Supplementary Information (SI) for Physical Chemistry Chemical Physics.


# Electronic Supplementary Information

## Reactions of hydrogen atoms with fluorene ($C_{13}H_{10}$): Infrared spectra of 9*H*-fluoren-9-yl ($C_{13}H_9$) and monohydrofluorenyl (1*H*-, 2*H*-, 3*H*-, and 4*H*-$C_{13}H_{11}$) radicals isolated in solid *para*-hydrogen

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**Table S1** Cartesian coordinates of optimized geometries of fluorene ($C_{13}H_{10}$), 9*H*-fluoren-9-yl ($C_{13}H_9$), and 9*H*-fluoren-9-ylidene ($C_{13}H_8$)

| $C_{13}H_{10}$[a] | | | | $C_{13}H_9$[a] | | | |
|---|---|---|---|---|---|---|---|
| | *x* | *y* | *z* | | *x* | *y* | *z* |
| C | 0.0000000 | 1.8294690 | 0.0001260 | C | 0.0000000 | 1.7436230 | -0.0000030 |
| C | 1.1833500 | 0.8848690 | 0.0000840 | C | 1.1599320 | 0.9065430 | 0.0000000 |
| C | -1.1833500 | 0.8848690 | 0.0000360 | C | -1.1599320 | 0.9065420 | 0.0000000 |
| C | 0.7345440 | -0.4502020 | -0.0000140 | C | 0.7338250 | -0.4602430 | -0.0000030 |
| C | -0.7345440 | -0.4502020 | -0.0000440 | C | -0.7338260 | -0.4602430 | -0.0000030 |
| C | 2.5422880 | 1.1711720 | 0.0001290 | C | 2.5268900 | 1.2161630 | 0.0000020 |
| C | -2.5422870 | 1.1711720 | 0.0000250 | C | -2.5268900 | 1.2161640 | 0.0000010 |
| C | 1.6507850 | -1.5025410 | -0.0000660 | C | 1.6683660 | -1.4832530 | -0.0000020 |
| C | -1.6507840 | -1.5025410 | -0.0000134 | C | -1.6683660 | -1.4832550 | -0.0000010 |
| C | 3.4581000 | 0.1155390 | 0.0000760 | C | 3.4548410 | 0.1761510 | 0.0000030 |
| C | -3.4581000 | 0.1155390 | -0.0000660 | C | -3.4548390 | 0.1761520 | 0.0000030 |
| C | 3.0140280 | -1.2095630 | -0.0000200 | C | 3.0326180 | -1.1583530 | 0.0000010 |
| C | -3.0140280 | -1.2095630 | -0.0001450 | C | -3.0326160 | -1.1583540 | 0.0000020 |
| H | -0.0000170 | 2.4833580 | 0.8799330 | H | -0.0000080 | 2.8256390 | -0.0000130 |
| H | 0.0000180 | 2.4834930 | -0.8795800 | H | 2.8588050 | 2.2489160 | 0.0000020 |
| H | 2.894165 | 2.1978250 | 0.0002030 | H | -2.8588060 | 2.2489170 | 0.0000010 |
| H | -2.8941660 | 2.1978250 | 0.0000850 | H | 1.3598720 | -2.5232600 | -0.0000030 |
| H | 1.3145150 | -2.5336850 | -0.0001400 | H | -1.3598700 | -2.5232610 | -0.0000020 |
| H | -1.3145150 | -2.5336850 | -0.0001950 | H | 4.5153400 | 0.4009830 | 0.0000050 |
| H | 4.5218050 | 0.3255980 | 0.0001090 | H | -4.5153400 | 0.4009780 | 0.0000040 |
| H | -4.5218050 | 0.3255980 | -0.0000770 | H | 3.7708070 | -1.9523650 | 0.0000020 |
| H | 3.7375510 | -2.0172215 | -0.0000590 | H | -3.7708110 | -1.9523620 | 0.0000030 |
| H | -3.7375510 | -2.0172150 | -0.0002150 | | | | |

| | $C_{13}H_8$ (triplet)[a] | | | | $C_{13}H_8$ (singlet)[a] | | |
|---|---|---|---|---|---|---|---|
| | *x* | *y* | *z* | | *x* | *y* | *z* |
| C | 0.0000000 | 0.0000000 | 1.7418490 | C | 0.0000000 | 0.0000000 | 1.8443380 |
| C | 0.0000000 | 1.1783000 | 0.9488630 | C | 0.0000000 | 1.1397790 | 0.9150290 |
| C | 0.0000000 | -1.1783000 | 0.9488630 | C | 0.0000000 | -1.1397790 | 0.9150290 |
| C | 0.0000000 | 0.7351170 | -0.4192180 | C | 0.0000000 | 0.7419980 | -0.4528240 |
| C | 0.0000000 | -0.7351170 | -0.4192180 | C | 0.0000000 | -0.7419980 | -0.4528240 |
| C | 0.0000000 | 2.5446790 | 1.2518510 | C | 0.0000000 | 2.4905970 | 1.2470160 |
| C | 0.0000000 | -2.5446790 | 1.2518510 | C | 0.0000000 | -2.4905970 | 1.2470160 |
| C | 0.0000000 | 1.6675730 | -1.4448510 | C | 0.0000000 | 1.6768500 | -1.4652530 |
| C | 0.0000000 | -1.6675730 | -1.4448510 | C | 0.0000000 | -1.6768500 | -1.4652530 |
| C | 0.0000000 | 3.4632090 | 0.2042110 | C | 0.0000000 | 3.4480850 | 0.2199920 |
| C | 0.0000000 | -3.4632090 | 0.2042110 | C | 0.0000000 | -3.4480850 | 0.2199920 |
| C | 0.0000000 | 3.0324920 | -1.1277110 | C | 0.0000000 | 3.0431920 | -1.1101750 |
| C | 0.0000000 | -3.0324920 | -1.1277110 | C | 0.0000000 | -3.0431920 | -1.1101750 |
| H | 0.0000000 | 2.8788350 | 2.2828210 | H | 0.0000000 | 2.7841560 | 2.2907780 |
| H | 0.0000000 | -2.8788350 | 2.2828210 | H | 0.0000000 | -2.7841560 | 2.2907780 |
| H | 0.0000000 | 1.3523730 | -2.4829890 | H | 0.0000000 | 1.3906830 | -2.5117140 |
| H | 0.0000000 | -1.3523730 | -2.4829890 | H | 0.0000000 | -1.3906830 | -2.5117140 |
| H | 0.0000000 | 4.5250500 | 0.4219530 | H | 0.0000000 | 4.5048860 | 0.4602190 |
| H | 0.0000000 | -4.5250500 | 0.4219530 | H | 0.0000000 | -4.5048860 | 0.4602190 |
| H | 0.0000000 | 3.7656070 | -1.9262090 | H | 0.0000000 | 3.7919750 | -1.8950020 |
| H | 0.0000000 | -3.7656070 | -1.9262090 | H | 0.0000000 | -3.7919750 | -1.8950020 |

[a] Optimized geometries were predicted with the B3LYP/6-311++G(d,p) method. The unit is in Å.

**Table S2** Cartesian coordinates of optimized geometries of six isomers of monohydrofluorenyl (1*H*-, 2*H*-, 3*H*-, 4*H*-, 4a*H*, and 9a*H*-$C_{13}H_{11}$) radicals

| | 1*H*-$C_{13}H_{11}$[a] | | | | 2*H*-$C_{13}H_{11}$[a] | | |
|---|---|---|---|---|---|---|---|
| | *x* | *y* | *z* | | *x* | *y* | *z* |
| C | -0.0231920 | 1.8091910 | 0.0000110 | C | -0.0528040 | 1.8444680 | 0.0000940 |
| C | 1.1355550 | 0.8486060 | 0.0000070 | C | 1.1441720 | 0.9074360 | 0.0000250 |
| C | -1.2220430 | 0.8848280 | 0.0000010 | C | -1.2310220 | 0.8916120 | 0.0000650 |
| C | 0.6921580 | -0.4568610 | -0.0000050 | C | 0.6727800 | -0.4498090 | -0.0000340 |
| C | -0.7811270 | -0.4525530 | -0.0000070 | C | -0.7686440 | -0.4488550 | -0.0000100 |
| C | 2.5833570 | 1.2110280 | 0.0000030 | C | 2.4655340 | 1.2063150 | 0.0000180 |
| C | -2.5774440 | 1.1813520 | 0.0000020 | C | -2.5875180 | 1.1696580 | 0.0001010 |
| C | 1.5931450 | -1.5481720 | -0.0000070 | C | 1.6056300 | -1.5247660 | -0.0001040 |
| C | -1.7016630 | -1.4990630 | -0.0000150 | C | -1.6917530 | -1.5065350 | -0.0000470 |
| C | 3.4764670 | 0.0007410 | 0.0000210 | C | 3.5070990 | 0.1198580 | -0.0000520 |
| C | -3.5005410 | 0.1301450 | -0.0000060 | C | -3.5033090 | 0.1091890 | 0.0000640 |
| C | 2.9849800 | -1.2737770 | 0.0000100 | C | 2.9407480 | -1.2732170 | -0.0001130 |
| C | -3.0646180 | -1.1964980 | -0.0000150 | C | -3.0529450 | -1.2152950 | -0.0000090 |
| H | -0.0116360 | 2.4696030 | 0.8783690 | H | -0.0570450 | 2.4968310 | 0.8801690 |
| H | -0.0116300 | 2.4696170 | -0.8783370 | H | -0.0570750 | 2.4969230 | -0.8799120 |
| H | 2.8193310 | 1.8551510 | 0.8670560 | H | 2.8082380 | 2.2367550 | 0.0000640 |
| H | -2.9229240 | 2.2102440 | 0.0000090 | H | -2.9437880 | 2.1949480 | 0.0001590 |
| H | 1.2362770 | -2.5705290 | -0.0000180 | H | 1.2494480 | -2.5501360 | -0.0001500 |
| H | -1.3719900 | -2.5323200 | -0.0000220 | H | -1.3543140 | -2.5371550 | -0.0001040 |
| H | 4.5480840 | 0.1689490 | 0.0000370 | H | 4.1804940 | 0.2434250 | 0.8660080 |
| H | -4.5629470 | 0.3467930 | -0.0000050 | H | -4.5675130 | 0.3157740 | 0.0000930 |
| H | 3.6810120 | -2.1066460 | 0.0000180 | H | 3.6478720 | -2.0963700 | -0.0001670 |
| H | -3.7931040 | -1.9997790 | -0.0000210 | H | -3.7746100 | -2.0248630 | -0.0000370 |
| H | 2.8193270 | 1.8551140 | -0.8670820 | H | 4.1804670 | 0.2435120 | -0.8661210 |

| | $3H$-$C_{13}H_{11}$[a] | | | | $4H$-$C_{13}H_{11}$[a] | | |
|---|---|---|---|---|---|---|---|
| | *x* | *y* | *z* | | *x* | *y* | *z* |
| C | -0.0649620 | 1.8457470 | 0.0000060 | C | 0.0506610 | 1.8564530 | 0.0002100 |
| C | 1.1258350 | 0.9208290 | -0.0000010 | C | -1.1400790 | 0.9188730 | 0.0000780 |
| C | -1.2348020 | 0.8818610 | 0.0000010 | C | 1.2273460 | 0.9061910 | 0.0001000 |
| C | 0.6988740 | -0.4435160 | 0.0000020 | C | -0.6992450 | -0.3986250 | -0.0000520 |
| C | -0.7750410 | -0.4477110 | 0.0000030 | C | 0.7476170 | -0.4265070 | -0.0000400 |
| C | 2.5033780 | 1.2340620 | -0.0000040 | C | -2.5015360 | 1.2413030 | 0.0001080 |
| C | -2.5971510 | 1.1558720 | -0.0000030 | C | 2.5869710 | 1.1658510 | 0.0001260 |
| C | 1.5897030 | -1.4785160 | 0.0000030 | C | -1.6422170 | -1.5603040 | -0.0002140 |
| C | -1.6820120 | -1.5075840 | 0.0000020 | C | 1.6489120 | -1.4984690 | -0.0001470 |
| C | 3.4392160 | 0.2398070 | -0.0000030 | C | -3.4568150 | 0.1801770 | 0.0000360 |
| C | -3.5037140 | 0.0929630 | -0.0000040 | C | 3.4854460 | 0.0897790 | 0.0000160 |
| C | 3.0707950 | -1.2184150 | -0.0000020 | C | -3.0841200 | -1.1286410 | -0.0000900 |
| C | -3.0479430 | -1.2283100 | -0.0000010 | C | 3.0168390 | -1.2265800 | -0.0001170 |
| H | -0.0809440 | 2.5044870 | 0.8787780 | H | 0.0519540 | 2.5101530 | -0.8795950 |
| H | -0.0809460 | 2.5045130 | -0.8787440 | H | 0.0519330 | 2.5098630 | 0.8802360 |
| H | 2.8222960 | 2.2724840 | -0.0000060 | H | -2.8339250 | 2.2727920 | 0.0002010 |
| H | -2.9575160 | 2.1796040 | -0.0000050 | H | 2.9594780 | 2.1852980 | 0.00022900 |
| H | 1.2538060 | -2.5102090 | 0.0000070 | H | -1.4456030 | -2.2135270 | -0.8683000 |
| H | -1.3353180 | -2.5353020 | 0.0000030 | H | 1.2948060 | -2.5236860 | -0.0002530 |
| H | 4.4954890 | 0.4875010 | -0.0000060 | H | -4.5129270 | 0.4303330 | 0.0000980 |
| H | -4.5692910 | 0.2937560 | -0.0000080 | H | 4.5527260 | 0.2801550 | 0.0000330 |
| H | 3.5416810 | -1.7183580 | 0.8654780 | H | -3.8384790 | -1.9082040 | -0.0001240 |
| H | -3.7639920 | -2.0426460 | -0.0000020 | H | 3.7268860 | -2.0463220 | -0.0002000 |
| H | 3.5416740 | -1.7183570 | -0.8654860 | H | -1.4455270 | -2.2138660 | 0.8675930 |

| | 4a*H*-$C_{13}H_{11}$[a] | | | | 9a*H*-$C_{13}H_{11}$[a] | | |
|---|---|---|---|---|---|---|---|
| | *x* | *y* | *z* | | *x* | *y* | *z* |
| C | 0.0117340 | 1.8621130 | 0.2793060 | C | 0.0304110 | -1.8045170 | -0.0866240 |
| C | -1.1861960 | 0.9434160 | 0.2558570 | C | 1.1784900 | -0.9053870 | 0.4528180 |
| C | 1.1626610 | 0.8892740 | 0.0811710 | C | -1.1681160 | -0.8786460 | -0.0350290 |
| C | -0.7426530 | -0.4539570 | 0.6359110 | C | 0.6953110 | 0.5059170 | 0.1847800 |
| C | 0.7343400 | -0.4339900 | 0.2538090 | C | -0.7491000 | 0.4655210 | 0.0944420 |
| C | -2.4474100 | 1.1916530 | -0.1945210 | C | 2.5876430 | -1.1423680 | 0.0049810 |
| C | 2.4912660 | 1.1628080 | -0.2256150 | C | -2.5171610 | -1.1869070 | -0.1464090 |
| C | -1.6529010 | -1.5290070 | 0.1193300 | C | 1.5864590 | 1.5372900 | -0.0167120 |
| C | 1.6276460 | -1.4900880 | 0.1180960 | C | -1.6965310 | 1.4989290 | 0.1002550 |
| C | -3.3572130 | 0.1247760 | -0.4128560 | C | 3.4216570 | -0.0870050 | -0.2094230 |
| C | 3.3894790 | 0.1021550 | -0.3679250 | C | -3.4578530 | -0.1525200 | -0.1291200 |
| C | -2.9109280 | -1.2191540 | -0.3113570 | C | 2.9572640 | 1.2619090 | -0.1531000 |
| C | 2.9604500 | -1.2148050 | -0.1987380 | C | -3.0463610 | 1.1797000 | -0.0091510 |
| H | -0.0363670 | 2.6394060 | -0.4888640 | H | 0.2368310 | -2.0973370 | -1.1237670 |
| H | 0.1112450 | 2.3767660 | 1.2476330 | H | -0.1048300 | -2.7202740 | 0.4939190 |
| H | -2.7432370 | 2.2030650 | -0.4586140 | H | 2.9547600 | -2.1619890 | -0.0557270 |
| H | 2.8292620 | 2.1850520 | -0.3624660 | H | -2.8429330 | -2.2169520 | -0.2496330 |
| H | -1.3246850 | -2.5614010 | 0.1739390 | H | 1.2297960 | 2.5537790 | -0.1517330 |
| H | 1.3017790 | -2.5165700 | 0.2493240 | H | -1.3860580 | 2.5330390 | 0.2022210 |
| H | -4.3627100 | 0.3338930 | -0.7567990 | H | 4.4628360 | -0.2667090 | -0.4575250 |
| H | 4.4255230 | 0.3032650 | -0.6168420 | H | -4.5141960 | -0.3833090 | -0.2089990 |
| H | -3.5832550 | -2.0161440 | -0.6127170 | H | 3.6564560 | 2.0725270 | -0.3196880 |
| H | 3.6654530 | -2.0302620 | -0.3164790 | H | -3.7887980 | 1.9699430 | 0.0052040 |
| H | -0.7646600 | -0.5282320 | 1.7470840 | H | 1.1634680 | -1.0342250 | 1.5554850 |

[a] Optimized geometries were predicted with the B3LYP/6-311++G(d,p) method. The unit is in Å.

