Supporting Information for:

Kinetics and Mechanisms of the Allyl + Allyl and Allyl + Propargyl Recombination Reactions

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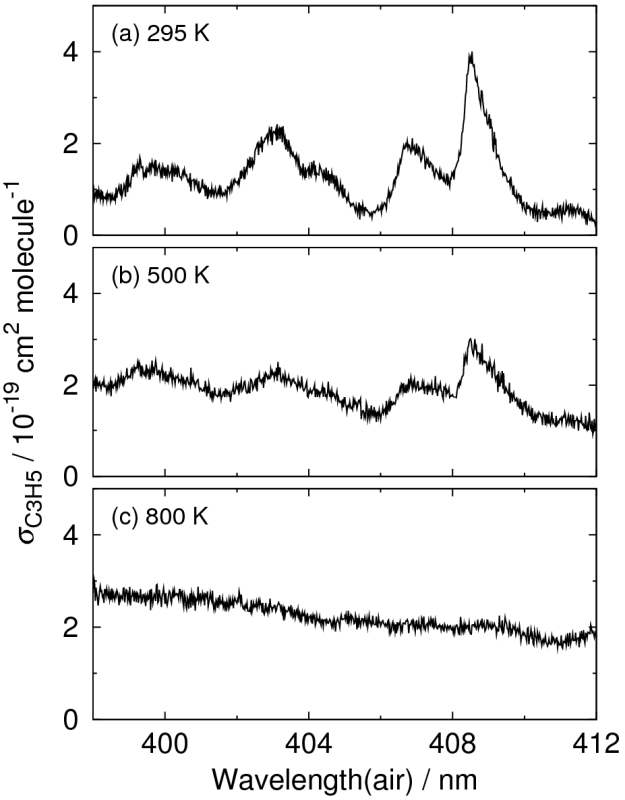


Figure S1. Absorption spectra of the allyl radical produced by the photolysis of 1,5-hexadiene at 295 K (a), 500 K (b) and 800 K (c).

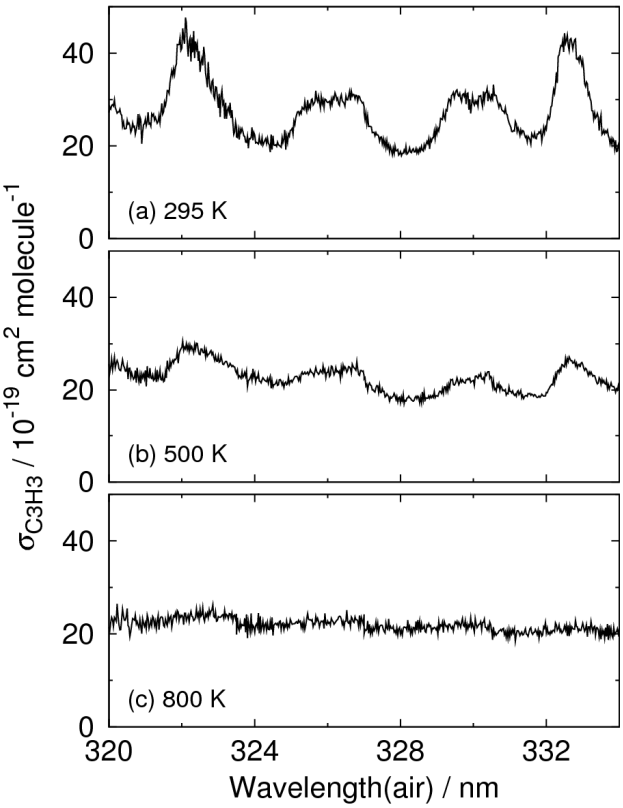


Figure S2. Absorption spectra of the propargyl radical produced by the photolysis of C_3H_3Cl at 295 K (a), 500 K (b) and 800 K (c).

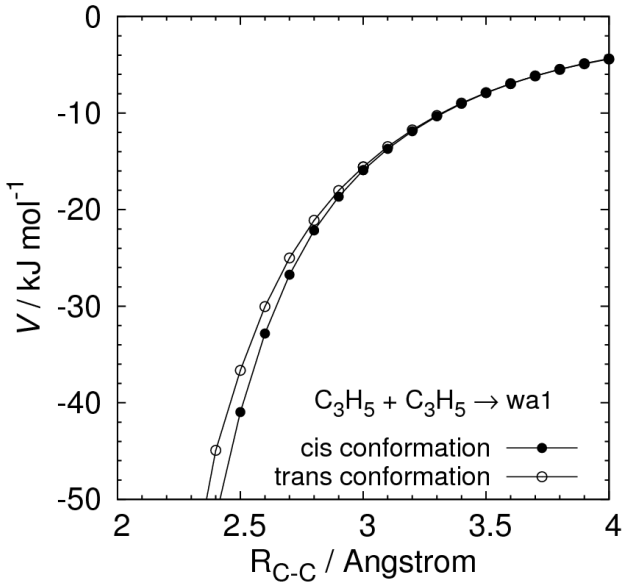


Figure S3. The potential energy curves for the C_3H_5 + C_3H_5 recombination as a function of the length of the newly formed C-C bond.

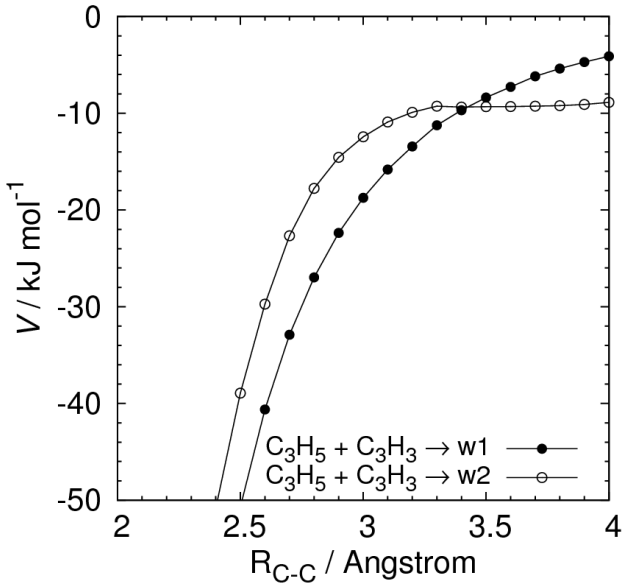


Figure S4. The potential energy curves for the C_3H_5 + C_3H_3 recombination as a function of the length of the newly formed C-C bond.

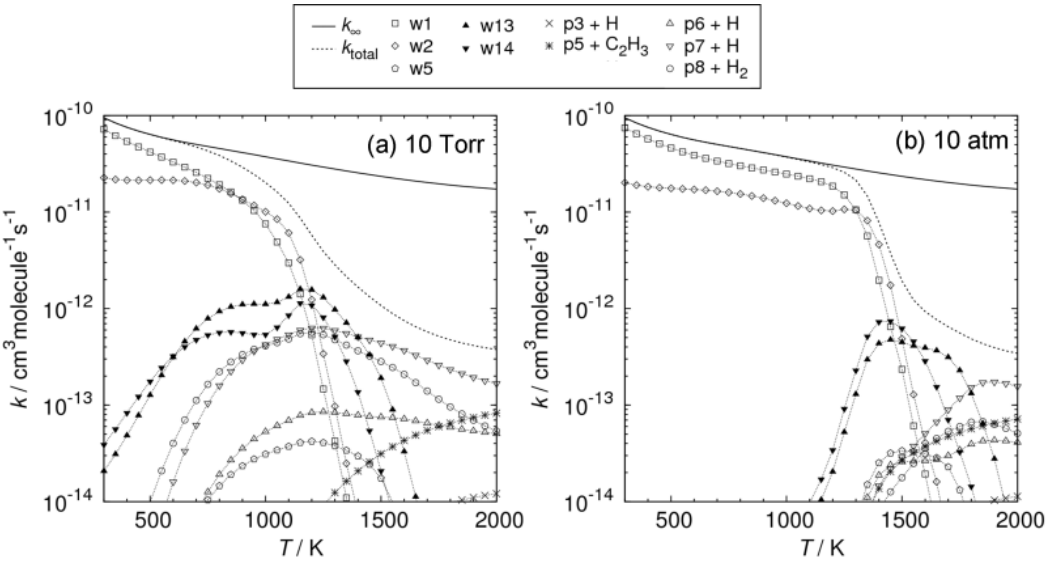


Figure S5. Product specific rate constants of C_3H_5 + C_3H_3 reaction at (a) 10 Torr and (b) 10 atm pressure (N_2).

