Supporting Information for

Exploring photochemistry of *p*-bromophenylsulfonyl, *p*-tolylsulfonyl and methylsulfonyl azides by ultrafast UV-pump – IR-probe spectroscopy and computations

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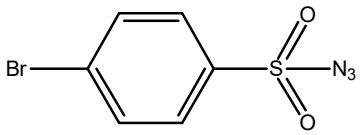
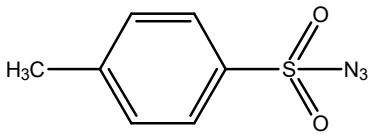
UV, FTIR, ^{1}H and ^{13}C NMR results

p-Bromobenzenesulfonyl azide (BsN_3).



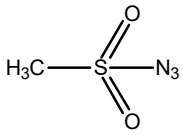
Yield 1.93 g, 7.83 mM (97%); light brown crystals. UV (EtOH) λ/nm: 278, 270, 266, 260, 241. IR (CCl_4), ν/cm^{-1}: 2955, 2127, 1576, 1473, 1392, 1387, 1190, 1176, 1089, 1069, 1012. ^{1}H NMR, δ: 7.77 (d, 2H, H2, H6), 7.81 (d, 2H, H3,H5) ppm. ^{13}C NMR, δ: 128.9 (C2, C6), 130.3 (C4), 133.1 (C3, C5), 137.5 (C1) ppm.

p-Toluenesulfonyl azide (TsN_3).



Yield 19.6 g, 99 mM (98%); colorless oil. UV (EtOH) λ/nm: 274, 266, 256, 236, 231. IR (CCl_4), ν/cm^{-1}: 2926, 2125, 1598, 1384, 1192, 1173, 1188. ^{1}H NMR, δ: 2.49 (s, 3H, CH_3), 7.42 (d, 2H, H2, H6), 7.85 (d, 2H, H3,H5) ppm. ^{13}C NMR, δ: 22.8 (CH_3), 128.6 (C2, C6), 131.3 (C3, C5), 136.6 (C1), 147.3 (C4) ppm.

Methanesulfonyl azide (MsN_3).



Yield 15.41 g, 127 mM (96%); colorless oil. UV (EtOH) λ/nm: 256, 211. IR (CCl_4), ν/cm^{-1}: 2936, 2136, 1376, 1325, 1200, 1174. ^{1}H NMR, δ: 3.26 (s, 3H, CH_3) ppm. ^{13}C NMR, δ: 43.8 (CH_3) ppm.

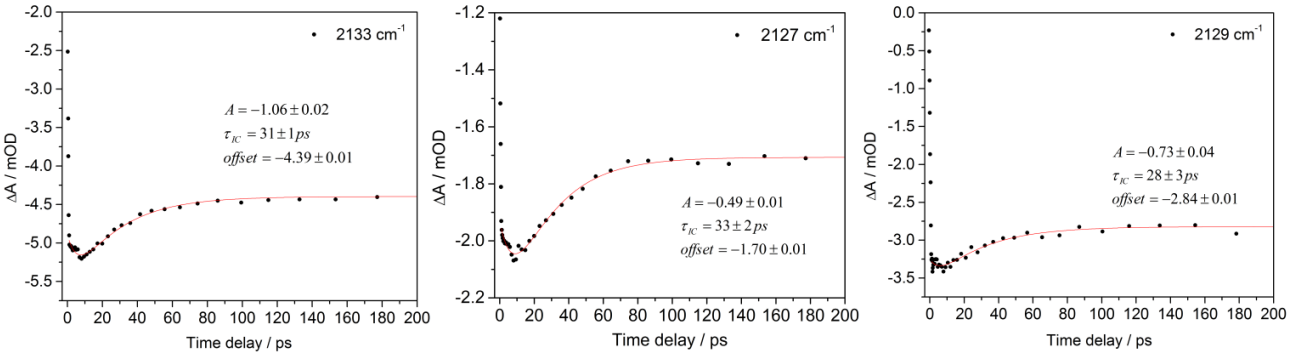


Figure S1. Transient kinetics of BsN_3 ground state recovery at 2133 cm^{-1} in CH_2Cl_2 (left) and of TsN_3 ground state recovery at 2127 cm^{-1} in CCl_4 (centre) and at 2129 cm^{-1} in CH_2Cl_2 (right).

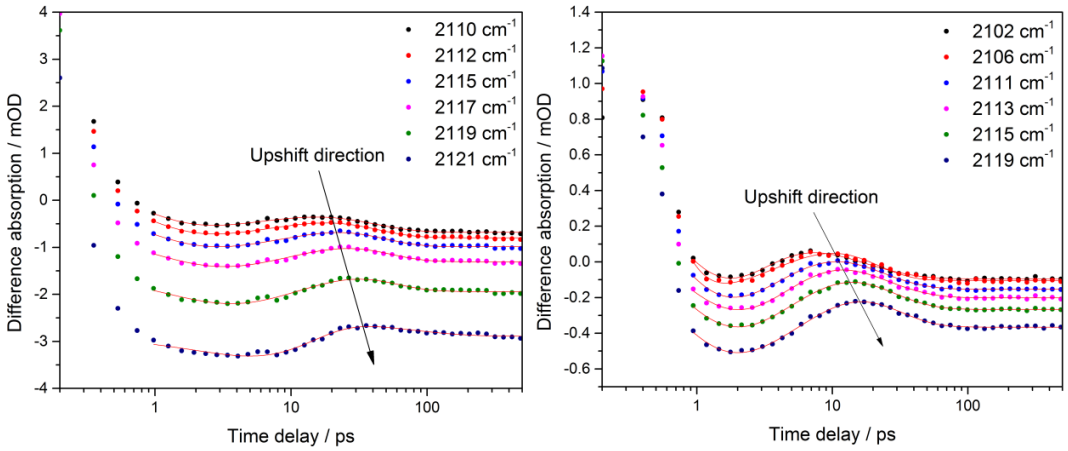


Figure S2. Vibrationally hot ground state in BsN_3 dissolved in CCl_4 (left) and in CH_2Cl_2 (right). The arrows indicate that the transient induced absorption continuously upshifts with increasing wavenumbers, which is interpreted as vibrational cooling. The red curves correspond to fits.

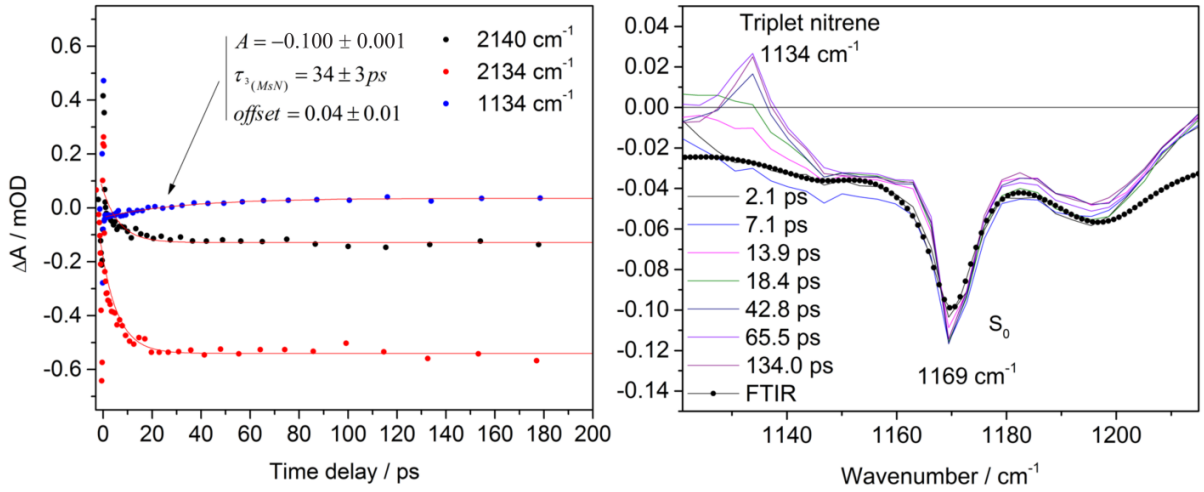


Figure S3. (left) Transient kinetics of MsN_3 ground state observed at 2134 cm^{-1} in CCl_4 and at 2140 cm^{-1} in CH_2Cl_2 and transient kinetics of ^{3}(MsN) at 1134 cm^{-1} observed in CH_2Cl_2. (right) Transient IR spectra in SO_2 sym. stretch regions produced upon MsN_3 photolysis in CH_2Cl_2 (λ_{ex} = 267 nm) at selected time delays.

Time trace fitting parameters

$$\Delta A = \sum_{n=1}^{n} A_n \exp(-t/\tau_n) + \text{ offset}$$

BsN_3, CCl_4

2110 cm^{-1}:

A_1 = 1.5±0.3; τ_1 = 1.0±0.1 ps; A_2 = -0.9±0.2; τ_2 = 9±2 ps; A_3 = 0.8±0.2; τ_3 = 28±4 ps; offset = -0.70±0.01;

2112 cm^{-1}:

A_1 = 1.5±0.3; τ_1 = 1.0±0.1 ps; A_2 = -1.8±2.1; τ_2 = 13±5 ps; A_3 = 1.7±2.2; τ_3 = 22±7 ps; offset = -0.80±0.01;

2115 cm^{-1}:

A_1 = 1.3±0.2; τ_1 = 1.0±0.2 ps; A_2 = -44.6±37.1; τ_2 = 18±17 ps; A_3 = 44.4±37.1; τ_3 = 18±16 ps; offset = -0.70±0.01;

2117 cm^{-1}:

A_1 = 1.1±0.1; τ_1 = 1.0±0.2 ps; A_2 = -52.6±60.2; τ_2 = 19±14 ps; A_3 = 52.3±60.2; τ_3 = 19±11 ps; offset = -1.30±0.01;

2119 cm^{-1}:

A_1 = 1.1±0.1; τ_1 = 2.0±0.3 ps; A_2 = -55.7±71.5; τ_2 = 20±19 ps; A_3 = 55.1±71.5; τ_3 = 21±20 ps; offset = -1.90±0.01;

2121 cm^{-1}:

A_1 = 88.1±142.8; τ_1 = 6±9 ps; A_2 = 0.4±0.1; τ_2 = 74±28 ps; A_3 = -88.5±142.8; τ_3 = 6±10 ps; offset = -2.90±0.02;

2128 cm^{-1}:

A_1 = 4.1±0.3; τ_1 = 4±1 ps; A_2 = -2.1±0.2; τ_2 = 45±2 ps; offset = -7.50±0.04;

1391 cm^{-1}:

A_1 = 88.8±129.3; τ_1 = 11±21 ps; A_2 = -1.7±0.1; τ_2 = 30±6 ps; offset = -6.5±0.4;

1365 cm^{-1}:

A_1 = 3.9±0.7; τ_1 = 0.2 ps; A_2 = -1.4±0.1; τ_2 = 18±2 ps; offset = -0.7±0.1;

1360 cm^{-1}:

A_1 = -3.4±0.1; τ_1 = 20±1 ps; A_2 = 1.7±0.1; τ_2 = 0.7±0.1 ns; offset = 0.2±0.1;

1347 cm^{-1}:

A_1 = -214.1; τ_1 = 14±17 ps; A_2 = 212.8±294.8; τ_2 = 15±18 ps; A_3 = -0.6±0.1; τ_3 = 0.70±0.23 ns; offset = 0.7±0.1;

1157 cm^{-1}:

A_1 = -0.5±0.1; τ_1 = 15±3 ps; A_2 = -1.7±0.1; τ_2 = 0.7±0.2 ns; offset = 0.4±0.1.

BsN_3, CH_2Cl_2

2102 cm^{-1}:

A_1 = 1.6±0.2; τ_1 = 1.0±0.1 ps; A_2 = -0.7±0.2; τ_2 = 7±0.4 ps; A_3 = 0.30±0.03; τ_3 = 15±1 ps; offset = -0.100±0.002;

2106 cm^{-1}:

A_1 = 4.1±2.2; τ_1 = 1.0±0.4 ps; A_2 = -1956.6±2725.3; τ_2 = 8.0±0.4 ps; A_3 = 1956.5±2725.3; τ_3 = 8±1 ps; offset = -0.100±0.001;

2111 cm^{-1}:

A_1 = 1.4±0.2; τ_1 = 1.0±0.4 ps; A_2 = -0.70±0.04; τ_2 = 4.0±0.4 ps; A_3 = 0.4±0.1; τ_3 = 16±1 ps; offset = -0.200±0.002;

2113 cm^{-1}:

A_1 = 1.0±0.1; τ_1 = 1.0±0.1 ps; A_2 = -0.8±0.1; τ_2 = 4±1 ps; A_3 = 0.4±0.1; τ_3 = 18±2 ps; offset = -0.200±0.002;

2115 cm^{-1}:

A_1 = 1.1±0.1; τ_1 = 1.0±0.1 ps; A_2 = -0.9±0.1; τ_2 = 6±1 ps; A_3 = 0.5±0.1; τ_3 = 17±2 ps; offset = -0.300±0.002;

2119 cm^{-1}:

A_1 = 1.1±0.2; τ_1 = 1 ps; A_2 = -1.2±0.5; τ_2 = 8±1 ps; A_3 = 0.8±0.5; τ_3 = 16±3 ps; offset = -0.40±0.02;

2133 cm^{-1}:

A_1 = 0.8±0.1; τ_1 = 6±1 ps; A_2 = -1.10±0.02; τ_2 = 31±1 ps; offset = -4.40±0.01;

1576 cm^{-1}:

A_1 = -1.2±0.1; τ_1 = 28±1 ps; offset = -0.60±0.01;

1564 cm^{-1}:

A_1 = 19.8±35.8; τ_1 = 4±10 ps; A_2 = -20.1±35.8; τ_2 = 4±11 ps; A_3 = 0.5±0.4; τ_3 = 18±7 ps; offset = 0.10±0.01;

1559 cm^{-1}:

A_1 = -0.5±0.2; τ_1 = 4±3 ps; A_2 = 0.40±0.04; τ_2 = 22±2 ps; offset = -0.010±0.003;

1393 cm^{-1}:

A_1 = -0.30±0.02; τ_1 = 32±2 ps; offset = -0.900±0.004;

1377 cm^{-1}:

A_1 = -0.20±0.03; τ_1 = 38±9 ps; offset = -1.10±0.01;

1360 cm^{-1}:

A_1 = -0.36±0.01; τ_1 = 17±1 ps; offset = 0.100±0.003;

1323 cm^{-1}:

A_1 = -0.5±0.1; τ_1 = 1.0±0.4 ps; A_2 = 0.7±0.1; τ_2 = 6±11 ps; A_3 = -0.9±0.1; τ_3 = 20±1 ps; offset = 0.700±0.003.