**Table S3** Cartesian coordinates of the transition-state structures TS9 and TS9′

| TS9[a] | | | | TS9′[a] | | | |
|---|---|---|---|---|---|---|---|
| | *x* | *y* | *z* | | *x* | *y* | *z* |
| C | 0.0000100 | 1.7700760 | -0.0713360 | C | -0.0000040 | 1.7358230 | 0.3018180 |
| C | 1.1805470 | 0.8465830 | -0.0631100 | C | -1.1550500 | 0.8585530 | 0.0665200 |
| C | -1.1805430 | 0.8465610 | -0.0634100 | C | 1.1550490 | 0.8585620 | 0.0665100 |
| C | 0.7348310 | -0.4902160 | 0.0163310 | C | -0.7386180 | -0.4993120 | 0.0015700 |
| C | -0.7348230 | -0.4902240 | 0.0161870 | C | 0.7386200 | -0.4993070 | 0.0015600 |
| C | 2.5389090 | 1.1376000 | -0.0988490 | C | -2.5123890 | 1.1744780 | 0.0629880 |
| C | -2.5389040 | 1.1375820 | -0.0990200 | C | 2.5123920 | 1.1744770 | 0.0629870 |
| C | 1.6541040 | -1.5365790 | 0.0603450 | C | -1.6688010 | -1.5249090 | -0.0237070 |
| C | -1.6540960 | -1.5365790 | 0.0604600 | C | 1.6687980 | -1.5249070 | -0.0237060 |
| C | 3.4571260 | 0.0852350 | -0.0566410 | C | -3.4502550 | 0.1409880 | -0.0170190 |
| C | -3.4571200 | 0.0852210 | -0.0566490 | C | 3.4502550 | 0.1409850 | -0.0170160 |
| C | 3.0171150 | -1.2386580 | 0.0241110 | C | -3.0316190 | -1.1903170 | -0.0484740 |
| C | -3.0171080 | -1.2386620 | 0.0242450 | C | 3.0316190 | -1.1903210 | -0.0484690 |
| H | -0.0001860 | 2.4111790 | 0.9340050 | H | -0.0000760 | 2.9832660 | -0.7292790 |
| H | 0.0001290 | 2.5373530 | -0.8490840 | H | -2.8301890 | 2.2097590 | 0.1192450 |
| H | 2.8863030 | 2.1638280 | -0.1567860 | H | 2.8301970 | 2.2097560 | 0.1192470 |
| H | -2.8863000 | 2.1638060 | -0.1570100 | H | -1.3650850 | -2.5662360 | -0.0287440 |
| H | 1.3228260 | -2.5677140 | 0.1173850 | H | 1.3650760 | -2.5662320 | -0.0287330 |
| H | -1.3228180 | -2.5677020 | 0.1176990 | H | -4.5093400 | 0.3705970 | -0.0359090 |
| H | 4.5199800 | 0.2969110 | -0.0858480 | H | 4.5093410 | 0.3705930 | -0.0359070 |
| H | -4.5199760 | 0.2968960 | -0.0857950 | H | -3.7726150 | -1.9813790 | -0.0840700 |
| H | 3.7433890 | -2.0430960 | 0.0567550 | H | 3.7726130 | -1.9813840 | -0.0840590 |
| H | -3.7433820 | -2.0430920 | 0.0570700 | H | 0.0000900 | 3.0224980 | -1.5251690 |
| H | -0.0002570 | 3.0839770 | 1.8956250 | | | | |

[a] Optimized geometries were predicted with the B3LYP/6-311++G(d,p) method. The unit is in Å.

**Table S4** Cartesian coordinates of the transition-state structures TS1, TS2, TS3, TS4, TS4a and TS9a

| TS1[a] | | | | TS2[a] | | | |
|---|---|---|---|---|---|---|---|
| | *x* | *y* | *z* | | *x* | *y* | *z* |
| C | 0.0082590 | 1.8094210 | -0.0562000 | C | 0.0424380 | 1.8303940 | -0.0285420 |
| C | -1.1573500 | 0.8495790 | -0.0526980 | C | -1.1406680 | 0.8850960 | -0.0372160 |
| C | 1.2045460 | 0.8815960 | -0.0282220 | C | 1.2259320 | 0.8865920 | -0.0067480 |
| C | -0.6966680 | -0.4756830 | -0.0081410 | C | -0.6871300 | -0.4523170 | -0.0237930 |
| C | 0.7728620 | -0.4586410 | 0.0026240 | C | 0.7778470 | -0.4497170 | -0.0021670 |
| C | -2.5315440 | 1.1280360 | -0.0306710 | C | -2.4931430 | 1.1706570 | -0.0636470 |
| C | 2.5595840 | 1.1850050 | -0.0295290 | C | 2.5842920 | 1.1736770 | 0.0076770 |
| C | -1.6010980 | -1.5404350 | 0.0070680 | C | -1.6019440 | -1.5100970 | -0.0554020 |
| C | 1.7010720 | -1.4994470 | 0.0348570 | C | 1.6954750 | -1.5020150 | 0.0184170 |
| C | -3.4358270 | 0.0444930 | -0.0770660 | C | -3.4198340 | 0.1069990 | -0.0294430 |
| C | 3.4879410 | 0.1408400 | 0.0030760 | C | 3.5004860 | 0.1184410 | 0.0276830 |
| C | -2.9711560 | -1.2661870 | -0.0364810 | C | -2.9603560 | -1.2267530 | -0.0782590 |
| C | 3.0605950 | -1.1892910 | 0.0352310 | C | 3.0576510 | -1.2074780 | 0.0331840 |
| H | 0.0088010 | 2.4565770 | -0.9410960 | H | 0.0530950 | 2.4789540 | -0.9120300 |
| H | -0.0179810 | 2.4706730 | 0.8188300 | H | 0.0295260 | 2.4888520 | 0.8475290 |
| H | -2.8909900 | 2.1374810 | -0.1959950 | H | -2.8490840 | 2.1952660 | -0.0802100 |
| H | 2.8988310 | 2.2155250 | -0.0536960 | H | 2.9356770 | 2.2004120 | 0.0039360 |
| H | -1.2521560 | -2.5666140 | 0.0382550 | H | -1.2600490 | -2.5391480 | -0.0728620 |
| H | 1.3775770 | -2.5343590 | 0.0591470 | H | 1.3600600 | -2.5333410 | 0.0238980 |
| H | -4.5009830 | 0.2406990 | -0.1150180 | H | -4.4724810 | 0.3120140 | -0.1808030 |
| H | 4.5489410 | 0.3640330 | 0.0039540 | H | 4.5639270 | 0.3292510 | 0.0397530 |
| H | -3.6811110 | -2.0856440 | -0.0475740 | H | -3.6821420 | -2.0348850 | -0.1059080 |
| H | 3.7941280 | -1.9873880 | 0.0605550 | H | 3.7820540 | -2.0140920 | 0.0496300 |
| H | -2.6923430 | 1.6333020 | 1.7895580 | H | -3.9468620 | 0.1758370 | 1.8166070 |

| TS3[a] | | | | TS4[a] | | | |
|---|---|---|---|---|---|---|---|
| | *x* | *y* | *z* | | *x* | *y* | *z* |
| C | 0.0632160 | 1.8441560 | 0.0309080 | C | 0.0354350 | 1.8522900 | 0.0365420 |
| C | -1.1318640 | 0.9175630 | -0.0059100 | C | -1.1554090 | 0.9176740 | 0.0107730 |
| C | 1.2335080 | 0.8833940 | 0.0178220 | C | 1.2103600 | 0.8981880 | 0.0079170 |
| C | -0.7015050 | -0.4266560 | -0.0293530 | C | -0.7161110 | -0.4169350 | -0.0261630 |
| C | 0.7679780 | -0.4449430 | -0.0179550 | C | 0.7480370 | -0.4328000 | -0.0258020 |
| C | -2.4886320 | 1.2267190 | -0.0455590 | C | -2.5122120 | 1.2168390 | 0.0038400 |
| C | 2.5961000 | 1.1517750 | 0.0366660 | C | 2.5716930 | 1.1702350 | 0.0152480 |
| C | -1.6255800 | -1.4634440 | -0.0715290 | C | -1.6466120 | -1.4725530 | -0.0266910 |
| C | 1.6697450 | -1.5093970 | -0.0340400 | C | 1.6528830 | -1.4953880 | -0.0469810 |
| C | -3.4199000 | 0.1941760 | -0.0825070 | C | -3.4412690 | 0.1692840 | -0.0563650 |
| C | 3.4975680 | 0.0842890 | 0.0189990 | C | 3.4759380 | 0.1046030 | -0.0093960 |
| C | -3.0004020 | -1.1543030 | -0.0336590 | C | -3.0171440 | -1.1547290 | -0.0924580 |
| C | 3.0364630 | -1.2346220 | -0.0160530 | C | 3.0186310 | -1.2158260 | -0.0390010 |
| H | 0.0799590 | 2.5224210 | -0.8303800 | H | 0.0386500 | 2.5329020 | -0.8225510 |
| H | 0.0629530 | 2.4745030 | 0.9280240 | H | 0.0412140 | 2.4781930 | 0.9363910 |
| H | -2.8212420 | 2.2596180 | -0.0583620 | H | -2.8543380 | 2.2462290 | 0.0292910 |
| H | 2.9613510 | 2.1732870 | 0.0648010 | H | 2.9347220 | 2.1925930 | 0.0411560 |
| H | -1.3063540 | -2.4991450 | -0.0975150 | H | -1.3213950 | -2.4947200 | -0.1795110 |
| H | 1.3197940 | -2.5356070 | -0.0591830 | H | 1.3055770 | -2.5224900 | -0.0664140 |
| H | -4.4794970 | 0.4193990 | -0.1152800 | H | -4.5015750 | 0.3937760 | -0.0845820 |
| H | 4.5638760 | 0.2800670 | 0.0330870 | H | 4.5417710 | 0.3033640 | -0.0035600 |
| H | -3.7260270 | -1.9400890 | -0.2057050 | H | -3.7467930 | -1.9545630 | -0.1437040 |
| H | 3.7493980 | -2.0514590 | -0.0283950 | H | 3.7342280 | -2.0302610 | -0.0546510 |
| H | -3.3843790 | -1.5152380 | 1.7619280 | H | -1.5173780 | -1.9903160 | 1.8393560 |

| TS4a[a] | | | | TS9a[a] | | | |
|---|---|---|---|---|---|---|---|
| | *x* | *y* | *z* | | *x* | *y* | *z* |
| C | 0.0103660 | 1.8359950 | 0.0734950 | C | 0.0076330 | 1.8214650 | -0.0656770 |
| C | -1.1765180 | 0.9007810 | 0.0559790 | C | -1.1744320 | 0.8763890 | 0.0975010 |
| C | 1.1897930 | 0.8874760 | 0.0130370 | C | 1.1912440 | 0.8789460 | -0.0311620 |
| C | -0.7303090 | -0.4494180 | 0.1761930 | C | -0.7141490 | -0.4694940 | 0.0301400 |
| C | 0.7483460 | -0.4453660 | 0.0698830 | C | 0.7489600 | -0.4583530 | 0.0079480 |
| C | -2.5250590 | 1.1840250 | -0.0609580 | C | -2.5460350 | 1.1508090 | -0.0446230 |
| C | 2.5461180 | 1.1738000 | -0.0808460 | C | 2.5490000 | 1.1705920 | -0.0487560 |
| C | -1.6534040 | -1.5045760 | -0.0164070 | C | -1.6256230 | -1.5212210 | -0.0083340 |
| C | 1.6594270 | -1.4979870 | 0.0306930 | C | 1.6707140 | -1.5072590 | 0.0221440 |
| C | -3.4426390 | 0.1283370 | -0.1324040 | C | -3.4450290 | 0.0918250 | -0.0855760 |
| C | 3.4607080 | 0.1185960 | -0.1249140 | C | 3.4689530 | 0.1191330 | -0.0323370 |
| C | -3.0019350 | -1.2021990 | -0.1326290 | C | -2.9900940 | -1.2338220 | -0.0484010 |
| C | 3.0194890 | -1.2060140 | -0.0712700 | C | 3.0315250 | -1.2083330 | 0.0012720 |
| H | -0.0057970 | 2.5407300 | -0.7646930 | H | -0.0544810 | 2.3343540 | -1.0336190 |
| H | 0.0316980 | 2.4368500 | 0.9926330 | H | 0.0560240 | 2.5928610 | 0.7065720 |
| H | -2.8727340 | 2.2101100 | -0.1244500 | H | -2.8999990 | 2.1756290 | -0.0760050 |
| H | 2.8955270 | 2.2002930 | -0.1241840 | H | 2.8962070 | 2.1983220 | -0.0759270 |
| H | -1.3157130 | -2.5345650 | -0.0243320 | H | -1.2857660 | -2.5508760 | -0.0293490 |
| H | 1.3241980 | -2.5281500 | 0.0800750 | H | 1.3389360 | -2.5392920 | 0.0535170 |
| H | -4.5011500 | 0.3419860 | -0.2268490 | H | -4.5086220 | 0.2904370 | -0.1540670 |
| H | 4.5214370 | 0.3286790 | -0.2039570 | H | 4.5316200 | 0.3338560 | -0.0452050 |
| H | -3.7246640 | -2.0034110 | -0.2393390 | H | -3.7083590 | -2.0453470 | -0.0799450 |
| H | 3.7416490 | -2.0139670 | -0.1073070 | H | 3.7591020 | -2.0121170 | 0.0148700 |
| H | -0.7207460 | -0.5192550 | 1.9432840 | H | -1.1606640 | 0.9581010 | 1.9543170 |

[a] Optimized geometries were predicted with the B3LYP/6-311++G(d,p) method. The unit is in Å.

**Table S5** Cartesian coordinates of the transition-state structures in hydrogen-atom transfer 1 → 2, 2 → 3, 3 → 4, 4 → 4a, and 4a → 9a

| | 1→2[a] | | | | 2→3[a] | | |
|---|---|---|---|---|---|---|---|
| | *x* | *y* | *z* | | *x* | *y* | *z* |
| C | -0.0490550 | -1.8309390 | -0.0263600 | C | 0.0468160 | 1.8500400 | -0.0031700 |
| C | 1.1269200 | -0.8834350 | -0.0036550 | C | -1.1566040 | 0.9281690 | -0.0028590 |
| C | -1.2366450 | -0.8922200 | -0.0090710 | C | 1.2166580 | 0.8811230 | -0.0004070 |
| C | 0.6838370 | 0.4266300 | 0.0130470 | C | -0.6853780 | -0.4762160 | -0.0064140 |
| C | -0.7680740 | 0.4431940 | 0.0159320 | C | 0.7646080 | -0.4586720 | 0.0002890 |
| C | 2.5090080 | -1.2166370 | 0.0173640 | C | -2.4791850 | 1.2255370 | -0.0235930 |
| C | -2.5913500 | -1.1686790 | -0.0232890 | C | 2.5750940 | 1.1664980 | 0.0005680 |
| C | 1.6304350 | 1.5349170 | -0.0186950 | C | -1.5849330 | -1.5083840 | -0.0487220 |
| C | -1.6805630 | 1.5046690 | 0.0290800 | C | 1.6947980 | -1.5081800 | 0.0065960 |
| C | 3.4941780 | -0.0594590 | -0.0172860 | C | -3.4710450 | 0.1827870 | -0.0003580 |
| C | -3.5041380 | -0.1017100 | -0.0086050 | C | 3.4975670 | 0.1158040 | 0.0041010 |
| C | 2.9703050 | 1.2710920 | -0.0581970 | C | -2.9890900 | -1.2531980 | -0.0120180 |
| C | -3.0469240 | 1.2167880 | 0.0171840 | C | 3.0538650 | -1.2118570 | 0.0077660 |
| H | -0.0393600 | -2.4673730 | -0.9196260 | H | 0.0644730 | 2.5059650 | -0.8830670 |
| H | -0.0377150 | -2.5040050 | 0.8391660 | H | 0.0630520 | 2.5081670 | 0.8750680 |
| H | 2.8745300 | -2.2189050 | -0.1616930 | H | -2.8198540 | 2.2558280 | -0.0653890 |
| H | -2.9512210 | -2.1925510 | -0.0450650 | H | 2.9233240 | 2.1946990 | -0.0006780 |
| H | 1.2722030 | 2.5565460 | -0.0404670 | H | -1.2509830 | -2.5392000 | -0.1094240 |
| H | -1.3394440 | 2.5338430 | 0.0478010 | H | 1.3637880 | -2.5412230 | 0.0122610 |
| H | 4.5357510 | -0.2729510 | -0.2103410 | H | -4.5174810 | 0.3768060 | -0.1871710 |
| H | -4.5691650 | -0.3034110 | -0.0175450 | H | 4.5604290 | 0.3292220 | 0.0053710 |
| H | 3.6794000 | 2.0893070 | -0.1282010 | H | -3.7072420 | -2.0322340 | -0.2305430 |
| H | -3.7643130 | 2.0303140 | 0.0276600 | H | 3.7789150 | -2.0184610 | 0.0127390 |
| H | 3.1117240 | -0.7160740 | 1.0436200 | H | -3.3574500 | -0.6402870 | 1.0401620 |

|  | 3→4[a] |  |  |  | 4→4a[a] |  |  |
|---|---|---|---|---|---|---|---|
|  | *x* | *y* | *z* |  | *x* | *y* | *z* |
| C | 0.0492420 | 1.8333510 | 0.0332800 | C | 0.0401490 | 1.8530300 | 0.0823740 |
| C | -1.1234750 | 0.8882310 | 0.0302370 | C | -1.1695880 | 0.9366830 | 0.0720860 |
| C | 1.2340160 | 0.8951210 | 0.0104090 | C | 1.2136330 | 0.8894070 | 0.0272270 |
| C | -0.6898050 | -0.4186010 | 0.0235400 | C | -0.6909810 | -0.4406940 | 0.1601480 |
| C | 0.7714480 | -0.4378600 | 0.0052030 | C | 0.7546850 | -0.4502680 | 0.0653900 |
| C | -2.5299340 | 1.2240670 | -0.0212700 | C | -2.4859840 | 1.2262080 | -0.0578480 |
| C | 2.5927230 | 1.1685920 | -0.0034300 | C | 2.5664780 | 1.1653570 | -0.0546440 |
| C | -1.6074340 | -1.5250910 | 0.0261850 | C | -1.7031510 | -1.5465520 | 0.0518330 |
| C | 1.6750270 | -1.5023540 | -0.0119800 | C | 1.6714220 | -1.5092580 | 0.0073590 |
| C | -3.4555100 | 0.2156380 | -0.0785420 | C | -3.4651790 | 0.1461630 | -0.1365310 |
| C | 3.4987900 | 0.1000160 | -0.0242660 | C | 3.4849030 | 0.1041240 | -0.1006940 |
| C | -3.0868480 | -1.1656880 | -0.0251450 | C | -3.0704460 | -1.1635210 | -0.1128350 |
| C | 3.0421980 | -1.2195110 | -0.0282750 | C | 3.0332720 | -1.2166420 | -0.0715490 |
| H | 0.0370990 | 2.5027350 | -0.8373900 | H | 0.0297940 | 2.5492990 | -0.7622670 |
| H | 0.0568560 | 2.4813310 | 0.9204550 | H | 0.0640950 | 2.4628560 | 0.9941650 |
| H | -2.8432110 | 2.2609890 | -0.0445460 | H | -2.8242980 | 2.2536140 | -0.1378070 |
| H | 2.9555760 | 2.1913520 | 0.0001550 | H | 2.9203010 | 2.1910010 | -0.0900220 |
| H | -1.3100600 | -2.5449150 | -0.1715840 | H | -1.3687180 | -2.5698820 | -0.0439480 |
| H | 1.3278120 | -2.5296850 | -0.0113390 | H | 1.3353320 | -2.5404340 | 0.0209350 |
| H | -4.5101640 | 0.4537310 | -0.1686440 | H | -4.5140600 | 0.3928280 | -0.2438260 |
| H | 4.5645020 | 0.2992160 | -0.0368610 | H | 4.5466710 | 0.3112780 | -0.1665080 |
| H | -3.7966920 | -1.9465780 | -0.2615350 | H | -3.8075190 | -1.9521520 | -0.2183480 |
| H | 3.7587590 | -2.0333710 | -0.0427630 | H | 3.7512230 | -2.0284590 | -0.1163500 |
| H | -2.4630980 | -1.4702690 | 1.0383820 | H | -1.2080940 | -1.0341760 | 1.1700790 |

| | 4a→9a[a] | | |
|---|---|---|---|
| | *x* | *y* | *z* |
| C | 0.0163580 | 1.8505170 | 0.0124600 |
| C | -1.1879590 | 0.9409310 | 0.1754460 |
| C | 1.1907020 | 0.8798120 | -0.0040420 |
| C | -0.6901990 | -0.5065920 | 0.2001580 |
| C | 0.7538240 | -0.4660570 | 0.0793160 |
| C | -2.5707840 | 1.1765660 | -0.0325980 |
| C | 2.5423660 | 1.1733420 | -0.0878150 |
| C | -1.6713360 | -1.5521760 | -0.0054030 |
| C | 1.6912310 | -1.5077860 | 0.0565150 |
| C | -3.4609300 | 0.1349550 | -0.1287130 |
| C | 3.4766580 | 0.1296060 | -0.1109940 |
| C | -2.9883570 | -1.2420500 | -0.1279180 |
| C | 3.0457040 | -1.1985880 | -0.0440600 |
| H | -0.0493420 | 2.4117880 | -0.9311790 |
| H | 0.1078770 | 2.5989780 | 0.8092410 |
| H | -2.9204540 | 2.2011210 | -0.1180030 |
| H | 2.8794840 | 2.2035880 | -0.1476860 |
| H | -1.3369960 | -2.5809850 | -0.0815390 |
| H | 1.3712540 | -2.5423090 | 0.1164420 |
| H | -4.5185600 | 0.3303550 | -0.2509130 |
| H | 4.5346680 | 0.3524360 | -0.1855080 |
| H | -3.7117660 | -2.0370350 | -0.2697220 |
| H | 3.7759160 | -2.0002510 | -0.0668610 |
| H | -1.0157460 | 0.1874310 | 1.2316160 |

[a] Optimized geometries were predicted with the B3LYP/6-311++G(d,p) method. The unit is in Å.

