Supplementary Information

A modified group contribution method for estimating thermodynamic parameters of methanol-to-olefins over SAPO-34 catalyst

Junyi Yu[1,2], Hua Li[1*], Mao Ye[1*] and Zhongmin Liu[1,2]

[1]National Engineering Laboratory for Methanol-to-Olefins, Dalian National Laboratory for Clean Energy, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, 116023 Dalian, China.

[2]University of Chinese Academy of Sciences, 10049 Beijing, China.

*Corresponding author: lihua@dicp.ac.cn & maoye@dicp.ac.cn

1. Names and abbreviations of species and reactions

Table S 1. Names and abbreviations of species

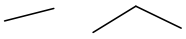
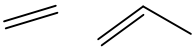
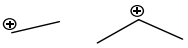
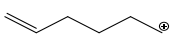
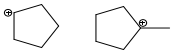
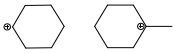
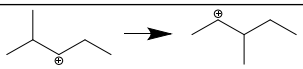
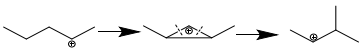
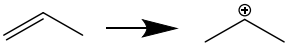
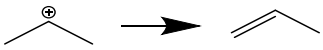
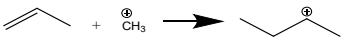
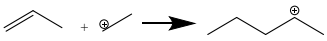
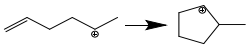
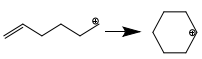
name	symbol	example	number
Alkanes	R		5
Olefins	O		50
Carbocation	C		72
Olefin carbocation	OC		33
Five-membered ring carbocation	N5C		20
Six-membered ring carbocation	NC		6

Table S 2. Names and abbreviations of reactions

name	symbol	example	number
Methyl shift	MSI		96
PCP branching	PCP		96
Protonation	PRO		18
Deprotonation	DEP		48
Hydrogen transfer	HTR		42
Methylation	MET		54
Alkylation	ALK		95
β-scission	BSC		264
Cyclization-five	CYC1		32
Cyclization-six	CYC2		8

2. The automatic generation method of the reaction network

The automatic generation method of the reaction network we used in this work includes the following three steps (as shown in the **Figure S 1** below through an example): convert the reactant species to Boolean matrix, formulate the reactions with matrix transformation, and establish the reaction network.

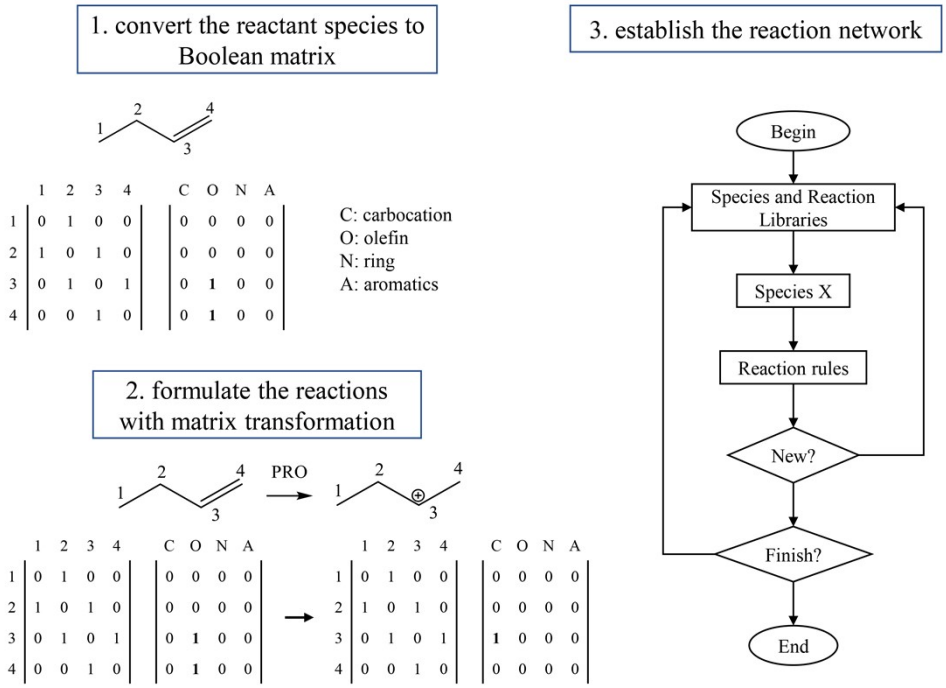


Figure S 1 A method for automatic generation of reaction network

Below we describe these processes in detail through an example.

(1) convert the reactant species to Boolean matrix. As shown in part 1 of the figure above, the matrix M represents the carbon-carbon bond adjacency matrix (if connected, it is "1"), and the auxiliary vector "CONA" is used to represent the specific structure of the species. For example, in 1-butene, the third and fourth lines of the "O" vector are "1", indicating that the third and fourth carbon atoms are double bonds.

