Halogen Derivatives of *m*-Phenylenecarbenonitrene: A Switch In Ground-State Multiplicity

Tomonori Enyo, §Athanassios Nicolaides,*¶and Hideo Tomioka*§

¶*Department of Chemistry, University of Cyprus, Nicosia 1678, Cyprus*

§*Chemistry Department for Materials, Faculty of Engineering, Mie University, Tsu, Mie 514-8507 Japan*

SUPPORTING INFORMATION

(Experimental Section, Tables S1-S4, Figures S1-S7, 36 total pages)

Experimental Section

3-Azidophenyldiazomethane (**3-H**) was prepared according to a modified procedure of Rees.[1] Thus, a mixture of 3-azidobenzaldehyde (190 mg, 1.3 mmol) and *p*-tosylhydrazine (250 mg, 3.4 mmol) in anhydrous tetrahydrofuran (10 mL) was stirred overnight at room temperature in the dark. After evaporation of the solvent, 3-azidobenzaldehyde tosylhydrazone was obtained as a white solid, which was used for the next step without further purification. To a stirred suspension of sodium hydride (60% oil supension, 52 mg, 1.3 mmol) in anhydrous tetrahydrofuran (10 mL) was added the hydrazone (410 mg, 1.3 mmol), and the mixture was stirred for 30 min at room temperature. The precipitate was collected by filtration and washed thoroughly with anhydrous ether to give sodium 3-azidobenzaldehyde tosylhydrozonate as a white solid (340 mg, 78%). The sodium salt (50 mg, 0.15 mmol) was placed in a micro sublimation apparatus and heated at 120 ^{o}C under 5x10^{-4} Torr. The diazo azido (**3-H**) was collected from a cold finger as a rather unstable red liquid (18 mg, 75%) and was immediately used for the matrix photolysis experiments: ^{1}H NMR ($CDCl_3$) δ 4.93 (s, 1H), 6.52 (dd, *J* = 2.02, 2.02 Hz, 1H), 6.65-6.75 (m, 2H), 7.25 (dd, *J* = 7.90, 7.90 Hz, 1H) ; IR (Ar, 13 K) ν 2121 (vs), 2068 (vs), 1616 (w), 1603 (m), 1582 (w), 1491 (m), 1452 (w), 1390 (w), 1370 (w), 1303 (m), 1296 (w), 1287 (w), 1265 (w), 1213 (w), 1203 (w), 1174 (w), 780 (w), 771 (w), 697 (w), 682 (w), 675 (w) cm^{-1}; UV (Ar, 10 K) λ_{max} 278, 257 nm.

3-(3-Azidophenyl)-3-chlorodiazirine (6-Cl). 3-Azidobenzonitrile was prepared following the literature procedure[2]. A mixture of 3-aminobenzonitrile (990 mg, 8.4 mmol), water (24 mL) and concentrated hydrochloric acid (24 mL) was stirred at 0-5 ^{o}C until a clear solution was obtained. To the amine hydrochloride solution was added dropwise a solution of sodium nitrite (700 mg) in water (9 mL). To the stirred solution of the diazonium salt was added a solution of sodium azide (1.1 g, 17 mmol) in water (9 mL) at 0-5 ^{o}C. After the reaction mixture was stirred for an additional hour, the resulting solution was extracted with CH_2Cl_2. The organic phase was washed (H_2O), dried (Na_2SO_4), filtered, evaporated, and dried in vacuo to give 3-azidobenzonitrile (1.2 g, 98%) as a light yellow solid : mp 55-56^{o}C; ^{1}H NMR ($CDCl_3$) δ 7.24-7.30 (m, 2H) 7.42 (ddd, *J* = 7.53, 1.65, 1.65 Hz, 1H), 7.47 (ddd, *J*

= 7.72, 7.72, 0.74 Hz, 1H); IR ν 2236 (m), 2195 (m), 2119 (s), 1600 (m), 1582 (m), 1486 (m), 1476 (m), 1430 (m), 1328 (m), 1299 (m), 1274 (m), 1216 (w), 1190 (w), 1112(w), 916(w), 894 (w), 868 (w), 791 (m), 757 (m), 679 (m), 600 (w), 534 (w) cm^{-1}. 3-Azidophenylimidate hydrochloride was prepared following the literature procedure[3]. Dry hydrogen chloride was passed into a solution of 3-azidobenzonitrile (1.1 g, 8.0 mmol) and absolute ethanol (0.47 mL, 8.0 mmol) in absolute $CHCl_3$ (2 mL) for 1 h. Then the flask was tightly stoppered and allowed to stand in a freezer. After 13 days, absolute Et_2O was added to the mixture under vigorous stirring. The precipitate was filtered, washed (Et_2O), and dried in vacuo to give 3-azidophenylimidate hydrochloride (1.6 g, 91%) as a white solid: mp 115-118 °C dec; ^{1}H NMR ($CDCl_3$) δ 1.63 (t, *J*=6.61 Hz, 3H), 4.92 (quart, *J*=6.80 Hz, 2H), 7.35 (d, *J* = 8.08 Hz, 1H), 7.57 (d, *J* = 7.90 Hz, 1H), 7.97 (s, 1H), 8.26 (d, *J* = 8.27 Hz, 1H) ; IR (KBr disk) ν 3200-2550 (bs), 2117 (s), 1639 (m), 1620 (m), 1605 (m), 1586 (m), 1497 (w), 1458 (m), 1450 (w), 1434 (w), 1390 (w), 1357 (w), 1300 (m), 1277 (m), 1171 (w), 1122 (m), 1074 (m), 997 (w), 884 (m), 851 (w), 800 (w), 784 (w), 735 (w), 685 (w), 670 (w), 556 (w), 530 (w) cm^{-1}. 3-Azidophenylamidine hydrochloride was prepared following the literature procedure.[3] To a solution of ethanol saturated with ammonia was added 3-azidophenylimidate hydrochloride (1.6 g, 7.2 mmol). After stirring overnight, the resulting mixture was filtered to remove an ammonium chloride. Removal of the solvent and drying of the solid in vacuo afforded 3-azidophenylamidine hydrochloride (1.5 g, quantitative) as a white solid: mp 183-184 °C (dec) ; IR (KBr disk) ν 3400-2900 (br.s), 2191 (w), 2168 (w), 2118 (s), 1673 (m), 1609 (w), 1584 (w), 1529 (w), 1478 (m), 1431 (w), 1322 (w), 1303 (m), 1280 (m), 1185 (w), 1109 (w), 1092 (w), 888 (w), 874 (w), 784 (w), 734 (m), 710 (m), 692 (m) cm^{-1}. **6-Cl** was prepared following the literature procedure.[4] A mixture of 3-azidophenylamidine hydrochloride (200 mg, 1.0 mmol), dimethylsulfoxide (3.5 mL) , LiCl (230 mg) and *n*-hexane (3 mL) was stirred at ~5 °C. A hypochlorite solution (8.0 mL) containing NaCl (1.4 g) was added rapidly to the stirred solution and the whole was stirred for an additional hour. Extraction with *n*-hexane and purification by gel permeation chromatography afforded **6-Cl** (90 mg, 46%) as a pale yellow liquid. ^{1}H NMR ($CDCl_3$) δ 6.78-6.82 (m, 2H), 7.06 (ddd, *J*=8.08, 2.02, 1.10 Hz, 1H), 7.37 (dd, *J* = 8.27 8.27 Hz, 1H);

^{13}C NMR ($CDCl_3$) δ 141, 138, 130, 122, 119, 116, 46; IR (Ar, 13 K) ν 2148 (m), 2137 (m), 2110 (s), 1613 (w), 1607 (w), 1592 (w), 1576 (m), 1494 (m), 1486 (m), 1442 (m), 1428 (w), 1327 (w), 1312 (m), 1284 (w), 1243 (w), 1179 (w), 1128 (w), 1105 (w), 1039 (w), 1025 (w), 999 (w), 989 (w), 978 (w), 951 (w), 944 (w), 894 (w), 880 (w), 853 (w), 835 (w), 815 (w), 788 (w), 781 (w), 714 (w), 687 (m), 654 (w), 535 (w); UV (Ar, 13 K) λ_{max} 386, 366, 348, 247, 220 nm.

3-(3-Azidophenyl)-3-bromodiazirine (6-Br) was prepared following the literature procedure.[5] A mixture of 3-azidophenylamidine hydrochloride (1.3 g, 6.5 mmol) dimethylsulfoxide (27 mL), LiBr**.**H_2O (3.31 g), and *n*-hexane (13 mL) was stirred at ~5 ^{o}C. A fresh solution of NaOBr, prepared by the slow addition of bromine (3.1 mL) to a stirred and cooled (-10 ^{o}C) solution of NaOH (7.3 g) and NaBr (20 g) in water (46 mL), was added rapidly to the stirred solution, and the whole mixture was stirred for an additional hour Extraction with *n*-hexane and purification by silica gel column chromatography afforded **6-Br** as a pale yellow liquid (540 mg, 45%): ^{1}H NMR ($CDCl_3$) δ 6.82-6.86 (m, 2H), 7.05 (ddd, *J* = 8.08, 2.02, 1.10 Hz, 1H), 7.35 (dd, *J* = 8.27, 8.27 Hz, 1H) ; ^{13}C NMR ($CDCl_3$) δ 141, 139, 130, 123, 120, 118, 117, 37; IR (Ar, 13 K) ν 2129 (s), 2121 (m), 2106 (s), 1614 (w), 1604 (w), 1590 (w), 1575 (w), 1494 (w), 1484 (w), 1440 (w), 1427 (w), 1327 (w), 1311 (s), 1285 (w), 1233 (w), 1178 (w), 1126 (w), 1104 (w), 1094 (w), 1069 (w), 1029 (w), 1018 (w), 1015 (w), 999 (w), 971 (w), 964 (w), 954 (w), 946 (w), 926 (w), 918 (w), 891 (w), 879 (w), 874 (w), 848 (w), 819 (w), 805 (w), 797 (w), 787 (w), 781 (w), 709 (w), 687 (w), 679 (w), 648 (w), 536 (w) cm^{-1}; UV (Ar, 13 K) λ_{max} 388, 370, 350, 247, 222 nm.

3-(3-Azidophenyl)-3-fluorodiazirine (6-F) was prepared following the literature procedure.[5] A mixture of **6-Br** (90 mg, 0.38 mmol), *n*-$Bu_4N^+F^-$ (460 mg, 1.8 mmol) and absolute acetonitrile (1 mL) was stirred at 25 ^{o}C in the dark for 4 h. The reaction was quenched with water (5 mL) and the resulting solution was extracted with *n*-hexane. Purification by gel permeation chromatography afforded **6-F** (7 mg, 10%) as a pale yellow liquid; ^{1}H NMR ($CDCl_3$) δ 6.68-6.76 (m, 2H), 7.10 (ddd, *J* = 8.08, 2.02, 1.10 Hz, 1H), 7.40 (dd, *J* = 8.27, 8.27 Hz, 1H); IR (Ar, 13 K) ν 2147 (w), 2125 (m), 2109 (s), 1614 (w), 1594 (w), 1568 (m), 1497 (w), 1490 (w), 1446 (w), 1327 (m), 1285 (w), 1271 (m), 1262 (w),

1170 (m), 1126 (w), 1043 (w), 873 (w), 791 (w), 734 (w), 688 (w), 661 (w), 558 (w), 536 (w) cm^{-1}; UV (Ar, 13 K) λ_{max} 384, 365, 348 sh, 293 sh, 247 nm.

3-Nitrenophenyldiazomethane (4-H): IR (Ar, 13 K) ν 2076, 1547, 1535, 1523, 1445, 1402, 1336, 1274, 1235, 1195, 1145, 837, 762, 651, 631 cm^{-1}.

***Z*-5-H**: IR (Ar, 13 K) ν 2208, 1733, 1594, 1588, 1505, 1304, 1107, 962, 955, 790, 732, 714, 704 cm^{-1}; UV (Ar, 13 K) λ_{max} 287 nm.

***E*-5-H:** IR (Ar, 13 K) ν 2223, 1769, 1741, 1624, 1605, 1520, 1352, 1170, 1090, 988, 968, 820, 686, 622 cm^{-1}; UV (Ar, 13 K) λ_{max} 283, 271, 260 sh nm.

3-Nitrenophenylfluorodiazomethane (4-F): IR (Ar, 13 K) ν 2029, 1303, 1287, 1208 cm^{-1}; UV (Ar, 13 K) λ_{max} 280 nm.

3-Nitrenophenylfluorocarbene (2-F): IR (Ar, 13 K) ν 1538, 1530, 1371, 1276, 1265, 1249, 1173, 1138, 1129, 1115, 1086, 1054, 890, 873, 785, 779, 649 cm^{-1}; UV (Ar, 13 K) λ_{max} 420, 245 nm max.

5-F: IR (Ar, 13 K) ν 2215, 1850, 1596, 1340, 1244, 1218, 762 cm^{-1}; UV (Ar, 13 K) λ_{max} 295 nm.

3-Azidophenylchlorocarbene (7-Cl): IR (Ar, 13 K) ν 2122, 1585, 1547, 1470, 1443, 1305, 1279, 1271, 1206, 1116, 1085, 936, 873, 795, 780, 730, 693, 670, 661, 564 cm^{-1}; UV (Ar, 13 K) λ_{max} 304 nm.

3-Nitrenophenylchlorocarbene (2-Cl): IR (Ar, 13 K) ν 1519, 1421, 1296, 1286, 1250, 1175, 1168, 1139, 951, 929, 893, 880, 800, 784, 771, 742, 719, 645, 589 cm^{-1}; UV (Ar, 13 K) λ_{max} 395, 257 nm.

5-Cl: IR (Ar, 13 K) ν 2212, 1798, 1593, 1538, 1407, 1125, 1047, 776, 708 cm^{-1}; UV (Ar, 13 K) λ_{max} 314 nm.

3-Azidophenylbromocarbene (3-Br): IR (Ar, 13 K) ν 2122, 1582, 1568, 1467, 1427, 1305, 1280, 1267, 1204, 1116, 994, 933, 776, 698, 657, 573, 551 cm^{-1}; UV (Ar, 13 K) λ_{max} 317 nm.

3-Nitrenophenylbromocarbene (2-Br): IR (Ar, 13 K) ν 1519, 1513, 1495, 1415, 1401, 1294, 1289, 1176, 1138, 893, 870, 794, 767, 753, 676, 668, 663, 644 cm^{-1}; UV (Ar, 13 K) λ_{max} 401 nm.

5-Br: IR (Ar, 13 K) ν 2203, 1773, 1531, 1111, 1044, 1032, 1017, 965, 926, 838, 792, 777, 744, 705 cm^{-1}; UV (Ar, 13 K) λ_{max} 314 nm.

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Table S1. Total Energies (hartrees) and Zero-Point Vibrational Energies (ZPE, hartrees) Using DFT and MCSCF Wavefunctions.

E-isomers	E(B3LYP)	ZPE	E(B3LYP) +ZPE [a]	E(MCSCF)[b]	E(CASPT2)[c]
2-H (^{1}A")				-322.32545	-323.24461
2-H (^{1}A')				-322.36260	-323.28887
2-H (^{3}A")	-324.27266	0.09316	-324.18130	-322.35479	-323.27652
2-H (^{3}A')				-322.36938	-323.29676
2-H (^{5}A')	-324.29221	0.09304	-324.20098	-322.37862	-323.30523
2-F (^{1}A")				-421.20937	-422.30328
2-F (^{1}A')				-421.20969	-422.31035
2-F (^{3}A")	-423.53869	0.08701	-423.45337	-421.23810	-422.33453
2-F (^{3}A')				-421.21626	-422.31770
2-F (^{5}A')	-423.52468	0.08660	-423.43976	-421.22559	-422.32602
2-Cl (^{1}A")				-781.24648	-782.31339
2-Cl (^{1}A')				-781.26601	-782.33852
2-Cl (^{3}A")	-783.89589	0.08552	-783.81203	-781.27521	-782.34452
2-Cl (^{3}A')				-781.27233	-782.34563
2-Cl (^{5}A')	-783.89620	0.08524	-783.81262	-781.28135	-782.35371
2-Br (^{1}A")				-2891.65340	-2892.72153
2-Br (^{1}A')				-2891.67350	-2892.74696
2-Br (^{3}A")	-2895.40573	0.08511	-2895.32227	-2891.68215	-2892.75267
2-Br (^{3}A')				-2891.67986	-2892.75407
2-Br (^{5}A')	-2895.40591	0.08472	-2895.32284	-2891.68888	-2892.76209
Z-isomers					
2-H (^{1}A")				-322.32534	-323.24455
2-H (^{1}A')				-322.36300	-323.28968
2-H (^{3}A")	-324.27333	0.09342	-324.18173	-322.35489	-323.27682
2-H (^{3}A')				-322.36992	-323.29787
2-H (^{5}A')	-324.29203	0.09309	-324.20075	-322.37861	-323.30513
2-F (^{1}A")				-421.20785	-422.30192
2-F (^{1}A')				-421.21009	-422.31121
2-F (^{3}A")	-423.53870	0.08694	-423.45344	-421.23787	-422.33435
2-F (^{3}A')				-421.21672	-422.31873
2-F (^{5}A')	-423.52434	0.08669	-423.43933	-421.22545	-422.32576
2-Cl (^{1}A")				-781.24430	-782.31137
2-Cl (^{1}A')				-781.26650	-782.33961
2-Cl (^{3}A")	-783.89575	0.08552	-783.81188	-781.27487	-782.34429
2-Cl (^{3}A')				-781.27284	-782.34675
2-Cl (^{5}A')	-783.89591	0.08530	-783.81226	-781.28124	-782.35356
2-Br (^{1}A")				-2891.65110	-2892.71924
2-Br (^{1}A')				-2891.67397	-2892.74798
2-Br (^{3}A")	-2895.40556	0.08507	-2895.32215	-2891.68179	-2892.75236
2-Br (^{3}A')				-2891.68035	-2892.75516
2-Br (^{5}A')	-2895.40562	0.08479	-2895.32248	-2891.68877	-2892.76193

[a] ZPE scaled by 0.961.

[c] The active space includes 10 (11) molecular orbitals (MOs) and 10 (12) electrons for **2-H** (**2-X**, X= F, Cl, Br).The 10 (12) MOs include the six π MOs of the ring, the two π and the two σ orbitals located on the reactive centers (and the MO corresponding to the π lone pair of the halogen substituent). The basis set used is 6-31G(d).

[d] Using the MCSCF/6-31G(d) wavefunction described above.