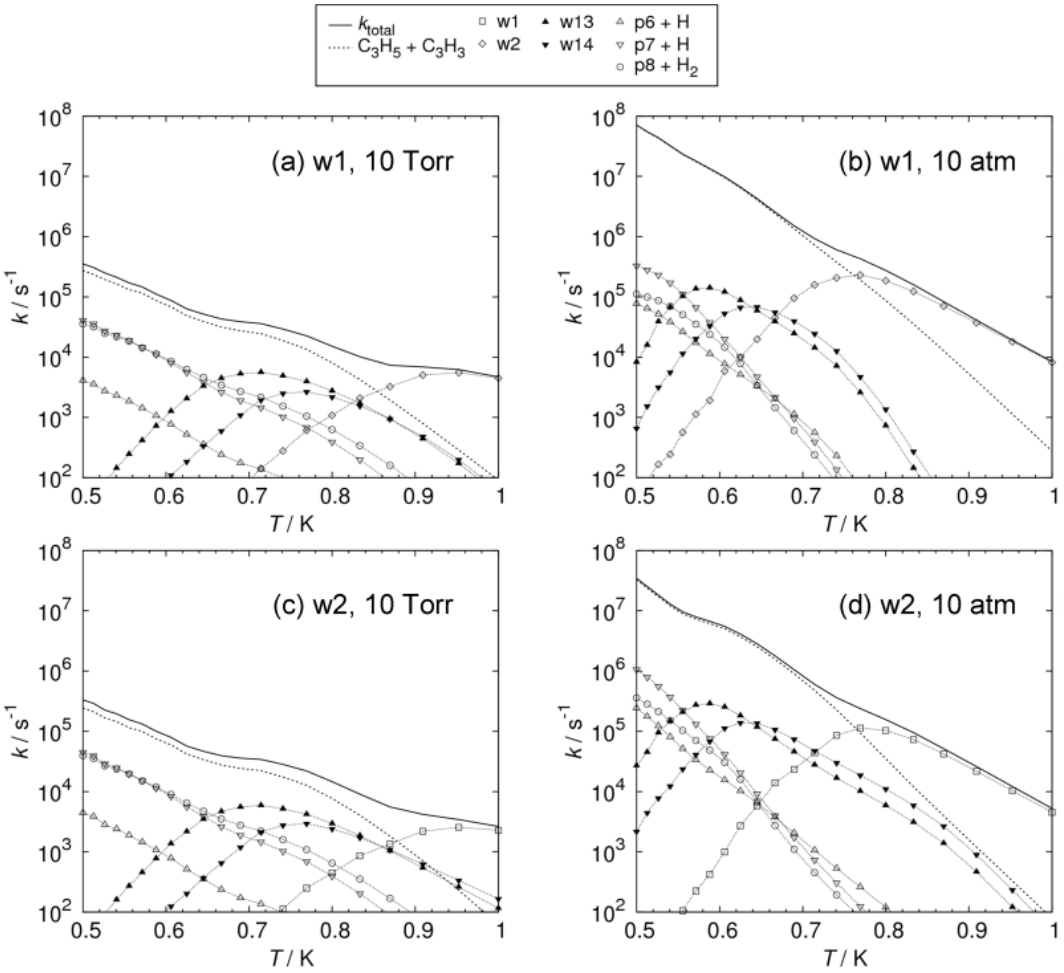


Figure S6. Product specific rate constants for the steady-state isomerization / dissociation reactions of w1and w2 at 10 Torr and 10 atm total pressure (N_2).

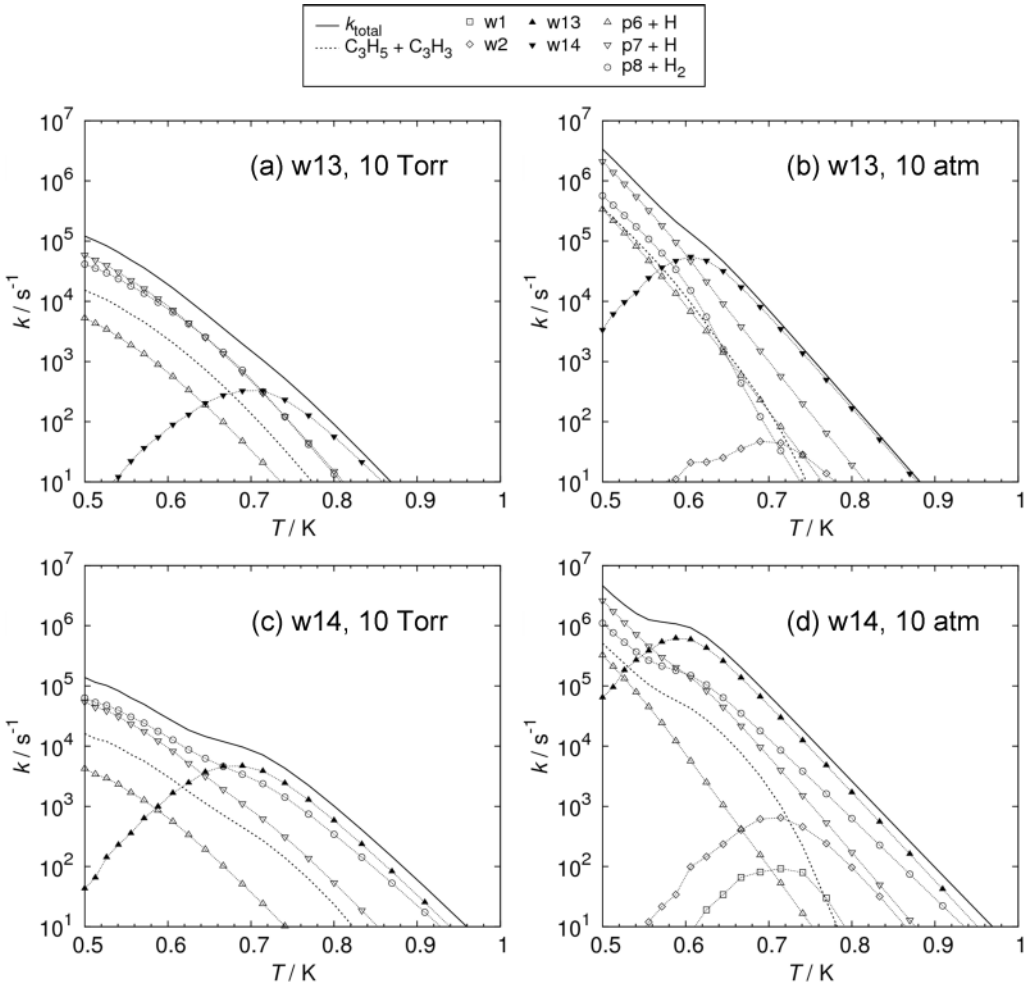


Figure S7. Product specific rate constants for the steady-state isomerization / dissociation reactions of w13and w14 at 10 Torr and 10 atm total pressure (N_2).

Table S1. Rotational constants and vibrational frequencies of the reactant, products, intermediates and the transition states for the $C_3H_5 + C_3H_5$ and $C_3H_5 + C_3H_3$ reactions.[a]

speies	rotational constant (GHz)	frequencies[b] (cm^{-1})
C_3H_5	55.07, 10.34, 8.70	429, 531, 552, 785, 811, 936, 1013, 1037, 1207, 1270, 1423, 1511, 1517, 3128, 3134, 3140, 3232, 3235
C_3H_3	290.03, 9.58, 9.27	351, 403, 468, 637, 682, 1031, 1089, 1455, 2011, 3139, 3229, 3468
wa1	12.85, 1.39, 1.35	75, 98, 116, 219, 348, 416, 438, 634, 665, 787, 930, 941, 945, 952, 963, 1022, 1032, 1034, 1090, 1177, 1242, 1276, 1311, 1323, 1329, 1363, 1449, 1452, 1481, 1496, 1706, 1709, 2998, 3001, 3049, 3066, 3111, 3112, 3125, 3125, 3207, 3207
wa2	8.49, 1.68, 1.49	76, 130, 157, 211, 280, 315, 465, 548, 600, 783, 893, 915, 944, 966, 1005, 1034, 1046, 1068, 1107, 1136, 1226, 1316, 1328, 1335, 1367, 1414, 1444, 1468, 1481, 1494, 1705, 1738, 2985, 3011, 3015, 3053, 3088, 3109, 3117, 3119, 3135, 3214
wa3	9.10, 2.07, 1.90	67, 191, 211, 272, 322, 400, 545, 654, 773, 812, 884, 902, 936, 957, 1015, 1026, 1064, 1092, 1107, 1127, 1139, 1196, 1233, 1330, 1351, 1412, 1431, 1454, 1491, 1494, 1504, 1701, 3015, 3071, 3078, 3104, 3115, 3121, 3132, 3135, 3202, 3214
wa4[c]	5.21, 3.63, 2.86	138, 156, 183, 338, 369, 389, 520, 669, 709, 793, 822, 886, 893, 909, 973, 995, 1036, 1043, 1062, 1128, 1173, 1206, 1244, 1271, 1301, 1331, 1353, 1370, 1457, 1470, 1472, 1498, 2926, 2972, 2992, 3007, 3022, 3034, 3087, 3128, 3188, 3230
wa5	5.27, 4.43, 3.97	307, 432, 499, 643, 822, 830, 833, 843, 849, 903, 940, 967, 972, 973, 1030, 1076, 1078, 1101, 1144, 1150, 1219, 1236, 1238, 1257, 1279, 1287, 1318, 1335, 1490, 1497, 1505, 1532, 3033, 3037, 3038, 3048, 3071, 3089, 3095, 3095, 3096, 3105
wa6	5.74, 3.48, 2.67	92, 255, 343, 383, 403, 684, 708, 778, 802, 893, 916, 936, 974, 975, 986, 1037, 1095, 1115, 1129, 1194, 1239, 1254, 1313, 1326, 1362, 1378, 1408, 1485, 1492, 1501, 1503, 1683, 2997, 2999, 3015, 3030, 3031, 3047, 3081, 3081, 3164, 3189
wa7	6.67, 3.16, 2.36	114, 237, 288, 342, 498, 588, 739, 760, 823, 852, 906, 943, 965, 978, 996, 1066, 1104, 1119, 1142, 1200, 1229, 1302, 1312, 1326, 1341, 1384, 1411, 1485, 1498, 1500, 1504, 1677, 2965, 2997, 3016, 3028, 3047, 3080, 3080, 3085, 3160, 3186
pa1	8.88, 1.74, 1.55	57, 127, 154, 269, 304, 469, 541, 546, 595, 758, 796, 875, 919, 947, 967, 998, 1035, 1061, 1129, 1205, 1210, 1285, 1310, 1329, 1374, 1442, 1464, 1500, 1520, 1704, 2964, 3014, 3113, 3120, 3132, 3136, 3139, 3214, 3234
pa2	6.65, 3.37, 2.51	73, 254, 313, 378, 503, 609, 658, 694, 800, 819, 896, 912, 948, 989, 1027, 1068, 1073, 1102, 1122, 1199, 1272, 1297, 1316, 1333, 1399, 1408, 1474, 1483, 1498, 1501, 2975, 2991, 3017, 3019, 3081, 3086, 3178, 3196, 3209
pa3	7.27, 3.14, 2.28	110, 142, 234, 317, 456, 591, 609, 771, 799, 858, 911, 922, 964, 975, 1002, 1041, 1077, 1147, 1220, 1225, 1281, 1294, 1309, 1413, 1427, 1463, 1471, 1473, 1491, 1517, 2982, 2990, 3001, 3006, 3010, 3025, 3088, 3172, 3208
TS(wa1-wa2)	8.89, 1.63, 1.47	1108i, 55, 127, 153, 256, 301, 442, 488, 507, 555, 602, 635, 756, 860, 907, 938, 954, 1033, 1050, 1128, 1161, 1234, 1267, 1278, 1300, 1324, 1368, 1435, 1451, 1465, 1554, 1703, 2617, 2931, 3004, 3098, 3115, 3132, 3155, 3159, 3212, 3265
TS(wa1-wa3)	7.83, 1.96, 1.83	1107i, 90, 187, 214, 313, 413, 551, 599, 607, 664, 741, 817, 852, 896, 945, 974, 1013, 1024, 1030, 1054, 1100, 1177, 1223, 1293, 1314, 1364, 1397, 1434, 1444, 1463, 1520, 1613, 1789, 2959, 2990, 2992, 3081, 3115, 3139, 3145, 3191, 3223
TS(wa1-wa4)[c]	5.93, 3.25, 2.43	632i, 133, 278, 327, 401, 412, 523, 545, 682, 696, 782, 868, 882, 914, 953, 967, 995, 1092, 1141, 1156, 1173, 1203, 1237, 1244, 1296, 1316, 1371, 1399, 1479, 1486, 1493, 1499, 2995, 3029, 3055, 3064, 3083, 3087, 3117, 3125, 3147, 3220
TS(wa4-wa5)[c]	4.97, 3.95, 3.19	230i, 186, 311, 374, 420, 532, 587, 692, 758, 804, 868, 895, 921, 948, 958, 973, 1019, 1044, 1073, 1142, 1151, 1209, 1249, 1255, 1293, 1329, 1333, 1359, 1461, 1476, 1484, 1507, 2925, 2957, 2960, 3035, 3038, 3057, 3082, 3120, 3169, 3224

