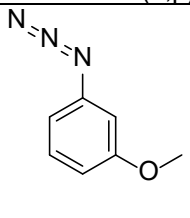
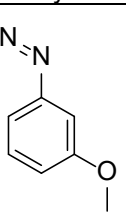
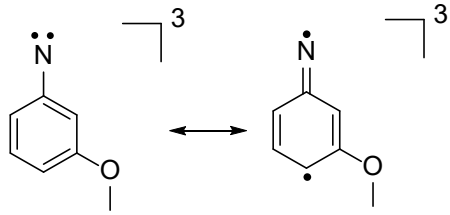
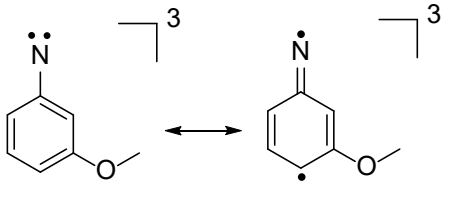
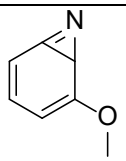
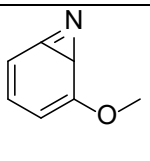
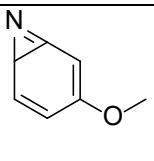
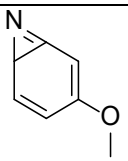
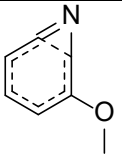
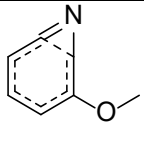
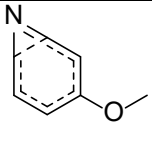
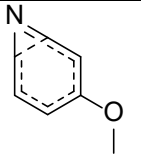
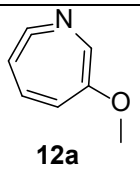
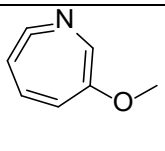
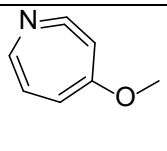
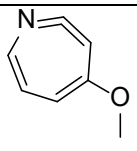


Figure S2. IR spectra highlighting the presence of different conformers of **12/13** in the matrix after initial photolysis of **8**. a) Experimental IR spectrum as recorded after photolysis of azide **8** with λ = 405 nm for 1 hr at 3 K in an argon matrix; for better comparison, residual intensities of **8** were removed from the spectrum via partial subtraction of the deposition spectrum. Peaks marked in green and red can be unanimously assigned to **11a** and **13a**, respectively, via the experimental difference spectrum recorded for the rearrangement **11a** → **13a**. b-e) Theoretical spectra of **12/13** at the B3LYP/6-311++G(d,p) level of theory.

Calculated energetic differences

Table S1. Relative energies of all species relevant to the photochemistry of azides **8a-d** as well as subsequent tunneling pathways, as calculated at the B3LYP/6-311++G(d,p) level of theory.

Azides	 **8a**	 **8b**	 **8c**	 **8d**
E_{rel} [kcal mol^{-1}]	0.2	0.3	0	0.2
μ_{tot} [D]	3.40	1.53	1.79	3.43
Triplet nitrenes	 **T-9a** **T-9a**		 **T-9b** **T-9b**	
E_{rel} [kcal mol^{-1}]	1.1		0	
μ_{tot} [D]	4.67		2.75	
Benzazirines	 **10a**	 **10b**	 **11a**	 **11b**
E_{rel} [kcal mol^{-1}]	0	1.1	1.5	5.0
μ_{tot} [D]	3.84	1.70	3.53	3.97
Transition states	 **TS(10a → 12a)**	 **TS(10b → 12b)**	 **TS(11a → 13a)**	 **TS(11b → 13b)**
E_{rel} [kcal mol^{-1}]	0.8	1.2	0	0.8
μ_{tot} [D]	3.44	1.81	2.95	3.16
Ketenimines	 **12a**	 **12b**	 **13a**	 **13b**

E_{rel} [kcal mol^{-1}]	7.1	5.3	1.1	0
μ_{tot} [D]	3.18	2.08	2.54	3.15

Kinetic Data

Table S2. Rate constants and (apparent) half-lives, as fitted to Equation (1) with β = 0.8, for the ring expansion of benzazirine **16** to ketenimine **17** in argon matrices.

T / K	k / 10^{-6} s^{-1}	τ_{app} / h	t_{final} / h
3	7.20 ± 0.07	24.4	48.0
8	4.70 ± 0.08	37.4	40.2
15	5.22 ± 0.03	33.7	56.0
20	5.71 ± 0.06	30.8	38.9

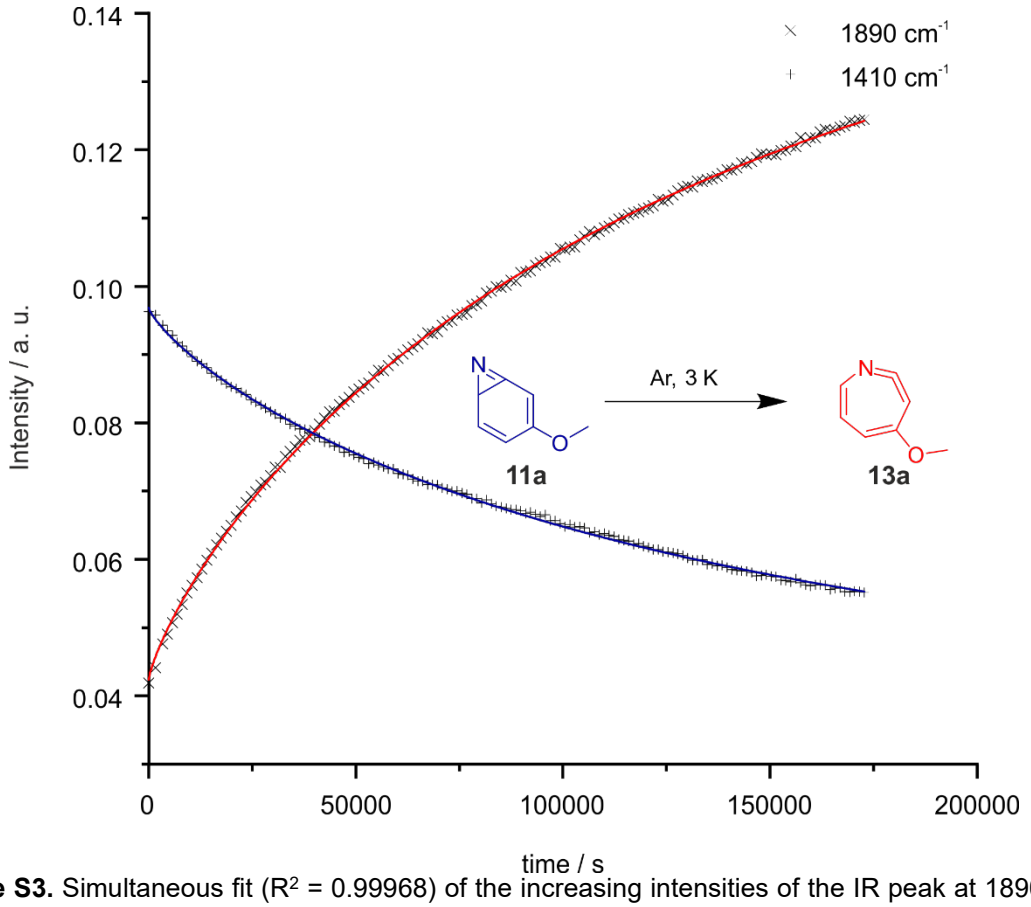


Figure S3. Simultaneous fit (R^2 = 0.99968) of the increasing intensities of the IR peak at 1890 cm^{-1} as well as the decreasing intensity of the IR peak at 1410 cm^{-1} to eq. 1 as recorded for an argon matrix at 3 K.

