Table S1. Calculated frequencies (in cm^{-1}) and $<s^2>$ values for the reactants, products, transition states, and hydrogen-bonded complexes for the title reactions at the B3LYP/I level.

species	B3LYP/I	$<s^2>$
CH_3I	528, 888, 889, 1277, 1469, 4169, 3082, 3192, 3193	0.0
C_2H_5I	252, 252, 495, 747, 968, 991, 1062, 1235, 1255, 1411, 1480, 1484, 1494, 3016, 3081, 3100, 3110, 3160	0.0
NO_3	272, 295, 800, 1092, 1118, 1135	0.756
CH_2I	166, 611, 849, 1351, 3159, 3315	0.756
CH_3CHI	141, 264, 339, 552, 991, 998, 1097, 1241, 1402, 1461, 1478, 2966, 3040, 3081, 3202	0.755
CH_2CH_2I	70, 114, 231, 836, 964, 993, 1005, 1239, 1362, 1474, 1639, 3139, 3147, 3218, 3244	0.752
HNO_3	457, 586, 648, 773, 896, 1319, 1348, 1756, 3729	0.0
CH_3NO_3	131, 198, 336, 569, 661, 768, 863, 1013, 1163, 1188, 1324, 1458, 1470, 1498, 1714, 3052, 3136, 3156	0.0
$CH_3CH_2NO_3$	84, 122, 223, 253, 370, 566, 704, 768, 827, 869, 919, 1023, 1139, 1175, 1288, 1315, 1398, 1423, 1484, 1499, 1519, 1704, 3043, 3058, 3101, 3110, 3126	0.0
TS1a	1428*i*, 24, 64, 72, 120, 414, 433, 602, 684, 736, 784, 893, 928, 994, 1191, 1307, 1368, 1379, 1626, 3107, 3220	0.756
TS2a	1536*i*, 15, 51, 79, 168, 406, 455, 595, 679, 711, 786, 907, 934, 988, 1197, 1305, 1379, 1394, 1624, 3100, 3213	0.756
TS3a	683*i*, 44, 64, 88, 125, 168, 223, 600, 680, 786, 858, 968, 985, 1060, 1261, 1377, 1404, 1551, 3123, 3296, 3325	0.774
TS1b	1193*i*, 28, 58, 73, 128, 172, 225, 272, 433, 549, 686, 740, 786, 809, 946, 975, 1051, 1069, 1199, 1275, 1308, 1348, 1400, 1471, 1480, 1613, 3018, 3080, 3109, 3128	0.756
TS2b	1072*i*, 36, 48, 54, 109, 148, 191, 474, 490, 549, 681, 760, 773, 784, 937, 981, 1028, 1068, 1188, 1247, 1257, 1309, 1339, 1464, 1493, 1617, 3078, 3123, 3156, 3201	0.758
TS3b	1370*i*, 23, 46, 86, 105, 192, 271, 432, 493, 504, 674, 727, 742, 780, 908, 972, 997, 1046, 1138, 1231, 1250, 1319, 1334, 1430, 1449, 1641, 3047, 3055, 3139, 3153	0.756
TS4b	563*i*, 33, 53, 64, 93, 142, 174, 202, 284, 608, 693, 793, 818, 893, 931, 975, 1025, 1069, 1197, 1259, 1403, 1447, 1475, 1491, 1526, 3035, 3103, 3139, 3172, 3260	0.777
EP1a	21, 30, 58, 63, 123, 225, 575, 606, 610, 631, 663, 779, 864, 910, 1333, 1357, 1366, 1738, 3135, 3281, 3446	0.755
EP2a	28, 36, 60, 80, 103, 241, 589, 604, 616, 628, 658, 779, 870, 903, 1326, 1345, 1359, 1731, 3118, 3262, 3481	0.755
EP3a	12, 23, 36, 142, 198, 337, 570, 663, 768, 864, 1012, 1168, 1189, 1323, 1457, 1470, 1497, 1711, 3055, 3140, 3158	0.752