1148 cm^{-1}:

A_1 = -0.50±0.01; τ_1 = 23±1 ps; offset = 0.500±0.004.

TsN_3, CCl_4

2127 cm^{-1}:

A_1 = 0.5±0.1; τ_1 = 8±2 ps; A_2 = -0.50±0.01; τ_2 = 33±2 ps; offset = -1.70±0.01;

1379 cm^{-1}:

A_1 = -0.4±0.1; τ_1 = 30±7 ps; offset = -1.20±0.01;

1349 cm^{-1}:

A_1 = -0.60±0.03; τ_1 = 19±2 ps; A_2 = 0.40±0.02; τ_2 = 0.67±0.10 ns; offset = 0.10±0.02;

1337 cm^{-1}:

A_1 = -0.9±0.1; τ_1 = 3±0 ps; A_2 = 0.5±0.1; τ_2 = 24±5 ps; A_3 = -0.10±0.03; τ_3 = 0.44±0.26 ns; offset = 0.09±0.02.

TsN_3, CH_2Cl_2

2129 cm^{-1}:

A_1 = 0.4±0.2; τ_1 = 6±3 ps; A_2 = -0.70±0.04; τ_2 = 28±3 ps; offset = -2.80±0.01;

1373 cm^{-1}:

A_1 = -0.20±0.02; τ_1 = 20±3 ps; offset = -0.50±0.01;

1353 cm^{-1}:

A_1 = -0.30±0.04; τ_1 = 14±3 ps; A_2 = 0.10±0.04; τ_2 = 84±51 ps; offset = 0.200±0.003;

1305 cm^{-1}:

A_1 = 0.2±0.1; τ_1 = 6±2 ps; A_2 = -0.20±0.01; τ_2 = 25±2 ps; offset = 0.600±0.002;

MsN_3, CCl_4

2134 cm^{-1}:

A_1 = 0.30±0.02; τ_1 = 7±1 ps; offset = -0.500±0.004;

1378 cm^{-1}:

A_1 = 0.10±0.01; τ_1 = 24±6 ps; offset = -0.30±0.01;

MsN_3, CH_2Cl_2

2140 cm^{-1}:

A_1 = 0.10±0.01; τ_1 = 9±1 ps; offset = -0.100±0.003;

1366 cm^{-1}:

A_1 = 0.040±0.004; τ_1 = 20±6 ps; offset = -0.200±0.002;

1134 cm^{-1}:

A_1 = -0.100±0.001; τ_1 = 34±3 ps; offset = 0.04±0.01;

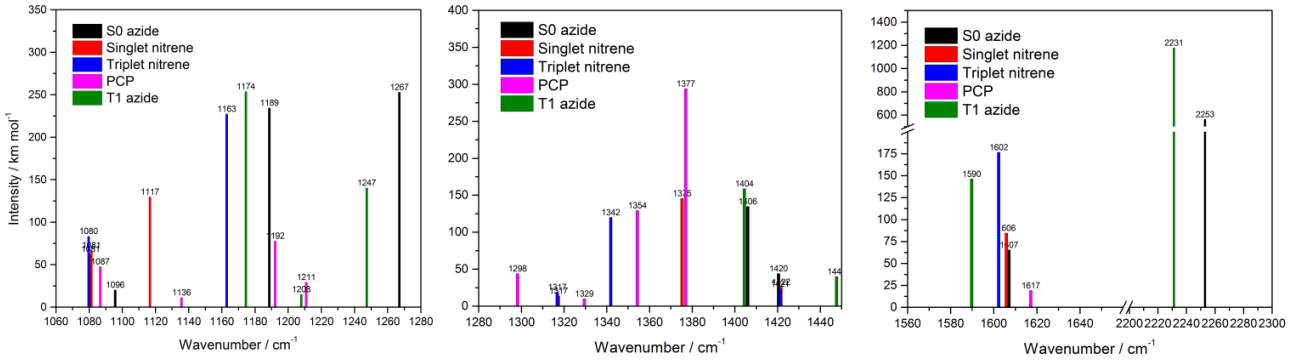


Figure S4. Calculated IR vibrational frequencies for BsN_3 and derived species at B3LYP/6-311++G(3df,3pd).

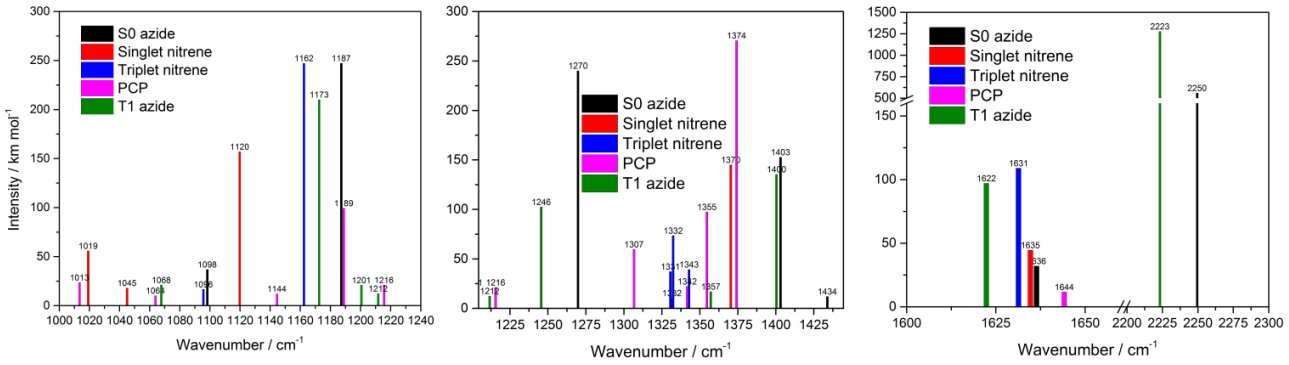


Figure S5. Calculated IR vibrational frequencies for TsN_3 and derived species at B3LYP/6-311++G(3df,3pd).

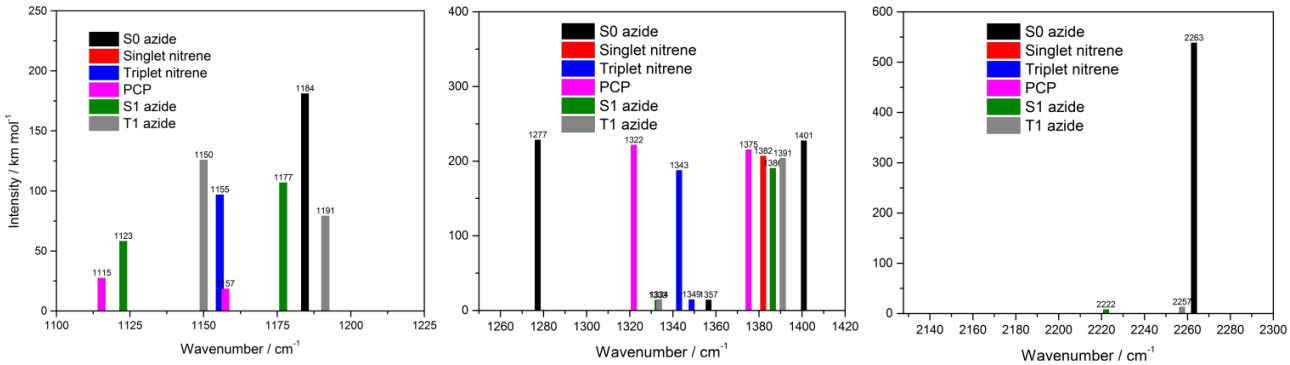


Figure S6. Calculated IR vibrational frequencies for MsN_3 and derived species at B3LYP/6-311++G(3df,3pd).

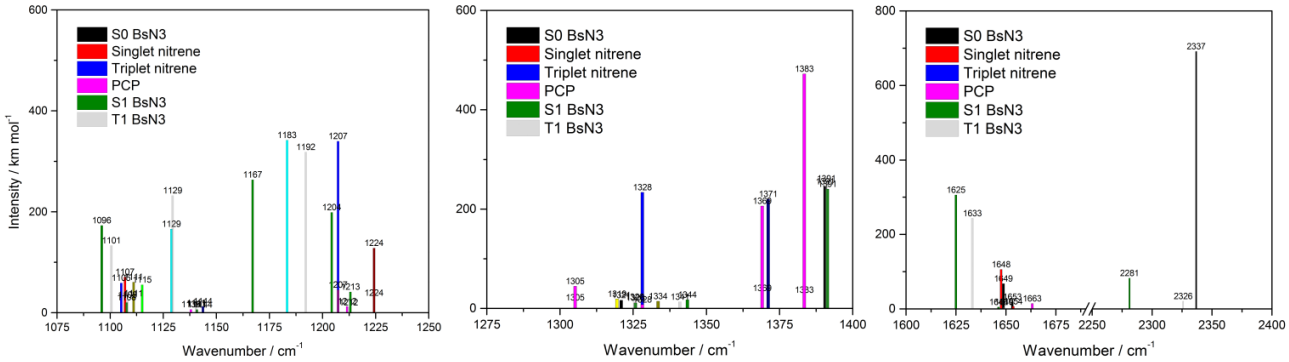


Figure S7. Calculated IR vibrational frequencies for BsN_3 and derived species at M06-2X/6-311++G(d,p).

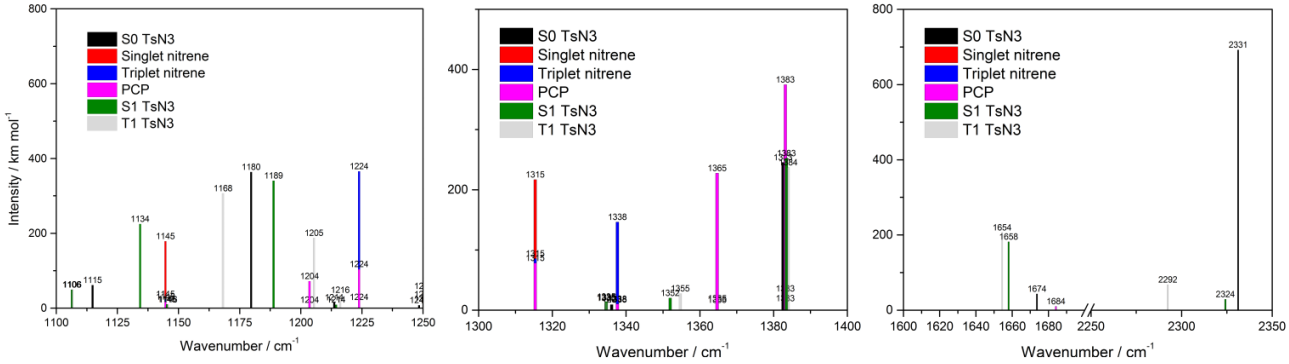


Figure S8. Calculated IR vibrational frequencies for TsN_3 and derived species at M06-2X/6-311++G(d,p).

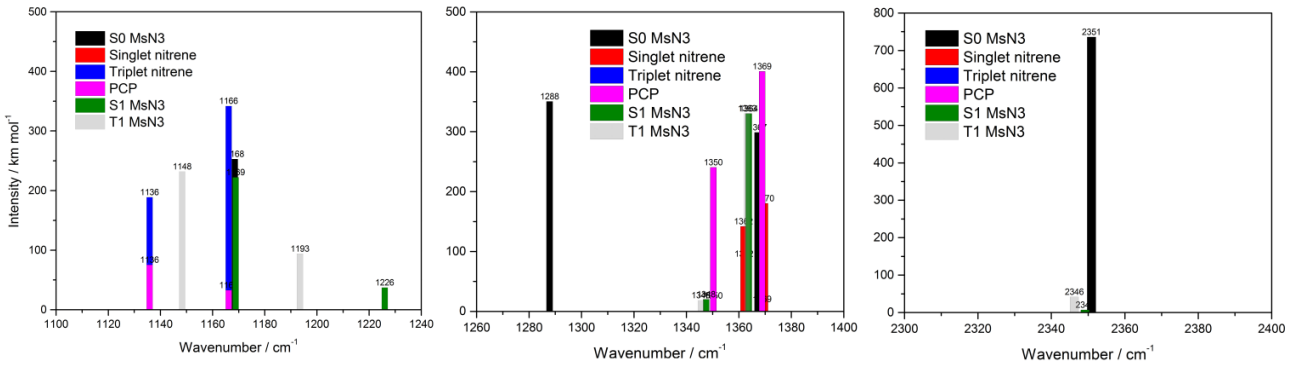


Figure S9. Calculated IR vibrational frequencies for MsN_3 and derived species at M06-2X/6-311++G(d,p).