IR Spectroscopic Data

Table S3. IR spectroscopic data of **11a**.

Mode	Calculated[a] ν/cm^{-1} (I_{abs})	Argon[b] ν/cm^{-1} (I_{rel})	Assignment[c]
15	818.5 (57)	794.8 (30)	C-H wag.
20	1033.2 (35)	1020.8 (18)	C-O stretch.
24	1180.5 (45)	1160.6 (14)	C-H scis.
27	1305.1 (51)	1281.1 (16)	C-H rock.
28	1338.6 (20)	1311.1 (13)	C-H rock.
29	1437.2 (66)	1406.8 (77)	C-H rock.
30	1473.1 (10)	1440.7 (2)	C-H (CH_3) wag.
33	1536.5 (75)	1520.0 +	C=C stretch.
34	1626.8 (93)	1597.6 (55) 1587.2 (100)	C=C stretch.
35	1804.9 (66)	1729.1 (32)	C=N stretch.

[a] Calculated at B3LYP/6-311++G(d,p) level of theory. [b] Argon matrix at 3 K. [c] Tentative assignment.

Table S4. IR spectroscopic data of **10a/b** and **11b**, calculated at B3LYP/6-311++G(d,p) level of theory.

Mode	**10a** ν/cm^{-1} (I_{abs})	**10b** ν/cm^{-1} (I_{abs})	**11b** ν/cm^{-1} (I_{abs})
15	835.5 (22)	858.6 (28)	806.2 (66)
20	1045.6 (78)	1019.8 (23)	1018.7 (11)
24	1167.9 (4)	1165.9 (3)	1191.6 (26)
27	1306.8 (30)	1310.1 (26)	1297.5 (70)
28	1383.4 (52)	1385.3 (121)	1335.5 (31)
29	1406.3 (3)	1399.4 (4)	1454.4 (74)
30	1465.1 (49)	1469.7 (39)	1477.9 (3)
33	1516.6 (236)	1513.6 (177)	1509.5 (33)
34	1604.2 (59)	1603.8 (68)	1619.4 (126)
35	1805.4 (52)	1806.6 (66)	1812.0 (77)

Table S5. IR spectroscopic data of **13a**.

Mode	Calculated[a] ν/cm^{-1} (I_{abs})	Argon[b] ν/cm^{-1} (I_{rel})	Assignment[c]
13	713.0 (66)	695.3 (50)	C-H wag.
15	818.2 (39)	799.6 (14)	C-H wag.
17	896.7 (7)	876.9 (12)	C-H wag.
20	1023.6 (23)	1006.2 (13)	C-O stretch.
21	1085.7 (28)	1066.0 (13)	C-O stretch.
24	1188.1 (77)	1169.2 (49)	C-H (CH_3) wag.
25	1232.4 (41)	1224.1 (47)	C-H scis.
26	1248.6 (333)	1230.0 (16)	C-O stretch.
28	1357.2 (98)	1338.4 + 1347.7 (60)	C-C stretch.
31	1494.2 (14)	1457.9 (3)	C-H (CH_3) scis.
32	1503.5 (30)	1467.1 (6)	C-H (CH_3) scis.
33	1561.6 (89)	1535.2 (28)	C=C stretch.
34	1609.8 (58)	1578.8 (34)	C=C stretch.
35	1952.7 (229)	1889.0 (100)	C=C=N stretch.

[a] Calculated at B3LYP/6-311++G(d,p) level of theory. [b] Argon matrix at 3 K. [c] Tentative assignment.

Table S6. IR spectroscopic data of **12a/b** and **13b**, calculated at B3LYP/6-311++G(d,p) level of theory.

Mode	**12a** ν/cm^{-1} (I_{abs})	**12b** ν/cm^{-1} (I_{abs})	**13b** ν/cm^{-1} (I_{abs})
13	719.8 (1)	705.0 (53)	726.0 (62)
15	822.6 (28)	812.5 (41)	806.6 (46)
17	900.3 (10)	892.5 (5)	893.4 (14)
20	1026.4 (2)	1035.8 (29)	1029.8 (56)
21	1046.8 (55)	1048.7 (25)	1066.4 (7)
24	1178.7 (59)	1200.0 (34)	1200.1 (35)
25	1198.2 (5)	1208.8 (5)	1232.1 (52)
26	1228.5 (100)	1238.2 (185)	1257.4 (323)
28	1333.6 (7)	1345.6 (8)	1369.8 (31)
31	1487.6 (10)	1490.5 (10)	1491.2 (11)
32	1503.0 (13)	1504.4 (17)	1502.4 (23)
33	1562.4 (12)	1566.4 (55)	1561.7 (152)
34	1619.2 (36)	1627.7 (38)	1609.5 (45)
35	1949.3 (186)	1948.7 (190)	1962.3 (219)

Table S7. IR spectroscopic data of **16**.

Mode	Calculated[a] ν/cm^{-1} (I_{abs})	Argon[b] ν/cm^{-1} (I_{rel})	Assignment[c]
11	677.5 (8)	662.9 (6)	ring torsion
13	776.8 (34)	753.8 (19)	C–H rock.
14	860.5 (43)	846.4 (22)	C–H rock.
15	910.7 (20)	894.7 (13)	C–H rock.
17	976.6 (40)	966.0 (16)	ring def.
19	1088.1 (24)	1085.1 (8)	C–C stretch.
20	1135.1 (169)	1131.9 (88)	C–H bend.
23	1355.3 (52)	1340.2 (34)	C–H bend.
24	1408.4 (97)	1381.7 (67)	C–H bend.
25	1541.0 (150)	1535.1 (89)	C=C stretch.
26	1639.6 (154)	1618.1 (100)	C=C stretch.
27	1813.4 (59)	1734.8 (25)	C=N stretch.

[a] Calculated at the B3LYP/6-311++G(d,p) level of theory. [b] Argon matrix at 3 K. [c] Tentative assignment.

Table S8. IR spectroscopic data of **17**.

Mode	Calculated[a] ν/cm^{-1} (I_{abs})	Argon[b] ν/cm^{-1} (I_{rel})	Assignment[c]
10	598.6 (25)	585.2 (15)	ring torsion
13	742.0 (74)	720.2 (47)	C–H rock.
14	862.3 (46)	835.5 (32)	C–H rock.
16	920.4 (11)	907 (6)	ring def.
17	968.1 (29)	957.5 (15)	ring def.
18	1047.3 (41)	1034.6 (15)	C–H bend.
19	1122.1 (168)	1119.5 (81)	C–H bend.
21	1222.1 (148)	1213.8 (71)	C–F stretch.
22	1275.3 (20)	1251.4 (9)	C–H bend.
23	1338.8 (36)	1320.5 (34)	C–H bend.
24	1386.1 (47)	1365.9 (21)	C–H bend.
25	1584.6 (69)	1560 (20)	C=C stretch.
26	1640.4 (94)	1607.7 (45)	C=C stretch.
27	1949.9 (198)	1888.4 (100)	C=C=N stretch.