**Table S6** Comparison of experimental vibrational wavenumbers and intensities of fluorene ($C_{13}H_{10}$) with scaled harmonic and anharmonic vibrational wavenumbers and IR intensities calculated with the B3LYP/6-311++G(d,p) method

| | Sym. | Computations | | | | Experiments | |
|---|---|---|---|---|---|---|---|
| | | Harmonic | | Anharmonic | | *p*-$H_2$ | Gas[a] |
| $\nu_1$ | $a_1$ | 3065[b] | (5)[c] | 3058 | (8)[c] | | |
| $\nu_2$ | $a_1$ | 3054 | (37) | 3056 | (10) | 3051.3[d] | 3053.9 (52)[e] |
| $\nu_3$ | $a_1$ | 3043 | (5) | 3064 | (11) | 3028.8[d] | 3031.3 (6) |
| $\nu_4$ | $a_1$ | 3036 | (8) | 3014 | (2) | 3025.4[d] | 3023.5 (14) |
| $\nu_5$ | $a_1$ | 2907 | (15) | 2906 | (2) | 2909.0[d] | 2909.9 (9) |
| $\nu_6$ | $a_1$ | 1612 | (0) | 1606 | (0) | 1607.1[d] | |
| $\nu_7$ | $a_1$ | 1583 | (1) | 1578 | (0) | | |
| $\nu_8$ | $a_1$ | 1477 | (0) | 1475 | (0) | | |
| $\nu_9$ | $a_1$ | 1447 | (9) | 1448 | (4) | 1451.6 (8)[e] | |
| $\nu_{10}$ | $a_1$ | 1421 | (12) | 1411 | (5) | 1408.6 (5) | 1420.2 (6) |
| $\nu_{11}$ | $a_1$ | 1347 | (0) | 1348 | (0) | 1336.7 (1) | |
| $\nu_{12}$ | $a_1$ | 1294 | (0) | 1295 | (0) | | |
| $\nu_{13}$ | $a_1$ | 1227 | (3) | 1228 | (4) | 1234.4 (1) | 1231.4 (2) |
| $\nu_{14}$ | $a_1$ | 1183 | (3) | 1185 | (3) | 1189.5[d] | |
| $\nu_{15}$ | $a_1$ | 1157 | (0) | 1167 | (0) | 1296.0[d] | |
| $\nu_{16}$ | $a_1$ | 1096 | (3) | 1097 | (2) | 1094.2 (2) | 1093.2 (1) |
| $\nu_{17}$ | $a_1$ | 1025 | (1) | 1026 | (1) | 1023.1 (0.4) | |
| $\nu_{18}$ | $a_1$ | 838 | (0) | 844 | (0) | | |
| $\nu_{19}$ | $a_1$ | 742 | (0) | 746 | (3) | 754.2 (0.5) | |
| $\nu_{20}$ | $a_1$ | 635 | (0) | 637 | (0) | | |
| $\nu_{21}$ | $a_1$ | 414 | (0) | 415 | (2) | | |
| $\nu_{22}$ | $a_1$ | 217 | (0) | 212 | (0) | | |
| $\nu_{23}$ | $a_2$ | 1139 | (0) | 1137 | (0) | | |
| $\nu_{24}$ | $a_2$ | 967 | (0) | 998 | (0) | | |
| $\nu_{25}$ | $a_2$ | 934 | (0) | 953 | (0) | | |
| $\nu_{26}$ | $a_2$ | 860 | (0) | 878 | (0) | | |
| $\nu_{27}$ | $a_2$ | 777 | (0) | 792 | (0) | | |
| $\nu_{28}$ | $a_2$ | 725 | (0) | 730 | (0) | | |
| $\nu_{29}$ | $a_2$ | 565 | (0) | 573 | (0) | | |
| $\nu_{30}$ | $a_2$ | 432 | (0) | 430 | (0) | | |
| $\nu_{31}$ | $a_2$ | 273 | (0) | 270 | (0) | | |
| $\nu_{32}$ | $a_2$ | 137 | (0) | 133 | (0) | | |
| $\nu_{33}$ | $b_1$ | 2930 | (7) | 2898 | (10) | 2926.6[d] | 2915.3 (12) |
| $\nu_{34}$ | $b_1$ | 969 | (0) | 998 | (0) | | |
| $\nu_{35}$ | $b_1$ | 955 | (4) | 967 | (4) | 956.5 (3) | 955.0 (2) |
| $\nu_{36}$ | $b_1$ | 913 | (0) | 922 | (0) | | |
| $\nu_{37}$ | $b_1$ | 853 | (1) | 859 | (1) | 856.8 (0.5) | 857.2 (1) |
| $\nu_{38}$ | $b_1$ | 739 | (133) | 746 | (113) | 742.2 (100) | 738.5 (100) |
| $\nu_{39}$ | $b_1$ | 698 | (5) | 702 | (17) | 695.5[d] | 695.4 (6) |
| $\nu_{40}$ | $b_1$ | 472 | (1) | 479 | (1) | | |
| $\nu_{41}$ | $b_1$ | 416 | (6) | 416 | (7) | | |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| $\nu_{42}$ | $b_1$ | 238 | (7) | 245 | (7) | | |
| $\nu_{43}$ | $b_1$ | 99 | (1) | 96 | (1) | | |
| $\nu_{44}$ | $b_2$ | 3064 | (43) | 3058 | (41) | 3074.3[d] | 3075.7 (60) |
| $\nu_{45}$ | $b_2$ | 3053 | (7) | 3054 | (1) | | |
| $\nu_{46}$ | $b_2$ | 3042 | (2) | 3042 | (7) | | |
| $\nu_{47}$ | $b_2$ | 3036 | (2) | 3007 | (0) | | |
| $\nu_{48}$ | $b_2$ | 1613 | (4) | 1609 | (3) | 1615.8[d] | |
| $\nu_{49}$ | $b_2$ | 1587 | (1) | 1581 | (1) | 1582.1 (1) | 1587.9 (3) |
| $\nu_{50}$ | $b_2$ | 1478 | (7) | 1479 | (6) | 1483.2 (6) | 1484.2 (5) |
| $\nu_{51}$ | $b_2$ | 1453 | (19) | 1454 | (18) | 1455.9 (16) | 1459.6 (24) |
| $\nu_{52}$ | $b_2$ | 1318 | (7) | 1313 | (4) | 1313.5 (2) | 1335.9 (5) |
| $\nu_{53}$ | $b_2$ | 1303 | (2) | 1301 | (0) | 1299.9 (5) | 1295.5 (5) |
| $\nu_{54}$ | $b_2$ | 1196 | (4) | 1193 | (4) | 1192.2[d] | 1191.0 (6) |
| $\nu_{55}$ | $b_2$ | 1169 | (3) | 1171 | (1) | 1171.9 (1) | 1170.7 (2) |
| $\nu_{56}$ | $b_2$ | 1153 | (0) | 1158 | (0) | 1151.6 (1) | |
| $\nu_{57}$ | $b_2$ | 1108 | (0) | 1110 | (0) | 1109.0 (0.4) | |
| $\nu_{58}$ | $b_2$ | 1032 | (6) | 1034 | (4) | 1030.0 (1) | 1029.2 (4) |
| $\nu_{59}$ | $b_2$ | 1004 | (5) | 1007 | (5) | 1005.5 (4) | 1005.6 (4) |
| $\nu_{60}$ | $b_2$ | 799 | (0) | 801 | (0) | 801.7 (0.3) | |
| $\nu_{61}$ | $b_2$ | 626 | (8) | 630 | (8) | 622.5 (5) | 626.6 (6) |
| $\nu_{62}$ | $b_2$ | 545 | (0) | 546 | (0) | | |
| $\nu_{63}$ | $b_2$ | 492 | (0) | 493 | (0) | | |
| $\nu_7 + \nu_{49}$ [f] | $b_2$ | | | 3162 | (6) | | |
| $\nu_{48} + \nu_{50}$ | $a_1$ | | | 3098 | (13) | | |
| $\nu_8 + \nu_{48}$ | $b_2$ | | | 3080 | (5) | | |
| $\nu_6 + \nu_8$ | $a_1$ | | | 3080 | (5) | | |
| $\nu_{48} + \nu_{51}$ | $a_1$ | | | 3045 | (11) | | |
| $\nu_6 + \nu_9$ | $a_1$ | | | 3044 | (6) | | |
| $\nu_6 + \nu_{11}$ | $a_1$ | | | 2952 | (19) | | |
| $\nu_{24} + \nu_{34}$ | $b_2$ | | | 2007 | (10) | | |
| $\nu_{60} + \nu_{61}$ | $a_1$ | | | 1431 | (7) | | |

[a] Gas-phase data from Chakraborty et al., *Vib. Spectrosc.* 2013, **68**, 162−169. [b] Harmonic vibrational wavenumbers ($cm^{-1}$) $x$ are scaled by equations $y = 0.9513\, x + 33.4$ for $x > 2000\ cm^{-1}$ and $y = 0.9765\, x + 5.0$ for $x < 2000\ cm^{-1}$. [c] IR intensity in km $mol^{-1}$. [d] Intensity could not be determined due to overlap with other bands. [e] Intensity relative to the most intense line ($\nu_{38}$) [f] Overtone and combination bands with IR intensities >5 km $mol^{-1}$ are listed.

**Table S7** Scaled harmonic and anharmonic vibrational wavenumbers and IR intensities of 9*H*-fluoren-9-yl ($C_{13}H_9$) radical calculated with the B3LYP/6-311++G(d,p) method

| Mode | Sym. | Scaled Harmonic[a] | | Anharmonic | |
|---|---|---|---|---|---|
| | | Wavenumber /cm$^{-1}$ | Intensity /km mol$^{-1}$ | Wavenumber /cm$^{-1}$ | Intensity /km mol$^{-1}$ |
| $\nu_1$ | $a_1$ | 3084 | (8) | 3080 | (8) |
| $\nu_2$ | $a_1$ | 3067 | (3) | 3055 | (0) |
| $\nu_3$ | $a_1$ | 3055 | (44) | 3059 | (51) |
| $\nu_4$ | $a_1$ | 3046 | (1) | 3035 | (1) |
| $\nu_5$ | $a_1$ | 3040 | (4) | 3040 | (8) |
| $\nu_6$ | $a_1$ | 1588 | (8) | 1583 | (3) |
| $\nu_7$ | $a_1$ | 1569 | (0) | 1559 | (0) |
| $\nu_8$ | $a_1$ | 1469 | (5) | 1465 | (2) |
| $\nu_9$ | $a_1$ | 1431 | (2) | 1428 | (0) |
| $\nu_{10}$ | $a_1$ | 1360 | (0) | 1361 | (0) |
| $\nu_{11}$ | $a_1$ | 1293 | (1) | 1292 | (0) |
| $\nu_{12}$ | $a_1$ | 1243 | (10) | 1243 | (9) |
| $\nu_{13}$ | $a_1$ | 1187 | (3) | 1192 | (1) |
| $\nu_{14}$ | $a_1$ | 1155 | (0) | 1161 | (0) |
| $\nu_{15}$ | $a_1$ | 1095 | (1) | 1095 | (0) |
| $\nu_{16}$ | $a_1$ | 1016 | (1) | 1018 | (0) |
| $\nu_{17}$ | $a_1$ | 870 | (0) | 875 | (0) |
| $\nu_{18}$ | $a_1$ | 739 | (0) | 742 | (0) |
| $\nu_{19}$ | $a_1$ | 645 | (1) | 649 | (1) |
| $\nu_{20}$ | $a_1$ | 422 | (0) | 423 | (0) |
| $\nu_{21}$ | $a_1$ | 217 | (0) | 215 | (0) |
| $\nu_{22}$ | $a_2$ | 959 | (0) | 983 | (0) |
| $\nu_{23}$ | $a_2$ | 931 | (0) | 941 | (0) |
| $\nu_{24}$ | $a_2$ | 861 | (0) | 874 | (0) |
| $\nu_{25}$ | $a_2$ | 764 | (0) | 771 | (0) |
| $\nu_{26}$ | $a_2$ | 739 | (0) | 735 | (0) |
| $\nu_{27}$ | $a_2$ | 561 | (0) | 560 | (0) |
| $\nu_{28}$ | $a_2$ | 437 | (0) | 407 | (0) |
| $\nu_{29}$ | $a_2$ | 280 | (0) | 267 | (0) |
| $\nu_{30}$ | $a_2$ | 135 | (0) | 130 | (0) |
| $\nu_{31}$ | $b_1$ | 962 | (0) | 982 | (0) |
| $\nu_{32}$ | $b_1$ | 930 | (4) | 941 | (4) |
| $\nu_{33}$ | $b_1$ | 857 | (1) | 865 | (2) |
| $\nu_{34}$ | $b_1$ | 776 | (59) | 792 | (21) |
| $\nu_{35}$ | $b_1$ | 721 | (83) | 726 | (107) |
| $\nu_{36}$ | $b_1$ | 698 | (8) | 686 | (2) |
| $\nu_{37}$ | $b_1$ | 532 | (6) | 539 | (7) |
| $\nu_{38}$ | $b_1$ | 411 | (8) | 408 | (9) |
| $\nu_{39}$ | $b_1$ | 300 | (3) | 297 | (3) |
| $\nu_{40}$ | $b_1$ | 108 | (2) | 105 | (2) |
| $\nu_{41}$ | $b_2$ | 3066 | (50) | 3055 | (62) |
| $\nu_{42}$ | $b_2$ | 3055 | (4) | 3060 | (1) |

| | | | | | |
|---|---|---|---|---|---|
| $\nu_{43}$ | $b_2$ | 3044 | (1) | 3030 | (0) |
| $\nu_{44}$ | $b_2$ | 3039 | (1) | 3041 | (2) |
| $\nu_{45}$ | $b_2$ | 1576 | (8) | 1570 | (11) |
| $\nu_{46}$ | $b_2$ | 1566 | (31) | 1560 | (23) |
| $\nu_{47}$ | $b_2$ | 1469 | (10) | 1468 | (8) |
| $\nu_{48}$ | $b_2$ | 1437 | (16) | 1438 | (15) |
| $\nu_{49}$ | $b_2$ | 1331 | (3) | 1328 | (1) |
| $\nu_{50}$ | $b_2$ | 1303 | (2) | 1304 | (1) |
| $\nu_{51}$ | $b_2$ | 1212 | (0) | 1214 | (0) |
| $\nu_{52}$ | $b_2$ | 1157 | (3) | 1164 | (1) |
| $\nu_{53}$ | $b_2$ | 1128 | (7) | 1132 | (6) |
| $\nu_{54}$ | $b_2$ | 1089 | (7) | 1092 | (3) |
| $\nu_{55}$ | $b_2$ | 1021 | (4) | 1023 | (3) |
| $\nu_{56}$ | $b_2$ | 987 | (1) | 990 | (0) |
| $\nu_{57}$ | $b_2$ | 838 | (3) | 843 | (2) |
| $\nu_{58}$ | $b_2$ | 619 | (1) | 623 | (1) |
| $\nu_{59}$ | $b_2$ | 537 | (5) | 538 | (3) |
| $\nu_{60}$ | $b_2$ | 492 | (0) | 493 | (0) |
| $\nu_{22} + \nu_{31}$ [b] | $b_2$ | | | 1978 | (14) |
| $\nu_{20} + \nu_{39}$ | $b_1$ | | | 720 | (5) |

[a] Harmonic vibrational wavenumbers ($cm^{-1}$) $x$ are scaled by equations $y = 0.9513\,x + 33.4$ for $x > 2000\ cm^{-1}$ and $y = 0.9765\,x + 5.0$ for $x < 2000\ cm^{-1}$. [b] Overtone and combination bands with IR intensities >5 km $mol^{-1}$ are listed.