EP1b	21, 39, 48, 67, 90, 135, 189, 271, 526, 585, 610, 660, 665, 782, 913, 988, 1003, 1090, 1247, 1333, 1368, 1399, 1468, 1473, 1734, 2976, 3053, 3096, 3172, 3404	0.755
EP2b	21, 23, 29, 47, 57, 70, 111, 112, 265, 561, 599, 658, 779, 837, 903, 991, 1012, 1033, 1241, 1332, 1358, 1363, 1474, 1640, 1746, 3134, 3142, 3213, 3239, 3594	0.752
EP3b	27, 40, 53, 55, 59, 68, 96, 134, 297, 581, 610, 671, 782, 836, 921, 987, 996, 1006, 1241, 1333, 1355, 1362, 1467, 1624, 1730, 3142, 3149, 3226, 3251, 3456	0.752
EP4b	23, 28, 58, 91, 124, 227, 251, 375, 567, 708, 768, 826, 875, 916, 1020, 1137, 1174, 1289, 1308, 1398, 1422, 1484, 1498, 1518, 1689, 3043, 3062, 3105, 3111, 3129	0.752

Table S2. The vertical excitation energy T_V in eV and oscillator strength f in atomic units for the first 15 excited states of CH_3I, C_2H_5I, EP1a, EP2a, EP1b, EP2b, and EP3b.

Excited states	CH_3I	C_2H_5I	EP1a	EP2a	EP1b	EP2b	EP3b
	T_V						
1	4.6555	4.6442	2.9140	2.9282	3.1866	0.5116	0.9295
2	4.6556	4.6811	3.6263	3.6422	3.3269	0.5553	1.1049
3	6.0560	5.9520	3.6671	3.7186	3.4963	3.4077	3.3507
4	6.0562	5.9920	3.7402	3.7775	3.7964	3.7339	3.5105
5	7.0910	6.6455	3.8959	3.9212	3.9235	3.9187	3.9302
6	7.0910	6.6852	4.1513	4.1441	4.1336	4.0398	4.0054
7	7.1176	6.8049	4.6406	4.6594	4.6565	4.1587	4.0744
8	7.1305	6.8252	4.7217	4.6714	4.7002	4.2451	4.1183
9	7.3913	6.8900	4.7398	4.7237	4.7751	4.2900	4.2667
10	7.3916	6.9069	4.8610	4.9283	4.8172	4.3318	4.4050
11	7.8962	7.4089	4.9117	4.9794	5.0019	4.4965	4.4623
12	7.8963	7.5430	5.1862	5.2116	5.0320	4.5398	4.4680
13	7.9586	7.5613	5.2807	5.2920	5.1004	4.5436	4.6358
14	8.0588	7.6038	5.3326	5.3369	5.1453	4.6827	4.6452
15	8.0880	7.7124	5.3717	5.3614	5.2649	4.7393	4.6733
	f						
1	0.0001	0.0	0.0	0.0	0.0	0.0	0.0002
2	0.0001	0.0	0.0089	0.0137	0.0002	0.0001	0.0
3	0.0565	0.045	0.0083	0.0002	0.0	0.2093	0.1272
4	0.0565	0.0573	0.055	0.0475	0.0569	0.0001	0.0786
5	0.0001	0.0059	0.0	0.0	0.0	0.0	0.0
6	0.0001	0.0038	0.0	0.0	0.0	0.0012	0.0029
7	0.0	0.0184	0.0	0.0	0.0	0.0	0.0
8	0.0387	0.0072	0.0001	0.0001	0.0	0.0	0.0
9	0.0696	0.0558	0.0	0.0024	0.0001	0.0029	0.0
10	0.0697	0.0576	0.0001	0.0001	0.0001	0.0	0.0012
11	0.0055	0.1918	0.0001	0.0001	0.0026	0.0	0.0001
12	0.0055	0.0013	0.0	0.0	0.001	0.0044	0.0
13	0.1251	0.0312	0.0011	0.0011	0.0004	0.0002	0.0013
14	0.0	0.0209	0.0001	0.0	0.0018	0.0004	0.0
15	0.0036	0.0799	0.0	0.0	0.0002	0.0	0.0

Figure S1. Classical potential energy curve (V_{MEP}), ground-state vibrational adiabatic energy curve (V_a^G), and zero-point energy curve (ZPE) as functions of s (amu)$^{1/2}$bohr at the CCSD(T)/II//B3LYP/I level for the reaction channels R1a (a), and R1b (b).