(2) formulate the reactions with matrix transformation. As shown in part 2 of the figure above, the process is the protonation of 1-butene. The No. 3 olefin position of 1-butene reacts to become a carbocation, and the corresponding matrix transformation process is: the third row of the "C" column of the carbocation become "1", and the "O" columns all become "0".

(3) establish the reaction network. As shown in part 3 of the figure above, the basic process of

establishing a reaction network is: establish a species and a reaction library, select the species in the species library in turn to obtain the product according to the reaction rules. Then these products and reactions are compared with the species library and reaction library to check the plausibility, detect whether new species or new reactions are generated, and add the generated new species and reactions to the database. When no new species is generated until all species in the reactant database participate in the reaction, the algorithm ends to obtain the final species library and reaction library.

3. Calculating thermodynamic of adsorption species

In this work, we used well-developed software to obtain the thermodynamic parameters of species at different temperatures. Specifically, we first used Gauss View 5.0 software to edit the structure of species, and then used Gaussian 09W and Shermo 2.0.5 software to calculate the thermodynamic parameters of species at different temperatures. Finally, in order to simplify calculations and improve model fitting, we propose the utilization of modified thermodynamic parameters. This approach is particularly beneficial when dealing with thermodynamic values obtained from DFT calculations, which tend to be excessively large and pose challenges for effective fitting.

We consider the structure of two cages of H-SAPO-34, to ensure the accuracy for thermodynamic calculations. In our research group, the structures of SAPO-34 molecular sieves have been well-studied and optimized to unveil the reaction mechanism of MTO (please refer to Zhang et al[1] and Gao et al[2].). As our purpose is to calculate the thermodynamic parameters of species at the active sites, here the acidic sites are essentially considered as the adsorption sites of molecular sieves. Thus, in the process of structure optimization, except for the terminal H atoms, all atoms are treated in a relaxed state in order to achieve more accurate calculations for adsorbed species (as shown in **Figure S 2** which includes ethylene carbocation in SAPO-34 molecular sieves). Basically, in GAUSS 09W software the species structure could also be optimized by automatically finding the optimal configuration of adsorbed species, through which the translation, rotation and vibration frequency at the corresponding temperature could be obtained via frequency calculation.

The intermediates in MTO reaction network over SAPO-34 catalyst herein refer to the carbocation species adsorbed on the active sites of molecular sieves. In MTO reaction, the gas phase reactants first enter the molecular sieves through diffusion, and then are adsorbed on the acidic sites where the reaction occurs in which the carbocation intermediates can be formed and further react with the reactants to generate products.

The interaction between the intermediates and molecular sieves is very important in the reaction. A key task of this work is to calculate the thermodynamic parameters of species at the active sites in which the adsorption sites are essentially the acid sites of molecular sieves. During the structure optimization, all atoms except the terminal H atoms are considered in a relaxed state.

Thus, the interaction between intermediates and molecular sieves can be directly treated as the chemical bonding between guest molecules and acid sites as shown in **Figure S 2**.

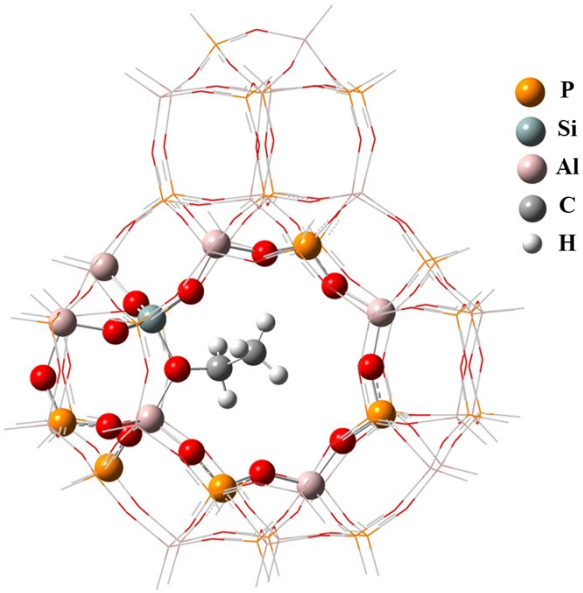


Figure S 2 Model of ethylene carbocation in SAPO-34 molecular sieve

4. Group parameter

The enthalpy and entropy values of the groups at different temperatures are shown in the following table.