Table S1. (Continued.)

speies	rotational constant (GHz)	frequencies[b] (cm^{-1})
TS(wa4-wa6)[c]	5.10, 3.97, 3.24	1556i, 271, 361, 418, 456, 487, 598, 689, 760, 788, 856, 882, 915, 933, 938, 961, 1024, 1051, 1058, 1113, 1140, 1155, 1210, 1252, 1277, 1291, 1313, 1336, 1398, 1453, 1468, 1508, 1688, 2994, 3022, 3026, 3042, 3091, 3107, 3129, 3187, 3199
TS(wa4-wa7)[c]	5.65, 3.60, 2.74	1734i, 133, 174, 353, 419, 538, 636, 650, 736, 771, 799, 852, 903, 911, 935, 960, 983, 1059, 1080, 1103, 1178, 1197, 1251, 1279, 1294, 1315, 1331, 1345, 1397, 1440, 1470, 1498, 1772, 2945, 3027, 3045, 3067, 3085, 3113, 3118, 3173, 3217
w1	17.66, 1.40, 1.38	78, 97, 153, 305, 343, 414, 513, 644, 664, 675, 776, 936, 949, 956, 999, 1019, 1034, 1134, 1230, 1282, 1311, 1328, 1367, 1454, 1477, 1492, 1709, 2222, 3017, 3025, 3047, 3076, 3113, 3127, 3209, 3477
w2	16.88, 1.42, 1.39	60, 87, 199, 295, 343, 406, 557, 572, 669, 870, 874, 910, 939, 948, 1008, 1020, 1035, 1124, 1146, 1239, 1299, 1324, 1369, 1449, 1476, 1477, 1703, 2051, 3017, 3060, 3112, 3119, 3122, 3131, 3182, 3208
w3	26.77, 1.34, 1.27	98, 148, 223, 253, 353, 445, 545, 615, 709, 900, 924, 930, 946, 966, 979, 1023, 1054, 1157, 1218, 1283, 1313, 1325, 1330, 1434, 1466, 1635, 1685, 1689, 3121, 3121, 3129, 3134, 3136, 3137, 3221, 3221
w4	15.02, 1.57, 1.42	102, 152, 163, 332, 352, 395, 604, 689, 733, 845, 893, 929, 933, 965, 983, 1027, 1039, 1102, 1213, 1286, 1309, 1343, 1390, 1435, 1488, 1622, 1678, 1687, 3125, 3132, 3133, 3145, 3147, 3159, 3220, 3221
w5	5.55, 2.87, 1.96	101, 151, 248, 305, 377, 504, 525, 637, 764, 781, 794, 925, 939, 943, 954, 1026, 1033, 1059, 1089, 1289, 1325, 1332, 1418, 1455, 1464, 1644, 1685, 1695, 3127, 3132, 3136, 3140, 3145, 3217, 3223, 3228
w6[c]	5.05, 3.92, 2.43	139, 149, 221, 314, 380, 527, 545, 570, 665, 698, 774, 782, 825, 896, 956, 974, 1034, 1065, 1162, 1176, 1208, 1253, 1311, 1341, 1400, 1462, 1468, 1506, 3008, 3039, 3051, 3130, 3136, 3180, 3228, 3233
w7[c]	6.51, 3.59, 2.55	124, 136, 354, 375, 390, 631, 650, 687, 768, 804, 813, 895, 905, 947, 979, 1049, 1085, 1121, 1150, 1205, 1249, 1279, 1326, 1346, 1452, 1467, 1488, 1702, 2927, 2972, 3001, 3024, 3046, 3105, 3188, 3242
w8[c]	7.34, 3.39, 2.39	150, 208, 347, 352, 465, 535, 629, 701, 736, 763, 864, 894, 922, 926, 935, 1013, 1046, 1110, 1132, 1215, 1275, 1306, 1338, 1375, 1430, 1456, 1468, 1508, 2928, 2935, 2956, 2960, 3138, 3186, 3201, 3229
w8(T)[d]	7.34, 3.39, 2.39	151, 208, 337, 354, 463, 538, 629, 696, 760, 764, 860, 881, 922, 924, 937, 1014, 1047, 1101, 1135, 1219, 1275, 1307, 1342, 1373, 1423, 1451, 1465, 1509, 2901, 2915, 2964, 2970, 3138, 3187, 3204, 3228
w9[c]	7.60, 3.29, 2.36	84, 179, 285, 466, 557, 607, 609, 620, 628, 776, 796, 808, 886, 941, 962, 988, 1061, 1117, 1124, 1205, 1235, 1281, 1328, 1335, 1457, 1459, 1479, 1588, 2980, 2985, 2989, 3004, 3146, 3191, 3196, 3234
w10	7.71, 3.38, 2.74	157, 344, 383, 519, 622, 722, 762, 793, 854, 888, 890, 919, 959, 976, 1029, 1041, 1067, 1080, 1133, 1196, 1212, 1239, 1297, 1335, 1441, 1473, 1494, 1743, 3031, 3082, 3098, 3128, 3170, 3179, 3191, 3208
w11	8.04, 3.08, 2.73	175, 216, 344, 558, 637, 641, 773, 787, 862, 889, 901, 948, 969, 988, 1006, 1038, 1078, 1155, 1169, 1223, 1229, 1244, 1284, 1304, 1464, 1485, 1507, 1819, 3043, 3050, 3088, 3106, 3122, 3149, 3157, 3203
w12	7.11, 4.02, 2.91	220, 336, 351, 561, 657, 751, 767, 836, 857, 888, 928, 945, 965, 996, 1042, 1077, 1088, 1132, 1173, 1209, 1267, 1299, 1313, 1352, 1465, 1476, 1487, 1719, 2996, 3022, 3059, 3076, 3087, 3107, 3168, 3168
w13	7.32, 3.46, 2.42	51, 294, 363, 517, 630, 674, 780, 790, 843, 851, 883, 912, 957, 979, 1008, 1029, 1121, 1169, 1244, 1259, 1278, 1327, 1368, 1452, 1473, 1498, 1643, 1698, 3015, 3033, 3050, 3082, 3132, 3176, 3199, 3213
w14	7.24, 3.50, 2.43	52, 368, 376, 437, 618, 692, 692, 792, 813, 910, 918, 946, 977, 980, 980, 1001, 1130, 1164, 1187, 1239, 1293, 1297, 1373, 1447, 1468, 1474, 1682, 1727, 3002, 3005, 3021, 3021, 3124, 3171, 3195, 3202
w15	5.00, 4.93, 2.68	135, 254, 398, 460, 511, 607, 662, 733, 818, 844, 891, 936, 977, 997, 1031, 1064, 1105, 1166, 1228, 1254, 1281, 1330, 1358, 1383, 1395, 1414, 1485, 1703, 2867, 2872, 2994, 3045, 3048, 3052, 3140, 3164
w16	5.15, 4.91, 2.59	115, 384, 406, 543, 580, 632, 722, 856, 890, 945, 966, 974, 987, 1002, 1021, 1044, 1181, 1220, 1222, 1227, 1366, 1381, 1402, 1438, 1469, 1473, 1705, 1751, 2975, 2976, 2979, 2980, 3131, 3131, 3154, 3156
w17	6.34, 4.50, 3.19	285, 355, 486, 682, 732, 768, 773, 811, 886, 926, 934, 954, 994, 1014, 1049, 1069, 1090, 1099, 1132, 1185, 1206, 1303, 1313, 1370, 1384, 1475, 1486, 1660, 3006, 3030, 3108, 3154, 3167, 3172, 3195, 3196
w18	6.18, 4.06, 2.90	130, 253, 302, 496, 618, 681, 741, 783, 821, 877, 904, 928, 973, 995, 1011, 1091, 1125, 1131, 1205, 1219, 1256, 1268, 1315, 1356, 1375, 1472, 1494, 1680, 2911, 2928, 3020, 3047, 3051, 3130, 3168, 3193

Table S1. (Continued.)