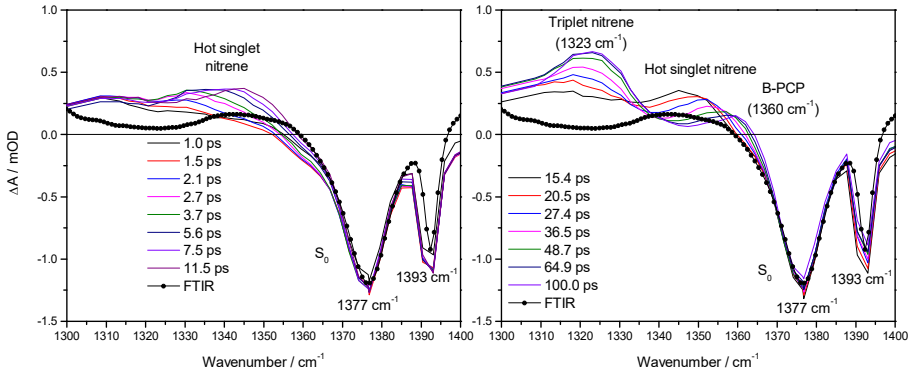


Figure S10. Transient IR spectra in SO_2 asym. stretch region produced upon BsN_3 photolysis in CH_2Cl_2 (λ_{ex} = 267 nm) at selected time delays.

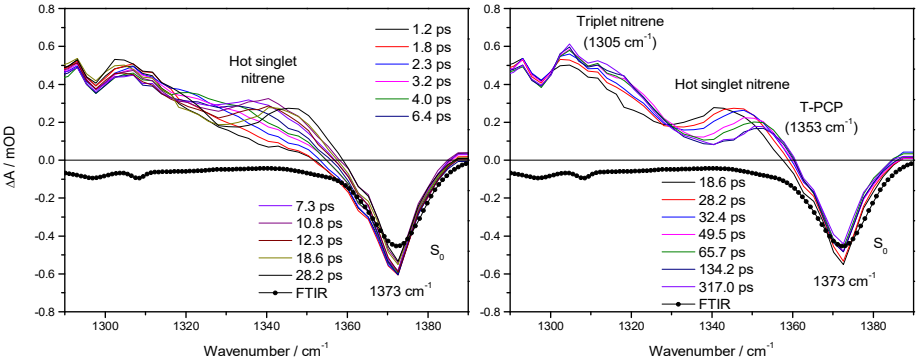


Figure S11. Transient IR spectra in SO_2 asym. stretch region produced upon TsN_3 photolysis in CCl_4 (λ_{ex} = 267 nm) at selected time delays.

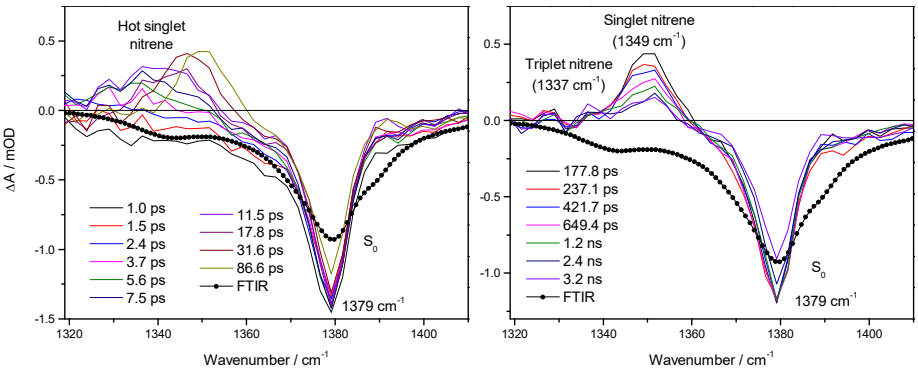


Figure S12. Transient IR spectra in SO_2 asym. stretch region produced upon TsN_3 photolysis in CH_2Cl_2 (λ_{ex} = 267 nm) at selected time delays.

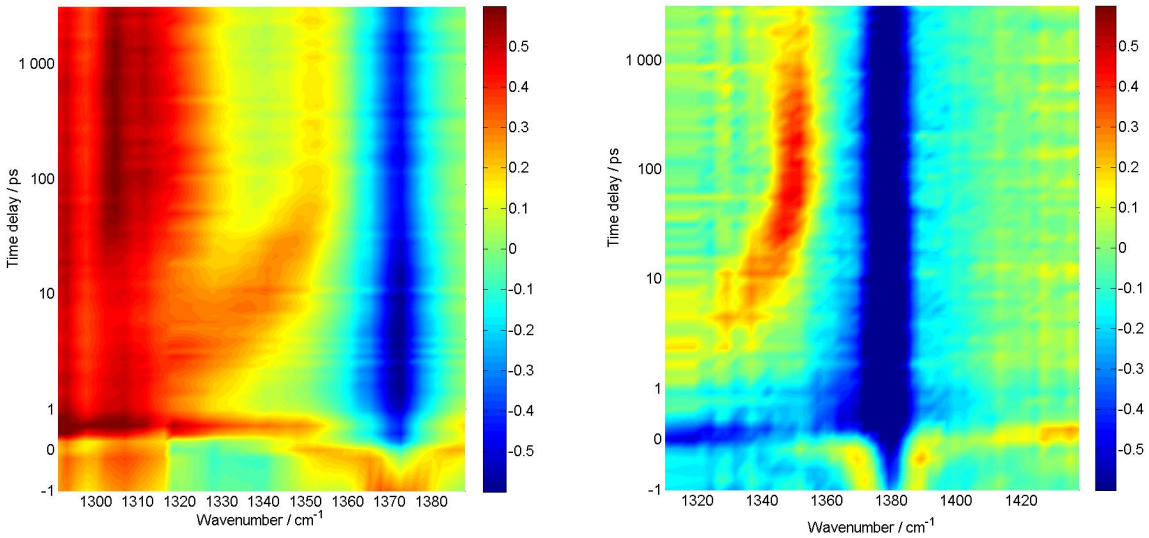


Figure S13. Transient kinetics surface plots in the range 1300–1400 cm^{-1} for TsN_3 solution in CH_2Cl_2 (a) and in CCl_4 (b).

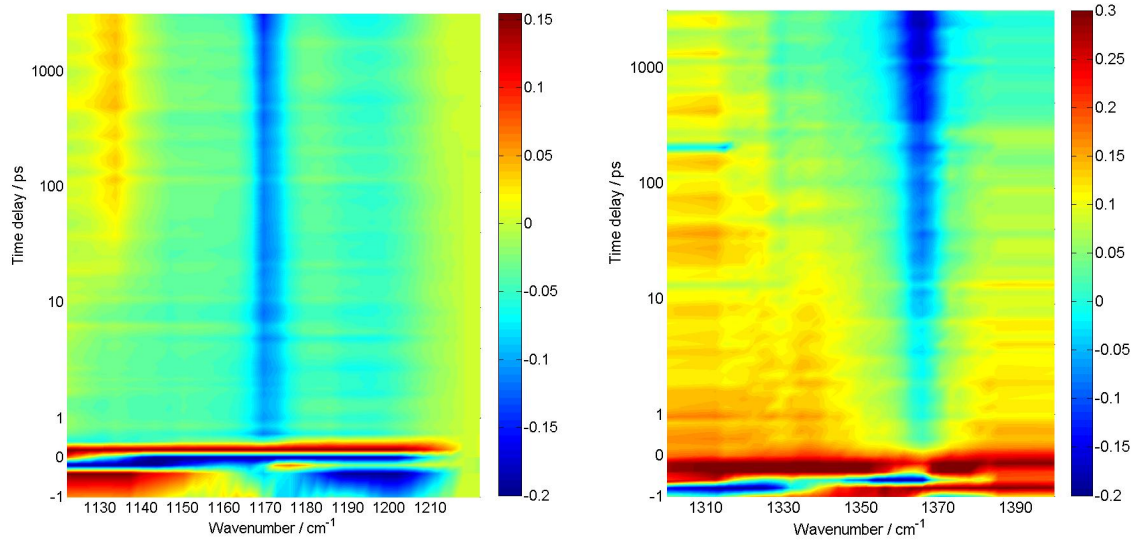


Figure S14. Transient kinetics surface plots in the range 1120–1240 cm^{-1} (a) and 1300–1400 cm^{-1} (b) for MsN_3 solution in CH_2Cl_2.

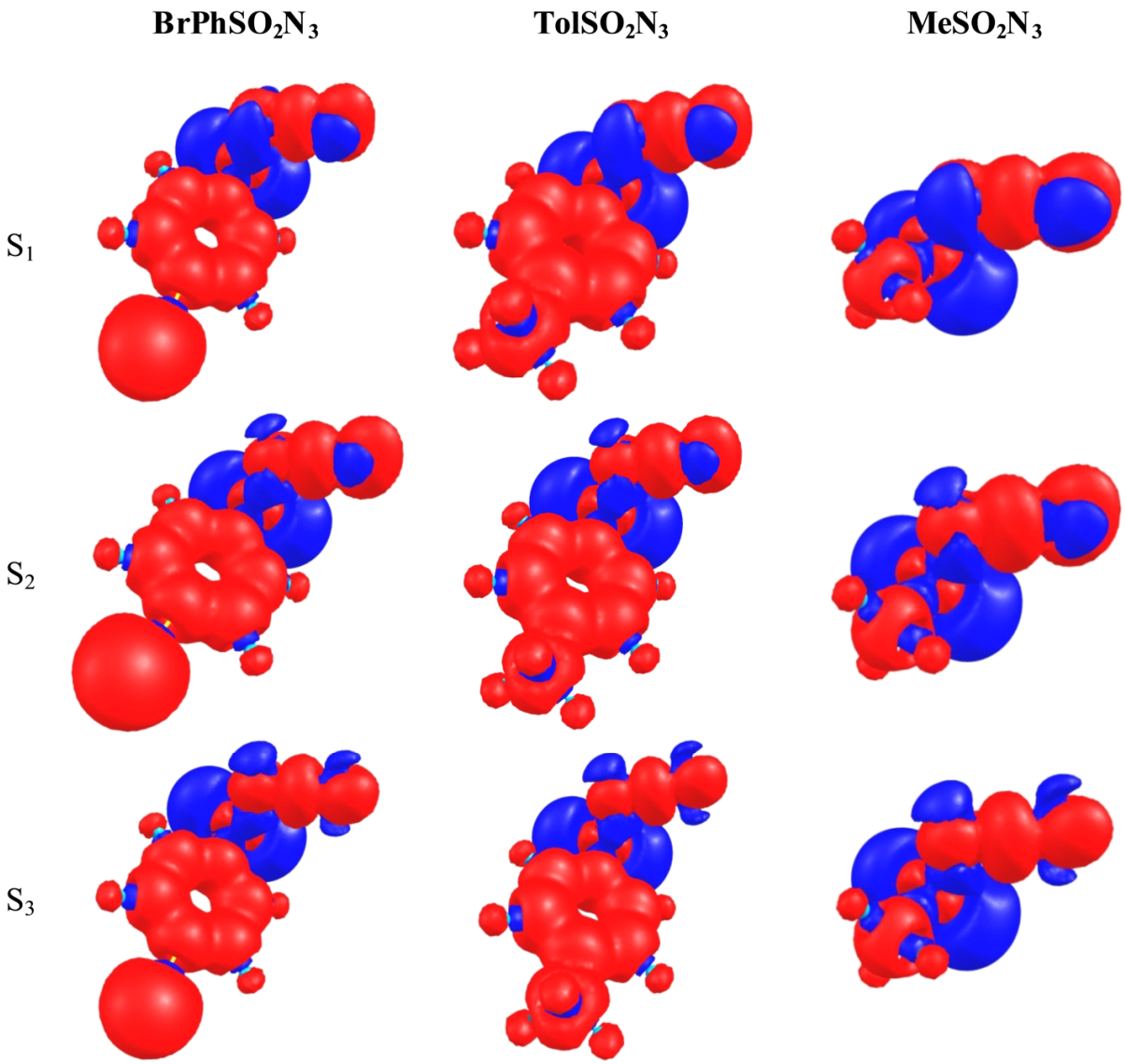


Figure S15. Relative to the S_0 ground state, electron density difference plots for the S_1−S_3 states for BsN_3, TsN_3 and MsN_3 as calculated at the TD-B3LYP/6-311++G(3df,3pd) level of theory. The red contours depict the accumulation of electron density in the excited state, and the blue contours illustrate the depletion of electron density from the S_0 ground state. The isocontour value is ±0.004 au.

Table S1. Results of assignment of experimentally observed and theoretically predicted IR frequencies.