[a] Calculated at the B3LYP/6-311++G(d,p) level of theory. [b] Argon matrix at 3 K. [c] Tentative assignment.

Potential energy surfaces and IRCs

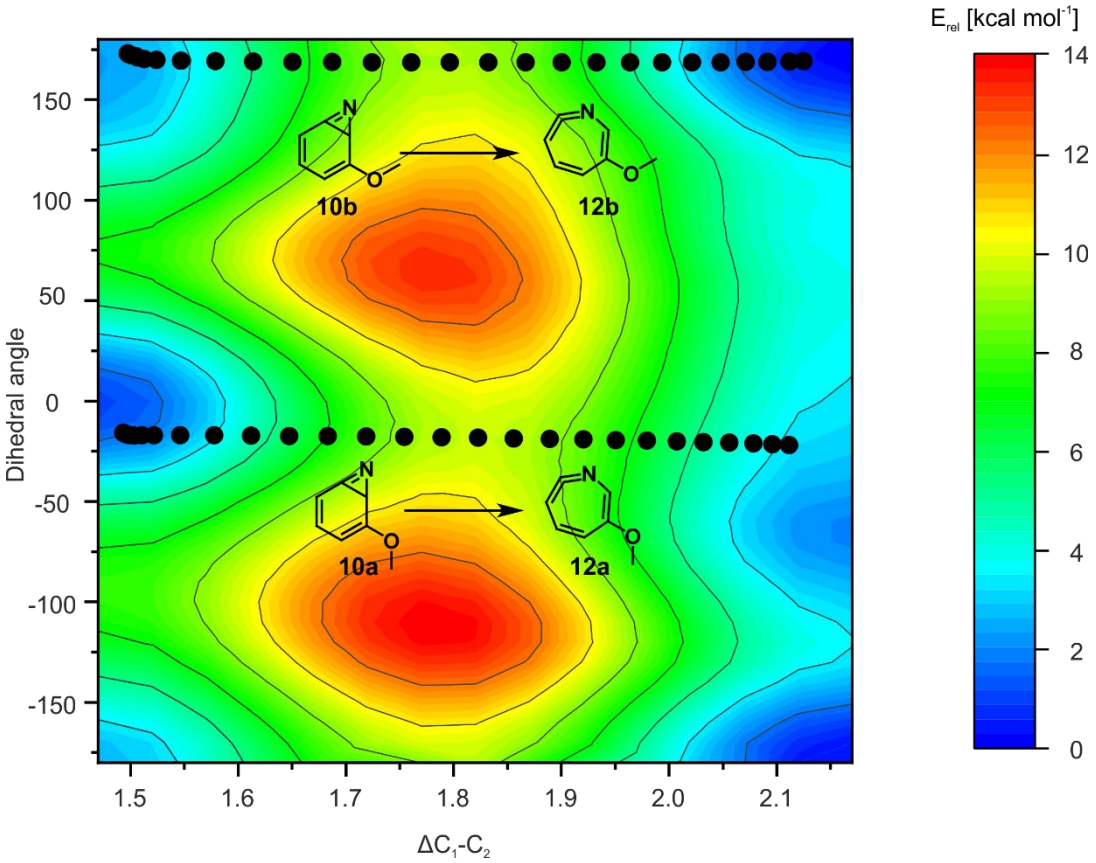


Figure S4. Heatmap depicting the potential energy surface for the ring expansions **10a/b** → **12a/b**.

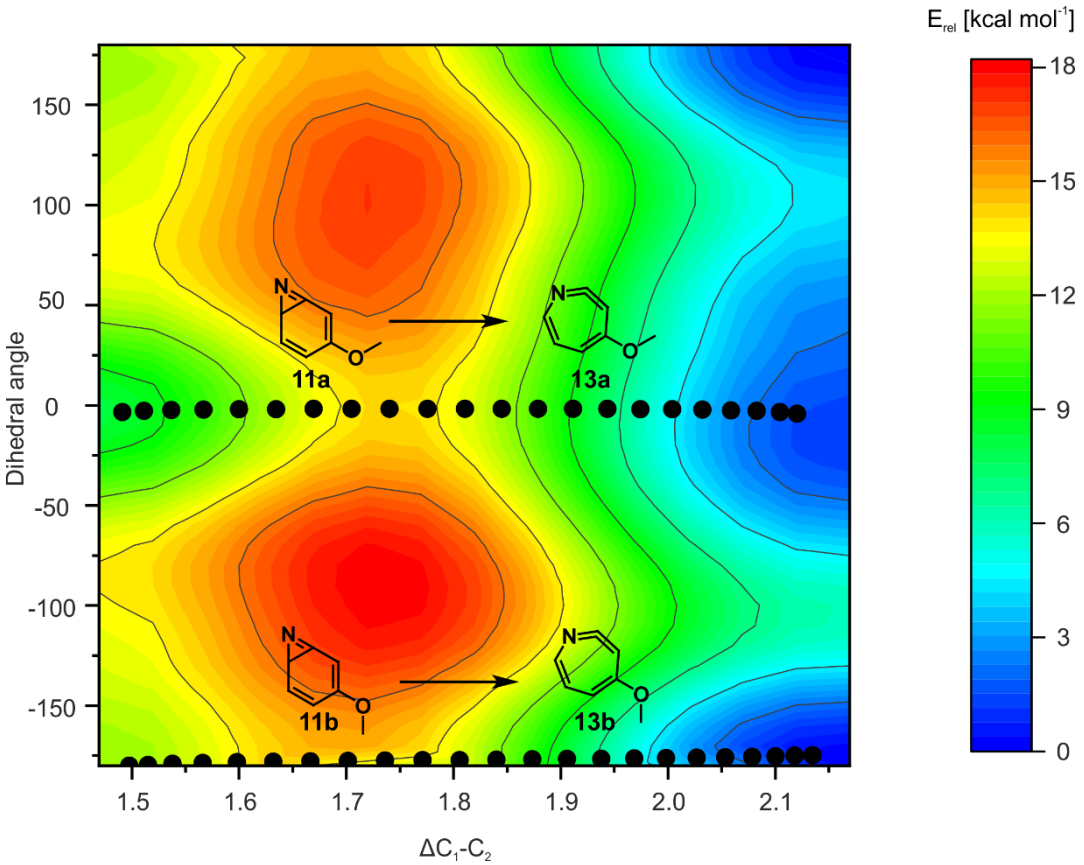


Figure S5. Heatmap depicting the potential energy surface for the ring expansions **11a/b** → **13a/b**.