**Table S8** Scaled harmonic and anharmonic vibrational wavenumbers σ and IR intensities of fluorene-1-hydryl (1*H*-$C_{13}H_{11}$) and fluorene-2-hydryl (2*H*-$C_{13}H_{11}$) radicals calculated with the B3LYP/6-311++G(d,p) method

| Mode | Sym. | 1*H*-$C_{13}H_{11}$ | | | | 2*H*-$C_{13}H_{11}$ | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | Scaled Harmonic[a] | | Anharmonic | | Scaled Harmonic[a] | | Anharmonic | |
| | | σ /$cm^{-1}$ | Intensity /km $mol^{-1}$ | σ /$cm^{-1}$ | Intensity /km $mol^{-1}$ | σ /$cm^{-1}$ | Intensity /km $mol^{-1}$ | σ /$cm^{-1}$ | Intensity /km $mol^{-1}$ |
| $\nu_1$ | *a*′ | 3069 | (14) | 3072 | (30) | 3064 | (24) | 3063 | (21) |
| $\nu_2$ | *a*′ | 3064 | (24) | 3054 | (34) | 3053 | (32) | 3083 | (5) |
| $\nu_3$ | *a*′ | 3053 | (19) | 3014 | (0) | 3049 | (13) | 3032 | (14) |
| $\nu_4$ | *a*′ | 3050 | (30) | 3029 | (22) | 3041 | (5) | 3007 | (1) |
| $\nu_5$ | *a*′ | 3042 | (5) | 3078 | (1) | 3035 | (8) | 3038 | (20) |
| $\nu_6$ | *a*′ | 3035 | (4) | 2989 | (2) | 3032 | (18) | 3017 | (16) |
| $\nu_7$ | *a*′ | 3032 | (6) | 3046 | (7) | 3031 | (4) | 3043 | (20) |
| $\nu_8$ | *a*′ | 2879 | (32) | 2875 | (8) | 2911 | (15) | 2902 | (13) |
| $\nu_9$ | *a*′ | 2803 | (60) | 2737 | (29) | 2821 | (69) | 2750 | (43) |
| $\nu_{10}$ | *a*′ | 1613 | (3) | 1606 | (0) | 1611 | (4) | 1602 | (2) |
| $\nu_{11}$ | *a*′ | 1587 | (1) | 1582 | (0) | 1584 | (5) | 1578 | (3) |
| $\nu_{12}$ | *a*′ | 1557 | (6) | 1551 | (0) | 1571 | (2) | 1564 | (0) |
| $\nu_{13}$ | *a*′ | 1504 | (7) | 1497 | (2) | 1519 | (1) | 1511 | (1) |
| $\nu_{14}$ | *a*′ | 1467 | (14) | 1465 | (11) | 1460 | (5) | 1460 | (2) |
| $\nu_{15}$ | *a*′ | 1458 | (7) | 1459 | (3) | 1453 | (15) | 1454 | (9) |
| $\nu_{16}$ | *a*′ | 1418 | (12) | 1410 | (5) | 1431 | (6) | 1431 | (2) |
| $\nu_{17}$ | *a*′ | 1408 | (1) | 1391 | (1) | 1424 | (6) | 1411 | (5) |
| $\nu_{18}$ | *a*′ | 1400 | (2) | 1403 | (2) | 1415 | (4) | 1396 | (6) |
| $\nu_{19}$ | *a*′ | 1382 | (4) | 1378 | (3) | 1358 | (2) | 1354 | (0) |
| $\nu_{20}$ | *a*′ | 1343 | (3) | 1333 | (1) | 1341 | (3) | 1336 | (2) |
| $\nu_{21}$ | *a*′ | 1310 | (2) | 1306 | (0) | 1317 | (4) | 1305 | (1) |
| $\nu_{22}$ | *a*′ | 1289 | (1) | 1286 | (1) | 1301 | (2) | 1298 | (1) |
| $\nu_{23}$ | *a*′ | 1277 | (2) | 1276 | (2) | 1283 | (5) | 1280 | (4) |
| $\nu_{24}$ | *a*′ | 1210 | (0) | 1207 | (0) | 1216 | (6) | 1215 | (5) |
| $\nu_{25}$ | *a*′ | 1184 | (5) | 1184 | (4) | 1198 | (3) | 1199 | (2) |
| $\nu_{26}$ | *a*′ | 1162 | (0) | 1168 | (0) | 1171 | (8) | 1172 | (6) |
| $\nu_{27}$ | *a*′ | 1156 | (0) | 1162 | (0) | 1153 | (0) | 1162 | (0) |
| $\nu_{28}$ | *a*′ | 1142 | (2) | 1146 | (2) | 1144 | (1) | 1147 | (1) |
| $\nu_{29}$ | *a*′ | 1132 | (2) | 1134 | (1) | 1118 | (0) | 1117 | (0) |
| $\nu_{30}$ | *a*′ | 1092 | (1) | 1093 | (1) | 1092 | (1) | 1094 | (1) |
| $\nu_{31}$ | *a*′ | 1038 | (2) | 1042 | (0) | 1025 | (5) | 1028 | (1) |
| $\nu_{32}$ | *a*′ | 1025 | (7) | 1029 | (3) | 1010 | (5) | 1013 | (4) |
| $\nu_{33}$ | *a*′ | 986 | (0) | 989 | (0) | 984 | (4) | 984 | (1) |
| $\nu_{34}$ | *a*′ | 911 | (3) | 912 | (2) | 876 | (17) | 876 | (14) |
| $\nu_{35}$ | *a*′ | 833 | (0) | 835 | (0) | 818 | (4) | 824 | (2) |
| $\nu_{36}$ | *a*′ | 783 | (0) | 784 | (0) | 781 | (2) | 780 | (2) |
| $\nu_{37}$ | *a*′ | 726 | (0) | 730 | (0) | 717 | (1) | 720 | (0) |
| $\nu_{38}$ | *a*′ | 624 | (2) | 627 | (2) | 622 | (1) | 624 | (1) |
| $\nu_{39}$ | *a*′ | 602 | (5) | 606 | (4) | 597 | (7) | 599 | (6) |
| $\nu_{40}$ | *a*′ | 528 | (2) | 529 | (1) | 528 | (1) | 532 | (0) |

| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| $\nu_{41}$ | *a′* | 478 | (0) | 480 | (0) | 490 | (0) | 492 | (0) |
| $\nu_{42}$ | *a′* | 392 | (0) | 393 | (0) | 408 | (0) | 409 | (0) |
| $\nu_{43}$ | *a′* | 209 | (0) | 205 | (0) | 213 | (0) | 209 | (0) |
| $\nu_{44}$ | *a″* | 2895 | (13) | 2857 | (17) | 2935 | (7) | 2902 | (10) |
| $\nu_{45}$ | *a″* | 2788 | (24) | 2724 | (32) | 2809 | (19) | 2749 | (25) |
| $\nu_{46}$ | *a″* | 1164 | (0) | 1159 | (0) | 1167 | (0) | 1159 | (0) |
| $\nu_{47}$ | *a″* | 1110 | (1) | 1107 | (1) | 1143 | (0) | 1143 | (0) |
| $\nu_{48}$ | *a″* | 967 | (0) | 992 | (0) | 961 | (0) | 988 | (0) |
| $\nu_{49}$ | *a″* | 947 | (0) | 951 | (0) | 951 | (5) | 962 | (4) |
| $\nu_{50}$ | *a″* | 946 | (1) | 960 | (1) | 949 | (1) | 951 | (0) |
| $\nu_{51}$ | *a″* | 923 | (2) | 931 | (1) | 921 | (4) | 928 | (2) |
| $\nu_{52}$ | *a″* | 871 | (2) | 876 | (0) | 910 | (3) | 910 | (6) |
| $\nu_{53}$ | *a″* | 850 | (2) | 854 | (3) | 846 | (0) | 858 | (0) |
| $\nu_{54}$ | *a″* | 775 | (6) | 791 | (2) | 764 | (0) | 799 | (1) |
| $\nu_{55}$ | *a″* | 746 | (37) | 759 | (21) | 757 | (8) | 738 | (0) |
| $\nu_{56}$ | *a″* | 715 | (27) | 717 | (34) | 727 | (100) | 730 | (98) |
| $\nu_{57}$ | *a″* | 656 | (60) | 662 | (29) | 702 | (0) | 706 | (0) |
| $\nu_{58}$ | *a″* | 608 | (1) | 611 | (5) | 605 | (7) | 611 | (8) |
| $\nu_{59}$ | *a″* | 508 | (0) | 514 | (0) | 499 | (1) | 507 | (0) |
| $\nu_{60}$ | *a″* | 450 | (0) | 452 | (0) | 431 | (0) | 426 | (1) |
| $\nu_{61}$ | *a″* | 420 | (3) | 419 | (3) | 410 | (9) | 409 | (9) |
| $\nu_{62}$ | *a″* | 281 | (1) | 282 | (2) | 289 | (0) | 290 | (1) |
| $\nu_{63}$ | *a″* | 249 | (8) | 255 | (7) | 231 | (8) | 233 | (7) |
| $\nu_{64}$ | *a″* | 185 | (0) | 186 | (0) | 201 | (0) | 199 | (0) |
| $\nu_{65}$ | *a″* | 122 | (0) | 121 | (1) | 120 | (0) | 117 | (0) |
| $\nu_{66}$ | *a″* | 94 | (1) | 90 | (0) | 85 | (1) | 79 | (1) |

| Mode[b] | Sym. | σ /cm$^{-1}$ | Intensity /km mol$^{-1}$ | Mode[b] | Sym. | σ /cm$^{-1}$ | Intensity /km mol$^{-1}$ |
|---|---|---|---|---|---|---|---|
| $\nu_{10} + \nu_{14}$ | *a′* | 3090 | (7) | $\nu_{10} + \nu_{13}$ | *a′* | 3116 | (12) |
| $\nu_{11} + \nu_{15}$ | *a′* | 3034 | (6) | $\nu_{11} + \nu_{13}$ | *a′* | 3092 | (7) |
| $\nu_{11} + \nu_{20}$ | *a′* | 2909 | (5) | $\nu_{13} + \nu_{20}$ | *a′* | 2846 | (12) |
| $\nu_{10} + \nu_{21}$ | *a′* | 2908 | (5) | $2\nu_{17}$ | *a’* | 2821 | (15) |
| $\nu_{13} + \nu_{16}$ | *a′* | 2902 | (5) | $2\nu_{48}$ | *a’* | 1988 | (6) |
| $\nu_{15} + \nu_{19}$ | *a′* | 2836 | (5) | $\nu_{54} + \nu_{55}$ | *a′* | 1534 | (5) |
| $2\nu_{16}$ | *a’* | 2812 | (19) | $\nu_{52} + \nu_{65}$ | *a′* | 1030 | (5) |
| $2\nu_{17}$ | *a’* | 2790 | (6) | | | | |
| $\nu_{17} + \nu_{18}$ | *a′* | 2789 | (5) | | | | |
| $2\nu_{48}$ | *a′* | 1996 | (5) | | | | |
| $\nu_{55} + \nu_{56}$ | *a′* | 1476 | (5) | | | | |
| $\nu_{54} + \nu_{57}$ | *a′* | 1454 | (7) | | | | |
| $\nu_{41} + \nu_{64}$ | *a″* | 666 | (26) | | | | |

[a] Harmonic vibrational wavenumbers (cm$^{-1}$) $x$ are scaled by equations $y = 0.9513\,x + 33.4$ for $x > 2000$ cm$^{-1}$ and $y = 0.9765\,x + 5.0$ for $x < 2000$ cm$^{-1}$. [b] Overtone and combination bands with IR intensities ≥5 km mol$^{-1}$ are listed.

**Table S9** Scaled harmonic and anharmonic vibrational wavenumbers σ and IR intensities of fluorene-3-hydryl (3$H$-$C_{13}H_{11}$) and fluorene-4-hydryl (4$H$-$C_{13}H_{11}$) radicals calculated with the B3LYP/6-311++G(d,p) method

| Mode | Sym. | 3$H$-$C_{13}H_{11}$ Scaled Harmonic[a] σ /cm$^{-1}$ | Intensity /km mol$^{-1}$ | 3$H$-$C_{13}H_{11}$ Anharmonic σ /cm$^{-1}$ | Intensity /km mol$^{-1}$ | 4$H$-$C_{13}H_{11}$ Scaled Harmonic[a] σ /cm$^{-1}$ | Intensity /km mol$^{-1}$ | 4$H$-$C_{13}H_{11}$ Anharmonic σ /cm$^{-1}$ | Intensity /km mol$^{-1}$ |
|---|---|---|---|---|---|---|---|---|---|
| $\nu_{1}$ | $a'$ | 3064 | (24) | 3062 | (14) | 3064 | (21) | 3062 | (46) |
| $\nu_{2}$ | $a'$ | 3053 | (26) | 3037 | (17) | 3061 | (24) | 3055 | (7) |
| $\nu_{3}$ | $a'$ | 3048 | (23) | 3031 | (11) | 3052 | (22) | 3024 | (19) |
| $\nu_{4}$ | $a'$ | 3043 | (0) | 2995 | (0) | 3049 | (26) | 3053 | (35) |
| $\nu_{5}$ | $a'$ | 3040 | (12) | 3091 | (6) | 3041 | (4) | 3078 | (14) |
| $\nu_{6}$ | $a'$ | 3035 | (4) | 3002 | (15) | 3035 | (7) | 3002 | (8) |
| $\nu_{7}$ | $a'$ | 3026 | (10) | 3026 | (46) | 3032 | (5) | 3024 | (8) |
| $\nu_{8}$ | $a'$ | 2880 | (33) | 2881 | (13) | 2909 | (13) | 2903 | (12) |
| $\nu_{9}$ | $a'$ | 2810 | (66) | 2737 | (44) | 2819 | (33) | 2760 | (0) |
| $\nu_{10}$ | $a'$ | 1612 | (0) | 1608 | (0) | 1599 | (7) | 1592 | (3) |
| $\nu_{11}$ | $a'$ | 1585 | (1) | 1580 | (1) | 1576 | (5) | 1569 | (2) |
| $\nu_{12}$ | $a'$ | 1582 | (2) | 1569 | (10) | 1567 | (1) | 1556 | (0) |
| $\nu_{13}$ | $a'$ | 1502 | (0) | 1493 | (0) | 1501 | (1) | 1493 | (1) |
| $\nu_{14}$ | $a'$ | 1466 | (14) | 1465 | (9) | 1458 | (5) | 1456 | (3) |
| $\nu_{15}$ | $a'$ | 1463 | (6) | 1463 | (12) | 1450 | (4) | 1448 | (2) |
| $\nu_{16}$ | $a'$ | 1427 | (3) | 1427 | (1) | 1418 | (15) | 1404 | (3) |
| $\nu_{17}$ | $a'$ | 1423 | (6) | 1410 | (5) | 1413 | (2) | 1399 | (3) |
| $\nu_{18}$ | $a'$ | 1411 | (4) | 1394 | (2) | 1400 | (2) | 1402 | (0) |
| $\nu_{19}$ | $a'$ | 1352 | (13) | 1351 | (2) | 1382 | (12) | 1377 | (4) |
| $\nu_{20}$ | $a'$ | 1327 | (2) | 1322 | (1) | 1353 | (1) | 1351 | (1) |
| $\nu_{21}$ | $a'$ | 1306 | (1) | 1305 | (0) | 1316 | (1) | 1314 | (1) |
| $\nu_{22}$ | $a'$ | 1288 | (20) | 1281 | (14) | 1295 | (0) | 1291 | (0) |
| $\nu_{23}$ | $a'$ | 1266 | (2) | 1265 | (3) | 1258 | (6) | 1256 | (3) |
| $\nu_{24}$ | $a'$ | 1221 | (0) | 1219 | (0) | 1217 | (6) | 1213 | (5) |
| $\nu_{25}$ | $a'$ | 1192 | (8) | 1195 | (2) | 1183 | (6) | 1180 | (2) |
| $\nu_{26}$ | $a'$ | 1179 | (9) | 1184 | (3) | 1166 | (1) | 1169 | (1) |
| $\nu_{27}$ | $a'$ | 1164 | (1) | 1167 | (0) | 1163 | (0) | 1167 | (0) |
| $\nu_{28}$ | $a'$ | 1153 | (1) | 1157 | (1) | 1150 | (0) | 1156 | (0) |
| $\nu_{29}$ | $a'$ | 1134 | (2) | 1137 | (2) | 1101 | (0) | 1103 | (0) |
| $\nu_{30}$ | $a'$ | 1096 | (4) | 1098 | (3) | 1098 | (3) | 1100 | (3) |
| $\nu_{31}$ | $a'$ | 1027 | (4) | 1030 | (2) | 1028 | (2) | 1030 | (2) |
| $\nu_{32}$ | $a'$ | 1000 | (8) | 1003 | (3) | 1022 | (6) | 1023 | (5) |
| $\nu_{33}$ | $a'$ | 983 | (4) | 987 | (3) | 992 | (2) | 994 | (1) |
| $\nu_{34}$ | $a'$ | 873 | (6) | 873 | (2) | 914 | (12) | 916 | (10) |
| $\nu_{35}$ | $a'$ | 824 | (1) | 826 | (0) | 830 | (3) | 834 | (3) |
| $\nu_{36}$ | $a'$ | 774 | (1) | 775 | (0) | 786 | (0) | 788 | (0) |
| $\nu_{37}$ | $a'$ | 730 | (0) | 733 | (0) | 718 | (4) | 720 | (3) |
| $\nu_{38}$ | $a'$ | 617 | (1) | 621 | (0) | 618 | (1) | 621 | (0) |
| $\nu_{39}$ | $a'$ | 612 | (7) | 615 | (6) | 599 | (1) | 599 | (0) |

| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| $\nu_{40}$ | $a'$ | 524 | (0) | 528 | (0) | 529 | (0) | 530 | (0) |
| $\nu_{41}$ | $a'$ | 482 | (0) | 482 | (0) | 485 | (1) | 486 | (1) |
| $\nu_{42}$ | $a'$ | 405 | (0) | 405 | (0) | 400 | (1) | 401 | (1) |
| $\nu_{43}$ | $a'$ | 213 | (0) | 209 | (0) | 206 | (0) | 204 | (0) |
| $\nu_{44}$ | $a''$ | 2895 | (14) | 2856 | (18) | 2934 | (7) | 2901 | (9) |
| $\nu_{45}$ | $a''$ | 2793 | (19) | 2730 | (27) | 2809 | (19) | 2754 | (25) |
| $\nu_{46}$ | $a''$ | 1160 | (0) | 1153 | (0) | 1162 | (0) | 1156 | (0) |
| $\nu_{47}$ | $a''$ | 1126 | (0) | 1125 | (0) | 1134 | (0) | 1132 | (0) |
| $\nu_{48}$ | $a''$ | 968 | (0) | 998 | (0) | 963 | (0) | 985 | (0) |
| $\nu_{49}$ | $a''$ | 950 | (3) | 964 | (1) | 950 | (1) | 955 | (1) |
| $\nu_{50}$ | $a''$ | 938 | (0) | 943 | (0) | 942 | (3) | 950 | (3) |
| $\nu_{51}$ | $a''$ | 914 | (5) | 920 | (0) | 920 | (2) | 919 | (0) |
| $\nu_{52}$ | $a''$ | 909 | (4) | 905 | (5) | 908 | (0) | 915 | (1) |
| $\nu_{53}$ | $a''$ | 856 | (0) | 868 | (1) | 847 | (0) | 853 | (0) |
| $\nu_{54}$ | $a''$ | 776 | (7) | 792 | (6) | 768 | (2) | 781 | (4) |
| $\nu_{55}$ | $a''$ | 737 | (56) | 741 | (48) | 752 | (32) | 760 | (4) |
| $\nu_{56}$ | $a''$ | 710 | (2) | 710 | (1) | 713 | (32) | 712 | (42) |
| $\nu_{57}$ | $a''$ | 689 | (44) | 694 | (34) | 670 | (65) | 672 | (58) |
| $\nu_{58}$ | $a''$ | 629 | (8) | 632 | (15) | 585 | (0) | 588 | (1) |
| $\nu_{59}$ | $a''$ | 500 | (4) | 509 | (4) | 514 | (0) | 516 | (0) |
| $\nu_{60}$ | $a''$ | 432 | (0) | 431 | (0) | 452 | (2) | 456 | (2) |
| $\nu_{61}$ | $a''$ | 408 | (5) | 408 | (5) | 424 | (2) | 424 | (2) |
| $\nu_{62}$ | $a''$ | 263 | (0) | 259 | (0) | 306 | (2) | 305 | (2) |
| $\nu_{63}$ | $a''$ | 244 | (4) | 256 | (4) | 237 | (9) | 243 | (8) |
| $\nu_{64}$ | $a''$ | 191 | (3) | 197 | (2) | 177 | (1) | 181 | (1) |
| $\nu_{65}$ | $a''$ | 111 | (1) | 98 | (1) | 138 | (0) | 134 | (0) |
| $\nu_{66}$ | $a''$ | 93 | (0) | 90 | (1) | 85 | (0) | 79 | (0) |