Experimentally observed band, cm^{-1}		Theoretically predicted band (unscaled), cm^{-1}		Band assignment
CH_2Cl_2	CCl_4	B3LYP*	M06-2X*	
BsN_3 experiment				
2133	2128	2253	2337	BsN_3 S_0 state, N_3 stretch
2095–2118	2110–2121	-	-	Vibrationally hot BsN_3 S_0 state, N_3 stretch
1576	**	1607	1651	BsN_3 S_0 state, in-ring C-C stretch
1564	**	1602	1651	^{3}(BsN), in-ring C-C stretch
1559	**	***	1625	BsN_3 S_1 state, in-ring C-C stretch
1393	1387	1267	1273	BsN_3 S_0 state, N_3 stretch
1377	1391	1406	1409	BsN_3 S_0 state, $\nu^{as}(SO_2)$
1340-1357	1325-1350	-	-	Vibrationally hot ^{1}(BsN)
-	1360	1375	1384	^{1}(BsN), $\nu^{as}(SO_2)$
1360	1365	1377	1383	B-PCP, $\nu^{as}(SO_2)$
1323	1347	1342	1373	^{3}(BsN), $\nu^{as}(SO_2)$
1148	1157	1163	1180	^{3}(BsN), $\nu^{s}(SO_2)$
TsN_3 experiment				
2129	2127	2250	2331	TsN_3 S_0 state, N_3 stretch
1373	1379	1403	1383	TsN_3 S_0 state, $\nu^{as}(SO_2)$
1353	1349	1374	1383	T-PCP, $\nu^{as}(SO_2)$
1330-1350	1330-1345	-	-	Vibrationally hot ^{1}(TsN)
-	1349	1370	1383	^{1}(TsN), $\nu^{as}(SO_2)$
1305	1337	1332	1338	^{3}(TsN), $\nu^{as}(SO_2)$
MsN_3 experiment				
2140	2134	2263	2351	MsN_3 S_0 state, N_3 stretch
1366	1378	1401	1368	MsN_3 S_0 state, $\nu^{as}(SO_2)$
1134	-	1155	1166	^{3}(MsN), $\nu^{s}(SO_2)$

* see the Experimental and Computational Details section for the used procedure

** not recorded

*** not calculated

Table S2. Calculated IR vibrational frequencies of BsN_3 S_0 and T_1 states and corresponding intensities (km mol^{-1}) at the TD-B3LYP/6-311++G(3df,3pd) level of theory.

BsN_3 S_0 state		**BsN_3 T_1 state**	
Wavenumber / cm^{-1}	Intensity / km mol^{-1}	**Wavenumber / cm^{-1}**	Intensity / km mol^{-1}
28.0	0.1	**-2549.8**	2212.5
37.8	0.2	**-227.7**	1.0
69.4	1.5	**-157.6**	0.3
133.7	2.4	**-68.5**	2.6
150.8	0.0	**-5.1**	0.1
182.9	0.4	**70.2**	4.1
213.0	0.0	**132.5**	2.7
261.0	0.1	**146.6**	2.0
330.2	3.1	**193.5**	1.5
343.4	0.8	**251.7**	1.2
414.9	7.9	**255.3**	31.4
415.8	14.2	**337.4**	1.1
437.1	1.9	**400.3**	17.2
454.8	1.4	**403.2**	10.0
501.8	4.9	**407.6**	9.8
578.1	82.6	**461.5**	0.4
586.5	2.2	**487.6**	84.9
614.1	278.7	**546.1**	41.4
636.2	0.6	**563.1**	16.4
712.8	5.5	**567.5**	75.7
730.8	25.5	**637.6**	16.9
753.6	163.6	**675.2**	86.3
850.1	2.6	**687.0**	101.2
853.0	18.6	**699.7**	3.0
985.9	0.4	**709.1**	20.2
1001.1	31.4	**953.5**	0.4
1001.9	0.2	**961.2**	0.4
1080.8	62.3	**969.0**	47.1
1095.6	20.3	**995.1**	4.3
1132.5	4.2	**1096.6**	4.0
1188.7	234.6	**1119.4**	8.2
1206.0	5.1	**1174.5**	253.9
1267.0	253.1	**1207.9**	15.1
1314.7	6.2	**1247.3**	140.5
1328.5	0.4	**1344.8**	6.5
1406.0	134.7	**1395.1**	8.6
1420.5	44.1	**1404.4**	158.9
1504.9	30.2	**1447.7**	39.9

1601.9	3.6	**1565.7**	9.5
1607.0	65.4	**1589.7**	146.3
2253.0	562.2	**2231.2**	1177.1
3204.4	0.8	**3199.7**	7.5
3206.4	0.5	**3205.8**	2.7
3217.9	0.4	**3218.0**	0.2
3219.4	1.5	**3219.6**	0.1

Table S3. Calculated IR vibrational frequencies of singlet ^{1}(BsN) and triplet ^{3}(BsN) nitrenes and *p*-$BrC_6H_5NSO_2$ and corresponding intensities (km mol^{-1}) at the B3LYP/6-311++G(3df,3pd) level of theory.

^{1}(BsN)		**^{3}(BsN)**		***p*-$BrC_6H_4NSO_2$**	
Wavenumber / cm^{-1}	Intensity / km mol^{-1}	**Wavenumber / cm^{-1}**	Intensity / km mol^{-1}	**Wavenumber / cm^{-1}**	Intensity / km mol^{-1}
48.9	0.4	**53.5**	0.0	**24.6**	0.0
67.4	2.1	**62.4**	2.1	**60.1**	0.7
130.6	2.8	**135.0**	2.8	**108.4**	0.8
194.3	0.7	**167.3**	0.1	**166.3**	0.1
212.6	0.2	**211.1**	0.3	**214.0**	1.3
258.9	0.8	**256.4**	0.1	**247.0**	3.4
298.1	3.5	**290.1**	3.5	**344.6**	1.7
385.3	6.0	**302.2**	3.1	**351.0**	6.0
411.5	12.2	**411.5**	0.1	**370.0**	20.6
414.2	0.4	**412.0**	21.7	**422.7**	1.0
417.0	14.1	**422.5**	2.4	**426.6**	22.3
459.9	6.2	**460.0**	2.6	**520.8**	12.8
519.1	31.6	**526.6**	39.7	**547.4**	18.7
567.1	103.4	**561.3**	68.5	**630.7**	6.1
635.1	0.2	**634.3**	0.3	**657.0**	11.0
704.5	1.5	**705.3**	7.8	**701.3**	0.3
743.4	58.3	**714.9**	12.4	**778.4**	10.1
848.6	3.6	**752.4**	38.5	**841.7**	0.7
852.1	36.6	**848.8**	0.1	**857.9**	47.0
956.7	13.5	**853.1**	33.0	**975.0**	0.4
987.3	1.2	**989.1**	0.3	**995.7**	0.1
991.4	75.9	**1003.5**	32.9	**996.2**	64.6
1003.0	0.0	**1003.5**	5.8	**1024.4**	1.5
1038.3	26.4	**1079.6**	83.6	**1086.7**	47.8
1081.3	66.8	**1093.2**	8.3	**1135.7**	11.2
1116.6	129.8	**1133.2**	3.8	**1192.1**	78.1
1132.8	4.2	**1162.9**	227.5	**1210.8**	29.5
1205.9	1.9	**1206.8**	1.9	**1298.2**	43.9

1317.4	13.8	**1316.8**	18.9	**1329.5**	10.0
1328.8	0.1	**1326.3**	6.5	**1354.3**	129.4
1375.3	145.7	**1341.9**	119.9	**1377.0**	294.0
1421.6	25.8	**1421.1**	23.5	**1433.0**	8.8
1503.7	28.3	**1501.0**	20.7	**1514.1**	103.1
1600.0	3.7	**1588.6**	3.4	**1595.6**	0.9
1605.9	84.5	**1602.3**	176.5	**1617.2**	19.1
3205.2	1.2	**3204.2**	1.4	**3199.2**	0.5
3208.4	0.4	**3205.8**	0.5	**3206.8**	0.3
3218.3	1.2	**3217.4**	0.6	**3214.5**	0.5
3223.2	2.3	**3218.8**	2.2	**3227.4**	1.4

Table S4. Calculated IR vibrational frequencies of TsN_3 S_0 and T_1 states and corresponding intensities (km mol^{-1}) at the TD-B3LYP/6-311++G(3df,3pd) level of theory.

TsN_3 S_0 state		**TsN_3 T_1 state**	
Wavenumber / cm^{-1}	Intensity / km mol^{-1}	**Wavenumber / cm^{-1}**	Intensity / km mol^{-1}
30.3	0.2	**-3510.1**	5777.5
33.8	0.1	**-170.7**	4.1
40.8	0.1	**-158.4**	0.5
89.2	0.3	**-130.4**	1.4
146.8	0.7	**-23.3**	0.3
167.5	0.3	**65.2**	5.0
204.0	1.0	**134.8**	1.9
283.3	1.7	**150.6**	7.6
312.6	0.1	**159.7**	1.7
344.1	2.7	**238.3**	25.6
365.9	1.2	**281.8**	4.2
416.1	0.0	**312.8**	0.7
436.0	1.8	**353.9**	0.3
458.0	1.2	**393.6**	15.2
503.6	7.9	**399.8**	5.5
544.6	70.9	**462.1**	0.5
588.0	17.6	**482.0**	97.9
597.8	190.7	**518.5**	36.9
649.0	0.7	**543.1**	9.6
660.0	134.3	**560.4**	31.0
715.7	4.5	**609.0**	52.6
736.3	87.8	**660.6**	4.3
816.9	15.2	**692.8**	30.7
839.6	17.6	**701.1**	29.5
860.0	0.0	**726.3**	63.6

985.8	0.4	**761.0**	8.8
1003.7	0.0	**952.9**	1.8
1010.3	3.0	**967.4**	0.8
1036.6	3.7	**970.5**	4.0
1066.0	5.2	**995.1**	9.0
1098.2	37.0	**1012.8**	5.4
1142.9	5.5	**1067.7**	21.1
1187.2	247.3	**1133.4**	7.8
1212.5	5.1	**1172.5**	210.2
1231.2	3.8	**1200.6**	21.0
1269.8	240.1	**1211.7**	12.4
1328.3	4.0	**1245.6**	102.4
1340.3	5.3	**1357.2**	16.9
1403.1	152.7	**1377.0**	7.9
1418.0	1.8	**1400.5**	135.4
1433.9	11.9	**1410.0**	7.3
1487.2	7.5	**1454.7**	14.6
1494.8	17.2	**1461.3**	34.4
1528.5	6.7	**1475.9**	17.8
1609.0	0.9	**1572.8**	2.3
1636.4	32.1	**1622.3**	97.1
2249.5	560.4	**2223.2**	1277.1
3031.3	16.1	**3009.7**	23.3
3082.0	9.7	**3056.3**	17.9
3115.2	12.2	**3113.7**	10.0
3175.1	8.1	**3175.4**	15.3
3179.8	7.3	**3182.6**	6.5
3211.7	0.9	**3209.8**	1.0
3213.7	1.8	**3213.1**	2.3

Table S5. Calculated IR vibrational frequencies of singlet ^{1}(TsN) and triplet ^{3}(TsN) nitrenes and *p*-TolNSO$_2$ and corresponding intensities (km mol^{-1}) at the B3LYP/6-311++G(3df,3pd) level of theory.

^{1}(TsN)		**^{3}(TsN)**		***p*-TolNSO$_2$**	
Wavenumber / cm^{-1}	Intensity / km mol^{-1}	**Wavenumber / cm^{-1}**	Intensity / km mol^{-1}	**Wavenumber / cm^{-1}**	Intensity / km mol^{-1}
19.0	0.2	**13.5**	0.2	**22.8**	0.2
49.5	0.1	**53.2**	0.0	**27.1**	0.0
91.0	0.4	**82.8**	0.4	**77.5**	0.0
158.3	1.4	**161.2**	1.1	**128.9**	1.3
212.0	1.5	**186.9**	0.5	**190.0**	0.9
284.5	1.4	**277.1**	1.3	**275.9**	4.4
306.7	4.2	**281.8**	2.1	**329.3**	0.7

329.3	0.7	**321.7**	2.2	**349.4**	8.1
397.8	2.3	**334.6**	2.6	**370.6**	14.2
413.9	0.1	**411.1**	0.0	**380.4**	4.3
419.6	1.1	**430.0**	1.9	**422.6**	1.1
460.6	8.3	**461.6**	4.4	**519.1**	36.0
514.5	42.5	**515.6**	52.8	**525.1**	13.6
533.7	82.7	**536.6**	51.5	**582.3**	3.1
646.4	39.4	**640.1**	35.8	**653.2**	0.4
648.4	11.6	**646.3**	1.0	**704.8**	0.6
705.0	1.6	**711.3**	0.5	**719.8**	11.1
812.8	2.5	**718.9**	4.5	**824.3**	1.8
837.3	36.1	**815.0**	1.9	**845.8**	42.6
858.6	0.8	**838.6**	29.1	**851.4**	1.4
952.8	15.1	**857.5**	0.3	**974.5**	1.3
987.2	0.2	**988.6**	0.3	**996.5**	0.0
1004.8	0.2	**1004.9**	0.6	**1007.3**	4.8
1009.5	0.4	**1008.3**	6.0	**1013.4**	23.7
1019.2	55.9	**1035.1**	4.9	**1037.9**	1.0
1045.0	18.1	**1063.8**	4.3	**1063.8**	10.3
1064.8	4.3	**1095.6**	16.7	**1144.5**	12.1
1119.7	157.2	**1142.8**	6.4	**1188.9**	99.5
1142.7	4.4	**1162.4**	247.3	**1215.6**	21.1
1211.7	2.1	**1212.3**	1.9	**1232.2**	1.4
1230.1	2.3	**1230.2**	1.0	**1306.7**	59.6
1331.7	10.3	**1330.7**	37.2	**1341.7**	22.1
1338.4	8.2	**1332.4**	73.4	**1354.6**	97.4
1370.4	145.0	**1342.9**	39.3	**1374.2**	270.6
1417.9	2.0	**1415.9**	2.2	**1417.3**	1.4
1435.5	9.2	**1435.6**	9.0	**1444.4**	1.0
1486.7	7.1	**1485.1**	7.2	**1488.5**	6.7
1495.0	17.6	**1492.3**	17.4	**1494.0**	10.9
1526.0	5.3	**1523.6**	1.1	**1536.7**	47.9
1607.3	1.0	**1596.2**	0.8	**1602.3**	2.8
1634.7	44.6	**1631.3**	108.9	**1644.2**	11.6
3032.8	14.5	**3032.2**	11.0	**3025.6**	25.1
3082.2	8.1	**3081.5**	7.4	**3078.1**	14.2
3116.4	12.4	**3117.0**	13.1	**3108.6**	13.0
3176.3	7.6	**3176.4**	7.1	**3169.4**	11.2
3180.0	6.9	**3180.1**	7.2	**3171.7**	11.7
3211.8	1.9	**3211.4**	0.0	**3202.4**	2.7
3219.5	2.2	**3212.1**	4.3	**3224.3**	0.8

Table S6. Calculated IR vibrational frequencies of MsN_3 S_0, S_1 and T_1 states and corresponding intensities (km mol^{-1}) at the TD-B3LYP/6-311++G(3df,3pd) level of theory.