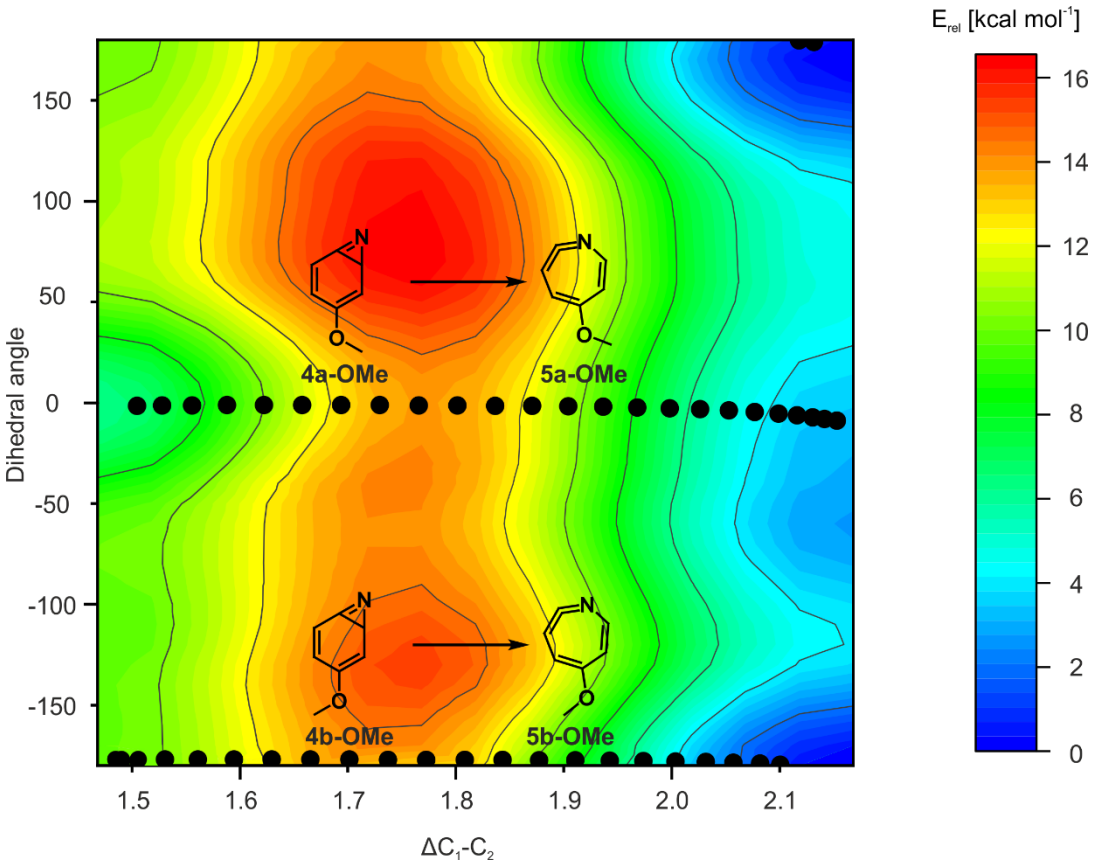


Figure S6. Heatmap depicting the potential energy surface for the ring expansions **4a/b-OMe** → **5a/b-OMe**.

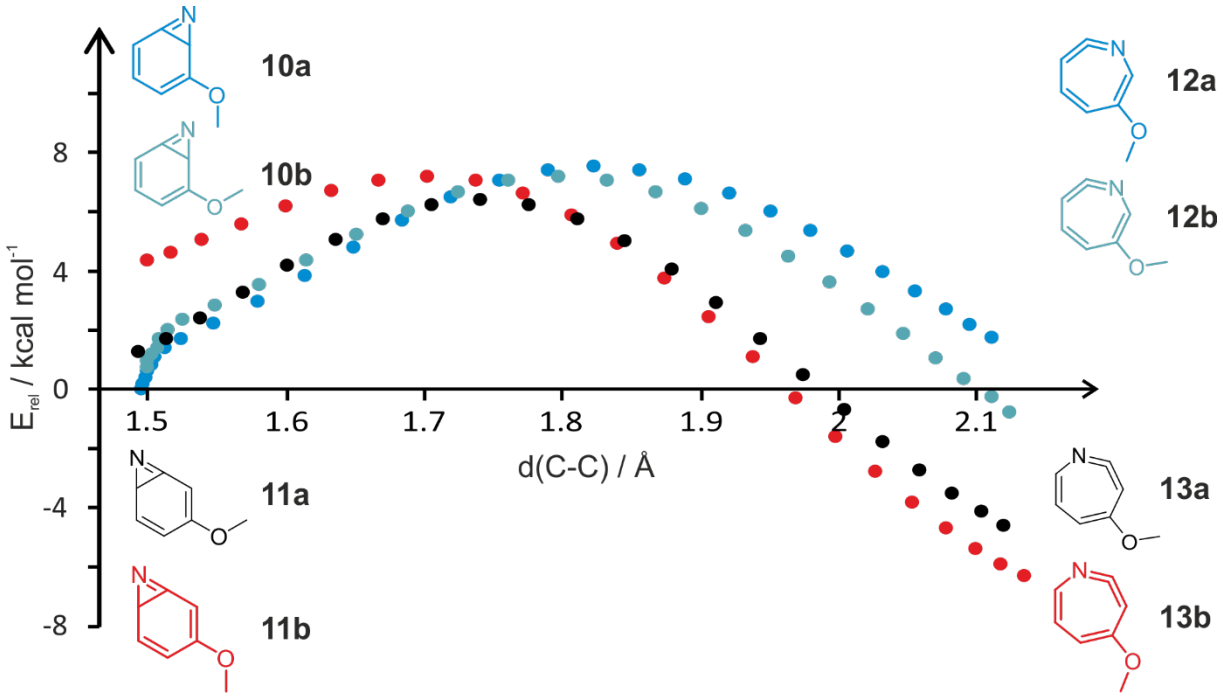


Figure S7. Alternative reaction coordinates along the C1-C2 distance for the ring expansions of benzazirines **10/11**, as calculated at the B3LYP/6-311++G(d,p) level of theory. All energies relative to the most stable benzazirine **10a**.

Optimized geometries at B3LYP/6-311++G(d,p) level of theory

Table S9. Cartesian coordinates of azide **8a**.

Atom	X	Y	Z
C	0.82155800	2.11872100	-0.00006300
C	-0.54930300	1.91139200	-0.00002500
C	-1.03491200	0.59773300	0.00009300
C	-0.15768100	-0.48370300	-0.00000500
C	1.22300000	-0.25591800	-0.00024400
C	1.72161900	1.04971300	-0.00015300
H	-1.24896500	2.73696100	0.00000200
H	-0.51058700	-1.50825200	0.00012900
H	2.78486200	1.24421700	-0.00008200
N	-2.44861500	0.45658200	0.00021900
N	-2.92944800	-0.67718700	0.00021900
N	-3.49797000	-1.65772600	-0.00024500
H	1.20707200	3.13192300	-0.00002800
O	1.99562600	-1.37856400	-0.00031600
C	3.41049800	-1.23326000	0.00034600
H	3.75676100	-0.70559500	0.89527700
H	3.81172400	-2.24522400	0.00025300
H	3.75768300	-0.70526200	-0.89406500
E = -510.49967083			

Table S10. Cartesian coordinates of azide **8b**.