| Mode[b] | Sym. | σ /cm$^{-1}$ | Intensity /km mol$^{-1}$ | Mode[b] | Sym. | σ /cm$^{-1}$ | Intensity /km mol$^{-1}$ |
|---|---|---|---|---|---|---|---|
| $\nu_{10}+\nu_{14}$ | $a'$ | 3085 | (18) | $\nu_{10}+\nu_{15}$ | $a'$ | 3049 | (27) |
| $\nu_{10}+\nu_{14}$ | $a'$ | 3072 | (13) | $\nu_{14}+\nu_{17}$ | $a'$ | 2856 | (5) |
| $\nu_{11}+\nu_{13}$ | $a'$ | 3067 | (7) | $\nu_{15}+\nu_{16}$ | $a'$ | 2849 | (30) |
| $\nu_{10}+\nu_{15}$ | $a'$ | 3057 | (20) | $\nu_{15}+\nu_{17}$ | $a'$ | 2844 | (10) |
| $\nu_{11}+\nu_{15}$ | $a'$ | 3039 | (7) | $\nu_{16}+\nu_{17}$ | $a'$ | 2796 | (5) |
| $2\nu_{14}$ | $a'$ | 2926 | (9) | $2\nu_{48}$ | $a'$ | 1981 | (6) |
| $\nu_{16}+\nu_{17}$ | $a'$ | 2827 | (5) | $2\nu_{54}$ | $a'$ | 1556 | (5) |
| $2\nu_{16}$ | $a'$ | 2812 | (6) | $\nu_{54}+\nu_{57}$ | $a'$ | 1447 | (5) |
| $\nu_{16}+\nu_{18}$ | $a'$ | 2809 | (10) | $2\nu_{56}$ | $a'$ | 1436 | (6) |
| $2\nu_{18}$ | $a'$ | 2808 | (18) | $\nu_{24}+\nu_{43}$ | $a'$ | 1419 | (8) |
| $2\nu_{48}$ | $a'$ | 2010 | (5) | $\nu_{38}+\nu_{65}$ | $a''$ | 756 | (8) |
| $\nu_{49}+\nu_{61}$ | $a'$ | 1367 | (13) | | | | |
| $\nu_{36}+\nu_{42}$ | $a'$ | 1175 | (5) | | | | |

[a] Harmonic vibrational wavenumbers (cm$^{-1}$) $x$ are scaled by equations $y = 0.9513\,x + 33.4$ for $x > 2000$ cm$^{-1}$ and $y = 0.9765\,x + 5.0$ for $x < 2000$ cm$^{-1}$. [b] Overtone and combination bands with IR intensities >5 km mol$^{-1}$ are listed.

**Table S10** Scaled harmonic and anharmonic vibrational wavenumbers σ and IR intensities of fluorene-4a-hydryl (4a*H*-$C_{13}H_{11}$) and fluoren-9a-hydryl (9a*H*-$C_{13}H_{11}$) radicals calculated with the B3LYP/6-311++G(d,p) method

| Mode | 4a*H*-$C_{13}H_{11}$ | | | | 9a*H*-$C_{13}H_{11}$ | | | |
|---|---|---|---|---|---|---|---|---|
| | Scaled Harmonic[a] | | Anharmonic[b] | | Scaled Harmonic[a] | | Anharmonic | |
| | σ /$cm^{-1}$ | Intensity /km $mol^{-1}$ | σ /$cm^{-1}$ | Intensity /km $mol^{-1}$ | σ /$cm^{-1}$ | Intensity /km $mol^{-1}$ | σ /$cm^{-1}$ | Intensity /km $mol^{-1}$ |
| $\nu_1$ | 3068 | (19) | | | 3062 | (17) | 3069 | (12) |
| $\nu_2$ | 3063 | (26) | | | 3060 | (28) | 3054 | (23) |
| $\nu_3$ | 3052 | (40) | | | 3050 | (22) | 3060 | (9) |
| $\nu_4$ | 3050 | (1) | | | 3043 | (27) | 3039 | (36) |
| $\nu_5$ | 3040 | (3) | | | 3039 | (3) | 3075 | (21) |
| $\nu_6$ | 3035 | (3) | | | 3033 | (6) | 3004 | (8) |
| $\nu_7$ | 3033 | (9) | | | 3030 | (5) | 3020 | (8) |
| $\nu_8$ | 3027 | (13) | | | 3026 | (5) | 3037 | (2) |
| $\nu_9$ | 2938 | (17) | | | 2954 | (22) | 2942 | (25) |
| $\nu_{10}$ | 2854 | (32) | | | 2895 | (25) | 2835 | (9) |
| $\nu_{11}$ | 2696 | (30) | | | 2734 | (27) | 2680 | (29) |
| $\nu_{12}$ | 1611 | (1) | | | 1599 | (3) | 1594 | (1) |
| $\nu_{13}$ | 1590 | (3) | | | 1572 | 0 | 1566 | 0 |
| $\nu_{14}$ | 1574 | (2) | | | 1559 | (1) | 1547 | 0 |
| $\nu_{15}$ | 1504 | (1) | | | 1502 | 0 | 1497 | 0 |
| $\nu_{16}$ | 1473 | (21) | | | 1462 | (5) | 1460 | (1) |
| $\nu_{17}$ | 1459 | (4) | | | 1460 | (7) | 1466 | (6) |
| $\nu_{18}$ | 1437 | (4) | | | 1448 | (8) | 1429 | (1) |
| $\nu_{19}$ | 1399 | (2) | | | 1396 | (3) | 1398 | (1) |
| $\nu_{20}$ | 1360 | (1) | | | 1365 | 0 | 1361 | 0 |
| $\nu_{21}$ | 1319 | (2) | | | 1327 | (3) | 1322 | (1) |
| $\nu_{22}$ | 1317 | (1) | | | 1301 | (1) | 1302 | 0 |
| $\nu_{23}$ | 1289 | (1) | | | 1299 | (3) | 1303 | (1) |
| $\nu_{24}$ | 1254 | (3) | | | 1285 | (10) | 1279 | (2) |
| $\nu_{25}$ | 1216 | (1) | | | 1248 | (4) | 1240 | (4) |
| $\nu_{26}$ | 1196 | (7) | | | 1222 | (6) | 1221 | (4) |
| $\nu_{27}$ | 1195 | (8) | | | 1200 | (5) | 1193 | (2) |
| $\nu_{28}$ | 1173 | (6) | | | 1173 | (3) | 1174 | (2) |
| $\nu_{29}$ | 1158 | 0 | | | 1158 | (1) | 1161 | 0 |
| $\nu_{30}$ | 1153 | (1) | | | 1155 | 0 | 1161 | 0 |
| $\nu_{31}$ | 1133 | (2) | | | 1137 | 0 | 1136 | 0 |
| $\nu_{32}$ | 1130 | (1) | | | 1104 | (4) | 1108 | (2) |
| $\nu_{33}$ | 1098 | 0 | | | 1093 | (1) | 1097 | (1) |
| $\nu_{34}$ | 1082 | (1) | | | 1052 | (4) | 1053 | (2) |
| $\nu_{35}$ | 1027 | (4) | | | 1035 | (3) | 1031 | (1) |
| $\nu_{36}$ | 1018 | (6) | | | 1024 | (4) | 1024 | (3) |
| $\nu_{37}$ | 982 | (4) | | | 985 | (6) | 988 | 0 |
| $\nu_{38}$ | 971 | 0 | | | 975 | (6) | 975 | (2) |
| $\nu_{39}$ | 960 | (2) | | | 968 | 0 | 988 | 0 |

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| $\nu_{40}$ | 945 | 0 | | | 962 | (2) | 960 | (3) |
| $\nu_{41}$ | 938 | (2) | | | 949 | (1) | 948 | (1) |
| $\nu_{42}$ | 920 | (3) | | | 929 | (1) | 934 | 0 |
| $\nu_{43}$ | 883 | (3) | | | 901 | (1) | 897 | (3) |
| $\nu_{44}$ | 865 | 0 | | | 858 | (1) | 864 | (1) |
| $\nu_{45}$ | 824 | (1) | | | 839 | (1) | 841 | (1) |
| $\nu_{46}$ | 815 | (2) | | | 798 | (2) | 801 | (1) |
| $\nu_{47}$ | 774 | (1) | | | 769 | 0 | 772 | (1) |
| $\nu_{48}$ | 749 | (7) | | | 753 | (44) | 759 | (29) |
| $\nu_{49}$ | 734 | (65) | | | 727 | (5) | 731 | (2) |
| $\nu_{50}$ | 713 | (1) | | | 715 | (11) | 713 | (15) |
| $\nu_{51}$ | 683 | (35) | | | 680 | (74) | 684 | (61) |
| $\nu_{52}$ | 649 | (24) | | | 651 | (7) | 647 | (19) |
| $\nu_{53}$ | 609 | (4) | | | 609 | (4) | 611 | (1) |
| $\nu_{54}$ | 590 | (3) | | | 604 | (2) | 605 | (1) |
| $\nu_{55}$ | 523 | 0 | | | 536 | 0 | 538 | 0 |
| $\nu_{56}$ | 516 | 0 | | | 516 | (1) | 518 | (1) |
| $\nu_{57}$ | 492 | (2) | | | 504 | 0 | 507 | 0 |
| $\nu_{58}$ | 453 | (1) | | | 446 | 0 | 445 | (1) |
| $\nu_{59}$ | 430 | (4) | | | 442 | (3) | 442 | (3) |
| $\nu_{60}$ | 409 | (1) | | | 402 | (4) | 400 | (4) |
| $\nu_{61}$ | 371 | (1) | | | 380 | (1) | 378 | (1) |
| $\nu_{62}$ | 259 | (3) | | | 262 | (1) | 259 | (1) |
| $\nu_{63}$ | 233 | (1) | | | 215 | (2) | 220 | 0 |
| $\nu_{64}$ | 190 | (1) | | | 210 | (1) | 200 | (2) |
| $\nu_{65}$ | 116 | 0 | | | 105 | 0 | 101 | 0 |
| $\nu_{66}$ | 70 | 0 | | | 93 | 0 | 90 | 0 |
| | | | | | Mode [c] | Sym. | σ /cm$^{-1}$ | Intensity /km mol$^{-1}$ |
| | | | | | $\nu_{13}+\nu_{14}$ | *a′* | 3117 | (14) |
| | | | | | $\nu_{12}+\nu_{15}$ | *a′* | 3094 | (12) |
| | | | | | $\nu_{14}+\nu_{15}$ | *a′* | 3030 | (5) |
| | | | | | $\nu_{12}+\nu_{17}$ | *a′* | 3028 | (31) |
| | | | | | $\nu_{15}+\nu_{18}$ | *a′* | 2938 | (12) |
| | | | | | $2\nu_{18}$ | *a′* | 2910 | (5) |
| | | | | | $2\nu_{37}$ | *a′* | 1986 | (5) |

[a] Harmonic vibrational wavenumbers (cm$^{-1}$) $x$ are scaled by equations $y = 0.9513\,x + 33.4$ for $x > 2000$ cm$^{-1}$ and $y = 0.9765\,x + 5.0$ for $x < 2000$ cm$^{-1}$. [b] Anharmonic vibrational calculation of 4a-$HC_{13}H_{10}$ do not converge.. [c] Overtone and combination bands with IR intensities >5 km mol$^{-1}$ are listed.

**Table S11** Scaled harmonic and anharmonic vibrational wavenumbers σ and IR intensities of the triplet and singlet fluoren-9-ylidene ($C_{13}H_8$) calculated with the B3LYP/6-311++G(d,p) method

| Mode | Sym. | $C_{13}H_8$ (triplet) | | | | $C_{13}H_8$ (singlet) | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | Scaled Harmonic[a] | | Anharmonic | | Scaled Harmonic[a] | | Anharmonic | |
| | | σ /$cm^{-1}$ | Intensity /km $mol^{-1}$ | σ /$cm^{-1}$ | Intensity /km $mol^{-1}$ | σ /$cm^{-1}$ | Intensity /km $mol^{-1}$ | σ /$cm^{-1}$ | Intensity /km $mol^{-1}$ |
| $\nu_1$ | $a_1$ | 3070 | (0) | 3056 | (0) | 3071 | (0) | 3066 | (0) |
| $\nu_2$ | $a_1$ | 3060 | (35) | 3065 | (26) | 3060 | (21) | 3055 | (26) |
| $\nu_3$ | $a_1$ | 3050 | (3) | 3044 | (2) | 3051 | (14) | 3073 | (0) |
| $\nu_4$ | $a_1$ | 3042 | (1) | 3029 | (3) | 3040 | (2) | 3023 | (6) |
| $\nu_5$ | $a_1$ | 1584 | (6) | 1577 | (3) | 1599 | (18) | 1592 | (8) |
| $\nu_6$ | $a_1$ | 1567 | (1) | 1558 | (1) | 1589 | (4) | 1580 | (9) |
| $\nu_7$ | $a_1$ | 1466 | (7) | 1464 | (3) | 1472 | (34) | 1466 | (15) |
| $\nu_8$ | $a_1$ | 1415 | (1) | 1407 | (0) | 1442 | (0) | 1441 | (1) |
| $\nu_9$ | $a_1$ | 1352 | (0) | 1353 | (0) | 1383 | (1) | 1382 | (2) |
| $\nu_{10}$ | $a_1$ | 1292 | (1) | 1294 | (1) | 1278 | (1) | 1282 | (1) |
| $\nu_{11}$ | $a_1$ | 1202 | (11) | 1205 | (9) | 1179 | (21) | 1183 | (10) |
| $\nu_{12}$ | $a_1$ | 1179 | (0) | 1181 | (0) | 1174 | (5) | 1174 | (0) |
| $\nu_{13}$ | $a_1$ | 1150 | (0) | 1153 | (0) | 1159 | (8) | 1162 | (10) |
| $\nu_{14}$ | $a_1$ | 1092 | (0) | 1092 | (0) | 1080 | (1) | 1081 | (1) |
| $\nu_{15}$ | $a_1$ | 1016 | (1) | 1016 | (1) | 1014 | (1) | 1019 | (1) |
| $\nu_{16}$ | $a_1$ | 862 | (0) | 865 | (0) | 648 | (0) | 649 | (0) |
| $\nu_{17}$ | $a_1$ | 737 | (0) | 740 | (0) | 419 | (0) | 418 | (1) |
| $\nu_{18}$ | $a_1$ | 640 | (0) | 643 | (0) | 854 | (1) | 857 | (0) |
| $\nu_{19}$ | $a_1$ | 422 | (1) | 422 | (1) | 737 | (0) | 740 | (0) |
| $\nu_{20}$ | $a_1$ | 217 | (1) | 215 | (1) | 218 | (1) | 215 | (1) |
| $\nu_{21}$ | $a_2$ | 960 | (0) | 984 | (0) | 982 | (0) | 996 | (0) |
| $\nu_{22}$ | $a_2$ | 930 | (0) | 939 | (0) | 958 | (0) | 955 | (0) |
| $\nu_{23}$ | $a_2$ | 857 | (0) | 872 | (0) | 889 | (0) | 890 | (0) |
| $\nu_{24}$ | $a_2$ | 753 | (0) | 780 | (0) | 772 | (0) | 783 | (0) |
| $\nu_{25}$ | $a_2$ | 732 | (0) | 727 | (0) | 748 | (0) | 740 | (0) |
| $\nu_{26}$ | $a_2$ | 558 | (0) | 558 | (0) | 551 | (0) | 545 | (0) |
| $\nu_{27}$ | $a_2$ | 428 | (0) | 398 | (0) | 430 | (0) | 390 | (0) |
| $\nu_{28}$ | $a_2$ | 276 | (0) | 262 | (0) | 264 | (0) | 247 | (0) |
| $\nu_{29}$ | $a_2$ | 134 | (0) | 129 | (0) | 124 | (0) | 115 | (0) |
| $\nu_{30}$ | $b_1$ | 962 | (0) | 985 | (0) | 985 | (0) | 995 | (0) |
| $\nu_{31}$ | $b_1$ | 930 | (3) | 940 | (3) | 955 | (6) | 958 | (6) |
| $\nu_{32}$ | $b_1$ | 853 | (0) | 862 | (0) | 878 | (0) | 880 | (0) |
| $\nu_{33}$ | $b_1$ | 748 | (98) | 767 | (36) | 762 | (125) | 769 | (69) |
| $\nu_{34}$ | $b_1$ | 708 | (43) | 713 | (85) | 710 | (21) | 719 | (48) |
| $\nu_{35}$ | $b_1$ | 562 | (3) | 573 | (4) | 493 | (6) | 494 | (5) |
| $\nu_{36}$ | $b_1$ | 412 | (7) | 410 | (8) | 394 | (1) | 392 | (2) |
| $\nu_{37}$ | $b_1$ | 327 | (0) | 323 | (0) | 214 | (10) | 212 | (7) |

| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| $\nu_{38}$ | $b_1$ | 108 | (2) | 104 | (2) | 86 | (8) | 86 | (8) |
| $\nu_{39}$ | $b_2$ | 3069 | (44) | 3065 | (18) | 3070 | (41) | 3068 | (21) |
| $\nu_{40}$ | $b_2$ | 3060 | (0) | 3058 | (7) | 3060 | (5) | 3053 | (2) |
| $\nu_{41}$ | $b_2$ | 3049 | (2) | 3036 | (22) | 3051 | (0) | 3064 | (30) |
| $\nu_{42}$ | $b_2$ | 3040 | (1) | 3023 | (0) | 3039 | (2) | 3029 | (0) |
| $\nu_{43}$ | $b_2$ | 1573 | (4) | 1570 | (5) | 1601 | (106) | 1597 | (69) |
| $\nu_{44}$ | $b_2$ | 1554 | (9) | 1546 | (6) | 1576 | (45) | 1570 | (29) |
| $\nu_{45}$ | $b_2$ | 1460 | (3) | 1461 | (3) | 1453 | (10) | 1455 | (9) |
| $\nu_{46}$ | $b_2$ | 1413 | (19) | 1407 | (15) | 1425 | (10) | 1430 | (5) |
| $\nu_{47}$ | $b_2$ | 1304 | (10) | 1301 | (5) | 1285 | (4) | 1284 | (11) |
| $\nu_{48}$ | $b_2$ | 1296 | (1) | 1295 | (0) | 1266 | (34) | 1265 | (20) |
| $\nu_{49}$ | $b_2$ | 1199 | (0) | 1199 | (0) | 1169 | (112) | 1170 | (48) |
| $\nu_{50}$ | $b_2$ | 1151 | (0) | 1158 | (0) | 1149 | (11) | 1156 | (11) |
| $\nu_{51}$ | $b_2$ | 1086 | (3) | 1087 | (1) | 1079 | (83) | 1081 | (72) |
| $\nu_{52}$ | $b_2$ | 1020 | (6) | 1022 | (3) | 1025 | (5) | 1028 | (4) |
| $\nu_{53}$ | $b_2$ | 981 | (1) | 985 | (1) | 994 | (2) | 997 | (1) |
| $\nu_{54}$ | $b_2$ | 876 | (1) | 880 | (1) | 845 | (15) | 851 | (13) |
| $\nu_{55}$ | $b_2$ | 616 | (0) | 620 | (0) | 618 | (0) | 621 | (0) |
| $\nu_{56}$ | $b_2$ | 554 | (1) | 557 | (1) | 536 | (10) | 539 | (9) |
| $\nu_{57}$ | $b_2$ | 488 | (1) | 487 | (1) | 504 | (7) | 501 | (7) |

[a] Harmonic vibrational wavenumbers ($cm^{-1}$) $x$ are scaled by equations $y = 0.9513\,x + 33.4$ for $x > 2000$ $cm^{-1}$ and $y = 0.9765\,x + 5.0$ for $x < 2000$ $cm^{-1}$.