[e] Modified G2(MP2,SVP) procedure (MCSCF/6-31G(d) optimized geometries, omission of higher-level correction. (See main text for details)

Table S2. Total Energies (hartrees) and Zero-Point Vibrational Energies (ZPE, hartrees) at Various Levels of Theory Based on HF wavefunctions.[a]

	^{5}A' **2-H**	^{5}A' **2-F**	^{5}A'**2-Cl**	^{5}A' **2-Br**	^{5}A' **1-CCl**
HF	-322.34376	-421.18910	-781.24615	-2891.65404	-1224.10659
HF-ZPE	0.09760	0.09089	0.0894	0.08880	0.09245
ROMP2[b,c]	-323.23501	-422.25131	-782.27145	-2892.66172	-1225.25033
ROMP2[b,c,d]	-323.56641	-422.69446	-782.68432	-2895.52217	-1225.73822
QCISD[c]	-323.30541	-422.31964	-782.34820	-2892.73573	-1225.32879
QCISD(T)[c]	-323.34401	-422.36149	-782.39212	-2892.77897	-1225.37797
E_{QCI} [c]	-323.58826	-422.72349	-782.72518	-2895.56012	-1225.78331
	^{3}A' **2-H**	^{3}A' **2-F**	^{3}A' **2-Cl**	^{3}A' **2-Br**	^{3}A' **1-CCl**
HF	-322.26526	-421.16923	-781.20734	-2891.61434	-1224.03217
HF-ZPE	0.10108	0.09148	0.08999	0.08944	0.09565
ROMP2[b,c]	-323.21393	-422.26904	-782.27199	-2892.66280	-1225.25567
ROMP2[b,c,d]	-323.55090	-422.71485	-782.68991	-2895.52570	-1225.75410
QCISD[c]	-323.27955	-422.33201	-782.34318	-2892.73095	-1225.32978
QCISD(T)[c]	-323.32255	-422.37814	-782.39217	-2892.77948	-1225.38854
E_{QCI} [c]	-323.56927	-422.74227	-782.72973	-2895.56252	-1225.80156
	^{1}A' **8-H**	^{1}A' **8-F**	^{1}A' **8-Cl**	^{1}A' **8-Br**	
HF	-268.44864	-367.32969	-727.36890	-2837.77619	
HF-ZPE	0.11016	0.10335	0.10182	0.10127	
ROMP2[b,c]	-269.30071	-368.35569	-728.35921	-2838.75029	
ROMP2[b,c,d]	-269.60086	-368.76461	-728.73994	-2841.57590	
QCISD(T) [c]	-269.39180	-368.44689	-728.46138	-2838.84895	
E_{QCI} [c]	-269.59359	-368.76353	-728.75120	-2841.58413	
	^{3}A" **8-H**	^{3}A" **8-F**	^{3}A" **8-Cl**	^{3}A" **8-Br**	
HF	-268.50298	-367.34901	-727.40634	-2837.81419	
HF-ZPE	0.10696	0.10031	0.09882	0.09825	
ROMP2[b,c]	-269.31549	-368.33243	-728.35279	-2838.74302	
ROMP2[b,c,d]	-269.60956	-368.73829	-728.72818	-2841.56595	
QCISD(T)[c]	-269.40196	-368.42014	-728.45103	-2838.83794	
E_{QCI} [c]	-269.60053	-368.73644	-728.73818	-2841.57314	

[a] With the 6-31G(d) basis set, unless otherwise specified.

[b] Restricted open-shell MP2 calculation as implemented in Gaussian 98.

[c] At the MCSCF/6-31G(d) optimized geometry.

[c] With the 6-311+G(3df,2p) basis set.

[d] $E_{QCI} = E_{QCISD(T)} + E_{ROMP2/6\text{-}311+G(3df,2p)} - E_{ROMP2/6\text{-}31G(d)} + 0.8929 * (HF\text{-}ZPE)$.

Table S3. Gaussian Archives of ^{5}A' and ^{3}A" states of **2-X**.

(The (U)B3LYP/6-31G(d) optimized structures of **2-X** were found to have zero imaginary frequencies).

^{5}A'**2-H**

1¥1¥GINC-NS118¥FOpt¥UB3LYP¥6-31G(d)¥C7H5N1(5)¥AXN501¥17-Nov-2000¥0¥¥#B
3LYP/6-31G* FOPT FREQ¥¥5-A'meta phenylenecarbenonitrene, anti-H,str+f
rq. anl¥¥0,5¥C,0.2614490339,1.2591945241,0.¥C,-0.9656019078,0.54450303
96,0.¥C,-0.9901036126,-0.8842017377,0.¥C,0.2614876813,-1.600656917,0.¥
C,1.4590045412,-0.8969203848,0.¥C,1.4837172505,0.4968009097,0.¥C,0.283
5304042,2.6461511346,0.¥N,-2.1409088536,-1.5380477318,0.¥H,-1.90698109
73,1.0828051354,0.¥H,2.4316900229,1.0259024745,0.¥H,0.23802207,-2.6848
374869,0.¥H,2.3985934288,-1.4433794658,0.¥H,1.064137206,3.3966200542,0
.¥¥Version=IBM-RS6000-G98RevA.9¥State=5-A'¥HF=-324.2922124¥S2=6.095438
¥S2-1=0.¥S2A=6.002792¥RMSD=6.867e-09¥RMSF=1.225e-05¥Dipole=1.2170722,0
.4729871,0.¥PG=CS [SG(C7H5N1)]¥¥@

^{5}A'**2-H**

1¥1¥GINC-AEGEAN¥SP¥UQCISD(T)-FC¥6-31G(d)¥C7H5N1(5)¥CYP0002¥04-Mar-2001
¥0¥¥#QCISD(T,E4)/6-31G* MAXDISK=900000000 IOP(5/15=2)¥¥5-A' E-m-phenyl
ene-.carbenonitrene, qcisd(t,e4)/6-31g*//CAS(12,11)/6-31G*¥¥0,5¥C,0,1.
2328813647,0.3441043003,0.¥C,0,0.0138562833,1.0580950952,0.¥C,0,-1.231
3236723,0.3727766843,0.¥C,0,-1.2447332926,-1.0597107762,0.¥C,0,-0.0433
062083,-1.7583916154,0.¥C,0,1.180957736,-1.0851349587,0.¥C,0,2.4618317
732,1.0260868666,0.¥N,0,-2.3729492051,1.0555218687,0.¥H,0,0.017526009,
2.1319719266,0.¥H,0,2.0994093561,-1.6427307826,0.¥H,0,-2.1886851202,-1
.5712731579,0.¥H,0,-0.0543116916,-2.8333450235,0.¥H,0,3.4650776679,0.6
483835726,0.¥¥Version=HP-PARisc-HPUX-G98RevA.9¥State=5-A'¥HF=-322.3435
387¥MP2=-323.2086019¥MP3=-323.2696672¥MP4D=-323.2898858¥MP4DQ=-323.271
8801¥MP4SDTQ=-323.3205417¥PUHF=-322.3728802¥PMP2-0=-323.2343919¥PMP3-0
=-323.2902394¥MP4SDQ=-323.2868166¥QCISD=-323.3054133¥QCISD(T)=-323.344
008¥S2=6.713889¥S2-1=6.510099¥S2A=6.184063¥RMSD=4.633e-09¥PG=CS [SG(C7
H5N1)]¥¥@

^{3}A"**2-H**

1¥1¥GINC-NS118¥FOpt¥UB3LYP¥6-31G(d)¥C7H5N1(3)¥AXN501¥08-Jun-2001¥0¥¥#B
3LYP/6-31G*,FOPT¥¥nitrenocarbene,triplet,E¥¥0,3¥C,-1.2557589745,0.4115
080213,0.¥C,-1.2411419988,-1.0231849789,0.¥C,-0.0434730108,-1.72623499
93,0.¥C,1.1734240009,-1.0405840199,0.¥C,1.218771025,0.3843539793,0.¥C,
0.000000037,1.091451,0.¥N,-2.404693963,1.0876210408,0.¥C,2.4259470386,
1.1847679588,0.¥H,3.2783320264,0.4665269444,0.¥H,-2.1937360077,-1.5442
679628,0.¥H,-0.0610190292,-2.812567999,0.¥H,2.1102859915,-1.5912630358
,0.¥H,0.0323860554,2.1757629995,0.¥¥Version=IBM-RS6000-G98RevA.9¥State
=3-A"¥HF=-324.272659¥S2=2.054472¥S2-1=0.¥S2A=2.001418¥RMSD=8.890e-09¥R
MSF=6.631e-05¥Dipole=0.0271478,-1.6155399,0.¥PG=CS [SG(C7H5N1)]¥¥@

^{3}A"**2-H**

1¥1¥GINC-AEGEAN¥SP¥UQCISD(T)-FC¥6-31G(d)¥C7H5N1(3)¥CYP0002¥04-Mar-2001
¥0¥¥#QCISD(T,E4)/6-31G* MAXDISK=900000000 IOP(5/15=2)¥¥3-A" E-m-phenyl
ene-.carbenonitrene, qcisd(t,e4)/6-31g*//CAS(12,11)/6-31G*¥¥0,3¥C,0,1.
2313921874,0.3556803767,0.¥C,0,0.0194384428,1.0580055804,0.¥C,0,-1.223
1566302,0.3702768259,0.¥C,0,-1.2207027144,-1.0532839796,0.¥C,0,-0.0201
40517,-1.7509340858,0.¥C,0,1.1973614602,-1.0602411161,0.¥C,0,2.4638249
78,1.1508785864,0.¥N,0,-2.3803151571,1.050287959,0.¥H,0,0.0354064778,2
.131211761,0.¥H,0,2.1227891993,-1.6070405359,0.¥H,0,-2.1607977765,-1.5
731773235,0.¥H,0,-0.0287662312,-2.8255496946,0.¥H,0,3.2998972808,0.440
2396459,0.¥¥Version=HP-PARisc-HPUX-G98RevA.9¥State=3-A"¥HF=-322.287941
9¥MP2=-323.1808343¥MP3=-323.241889¥MP4D=-323.2640503¥MP4DQ=-323.244247
7¥MP4SDTQ=-323.2968709¥PUHF=-322.3252155¥PMP2-0=-323.2146278¥PMP3-0=-3

23.2699202¥MP4SDQ=-323.2598655¥QCISD=-323.2795545¥QCISD(T)=-323.3225549¥S2=2.720221¥S2-1=2.548319¥S2A=2.319371¥RMSD=9.059e-09¥PG=CS [SG(C7H5N1)]¥¥@

^{5}A'**2-F**

1¥1¥GINC-DRAGON2¥Freq¥UB3LYP¥6-31G(d)¥C7H4F1N1(5)¥AXN501¥16-May-1900¥0¥¥#B3LYP/6-31G*,FREQ¥¥m-F.q.nitrenocarbene¥¥0,5¥C,1.0375189516,-1.4270599194,0.¥C,-0.2785370484,-2.0175899194,0.¥C,-1.4022900484,-1.2006299194,0.¥C,-1.2943270484,0.1884900806,0.¥C,-0.0000000484,0.8123530806,0.¥C,1.1560979516,-0.0038989194,0.¥N,2.1177249516,-2.1924299194,0.¥C,0.1143429516,2.2039920806,0.¥F,-0.8927110484,3.0567500806,0.¥H,-2.1803880484,0.8136280806,0.¥H,2.1453019516,0.4401660806,0.¥H,-2.3907000484,-1.6527259194,0.¥H,-0.3607230484,-3.0987489194,0.¥¥Version=DEC-AXP-OSF/1-G94RevD.4¥State=5-A'¥HF=-423.5246839¥S2=6.09¥S2-1=0.¥S2A=6.002¥RMSD=6.103e-09¥RMSF=2.256e-06¥Dipole=-0.9208402,0.3224304,0.¥ PG=CS [SG(C7H4F1N1)]¥NImag=0¥

^{5}A'**2-F**

1¥1¥GINC-NS118¥SP¥UQCISD(T)-FC¥6-31G(d)¥C7H4F1N1(5)¥AXN501¥23-Jan-2001¥0¥¥#QCISD(T,E4)/6-31G* MAXDISK=900000000¥¥5-A' E-m-phenylene-F.carbenonitrene, qcisd(t)/6-31g*//CAS(12,11)/6-31G*¥¥0,5¥C,0,0.7479412572,0.3405391946,0.¥C,0,0.7285519256,-1.0866785734,0.¥C,0,-0.4886231718,-1.7724628219,0.¥C,0,-1.6989382634,-1.08952032,0.¥C,0,-1.7063705419,0.3430623713,0.¥C,0,-0.4723976648,1.0467991178,0.¥C,0,1.9661605131,1.0425759679,0.¥N,0,-2.8571555734,1.0109684541,0.¥F,0,3.1457357937,0.4675591523,0.¥H,0,1.6562566239,-1.6252314028,0.¥H,0,-0.4858879342,-2.8471692422,0.¥H,0,-2.6355989172,-1.6140651161,0.¥H,0,-0.4826740468,2.1206232181,0.¥¥Version=IBM-RS6000-G98RevA.9¥State=5-A'¥HF=-421.1889369¥MP2=-422.2243649¥MP3=-422.2785809¥MP4D=-422.3008732¥MP4DQ=-422.2816899¥MP4SDTQ=-422.3393325¥PUHF=-421.2176587¥PMP2-0=-422.2496103¥PMP3-0=-422.2986821¥MP4SDQ=-422.3004128¥QCISD=-422.3196369¥QCISD(T)=-422.3614895¥S2=6.703204¥S2-1=6.503227¥S2A=6.176271¥RMSD=5.414e-09¥PG=CS [SG(C7H4F1N1)]¥¥@

^{3}A"**2-F**

1¥1¥GINC-DRAGON2¥Freq¥UB3LYP¥6-31G(d)¥C7H4F1N1(3)¥ROOT¥03-May-1900¥0¥¥#B3LYP/6-31G*,FREQ¥¥triplet,freq.m-f¥¥0,3¥C,1.0076010968,-1.4206530161,0.¥C,-0.3138479032,-1.9778630161,0.¥C,-1.4329939032,-1.1543700161,0.¥C,-1.2916489032,0.2344659839,0.¥C,0.0000000968,0.8175699839,0.¥C,1.1336670968,0.0041489839,0.¥N,2.0846470968,-2.2037510161,0.¥C,0.2866020968,2.2670789839,0.¥F,-0.8940469032,2.9020819839,0.¥H,-2.1616269032,0.8823769839,0.¥H,2.1176070968,0.4620129839,0.¥H,-2.4236949032,-1.6005180161,0.¥H,-0.4146709032,-3.0586200161,0.¥¥Version=DEC-AXP-OSF/1-G94RevD.4¥State=3-A"¥HF=-423.538689¥S2=2.055¥S2-1=0.¥S2A=2.001¥RMSD=6.142e-09¥RMSF=1.324e-04¥Dipole=-1.2096458,-0.6218342,0.¥PG=CS [SG(C7H4F1N1)]¥NImag=0

^{3}A"**2-F**

1¥1¥GINC-NS118¥SP¥UQCISD(T)-FC¥6-31G(d)¥C7H4F1N1(3)¥AXN501¥22-Jan-2001¥0¥¥#QCISD(T,E4)/6-31G* MAXDISK=900000000¥¥3-A" E-m-phenylene-F.carbenonitrene, qcisd(t)/6-31g*//CAS(12,11)/6-31G*¥¥0,3¥C,0,0.7458286872,0.3313737013,0.¥C,0,0.7387890095,-1.0823032616,0.¥C,0,-0.4760513127,-1.7743419751,0.¥C,0,-1.683194831,-1.084548226,0.¥C,0,-1.6960386031,0.3377508648,0.¥C,0,-0.4552849972,1.034158729,0.¥C,0,1.9695689061,1.1681974725,0.¥N,0,-2.8542668798,1.0127804099,0.¥F,0,3.0060560437,0.3646190188,0.¥H,0,1.6675025734,-1.6185941701,0.¥H,0,-0.4789878507,-2.8488672456,0.¥H,0,-2.6193742834,-1.6112882994,0.¥H,0,-0.4475464621,2.1080629815,0.¥¥Version=IBM-RS6000-G98RevA.9¥State=3-A"¥HF=-421.169076¥MP2=-422.2365589¥MP3=-422.2895163¥MP4D=-422.314218¥MP4DQ=-422.293065¥MP4SDTQ=-422.3560347¥PUHF=-421.2063731¥PMP2-0=-422.2702975¥PMP3-0=-422.3173783¥MP4SDQ=-422.3129898¥QCISD=-422.3320122¥QCISD(T)=-422.3781429¥S2=2.706367¥S2-1=2.534792¥S2A=2.307554¥RMSD=3.606e-09¥PG=CS [SG(C7H4F1N1)]¥¥@

^{5}A'**2-Cl**

1¥1¥GINC-LEONARDO¥FOpt¥UB3LYP¥6-31G(d)¥C7H4Cl1N1(5)¥AXN501¥08-Jan-1901
¥0¥¥#B3LYP/6-31G*,FREQ FOPT¥¥m-Cl.q.nitrenocarbene¥¥0,5¥C,1.1461022952
,-1.8820785158,0.¥C,-0.1711467203,-2.4677245436,0.¥C,-1.290379353,-1.6
462383054,0.¥C,-1.175592746,-0.2565753044,0.¥C,0.116848845,0.368117376
6,0.¥C,1.2676147826,-0.458914319,0.¥N,2.2251396866,-2.6495799125,0.¥C,
0.2780070129,1.7566173539,0.¥Cl,-0.838861557,3.0212180372,0.¥H,-2.0631
533506,0.3670678608,0.¥H,2.258100217,-0.017941,0.¥H,-2.2809383697,-2.0
934091323,0.¥H,-0.258064532,-3.5485874274,0.¥¥Version=SGI-G94RevD.4¥St
ate=5-A'¥HF=-783.8962005¥S2=6.091¥S2-1=0.¥S2A=6.003¥RMSD=5.135e-09¥RMS
F=2.732e-05¥Dipole=-1.0332073,0.2777993,0.¥PG=CS [SG(C7H4Cl1N1)]¥¥@

^{5}A'**2-Cl**

1¥1¥GINC-NS118¥SP¥UQCISD(T)-FC¥6-31G(d)¥C7H4Cl1N1(5)¥AXN501¥20-Jan-200
1¥0¥¥#QCISD(T)/6-31G* MAXDISK=11000000000¥¥5-A' E-m-phenylene-Cl.carben
onitrene, qcisd(t)/6-31g*//CAS(12,11)/6-31G*¥¥0,5¥C,0,0.31188565,0.283
1590329,0.¥C,0,-0.9040336669,1.000741371,0.¥C,0,-2.1469202718,0.313467
9881,0.¥C,0,-2.1570009245,-1.1185509133,0.¥C,0,-0.9550841822,-1.814497
1953,0.¥C,0,0.2710165864,-1.1427034012,0.¥C,0,1.5209649196,1.008806667
1,0.¥N,0,-3.2891786704,0.9968167742,0.¥Cl,0,3.1247162841,0.4565121899,
0.¥H,0,-0.900855238,2.0744306784,0.¥H,0,1.1885318706,-1.6985814646,0.¥
H,0,-0.9634840738,-2.8891680079,0.¥H,0,-3.0995582833,-1.6324337193,0.¥
¥Version=IBM-RS6000-G98RevA.9¥State=5-A'¥HF=-781.2459551¥MP2=-782.2430
993¥MP3=-782.3107714¥MP4D=-782.333134¥MP4DQ=-782.3119628¥PUHF=-781.275
3531¥PMP2-0=-782.26894¥PMP3-0=-782.3313581¥MP4SDQ=-782.3287922¥QCISD=-
782.3482045¥QCISD(T)=-782.392115¥S2=6.715338¥S2-1=6.511059¥S2A=6.18542
5¥RMSD=8.115e-09¥PG=CS [SG(C7H4Cl1N1)]¥¥@