Table S 3. Group parameters (H_f) at different temperatures

seq	name	H_f(kJ/mol)			
		698K	723K	748K	763K
1	C-CH_3	-829.3977993	-829.7755397	-830.1227309	-830.3185241
2	C-C_2H_2	-795.0970824	-795.2652758	-795.4086709	-795.4842653
3	C-C_3H	-764.7575959	-764.6954422	-764.6163545	-764.5608351
4	C-C_4	-730.8145863	-730.5182295	-730.2135389	-730.0260794
5	Cdb-H_2	-748.703308	-748.9866746	-749.2513899	-749.4016177
6	Cdb-CH	-719.8647313	-719.9406003	-720.0039446	-720.0355541
7	Cdb-C_2	-697.9646688	-697.8118031	-697.6541911	-697.5555911
8	C+-CH_2	-794.121494	-794.1237742	-794.1030213	-794.0831953
9	C+-C_2H	-780.8353557	-780.5895489	-780.3294897	-780.1693286
10	C+-C_3	-703.5830376	-703.0703036	-702.5531875	-702.2420279
11	Cc-C_2H_2	-779.4486998	-779.6902338	-779.9065449	-780.0259418
12	Cc-C_3H	-737.3559827	-737.3902601	-737.4067942	-737.409261
13	Cc-C_4	-689.9559673	-689.7657167	-689.5656332	-689.4413749
14	Cc+-C_2H	-746.6328487	-746.4534229	-746.2584423	-746.1378692
15	Cc+-C_3	-718.8948098	-718.4551555	-718.0098626	-717.7427371
16	$f_{[O]}$	0.89	0.89	0.89	0.89
17	$f_{[C]}$	1.55	1.55	1.55	1.55
18	$f_{[NC]}$	1.89	1.89	1.89	1.89
18	$P_{[O]}$	-8.26692428	-8.27885571	-8.289581614	-8.296331291
19	$P_{[C]}$	-1.914286015	-1.91531117	-1.91621622	-1.916737283
20	$P_{[O\_OC]}$	9.767658273	9.757983099	9.749229873	9.744413992
21	$P_{[C\_OC]}$	-1.471042501	-1.47135976	-1.471540635	-1.47172929
22	$P_{[NC]}$	-3.070406526	-3.069999533	-3.069603372	-3.069332325

Table S 4. Group parameters (S_f) at different temperatures

seq	name	S_f(J/mol)			
		698K	723K	748K	763K
1	C-CH_3	-252.7822	-253.3095	-253.7806	-254.0396
2	C-C_2H_2	-261.249	-261.4936	-261.6967	-261.8022
3	C-C_3H	-273.2257	-273.157	-273.0656	-273.0026
4	C-C_4	-285.9293	-285.5427	-285.1522	-284.92
5	Cdb-H_2	-184.9955	-185.3904	-185.7485	-185.9459
6	Cdb-CH	-189.114	-189.2297	-189.3231	-189.3693
7	Cdb-C_2	-196.5502	-196.3563	-196.1585	-196.038
8	C+-CH_2	-267.6497	-267.6754	-267.6619	-267.6415
9	C+-C_2H	-262.1893	-261.8738	-261.5403	-261.338
10	C+-C_3	-286.0978	-285.4198	-284.7467	-284.3507
11	Cc-C_2H_2	-250.0055	-250.3195	-250.5887	-250.7336
12	Cc-C_3H	-251.7241	-251.7306	-251.7072	-251.6865
13	Cc-C_4	-260.0722	-259.7469	-259.4081	-259.2101
14	Cc+-C_2H	-266.8928	-266.629	-266.3384	-266.1652
15	Cc+-C_3	-272.3042	-271.6449	-270.9791	-270.5941
16	$f_{[O]}$	0.79	0.79	0.79	0.79
17	$f_{[C]}$	0.71	0.71	0.71	0.71
18	$f_{[NC]}$	0.72	0.72	0.72	0.72
18	$P_{[O]}$	-3.87271	-3.881449	-3.890302	-3.896003
19	$P_{[C]}$	-31.78426	-31.77361	-31.76409	-31.75908
20	$P_{[O\_OC]}$	-0.856255	-0.858362	-0.858855	-0.860788
21	$P_{[C\_OC]}$	-33.87516	-33.87345	-33.87325	-33.87265
22	$P_{[NC]}$	-12.19864	-12.24022	-12.28662	-12.31117

5. Thermodynamic parameters of species

Table S 5. Thermodynamic parameters of species at different temperatures by density functional theory (Definition: $Y_f^o(ZHC_xH_y) = Y_f^o(ZHC_xH_y) - Y_f^o(ZH) - x \times Y_f^o(C,g) - \frac{y}{2} \times Y_f^o(H_2,g)$, Y represents the thermodynamic parameters enthalpy and entropy. Nomenclature: Numbers after 'C' represent carbon chain lengths, front brackets for alkene positions, back brackets for carbocation positions, R1 and R2 for methyl and ethyl groups, and N for cyclic hydrocarbons)