**Table S12** Lines of fluorene ($C_{13}H_{10}$), 9*H*-fluoren-9-yl ($C_{13}H_9$) and hydrofluorenyl (1*H*-, 2*H*-, 3*H*-, and 4*H*-$C_{13}H_{11}$) radicals integrated for mixing ratio calculations

| Group | Assignment | Mixing ratio /ppm | Lines integrated (region) /$cm^{-1}$ |
|---|---|---|---|
| Parent | $C_{13}H_{10}$ | 45.0 ± 7.4 | 1483.2 (1484.07−1481.91) |
| | | | 1455.9 (1456.9−1454.73) |
| | | | 1234.4 (1235.87−1233.29) |
| | | | 1005.5 (1006.7−1004.2) |
| | | | 956.5 (958.2−955.14) |
| | | | 742.2 (744.28−739.97) |
| | | | 622.5 (623.59−621.1) |
| A | $C_{13}H_9$ | 2.7 ± 0.4 | 1566.4 (1570.7−1564.52) |
| | | | 1248.0 (1249.13−1246.96) |
| | | | 780.6 (781.46−779.75) |
| | | | 722.8 (724.225−721.1) |
| B | 1*H*-$C_{13}H_{11}$ | 2.6 ± 0.4 | 748.8 (749.81−747.38) |
| | | | 657.6 (660.71−656.73) |
| C | 2*H*-$C_{13}H_{11}$ | 7.4 ± 1.5 | 882.8 (885.19−881.19) |
| | | | 728.6 (730.421−726.67) |
| | | | 602.5 (603.11−601.36) |
| | | | 593.4 (594.1−592.78) |
| D | 3*H*-$C_{13}H_{11}$ | 5.7 ± 1.4 | 1290.3 (1293.11−1288.78) |
| | | | 738.0 (738.87−736.44) |
| | | | 689.7 (691.28−687.83) |
| | | | 626.7 (627.28−625.89) |
| E | 4*H*-$C_{13}H_{11}$ | 7.1 ± 5.5 | 754.4 (756.57−751.71) |
| | | | 668.0 (671.05−667.34) |

**Table S13** Vertical excitation wavelength λ and oscillator strength *f* of fluorene ($C_{13}H_{10}$) and the 9*H*-fluoren-9-yl ($C_{13}H_9$) radical calculated with the TD-B3LYP/6-311++G(d,p) method

| State | $C_{13}H_{10}$ | | | $C_{13}H_9$ | | |
|---|---|---|---|---|---|---|
| | λ /nm | $f$ /$10^{-1}$ | Assignment | λ /nm | $f$ /$10^{-1}$ | Assignment |
| 1 | 276.9 | 1.61 | HOMO→ LUMO | 717.3 | 0.01 | HOMO(β)→LUMO(β) |
| 2 | 265.6 | 2.80 | HOMO→ LUMO<br>HOMO → LUMO+1 | 452.4 | 0.50 | HOMO−1(β)→ LUMO(β) |
| 3 | 256.6 | 0.07 | HOMO−1→ LUMO<br>HOMO→ LUMO+3 | 410.7 | 0.05 | HOMO(α)→LUMO(α) |
| 4 | 235.8 | 0.00 | HOMO →LUMO+2 | 365.4 | 0.02 | HOMO−1(α)→LUMO(α)<br>HOMO(β)→LUMO+1(β) |
| 5 | 227.5 | 0.04 | HOMO−2→LUMO | 355.0 | 0.00 | HOMO−2(β) → LUMO(β) |
| 6 | 226.1 | 0.10 | HOMO →LUMO+4 | 335.5 | 0.14 | HOMO−3(β)→ LUMO(β) |
| 7 | 226.0 | 0.15 | HOMO−1→LUMO+1 | 317.4 | 0.33 | HOMO(α)→LUMO+1(α)<br>HOMO (β) →LUMO+1(β) |
| 8 | 223.0 | 0.00 | HOMO→ LUMO+5 | 284.7 | 0.15 | HOMO−1(β) →LUMO+1(β)<br>HOMO−2(α) → LUMO(α) |
| 9 | 215.6 | 1.12 | HOMO→ LUMO+3 | 278.4 | 0.01 | HOMO(α) →LUMO+2(α) |
| 10 | 215.4 | 1.51 | HOMO−2→LUMO+1 | 277.0 | 0.00 | HOMO−1(α)→LUMO+1(α)<br>HOMO (β) →LUMO+3(β) |
| 11 | 208.6 | 0.00 | HOMO→ LUMO+6 | 271.1 | 0.10 | HOMO−3(α)→ LUMO(α)<br>HOMO (β)→ LUMO+3(β) |
| 12 | 208.1 | 0.02 | HOMO−1→LUMO+2 | 265.0 | 0.00 | HOMO(α)→LUMO+3(α) |

**Table S14** Vertical excitation wavelength λ and oscillator strength *f* of 1*H*-$C_{13}H_{11}$ and 2*H*-$C_{13}H_{11}$ radicals calculated with the TD-B3LYP/6-311++G(d,p) method

| | 1*H*-$C_{13}H_{11}$ | | | 2*H*-$C_{13}H_{11}$ | | |
|---|---|---|---|---|---|---|
| State | λ /nm | *f* | Assignment | λ /nm | *f* | Assignment |
| 1 | 531.8 | 0.004 | HOMO(α) → LUMO(α) | 493.9 | 0.007 | HOMO(α) → LUMO(α) |
| 2 | 401.1 | 0.051 | HOMO(α) → LUMO(α)<br>HOMO(β)→ LUMO(β) | 420.6 | 0.002 | HOMO(α) → LUMO+2(α) |
| 3 | 362.3 | 0.007 | HOMO−1(α)→ LUMO (α)<br>HOMO(β)→ LUMO+1(β) | 400.1 | 0.000 | HOMO(α) → LUMO+1(α)<br>HOMO−1(β) → LUMO(β) |
| 4 | 345.9 | 0.008 | HOMO(α)→ LUMO+1(α) | 364.7 | 0.000 | HOMO(α) →LUMO+1(α) |
| 5 | 342.7 | 0.003 | HOMO(α)→ LUMO+2(α) | 344.3 | 0.014 | HOMO−1(β)→ LUMO(β) |
| 6 | 325.9 | 0.002 | HOMO(α) →LUMO+5(α)<br>HOMO−2(β)→ LUMO(β) | 330.3 | 0.055 | HOMO−2(β) → LUMO(β) |
| 7 | 317.6 | 0.001 | HOMO−1(β) → LUMO(β) | 328.8 | 0.000 | HOMO(α) →LUMO+1(α) |
| 8 | 305.3 | 0.000 | HOMO(α) →LUMO+4(α) | 324.5 | 0.000 | HOMO(α)→LUMO+5(α) |
| 9 | 299.6 | 0.001 | HOMO(α)→ LUMO+3(α) | 316.4 | 0.477 | HOMO(α) →LUMO+2(α)<br>HOMO(β)→ LUMO(β) |
| 10 | 292.1 | 0.000 | HOMO(β) →LUMO+2(β) | 298.1 | 0.030 | HOMO−1(α)→ LUMO(α)<br>HOMO−1(β)→ LUMO+1(β) |
| 11 | 286.5 | 0.021 | HOMO−2(α)→LUMO+1(α)<br>HOMO(α) → LUMO+5(α)<br>HOMO−1(β)→LUMO+2(β) | 293.8 | 0.003 | HOMO(α)→ LUMO+6(α) |
| 12 | 278.6 | 0.032 | HOMO−2(β) → LUMO(β) | 288.8 | 0.000 | HOMO(α) → LUMO+7(α) |

**Table S15** Vertical excitation wavelength λ and oscillator strength *f* of 3*H*-$C_{13}H_{11}$ and 4*H*-$C_{13}H_{11}$ radicals calculated with the TD-B3LYP/6-311++G(d,p) method

| State | 3*H*-$C_{13}H_{11}$ | | | 4*H*-$C_{13}H_{11}$ | | |
|---|---|---|---|---|---|---|
| | λ /nm | *f* | Assignment | λ /nm | *f* | Assignment |
| 1 | 560.7 | 0.008 | HOMO(α) → LUMO(α) | 533.6 | 0.000 | HOMO(α)→ LUMO(α)<br>HOMO(β)→LUMO(β) |
| 2 | 398.1 | 0.021 | HOMO(β)→LUMO(β)<br>HOMO(α)→ LUMO(α) | 405.3 | 0.102 | HOMO(α)→LUMO+1(α)<br>HOMO(β)→LUMO(β) |
| 3 | 368.5 | 0.010 | HOMO(α)→LUMO+1(α) | 374.3 | 0.229 | HOMO(α)→LUMO+1(α) |
| 4 | 360.5 | 0.005 | HOMO−1(α)→ LUMO(α)<br>HOMO(α)→LUMO+1(α)<br>HOMO(β)→LUMO+1(β) | 353.7 | 0.014 | HOMO−1(α) →LUMO(α)<br>HOMO(β)→LUMO+1(β) |
| 5 | 353.6 | 0.001 | HOMO(α)→LUMO+2(α) | 351.0 | 0.002 | HOMO(α)→LUMO+2(α) |
| 6 | 326.1 | 0.001 | HOMO(α) →LUMO+5(α) | 344.6 | 0.007 | HOMO−1(β)→LUMO(β) |
| 7 | 317.3 | 0.002 | HOMO(α)→LUMO+3(α)<br>HOMO (α)→LUMO+4(α) | 317.1 | 0.000 | HOMO(α)→LUMO+4(α) |
| 8 | 311.4 | 0.000 | HOMO(α)→LUMO+3(α) | 315.2 | 0.000 | HOMO(α)→LUMO+3(α) |
| 9 | 306.4 | 0.002 | HOMO−1(β) →LUMO(β) | 304.3 | 0.005 | HOMO (α)→LUMO+6(α)<br>HOMO(β) →LUMO+1(β)<br>HOMO−1(α) → LUMO(α) |
| 10 | 295.5 | 0.005 | HOMO−1(β)→ LUMO(β)<br>HOMO (β)→LUMO+2(β) | 292.7 | 0.000 | HOMO−2(α)→LUMO+1(α) |
| 11 | 287.0 | 0.001 | HOMO−2(α)→LUMO(α)<br>HOMO (β)→LUMO+2(β) | 286.8 | 0.003 | HOMO(α)→LUMO+5(α) |
| 12 | 284.5 | 0.000 | HOMO(α)→LUMO+6(α) | 279.4 | 0.003 | HOMO(α)→LUMO+5(α) |

**Table S16** Vertical excitation wavelength λ and oscillator strength *f* of 9a*H*-$C_{13}H_{11}$ and 4a*H*-$C_{13}H_{11}$ radicals calculated with the TD-B3LYP/6-311++G(d,p) method

| State | 9a*H*-$C_{13}H_{11}$ | | | 4a*H*-$C_{13}H_{11}$ | | |
|---|---|---|---|---|---|---|
| | λ /nm | *f* | Assignment | λ /nm | *f* | Assignment |
| 1 | 547.7 | 0.007 | HOMO(α) → LUMO(α) | 466.8 | 0.001 | HOMO(α)→ LUMO(α)<br>HOMO-1(β)→LUMO(β) |
| 2 | 410.1 | 0.144 | HOMO(α)→ LUMO(α)<br>HOMO(α)→LUMO+1(α)<br>HOMO(β) → LUMO(β) | 369.2 | 0.021 | HOMO(α)→LUMO(α) |
| 3 | 380.2 | 0.090 | HOMO(α) → LUMO+1(α) | 348.7 | 0.007 | HOMO(α)→LUMO+1(α)<br>HOMO(β)→LUMO(β) |
| 4 | 358.8 | 0.002 | HOMO−1(α)→LUMO+1(α) | 339.8 | 0.003 | HOMO(α) →LUMO+1(α)<br>HOMO-1(β)→LUMO(β) |
| 5 | 345 | 0.008 | HOMO−1(α)→LUMO(α)<br>HOMO(α)→LUMO+6(α) | 333.7 | 0.002 | HOMO(β)→LUMO+2(β)<br>HOMO-2(β)→LUMO+1(β) |
| 6 | 337.6 | 0.004 | HOMO(α)→ LUMO+2(α) | 326.5 | 0.005 | HOMO(α)→LUMO+2(α) |
| 7 | 311.7 | 0.005 | HOMO(α)→ LUMO+4(α)<br>HOMO−1(α) → LUMO(α) | 319.0 | 0.026 | HOMO(α)→LUMO+3(α) |
| 8 | 309.6 | 0.001 | HOMO(α)→ LUMO+3(α) | 308.1 | 0.000 | HOMO-2(β) →LUMO(β) |
| 9 | 307.5 | 0.002 | HOMO(α)→ LUMO+4(α)<br>HOMO(α)→ LUMO+6(α) | 298.6 | 0.006 | HOMO(α)→LUMO+5(α) |
| 10 | 297.5 | 0.001 | HOMO−1(α)→LUMO+1(α)<br>HOMO−1(β)→LUMO+2(β) | 296.7 | 0.004 | HOMO(α)→LUMO+4(α)<br>HOMO(α)→LUMO+6(α) |
| 11 | 290.3 | 0.010 | HOMO(α)→LUMO+5(α) | 290.7 | 0.003 | HOMO-3(β) →LUMO(β)<br>HOMO-3(α)→LUMO(α) |
| 12 | 280.6 | 0.020 | HOMO−2(β)→ LUMO(β) | 281.8 | 0.000 | HOMO(β) →LUMO+1(β) |

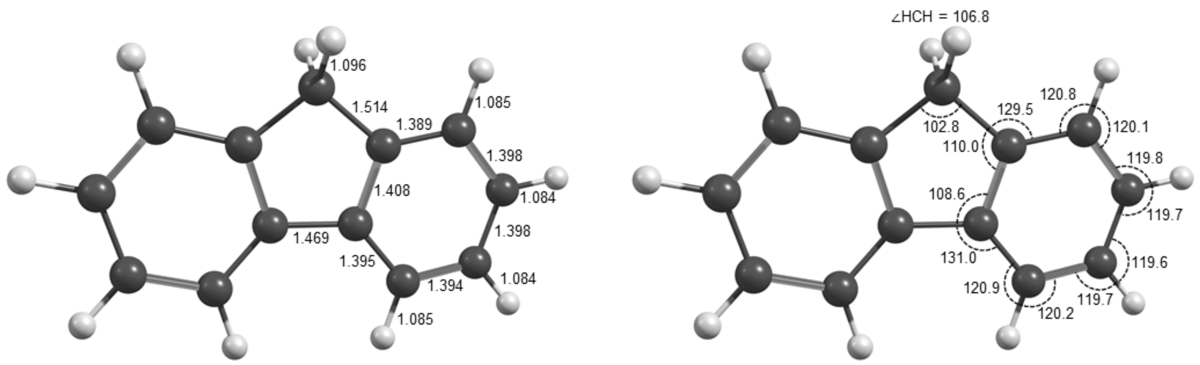



**Fig. S1** Optimized geometry of fluorene ($C_{13}H_{10}$) calculated at the B3LYP/6-311++G(d,p) level of theory. Bond lengths in Å are on the left and bond angles in degrees are on the right.