^{3}A"**2-Cl**

1¥1¥GINC-DRAGON1¥Freq¥UB3LYP¥6-31G(d)¥C7H4Cl1N1(3)¥MATSUOKA¥19-Apr-199
9¥0¥¥#B3LYP/6-31G*,FREQ¥¥triplet.nitrenocarbene¥¥0,3¥C,1.6621768286,-1
.3965949,0.¥C,0.5826008286,-2.3385309,0.¥C,-0.7375031714,-1.9031129,0.
¥C,-1.0402421714,-0.5418119,0.¥C,-0.0000001714,0.4278231,0.¥C,1.334532
8286,-0.0044049,0.¥N,2.9314778286,-1.7995489,0.¥C,-0.0970451714,1.8888
451,0.¥Cl,-1.7695761714,2.4300281,0.¥H,-2.0734151714,-0.2120449,0.¥H,2
.1258458286,0.7374481,0.¥H,-1.5401461714,-2.6352989,0.¥H,0.8230468286,
-3.3970159,0.¥¥Version=DEC-AXP-OSF/1-G94RevD.4¥State=3-A"¥HF=-783.8958
886¥S2=2.056¥S2-1=0.¥S2A=2.001¥RMSD=5.922e-09¥RMSF=7.356e-05¥Dipole=-0
.8867376,-1.1814845,0.¥G=CS [SG(C7H4Cl1N1)]¥NImag=0¥

^{3}A"**2-Cl**

1¥1¥GINC-NS118¥SP¥UQCISD(T)-FC¥6-31G(d)¥C7H4Cl1N1(3)¥AXN501¥17-Jan-200
1¥0¥¥#QCISD(T)/6-31G* MAXDISK=900000000¥¥3-A" E-m-phenylene-Cl.carbeno
nitrene, qcisd(t)/6-31g*//CAS(12,11)/6-31G*¥¥0,3¥C,0,0.3140372319,0.28
35644699,0.¥C,0,-0.8903698337,0.9902967039,0.¥C,0,-2.1374763851,0.3061
534956,0.¥C,0,-2.1375937964,-1.1141488845,0.¥C,0,-0.9341782403,-1.8117
890336,0.¥C,0,0.2865043639,-1.1334339253,0.¥C,0,1.4901483954,1.1690141
754,0.¥N,0,-3.2886113073,0.9948766686,0.¥Cl,0,2.9898143316,0.298833818
4,0.¥H,0,-0.8733161105,2.0633655691,0.¥H,0,1.2035257314,-1.6878407556,
0.¥H,0,-0.9443590551,-2.8861876845,0.¥H,0,-3.0771253259,-1.6347046174,
0.¥¥Version=IBM-RS6000-G98RevA.9¥State=3-A"¥HF=-781.2071521¥MP2=-782.2
394061¥MP3=-782.3047463¥MP4D=-782.3293352¥MP4DQ=-782.3057338¥PUHF=-781
.2440784¥PMP2-0=-782.2728388¥PMP3-0=-782.3323768¥MP4SDQ=-782.3238887¥Q
CISD=-782.3431813¥QCISD(T)=-782.3921658¥S2=2.70815¥S2-1=2.537517¥S2A=2
.308765¥RMSD=4.712e-09¥PG=CS [SG(C7H4Cl1N1)]¥¥@

^{5}A'**2-Br**

1¥1¥GINC-AEGEAN 41¥FOpt¥UB3LYP¥6-31G(d)¥C7H4Br1N1(5)¥CYP0002¥19-Jan-
2001¥0¥¥#B3LYP/6-31G*,OPT=FCCARDS FREQ¥¥5-A',m-Br.nitrenocarbene, E-is
omer, str+frq.¥¥0,5¥C,0.992474935,2.7086926944,0.¥C,2.3067098655,2.116
2471586,0.¥C,2.43970589,0.7341466891,0.¥C,1.3265714612,-0.1048617185,0
.¥C,-0.0009584756,0.4420212411,0.¥C,-0.1504882724,1.851534779,0.¥N,0.8
460591082,4.0246224628,0.¥C,-1.1419821974,-0.3641566334,0.¥Br,-1.35613

73668,-2.1900933842,0.¥H,3.1706275785,2.7716290235,0.¥H,3.433033121,0.
2931071008,0.¥H,1.4453528158,-1.1828996183,0.¥H,-1.1388186722,2.297329
4394,0.¥¥Version=HP-PARisc-HPUX-G98RevA.9¥State=5-A'¥HF=-2895.4059112¥
S2=6.091105¥S2-1=0.¥S2A=6.002574¥RMSD=4.051e-09¥RMSF=3.450e-06¥Dipole=
0.4454085,-1.0498633,0.¥PG=CS [SG(C7H4Br1N1)]¥¥@

^{5}A'**2-Br**

1¥1¥GINC-NS118¥SP¥UQCISD(T)-FC¥6-31G(d)¥C7H4Br1N1(5)¥AXN501¥14-Feb-200
1¥0¥¥#QCISD(T)/6-31G* MAXDISK=900000000¥¥5-A' E-m-phenylene-Br.carbeno
nitrene, qcisd(t)/6-31g*//CAS(12,11)/6-31G*¥¥0,5¥C,0,-0.3652550232,0.2
357816148,0.¥C,0,-1.5996135565,0.9216892325,0.¥C,0,-2.824435546,0.2022
444582,0.¥C,0,-2.7975612302,-1.229465251,0.¥C,0,-1.5779215948,-1.89412
71604,0.¥C,0,-0.3700147202,-1.1908275923,0.¥C,0,0.8249609025,0.9912495
108,0.¥N,0,-3.9838045083,0.8559665517,0.¥Br,0,2.5920075929,0.441479257
1,0.¥H,0,-1.6245632712,1.9951332099,0.¥H,0,0.5634629311,-1.719014073,0
.¥H,0,-1.558694846,-2.9686336355,0.¥H,0,-3.7265671302,-1.7674761228,0.
¥¥Version=IBM-RS6000-G98RevA.9¥State=5-A'¥HF=-2891.65385¥MP2=-2892.632
9728¥MP3=-2892.6978414¥MP4D=-2892.719981¥MP4DQ=-2892.6989036¥PUHF=-289
1.6834367¥PMP2-0=-2892.6589729¥PMP3-0=-2892.7185472¥MP4SDQ=-2892.71620
48¥QCISD=-2892.7357253¥QCISD(T)=-2892.7789699¥S2=6.718603¥S2-1=6.51270
6¥S2A=6.18848¥RMSD=4.446e-09¥PG=CS [SG(C7H4Br1N1)]¥¥@

^{3}A"**2-Br**

1¥1¥GINC-AEGEAN 41¥FOpt¥UB3LYP¥6-31G(d)¥C7H4Br1N1(3)¥CYP0002¥16-Jan-
2001¥0¥¥#UB3LYP/6-31G* FOPT FREQ¥¥3-A" m-Br.nitrenocarbene, E-isomer,
str+frq.¥¥0,3¥C,-0.3553697142,0.2380977709,0.¥C,-1.5858139558,0.915786
0129,0.¥C,-2.8253621212,0.2025336501,0.¥C,-2.7744460007,-1.2290031681,
0.¥C,-1.553706332,-1.8944550635,0.¥C,-0.3539344248,-1.1848652095,0.¥C,
0.7675260117,1.1731552932,0.¥N,-3.9873082382,0.8538231662,0.¥Br,2.4639
834278,0.2617534325,0.¥H,-1.5878457502,2.0005442153,0.¥H,0.5962564356,
-1.7079169183,0.¥H,-1.5388357384,-2.980809302,0.¥H,-3.7111980316,-1.77
74460126,0.¥¥Version=HP-PARisc-HPUX-G98RevA.9¥State=3-A"¥HF=-2895.4057
324¥S2=2.056426¥S2-1=0.¥S2A=2.001492¥RMSD=6.303e-09¥RMSF=7.441e-05¥Dip
ole=-0.2306745,-1.4278535,0.¥PG=CS [SG(C7H4Br1N1)]¥¥@

^{3}A"**2-Br**

1¥1¥GINC-NS118¥SP¥UQCISD(T)-FC¥6-31G(d)¥C7H4Br1N1(3)¥AXN501¥04-Mar-200
1¥4¥¥#QCISD(T)/6-31G* MAXDISK=900000000 IOP(5/15=2) SCF=QC GUESS=ALTER
¥¥3-A' E-m-phenylene-Br.carbenonitrene, qcisd(t)/6-31g*//CAS(12,11)/6-
31G*¥¥0,3¥C,0,-0.3621907103,0.2374313169,0.¥C,0,-1.5869845344,0.911603
1849,0.¥C,0,-2.8152262327,0.1943338676,0.¥C,0,-2.7774567665,-1.2252091
804,0.¥C,0,-1.555640247,-1.8903979487,0.¥C,0,-0.3537641753,-1.18030161
5,0.¥C,0,0.780751083,1.1604301646,0.¥N,0,-3.9842569716,0.8527817374,0.
¥Br,0,2.4671938606,0.270691229,0.¥H,0,-1.6001107134,1.9847688266,0.¥H,
0,0.5790456317,-1.7067367725,0.¥H,0,-1.5366445788,-2.964649032,0.¥H,0,
-3.7027156454,-1.7707457783,0.¥¥¥43,44¥¥Version=IBM-RS6000-G98RevA.9¥S
tate=3-A"¥HF=-2891.6141519¥MP2=-2892.6300476¥MP3=-2892.6919868¥MP4D=-2
892.7165112¥MP4DQ=-2892.6928364¥PUHF=-2891.6509767¥PMP2-0=-2892.663399
5¥PMP3-0=-2892.719559¥MP4SDQ=-2892.7117403¥QCISD=-2892.7309539¥QCISD(T
)=-2892.7794802¥S2=2.709165¥S2-1=2.538788¥S2A=2.309584¥RMSD=0.000e+00¥
PG=CS [SG(C7H4Br1N1)]¥¥@

Table S4. Coordinates of MCSCF/6-31G(d) Optimized Geometries of **2-X**.

^{5}A'**2-H**
C,1.2328813647,0.3441043003,0.0000000000¥C,0.0138562833,1.0580950952,0
.0000000000¥C,-1.2313236723,0.3727766843,0.0000000000¥C,-1.2447332926,
-1.0597107762,0.0000000000¥C,-0.0433062083,-1.7583916154,0.0000000000¥
C,1.1809577360,-1.0851349587,0.0000000000¥C,2.4618317732,1.0260868666,
0.0000000000¥N,-2.3729492051,1.0555218687,0.0000000000¥H,0.0175260090,
2.1319719266,0.0000000000¥H,2.0994093561,-1.6427307826,0.0000000000¥H,
-2.1886851202,-1.5712731579,0.0000000000¥H,-0.0543116916,-2.8333450235
,0.0000000000¥H,3.4650776679,0.6483835726,0.0000000000¥
^{1}A'**2-H**
C,1.2194324316,0.3329736629,0.0000000000¥C,0.0106827054,1.0441040245,0
.0000000000¥C,-1.2218687273,0.3592664069,0.0000000000¥C,-1.2436012999,
-1.0505373122,0.0000000000¥C,-0.0430922496,-1.7547692367,0.0000000000¥
C,1.1773902829,-1.0764626326,0.0000000000¥C,2.4846236289,1.0365111285,
0.0000000000¥N,-2.3984138390,1.0619246897,0.0000000000¥H,0.0148168246,
2.1183731642,0.0000000000¥H,2.0970940250,-1.6332123153,0.0000000000¥H,
-2.1876710727,-1.5631427727,0.0000000000¥H,-0.0541815499,-2.8295563972
,0.0000000000¥H,3.4810198400,0.6408815901,0.0000000000¥
^{1}A"**2-H**
C,1.2336219670,0.3711904225,0.0000000000¥C,0.0464398683,1.0754456879,0
.0000000000¥C,-1.2521754690,0.3839994782,0.0000000000¥C,-1.2340296808,
-1.0875752897,0.0000000000¥C,-0.0425396627,-1.7622848255,0.0000000000¥
C,1.1974899671,-1.0675418526,0.0000000000¥C,2.4646948984,1.1720410588,
0.0000000000¥N,-2.3464609888,1.0427575291,0.0000000000¥H,0.0602065670,
2.1478040859,0.0000000000¥H,2.1200964387,-1.6166810114,0.0000000000¥H,
-2.1754733005,-1.6027714242,0.0000000000¥H,-0.0416081056,-2.8371972653
,0.0000000000¥H,3.3059685009,0.4671674064,0.0000000000¥
^{3}A'**2-H**
C,1.2278072724,0.3393340951,0.0000000000¥C,0.0131926432,1.0527487009,0
.0000000000¥C,-1.2283539063,0.3676859765,0.0000000000¥C,-1.2446006890,
-1.0565310868,0.0000000000¥C,-0.0440138901,-1.7570681768,0.0000000000¥
C,1.1794268195,-1.0816312561,0.0000000000¥C,2.4706325307,1.0299688288,
0.0000000000¥N,-2.3816890041,1.0570897491,0.0000000000¥H,0.0171876732,
2.1267184938,0.0000000000¥H,2.0982112138,-1.6392171474,0.0000000000¥H,
-2.1886478644,-1.5682901851,0.0000000000¥H,-0.0548930911,-2.8319211887
,0.0000000000¥H,3.4719712923,0.6474671966,0.0000000000¥
^{3}A"**2-H**
C,1.2313921874,0.3556803767,0.0000000000¥C,0.0194384428,1.0580055804,0
.0000000000¥C,-1.2231566302,0.3702768259,0.0000000000¥C,-1.2207027144,
-1.0532839796,0.0000000000¥C,-0.0201405170,-1.7509340858,0.0000000000¥
C,1.1973614602,-1.0602411161,0.0000000000¥C,2.4638249780,1.1508785864,
0.0000000000¥N,-2.3803151571,1.0502879590,0.0000000000¥H,0.0354064778,
2.1312117610,0.0000000000¥H,2.1227891993,-1.6070405359,0.0000000000¥H,
-2.1607977765,-1.5731773235,0.0000000000¥H,-0.0287662312,-2.8255496946
,0.0000000000¥H,3.2998972808,0.4402396459,0.0000000000¥
^{5}A'**2-F**
C,.7479412572,.3405391946,.0000000000¥C,.7285519256,-1.0866785734,.000
0000000¥C,-.4886231718,-1.7724628219,.0000000000¥C,-1.6989382634,-1.08
95203200,.0000000000¥C,-1.7063705419,.3430623713,.0000000000¥C,-.47239
76648,1.0467991178,.0000000000¥C,1.9661605131,1.0425759679,.0000000000
¥N,-2.8571555734,1.0109684541,.0000000000¥F,3.1457357937,.4675591523,.
0000000000¥H,1.6562566239,-1.6252314028,.0000000000¥H,-.4858879342,-2.
8471692422,.0000000000¥H,-2.6355989172,-1.6140651161,.0000000000¥H,-.4
826740468,2.1206232181,.0000000000¥
^{1}A'**2-F**
C,.7349401258,.3313669866,.0000000000¥C,.7261589645,-1.0757410192,.000
0000000¥C,-.4869622833,-1.7677005942,.0000000000¥C,-1.6972725248,-1.08
10355193,.0000000000¥C,-1.6975428089,.3291922163,.0000000000¥C,-.47648
59510,1.0330790206,.0000000000¥C,1.9909556292,1.0573921599,.0000000000
¥N,-2.8833813855,1.0165163771,.0000000000¥F,3.1553216655,.4492232965,.

0000000000¥H,1.6553504276,-1.6127052657,.0000000000¥H,-.4828285463,-2.
8423511376,.0000000000¥H,-2.6334506373,-1.6076824841,.0000000000¥H,-.4
878026755,2.1074459631,.0000000000¥

^{1}A"**2-F**

C,.7469881319,.3487621200,.0000000000¥C,.7397311202,-1.0882353266,.000
0000000¥C,-.4976736834,-1.7852861041,.0000000000¥C,-1.6945227222,-1.11
82407941,.0000000000¥C,-1.7242218361,.3536708272,.0000000000¥C,-.42993
39934,1.0534727658,.0000000000¥C,1.9717648022,1.1856255156,.0000000000
¥N,-2.8213625982,1.0065517276,.0000000000¥F,3.0056776373,.3798940640,.
0000000000¥H,1.6664390022,-1.6254243705,.0000000000¥H,-.4909475330,-2.
8600891654,.0000000000¥H,-2.6321081767,-1.6402938348,.0000000000¥H,-.4
228301508,2.1265925753,.0000000000¥

^{3}A'**2-F**

C,.7424885469,.3369851844,.0000000000¥C,.7275697299,-1.0814526568,.000
0000000¥C,-.4884083357,-1.7702158748,.0000000000¥C,-1.6984159196,-1.08
63231770,.0000000000¥C,-1.7035604720,.3375615808,.0000000000¥C,-.47372
15136,1.0414059640,.0000000000¥C,1.9767164317,1.0485823745,.0000000000
¥N,-2.8671611271,1.0120384327,.0000000000¥F,3.1497115274,.4592538646,.
0000000000¥H,1.6557594597,-1.6194604786,.0000000000¥H,-.4845321176,-2.
8449262622,.0000000000¥H,-2.6347892125,-1.6118422516,.0000000000¥H,-.4
846569975,2.1153933002,.0000000000¥

^{3}A"**2-F**

C,.7458286872,.3313737013,.0000000000¥C,.7387890095,-1.0823032616,.000
0000000¥C,-.4760513127,-1.7743419751,.0000000000¥C,-1.6831948310,-1.08
45482260,.0000000000¥C,-1.6960386031,.3377508648,.0000000000¥C,-.45528
49972,1.0341587290,.0000000000¥C,1.9695689061,1.1681974725,.0000000000
¥N,-2.8542668798,1.0127804099,.0000000000¥F,3.0060560437,.3646190188,.
0000000000¥H,1.6675025734,-1.6185941701,.0000000000¥H,-.4789878507,-2.
8488672456,.0000000000¥H,-2.6193742834,-1.6112882994,.0000000000¥H,-.4
475464621,2.1080629815,.0000000000¥

^{5}A'**2-Cl**

C,0.3118856500,0.2831590329,0.0000000000¥C,-0.9040336669,1.0007413710,
0.0000000000¥C,-2.1469202718,0.3134679881,0.0000000000¥C,-2.1570009245
,-1.1185509133,0.0000000000¥C,-0.9550841822,-1.8144971953,0.0000000000
¥C,0.2710165864,-1.1427034012,0.0000000000¥C,1.5209649196,1.0088066671
,0.0000000000¥N,-3.2891786704,0.9968167742,0.0000000000¥Cl,3.124716284
1,0.4565121899,0.0000000000¥H,-0.9008552380,2.0744306784,0.0000000000¥
H,1.1885318706,-1.6985814646,0.0000000000¥H,-0.9634840738,-2.889168007
9,0.0000000000¥H,-3.0995582833,-1.6324337193,0.0000000000¥