Atom	X	Y	Z
C	0.92702600	-2.31804700	0.00004300
C	-0.44170000	-2.05287200	-0.00002800
C	-0.86966100	-0.72753100	-0.00004500
C	0.05208300	0.32952400	-0.00005700
C	1.41811800	0.04102700	-0.00006000
C	1.85814000	-1.28919000	0.00005200
H	-1.17435700	-2.84923100	-0.00001800
H	-0.29950400	1.35257800	-0.00005500
H	2.92278900	-1.48547400	0.00014000
N	-2.27619800	-0.52261600	-0.00004600
N	-2.70884800	0.62914000	0.00001000
N	-3.23428900	1.63449200	0.00008200
H	1.27001000	-3.34633200	0.00009400
O	2.39604500	0.98934500	0.00000900
C	2.02273600	2.36160000	0.00000400
H	1.44584500	2.61850200	0.89490600
H	2.95569600	2.92238800	0.00008200

H	1.44605600	2.61863200	-0.89500300
E = -510.49956608			

Table S11. Cartesian coordinates of azide **8c**.

Atom	X	Y	Z
C	-0.06555100	2.11575700	0.00011600
C	1.03230000	1.25336900	0.00001800
C	0.80195400	-0.12210300	-0.00008800
C	-0.50054700	-0.63604300	-0.00020000
C	-1.58223200	0.24336100	-0.00020300
C	-1.36358100	1.62850000	0.00003500
H	2.04055200	1.64994500	0.00012700
H	-0.62906900	-1.70887500	-0.00025200
H	-2.21897300	2.29207400	0.00013300
N	1.83706300	-1.09692800	-0.00012500
N	3.00726200	-0.71362200	0.00025500
N	4.11987800	-0.49684500	-0.00005800
H	0.10134200	3.18688200	0.00026200
O	-2.88549600	-0.15176400	-0.00022400
C	-3.17806400	-1.54389800	0.00029000
H	-2.78043400	-2.03449200	0.89500200
H	-4.26406800	-1.61811100	0.00026900
H	-2.78048400	-2.03520300	-0.89405500
E = -510.49995186			

Table S12. Cartesian coordinates of azide **8d**.

Atom	X	Y	Z
C	0.26322200	1.85787200	-0.00001400
C	-0.94920500	1.18166700	-0.00006400
C	-0.93792100	-0.22071300	-0.00005500
C	0.26381800	-0.92072700	-0.00005900
C	1.47492400	-0.22346600	-0.00007000
C	1.48103800	1.17544800	-0.00000600
H	-1.88294000	1.73124500	-0.00003500
H	0.26750400	-2.00280800	-0.00005900
H	2.40676100	1.73352700	0.00001300
N	-2.11608600	-1.01512200	-0.00016200
N	-3.20953600	-0.44940800	0.00010800
N	-4.27394200	-0.05919500	0.00012300
H	0.26640800	2.94201200	0.00004200
O	2.59464600	-0.99966300	0.00007800
C	3.86638300	-0.36327300	0.00005700
H	4.00431600	0.25322100	0.89462300

H	4.59973900	-1.16774000	0.00016900
H	4.00443700	0.25307400	-0.89459200
E = -510.49956758			

Table S13. Cartesian coordinates of triplet nitrene **T-9a**.

Atom	X	Y	Z
C	-0.68806100	-0.23063100	0.00004000
C	0.42904000	-1.05766600	0.00006400
C	1.73842200	-0.49543700	-0.00001200
C	1.88442800	0.93212600	-0.00001200
C	0.75700100	1.72341400	-0.00000900
C	-0.53180100	1.16490600	0.00001000
H	0.30387100	-2.13268300	0.00011800
H	2.88001000	1.35630500	-0.00003800
H	-1.39173400	1.82006000	0.00003900
N	2.80964700	-1.27853600	-0.00000800
H	0.85883500	2.80288500	-0.00002500
O	-1.89428200	-0.86465300	-0.00011700
C	-3.08274400	-0.08239100	0.00003700
H	-3.90473200	-0.79589900	-0.00018300
H	-3.14861200	0.54497300	0.89527500
H	-3.14861800	0.54540800	-0.89490300
E = -400.93752485			

Table S14. Cartesian coordinates of triplet nitrene **T-9b**.

Atom	X	Y	Z
C	0.72323600	0.35724300	-0.00005700
C	0.03230000	-0.84019600	-0.00002700
C	-1.40359200	-0.83174500	0.00000200
C	-2.09630500	0.42127600	-0.00001700
C	-1.36918000	1.59958700	0.00001900
C	0.02470700	1.58458200	0.00003200
H	0.53251900	-1.79799900	0.00001600
H	-3.17852900	0.41888600	-0.00000500
H	0.59870000	2.50274000	0.00010200
N	-2.07842800	-1.96867400	0.00001100
H	-1.88886400	2.55104400	0.00005800
O	2.07976700	0.46839900	-0.00007100
C	2.85884700	-0.72328600	0.00006400
H	3.89745300	-0.39800400	-0.00062800
H	2.66513500	-1.32354500	0.89505900
H	2.66437000	-1.32437100	-0.89421900

E = -400.93943311

Table S15. Cartesian coordinates of benzazirine **10a**.

Atom	X	Y	Z
C	0.60002000	-0.18913900	-0.02144500
C	0.24321700	1.12073000	0.20622300
C	-1.10639000	1.59955400	0.00674700
C	-2.17873700	0.78301500	-0.20848800
C	-1.76877500	-0.58289700	-0.10992000
C	-0.43584900	-1.15040100	-0.39363600
H	0.99517000	1.85894100	0.45010400
H	-3.19213400	1.12355500	-0.36403400
H	-0.24118200	-1.85354300	-1.19607800
N	-1.53185400	-1.56808000	0.63716700
H	-1.26558700	2.67157900	0.06493800
O	1.86370000	-0.65912800	-0.09420600
C	2.94862800	0.25715800	0.04075000
H	2.96165200	0.70384900	1.03949700
H	3.85326500	-0.32937000	-0.10699600
H	2.88951600	1.04645600	-0.71533800
E = -400.91427663			

Table S16. Cartesian coordinates of benzazirine **10b**.

Atom	X	Y	Z
C	0.55550700	-0.43040200	0.00448800
C	-0.37733200	-1.41359300	-0.22399100
C	-1.78633600	-1.21017300	-0.00950900
C	-2.34935600	0.01719000	0.21105700
C	-1.34913400	1.02923800	0.11305300
C	0.09720800	0.90209200	0.39761200
H	-0.02521400	-2.40759100	-0.47192800
H	-3.40346300	0.19494500	0.36624800
H	0.56999600	1.41822000	1.22675900
N	-0.67995800	1.81420800	-0.60893400
H	-2.43211000	-2.08041100	-0.06902000
O	1.86351400	-0.78309300	0.03383900
C	2.84538000	0.25903300	0.00189800
H	2.95475000	0.72859200	0.98325400
H	3.78239000	-0.22531000	-0.26844500
H	2.58962600	1.01653400	-0.74268800
E = -400.91229105			

Table S17. Cartesian coordinates of benzazirine **11a**.