speies	rotational constant (GHz)	frequencies[b] (cm^{-1})
w19	6.51, 4.89, 3.62	243, 456, 618, 737, 752, 766, 786, 851, 855, 895, 915, 947, 986, 998, 1015, 1074, 1117, 1123, 1179, 1205, 1241, 1248, 1272, 1301, 1331, 1441, 1491, 1512, 3030, 3042, 3062, 3082, 3165, 3166, 3237, 3252
w20	5.07, 5.06, 2.69	195, 302, 480, 522, 572, 673, 761, 776, 852, 930, 962, 974, 989, 1010, 1041, 1068, 1173, 1190, 1201, 1268, 1356, 1358, 1401, 1437, 1470, 1481, 1638, 1703, 2959, 2972, 3058, 3059, 3146, 3153, 3168, 3177
H_2	1811.32	4420
C_2H_3	237.30, 32.67, 28.72	709, 819, 921, 1044, 1391, 1651, 3037, 3134, 3238
p1	13.73, 1.51, 1.43	55, 134, 236, 284, 331, 445, 532, 552, 666, 679, 742, 795, 888, 946, 962, 995, 1106, 1204, 1210, 1283, 1294, 1371, 1459, 1496, 1517, 2222, 2975, 3043, 3116, 3140, 3153, 3236, 3478
p2	17.91, 1.46, 1.44	34, 86, 200, 308, 388, 402, 446, 538, 620, 644, 667, 861, 931, 948, 1004, 1034, 1115, 1144, 1238, 1291, 1323, 1398, 1447, 1470, 1699, 2013, 3001, 3058, 3123, 3134, 3151, 3209, 3468
p3	24.71, 1.36, 1.30	117, 129, 216, 303, 309, 458, 544, 571, 601, 821, 851, 880, 910, 962, 991, 1008, 1061, 1167, 1222, 1261, 1293, 1401, 1454, 1486, 1547, 1957, 3087, 3105, 3120, 3138, 3150, 3156, 3231
p4	6.89, 2.20, 1.71	63, 99, 243, 315, 317, 481, 489, 669, 747, 869, 876, 880, 892, 910, 1009, 1012, 1091, 1193, 1349, 1380, 1473, 1475, 2024, 2047, 3103, 3103, 3123, 3136, 3171, 3172
p5	42.24, 4.41, 4.11	207, 214, 495, 525, 573, 741, 883, 907, 938, 981, 1090, 1193, 1377, 1449, 1492, 1909, 3068, 3112, 3127, 3151, 3251
p6	8.01, 3.52, 2.48	216, 349, 356, 531, 585, 643, 655, 743, 772, 791, 915, 918, 939, 952, 960, 1015, 1106, 1126, 1250, 1273, 1319, 1365, 1429, 1442, 1512, 1628, 2985, 2996, 3143, 3186, 3207, 3211, 3235
p7	7.97, 3.56, 2.50	183, 354, 394, 528, 617, 638, 660, 778, 819, 820, 856, 927, 943, 952, 986, 1043, 1108, 1145, 1256, 1268, 1308, 1395, 1415, 1442, 1509, 1566, 3016, 3039, 3136, 3189, 3207, 3219, 3223
p8	8.21, 3.82, 2.60	208, 345, 492, 636, 679, 690, 778, 790, 808, 909, 929, 943, 961, 962, 1000, 1102, 1104, 1252, 1334, 1368, 1452, 1531, 1615, 1700, 3136, 3196, 3206, 3221, 3224, 3229
p9	5.35, 5.26, 2.69	172, 384, 526, 565, 593, 636, 726, 774, 869, 933, 967, 967, 974, 987, 996, 1110, 1171, 1181, 1197, 1306, 1368, 1415, 1436, 1455, 1544, 1610, 2901, 2917, 3149, 3151, 3169, 3170, 3193
p10	5.71, 5.71, 2.85	412, 412, 623, 623, 687, 722, 861, 861, 980, 980, 1013, 1015, 1023, 1060, 1060, 1174, 1197, 1197, 1335, 1382, 1513, 1513, 1637, 1637, 3155, 3165, 3165, 3180, 3180, 3191
TS(w1-w2)	4.81, 4.52, 2.56	519i, 176, 258, 378, 407, 412, 485, 603, 686, 790, 847, 887, 913, 991, 1024, 1051, 1067, 1085, 1104, 1124, 1192, 1258, 1283, 1429, 1480, 1521, 1547, 1906, 3077, 3092, 3100, 3130, 3136, 3166, 3174, 3297
TS(w1-w7)	6.42, 3.51, 2.47	718i, 65, 278, 330, 414, 502, 578, 611, 673, 705, 774, 869, 914, 928, 961, 972, 1096, 1112, 1169, 1190, 1245, 1268, 1316, 1376, 1475, 1490, 1504, 1789, 3006, 3037, 3060, 3072, 3094, 3148, 3168, 3333
TS(w2-w3)	14.64, 1.49, 1.45	1735i, 100, 167, 232, 337, 386, 457, 554, 647, 723, 822, 873, 895, 936, 944, 1009, 1026, 1099, 1145, 1166, 1206, 1311, 1319, 1383, 1466, 1475, 1649, 1665, 1822, 3115, 3118, 3129, 3133, 3139, 3201, 3219
TS(w2-w6)[c]	5.17, 3.60, 2.33	869i, 152, 219, 294, 386, 402, 445, 489, 685, 689, 736, 743, 863, 897, 960, 981, 1002, 1060, 1116, 1145, 1242, 1263, 1293, 1387, 1453, 1468, 1496, 1594, 3006, 3036, 3094, 3119, 3129, 3152, 3204, 3221
TS(w2-w8)[c]	6.74, 3.37, 2.46	861i, 209, 249, 291, 432, 495, 543, 621, 675, 751, 819, 880, 928, 945, 959, 1001, 1028, 1101, 1139, 1198, 1243, 1251, 1319, 1397, 1464, 1497, 1518, 1714, 2970, 3061, 3081, 3121, 3144, 3162, 3181, 3200
TS(w3-w4)	18.60, 1.37, 1.35	506i, 113, 131, 320, 327, 389, 478, 548, 585, 679, 760, 801, 808, 908, 983, 986, 1002, 1105, 1198, 1201, 1257, 1282, 1290, 1335, 1464, 1482, 1513, 1517, 3079, 3081, 3129, 3130, 3138, 3138, 3234, 3234
TS(w4-p4)	7.10, 2.09, 1.69	1100i, 110, 242, 323, 332, 430, 540, 627, 649, 687, 755, 797, 846, 888, 892, 929, 952, 998, 1025, 1042, 1087, 1157, 1191, 1381, 1400, 1474, 1477, 1846, 1891, 2521, 3107, 3107, 3131, 3146, 3189, 3189
TS(w4-w20)	5.05, 4.16, 2.40	579i, 100, 351, 368, 522, 573, 685, 687, 839, 845, 861, 924, 957, 984, 999, 1006, 1033, 1076, 1122, 1202, 1267, 1281, 1417, 1461, 1505, 1512, 1559, 1610, 3101, 3102, 3122, 3127, 3134, 3153, 3232, 3281

Table S1. (Continued.)