^{1}A'**2-Cl**

C,.2991203508,.2729600118,.0000000000¥C,-.9080269217,.9872789866,.0000
000000¥C,-2.1377958748,.3000337520,.0000000000¥C,-2.1549642101,-1.1108
154005,.0000000000¥C,-.9537795579,-1.8106833963,.0000000000¥C,.2689527
704,-1.1330111857,.0000000000¥C,1.5431204040,1.0246551500,.0000000000¥
N,-3.3138728082,1.0025429151,.0000000000¥Cl,3.1348789326,.4426982736,.
0000000000¥H,-.9055410554,2.0614555920,.0000000000¥H,1.1877146915,-1.6
877843954,.0000000000¥H,-.9614120847,-2.8852409096,.0000000000¥H,-3.09
73946365,-1.6260893934,.0000000000¥

^{1}A"**2-Cl**

C,.3160174946,.3016621937,.0000000000¥C,-.8638462553,1.0091938235,.000
0000000¥C,-2.1646108843,.3218311801,.0000000000¥C,-2.1497823111,-1.148
8043125,.0000000000¥C,-.9566256649,-1.8227644632,.0000000000¥C,.287005
0862,-1.1398153900,.0000000000¥C,1.4921185972,1.1882473316,.0000000000
¥N,-3.2523336271,.9905064085,.0000000000¥Cl,2.9875259250,.3130887683,.
0000000000¥H,-.8490837164,2.0815257039,.0000000000¥H,1.2019682412,-1.6
949683938,.0000000000¥H,-.9566141835,-2.8974336273,.0000000000¥H,-3.09
07387017,-1.6642692226,.0000000000¥

^{3}A'**2-Cl**

C,0.3065697774,0.2789063533,0.0000000000¥C,-0.9051376885,0.9952297509,
0.0000000000¥C,-2.1437274490,0.3080363140,0.0000000000¥C,-2.1563582464
,-1.1156333131,0.0000000000¥C,-0.9550627266,-1.8127264803,0.0000000000
¥C,0.2701181666,-1.1381401445,0.0000000000¥C,1.5302792483,1.0152738773
,0.0000000000¥N,-3.2984403230,0.9978958275,0.0000000000¥Cl,3.128845077

9,0.4513488584,0.0000000000¥H,-0.9020628131,2.0690100121,0.0000000000¥
H,1.1880029336,-1.6937619889,0.0000000000¥H,-0.9631379577,-2.887294454
8,0.0000000000¥H,-3.0988879993,-1.6301446118,0.0000000000¥

^{3}A"**2-Cl**

C,0.3140372319,0.2835644699,0.0000000000¥C,-0.8903698337,0.9902967039,
0.0000000000¥C,-2.1374763851,0.3061534956,0.0000000000¥C,-2.1375937964
,-1.1141488845,0.0000000000¥C,-0.9341782403,-1.8117890336,0.0000000000
¥C,0.2865043639,-1.1334339253,0.0000000000¥C,1.4901483954,1.1690141754
,0.0000000000¥N,-3.2886113073,0.9948766686,0.0000000000¥Cl,2.989814331
6,0.2988338184,0.0000000000¥H,-0.8733161105,2.0633655691,0.0000000000¥
H,1.2035257314,-1.6878407556,0.0000000000¥H,-0.9443590551,-2.886187684
5,0.0000000000¥H,-3.0771253259,-1.6347046174,0.0000000000¥

^{5}A'**2-Br**

C,-.3652550232,.2357816148,.0000000000¥C,-1.5996135565,.9216892325,.00
00000000¥C,-2.8244355460,.2022444582,.0000000000¥C,-2.7975612302,-1.22
94652510,.0000000000¥C,-1.5779215948,-1.8941271604,.0000000000¥C,-.370
0147202,-1.1908275923,.0000000000¥C,.8249609025,.9912495108,.000000000
0¥N,-3.9838045083,.8559665517,.0000000000¥Br,2.5920075929,.4414792571,
.0000000000¥H,-1.6245632712,1.9951332099,.0000000000¥H,.5634629311,-1.
7190140730,.0000000000¥H,-1.5586948460,-2.9686336355,.0000000000¥H,-3.
7265671302,-1.7674761228,.0000000000¥

^{1}A'**2-Br**

C,-.3781785011,.2255833302,.0000000000¥C,-1.6034177550,.9083588588,.00
00000000¥C,-2.8151562733,.1891092105,.0000000000¥C,-2.7955781898,-1.22
14937342,.0000000000¥C,-1.5764496084,-1.8903138336,.0000000000¥C,-.372
3665334,-1.1810785198,.0000000000¥C,.8469731280,1.0074232046,.00000000
00¥N,-4.0091467586,.8605141470,.0000000000¥Br,2.6028744882,.4273788890
,.0000000000¥H,-1.6294635071,1.9822456922,.0000000000¥H,.5624160518,-1
.7079860659,.0000000000¥H,-1.5561714496,-2.9647317598,.0000000000¥H,-3
.7243350917,-1.7610094190,.0000000000¥

^{1}A"**2-Br**

C,-.3606577192,.2555336816,.0000000000¥C,-1.5609601530,.9306468232,.00
00000000¥C,-2.8428799687,.2087526175,.0000000000¥C,-2.7887310654,-1.26
07769933,.0000000000¥C,-1.5773380580,-1.9020133065,.0000000000¥C,-.352
6740566,-1.1869431247,.0000000000¥C,.7813593576,1.1810801833,.00000000
00¥N,-3.9471270485,.8500189470,.0000000000¥Br,2.4633736182,.2866574322
,.0000000000¥H,-1.5773940686,2.0030361625,.0000000000¥H,.5780801830,-1
.7145038607,.0000000000¥H,-1.5475892600,-2.9762455354,.0000000000¥H,-3
.7154617607,-1.8012430267,.0000000000¥

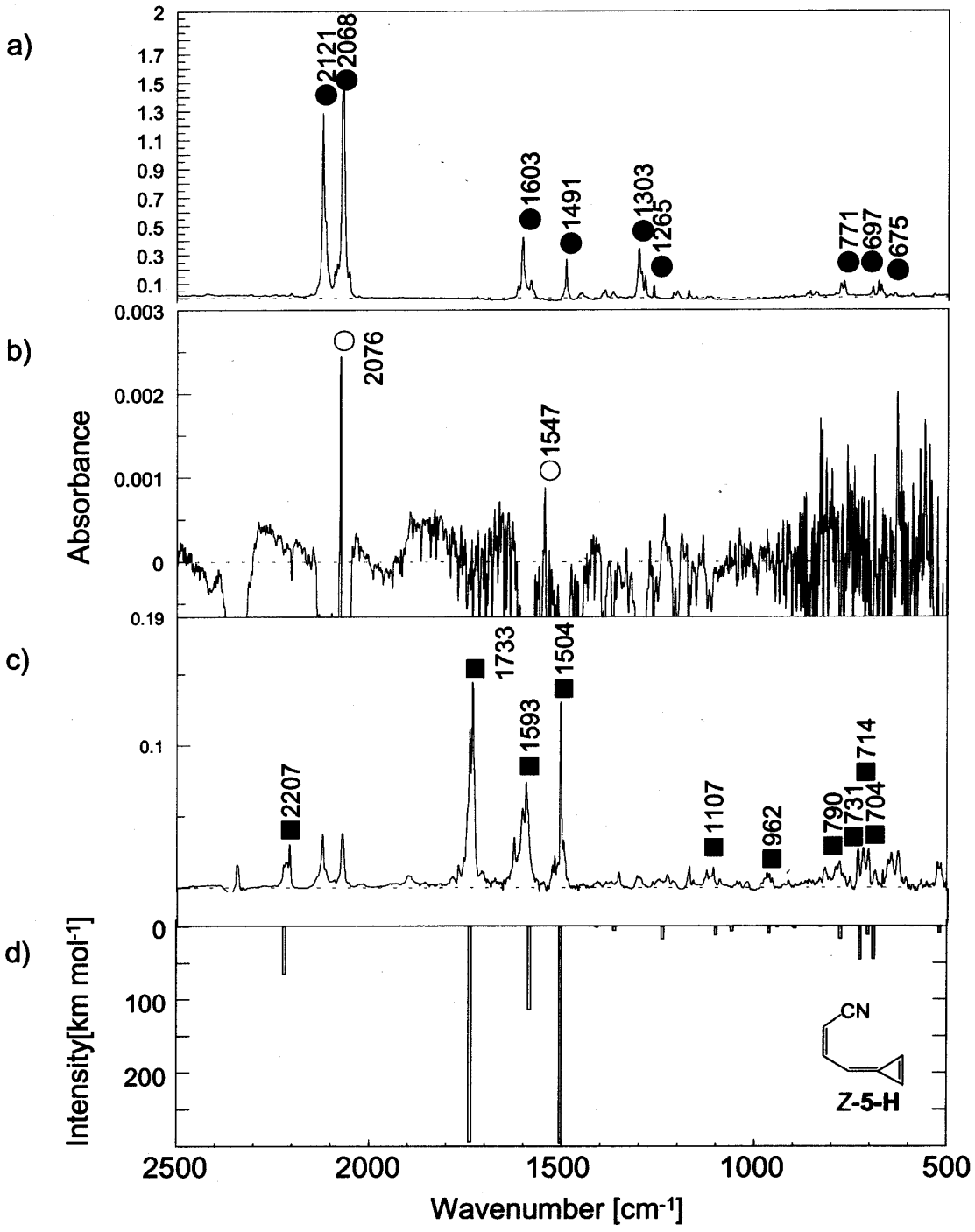
^{3}A'**2-Br**

C,-0.3705994227,0.2315114404,0.0000000000¥C,-1.6007966960,0.9164247901
,0.0000000000¥C,-2.8212248135,0.1970846430,0.0000000000¥C,-2.796847948
5,-1.2263832468,0.0000000000¥C,-1.5778270203,-1.8925110708,0.000000000
0¥C,-0.3710344360,-1.1863556068,0.0000000000¥C,0.8342827493,0.99748182
49,0.0000000000¥N,-3.9933952728,0.8568362596,0.0000000000¥Br,2.5966360
556,0.4361559231,0.0000000000¥H,-1.6264853430,1.9899666306,0.000000000
0¥H,0.5628589818,-1.7142986555,0.0000000000¥H,-1.5577703046,-2.9670064
622,0.0000000000¥H,-3.7257965293,-1.7649064696,0.0000000000¥

^{3}A"**2-Br**

C,-0.3621907103,0.2374313169,0.0000000000¥C,-1.5869845344,0.9116031849
,0.0000000000¥C,-2.8152262327,0.1943338676,0.0000000000¥C,-2.777456766
5,-1.2252091804,0.0000000000¥C,-1.5556402470,-1.8903979487,0.000000000
0¥C,-0.3537641753,-1.1803016150,0.0000000000¥C,0.7807510830,1.16043016
46,0.0000000000¥N,-3.9842569716,0.8527817374,0.0000000000¥Br,2.4671938
606,0.2706912290,0.0000000000¥H,-1.6001107134,1.9847688266,0.000000000
0¥H,0.5790456317,-1.7067367725,0.0000000000¥H,-1.5366445788,-2.9646490
320,0.0000000000¥H,-3.7027156454,-1.7707457783,0.0000000000¥

Figure S1. Photolysis (λ>350 nm) of **3-H** in Ar matrix at 13 K. a) Total IR spectrum of **3-H** before irradiation. b) Difference spectrum between **3-H** (lower part) and photoproduct (H1, upper part) obtained after 60 sec of irradiation. c) Total spectrum obtained after 505 min of irradiation (H2, '■'). d) Calculated (B3LYP/6-31G(d)) spectrum of *Z*-**5-H**. e) Total IR spectrum of photoproduct H3 ('★') obtained after additional 215 min of irradiation with shorter wave-length (λ > 300 nm). f) Calculated spectrum of *E*-**5-H**. g) Calculated spectrum of ^{5}A'-**2-H**. h) Calculated spectrum of ^{3}A''-**2-H**.



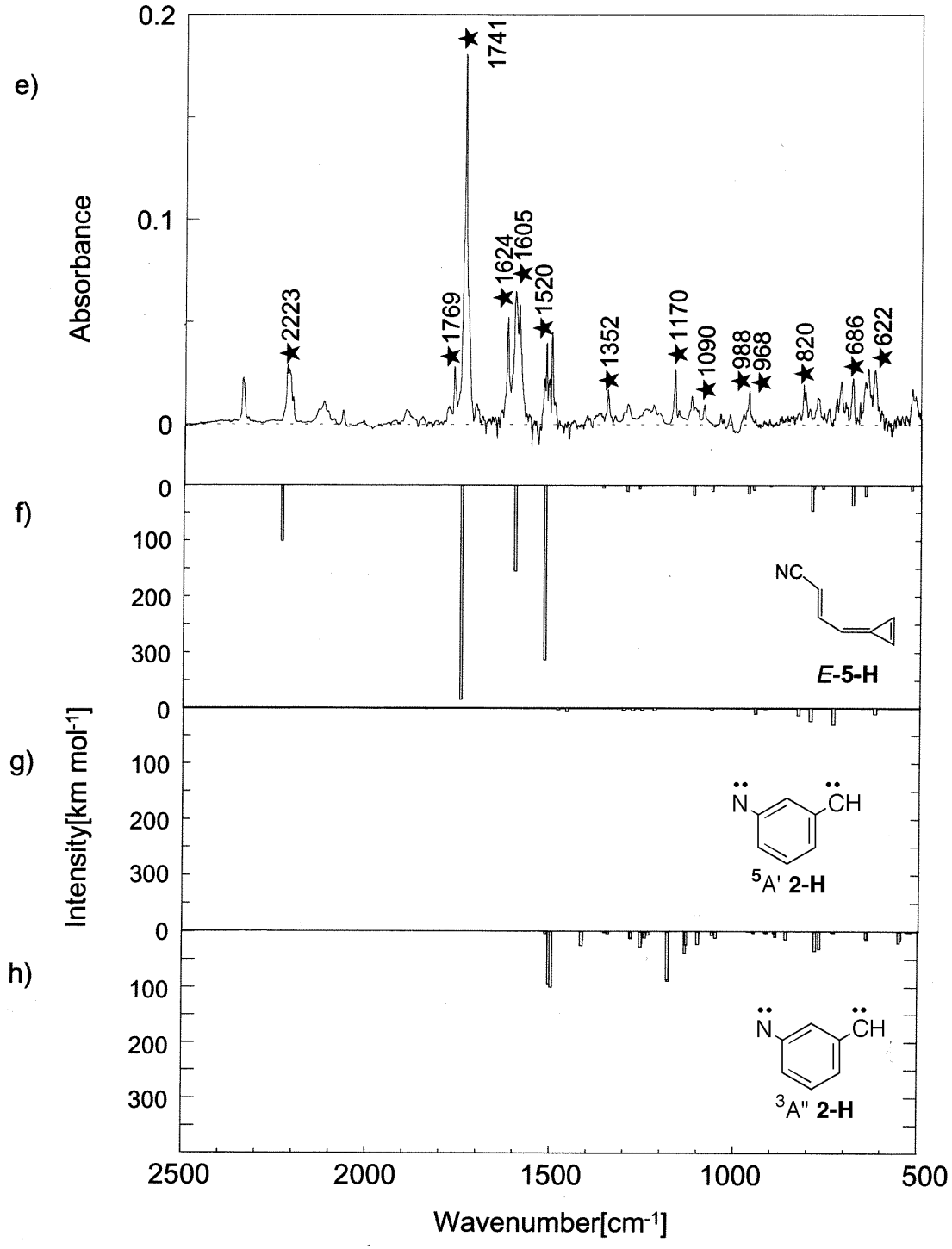
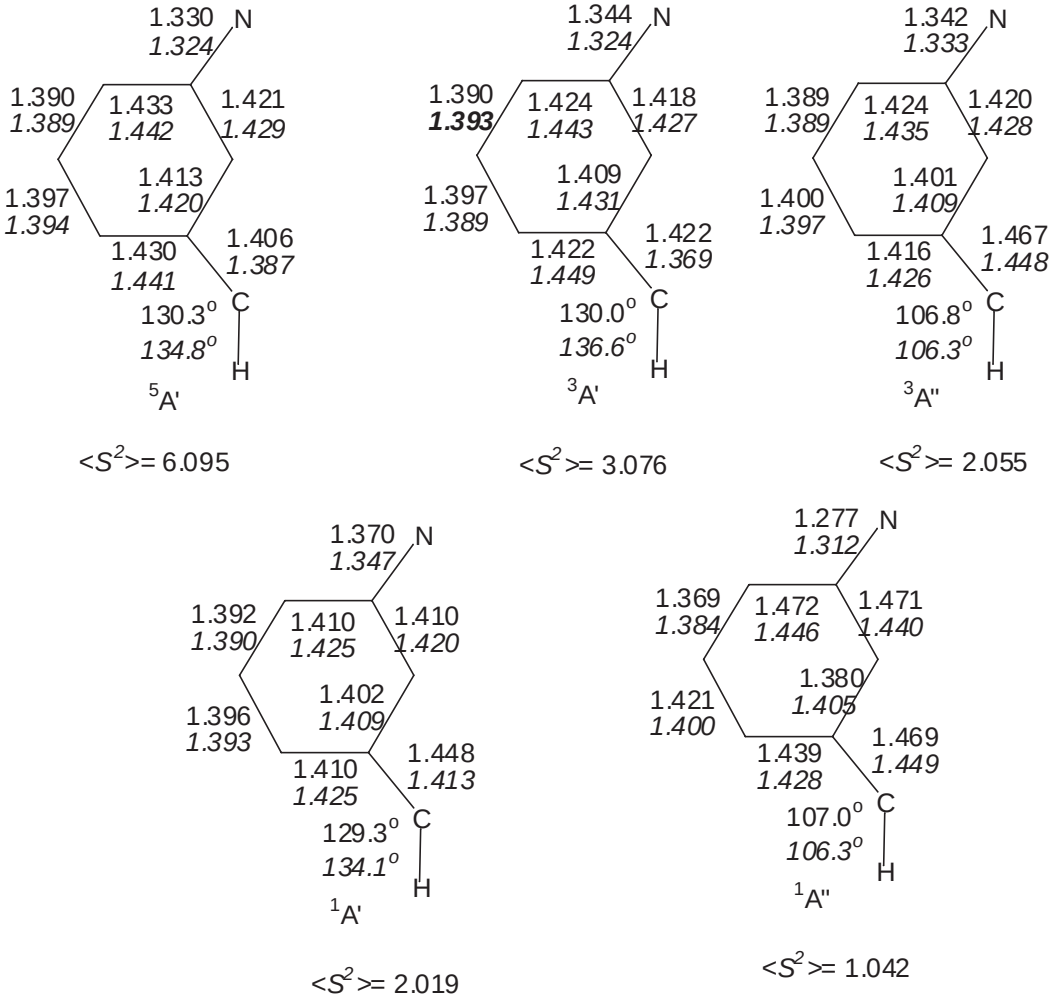
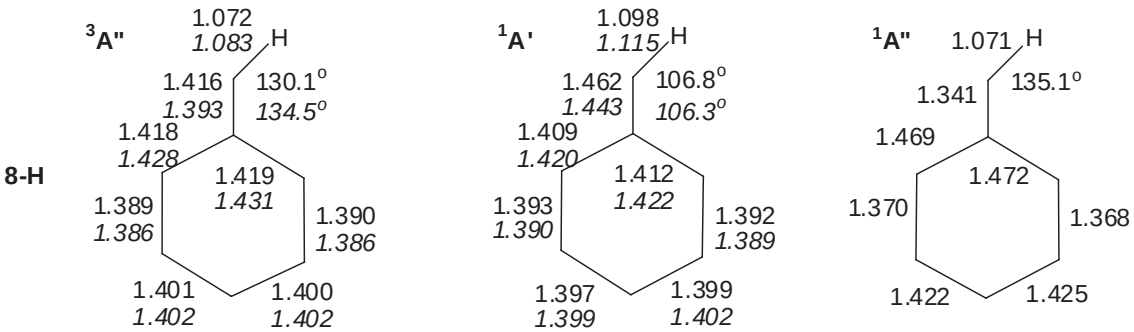

e)
f)
g)
h)
Absorbance
Intensity[km mol-1]
Wavenumber[cm-1]
0.2
0.1
0
2223
1769
1741
1624
1605
1520
1352
1170
1090
988
968
820
686
622
NC
E-5-H
N
CH
5A' 2-H
3A" 2-H
2500
2000
1500
1000
500

Figure S2. Selected geometrical parameters (distances in Å, angles in degrees) for the ^{5}A', ^{3}A', ^{3}A", ^{1}A' and ^{1}A" states of **2-H** at the MCSCF and UB3LYP (in italics) levels of theory with the 6-31G(d) basis set and UB3LYP spin-squared expectation values (<S^2>).