Atom	X	Y	Z
C	-1.52325900	1.32899100	0.04814600
C	-0.18451000	1.38208300	-0.17918000
C	0.70624200	0.23465100	-0.01562900
C	0.23763500	-1.03746100	0.18673700
C	-1.18937000	-1.04005500	0.10920100
C	-2.12874700	0.04786700	0.41416700
H	-2.09636400	2.25131100	0.08608300
H	0.30623000	2.32222700	-0.40292200
H	0.84728900	-1.92276800	0.28402200
H	-2.85255200	-0.00389600	1.22017800
N	-2.21390000	-1.14142100	-0.61659300
O	2.01287600	0.57555400	-0.11584000
C	2.98889300	-0.44661800	0.06114100
H	2.88069200	-1.22577100	-0.70059900
H	3.95546500	0.04085600	-0.04888000
H	2.91222200	-0.89318800	1.05748500
E = -400.91166371			

Table S18. Cartesian coordinates of benzazirine **11b**.

Atom	X	Y	Z
C	1.01942600	1.48463000	-0.06342500
C	-0.26736200	1.06106600	0.11289900
C	-0.68322600	-0.32338200	-0.07833300
C	0.22746000	-1.33612200	-0.24341000
C	1.55109200	-0.84722900	-0.07787800
C	2.06291400	0.51494100	-0.35855300
H	1.21825300	2.55129100	-0.12738900
H	-1.03445600	1.80204100	0.29292900
H	-0.05705100	-2.36854700	-0.38783500
H	2.80687200	0.72517600	-1.11908200
N	2.50200700	-0.56381500	0.69640200
O	-1.99628800	-0.67833800	-0.09054700
C	-3.01127200	0.29490500	0.14131200
H	-3.95035100	-0.25419600	0.10145700
H	-2.90769300	0.75748400	1.12756200
H	-3.01351000	1.06730600	-0.63373900
E = -400.90591504			

Table S19. Cartesian coordinates of **TS(10a→ 12a)**.

Atom	X	Y	Z

C	0.57158000	-0.31613900	0.16120300
C	0.20235600	1.01429400	0.50218400
C	-0.99851100	1.59749900	0.10788300
C	-2.05872200	0.86426600	-0.46976100
C	-1.91917500	-0.45609600	-0.17194300
C	-0.31827900	-1.32763100	-0.18540500
H	0.96031100	1.66400300	0.92005200
H	-2.85069200	1.28432600	-1.07137300
H	-0.02222000	-2.13640100	-0.84309500
N	-1.63505700	-1.46006400	0.49541400
H	-1.11274100	2.67190200	0.22008800
O	1.88249700	-0.66981000	-0.00911500
C	2.85995600	0.34574700	-0.23350300
H	3.10069100	0.87912800	0.69098100
H	3.75074700	-0.17440600	-0.58343500
H	2.52409100	1.05873800	-0.99214600
E = -400.90029863 v^{TS} = -453.57 cm^{-1}			

Table S20. Cartesian coordinates of **TS(10b→ 12b)**.

Atom	X	Y	Z
C	-0.56598900	0.29265600	-0.10491000
C	0.36352200	1.32649200	-0.38944400
C	1.70030300	1.27003300	-0.01118200
C	2.32177100	0.09083000	0.45272900
C	1.57312500	-0.99270300	0.09851000
C	-0.22194400	-1.03484900	0.15307500
H	-0.05620700	2.27594000	-0.69842800
H	3.23784800	0.05152500	1.02228900
H	-0.80210000	-1.67591800	0.80509700
N	0.86664400	-1.71493800	-0.61836700
H	2.28647400	2.18379200	-0.04228100
O	-1.84043400	0.74326300	0.09285500
C	-2.90849500	-0.20193300	0.14149400
H	-2.95970600	-0.69602300	1.11653400
H	-3.82227100	0.37053800	-0.01355100
H	-2.80083500	-0.95454900	-0.64556800
E = -400.90083757 v^{TS} = -473.44 cm^{-1}			

Table S21. Cartesian coordinates of **TS(11a→ 13a)**.

Atom	X	Y	Z
C	-1.55137900	1.26538900	0.15079600

C	-0.20450800	1.33931700	-0.20986000
C	0.69636500	0.26494000	-0.04600300
C	0.26132900	-1.02990800	0.29686600
C	-1.07749600	-1.15478500	0.02123700
C	-2.26983600	0.07802500	0.31588000
H	-2.03474500	2.18368400	0.47833500
H	0.24272000	2.30718000	-0.40155800
H	0.86413800	-1.80456400	0.74459400
H	-3.09009300	-0.01123700	1.01888900
N	-2.12810400	-1.08934700	-0.62912000
O	2.00869800	0.59306500	-0.17976000
C	2.99107400	-0.40557300	0.07252700
H	2.83023100	-1.28425800	-0.56060900
H	3.94854400	0.05081200	-0.17204100
H	2.99306300	-0.70514100	1.12564600
E = -400.902122			
v^{TS} = -526.39 cm^{-1}			

Table S22. Cartesian coordinates of **TS(11b→ 13b)**.

Atom	X	Y	Z
C	-1.55137900	1.26538900	0.15079600
C	-0.20450800	1.33931700	-0.20986000
C	0.69636500	0.26494000	-0.04600300
C	0.26132900	-1.02990800	0.29686600
C	-1.07749600	-1.15478500	0.02123700
C	-2.26983600	0.07802500	0.31588000
H	-2.03474500	2.18368400	0.47833500
H	0.24272000	2.30718000	-0.40155800
H	0.86413800	-1.80456400	0.74459400
H	-3.09009300	-0.01123700	1.01888900
N	-2.12810400	-1.08934700	-0.62912000
O	2.00869800	0.59306500	-0.17976000
C	2.99107400	-0.40557300	0.07252700
H	2.83023100	-1.28425800	-0.56060900
H	3.94854400	0.05081200	-0.17204100
H	2.99306300	-0.70514100	1.12564600
E = -400.902122			
v^{TS} = -493.97 cm^{-1}			

Table S23. Cartesian coordinates of ketenimine **12a**.

Atom	X	Y	Z
C	-0.60992100	-0.29383900	-0.24596200
C	-0.04867600	1.01105900	-0.62053900
C	1.15617300	1.53046100	-0.27634900
C	2.06695400	0.77705300	0.60337700

C	1.97954200	-0.50323700	0.29896800
C	0.06639300	-1.45583600	-0.03657200
H	-0.70408500	1.60601700	-1.25109200
H	2.61630500	1.19963300	1.43215000
H	-0.46254500	-2.38454300	0.13919400
N	1.47585000	-1.51016800	-0.22434300
H	1.44746800	2.50370100	-0.66477200
O	-1.98535700	-0.39944100	-0.31322400
C	-2.71170900	0.42659300	0.59976600
H	-2.47376100	1.48657600	0.46328400
H	-3.76709700	0.26202200	0.38622500
H	-2.49691600	0.13977400	1.63506500
E = -400.91283412			

Table S24. Cartesian coordinates of ketenimine **12b**.

Atom	X	Y	Z
C	0.59277300	-0.20311500	-0.08661700
C	-0.38010900	-1.27326900	-0.36194900
C	-1.70783700	-1.28432400	-0.09942600
C	-2.35324300	-0.13141500	0.55271800
C	-1.78652100	0.97705800	0.11809300
C	0.37008300	1.14358100	-0.10871600
H	0.07358800	-2.15991400	-0.79383500
H	-3.07277300	-0.20551800	1.35531500
H	1.15627100	1.87533800	0.01035900
N	-0.91688800	1.64492600	-0.46301600
H	-2.29339600	-2.15991300	-0.37003500
O	1.83927500	-0.74624400	0.07266000
C	2.94896700	0.12390500	0.24847000
H	2.84029700	0.72863100	1.15530500
H	3.82067800	-0.52097300	0.34494300
H	3.07466800	0.78329700	-0.61765800
E = -400.91594259			

Table S25. Cartesian coordinates of ketenimine **13a**.