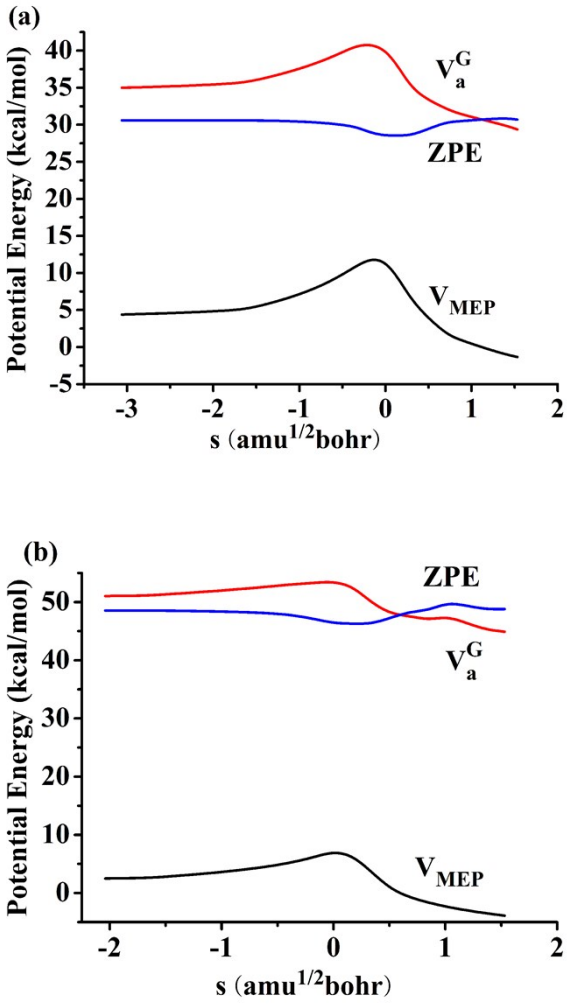

Figure S2. Changes of generalized normal-mode vibrational frequencies as functions of *s* (amu)$^{1/2}$bohr at the CCSD(T)/II//B3LYP/I level for reaction R1a via TS1a (a), and R1b via TS1b (b).

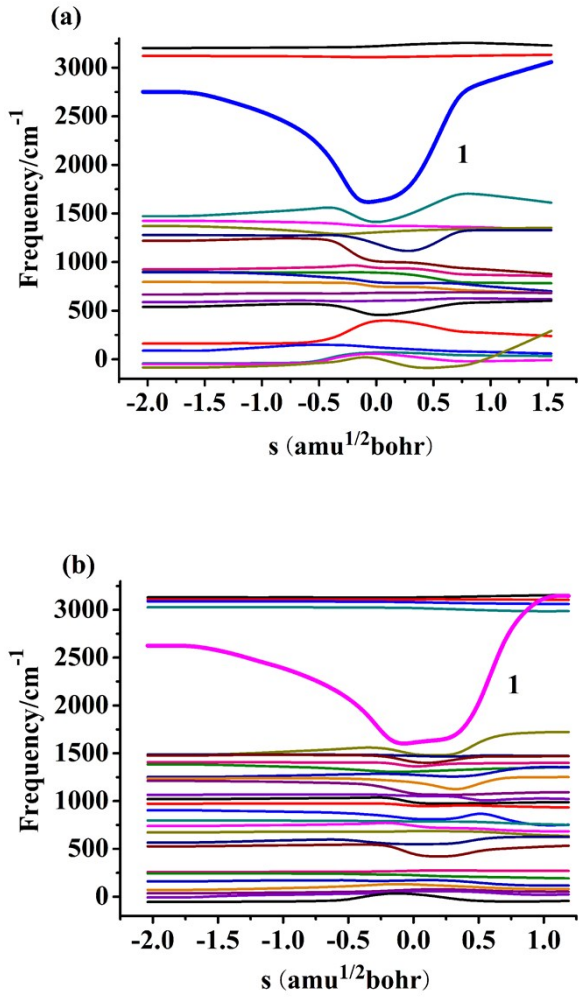

Figure S3. The wavelength in nm and oscillator strength in atomic unit at the TD-B3LYP level (a) for CH_3I, C_2H_5I; (b) for EP1a, EP2a; (c) for EP1b, EP2b, and EP3b.