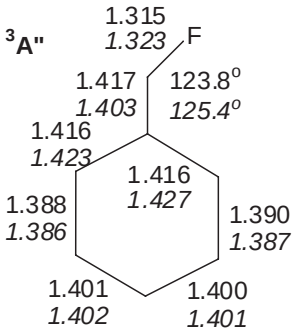
Figure S3. Selected geometrical parameters (distances in Å, angles in degrees) for the

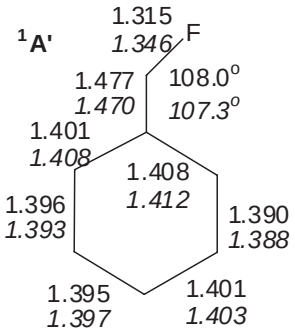


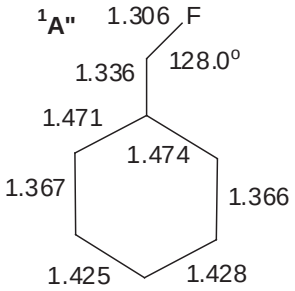
^{3}A", ^{1}A' and ^{1}A" states of **8-X** and for the $^3A_2$, $^1A_1$ and $^1A_2$ states of **9** at the MCSCF and UB3LYP (in italics) levels of theory with the 6-31G(d) basis set.



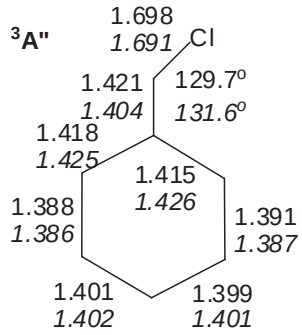
8-F

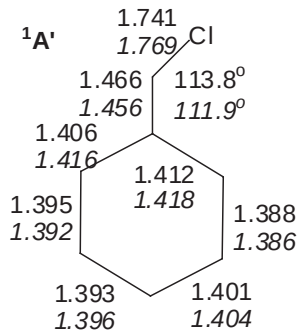

3A"
1.315
1.323
F
1.417
1.403
123.8°
125.4°
1.416
1.423
1.416
1.427
1.388
1.386
1.390
1.387
1.401
1.402
1.400
1.401

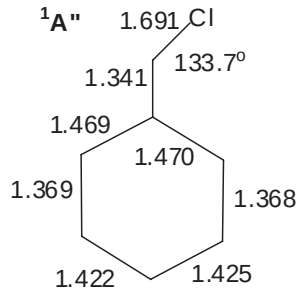

1A'
1.315
1.346
F
1.477
1.470
108.0°
107.3°
1.401
1.408
1.408
1.412
1.396
1.393
1.390
1.388
1.395
1.397
1.401
1.403


1A"
1.306
F
1.336
128.0°
1.471
1.474
1.367
1.366
1.425
1.428

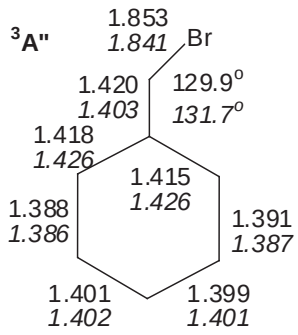
8-Cl

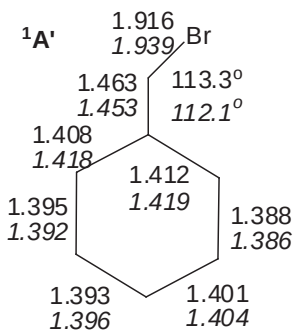

3A"
1.698
1.691
Cl
1.421
1.404
129.7°
131.6°
1.418
1.425
1.415
1.426
1.388
1.386
1.391
1.387
1.401
1.402
1.399
1.401

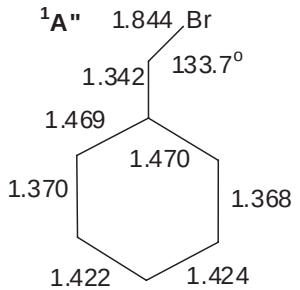

1A'
1.741
1.769
Cl
1.466
1.456
113.8°
111.9°
1.406
1.416
1.412
1.418
1.395
1.392
1.388
1.386
1.393
1.396
1.401
1.404


1A"
1.691
Cl
1.341
133.7°
1.469
1.470
1.369
1.368
1.422
1.425

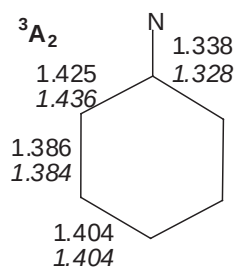
8-Br

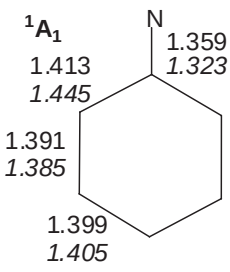

3A"
1.853
1.841
Br
1.420
1.403
129.9°
131.7°
1.418
1.426
1.415
1.426
1.388
1.386
1.391
1.387
1.401
1.402
1.399
1.401


1A'
1.916
1.939
Br
1.463
1.453
113.3°
112.1°
1.408
1.418
1.412
1.419
1.395
1.392
1.388
1.386
1.393
1.396
1.401
1.404


1A"
1.844
Br
1.342
133.7°
1.469
1.470
1.370
1.368
1.422
1.424

9


3A2
N
1.338
1.328
1.425
1.436
1.386
1.384
1.404
1.404


1A1
N
1.359
1.323
1.413
1.445
1.391
1.385
1.399
1.405

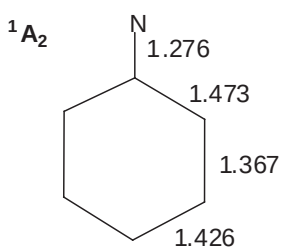
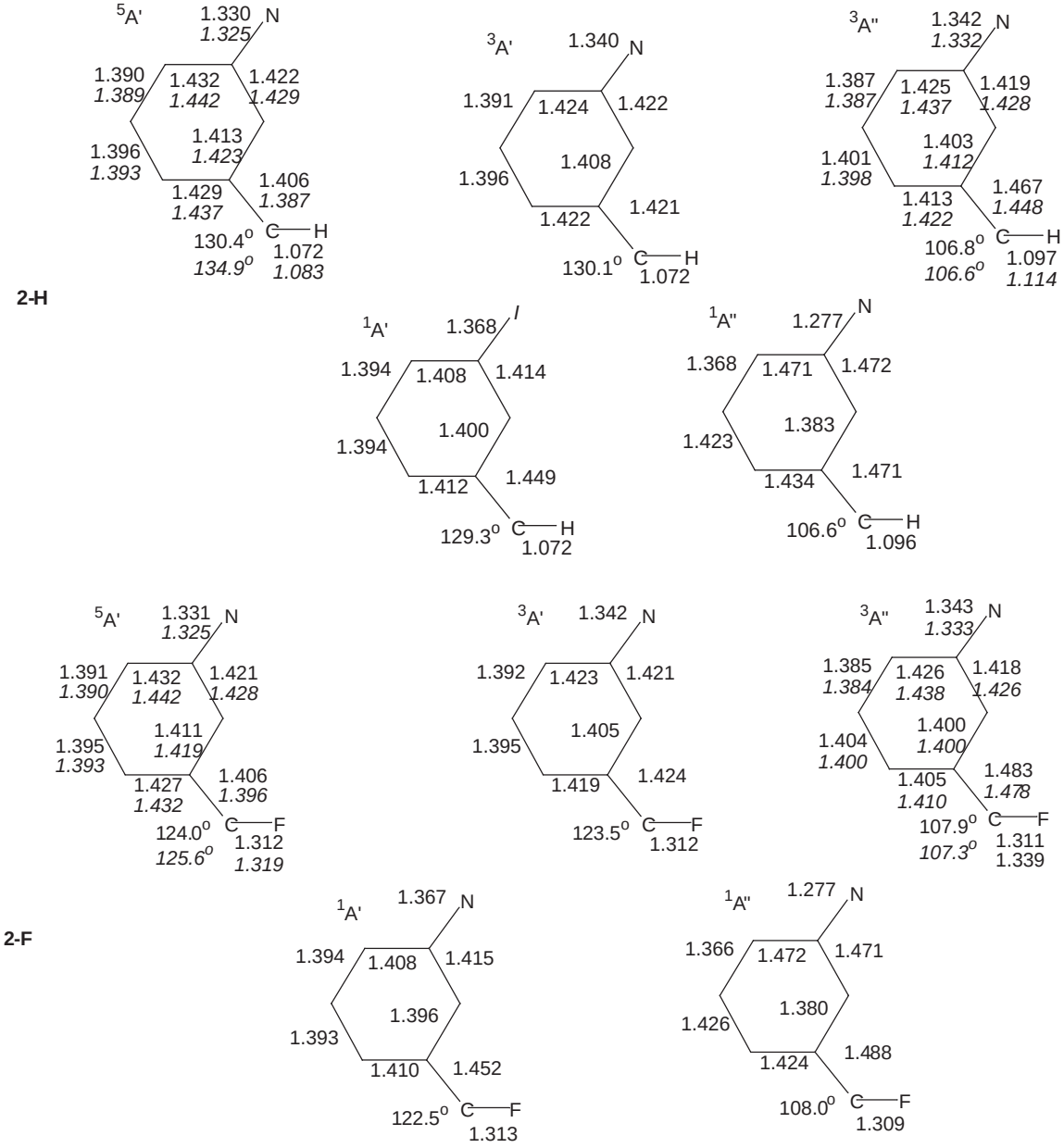
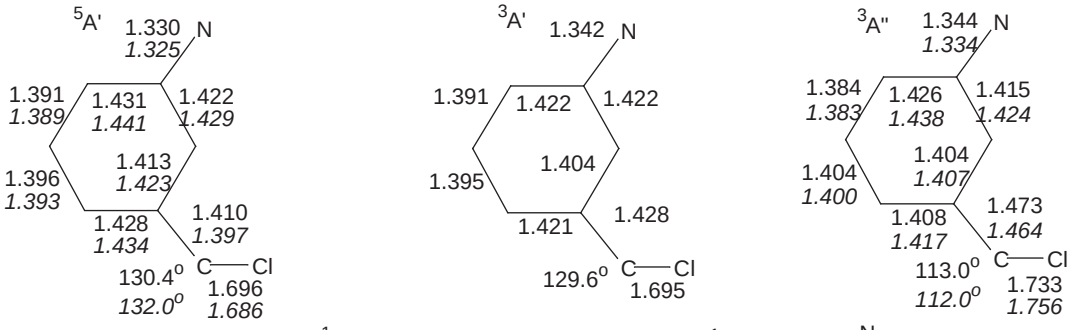
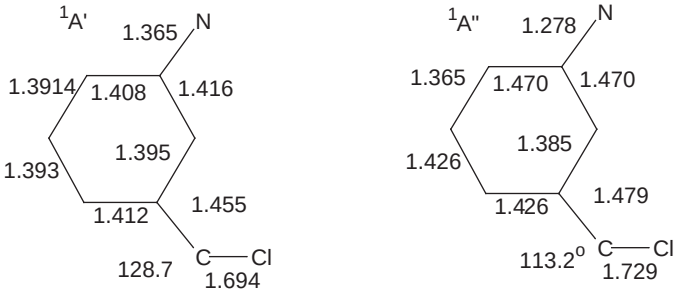

1A2
N
1.276
1.473
1.367
1.426

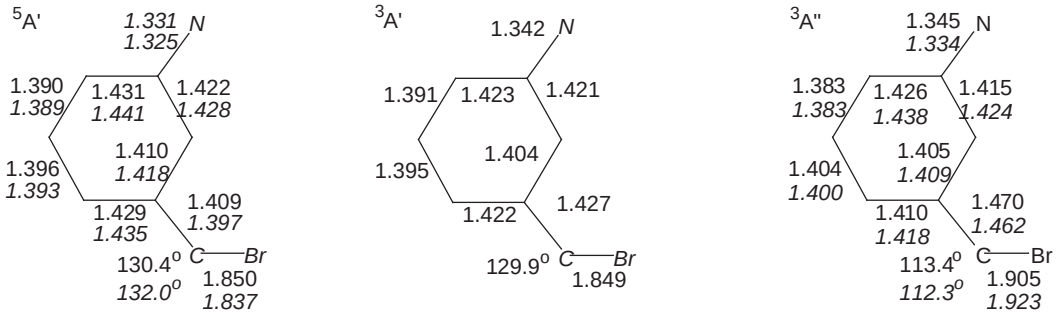
Figure S4. Selected geometrical parameters (distances in Å, angles in degrees) for the ^{5}A', ^{3}A', ^{3}A", ^{1}A' and ^{1}A" states of **2-X** (*syn* isomers) at the MCSCF and UB3LYP (in italics) levels of theory with the 6-31G(d) basis set.




5A'
1.330 N
1.325
1.391
1.389
1.431
1.441
1.422
1.429
1.413
1.423
1.396
1.393
1.428
1.434
1.410
1.397
130.4°
C—Cl
1.696
132.0°
1.686
3A'
1.342 N
1.391
1.422
1.422
1.404
1.395
1.421
1.428
129.6°
C—Cl
1.695
3A"
1.344 N
1.334
1.384
1.383
1.426
1.438
1.415
1.424
1.404
1.404
1.400
1.407
1.408
1.417
1.473
1.464
113.0°
C—Cl
1.733
112.0°
1.756

2-Cl


1A'
1.365 N
1.3914
1.408
1.416
1.395
1.393
1.412
1.455
C—Cl
128.7
1.694
1A"
1.278 N
1.365
1.470
1.470
1.385
1.426
1.426
1.479
113.2°
C—Cl
1.729


5A'
1.331 N
1.325
1.390
1.389
1.431
1.441
1.422
1.428
1.410
1.418
1.396
1.393
1.429
1.435
1.409
1.397
130.4°
C—Br
1.850
132.0°
1.837
3A'
1.342 N
1.391
1.423
1.421
1.404
1.395
1.422
1.427
129.9°
C—Br
1.849
3A"
1.345 N
1.334
1.383
1.383
1.426
1.438
1.415
1.424
1.404
1.404
1.400
1.405
1.409
1.410
1.418
1.470
1.462
113.4°
C—Br
1.905
112.3°
1.923