Atom	X	Y	Z
C	-1.65661400	1.17966400	0.24267200
C	-0.23560300	1.29925100	-0.01631900
C	0.70563100	0.30846100	0.04253300
C	0.32040200	-1.04788300	0.47472500
C	-0.86487700	-1.32807500	-0.03231400
C	-2.47310400	0.11119000	0.03835200
H	-2.15517900	2.09816100	0.53930300
H	0.12619500	2.28965000	-0.27458700

H	0.82634700	-1.62642100	1.23478700
H	-3.54203600	0.15903400	0.20724300
N	-1.97587600	-1.09488800	-0.53418300
O	1.97292800	0.61352500	-0.33979300
C	3.01959100	-0.29436000	0.00269200
H	3.91786900	0.09735800	-0.47084100
H	3.17005200	-0.33346100	1.08644500
H	2.81190100	-1.29778800	-0.37877200
E = -400.92279371			

Table S26. Cartesian coordinates of ketenimine **13b**.

Atom	X	Y	Z
C	-1.19930900	1.37352300	-0.30240500
C	0.19780500	1.00053600	-0.12414400
C	0.72306400	-0.26320300	-0.18151600
C	-0.14682600	-1.40891300	-0.47629500
C	-1.31024800	-1.23201500	0.11733600
C	-2.31764900	0.67551700	0.02084400
H	-1.36562800	2.38846500	-0.65267800
H	0.87302400	1.83370200	0.03183400
H	0.10667900	-2.18622000	-1.18295000
H	-3.31355500	1.08377200	-0.10125400
N	-2.22080700	-0.59372600	0.66630700
O	2.02836500	-0.58103000	-0.01711300
C	2.95460400	0.45206500	0.31163100
H	3.91995600	-0.03814800	0.42224500
H	3.01209600	1.19735500	-0.48804000
H	2.67751300	0.94033900	1.25089100
E = -400.92470003			

Table S27. Cartesian coordinates of 3,5-difluorophenyl azide.

Atom	X	Y	Z
C	0.89127800	1.34279400	-0.00001300
C	-0.41722000	0.88799900	-0.00006200
C	-0.63140100	-0.49571300	-0.00006500
C	0.44650800	-1.38621400	-0.00002100
C	1.72636900	-0.86138000	0.00002800
C	1.99254700	0.50078700	0.00003500
H	-1.23109200	1.60179700	-0.00010800
H	0.28376100	-2.45508300	-0.00002800
H	3.00295800	0.88479900	0.00007300
F	2.77129300	-1.71619000	0.00006300
F	1.10410600	2.67633500	-0.00001100

N	-1.91614200	-1.08737600	-0.00011800
N	-2.90476900	-0.34845900	-0.00007000
N	-3.89090400	0.20691200	0.00021300
E = -594.47755547			

Table S28. Cartesian coordinates of triplet 3,5-difluorophenyl nitrene.

Atom	X	Y	Z
C	1.19122900	-0.59619600	-0.00000100
C	1.23723000	0.77770400	0.00002100
C	-0.00002500	1.49881500	0.00002700
C	-1.23726200	0.77765400	-0.00001200
C	-1.19120400	-0.59623800	-0.00002900
C	0.00003000	-1.32214800	-0.00002200
H	2.18015200	1.30689800	-0.00000600
H	-2.18019700	1.30682200	-0.00004200
H	0.00004000	-2.40347400	-0.00002000
F	-2.34817200	-1.28991000	0.00002600
F	2.34823100	-1.28980900	0.00000100
N	-0.00007200	2.82423800	-0.00001200
E = -484.91482049			

Table S29. Cartesian coordinates of benzazirine **16**.

Atom	X	Y	Z
C	1.04231500	-0.67223200	-0.00456400
C	-0.22986800	-1.11259100	-0.19465700
C	-1.35020200	-0.23003400	0.02191600
C	-1.26276800	1.10894100	0.24214800
C	0.10375700	1.50213800	0.12200200
C	1.32407000	0.70023900	0.37205800
H	-0.43068600	-2.15261500	-0.41638100
H	-2.11164300	1.75976000	0.38934800
H	2.02628200	0.90156000	1.17366700
N	1.04798800	1.87527900	-0.62031600
F	-2.56052800	-0.81533100	-0.04528400
F	2.05122900	-1.56405000	0.02774600
E = -484.88817066			

Table S30. Cartesian coordinates of **TS**(**16** → **17**).

Atom	X	Y	Z
C	1.07184400	-0.61664600	-0.05411600
C	-0.22797000	-1.04728600	-0.33589000
C	-1.32747100	-0.25385700	-0.00980300

C	-1.25559700	1.07608300	0.41609100
C	-0.02343500	1.57563600	0.08728300
C	1.49223700	0.68582800	0.19546800
H	-0.39428400	-2.07967000	-0.61355000
H	-2.03954400	1.59566800	0.94584900
H	2.31672100	0.89227500	0.86760100
N	0.96922500	1.83625700	-0.60616300
F	1.98351500	-1.59033500	0.20061600
F	-2.54408400	-0.82973400	-0.06183300
E = -484.87910862 v^{TS} = -483.29 cm^{-1}			

Table S31. Cartesian coordinates of ketenimine **17**.

Atom	X	Y	Z
C	1.16510600	-0.50907700	0.03337000
C	-0.16891100	-1.03134200	-0.19654700
C	-1.31842100	-0.35196900	0.02811900
C	-1.35459200	1.00201500	0.56578400
C	-0.32128100	1.65623200	0.06746100
C	1.64181300	0.75527100	-0.07867000
H	-0.22585400	-2.05014100	-0.56348000
H	-2.00313800	1.32351400	1.36811400
H	2.69451100	0.97699300	0.03773600
N	0.77031300	1.79289000	-0.50445800
F	-2.49644800	-0.95086900	-0.24668500
F	2.08311500	-1.48550600	0.26576700
E = -484.89712495			

Table S32. Cartesian coordinates of parent benzazirine.

Atom	X	Y	Z
C	-0.02440500	1.46142600	0.05769400
C	1.20306800	0.92651000	-0.22236000
C	1.51310000	-0.47660400	-0.03383900
C	0.55776100	-1.41706600	0.21432800
C	-0.74521300	-0.83428300	0.11652800
C	-1.12084000	0.57602600	0.41309100
H	2.02596600	1.58702100	-0.47146500
H	0.75832100	-2.45511800	0.44111300
H	-1.82920700	0.83994500	1.18972000
N	-1.66774200	-0.44997300	-0.64298300
H	-0.13667000	2.53859500	0.14221000
H	2.55496000	-0.77668800	-0.07335000
E = -286.35163155			

Table S33. Cartesian coordinates of TS(parent benzazirine → parent ketenimine).