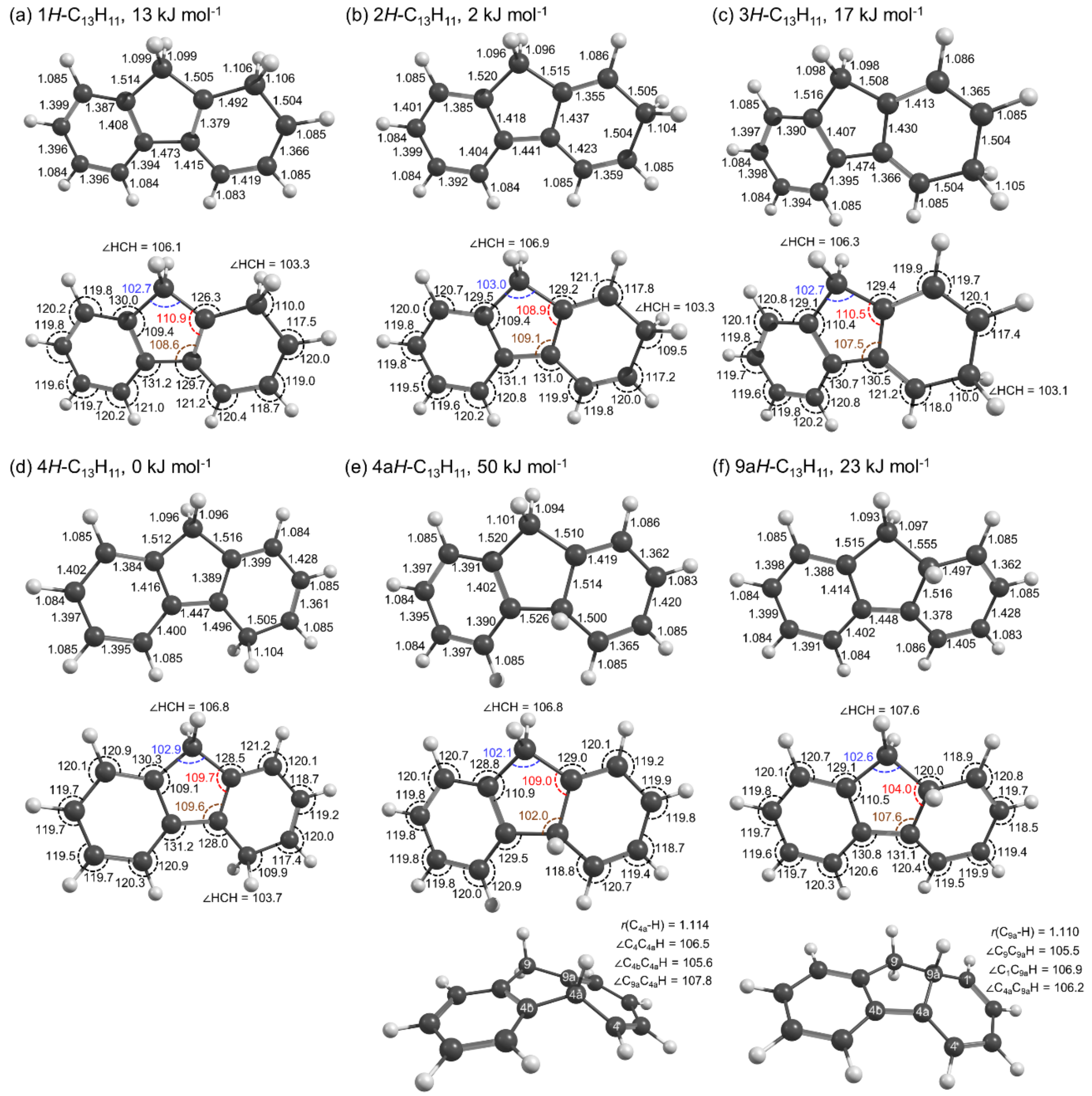



**Fig. S2** Optimized geometries of isomers of monohydrofluorenyl ($C_{13}H_{11}$) radicals calculated at the B3LYP/6-311++G(d,p) level of theory. (a) 1*H*-$C_{13}H_{11}$, (b) 2*H*-$C_{13}H_{11}$, (c) 3*H*-$C_{13}H_{11}$, (d) 4*H*-$C_{13}H_{11}$, (e) 9a*H*-$C_{13}H_{11}$, (f) 4a*H*-$C_{13}H_{11}$. Bond lengths in Å are on top, and bond angles in degrees are shown below.

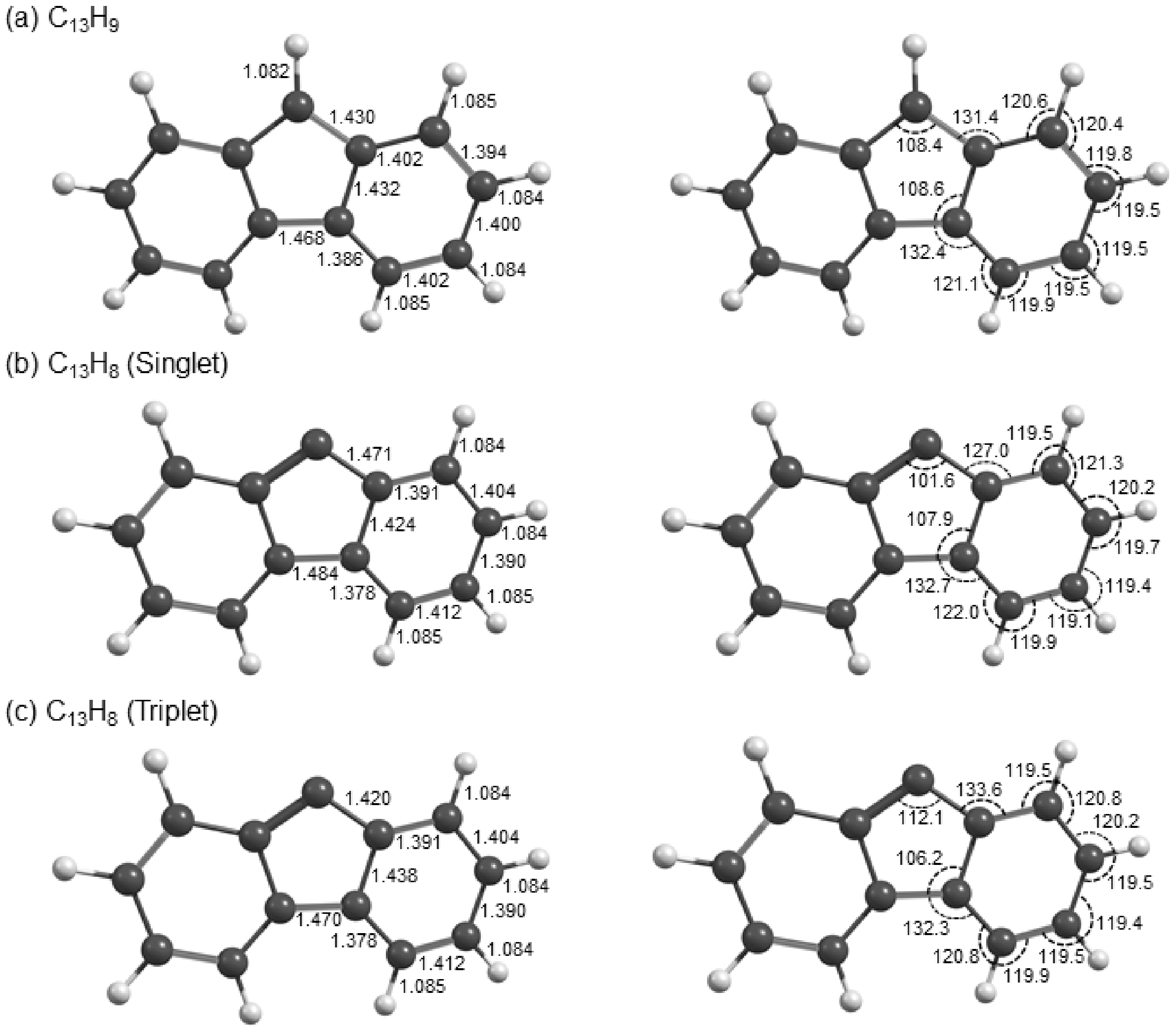



**Fig. S3** Optimized geometries of (a) $C_{13}H_9$, (b) $C_{13}H_8$ (singlet), and (c) $C_{13}H_8$ (triplet) calculated at the B3LYP/6-311++G(d,p) level of theory. Bond lengths in Å are on the left and bond angles in degrees are on the right.

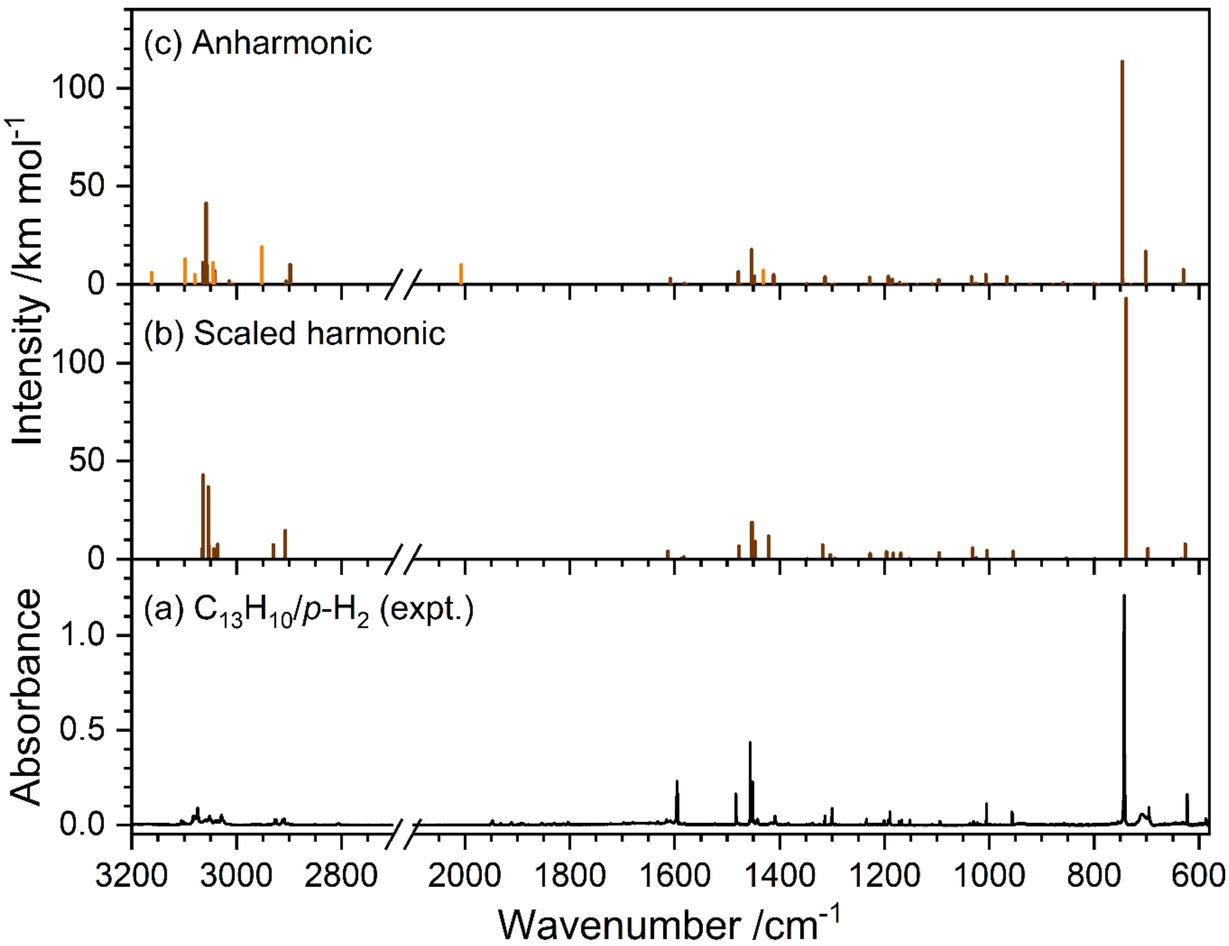
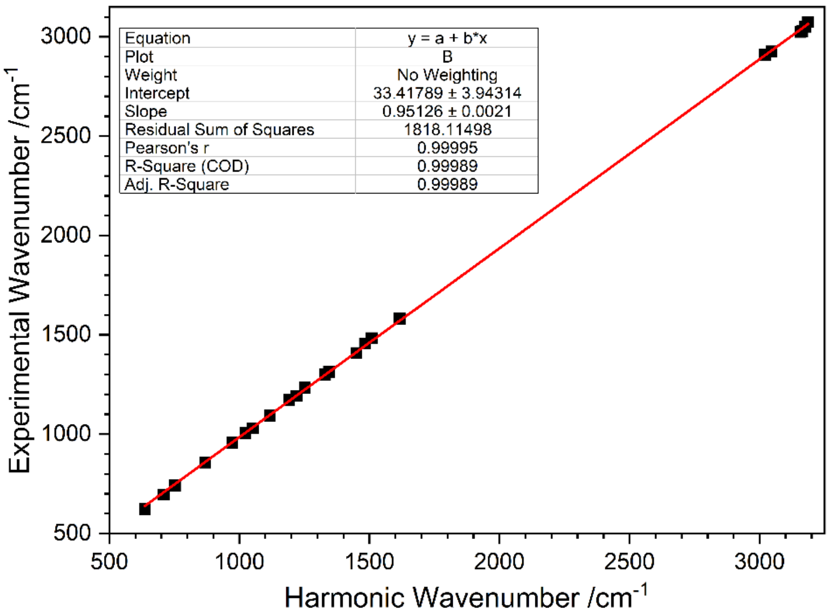



**Fig. S4** Comparison of experimental IR spectrum of fluorene ($C_{13}H_{10}$) in solid *p*-$H_2$ with scaled harmonic and anharmonic stick spectra computed using the B3LYP/6-311++G(d,p) method. The scaling equations for harmonic vibrational wavenumbers $x$ are $y = 0.9513\ x + 33.4$ for $x > 2000$ $cm^{-1}$ and $y = 0.9765\ x + 5.0$ for $x < 2000\ cm^{-1}$. Overtones and combination bands with an intensity $\geq 5$ km $mol^{-1}$ in the simulated anharmonic spectrum are indicated by orange sticks.

(a)




(b)