2-Br

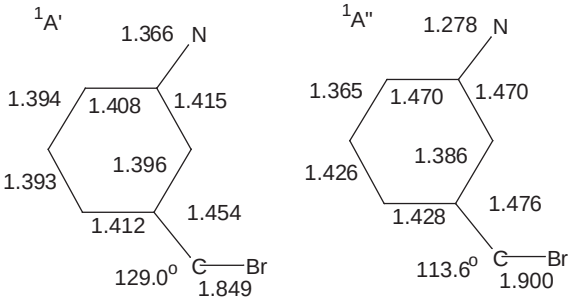
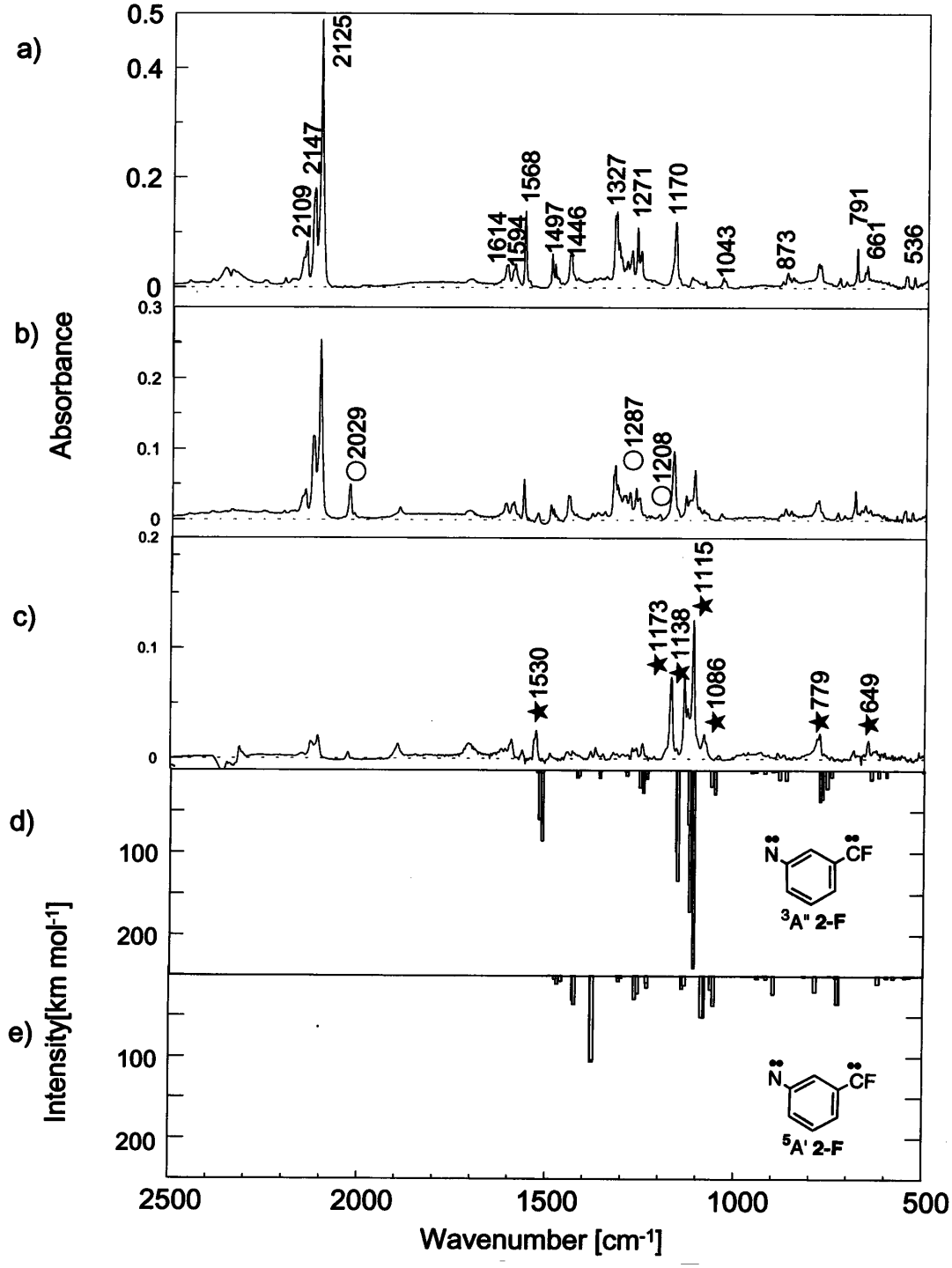
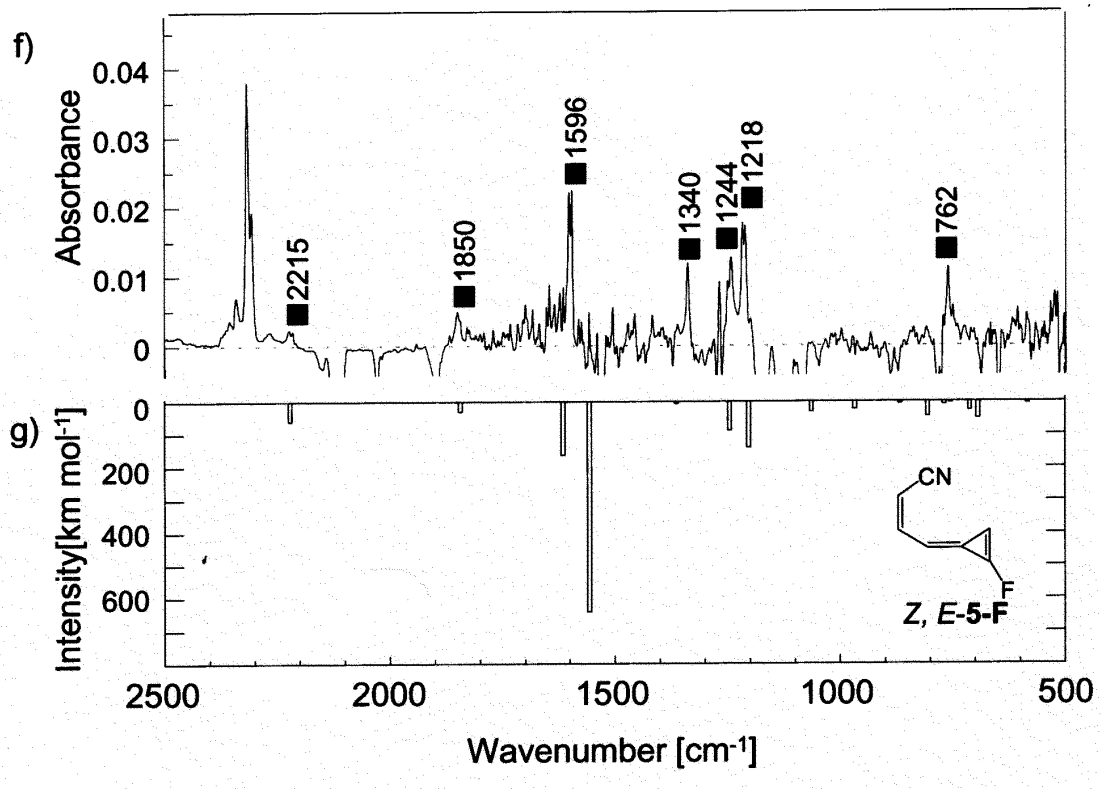
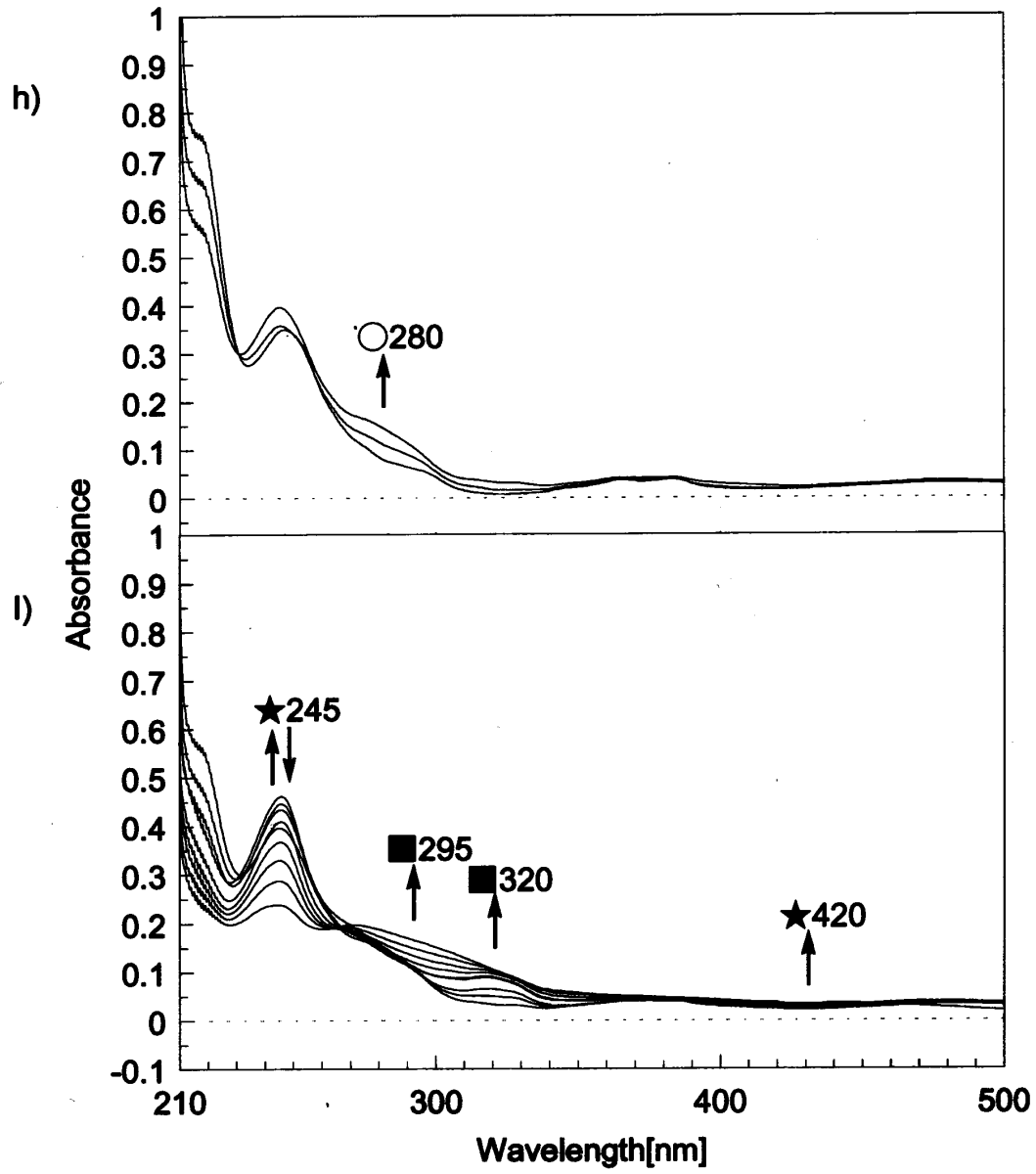

1A'
1.366 N
1.394
1.408
1.415
1.396
1.393
1.412
1.454
129.0°
C—Br
1.849
1A"
1.278 N
1.365
1.470
1.470
1.386
1.426
1.428
1.476
113.6°
C—Br
1.900

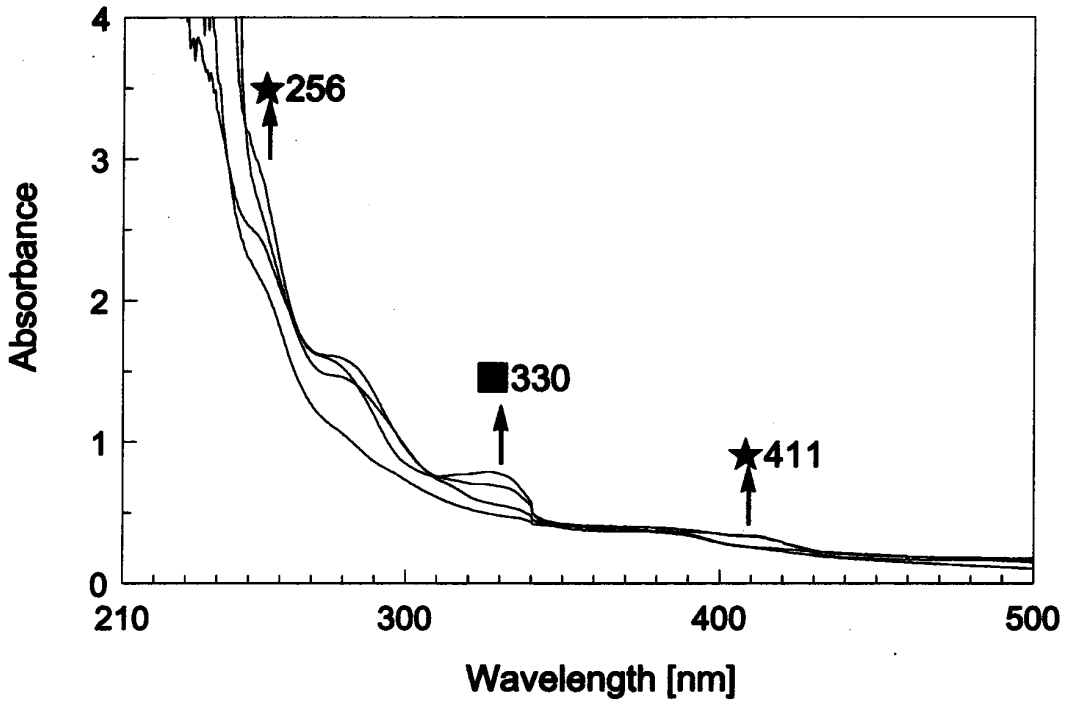
Figure S5. Photolysis (λ > 300 nm) of **6-F** in Ar matrix at 13 K. a) IR spectrum of **6-F**. b) IR spectrum obtained after 50 sec of irradiation. (Primary photoproduct (**4-F**, '○')). c) IR spectrum obtained after 6 min. (Secondary photoproduct (**2-F**, '★'). d) Calculated spectrum of ^{3}A" **2-F**. e) Calculated spectrum of ^{5}A' **2-F**. f) Difference spectrum of **2-F** (lower part) and photoproduct formed after 105 min of irradiation (**5-F**, '■'). g) Calculated spectrum of **5-F**. h) UV spectra (0-15 sec). i) UV spectra (15 sec to 23 min). j) UV spectra (triacetin, 10^{-3}M, 77 K, 0-6 min) k) ESR spectrum of **2-F** (triacetin, 10^{-3}M, 77 K, 16 min) (Freq=9.23470 GHz, St=2min, Amp=50, H0=330 mT, H=695 mT).




f)
Absorbance
0.04
0.03
0.02
0.01
0
2215
1850
1596
1340
1244
1218
762
g)
Intensity[km mol-1]
0
200
400
600
CN
F
Z, E-5-F
2500
2000
1500
1000
500
Wavenumber [cm-1]


h)
l)
Absorbance
Wavelength[nm]
280
245
295
320
420
1
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
-0.1
210
300
400
500

j)


Absorbance
Wavelength [nm]
256
330
411
0
1
2
3
4
210
300
400
500

k)