Atom	X	Y	Z
C	-0.26075800	1.41363300	0.12683800
C	1.04308500	1.06057900	-0.26076600
C	1.56293700	-0.22996200	-0.07678100
C	0.76867600	-1.32248500	0.29711000
C	-0.55401500	-1.05615700	0.04015700
C	-1.29155100	0.49886100	0.32866200
H	1.74235200	1.85677300	-0.48784900
H	1.13469000	-2.22861400	0.75715900
H	-2.08765600	0.65485800	1.04778900
N	-1.51540100	-0.64746400	-0.62405600
H	2.63709400	-0.37111400	-0.14473800
H	-0.42891200	2.43352400	0.46471500
E = -286.34524832 ν^{TS} = -479.23 cm^{-1}			

Table S34. Cartesian coordinates of parent ketenimine.

Atom	X	Y	Z
C	-0.78433900	1.20084500	0.23434200
C	0.61483700	1.31731400	-0.17586000
C	1.56773600	0.34975000	-0.14921700
C	1.24207500	-0.99748900	0.34939500
C	0.01971200	-1.31030400	-0.03496400
C	-1.59118500	0.11541000	0.14665700
H	0.91674300	2.30813700	-0.50484800
H	1.86575200	-1.57681500	1.01473900
H	-2.63704600	0.14354200	0.43151400
N	-1.12497600	-1.08953100	-0.46197100
H	2.57429000	0.57712100	-0.49225800
H	-1.25792400	2.12158100	0.56253800
E = -286.36220413			

Table S35. Cartesian coordinates of benzazirine **4a-OMe**.

Atom	X	Y	Z
C	-0.17743800	-1.00714400	0.25859400
C	-0.66389700	0.25481800	0.04587800
C	0.17237400	1.45094600	0.09347100
C	1.52741800	1.39894700	0.12276300
C	1.98370200	0.04179300	0.01288600
C	1.26390700	-1.16523000	0.43771600

H	2.16561200	2.26877600	0.20074600
H	1.65662600	-1.83074300	1.19804600
N	2.24502200	-0.90636000	-0.77333600
H	-0.34955100	2.40103500	0.09621000
H	-0.84495300	-1.84499500	0.41769200
O	-1.97813300	0.57455200	-0.13440400
C	-2.93137200	-0.48015100	-0.13751600
H	-2.97942700	-0.97448100	0.83869800
H	-3.89098200	-0.01500800	-0.35600700
H	-2.69558200	-1.22035000	-0.90954900

E = -400.785583

Table S36. Cartesian coordinates of benzazirine **4b-OMe**.

Atom	X	Y	Z
C	-0.30786800	-1.29087500	-0.23255300
C	0.63937600	-0.30363600	-0.13301200
C	0.31046100	1.10713500	-0.27011100
C	-0.97166800	1.56723200	-0.24765900
C	-1.89139200	0.50636300	0.02684700
C	-1.70730400	-0.92173000	-0.31917100
H	-1.24570500	2.59750700	-0.42932700
H	-2.38845000	-1.44820200	-0.97728100
N	-2.40679300	-0.22268300	0.91201100
H	1.11674600	1.81330800	-0.42405300
H	0.02517900	-2.31273100	-0.38171800
O	1.94919700	-0.70540100	-0.08365000
C	2.94341200	0.21236200	0.35634100
H	2.65452100	0.69639000	1.29488500
H	3.84232900	-0.38091100	0.51820800
H	3.15926300	0.97552300	-0.39968600

E = -400.780377

Table S37. Cartesian coordinates of **TS(4a-OMe → 5a-OMe)**.

Atom	X	Y	Z
C	0.16626400	-0.96344200	-0.37661300
C	0.62787200	0.32162000	-0.01782000
C	-0.19993900	1.45316200	-0.05960800
C	-1.59358200	1.37082800	-0.21266800
C	-2.04390400	0.12711900	0.12523800
C	-1.17309500	-1.34166900	-0.35099500
H	-2.21526400	2.17012800	-0.58940400
H	-1.58146900	-2.07442300	-1.03875900
N	-2.07798800	-0.93636900	0.76544300

H	0.28654900	2.42269000	-0.04991700
H	0.85202800	-1.62922000	-0.89038400
O	2.89294200	-0.46589400	0.14706000
C	3.83747600	-0.04286700	0.48677100
H	2.58162100	-1.26560100	0.82837400
H	3.03172200	-0.87948200	-0.85847000
H	1.96173700	0.60537700	0.15326400

E = -400.775326
v^{TS} = -522.22 cm^{-1}

Table S38. Cartesian coordinates of **TS(4b-OMe → 5b-OMe)**.

Atom	X	Y	Z
C	-0.33035900	-1.25425800	-0.30678100
C	0.62110200	-0.25773100	-0.01297300
C	0.32329800	1.11174500	-0.12954400
C	-0.99009400	1.58781300	-0.28247900
C	-1.90307600	0.63557900	0.08703700
C	-1.70576800	-1.03990300	-0.29448700
H	-1.24054800	2.55413200	-0.69555700
H	-2.38336200	-1.57547200	-0.95019800
N	-2.36769300	-0.26183200	0.80880500
H	1.13060100	1.83074200	-0.18755200
H	0.05270600	-2.17028900	-0.74686000
O	1.90144200	-0.73267300	0.13961900
C	2.98071000	0.18821700	0.15705200
H	3.87946400	-0.41103800	0.29485000
H	3.05791300	0.73968400	-0.78751700
H	2.89066300	0.89767500	0.98729400

E = -400.774852
v^{TS} = -505.39 cm^{-1}

Table S39. Cartesian coordinates of ketenimine **5a-OMe**.

Atom	X	Y	Z
C	0.07476900	0.97186800	0.64970000
C	0.60361600	-0.34777200	0.27868500
C	-0.11627000	-1.47397400	0.02124800
C	-1.58115600	-1.44010300	0.12240000
C	-2.02741600	-0.29329600	-0.35327200
C	-1.08497200	1.54903400	0.25621400
H	-2.18418400	-2.19441400	0.60803000
H	-1.36441100	2.54920700	0.56932600
N	-1.94773200	0.90478400	-0.67772100
H	0.41875700	-2.38205900	-0.24106500
H	0.73791700	1.57296200	1.26417300

O	1.97660900	-0.47132400	0.30999000
C	2.71027300	0.38543000	-0.56931900
H	2.49743900	1.44228500	-0.38013000
H	3.76395600	0.18881800	-0.37568400
H	2.47871600	0.15318200	-1.61445100
E = -400.791792			

Table S40. Cartesian coordinates of ketenimine **5b-OMe**.

Atom	X	Y	Z
C	-0.36666800	-1.24704100	-0.40991700
C	0.60542600	-0.17725600	-0.13554400
C	0.35781300	1.16445400	-0.07947000
C	-1.00335200	1.65143900	-0.35360600
C	-1.89143900	0.84537700	0.19428300
C	-1.67717600	-1.29294700	-0.07929900
H	-1.23552700	2.48327500	-1.00420500
H	-2.28023300	-2.17355800	-0.27181100
N	-2.30031500	-0.23970400	0.64429500
H	1.14598900	1.86387400	0.17462700
H	0.07326800	-2.14725000	-0.82549700
O	1.84420800	-0.72873000	0.03851400
C	2.95653100	0.13385900	0.23740500
H	2.85494500	0.70502100	1.16616000
H	3.82805900	-0.51504900	0.30431000
H	3.07522900	0.82414300	-0.60487900
E = -400.795457			