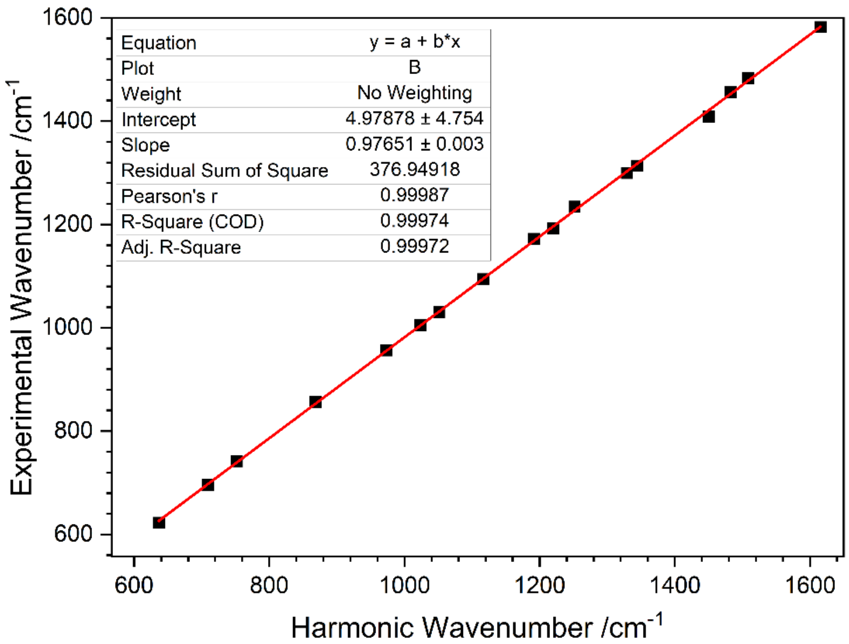
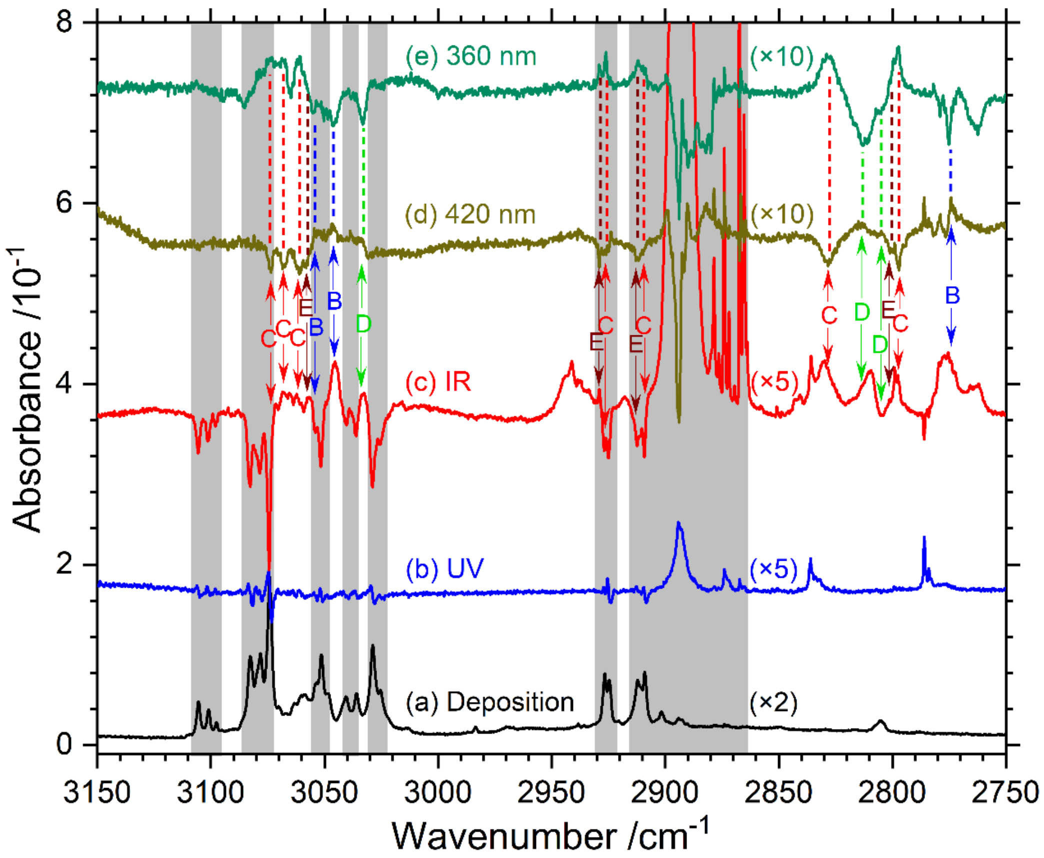
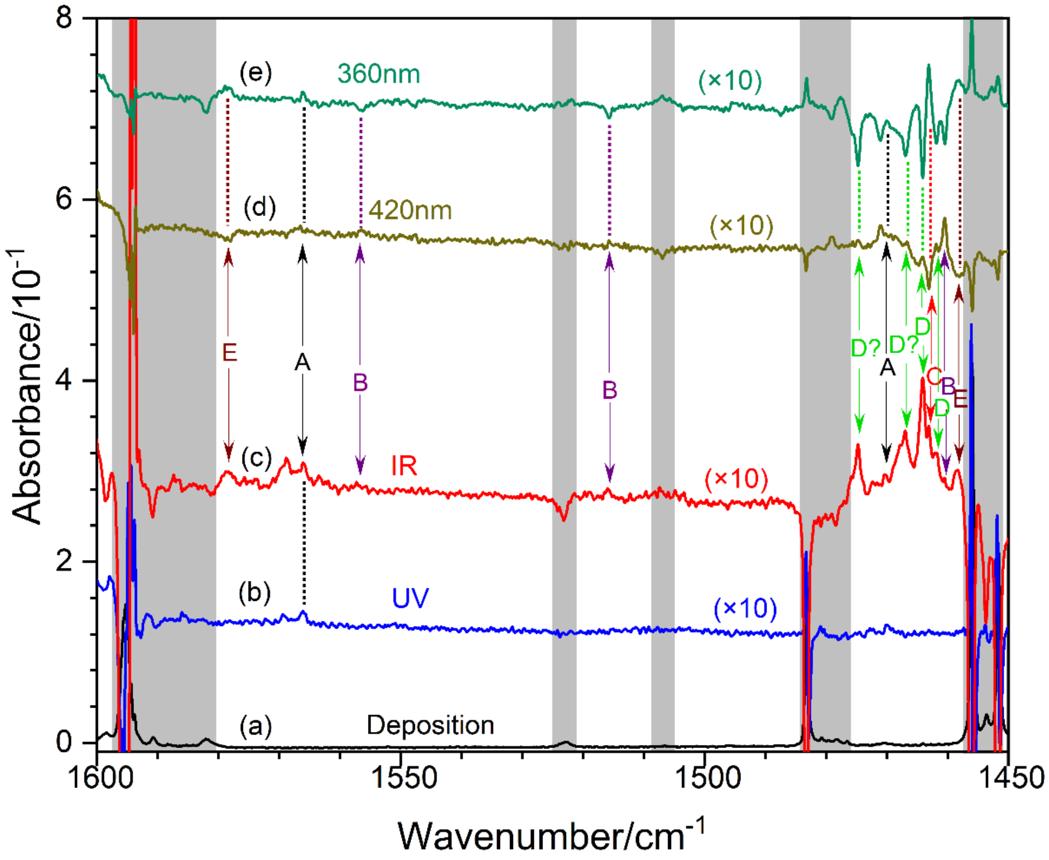
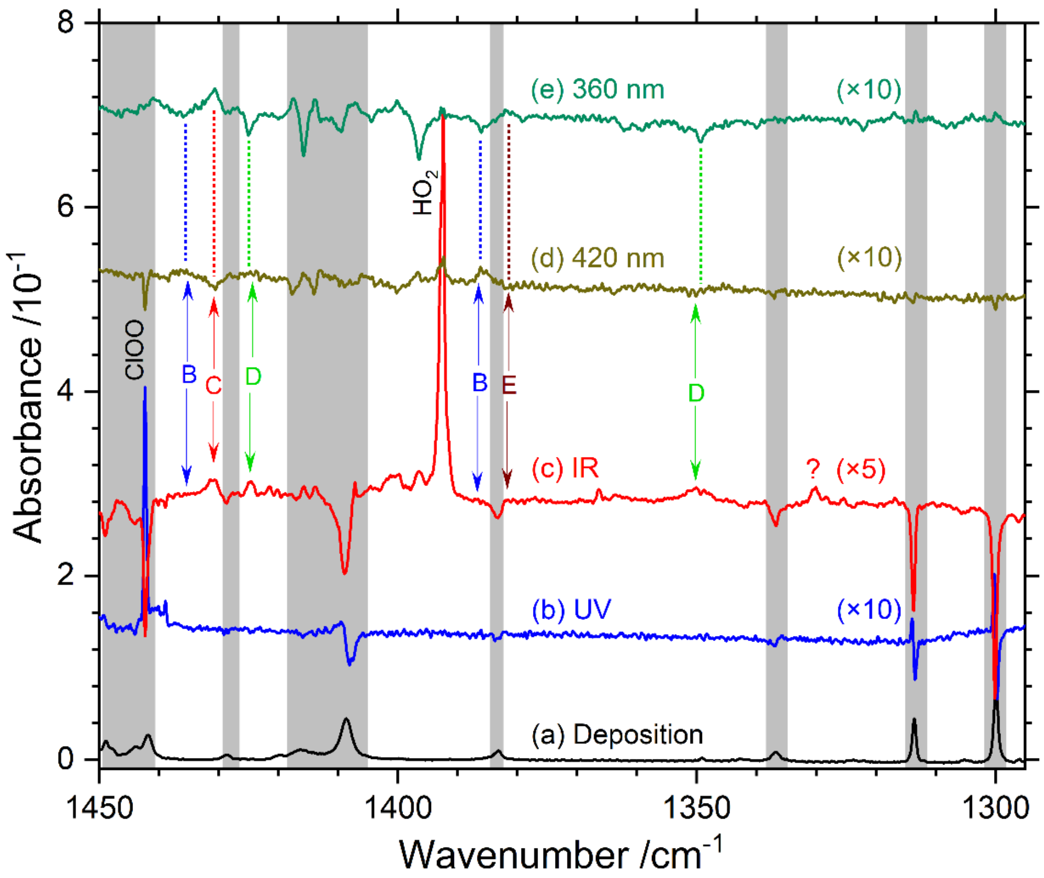
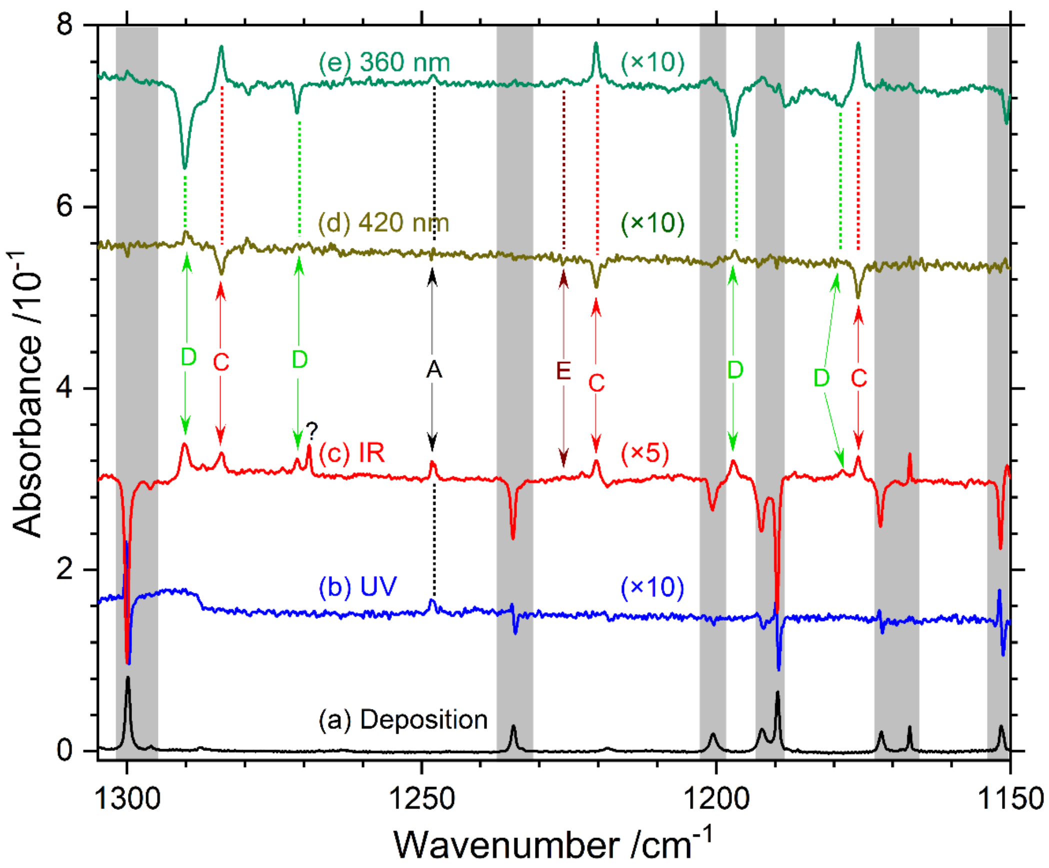



**Fig. S5** Linear plots of experimental wavenumbers of fluorene versus harmonic vibrational wavenumbers in (a) 600−3200 cm$^{-1}$ and (b) 600−2000 cm$^{-1}$ range. Harmonic vibrational wavenumbers $x$ were derived with the B3LYP/6-311++G(d,p) method. The linear regression yielded the following equations: $y = 0.9513\,x + 33.4$ for $x > 2000$ cm$^{-1}$ and $y = 0.9765\,x + 5.0$ for $x < 2000$ cm$^{-1}$.


(e) 360 nm
(×10)
(d) 420 nm
(×10)
(c) IR
(×5)
(b) UV
(×5)
(a) Deposition
(×2)
Absorbance /10-1
Wavenumber /cm-1


(e) 360nm
(×10)
(d) 420nm
(×10)
(c) IR
(×10)
(b) UV
(×10)
(a) Deposition
Absorbance/10-1
Wavenumber/cm-1


(e) 360 nm
(×10)
(d) 420 nm
(×10)
(c) IR
? (×5)
(b) UV
(×10)
(a) Deposition
ClOO
HO2
B
C
D
E
Absorbance /10-1
Wavenumber /cm-1


(e) 360 nm
(×10)
(d) 420 nm
(×10)
(c) IR
(×5)
(b) UV
(×10)
(a) Deposition
A
C
D
E
?
Absorbance /10-1
Wavenumber /cm-1

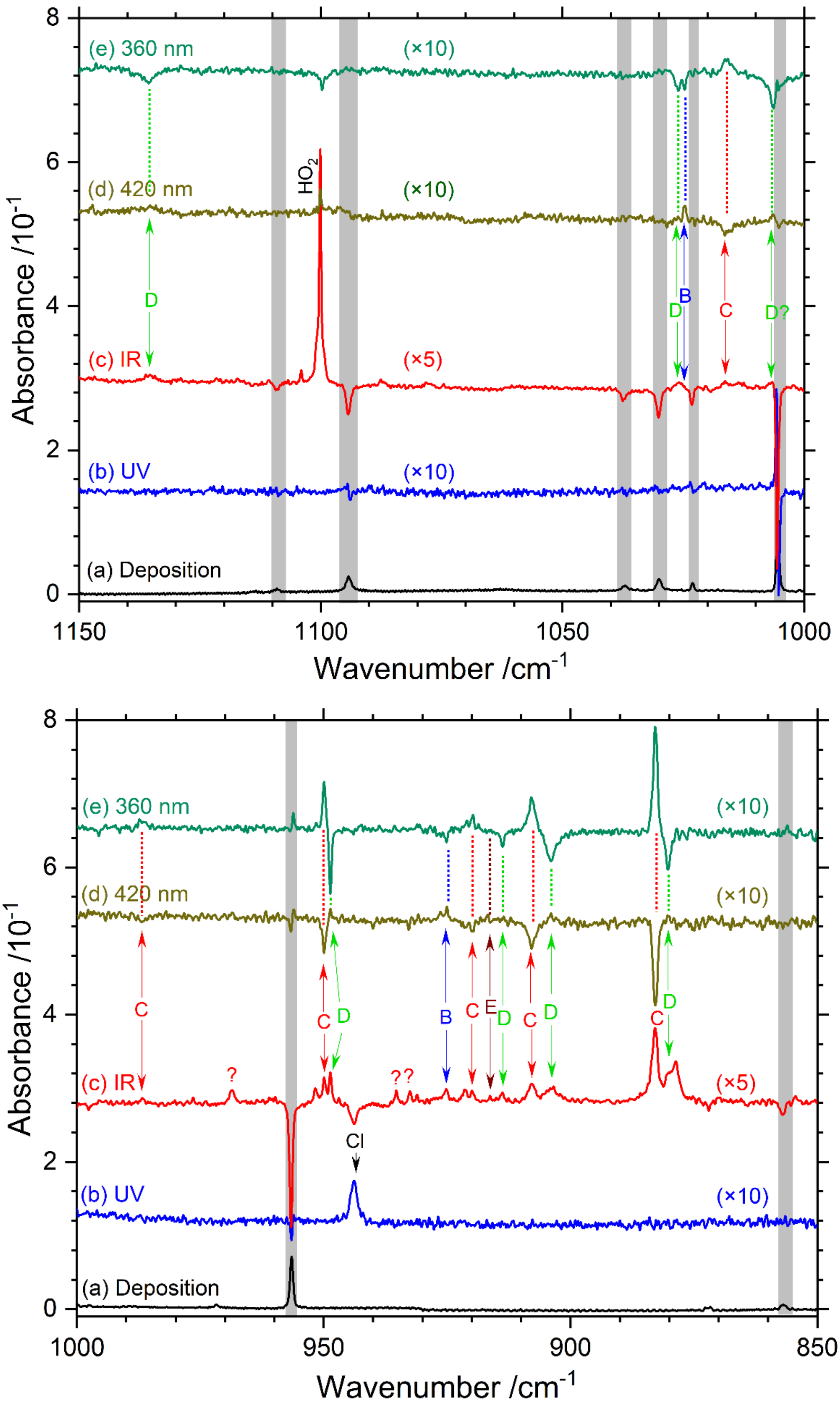

(e) 360 nm
(×10)
(d) 420 nm
(×10)
HO2
D
B
C
D?
(c) IR
(×5)
(b) UV
(×10)
(a) Deposition
Absorbance /10-1
Wavenumber /cm-1
1150
1100
1050
1000
0
2
4
6
8
(e) 360 nm
(×10)
(d) 420 nm
(×10)
C
C
D
B
C
E
D
C
D
C
D
?
??
(c) IR
(×5)
Cl
(b) UV
(×10)
(a) Deposition
Absorbance /10-1
Wavenumber /cm-1
1000
950
900
850

**Fig. S6** IR spectra of a $C_{13}H_{10}/Cl_2/p\text{-}H_2$ matrix in regions 3150−2750 and 1600−850 cm$^{-1}$ after various stages of the experiment. (a) After deposition at 3.5 K for 5 h. Difference spectra of the matrix after UV irradiation at 365 nm for 2 h (b), after subsequent IR irradiation for 170 min (c), after irradiation at 420 nm for 2h (d), and after irradiation at 360 nm for 75 min (e). The peak at 1442.3 cm$^{-1}$ is due to ClOO radical [Raston, Kettwich, and Anderson, *J. Mol. Spectrosc.* 2015, 310, 72]. The peak at 943.9 cm$^{-1}$ is due to the spin-orbit transition of the Cl atom [Raston and Anderson, *J. Chem. Phys*. 2007, 126, 021106]. Peaks at 1100.1 cm$^{-1}$ and 1392.4 cm$^{-1}$ are due to the $HO_2$ radical [Joshi and Lee, *J. Am. Chem. Soc.* 2024, 146, 23306]; the mixing ratio was estimated to be (16 ± 4) ppm. Lines in groups A ($C_{13}H_9$), B (1*H*-$C_{13}H_{11}$), C (2*H*-$C_{13}H_{11}$), D (3*H*-$C_{13}H_{11}$), and E (4*H*-$C_{13}H_{11}$) are labelled and designated with color-coded dashed lines. The regions interfered with by the intense absorption of the parent $C_{13}H_{10}$ are shaded gray.

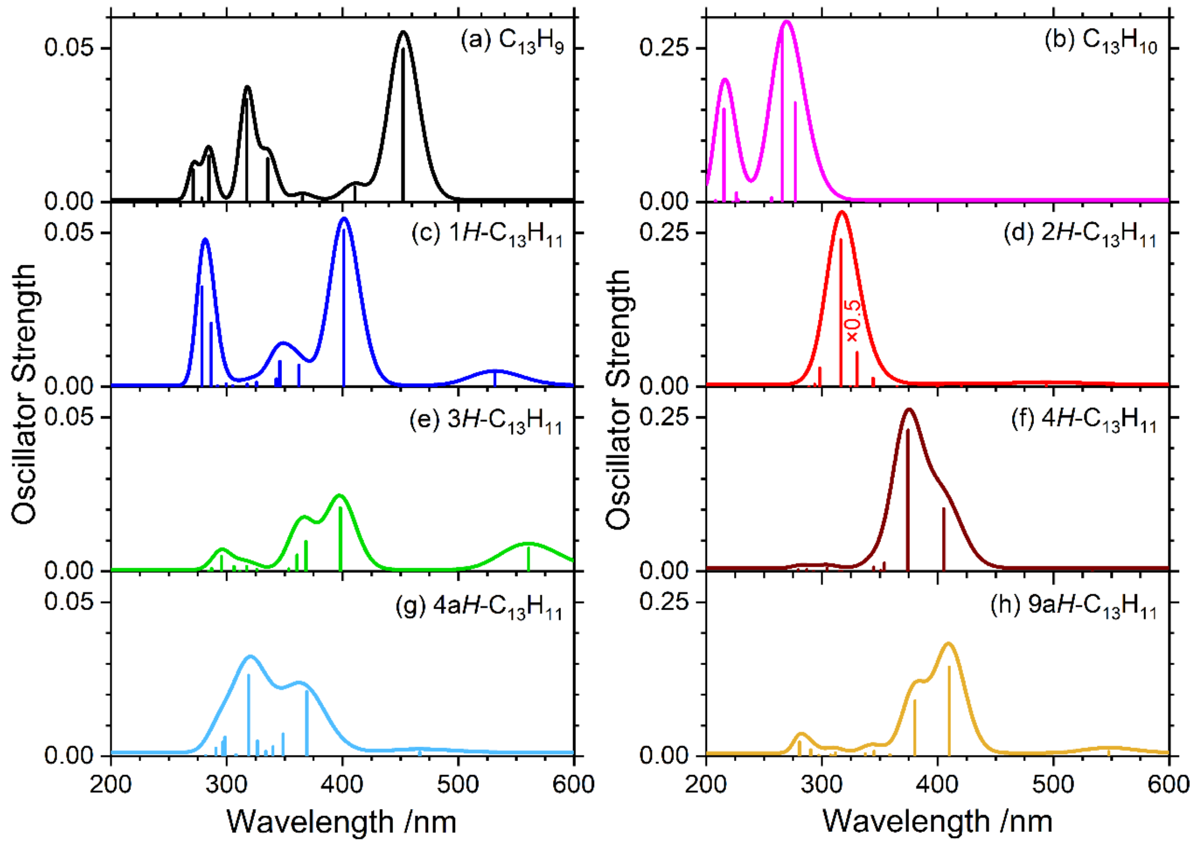



**Fig. S7** Predicted vertical electronic excitation spectra of fluorene ($C_{13}H_{10}$), 9*H*-fluoren-9-yl ($C_{13}H_9$) and monohydrofluorenyl (1*H*-, 2*H*-, 3*H*-, 4*H*-, 9a*H*-, and 4a*H*-$C_{13}H_{11}$) radicals using the TD-B3LYP/6-311++g(d,p) method. The spectra are fitted with a Gaussian function having a full width at half maximum (FWHM) of 30 $cm^{-1}$.