MsN_3 S_0 state		**MsN_3 S_1 state**		**MsN_3 T_1 state**	
Wavenumber / cm^{-1}	Intensity / km mol^{-1}	**Wavenumber / cm^{-1}**	Intensity / km mol^{-1}	**Wavenumber / cm^{-1}**	Intensity / km mol^{-1}
33.4	3.1	**-923.1**	36.9	**-968.0**	33.2
155.6	0.1	**-406.5**	14.5	**-436.0**	7.5
213.2	0.1	**-234.6**	16.2	**-169.4**	10.0
274.0	0.7	**109.1**	2.0	**119.2**	2.5
308.5	0.2	**154.5**	1.1	**159.2**	0.6
399.0	2.1	**163.6**	0.7	**173.1**	2.0
435.9	0.2	**243.5**	17.9	**267.4**	13.4
500.5	38.8	**322.2**	6.1	**332.4**	11.9
567.3	142.9	**420.8**	18.3	**444.5**	29.4
581.6	6.2	**477.6**	20.9	**481.4**	26.9
721.2	16.9	**504.4**	28.3	**534.5**	12.4
753.8	123.4	**699.3**	36.2	**701.0**	42.6
978.4	46.7	**942.8**	31.3	**950.4**	41.4
985.7	12.7	**970.1**	2.1	**969.6**	2.0
1184.4	181.2	**1122.7**	58.4	**1150.0**	125.8
1277.3	228.5	**1177.0**	107.0	**1191.4**	79.3
1356.6	14.2	**1332.9**	13.8	**1333.6**	14.5
1400.9	227.5	**1386.4**	190.4	**1391.0**	203.9
1455.2	4.2	**1442.4**	0.8	**1445.0**	0.4
1456.9	0.1	**1450.7**	6.0	**1451.5**	5.3
2263.0	538.4	**2222.1**	7.9	**2257.5**	13.2
3063.9	0.3	**3061.3**	2.9	**3061.3**	1.8
3158.7	0.2	**3156.9**	4.9	**3156.9**	3.0
3175.2	0.1	**3172.8**	0.1	**3172.9**	0.1

Table S7. Calculated IR vibrational frequencies of singlet ^{1}(MsN) and triplet ^{3}(MsN) nitrenes and $MeNSO_2$ and corresponding intensities (km mol^{-1}) at the B3LYP/6-311++G(3df,3pd) level of theory.

^{1}(MsN)		**^{3}(MsN)**		**$MeNSO_2$**	
Wavenumber / cm^{-1}	Intensity / km mol^{-1}	**Wavenumber / cm^{-1}**	Intensity / km mol^{-1}	**Wavenumber / cm^{-1}**	Intensity / km mol^{-1}
171.7	0.1	**179.5**	0.0	**86.6**	0.0
269.7	0.6	**261.2**	3.1	**214.1**	1.5
325.4	0.7	**272.9**	3.3	**233.3**	7.5
386.5	5.0	**341.9**	2.5	**427.5**	23.1
434.1	16.1	**446.2**	38.1	**487.4**	26.5
478.1	47.8	**479.2**	30.5	**549.8**	9.9

717.9	30.2	**657.5**	2.5	**835.8**	16.3
934.7	4.2	**740.3**	46.6	**1115.3**	27.6
984.3	5.7	**964.5**	17.3	**1128.8**	0.0
993.8	15.0	**970.7**	1.7	**1157.3**	18.5
1059.0	76.1	**1155.5**	97.0	**1321.9**	221.6
1352.6	9.4	**1342.9**	187.6	**1375.2**	215.4
1382.0	206.9	**1348.7**	14.6	**1461.0**	2.7
1451.3	8.8	**1446.8**	3.8	**1492.4**	7.7
1455.7	1.1	**1452.2**	8.7	**1496.9**	13.6
3061.3	0.2	**3056.5**	1.9	**3039.1**	26.5
3148.8	0.3	**3148.7**	2.2	**3108.9**	6.8
3182.9	0.6	**3170.9**	0.2	**3118.2**	5.0

Table S8. Calculated IR vibrational frequencies of BsN_3 S_0, S_1 and T_1 states and corresponding intensities (km mol^{-1}) at the TD-M06-2X/6-311G(d,p) level of theory.

BsN_3 S_0 state		**BsN_3 S_1 state**		**BsN_3 T_1 state**	
Wavenumber / cm^{-1}	Intensity / km mol^{-1}	**Wavenumber / cm^{-1}**	Intensity / km mol^{-1}	**Wavenumber / cm^{-1}**	Intensity / km mol^{-1}
8.7	0.4	**-926.5**	34.7	**-975.4**	42.0
21.6	0.4	**-464.7**	10.1	**-456.8**	9.7
68.3	2.2	**-98.6**	4.6	**-159.4**	6.0
138.5	4.0	**-57.9**	0.3	**-78.0**	0.8
149.7	0.2	**103.0**	1.4	**36.1**	1.8
185.4	0.3	**127.0**	4.7	**99.6**	2.1
218.4	0.1	**142.9**	2.6	**127.3**	4.7
267.9	0.1	**167.6**	2.4	**157.3**	1.5
332.2	3.7	**212.4**	0.8	**210.2**	1.7
343.6	1.0	**260.2**	0.1	**259.4**	1.7
411.7	0.1	**265.8**	2.3	**261.4**	3.5
425.5	45.2	**336.2**	11.3	**330.5**	22.8
445.9	1.3	**412.1**	35.0	**407.2**	57.2
455.9	2.4	**413.2**	23.4	**410.5**	14.2
508.0	8.0	**419.1**	14.2	**415.0**	23.3
578.6	84.9	**464.7**	6.0	**464.0**	7.6
589.0	38.4	**534.2**	71.2	**532.1**	110.0
616.9	331.0	**540.2**	99.2	**535.7**	74.2
631.6	1.2	**630.3**	3.9	**624.5**	20.6
736.3	17.1	**645.2**	22.9	**633.8**	11.0
751.5	28.4	**730.2**	13.8	**729.7**	12.3
774.5	238.7	**751.1**	43.9	**748.3**	42.8
848.4	34.4	**845.1**	36.1	**846.7**	36.3
856.2	0.0	**853.7**	0.3	**854.6**	0.1

987.1	0.6	**988.2**	1.9	**988.4**	3.4
1007.3	0.3	**1008.2**	0.1	**1008.1**	0.1
1022.5	42.9	**1024.8**	52.6	**1022.0**	47.1
1107.0	70.6	**1096.1**	172.9	**1100.6**	132.9
1115.1	55.4	**1107.7**	20.5	**1108.2**	25.4
1140.8	6.3	**1140.9**	6.3	**1129.4**	232.1
1183.2	341.7	**1167.0**	263.3	**1140.5**	9.1
1211.5	12.3	**1204.3**	199.0	**1192.1**	318.3
1262.7	376.8	**1213.1**	41.4	**1212.2**	10.3
1320.9	16.2	**1325.7**	11.2	**1325.5**	13.1
1329.1	0.2	**1343.5**	17.2	**1341.0**	13.0
1390.5	245.3	**1391.3**	240.2	**1391.0**	251.3
1438.9	35.8	**1437.6**	35.8	**1436.9**	36.2
1519.5	37.6	**1515.5**	33.1	**1516.3**	34.3
1648.8	67.8	**1625.0**	305.7	**1633.2**	242.8
1653.2	18.8	**1646.3**	5.0	**1649.1**	4.7
2336.8	691.3	**2281.2**	82.7	**2326.0**	20.4
3214.8	5.1	**3214.3**	6.4	**3215.3**	6.6
3216.0	1.2	**3215.5**	1.3	**3216.6**	0.6
3228.1	5.0	**3227.3**	6.8	**3229.0**	7.4
3243.8	1.0	**3242.7**	1.2	**3244.1**	1.2

Table S9. Calculated IR vibrational frequencies of singlet ^{1}(BsN) and triplet ^{3}(BrsN) nitrenes and *p*-$BrC_6H_4NSO_2$ and corresponding intensities (km mol^{-1}) at the M06-2X/6-311G(d,p) level of theory.

^{1}(BsN)		**^{3}(BsN)**		***p*-$BrC_6H_4NSO_2$**	
Wavenumber / cm^{-1}	Intensity / km mol^{-1}	**Wavenumber / cm^{-1}**	Intensity / km mol^{-1}	**Wavenumber / cm^{-1}**	Intensity / km mol^{-1}
52.1	0.6	**52.3**	0.1	**37.8**	0.2
72.4	2.3	**63.8**	2.1	**64.7**	0.7
131.5	3.5	**139.6**	3.1	**109.7**	0.8
200.4	1.3	**172.8**	0.1	**162.0**	0.5
216.4	0.2	**215.9**	0.1	**224.4**	1.0
263.0	0.7	**262.4**	0.1	**253.5**	3.2
297.8	3.3	**298.7**	5.2	**331.8**	5.2
399.2	9.3	**314.8**	6.2	**365.5**	9.4
410.0	1.8	**417.2**	0.0	**393.5**	31.8
416.2	21.9	**420.5**	33.4	**423.1**	4.8
422.7	17.5	**428.5**	4.4	**433.2**	21.2
491.6	14.3	**462.0**	6.0	**514.9**	10.3
515.4	29.1	**530.7**	48.5	**549.1**	28.3
584.6	112.2	**569.1**	94.7	**635.6**	3.1
633.6	0.5	**631.5**	0.2	**662.3**	17.8

716.4	1.1	**724.0**	12.4	**720.0**	0.6
755.7	62.1	**757.8**	39.0	**802.0**	7.8
842.1	49.9	**772.7**	61.9	**846.1**	7.4
856.2	4.1	**852.1**	34.6	**856.5**	54.6
934.8	23.9	**860.6**	0.1	**977.0**	0.1
980.4	0.1	**992.4**	0.1	**1001.4**	0.6
1005.3	0.3	**1010.6**	0.0	**1020.2**	62.7
1015.6	83.3	**1025.1**	33.5	**1049.5**	3.7
1055.5	26.3	**1107.0**	51.9	**1113.5**	47.4
1107.5	40.1	**1115.6**	24.9	**1143.0**	9.1
1132.9	118.0	**1137.7**	4.3	**1207.0**	30.3
1136.6	10.7	**1180.2**	262.9	**1226.5**	99.6
1208.3	0.3	**1210.5**	3.4	**1306.8**	33.8
1319.2	11.4	**1320.9**	12.8	**1326.9**	3.8
1333.2	8.1	**1334.2**	7.0	**1375.4**	139.4
1383.7	163.1	**1373.3**	181.0	**1395.7**	389.6
1442.0	28.2	**1440.2**	24.9	**1452.0**	8.9
1515.8	30.6	**1516.5**	21.9	**1532.5**	135.9
1651.1	69.7	**1650.6**	107.0	**1646.2**	0.2
1654.9	8.3	**1651.7**	4.3	**1666.0**	12.0
3208.8	6.9	**3209.1**	6.0	**3207.0**	0.2
3209.9	2.5	**3209.9**	3.2	**3211.7**	1.2
3220.9	4.9	**3226.3**	3.3	**3231.4**	0.4
3231.0	1.4	**3227.3**	0.2	**3234.0**	0.4

Table S10. Calculated IR vibrational frequencies of TsN_3 S_0, S_1 and T_1 states and corresponding intensities (km mol^{-1}) at the TD-M06-2X/6-311G(d,p) level of theory.