speies	rotational constant (GHz)	frequencies[b] (cm^{-1})
TS(w5-w9)[c]	6.58, 3.40, 2.37	1027i, 57, 329, 332, 408, 594, 607, 630, 715, 730, 775, 779, 837, 849, 914, 970, 1010, 1050, 1063, 1183, 1210, 1269, 1344, 1366, 1454, 1505, 1509, 1614, 3082, 3082, 3141, 3142, 3144, 3176, 3178, 3228
TS(w6-w5)[c]	4.68, 3.96, 2.38	867i, 130, 249, 285, 365, 419, 489, 582, 643, 659, 674, 736, 801, 807, 915, 961, 984, 1012, 1051, 1116, 1238, 1271, 1324, 1385, 1421, 1463, 1494, 1532, 3054, 3084, 3117, 3133, 3139, 3158, 3228, 3230
TS(w7-w13)[c]	6.25, 3.91, 2.77	2131i, 195, 302, 351, 541, 606, 656, 701, 731, 798, 828, 852, 881, 897, 968, 983, 1076, 1110, 1151, 1188, 1205, 1262, 1279, 1309, 1384, 1457, 1485, 1628, 1747, 2977, 3029, 3043, 3087, 3105, 3177, 3187
TS(w8-p6)[c]	7.24, 3.41, 2.44	491i, 204, 256, 303, 354, 391, 531, 613, 655, 657, 735, 771, 788, 911, 919, 940, 952, 964, 1016, 1100, 1125, 1250, 1273, 1320, 1367, 1429, 1445, 1512, 1560, 2977, 2994, 3146, 3195, 3208, 3216, 3238
TS(w8-p7)[c]	7.53, 3.37, 2.43	1257i, 187, 298, 319, 361, 459, 540, 570, 640, 717, 747, 782, 813, 869, 929, 947, 990, 1011, 1038, 1110, 1145, 1248, 1265, 1339, 1380, 1403, 1433, 1509, 1525, 3001, 3029, 3141, 3189, 3210, 3217, 3231
TS(w8-p8)[c]	7.62, 3.56, 2.65	1980i, 205, 336, 423, 555, 632, 649, 703, 725, 788, 858, 879, 884, 951, 964, 987, 1001, 1040, 1068, 1123, 1239, 1308, 1318, 1337, 1371, 1414, 1452, 1470, 1499, 1650, 3142, 3168, 3180, 3184, 3226, 3229
TS(w8-w10)[c]	7.45, 3.40, 2.54	480i, 161, 347, 361, 456, 542, 599, 625, 735, 810, 837, 899, 926, 941, 1007, 1048, 1098, 1133, 1201, 1244, 1250, 1266, 1335, 1346, 1438, 1480, 1504, 1582, 2952, 2985, 3088, 3094, 3133, 3165, 3203, 3219
TS(w8-w13)[c] (lower)	7.42, 3.45, 2.42	1813i, 118, 344, 362, 405, 547, 597, 625, 673, 777, 785, 835, 886, 917, 928, 975, 1009, 1065, 1146, 1226, 1237, 1270, 1313, 1347, 1404, 1434, 1453, 1574, 2270, 2970, 3015, 3136, 3164, 3220, 3222, 3246
TS(w8-w13)[c] (higher)	7.53, 3.43, 2.55	2049i, 203, 322, 354, 574, 607, 646, 652, 744, 804, 816, 849, 883, 937, 953, 987, 1002, 1045, 1080, 1187, 1212, 1243, 1268, 1328, 1386, 1401, 1460, 1498, 1709, 2964, 3064, 3137, 3156, 3172, 3220, 3225
TS(w8-w14)[c]	7.48, 3.43, 2.42	1845i, 133, 358, 362, 449, 547, 586, 626, 670, 775, 795, 839, 885, 925, 930, 980, 1000, 1075, 1146, 1205, 1230, 1270, 1298, 1343, 1426, 1437, 1456, 1584, 2139, 2966, 2999, 3137, 3174, 3222, 3230, 3235
TS(w8-w17)[c]	7.71, 3.34, 2.39	1584i, 177, 310, 332, 423, 470, 509, 545, 635, 638, 722, 769, 859, 866, 917, 940, 1014, 1017, 1090, 1098, 1123, 1248, 1264, 1316, 1406, 1411, 1487, 1545, 1843, 2894, 2950, 3157, 3205, 3225, 3229, 3249
TS(w8-w9)[c]	7.60, 3.35, 2.39	1907i, 190, 276, 339, 463, 549, 595, 620, 643, 706, 754, 792, 855, 890, 918, 927, 1011, 1049, 1100, 1203, 1225, 1257, 1264, 1313, 1343, 1425, 1446, 1536, 2163, 2934, 2983, 3146, 3194, 3199, 3207, 3234
TS(w8(T)-p6)[d]	7.26, 3.42, 2.44	654i, 213, 270, 312, 352, 409, 535, 616, 653, 661, 736, 775, 792, 906, 916, 940, 953, 976, 1017, 1100, 1122, 1248, 1272, 1318, 1366, 1421, 1439, 1511, 1569, 2972, 2989, 3145, 3195, 3208, 3216, 3238
TS(w8(T)-p7)[d]	7.35, 3.39, 2.44	406i, 171, 254, 348, 366, 429, 532, 613, 639, 651, 779, 815, 823, 857, 922, 943, 968, 988, 1046, 1093, 1147, 1261, 1266, 1317, 1396, 1408, 1441, 1480, 1559, 3010, 3035, 3138, 3197, 3210, 3223, 3225
TS(w9-p6)[c]	7.42, 3.34, 2.42	531i, 203, 245, 328, 357, 405, 534, 582, 653, 669, 763, 789, 796, 910, 920, 933, 950, 965, 1018, 1102, 1128, 1248, 1274, 1312, 1366, 1425, 1439, 1507, 1581, 2986, 3011, 3146, 3194, 3207, 3217, 3238
TS(w9-p8)[c]	7.77, 3.40, 2.46	1981i, 196, 331, 392, 499, 562, 640, 652, 687, 751, 772, 794, 896, 911, 944, 956, 960, 1065, 1086, 1096, 1124, 1239, 1301, 1326, 1330, 1428, 1499, 1537, 1607, 1656, 3147, 3158, 3162, 3195, 3197, 3230
TS(w9-w11)[c]	7.86, 3.19, 2.47	562i, 168, 243, 338, 598, 610, 658, 713, 756, 776, 785, 901, 917, 970, 1003, 1014, 1060, 1142, 1200, 1239, 1249, 1296, 1327, 1333, 1460, 1474, 1495, 1698, 2976, 2982, 3060, 3075, 3140, 3166, 3169, 3225
TS(w9-w12)[c]	7.24, 3.55, 2.59	622i, 189, 290, 443, 469, 607, 651, 699, 701, 704, 842, 887, 928, 962, 990, 1008, 1042, 1137, 1166, 1233, 1243, 1281, 1305, 1375, 1444, 1457, 1494, 1644, 2978, 2999, 3055, 3062, 3132, 3204, 3210, 3237
TS(w13-p8)	7.60, 3.46, 2.46	2070i, 204, 350, 390, 534, 582, 638, 668, 691, 714, 793, 814, 827, 914, 956, 968, 989, 1048, 1103, 1113, 1150, 1252, 1308, 1321, 1354, 1375, 1456, 1599, 1653, 1991, 3145, 3174, 3199, 3230, 3234, 3240
TS(w13-w14)	7.44, 3.43, 2.42	438i, 71, 290, 347, 369, 431, 540, 593, 625, 694, 782, 805, 835, 909, 930, 983, 1008, 1061, 1141, 1238, 1255, 1268, 1305, 1348, 1397, 1435, 1440, 1599, 2743, 2933, 3022, 3138, 3139, 3222, 3225, 3250
TS(w13-w15)	5.81, 4.63, 3.12	368i, 128, 364, 405, 525, 641, 749, 801, 827, 855, 902, 972, 989, 1024, 1039, 1102, 1123, 1156, 1160, 1205, 1259, 1318, 1319, 1360, 1466, 1500, 1521, 1607, 2957, 2996, 3012, 3055, 3075, 3108, 3159, 3215

Table S1. (Continued.)

speies	rotational constant (GHz)	frequencies[b] (cm^{-1})
TS(w13-w18)	6.15, 3.79, 2.78	325i, 128, 315, 401, 518, 672, 711, 745, 795, 849, 907, 952, 960, 976, 1016, 1046, 1085, 1120, 1130, 1205, 1248, 1289, 1308, 1325, 1360, 1479, 1498, 1663, 2873, 2899, 3018, 3043, 3059, 3108, 3172, 3200
TS(w14-p8)	7.41, 3.57, 2.67	1699i, 230, 335, 574, 672, 687, 730, 731, 764, 817, 893, 926, 947, 960, 976, 977, 993, 1064, 1080, 1125, 1236, 1295, 1319, 1335, 1353, 1447, 1464, 1500, 1708, 1761, 3138, 3188, 3193, 3205, 3220, 3221
TS(w15-w16)	5.07, 4.93, 2.65	882i, 117, 395, 404, 508, 572, 663, 739, 830, 879, 886, 928, 971, 998, 999, 1038, 1179, 1187, 1197, 1258, 1326, 1349, 1391, 1402, 1437, 1454, 1471, 1713, 2202, 2969, 2991, 3034, 3035, 3073, 3132, 3160
TS(w15-w20)	5.08, 4.98, 2.70	918i, 171, 300, 475, 512, 556, 695, 751, 813, 848, 908, 938, 983, 992, 1013, 1050, 1154, 1173, 1243, 1257, 1314, 1358, 1366, 1406, 1429, 1453, 1476, 1686, 2158, 2961, 2974, 3051, 3058, 3089, 3146, 3169
TS(w16-p10)	5.64, 5.06, 2.96	1605i, 491, 500, 641, 649, 718, 734, 773, 869, 911, 943, 952, 971, 1018, 1027, 1070, 1077, 1084, 1135, 1141, 1171, 1308, 1321, 1344, 1356, 1428, 1478, 1555, 1601, 1700, 3152, 3155, 3180, 3183, 3198, 3202
TS(w16-w17)	5.36, 4.98, 2.83	1133i, 236, 419, 431, 551, 594, 627, 687, 757, 834, 882, 919, 957, 970, 982, 1080, 1099, 1115, 1171, 1227, 1268, 1316, 1338, 1397, 1440, 1486, 1496, 1568, 2344, 2910, 3084, 3121, 3143, 3162, 3184, 3208
TS(w17-w20)	5.38, 4.96, 2.83	1030i, 259, 416, 443, 544, 583, 654, 697, 733, 831, 899, 929, 953, 965, 1015, 1076, 1103, 1138, 1165, 1236, 1254, 1316, 1332, 1401, 1427, 1467, 1474, 1565, 2420, 2870, 3088, 3132, 3140, 3175, 3192, 3207
TS(w18-w19)	5.95, 3.93, 2.93	376i, 135, 293, 420, 505, 682, 718, 786, 800, 867, 893, 943, 969, 984, 1007, 1082, 1128, 1147, 1212, 1244, 1275, 1312, 1326, 1349, 1363, 1485, 1500, 1660, 2887, 3012, 3023, 3043, 3053, 3083, 3174, 3205
TS(w19-w20)	5.72, 4.80, 3.19	264i, 196, 362, 446, 627, 705, 735, 820, 841, 882, 911, 927, 971, 995, 1016, 1050, 1133, 1165, 1203, 1215, 1261, 1289, 1310, 1349, 1440, 1472, 1492, 1526, 3009, 3026, 3043, 3062, 3085, 3114, 3120, 3152
TS(w20-p10)	5.26, 5.08, 2.73	2364i, 201, 396, 498, 549, 606, 635, 682, 729, 766, 857, 918, 951, 973, 982, 1001, 1028, 1099, 1126, 1165, 1190, 1227, 1311, 1353, 1363, 1437, 1492, 1574, 1631, 1941, 3153, 3157, 3165, 3192, 3201, 3211

[a] Computed at the (U)B3LYP/6-311G(d,p) level.
[b] Unscaled harmonic frequencies.
[c] Properties of open-singlet diradicals were computed by the UB3LYP/6-311G(d,p) method.
[d] Triplet states.