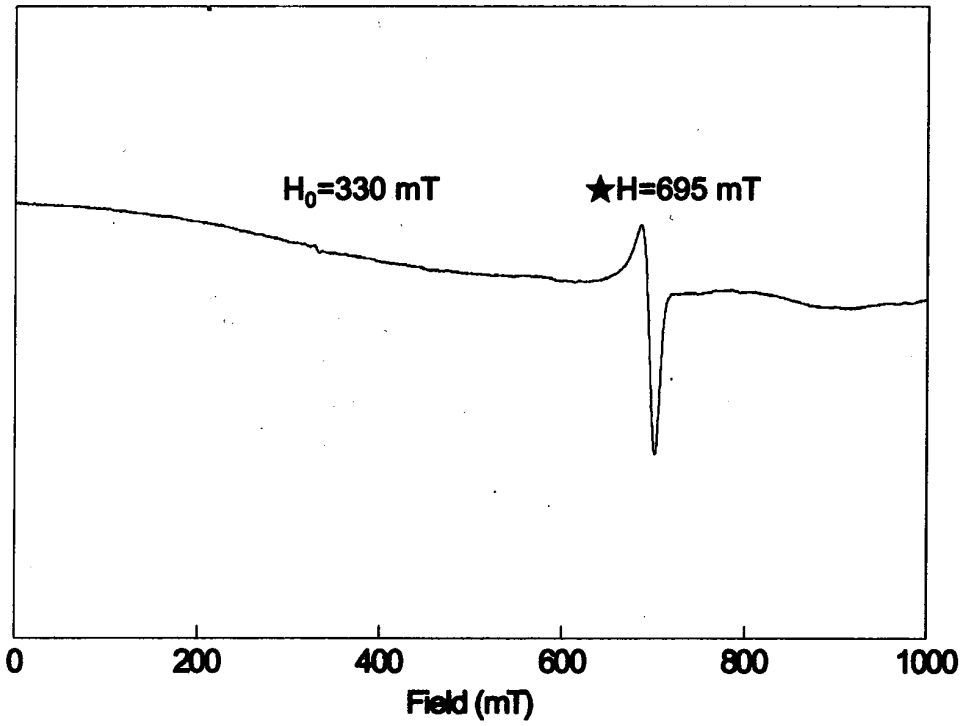
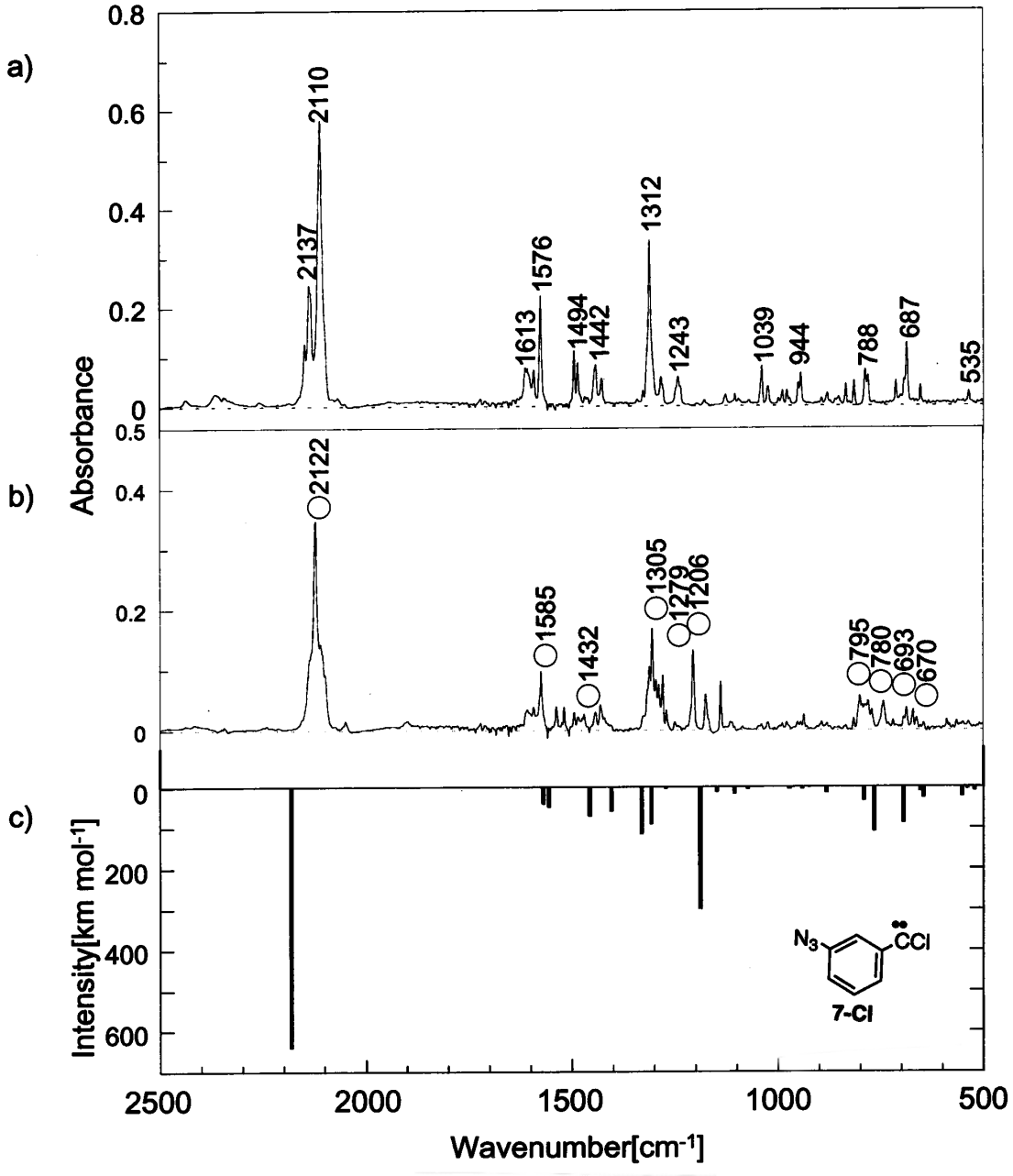
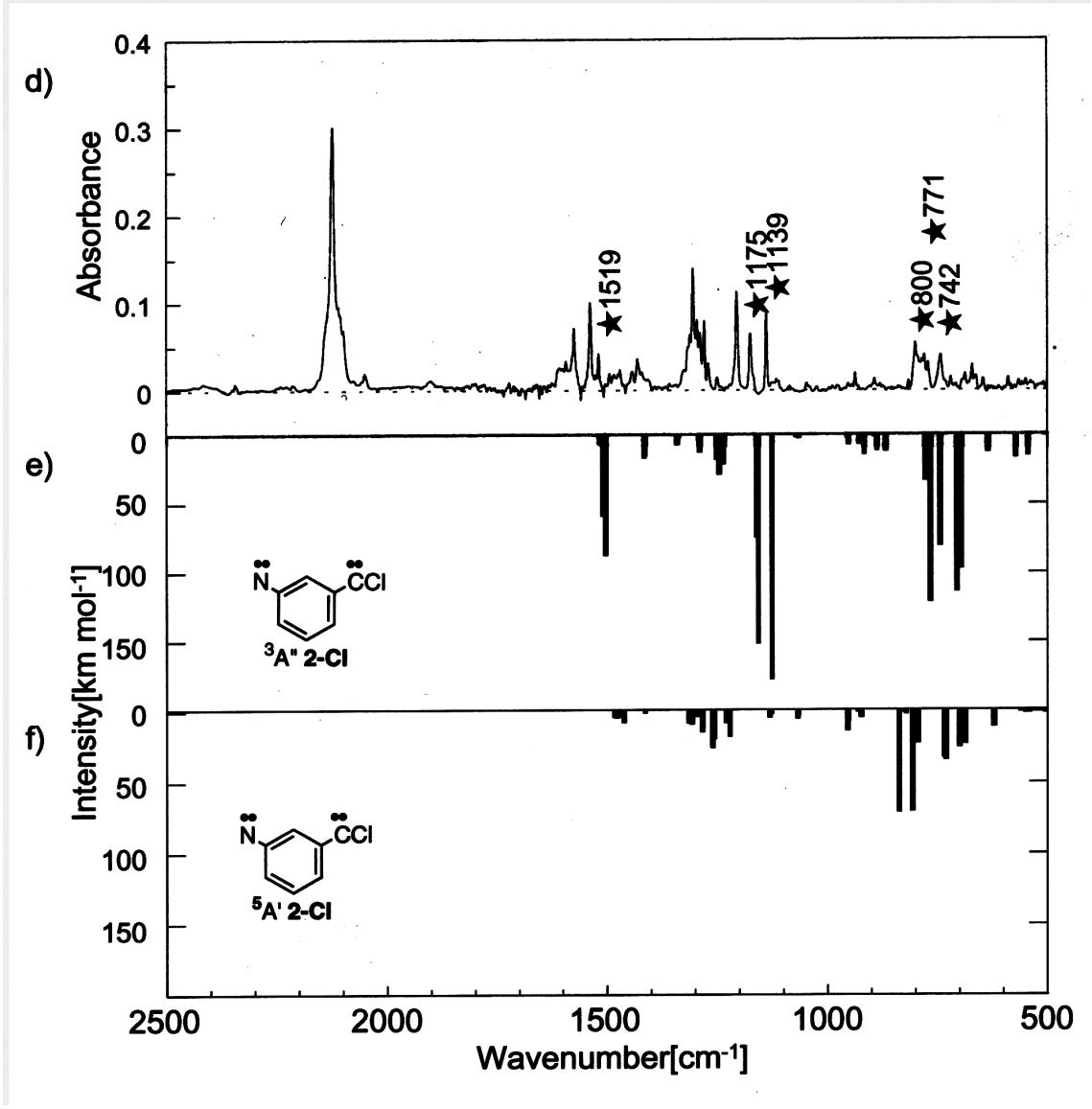
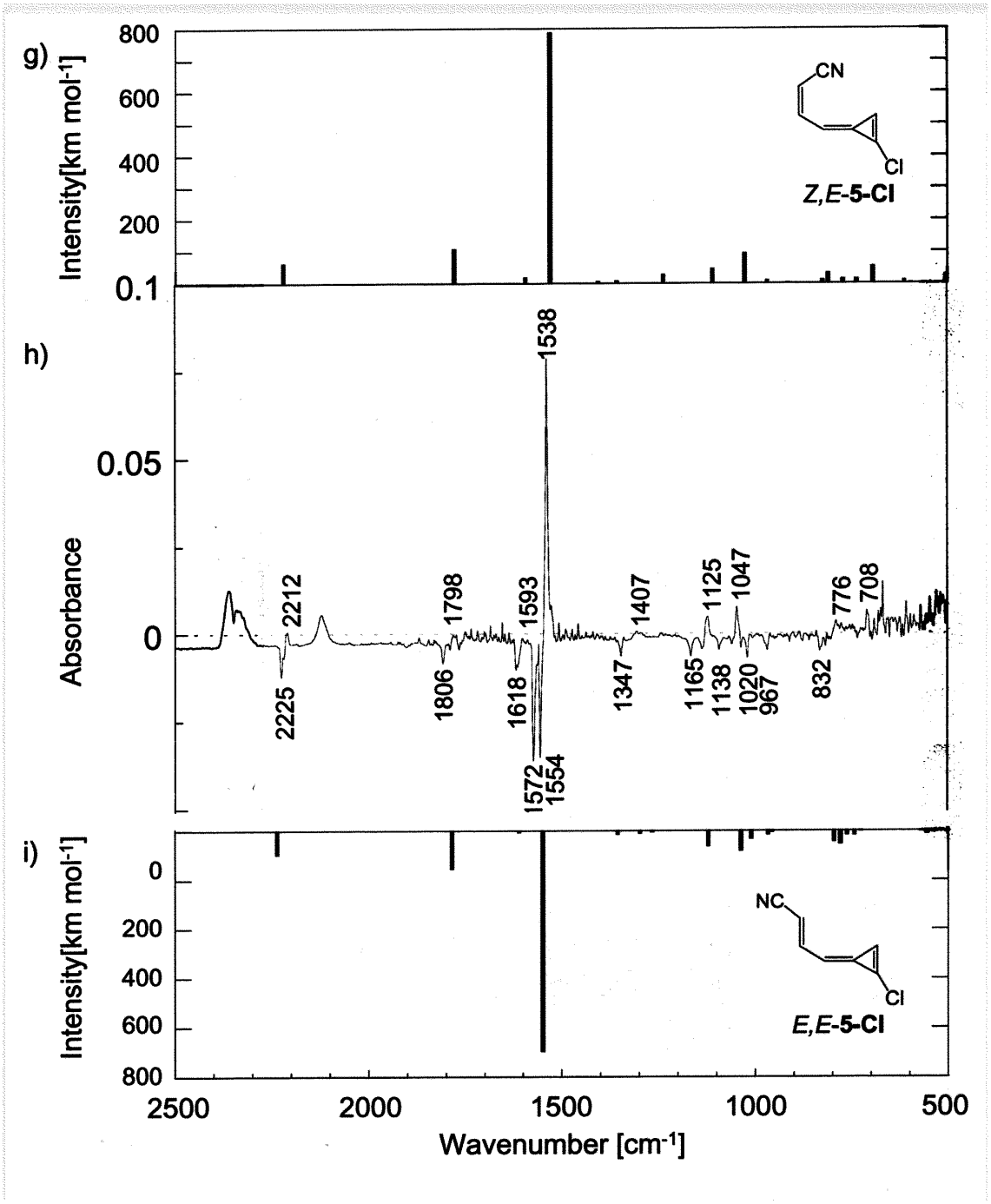
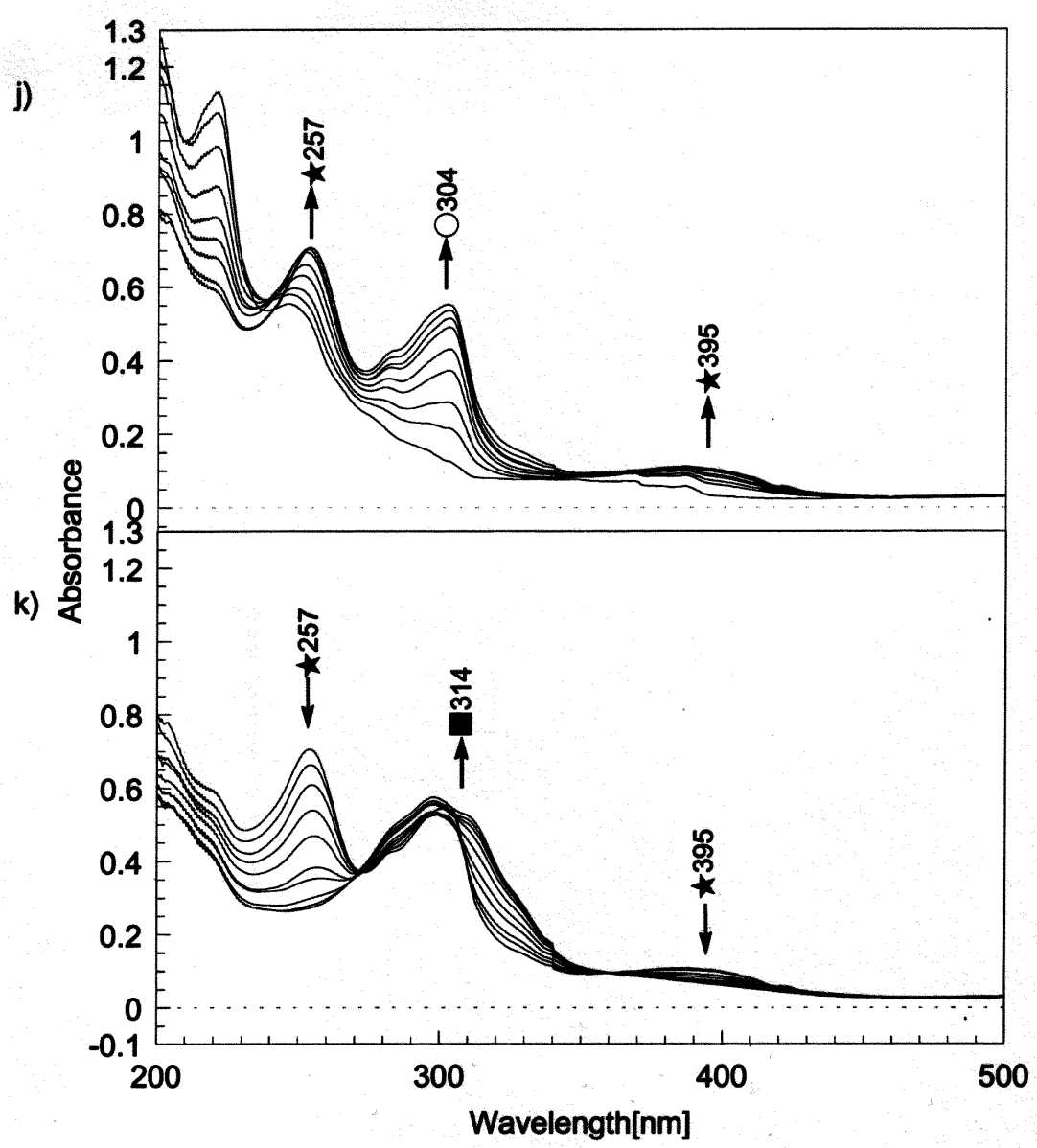

H0=330 mT
H=695 mT
Field (mT)
0
200
400
600
800
1000

Figure S6. Photolysis (l > 350 nm) of 6-Cl in Ar matrix at 13 K. a) IR spectrum of 6-Cl before irradiation. b) Total spectrum obtained after 5 min of irradiation. Bands due to primary photoproduct (7-Cl) are marked with '('. c) Calculated spectrum of singlet 7-Cl. d) Total spectrum obtained after 10 min of irradiation. Bands due to secondary photoproduct (2-Cl) are marked with '('. e) Calculated spectrum of 3A" 2-Cl. f) Calculated spectrum of 5A' 2-Cl. g) Calculated spectrum of Z,E 5-Cl. h) Difference spectrum obtained between photoproduct formed after 220 min of irradiation with l > 350 nm and photoproduct formed after 95 min of irradiation with l > 300 nm. i) Calculated spectrum of E,E 5-Cl. j) UV spectra (0-4 min). k) UV spectra (4–90 min). l) UV spectra (triacetin, 10-2M, 77 K, 0-4 min). m) ESR spectrum of 2-Cl (triacetin, 10-2M, 77 K, 10 min) (Freq=9.23231 GHz, St=2min, Amp=50, H0=329 mT, H=695 mT).




d)
e)
f)
Absorbance
Intensity[km mol-1]
Wavenumber[cm-1]
1519
1175
1139
800
771
742
3A" 2-Cl
5A' 2-Cl
N
CCl
0.4
0.3
0.2
0.1
0
50
100
150
2500
2000
1500
1000
500


g)
Intensity[km mol-1]
800
600
400
200
0.1
CN
Cl
Z,E-5-Cl
h)
Absorbance
0.05
0
2225
2212
1806
1798
1618
1593
1572
1554
1538
1347
1407
1165
1138
1125
1047
1020
967
832
776
708
i)
Intensity[km mol-1]
0
200
400
600
800
NC
Cl
E,E-5-Cl
2500
2000
1500
1000
500
Wavenumber [cm-1]


j)
k)
Absorbance
Wavelength[nm]
257
304
395
257
314
395
1.3
1.2
1
0.8
0.6
0.4
0.2
0
-0.1
200
300
400
500