TsN_3 S_0 state		**TsN_3 S_1 state**		**TsN_3 T_1 state**	
Wavenumber / cm^{-1}	Intensity / km mol^{-1}	**Wavenumber / cm^{-1}**	Intensity / km mol^{-1}	**Wavenumber / cm^{-1}**	Intensity / km mol^{-1}
-35.1	0.3	**-928.2**	32.9	**-974.7**	36.2
-20.0	0.6	**-460.6**	9.9	**-450.1**	9.8
85.3	0.3	**-82.3**	2.1	**-154.4**	4.7
109.5	0.1	**-58.6**	0.2	**-79.1**	0.4
145.8	1.6	**100.8**	0.1	**31.0**	1.2
170.1	0.7	**118.3**	3.2	**102.5**	0.0
205.4	1.5	**137.1**	4.3	**114.6**	6.1
287.9	4.7	**151.1**	2.5	**142.2**	2.5
314.5	0.1	**177.0**	0.2	**169.1**	0.2
343.0	2.9	**261.1**	1.4	**256.9**	2.2
366.0	1.8	**302.2**	1.3	**298.3**	3.8
409.5	0.0	**310.2**	1.4	**309.9**	2.2

445.5	0.4	**359.4**	10.9	**352.6**	26.7
458.3	2.1	**412.1**	0.5	**408.4**	2.9
507.3	12.5	**423.7**	25.6	**414.1**	44.1
536.6	110.8	**463.3**	14.9	**461.3**	16.7
590.2	18.8	**500.2**	84.7	**498.3**	91.4
603.0	251.6	**538.6**	97.4	**532.2**	101.9
640.3	0.7	**622.4**	34.1	**610.4**	34.2
665.6	147.1	**639.9**	1.0	**637.6**	1.8
734.2	14.7	**659.8**	5.9	**651.3**	9.7
767.3	135.4	**728.4**	6.4	**727.7**	5.4
824.7	36.2	**822.1**	2.2	**818.6**	2.2
835.8	18.3	**834.8**	28.8	**834.8**	28.8
862.2	0.1	**860.7**	0.2	**861.0**	0.2
983.6	0.3	**986.5**	1.7	**986.5**	2.8
1007.9	0.0	**1010.6**	0.0	**1009.9**	0.1
1015.4	2.3	**1015.7**	5.9	**1015.0**	5.8
1034.0	5.3	**1037.1**	1.4	**1034.7**	1.5
1066.6	10.1	**1064.0**	12.3	**1064.1**	11.5
1114.8	61.6	**1106.5**	49.5	**1106.3**	49.3
1145.2	9.9	**1145.7**	9.8	**1134.3**	225.1
1179.7	363.7	**1168.2**	306.9	**1145.2**	10.4
1213.6	15.1	**1205.4**	187.6	**1188.8**	341.0
1248.4	7.8	**1216.1**	34.9	**1214.4**	9.2
1266.6	357.4	**1247.3**	3.4	**1247.1**	3.4
1334.6	11.8	**1334.7**	12.4	**1334.6**	14.0
1336.1	9.1	**1354.7**	27.7	**1351.9**	20.1
1382.6	245.5	**1384.0**	237.0	**1383.5**	252.2
1416.8	3.8	**1414.7**	4.2	**1415.4**	4.0
1444.9	9.3	**1443.3**	9.7	**1442.5**	10.0
1488.4	15.5	**1487.1**	15.9	**1487.1**	15.9
1499.2	21.2	**1497.9**	22.2	**1497.9**	21.3
1541.4	9.1	**1536.3**	2.0	**1536.7**	2.5
1653.1	1.7	**1646.7**	3.1	**1648.6**	2.9
1673.7	43.4	**1654.5**	206.4	**1658.0**	181.6
2331.2	692.2	**2292.4**	67.9	**2324.2**	28.9
3059.0	10.6	**3059.7**	5.3	**3059.3**	6.0
3127.3	7.8	**3127.7**	9.8	**3127.8**	9.0
3150.9	7.6	**3151.4**	8.0	**3151.4**	7.3
3188.9	3.2	**3189.2**	3.3	**3189.9**	3.2
3198.7	3.2	**3198.1**	3.9	**3199.3**	3.4
3209.8	2.7	**3209.0**	5.2	**3210.8**	4.8
3213.1	3.9	**3213.0**	6.6	**3213.5**	6.8

Table S11. Calculated IR vibrational frequencies of singlet ^{1}(TsN) and triplet ^{3}(TsN) nitrenes and *p*-TolNSO$_2$ and corresponding intensities (km mol^{-1}) at the M06-2X/6-311G(d,p) level of theory.

^{1}(TsN)		^{3}(TsN)		*p*-TolNSO$_2$	
Wavenumber / cm^{-1}	Intensity / km mol^{-1}	**Wavenumber / cm^{-1}**	Intensity / km mol^{-1}	**Wavenumber / cm^{-1}**	Intensity / km mol^{-1}
49.2	0.2	**34.4**	0.2	**38.6**	0.2
74.3	0.2	**47.5**	0.1	**60.4**	0.2
89.0	0.5	**82.3**	0.4	**74.4**	0.0
157.0	1.9	**163.6**	1.3	**133.9**	0.6
214.4	2.4	**192.2**	0.7	**183.2**	1.9
285.3	3.3	**282.4**	4.2	**283.5**	4.2
302.8	4.7	**287.7**	2.8	**329.9**	1.4
327.5	0.7	**328.5**	3.6	**350.8**	6.1
407.6	0.1	**340.4**	3.8	**374.6**	20.7
412.7	1.0	**416.4**	0.0	**397.6**	18.3
422.2	4.6	**434.7**	3.6	**425.5**	1.5
487.1	34.6	**462.2**	8.4	**517.1**	15.2
499.6	43.6	**518.1**	77.9	**518.6**	39.8
553.4	74.0	**538.7**	61.4	**584.0**	6.1
642.6	0.4	**639.6**	0.3	**650.0**	0.5
657.8	65.7	**648.1**	46.4	**722.5**	2.9
712.2	1.5	**737.0**	30.1	**744.7**	10.3
823.8	7.6	**757.0**	18.3	**839.1**	15.7
828.4	40.5	**823.0**	13.7	**848.9**	35.2
863.1	1.3	**841.1**	21.8	**861.2**	6.5
934.0	24.8	**868.0**	0.2	**979.1**	1.6
980.1	0.6	**991.1**	0.4	**1005.9**	0.2
1007.1	0.0	**1012.2**	0.0	**1013.1**	0.1
1010.7	1.5	**1015.2**	2.6	**1028.3**	25.6
1025.8	37.4	**1036.0**	3.1	**1054.7**	7.7
1058.6	37.1	**1067.7**	8.5	**1066.2**	9.2
1062.6	5.2	**1116.6**	18.3	**1147.2**	12.6
1136.1	121.5	**1143.5**	5.9	**1208.6**	53.0
1143.4	12.2	**1179.0**	276.6	**1227.2**	70.8
1211.8	1.0	**1213.6**	3.0	**1251.9**	11.1
1248.6	2.5	**1248.2**	1.4	**1316.2**	50.1
1331.5	9.1	**1331.4**	14.4	**1340.3**	6.5
1341.0	11.4	**1344.9**	17.2	**1373.4**	144.2
1381.9	164.5	**1369.2**	170.8	**1393.6**	343.4
1416.4	3.7	**1421.1**	3.8	**1418.8**	2.0
1448.6	8.2	**1447.6**	7.3	**1457.9**	1.6
1490.4	9.4	**1493.0**	12.2	**1493.7**	8.7
1500.0	21.7	**1501.0**	17.3	**1503.7**	13.0

1539.1	8.3	**1539.1**	3.4	**1555.8**	66.4
1655.9	2.1	**1654.0**	1.7	**1651.1**	2.3
1674.6	38.0	**1673.8**	60.4	**1686.8**	6.1
3053.7	7.9	**3059.9**	7.8	**3051.6**	16.4
3118.0	3.8	**3128.7**	6.7	**3118.7**	8.2
3148.7	8.1	**3152.8**	6.4	**3144.5**	7.9
3182.9	2.9	**3188.4**	2.9	**3182.5**	5.9
3193.7	2.9	**3191.7**	2.9	**3186.9**	6.4
3210.3	4.1	**3211.5**	2.0	**3218.0**	0.3
3215.5	5.2	**3212.5**	5.3	**3223.8**	0.9

Table S12. Calculated IR vibrational frequencies of MsN_3 S_0, S_1 and T_1 states and corresponding intensities (km mol^{-1}) at the TD-M06-2X/6-311G(d,p) level of theory.

MsN_3 S_0 state		**MsN_3 S_1 state**		**MsN_3 T_1 state**	
Wavenumber / cm^{-1}	Intensity / km mol^{-1}	**Wavenumber / cm^{-1}**	Intensity / km mol^{-1}	**Wavenumber / cm^{-1}**	Intensity / km mol^{-1}
41.3	4.8	**-944.6**	22.5	**-981.2**	24.3
156.7	1.2	**-474.0**	8.7	**-451.9**	6.3
188.4	0.2	**119.7**	10.1	**-20.0**	10.3
272.0	1.5	**137.9**	1.1	**116.9**	1.4
304.6	0.4	**167.6**	2.3	**148.0**	2.0
396.8	6.3	**229.6**	7.2	**219.9**	6.3
446.7	9.9	**276.3**	11.4	**265.9**	23.2
497.9	60.4	**338.3**	15.6	**331.0**	17.3
559.4	26.8	**462.0**	54.7	**459.0**	57.4
579.7	175.1	**495.3**	54.6	**491.1**	49.4
742.4	52.3	**598.5**	20.6	**577.4**	35.5
782.2	142.3	**752.7**	53.9	**751.4**	51.8
992.7	16.8	**977.8**	21.9	**976.9**	28.1
997.2	63.6	**980.1**	18.6	**979.6**	6.3
1168.5	252.9	**1168.8**	222.2	**1148.4**	231.8
1287.9	350.3	**1226.0**	37.3	**1193.5**	93.8
1362.0	87.8	**1347.5**	20.0	**1345.5**	18.4
1367.1	298.6	**1363.8**	330.2	**1363.2**	330.3
1444.2	7.3	**1439.2**	7.3	**1439.2**	9.1
1450.0	2.8	**1441.5**	4.8	**1441.5**	3.4
2350.9	735.8	**2349.2**	7.1	**2346.2**	41.4
3078.1	2.5	**3077.3**	6.1	**3076.7**	5.1
3187.6	3.5	**3186.1**	8.6	**3186.4**	8.3
3201.2	3.0	**3198.2**	2.6	**3200.0**	2.9

Table S13. Calculated IR vibrational frequencies of singlet ^{1}(MsN) and triplet ^{3}(MsN) nitrenes and $MeNSO_2$ and corresponding intensities (km mol^{-1}) at the M06-2X/6-311G(d,p) level of theory.

^{1}(MsN)		**^{3}(MsN)**		**$MeNSO_2$**	
Wavenumber / cm^{-1}	Intensity / km mol^{-1}	**Wavenumber / cm^{-1}**	Intensity / km mol^{-1}	**Wavenumber / cm^{-1}**	Intensity / km mol^{-1}
170.6	0.1	**171.8**	0.1	**132.2**	0.2
275.1	0.6	**265.8**	2.1	**206.3**	1.3
320.6	0.6	**276.2**	4.1	**239.4**	8.2
399.4	17.3	**346.8**	7.3	**405.7**	37.4
453.4	40.9	**442.9**	48.6	**484.0**	35.1
514.5	35.1	**483.2**	49.0	**553.4**	12.6
743.0	29.7	**683.9**	3.4	**871.8**	20.7
918.6	14.6	**766.2**	55.8	**1129.5**	0.0
995.4	22.1	**979.0**	26.5	**1140.4**	51.2
1002.5	6.0	**983.9**	2.2	**1168.1**	28.9
1065.3	73.0	**1175.7**	148.9	**1355.4**	202.1
1361.4	7.7	**1357.5**	17.0	**1384.3**	308.0
1384.3	238.4	**1374.0**	264.3	**1466.1**	13.6
1445.7	9.8	**1447.4**	9.1	**1500.7**	10.5
1461.3	3.0	**1448.0**	3.1	**1509.2**	21.0
3081.4	1.1	**3073.2**	2.8	**3065.6**	18.8
3185.1	2.6	**3179.8**	4.5	**3151.5**	1.4
3208.8	4.2	**3190.8**	2.0	**3154.7**	3.2

Geometries and energies of azides and related species calculated at B3LYP/6-311++G(3df,3pd) level of theory

***p*-Bromobenzenesulfonylazide**, S_0 state, BsN_3, B3LYP/6-311++G(3df,3pd)

E_{total} = -3518.2167425 au, μ = 3.43 D.

S_1 state

E_{total} = -3518.0530664 au.

T_1 state

E_{total} = -3518.0760442 au, μ = 5.16 D.