Table S2. Enthalpies of formation of the selected species.

species	$\Delta H_f^\circ{}_{298}$ (kJ mol^{-1}) present study[a]	literature (exp.)	literature (calc.)
C_3H_5	171.52	171 ± 3[b]	
C_3H_3	355.62	339 ± 4[b] 345.2 ± 12.6[c]	352.2 ± 1.0[d]
wa1	94.68	85.4 ± 1.7[e]	
w1	262.72		
w2	257.80		
w13	121.11		
w14	137.46		
p6	253.44		
p7	229.63		
p8	225.72	224[f]	214.1 ± 1.6[g]

[a] Estimated by an atomization method; $\Delta H_f^\circ{}_{298}$ (C) = 716.67 kJ mol^{-1} and $\Delta H_f^\circ{}_{298}$ (H) = 218.00 kJ mol^{-1}, taken form [Chase, M. W., Jr. *J. Phys. Chem. Ref. Data, Monogr.* **1998**, *9*, 1–1951.], were used. [b] Tsang, W. *Heats of Formation of Organic Free Radicals by Kinetic Methods in Energetics of Organic Free Radicals*: Martinho Simoes, J.A.; Greenberg, A.; Liebman, J.F., eds., Blackie Academic and Professional, London, **1996**, 22-58. [c] Robinson, M. S.; Polak, M. L.; DePuy, C. H.; Lineberger, W. C. *J. Am. Chem. Soc*. **1995**, *117*, 6766. [d] Vazquez, J.; Harding, M. E.; Gauss, J.; Stanton, J. F. *J. Phys. Chem. A* **2009**, *113*, 12447-12453. [e] Fang, W.; Rogers, D.W. *J. Org. Chem.* **1992**, *57*, 22942297. [f] Roth, W.R.; Adamczak, O.; Breuckmann, R.; Lennartz, H.-W.; Boese, R. *Chem. Ber.* **1991**, *124*, 24992521. [g] Lories, X.; Vandooren, J.; Peeters, D. *Chem. Phys. Lett.* **2008**, *452*, 2932.

Table S3. Entropies and heat capacities of the selected species.

species	S°_{298} (J K^{-1} mol^{-1})	C_p° (J K^{-1} mol^{-1}) 300 K	400 K	500 K	600 K	800 K	1000 K	1500 K	2000 K
C_3H_5	258.579 (259.47)[a]	63.505	79.764	93.382	104.478	121.502	134.138	154.149	164.622
C_3H_3	255.005 (253.25)[a]	63.349	72.926	80.316	86.267	95.636	102.889	114.885	121.379
wa1	373.443	122.727	155.350	183.706	207.278	243.738	270.589	312.206	333.503
w1	363.392	117.518	145.984	169.908	189.499	219.578	241.700	276.095	293.783
w2	363.774	116.559	144.706	168.496	188.141	218.566	241.036	275.894	293.726
w13	318.060	99.298	132.789	161.454	184.840	219.953	244.905	282.300	300.998
w14	311.534	99.759	133.305	161.940	185.295	220.387	245.327	282.640	301.246
p6	312.113	100.635	132.620	158.833	179.658	210.275	231.783	263.990	280.162
p7	311.977	99.409	131.574	158.029	179.041	209.867	231.473	263.800	280.035
p8	294.340	91.806	121.621	146.078	165.461	193.767	213.482	242.851	257.588

[a] Experimental values taken from [Baulch, D. L.; Bowman, C. T.; Cobos, C. J.; Cox, R. A.; Just, T.; Kerr, J. A.; Pilling, M. J.; Stocker, D.; Troe, J.; Tsang, W.; Walker, R. W.; Warnatz, J. *J. Phys. Chem. Ref. Data* **2005**, *34*, 757-1397].

Table S4. Chebyshev-polynomial coefficients for the C_3H_5 + C_3H_3 recombination and thermal isomerization / decomposition reactions of w1, w2, w13 and w14.

reactants	products	N^a	M^b	Chebyshev coefficients[c, d]
C_3H_5+C_3H_3	w1	12	4	-11.639500, 0.687058, -0.095780, 0.024807 -2.576810, 1.117210, -0.077385, 0.002848 -1.905880, 0.757900, 0.002824, -0.005372 -1.366040, 0.381319, 0.053164, -0.003905 -0.873799, 0.079298, 0.066088, 0.000825 -0.468326, -0.101343, 0.047183, 0.005792 -0.177756, -0.163260, 0.013661, 0.007705 -0.003965, -0.140139, -0.016548, 0.005312 0.073830, -0.075141, -0.032736, 0.000202 0.086882, -0.006432, -0.032573, -0.004939 0.066011, 0.040767, -0.019966, -0.008010 0.035050, 0.057062, -0.002155, -0.008108
C_3H_5+C_3H_3	w2	12	4	-11.809800, 0.511696, -0.024172, -0.001705 -2.162540, 1.128930, -0.145591, 0.039258 -1.753630, 0.818930, -0.036483, -0.004767 -1.300220, 0.448890, 0.051436, -0.019510 -0.852123, 0.140509, 0.082180, -0.009932 -0.485243, -0.063367, 0.068419, 0.004756 -0.220004, -0.159398, 0.032528, 0.013398 -0.052349, -0.165663, -0.006479, 0.013582 0.033150, -0.113361, -0.035119, 0.007338 0.058762, -0.038647, -0.045944, -0.001828 0.049204, 0.026462, -0.038063, -0.010254 0.026457, 0.062077, -0.016893, -0.014856
C_3H_5+C_3H_3	w13	12	5	-14.736200, -2.322100, -0.250672, 0.053149, 0.033602 1.144970, 2.334110, -0.162887, -0.073302, -0.056567 -0.262242, 1.434330, 0.028011, 0.010178, -0.007354 -0.551789, 0.778278, 0.079069, -0.018317, 0.016091 -0.490634, 0.371918, 0.082840, -0.024796, -0.003639 -0.402859, 0.133744, 0.062207, -0.007399, -0.014021 -0.321207, -0.001876, 0.037194, 0.004699, -0.008514 -0.230636, -0.070520, 0.018758, 0.006366, -0.001396 -0.135011, -0.091043, 0.007699, 0.004380, 0.001146 -0.051008, -0.079186, 0.002068, 0.003086, 0.000768 0.007073, -0.051416, 0.000445, 0.002971, -0.000092 0.034550, -0.022878, 0.001514, 0.003436, -0.000515
C_3H_5+C_3H_3	w14	13	5	-14.771000, -2.084200, -0.308234, 0.070543, 0.031262 0.679707, 2.527910, -0.136822, -0.091153, -0.046691 -0.535640, 1.401480, 0.103103, 0.005216, -0.011075 -0.734782, 0.700404, 0.113244, 0.002413, 0.009911 -0.633105, 0.312603, 0.082735, -0.006104, -0.000169 -0.505377, 0.079159, 0.056698, -0.001832, -0.006506 -0.377247, -0.066016, 0.033734, 0.004470, -0.004425 -0.243096, -0.140270, 0.011395, 0.007148, -0.000888 -0.115627, -0.152717, -0.008738, 0.006457, 0.001140 -0.015943, -0.118841, -0.023177, 0.003669, 0.001885 0.042167, -0.061029, -0.028621, -0.000349, 0.001797 0.058930, -0.003491, -0.024035, -0.004475, 0.000977 0.046177, 0.034811, -0.011818, -0.007132, -0.000404

Table S4. (Continued.)

reactants	products	N^a	M^b	Chebyshev coefficients[c, d]
C_3H_5+C_3H_3	p5+C_2H_3	7	4	-20.918400, -1.580640, -0.216329, 0.053108 8.006320, 1.126850, -0.035869, -0.066301 0.115899, 0.428774, 0.146418, -0.040651 -0.092956, 0.112812, 0.110163, 0.020028 -0.075433, 0.004233, 0.040809, 0.034383 -0.055515, -0.032356, 0.000853, 0.020846 -0.046074, -0.042166, -0.016293, 0.005063
C_3H_5+C_3H_3	p6+H	8	5	-16.514700, -2.622850, -0.171415, 0.034562, 0.036514 2.965140, 1.581040, -0.039715, -0.073747, -0.048700 0.472594, 0.806757, 0.067045, 0.036140, -0.003983 -0.058355, 0.319716, 0.061698, 0.000009, 0.022828 -0.068314, 0.057831, 0.052985, -0.016004, 0.002990 -0.051792, -0.054071, 0.025604, -0.001545, -0.008986 -0.052569, -0.085048, -0.004605, 0.007263, -0.005183 -0.047954, -0.080052, -0.021984, 0.003618, 0.000606
C_3H_5+C_3H_3	p7+H	8	5	-16.634000, -3.814200, -0.072125, 0.120709, 0.024554 3.560310, 2.208760, -0.336292, -0.138583, -0.018067 0.526222, 1.132840, 0.076109, -0.037312, -0.011065 -0.056666, 0.463456, 0.138004, -0.015393, -0.000609 -0.060504, 0.132451, 0.102781, 0.001307, -0.008537 -0.039461, -0.001813, 0.053288, 0.011801, -0.007283 -0.037444, -0.046338, 0.015731, 0.010270, -0.002018 -0.035886, -0.056570, -0.005458, 0.003931, 0.000210
C_3H_5+C_3H_3	p8+H_2	9	5	-16.501900, -4.345030, -0.323014, 0.055772, 0.029009 3.081960, 2.647500, -0.123021, -0.106127, -0.039677 0.495864, 1.253640, 0.149297, -0.003543, -0.005246 -0.069350, 0.483252, 0.138634, 0.000415, 0.008780 -0.081308, 0.148505, 0.088682, 0.001013, -0.003668 -0.059991, 0.009223, 0.050245, 0.007937, -0.005897 -0.058641, -0.049260, 0.021513, 0.009730, -0.001561 -0.056632, -0.071530, -0.000225, 0.006304, 0.000951 -0.046388, -0.073946, -0.015105, 0.001776, 0.001002
w1	w2	9	4	0.633501, 0.804739, -0.064472, 0.012777 2.745180, 1.275060, -0.052842, 0.012920 -1.789380, 0.538928, 0.078002, 0.001298 -0.909867, -0.100918, 0.119745, 0.013973 -0.274899, -0.355147, 0.049537, 0.033072 0.023205, -0.269601, -0.047671, 0.031288 0.082982, -0.066384, -0.087698, 0.007158 0.048243, 0.069553, -0.057369, -0.017561 0.009288, 0.090034, -0.002560, -0.023500
w1	w13	9	4	-3.213670, -1.826130, -0.253835, 0.061041 8.052500, 2.948640, -0.125186, -0.127788 -0.701738, 1.201590, 0.223727, -0.006889 -0.740323, 0.260881, 0.134014, 0.002841 -0.507204, -0.121838, 0.067193, -0.000651 -0.262729, -0.196956, 0.021476, 0.009674 -0.074425, -0.116704, -0.000536, 0.010623 0.018350, -0.021428, 0.003106, 0.008704 0.026526, 0.012263, 0.010941, 0.011628