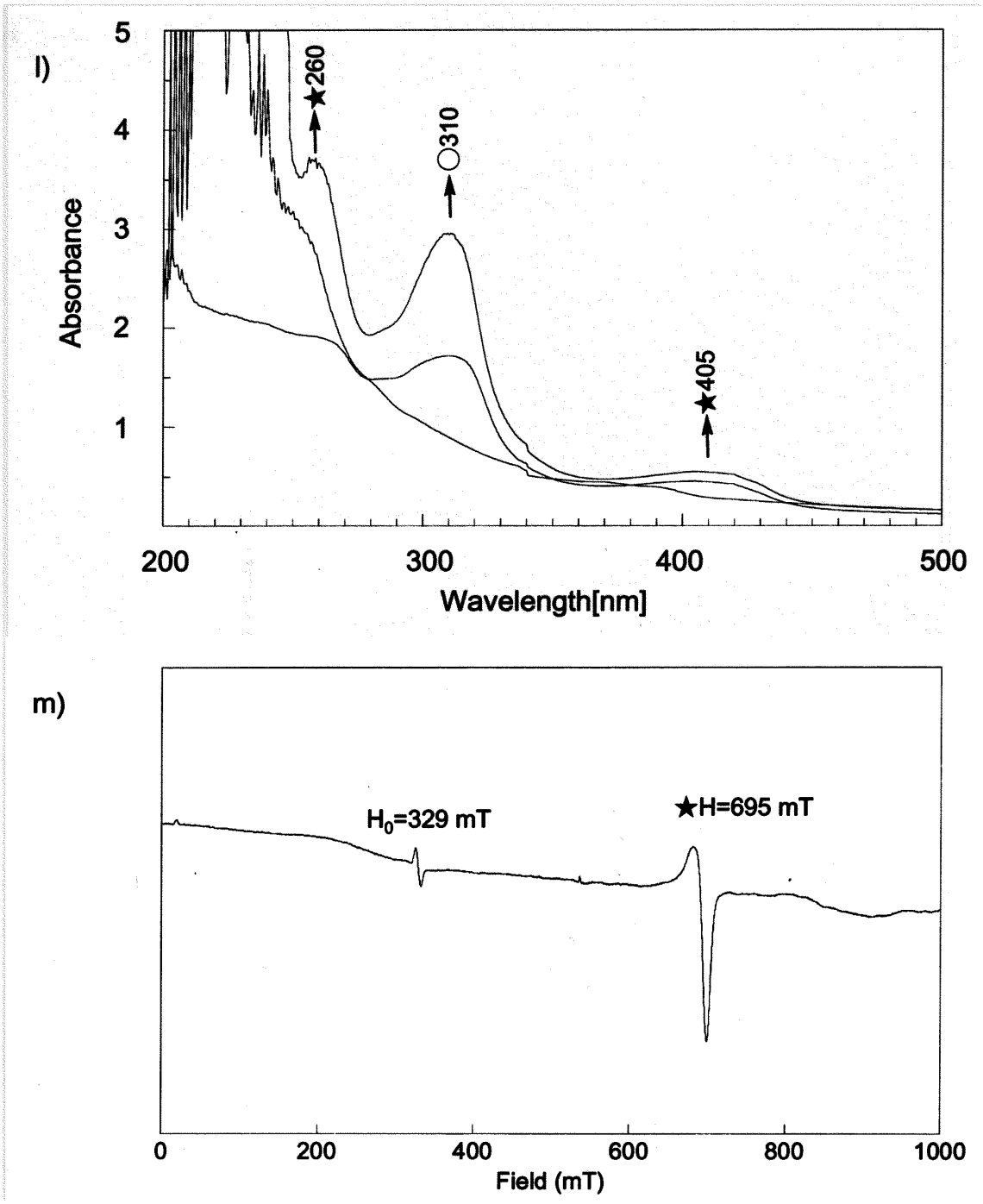
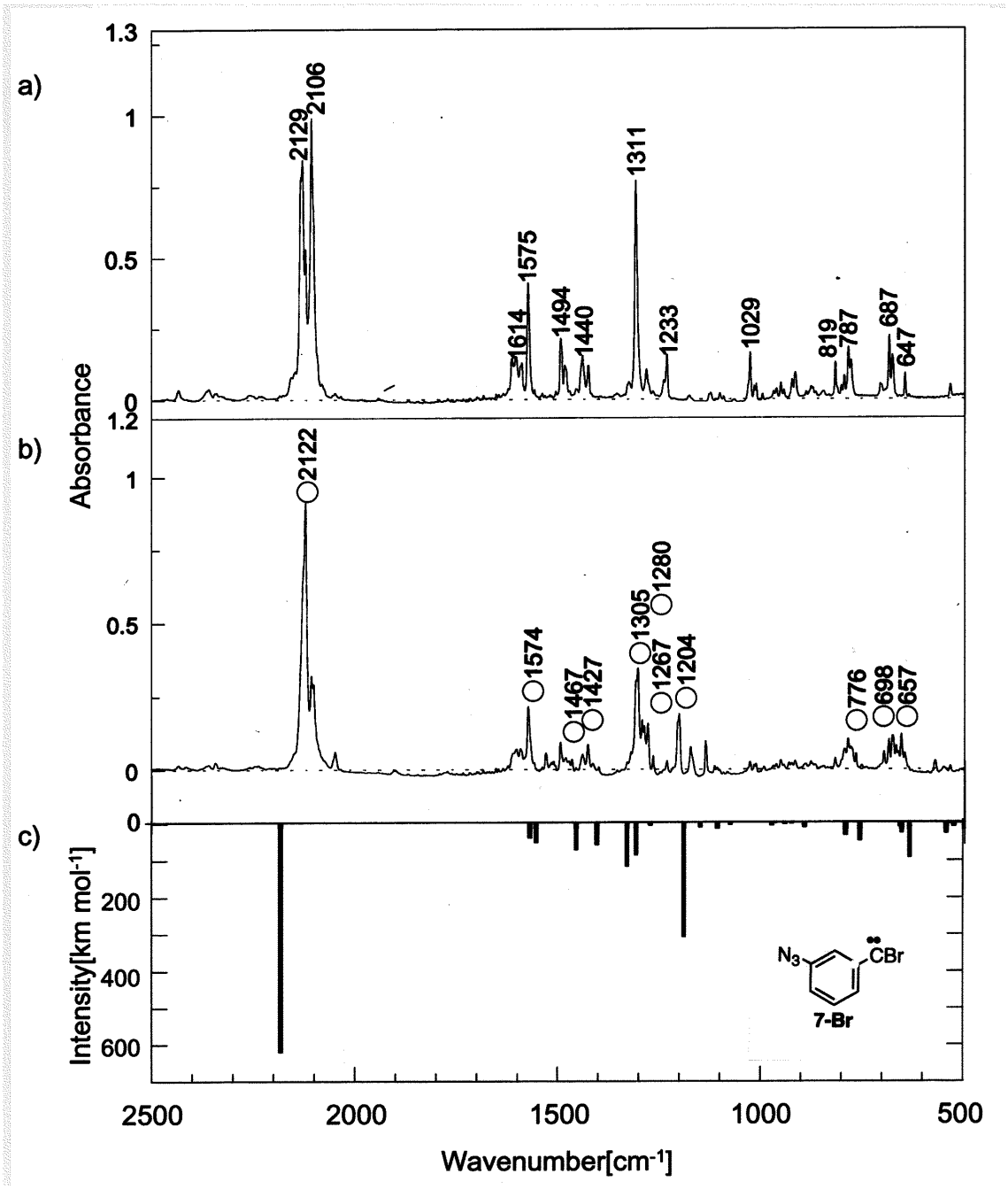
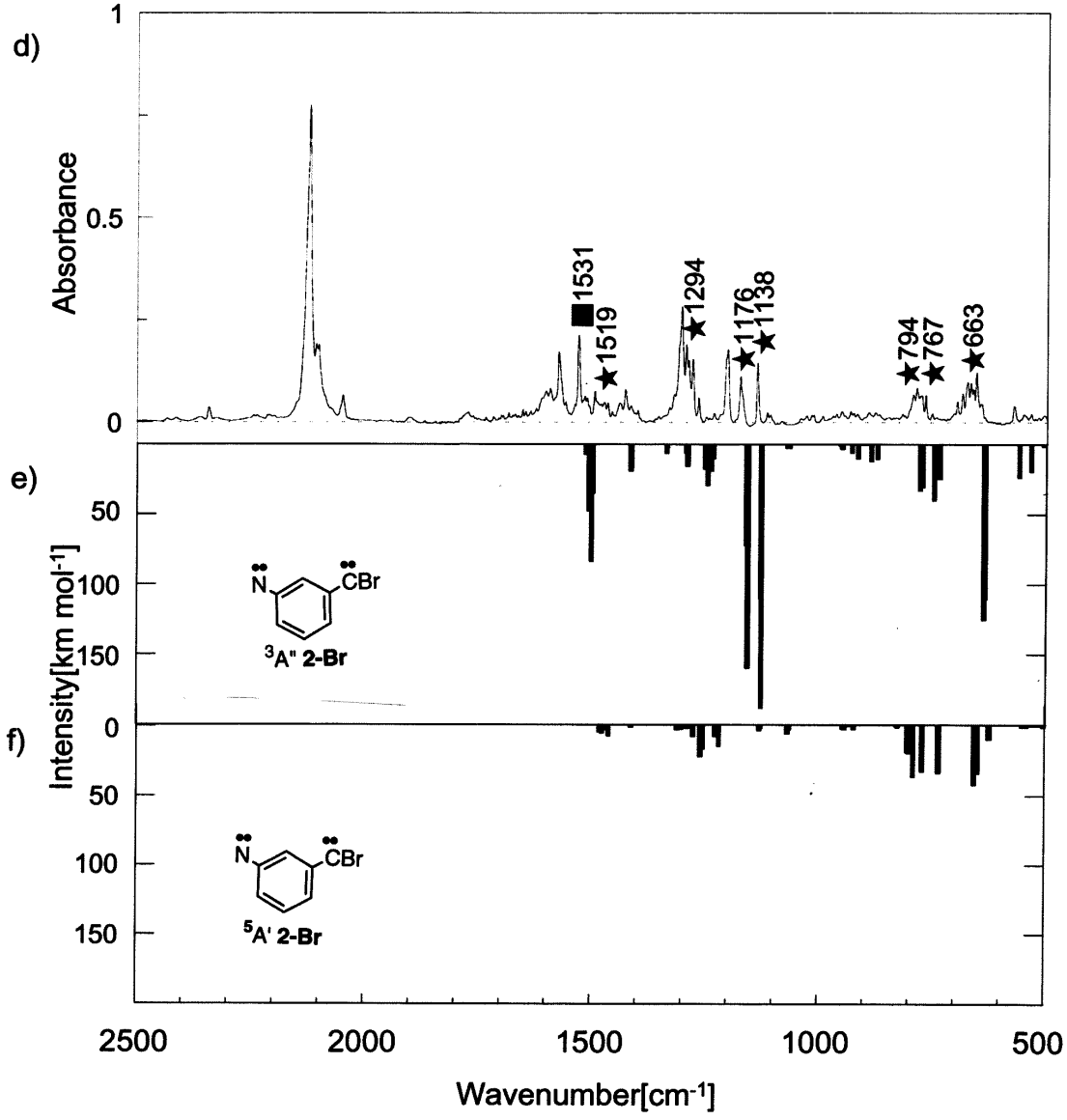
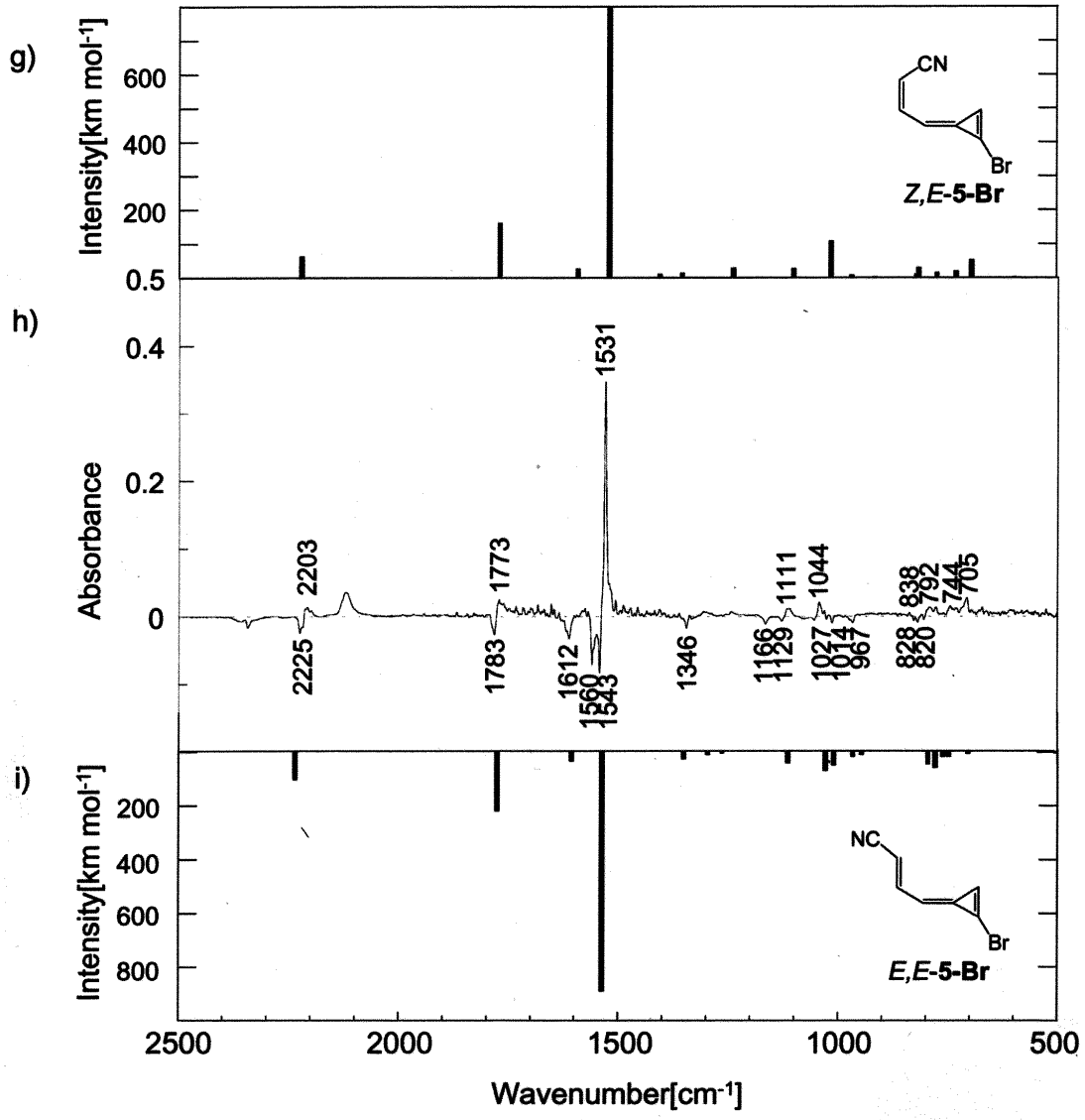
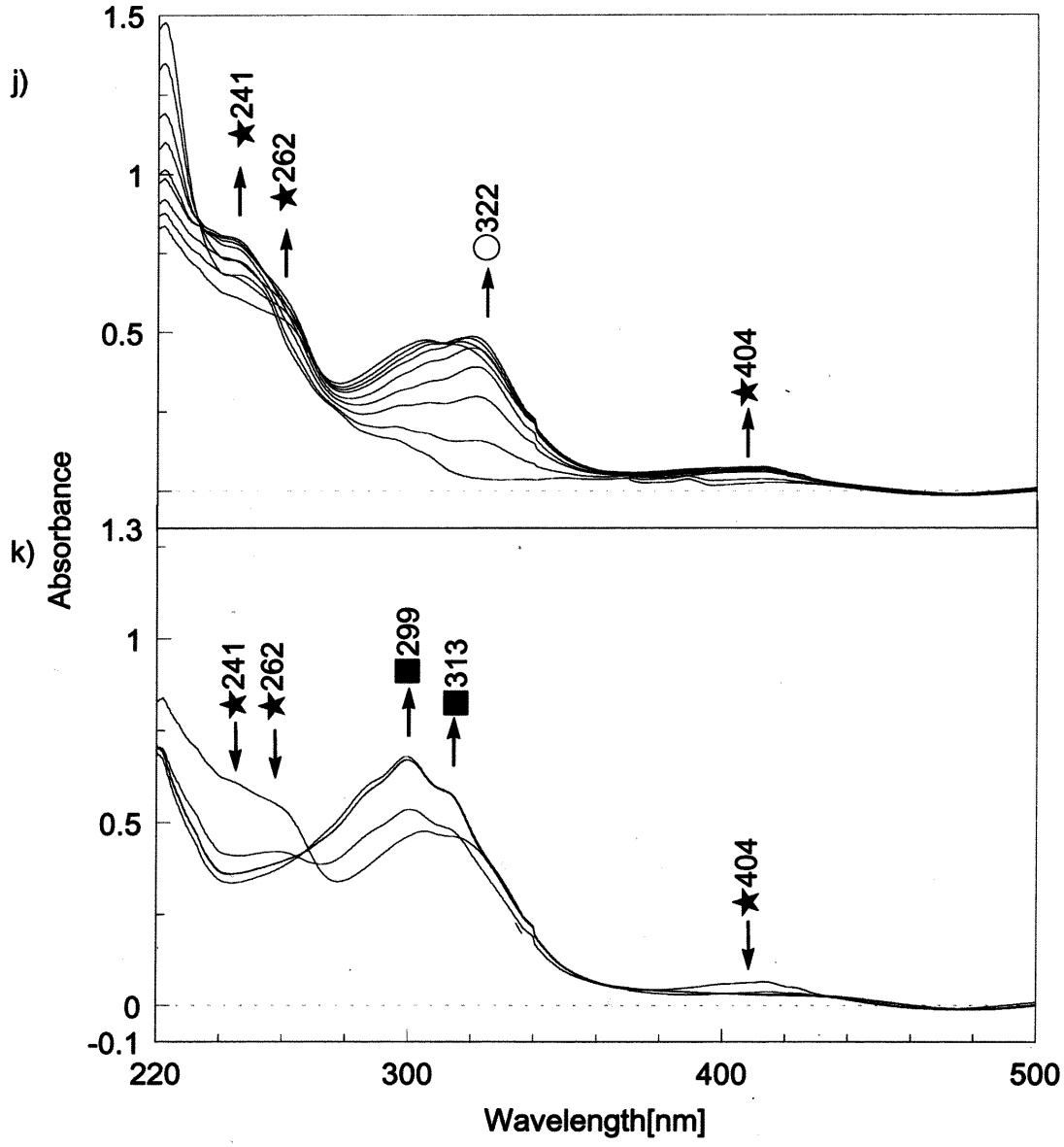

l)
Absorbance
5
4
3
2
1
★260
○310
★405
200
300
400
500
Wavelength[nm]
m)
H0=329 mT
★H=695 mT
0
200
400
600
800
1000
Field (mT)

Figure S7. Photolysis (λ > 350 nm) of **6-Br** in Ar matrix at 13 K. a) IR spectrum of **6-Br**. b) IR spectrum obtained after 4 min. (Primary photoproduct (**7-Br**, '❍'). c) Calculated spectrum of singlet **7-Br**. d) IR spectrum after 10 min. (Secondary photoproduct (**2-Br**, '★') and final photoproduct (**5-Br**, '■')). e) Calculated spectrum of ^{3}A" **2-Br**. f) Calculated spectrum of ^{5}A' **2-Br**. g) Calculated spectrum of *Z,E* **5-Br**. h) Difference spectrum obtained between photoproduct (**5-Br**, upper) formed after 310 min (l > 350 nm) and photoproduct formed after additional 540 min (l > 300 nm). i) Calculated spectrum of *E,E* **5-Br**. j) UV spectra (0-10 min). k) UV spectra (10 - 20 min). l) UV spectra (triacetin, 10^{-2}M, 77 K, 0-2 min). m) ESR spectrum of **2-Br** (triacetin, 10^{-2}M, 77 K, 20 min) (Freq=9.20696 GHz, St=2min, Amp=50, H0=328 mT, H=684 mT).

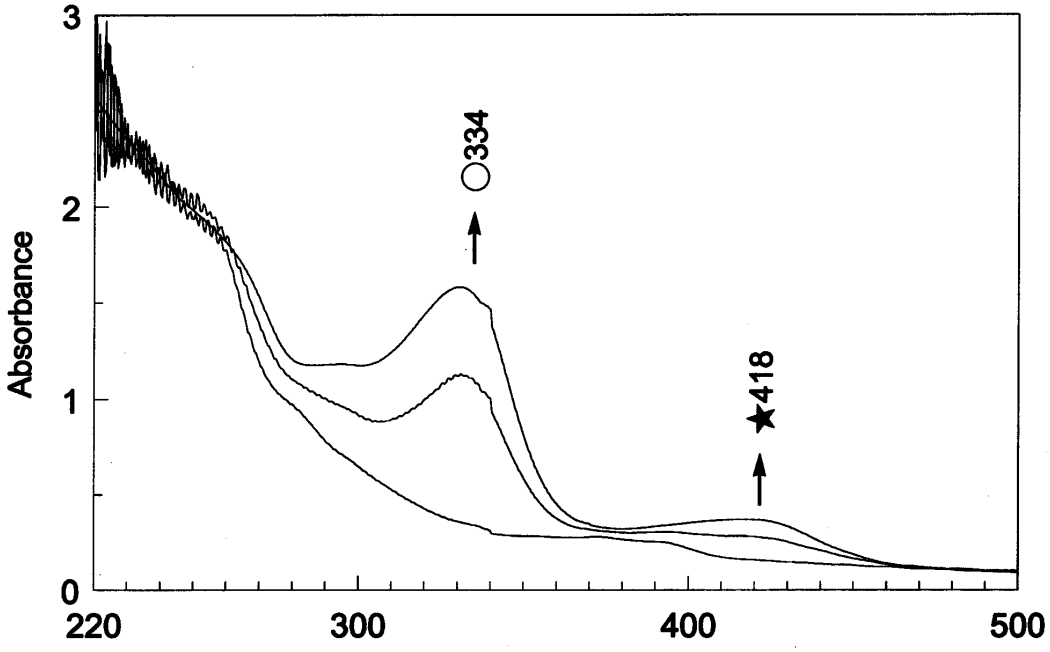



d)
e)
f)
Absorbance
Intensity[km mol-1]
Wavenumber[cm-1]
1531
1519
1294
1176
1138
794
767
663
3A" 2-Br
5A' 2-Br
CBr
N
2500
2000
1500
1000
500

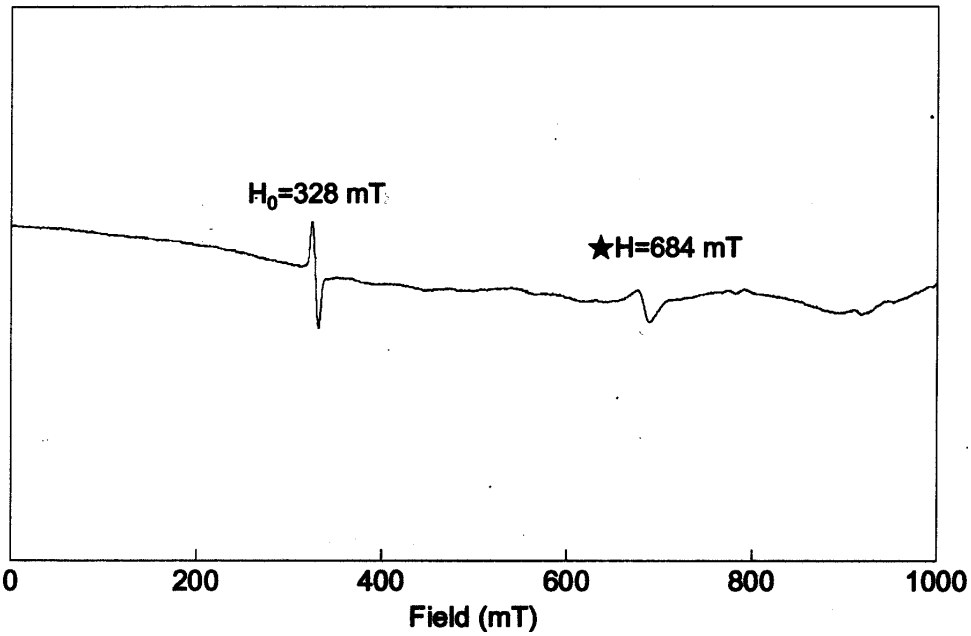

g)
Intensity[km mol-1]
600
400
200
0.5
CN
Br
Z,E-5-Br
h)
Absorbance
0.4
0.2
0
2203
1773
1531
1111
1044
838
792
744
705
2225
1783
1612
1560
1543
1346
1166
1129
1027
1014
967
828
820
i)
Intensity[km mol-1]
200
400
600
800
NC
Br
E,E-5-Br
2500
2000
1500
1000
500
Wavenumber[cm-1]


j)
k)
Absorbance
Wavelength[nm]
★241
★262
○322
★404
■299
■313
1.5
1
0.5
1.3
0
-0.1
220
300
400
500

l)


Absorbance
3
2
1
0
220
300
400
500
○334
★418

m)


H0=328 mT
★H=684 mT
0
200
400
600
800
1000
Field (mT)