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	16	0	2.529278	-0.676835	0.287119
2	8	0	2.836518	-2.017907	-0.090245
3	8	0	3.017871	-0.082459	1.497211
4	7	0	3.111083	0.252895	-1.046202
5	7	0	3.318006	1.448254	-0.801965
6	7	0	3.540919	2.541300	-0.677691
7	6	0	0.777359	-0.432664	0.194371
8	6	0	0.032893	-1.187699	-0.707286
9	6	0	0.171643	0.509627	1.018697
10	6	0	-1.337433	-0.993310	-0.788832
11	6	0	-1.200832	0.703584	0.937705
12	6	0	-1.940726	-0.047203	0.032953
13	1	0	0.518549	-1.925962	-1.328292
14	1	0	0.763155	1.071510	1.726286
15	1	0	-1.929904	-1.573808	-1.479712
16	1	0	-1.686831	1.426427	1.575398
17	35	0	-3.822172	0.217799	-0.079656

Transition state between ground state BsN_3 and ^{1}(BsN) + N_2, B3LYP/6-311++G(3df,3pd)

E_{total} = -3518.1551855 au, μ = 3.70 D, Negative frequency at -368.2 cm^{-1} (104.1 km mol^{-1})

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z

1	16	0	2.507769	-0.779211	0.094217
2	8	0	2.828293	-1.820638	-0.888955
3	8	0	2.905953	-0.882141	1.465457
4	7	0	3.281791	0.225401	-0.880751
5	7	0	3.700283	2.968042	0.003945
6	7	0	3.345751	1.935340	-0.045882
7	6	0	0.759895	-0.489992	0.067408
8	6	0	0.063021	-0.350794	1.261723
9	6	0	0.102832	-0.410407	-1.158711
10	6	0	-1.308136	-0.127515	1.234398
11	6	0	-1.264532	-0.190074	-1.188993
12	6	0	-1.957208	-0.049079	0.009991
13	1	0	0.588855	-0.423218	2.201956
14	1	0	0.656923	-0.523137	-2.079202
15	1	0	-1.861212	-0.019713	2.155245
16	1	0	-1.786973	-0.129077	-2.131742
17	35	0	-3.836168	0.256870	-0.033195

Transition state between ground state BsN_3 and *p*-$BrNSO_2$ + N_2, B3LYP/6-311++G(3df,3pd)

E_{total} = -3518.1521655 au, μ = 4.00 D, Negative frequency at -514.6 cm^{-1} (354.7 km mol^{-1})

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.672537	-0.341090	0.000279
2	16	0	2.426433	-0.745641	0.000581
3	8	0	2.813558	-1.384079	-1.231838
4	8	0	2.813783	-1.381719	1.234148
5	7	0	2.443271	0.869719	-0.000923
6	7	0	4.210228	1.363454	-0.001235
7	7	0	4.976387	2.145010	-0.001559
8	6	0	-0.007493	-0.241732	-1.217661
9	6	0	-0.007424	-0.239327	1.218060
10	6	0	-1.378734	-0.063539	-1.218306
11	6	0	-1.378666	-0.061140	1.218434
12	6	0	-2.049932	0.025769	-0.000005
13	1	0	0.543678	-0.319904	-2.143225
14	1	0	0.543803	-0.315649	2.143745
15	1	0	-1.923655	0.007463	-2.147416
16	1	0	-1.923533	0.011688	2.147433
17	35	0	-3.931225	0.272918	-0.000202

Singlet ^{1}(BsN) nitrene, B3LYP/6-311++G(3df,3pd)

E_{total} = -3408.5982704 au, μ = 4.16 D.

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	16	0	2.958708	0.126737	-0.065342
2	8	0	3.483465	-0.852099	0.977670
3	8	0	3.383918	1.490303	-0.097403
4	7	0	3.634491	-1.078920	-0.769620
5	6	0	1.198748	0.091440	-0.039659
6	6	0	0.550710	-1.141664	-0.087108
7	6	0	0.482829	1.282915	0.015072
8	6	0	-0.833113	-1.181430	-0.066603
9	6	0	-0.904555	1.242324	0.030930
10	6	0	-1.548087	0.011879	-0.008257
11	1	0	1.128045	-2.052703	-0.145596
12	1	0	1.005879	2.226746	0.045819
13	1	0	-1.351818	-2.127466	-0.100743
14	1	0	-1.475440	2.157506	0.073450
15	35	0	-3.448734	-0.046224	0.012900

Triplet ^{3}(BsN) nitrene, B3LYP/6-311++G(3df,3pd)

E_{total} = -3408.6214466 au, μ = 4.25 D.

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	16	0	-2.984248	0.000010	-0.059742
2	8	0	-3.465291	-1.253280	-0.576703
3	8	0	-3.465570	1.254112	-0.574485
4	7	0	-3.293530	-0.001475	1.584639
5	6	0	-1.221414	0.000196	-0.053591
6	6	0	-0.535531	1.214700	-0.040529
7	6	0	-0.535395	-1.214515	-0.040467
8	6	0	0.849777	1.214773	-0.023859
9	6	0	0.849669	-1.214509	-0.023738
10	6	0	1.529169	0.000243	-0.013294
11	1	0	-1.084469	2.144742	-0.060275
12	1	0	-1.084567	-2.144418	-0.060279
13	1	0	1.396076	2.145839	-0.022441

14	1	0	1.396339	-2.145357	-0.022214
15	35	0	3.428815	-0.000075	0.011742

p-Bromo-*N*-sulfonylaniline, $BrPhNSO_2$, B3LYP/6-311++G(3df,3pd)

E_{total} = -3408.7051213 au, μ = 1.57 D.

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	16	0	-3.580582	-0.119154	0.000669
2	8	0	-4.867486	0.507369	-0.001277
3	8	0	-3.477823	-1.554693	0.003928
4	7	0	-2.395650	0.801151	-0.002163
5	6	0	-1.024939	0.464040	-0.001224
6	6	0	-0.494179	-0.829290	-0.002800
7	6	0	-0.158065	1.560726	0.000812
8	6	0	0.880776	-1.015358	-0.002359
9	6	0	1.215114	1.376609	0.001373
10	6	0	1.726545	0.085582	-0.000246
11	1	0	-1.146792	-1.687985	-0.004306
12	1	0	-0.577334	2.556463	0.001875
13	1	0	1.287819	-2.015350	-0.003628
14	1	0	1.878006	2.228735	0.002991
15	35	0	3.614518	-0.178820	0.000370

Nitrogen molecule, N_2, B3LYP/6-311++G(3df,3pd)

E_{total} = -109.5673717 au, μ = 0.00 D.

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	7	0	0.000000	0.000000	0.545592
2	7	0	0.000000	0.000000	-0.545592

***p*-Toluenesulfonylazide**, S_0 state, TsN_3, B3LYP/6-311++G(3df,3pd)

E_{total} = -984.0045916 au, μ = 5.64 D.

S_1 state

E_{total} = -983.8401351 au.

T_1 state

E_{total} = -983.8589370 au, μ = 6.50 D.

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	16	0	1.489380	-0.722003	0.306407
2	8	0	1.721646	-2.082034	-0.058970
3	8	0	1.998235	-0.153951	1.521417
4	7	0	2.166704	0.159148	-1.021322
5	7	0	2.409057	1.349035	-0.790179
6	7	0	2.667135	2.436047	-0.674684
7	6	0	-0.236272	-0.361354	0.175600
8	6	0	-1.014270	-1.071921	-0.735846
9	6	0	-0.794456	0.627093	0.977309
10	6	0	-2.363204	-0.778547	-0.839249
11	6	0	-2.150091	0.904985	0.857814
12	6	0	-2.953003	0.214463	-0.049638
13	1	0	-0.567122	-1.847919	-1.339460
14	1	0	-0.181481	1.153791	1.693576
15	1	0	-2.972444	-1.333427	-1.540958
16	1	0	-2.589923	1.667760	1.486566
17	6	0	-4.418080	0.526858	-0.187006
18	1	0	-5.020141	-0.381086	-0.137633
19	1	0	-4.757465	1.203197	0.595139
20	1	0	-4.624563	0.998532	-1.149937

Transition state between ground state TsN_3 and ^{1}(TsN) + N_2, B3LYP/6-311++G(3df,3pd)

E_{total} = -983.942662 au, μ = 5.71 D, Negative frequency at -378.6 cm^{-1} (99.3 km mol^{-1})

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	16	0	1.446413	-0.831639	0.098032
2	8	0	1.696861	-1.891856	-0.886636

3	8	0	1.827534	-0.974273	1.471480
4	7	0	2.314348	0.111113	-0.863087
5	7	0	2.930514	2.806136	0.023445
6	7	0	2.499704	1.802711	-0.028368
7	6	0	-0.267958	-0.398976	0.056976
8	6	0	-0.965787	-0.216902	1.243544
9	6	0	-0.904783	-0.249335	-1.174754
10	6	0	-2.314072	0.117141	1.193235
11	6	0	-2.247502	0.081362	-1.204746
12	6	0	-2.975507	0.270614	-0.023636
13	1	0	-0.458644	-0.342165	2.188435
14	1	0	-0.350640	-0.394176	-2.090726
15	1	0	-2.858132	0.257047	2.118030
16	1	0	-2.743163	0.195070	-2.160341
17	6	0	-4.437443	0.621058	-0.078441
18	1	0	-4.606277	1.507040	-0.692242
19	1	0	-5.015463	-0.192099	-0.521695
20	1	0	-4.839098	0.815055	0.914286

Transition state between ground state TsN_3 and *p*-$TolNSO_2$ + N_2, B3LYP/6-311++G(3df,3pd)

E_{total} = -983.940417 au, μ = 5.97 D, Negative frequency at -521.0. cm^{-1} (321.4 km mol^{-1})

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.364510	-0.246227	0.000060
2	16	0	-1.352523	-0.765861	0.000339
3	8	0	-1.700425	-1.427195	1.233401
4	8	0	-1.700423	-1.428262	-1.232151
5	7	0	-1.492952	0.845122	-0.000323
6	7	0	-3.281994	1.206257	-0.000437
7	7	0	-4.097914	1.936298	-0.000871
8	6	0	1.037588	-0.094043	1.216924
9	6	0	1.037545	-0.095253	-1.216923
10	6	0	2.391348	0.181715	1.205862
11	6	0	2.391371	0.180497	-1.206142
12	6	0	3.089626	0.321932	-0.000241
13	1	0	0.492903	-0.207149	2.142628
14	1	0	0.492845	-0.209285	-2.142504
15	1	0	2.920049	0.295544	2.143009
16	1	0	2.920053	0.293361	-2.143406
17	6	0	4.566187	0.593782	-0.000180
18	1	0	4.868184	1.157333	0.881357
19	1	0	5.123560	-0.346513	0.006738

20	1	0	4.870536	1.145992	-0.887999

Singlet ^{1}(TsN) nitrene, B3LYP/6-311++G(3df,3pd)

E_{total} = -874.3864079 au, μ = 6.40 D.

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	16	0	1.913397	0.141858	-0.069890
2	8	0	2.468636	-0.814534	0.980461
3	8	0	2.319065	1.512011	-0.116643
4	7	0	2.612594	-1.057741	-0.763235
5	6	0	0.157208	0.076732	-0.038323
6	6	0	-0.471991	-1.164446	-0.085942
7	6	0	-0.580843	1.256136	0.023587
8	6	0	-1.856192	-1.215631	-0.058307
9	6	0	-1.964201	1.181373	0.045818
10	6	0	-2.624066	-0.049945	0.006767
11	1	0	0.119483	-2.065969	-0.149560
12	1	0	-0.072991	2.208181	0.054093
13	1	0	-2.349790	-2.177640	-0.093280
14	1	0	-2.541455	2.095556	0.094254
15	6	0	-4.126667	-0.109770	0.029507
16	1	0	-4.486256	-1.136506	0.010199
17	1	0	-4.522256	0.371120	0.925560
18	1	0	-4.550336	0.413197	-0.829570

Triplet ^{3}(TsN) nitrene, B3LYP/6-311++G(3df,3pd)

E_{total} = -874.4097443 au, μ = 6.42 D.

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	16	0	-1.947271	-0.001021	-0.063158
2	8	0	-2.430445	-1.253731	-0.581473
3	8	0	-2.434152	1.252251	-0.576627
4	7	0	-2.264183	-0.004278	1.579632
5	6	0	-0.187841	0.001348	-0.051572
6	6	0	0.497823	1.214884	-0.035414
7	6	0	0.502991	-1.212289	-0.035119

8	6	0	1.883486	1.205735	-0.013967
9	6	0	1.885637	-1.198880	-0.013625
10	6	0	2.598590	0.005904	-0.000344
11	1	0	-0.052126	2.144233	-0.057090
12	1	0	-0.044807	-2.142904	-0.056837
13	1	0	2.419772	2.145294	-0.010921
14	1	0	2.425082	-2.137123	-0.010450
15	6	0	4.101428	-0.002073	0.025755
16	1	0	4.507455	1.007281	0.020874
17	1	0	4.471644	-0.512480	0.916605
18	1	0	4.502684	-0.533950	-0.838565

p-Methyl-*N*-sulfonylaniline, *p*-TolNSO$_2$, B3LYP/6-311++G(3df,3pd)

E_{total} = -874.4914838 au, μ = 3.94 D.

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	16	0	2.498476	0.054762	0.002743
2	8	0	3.754546	-0.634608	0.003488
3	8	0	2.472170	1.494732	0.005667
4	7	0	1.269781	-0.804221	-0.001892
5	6	0	-0.085147	-0.402449	-0.002911
6	6	0	-0.554925	0.912709	-0.009390
7	6	0	-1.004872	-1.455475	-0.002066
8	6	0	-1.921983	1.152865	-0.012407
9	6	0	-2.364476	-1.195172	-0.005010
10	6	0	-2.852029	0.113540	-0.007802
11	1	0	0.137340	1.739885	-0.014470
12	1	0	-0.633355	-2.470161	-0.001752
13	1	0	-2.270624	2.177667	-0.020411
14	1	0	-3.059705	-2.025106	-0.007317
15	6	0	-4.331628	0.387596	0.015633
16	1	0	-4.552493	1.408334	-0.292486
17	1	0	-4.871550	-0.291322	-0.644759
18	1	0	-4.737056	0.251383	1.021024

***p*-Methanesulfonylazide**, S_0 state, MsN_3, B3LYP/6-311++G(3df,3pd)

E_{total} = -752.8803767 au, μ = 3.71 D.

S_1 state

E_{total} = -752.7035065 au, μ = 3.92 D.

T_1 state

E_{total} = -752.7204012 au, μ = 3.91 D.