Table S4. (Continued.)

reactants	products	N^a	M^b	Chebyshev coefficients[c, d]
w1	w14	9	4	-3.251890, -1.674420, -0.263184, 0.067209 7.517960, 3.112810, -0.102974, -0.120882 -1.042890, 1.181180, 0.268044, 0.004777 -0.924955, 0.154421, 0.159040, 0.020304 -0.585674, -0.244384, 0.063960, 0.014246 -0.266598, -0.304137, -0.003103, 0.018406 -0.039273, -0.183291, -0.039223, 0.012814 0.057610, -0.033494, -0.037959, 0.002970 0.050584, 0.045128, -0.017912, -0.001395
w1	C_3H_5+C_3H_3	7	3	-1.549620, 0.683110, -0.160048 8.902870, 0.925599, -0.123183 -0.626322, 0.430516, 0.007502 -0.231480, 0.093624, 0.055568 -0.034564, -0.045904, 0.046875 0.033169, -0.066598, 0.024925 0.036581, -0.043713, 0.008123
w1	p6+H	9	4	-5.276000, -1.708080, -0.380215, 0.045484 9.984000, 2.354300, -0.023255, -0.100002 -0.180633, 0.719069, 0.134006, 0.014758 -0.248282, 0.027461, 0.049996, -0.001422 -0.141570, -0.202273, 0.003184, -0.005002 -0.058494, -0.195144, -0.028205, -0.003488 0.003435, -0.082598, -0.034048, -0.008628 0.035524, 0.027505, -0.014306, -0.010720 0.031348, 0.074975, 0.010813, -0.004820
w1	p7+H	7	4	-5.209340, -2.902130, -0.313069, 0.107504 10.638900, 2.910970, -0.224569, -0.164723 -0.113187, 0.931592, 0.190985, -0.027103 -0.196610, 0.129677, 0.122121, 0.003603 -0.105205, -0.144415, 0.041301, 0.010341 -0.051494, -0.171173, -0.007035, 0.006926 -0.013380, -0.094825, -0.024673, 0.000870
w1	p8+H_2	7	4	-4.973790, -3.545000, -0.433521, 0.043402 10.213300, 3.274770, -0.045387, -0.114888 -0.075290, 0.975744, 0.245638, 0.004403 -0.221479, 0.100418, 0.127617, 0.007892 -0.128862, -0.159926, 0.047231, 0.012997 -0.072666, -0.192647, -0.008120, 0.012746 -0.028214, -0.119314, -0.035795, 0.002918
w2	w1	9	4	0.179040, 0.778184, -0.065434, 0.021111 2.736830, 1.213910, -0.054533, 0.028211 -1.933910, 0.466492, 0.074962, 0.013029 -0.978382, -0.165004, 0.111594, 0.021000 -0.289255, -0.385998, 0.035728, 0.034960 0.032442, -0.261834, -0.061278, 0.028479 0.098268, -0.038680, -0.093669, 0.001724 0.065752, 0.092608, -0.054502, -0.022392 0.029606, 0.097474, 0.002862, -0.025677

Table S4. (Continued.)

reactants	products	N^a	M^b	Chebyshev coefficients[c, d]
w2	w13	9	4	-1.391910, -0.281560, -0.054072, 0.059477 6.358460, 1.834410, -0.198719, -0.122263 -0.841107, 0.857919, 0.165337, -0.022310 -0.636036, 0.235173, 0.083872, 0.018498 -0.361506, 0.020869, 0.034246, -0.011248 -0.159411, -0.032820, 0.044657, -0.013760 -0.049172, -0.036862, 0.053343, 0.006101 -0.014032, -0.043536, 0.037737, 0.024821 -0.014818, -0.057010, 0.002121, 0.028879
w2	w14	9	4	-1.416890, -0.152948, -0.060610, 0.067163 5.835820, 2.000330, -0.182311, -0.112493 -1.201320, 0.857939, 0.204147, -0.012837 -0.820891, 0.125398, 0.114582, 0.032326 -0.428393, -0.116029, 0.033769, 0.005417 -0.159035, -0.141172, 0.015269, -0.002422 -0.018521, -0.095619, 0.011558, 0.006893 0.021365, -0.052710, -0.000583, 0.015963 0.010419, -0.028333, -0.022901, 0.01482
w2	C_3H_5+C_3H_3	7	3	-2.027360, 0.472664, -0.111868 9.248520, 0.910879, -0.209558 -0.651359, 0.446374, -0.011106 -0.263058, 0.107623, 0.065965 -0.064124, -0.057798, 0.058888 0.016487, -0.100063, 0.023507 0.038030, -0.071831, -0.0096311
w2	p6+H	7	4	-3.947750, -0.213830, -0.224564, 0.038510 8.836990, 1.284630, -0.007985, -0.112300 -0.315774, 0.380977, 0.049048, 0.040206 -0.199155, 0.039948, -0.028713, 0.000157 -0.039359, -0.065619, -0.010772, -0.032999 0.036582, -0.062188, 0.012025, -0.021785 0.044117, -0.017415, 0.015131, -0.002484
w2	p7+H	7	4	-3.984460, -1.497390, -0.124701, 0.100289 9.594210, 1.917150, -0.238621, -0.162125 -0.215530, 0.618956, 0.077922, -0.013685 -0.155614, 0.153465, 0.056811, -0.009607 -0.014153, -0.022748, 0.040063, -0.010563 0.035074, -0.052312, 0.030393, -0.001310 0.026443, -0.031669, 0.017592, 0.007033
w2	p8+H_2	7	4	-3.573550, -2.143250, -0.247760, 0.044391 8.951880, 2.265060, -0.092276, -0.124710 -0.144079, 0.702580, 0.179078, 0.015121 -0.170328, 0.098628, 0.063314, 0.008378 -0.032207, -0.045807, 0.029838, -0.009161 0.015346, -0.065841, 0.022775, -0.001156 0.008628, -0.049024, 0.009864, 0.006522

Table S4. (Continued.)

reactants	products	N^a	M^b	Chebyshev coefficients[c, d]
w13	w1	9	4	-10.723600, -1.774470, -0.236140, 0.080217 12.241100, 2.972800, -0.091647, -0.090918 -1.771020, 1.049560, 0.244205, 0.026287 -1.299730, -0.031019, 0.119564, 0.030652 -0.646904, -0.417786, 0.002797, 0.018400 -0.173553, -0.364744, -0.080629, 0.014571 0.072206, -0.112913, -0.101367, -0.001765 0.127713, 0.099506, -0.055078, -0.016642 0.078891, 0.153997, 0.011682, -0.014894
w13	w2	9	4	-8.447210, -0.204007, -0.035227, 0.070729 10.555700, 1.918490, -0.163189, -0.099858 -1.765650, 0.777374, 0.188963, -0.000039 -1.126830, 0.006744, 0.077475, 0.040066 -0.486887, -0.244509, -0.016579, 0.006583 -0.079656, -0.208358, -0.044101, -0.005585 0.081849, -0.060541, -0.041669, -0.000642 0.077392, 0.054676, -0.023248, 0.004248 0.016750, 0.077607, -0.002237, 0.004256
w13	w14	9	3	-5.574560, 0.647629, -0.072903 10.140300, 1.139030, -0.100671 -1.142170, 0.762417, -0.005795 -0.803036, 0.365841, 0.060515 -0.476388, 0.081252, 0.070658 -0.237813, -0.070249, 0.046001 -0.087390, -0.119892, 0.013295 -0.008761, -0.105652, -0.013372 0.019192, -0.060894, -0.028563
w13	C_3H_5+C_3H_3	10	3	-10.916800, -1.908620, -0.349439 16.658100, 2.230570, -0.113464 -0.337132, 0.874509, 0.059727 -0.331148, 0.201868, 0.054767 -0.254408, -0.070219, 0.006150 -0.163670, -0.138786, -0.028405 -0.054930, -0.098814, -0.038270 0.025865, -0.018009, -0.028376 0.050754, 0.044925, -0.007269 0.031354, 0.058014, 0.013400
w13	p6+H	5	3	-8.171530, 0.355238, -0.114739 13.245700, 0.603980, -0.180460 -0.294537, 0.375939, -0.086652 -0.188859, 0.173422, -0.019445 -0.088612, 0.058253, 0.004748
w13	p7+H	5	3	-6.636110, 0.252997, -0.088108 12.575500, 0.466258, -0.155304 -0.238886, 0.347597, -0.095068 -0.164890, 0.198376, -0.029153 -0.079124, 0.083224, 0.007675

Table S4. (Continued.)

reactants	products	N^a	M^b	Chebyshev coefficients[c, d]
w13	p8+H_2	7	3	-8.156350, -1.543290, -0.164267 13.747300, 1.526080, -0.192828 -0.063901, 0.790105, 0.008426 -0.201814, 0.276285, 0.071451 -0.106702, 0.061757, 0.043923 -0.064545, -0.008649, 0.013103 -0.048047, -0.035673, -0.001810
w14	w1	9	4	-9.260550, -1.645060, -0.248548, 0.085336 11.214500, 3.102280, -0.076111, -0.086147 -1.975360, 1.019730, 0.281000, 0.035673 -1.393450, -0.117591, 0.137770, 0.045570 -0.680951, -0.499562, -0.003640, 0.030510 -0.167760, -0.426549, -0.102225, 0.020636 0.098735, -0.145868, -0.130511, -0.001416 0.154697, 0.099816, -0.082619, -0.022630 0.095636, 0.178236, -0.004288, -0.026245
w14	w2	9	4	-6.970600, -0.098148, -0.044496, 0.077069 9.541640, 2.048840, -0.152792, -0.092812 -1.988460, 0.767092, 0.220939, 0.006584 -1.220230, -0.084000, 0.102063, 0.050820 -0.508854, -0.341467, -0.019583, 0.020009 -0.069149, -0.272131, -0.069899, 0.002746 0.104322, -0.086407, -0.073422, -0.001900 0.100927, 0.057227, -0.047707, -0.004944 0.035037, 0.097132, -0.014192, -0.008111
w14	w13	9	3	-4.073320, 0.625400, -0.076057 9.648130, 1.104470, -0.107527 -1.005390, 0.753081, -0.013481 -0.712144, 0.385812, 0.053530 -0.432008, 0.122147, 0.067276 -0.228221, -0.024708, 0.048809 -0.096086, -0.086105, 0.022705 -0.021077, -0.093192, 0.000097 0.011890, -0.069535, -0.015651
w14	C_3H_5+C_3H_3	5	3	-9.589530, -1.587630, -0.426283 15.665500, 2.270980, -0.022211 -0.480790, 0.774851, 0.100669 -0.434960, 0.147546, 0.047421 -0.317638, -0.114987, -0.000079
w14	p6+H	5	3	-8.704250, -0.408806, -0.208814 13.815200, 1.328200, -0.158728 -0.320665, 0.533479, -0.028160 -0.250011, 0.146749, -0.024520 -0.108729, 0.021675, -0.007798
w14	p7+H	5	3	-5.434020, 0.380720, -0.103989 11.583400, 0.616695, -0.149152 -0.391785, 0.335972, -0.053774 -0.214131, 0.118146, -0.005424 -0.092802, 0.015180, -0.002275

Table S4. (Continued.)

reactants	products	N^a	M^b	Chebyshev coefficients[c, d]
w14	p8+H_2	5	3	-3.336230, 0.265888, -0.058930
				9.264080, 0.459176, -0.094544
				-0.287123, 0.288240, -0.044860
				-0.225164, 0.114056, -0.005966
				-0.100985, 0.002221, 0.004739

[a] Number of basis functions along the temperature axis. Temperature range is 300–2000 K for recombination reactions and 500–2000 K for isomerization / decomposition reactions.
[b] Number of basis functions along the pressure axis. Pressure range is 0.001–100 atm.
[c] $N \times M$ coefficients, $\{a_{ij}\}$, are ordered as a_{11}, a_{12}, ..., a_{1M}, a_{21}, a_{22}, ..., a_{2M}, ..., ..., a_{N1}, a_{N2}, .., a_{NM}.
[d] Units of the rate constants are cm^3 $molecule^{-1}$ s^{-1} and s^{-1} for recombination and isomerization / decomposition reactions, respectively.

Table S5. Chebyshev-polynomial coefficients for the "lumped" kinetic mechanisms for the C_3H_5 + C_3H_3 recombination and related thermal isomerization / decomposition reactions.

reactants	products	N^a	M^b	Chebyshev coefficients[c, d]
C_3H_5+C_3H_3	(w1+w2)	12	3	-11.380100, 0.617382, -0.069575 -2.384950, 1.101490, -0.098087 -1.813840, 0.783121, -0.017278 -1.323640, 0.416671, 0.048629 -0.862312, 0.112587, 0.071998 -0.480239, -0.079194, 0.057315 -0.203645, -0.158349, 0.023900 -0.033294, -0.151322, -0.009780 0.048329, -0.094532, -0.032076 0.067841, -0.024072, -0.038229 0.053022, 0.031891, -0.029284 0.026910, 0.058467, -0.010854
C_3H_5+C_3H_3	(w13+w14)	12	5	-14.395200, -2.220200, -0.277459, 0.059281, 0.032707 0.985978, 2.386360, -0.141962, -0.087417, -0.051882 -0.334150, 1.389500, 0.060424, 0.009918, -0.011643 -0.592977, 0.730644, 0.083960, -0.005781, 0.012797 -0.524098, 0.343825, 0.074002, -0.017615, -0.000503 -0.428086, 0.114386, 0.055458, -0.008309, -0.010086 -0.335166, -0.019362, 0.033697, 0.002000, -0.007732 -0.233246, -0.085744, 0.014679, 0.005177, -0.002489 -0.128633, -0.101378, 0.001207, 0.004002, 0.000370 -0.039635, -0.082385, -0.006065, 0.002013, 0.000868 0.018948, -0.046812, -0.007127, 0.000527, 0.000296 0.043408, -0.012008, -0.003065, -0.000098, -0.000551
C_3H_5+C_3H_3	(p6+p7)+H	8	5	-16.039500, -3.136230, -0.021399, 0.026175, 0.018026 3.123600, 1.722250, -0.245201, -0.015024, -0.034890 0.479483, 1.001960, 0.012241, -0.013441, 0.019426 -0.057697, 0.423812, 0.089329, -0.036251, 0.010722 -0.062270, 0.114313, 0.081929, -0.019380, -0.014946 -0.044550, -0.017247, 0.043661, 0.002689, -0.015116 -0.045060, -0.062177, 0.008665, 0.008512, -0.004820 -0.042210, -0.068589, -0.011290, 0.004015, 0.000853
C_3H_5+C_3H_3	p8+H_2	9	5	-16.501900, -4.345030, -0.323014, 0.055772, 0.029009 3.081960, 2.647500, -0.123021, -0.106127, -0.039677 0.495864, 1.253640, 0.149297, -0.003543, -0.005246 -0.069350, 0.483252, 0.138634, 0.000415, 0.008780 -0.081308, 0.148505, 0.088682, 0.001013, -0.003668 -0.059991, 0.009223, 0.050245, 0.007937, -0.005897 -0.058641, -0.049260, 0.021513, 0.009730, -0.001561 -0.056632, -0.071530, -0.000225, 0.006304, 0.000951 -0.046388, -0.073946, -0.015105, 0.001776, 0.001002
(w1+w2)	(w13+w14)	8	4	-1.153160, -0.278090, -0.054709, 0.061783 6.200160, 1.836910, -0.196678, -0.117541 -0.926832, 0.840925, 0.169826, -0.018444 -0.686834, 0.199838, 0.091492, 0.020412 -0.388001, -0.021830, 0.037158, -0.008572 -0.165910, -0.068179, 0.037385, -0.010429 -0.042270, -0.054480, 0.038454, 0.007328 -0.002438, -0.040663, 0.023355, 0.021748

Table S5. (Continued.)

reactants	products	N^a	M^b	Chebyshev coefficients[c, d]
(w1+w2)	C_3H_5+C_3H_3	6	4	-1.804180, 0.593819, -0.137492, 0.012330 9.101010, 0.911238, -0.156129, -0.011937 -0.640882, 0.441823, -0.002710, -0.033999 -0.247985, 0.103199, 0.060177, -0.022089 -0.048128, -0.048770, 0.053453, -0.004670 0.027341, -0.080310, 0.025997, 0.003604
(w1+w2)	(p6+p7)+H	6	4	-3.490160, -0.873538, -0.033623, 0.018324 9.111050, 1.321360, -0.219967, -0.036646 -0.234229, 0.551939, -0.007126, -0.007214 -0.168892, 0.122899, 0.015863, -0.038389 -0.029908, -0.042930, 0.034917, -0.028923 0.027436, -0.058160, 0.033041, -0.003175
(w1+w2)	p8+H_2	6	4	-3.675590, -2.205330, -0.238536, 0.044928 8.972520, 2.218190, -0.103878, -0.116336 -0.126762, 0.717550, 0.163194, 0.016957 -0.174716, 0.111512, 0.067115, 0.003650 -0.043280, -0.049769, 0.041714, -0.010312 0.005027, -0.076809, 0.028565, 0.002857
(w13+w14)	(w1+w2)	9	4	-8.064190, -0.190688, -0.034508, 0.073763 10.406900, 1.935560, -0.157675, -0.093910 -1.861210, 0.765856, 0.196936, 0.004926 -1.175090, -0.027274, 0.086499, 0.043040 -0.506067, -0.282987, -0.015182, 0.009926 -0.081170, -0.234823, -0.054026, -0.002507 0.090196, -0.069382, -0.057630, -0.000534 0.089424, 0.060195, -0.036336, 0.000030 0.027969, 0.089931, -0.006425, -0.002379
(w13+w14)	C_3H_5+C_3H_3	10	3	-10.638200, -1.763430, -0.379911 16.490000, 2.214680, -0.063125 -0.394389, 0.816561, 0.068030 -0.368570, 0.172973, 0.045384 -0.277543, -0.090035, 0.001875 -0.168871, -0.156529, -0.032802 -0.045813, -0.109392, -0.047223 0.039555, -0.016309, -0.038751 0.060204, 0.057124, -0.012836 0.034043, 0.072758, 0.015950
(w13+w14)	(p6+p7)+H	5	3	-6.410370, 0.296829, -0.094130 12.451100, 0.512818, -0.152191 -0.281385, 0.336907, -0.080781 -0.175206, 0.170463, -0.024484 -0.083285, 0.064785, 0.000529
(w13+w14)	p8+H_2	5	3	-4.623500, 0.196383, -0.059168 10.127000, 0.351453, -0.101624 -0.124406, 0.251544, -0.063388 -0.136792, 0.142655, -0.026629 -0.072383, 0.061434, -0.005199

[a] Number of basis functions along the temperature axis. Temperature range is 300–2000 K for recombination reactions and 500–2000 K for isomerization / decomposition reactions.

[b] Number of basis functions along the pressure axis. Pressure range is 0.001–100 atm.

[c] $N \times M$ coefficients, $\{a_{ij}\}$, are ordered as a_{11}, a_{12}, ..., a_{1M}, a_{21}, a_{22}, ..., a_{2M}, ..., ..., a_{N1}, a_{N2}, .., a_{NM}.

[d] Units of the rate constants are cm^3 $molecule^{-1}$ s^{-1} and s^{-1} for recombination and isomerization / decomposition reactions, respectively.