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-1.377329	1.441986	-0.007729
2	1	0	-2.324989	1.384326	0.523779
3	1	0	-0.707311	2.143821	0.480097
4	1	0	-1.537347	1.698822	-1.050477
5	16	0	-0.668310	-0.186959	0.068803
6	8	0	-1.500129	-1.083365	-0.667911
7	8	0	-0.258083	-0.467255	1.414697
8	7	0	0.739727	0.031874	-0.906686
9	7	0	1.807310	0.073331	-0.282372
10	7	0	2.823289	0.111570	0.191607

Transition state between ground state MsN_3 and ^{1}(MsN) + N_2, B3LYP/6-311++G(3df,3pd)

E_{total} = -752.8176507 au, μ = 4.13 D, Negative frequency at -352.2 cm^{-1} (94.5 km mol^{-1})

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	16	0	-0.736742	-0.100583	0.132461
2	8	0	-1.570440	-1.152776	-0.460420
3	8	0	-0.677246	0.117846	1.545753
4	7	0	0.496138	-0.790912	-0.616369
5	6	0	-1.177981	1.446831	-0.629308
6	1	0	-0.436639	2.192555	-0.353578
7	1	0	-1.215138	1.301876	-1.704011
8	1	0	-2.151369	1.733133	-0.236818
9	7	0	3.200038	0.132478	-0.001287
10	7	0	2.109594	0.084181	-0.058314

Transition state between ground state MsN_3 and *p*-$MeNSO_2$ + N_2, B3LYP/6-311++G(3df,3pd)

E_{total} = -752.8009486 au, μ = 3.02 D, Negative frequency at -505.7 cm^{-1} (141.0 km mol^{-1})

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-1.754931	1.286319	0.000680
2	1	0	-2.687161	0.713808	-0.034166
3	1	0	-1.683924	1.841985	0.925574
4	1	0	-1.649065	1.883891	-0.894549
5	16	0	-0.650730	-0.259335	-0.000109
6	8	0	-0.846229	-0.984490	-1.227860
7	8	0	-0.843823	-0.978084	1.231846
8	7	0	0.397474	0.934511	-0.005055
9	7	0	2.146768	0.081622	-0.000133
10	7	0	3.238876	0.082775	0.000749

Singlet ^{1}(MsN) nitrene, B3LYP/6-311++G(3df,3pd)

E_{total} = -643.2594312 au, μ = 4.24 D.

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	16	0	0.016568	0.160879	-0.056563
2	8	0	1.030806	-0.486238	0.873645
3	8	0	-0.383435	1.526403	0.064602
4	7	0	1.201177	-0.388991	-0.894302
5	6	0	-1.445945	-0.847720	-0.038003
6	1	0	-2.036506	-0.585641	-0.913143
7	1	0	-1.135484	-1.886580	-0.065389
8	1	0	-2.004630	-0.613899	0.865683

Triplet ^{3}(MsN) nitrene, B3LYP/6-311++G(3df,3pd)

E_{total} = -643.2814844 au, μ = 3.92 D.

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	16	0	-0.139476	0.000011	-0.073067
2	8	0	-0.598407	-1.250097	-0.615069
3	8	0	-0.598420	1.250221	-0.614817
4	7	0	-0.561651	-0.000174	1.563597
5	6	0	1.636879	0.000006	0.008873
6	1	0	1.968975	0.900676	0.517554
7	1	0	1.968968	-0.900621	0.517638
8	1	0	1.978571	-0.000053	-1.025453

N-Sulfonylmethanamine, CH_3NSO_2, B3LYP/6-311++G(3df,3pd)

E_{total} = -643.3602273 au, μ = 2.94 D.

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	16	0	0.481766	-0.007144	0.000126
2	6	0	-2.098389	-0.022237	-0.000041
3	8	0	0.569485	1.428578	-0.000073
4	8	0	1.674171	-0.796540	-0.000115
5	7	0	-0.823310	-0.744064	-0.000023
6	1	0	-2.657431	-0.330306	0.882295
7	1	0	-1.988865	1.061096	-0.000417
8	1	0	-2.657701	-0.330911	-0.881987

Geometries and energies of azides and related species at M06-2X/6-311G(d,p) level of theory

***p*-Bromobenzenesulfonylazide**, S_0 state, BsN_3, M06-2X/6-311G(d,p)

E_{total} = -3517.8996359 au, μ = 4.24 D.

S_1 state

E_{total} = -3517.7363467 au, μ = 4.79 D.

T_1 state

E_{total} = -3517.7393952 au, μ = 4.67 D.

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	16	0	2.536737	-0.662382	0.279953
2	8	0	2.861737	-2.020312	-0.067427
3	8	0	3.031646	-0.027580	1.482618
4	7	0	3.097553	0.245339	-1.076022
5	7	0	3.224036	1.457721	-0.820696
6	7	0	3.369776	2.554450	-0.680263
7	6	0	0.779678	-0.439737	0.204636
8	6	0	0.038539	-1.253223	-0.645039
9	6	0	0.194624	0.556780	0.976302
10	6	0	-1.332305	-1.057329	-0.730285
11	6	0	-1.178217	0.750995	0.889405
12	6	0	-1.922394	-0.057048	0.036880
13	1	0	0.525700	-2.030363	-1.221576
14	1	0	0.798676	1.157873	1.645294
15	1	0	-1.936997	-1.678498	-1.377631
16	1	0	-1.663182	1.514854	1.482512
17	35	0	-3.793662	0.206062	-0.076626

Singlet ^{1}(BsN) nitrene, M06-2X/6-311G(d,p)

E_{total} = -3408.3214841 au, μ = 4.54 D.

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	16	0	2.947549	0.144031	-0.078747

2	8	0	3.447503	-0.928210	0.921244
3	8	0	3.388943	1.512436	-0.033328
4	7	0	3.647056	-1.080482	-0.741516
5	6	0	1.183200	0.107879	-0.040864
6	6	0	0.556260	-1.133419	-0.082029
7	6	0	0.474956	1.301078	0.007621
8	6	0	-0.828338	-1.178997	-0.059358
9	6	0	-0.913353	1.251148	0.023010
10	6	0	-1.546860	0.014230	-0.008956
11	1	0	1.150451	-2.038892	-0.130070
12	1	0	1.002709	2.246355	0.035644
13	1	0	-1.348726	-2.127091	-0.086112
14	1	0	-1.495771	2.162154	0.059482
15	35	0	-3.435588	-0.052256	0.012336

Triplet ^{3}(BsN) nitrene, M06-2X/6-311G(d,p)

E_{total} = -3408.3482284 au, μ = 4.06 D.

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	16	0	-2.977359	0.000022	-0.064374
2	8	0	-3.464428	-1.267379	-0.562733
3	8	0	-3.464427	1.267654	-0.562141
4	7	0	-3.255645	-0.000417	1.631048
5	6	0	-1.208512	0.000029	-0.081022
6	6	0	-0.536293	1.218072	-0.065344
7	6	0	-0.536310	-1.218026	-0.065354
8	6	0	0.850812	1.216873	-0.036929
9	6	0	0.850793	-1.216851	-0.036924
10	6	0	1.526469	0.000006	-0.020890
11	1	0	-1.094900	2.146237	-0.091208
12	1	0	-1.094922	-2.146188	-0.091243
13	1	0	1.403907	2.146666	-0.031422
14	1	0	1.403873	-2.146653	-0.031407
15	35	0	3.415954	-0.000009	0.019877

p-Bromo-*N*-sulfonylaniline, $BrPhNSO_2$, M06-2X/6-311G(d,p)

E_{total} = -3408.4275113 au, μ = 1.70 D.

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	16	0	-3.545655	-0.121100	0.054378
2	8	0	-4.866675	0.422651	-0.097364
3	8	0	-3.363966	-1.511857	0.399598
4	7	0	-2.401087	0.814446	-0.214304
5	6	0	-1.026770	0.477667	-0.128057
6	6	0	-0.501661	-0.806270	-0.286839
7	6	0	-0.172476	1.562442	0.073755
8	6	0	0.872827	-0.997263	-0.235992
9	6	0	1.199211	1.372062	0.130752
10	6	0	1.711753	0.089317	-0.025990
11	1	0	-1.151732	-1.656264	-0.445165
12	1	0	-0.601883	2.550675	0.180512
13	1	0	1.288206	-1.989008	-0.359574
14	1	0	1.864807	2.210318	0.289802
15	35	0	3.585329	-0.181524	0.039453

Nitrogen molecule, N_2, M06-2X/6-311G(d,p)

E_{total} = -109.5596937 au, μ = 0.00 D.

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	7	0	0.000000	0.000000	0.547789
2	7	0	0.000000	0.000000	-0.547789

***p*-Toluenesulfonylazide**, S_0 state, TsN_3, M06-2X/6-311G(d,p)

E_{total} = -983.6376418 au, μ = 6.82 D.

S_1 state

E_{total} = -983.4756209 au, μ = 7.38 D.

T_1 state

E_{total} = -983.4786614 au, μ = 7.30 D.

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	16	0	1.516127	-0.706888	0.293745
2	8	0	1.777675	-2.079285	-0.054311
3	8	0	2.036938	-0.104309	1.502876
4	7	0	2.154932	0.171248	-1.053926
5	7	0	2.287851	1.383675	-0.810080
6	7	0	2.439814	2.480947	-0.674489
7	6	0	-0.218688	-0.379915	0.191783
8	6	0	-0.995498	-1.141853	-0.676180
9	6	0	-0.757672	0.649861	0.952348
10	6	0	-2.346102	-0.851163	-0.781163
11	6	0	-2.115181	0.922551	0.829846
12	6	0	-2.922631	0.184154	-0.036259
13	1	0	-0.546071	-1.947405	-1.244531
14	1	0	-0.132203	1.210293	1.636893
15	1	0	-2.968241	-1.440456	-1.445837
16	1	0	-2.553468	1.716599	1.423530
17	6	0	-4.387586	0.494181	-0.181320
18	1	0	-4.982105	-0.420872	-0.168653
19	1	0	-4.735533	1.146541	0.619341
20	1	0	-4.575336	0.996275	-1.134064

Singlet ^{1}(TsN) nitrene, M06-2X/6-311G(d,p)

E_{total} = -874.0596506 au, μ = 6.86 D.

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	16	0	1.906463	0.161508	-0.082557
2	8	0	2.438333	-0.890474	0.924761
3	8	0	2.326386	1.538091	-0.048199
4	7	0	2.634358	-1.052657	-0.735992

5	6	0	0.146180	0.091642	-0.042622
6	6	0	-0.459178	-1.158718	-0.083429
7	6	0	-0.587721	1.271079	0.013566
8	6	0	-1.844200	-1.220122	-0.052091
9	6	0	-1.971704	1.183148	0.036426
10	6	0	-2.616369	-0.056445	0.005666
11	1	0	0.151552	-2.052880	-0.135981
12	1	0	-0.077870	2.226095	0.041257
13	1	0	-2.334960	-2.186197	-0.078629
14	1	0	-2.562719	2.091580	0.079096
15	6	0	-4.119329	-0.123293	0.030100
16	1	0	-4.471563	-1.154400	0.017649
17	1	0	-4.511260	0.362334	0.926533
18	1	0	-4.540921	0.393249	-0.835256

Triplet ^{3}(TsN) nitrene, M06-2X/6-311G(d,p)

E_{total} = -874.0862932 au, μ = 6.36 D.

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	16	0	-1.944671	-0.000868	-0.067837
2	8	0	-2.434875	-1.266435	-0.570285
3	8	0	-2.438897	1.266728	-0.561069
4	7	0	-2.230764	-0.007692	1.625872
5	6	0	-0.179757	0.001735	-0.080181
6	6	0	0.497612	-1.215132	-0.061492
7	6	0	0.493033	1.218418	-0.061597
8	6	0	1.882602	-1.200531	-0.027049
9	6	0	1.880741	1.208462	-0.026874
10	6	0	2.590493	0.006067	-0.004280
11	1	0	-0.059577	-2.144055	-0.091656
12	1	0	-0.066363	2.146055	-0.091293
13	1	0	2.428048	-2.137876	-0.022085
14	1	0	2.421732	2.147819	-0.022178
15	6	0	4.093748	-0.003739	0.054210
16	1	0	4.506670	-0.706265	-0.672094
17	1	0	4.506016	0.984863	-0.147178
18	1	0	4.432893	-0.316834	1.045173

p-Methyl-*N*-sulfonylaniline, *p*-TolNSO$_2$, M06-2X/6-311G(d,p)

E_{total} = -874.1636535 au, μ = 4.14 D.

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	16	0	2.473227	-0.055464	0.043638
2	8	0	3.766782	0.553845	-0.112561
3	8	0	2.368849	-1.456928	0.382107
4	7	0	1.281937	0.820783	-0.215996
5	6	0	-0.075668	0.417194	-0.119876
6	6	0	-0.538294	-0.891063	-0.257700
7	6	0	-0.984047	1.458581	0.079559
8	6	0	-1.903635	-1.140713	-0.186837
9	6	0	-2.340264	1.188419	0.153728
10	6	0	-2.824762	-0.115446	0.020281
11	1	0	0.152734	-1.709240	-0.410274
12	1	0	-0.603336	2.468023	0.173280
13	1	0	-2.257154	-2.160521	-0.292793
14	1	0	-3.037974	2.003295	0.315473
15	6	0	-4.303406	-0.392662	0.078204
16	1	0	-4.500671	-1.457325	0.206181
17	1	0	-4.770919	0.144616	0.905612
18	1	0	-4.792453	-0.068110	-0.844243