No.	Name	Calculated value(kJ/mol)				Calculated value(J/mol)			
		H_f_698K	H_f_723K	H_f_748K	H_f_763K	S_f_698K	S_f_723K	S_f_748K	S_f_763K
1	[R-1]1: C1	-892.73	-893.29	-893.82	-894.12	-253.32	-254.11	-254.83	-255.23
2	[R-2]2: C2	-1666.90	-1667.67	-1668.37	-1668.77	-509.72	-510.80	-511.75	-512.28
3	[R-3]3: C3	-2449.75	-2450.68	-2451.53	-2452.00	-764.65	-765.96	-767.11	-767.74
4	[R-4]4: C4	-3232.28	-3233.38	-3234.36	-3234.91	-1023.26	-1024.80	-1026.15	-1026.88
5	[R-5]4: 2-R1-C3	-3237.44	-3238.51	-3239.48	-3240.01	-1033.80	-1035.30	-1036.62	-1037.33
6	[O-1]2: (12)C2	-1496.65	-1497.24	-1497.79	-1498.10	-375.41	-376.23	-376.98	-377.39
7	[O-2]3: (12)C3	-2309.98	-2310.73	-2311.42	-2311.81	-623.85	-624.90	-625.84	-626.36
8	[O-3]4: (12)C4	-3109.23	-3110.16	-3111.00	-3111.47	-886.89	-888.19	-889.34	-889.96
9	[O-4]4: (23)C4	-3121.26	-3122.18	-3123.02	-3123.48	-890.73	-892.02	-893.16	-893.78
10	[O-5]4: 2-R1-(12)C3	-3124.92	-3125.82	-3126.64	-3127.10	-892.03	-893.30	-894.41	-895.02
11	[O-6]5: (12)C5	-3910.16	-3911.26	-3912.25	-3912.80	-1156.69	-1158.23	-1159.58	-1160.31
12	[O-7]5: (23)C5	-3920.77	-3921.88	-3922.88	-3923.44	-1154.40	-1155.96	-1157.32	-1158.06
13	[O-8]5: 2-R1-(12)C4	-3922.60	-3923.69	-3924.66	-3925.20	-1152.66	-1154.19	-1155.51	-1156.24

No.	Name	Calculated value(kJ/mol)				Calculated value(J/mol)			
		H_f_698K	H_f_723K	H_f_748K	H_f_763K	S_f_698K	S_f_723K	S_f_748K	S_f_763K
14	[O-9]5: 2-R1-(23)C4	-3929.60	-3930.68	-3931.64	-3932.17	-1137.87	-1139.38	-1140.69	-1141.40
15	[O-10]5: 2-R1-(34)C4	-3913.60	-3914.67	-3915.64	-3916.17	-1157.44	-1158.95	-1160.26	-1160.97
16	[O-11]6: (12)C6	-4708.09	-4709.38	-4710.53	-4711.16	-1426.47	-1428.28	-1429.85	-1430.69
17	[O-12]6: (23)C6	-4722.84	-4724.13	-4725.28	-4725.91	-1419.83	-1421.63	-1423.19	-1424.03
18	[O-13]6: (34)C6	-4719.88	-4721.18	-4722.33	-4722.96	-1424.18	-1425.99	-1427.56	-1428.41
19	[O-14]6: 2-R1-(12)C5	-4721.80	-4723.07	-4724.19	-4724.81	-1426.77	-1428.55	-1430.08	-1430.91
20	[O-15]6: 2-R1-(23)C5	-4728.70	-4729.97	-4731.10	-4731.72	-1415.31	-1417.09	-1418.63	-1419.46
21	[O-16]6: 2-R1-(34)C5	-4721.64	-4722.89	-4724.00	-4724.61	-1400.81	-1402.56	-1404.08	-1404.89
22	[O-17]6: 2-R1-(45)C5	-4717.95	-4719.20	-4720.31	-4720.92	-1420.54	-1422.29	-1423.80	-1424.61
23	[O-18]6: 3-R1-(12)C5	-4716.99	-4718.24	-4719.35	-4719.96	-1419.18	-1420.93	-1422.44	-1423.26
24	[O-19]6: 3-R1-(23)C5	-4727.35	-4728.60	-4729.71	-4730.33	-1403.48	-1405.23	-1406.76	-1407.57
25	[O-20]6: 3-R1-(36)C5	-4717.76	-4719.02	-4720.15	-4720.76	-1423.45	-1425.23	-1426.76	-1427.58
26	[O-21]6: 22-R1-(34)C4	-4721.05	-4722.25	-4723.32	-4723.90	-1426.23	-1427.91	-1429.37	-1430.14
27	[O-22]6: 23-R1-(12)C4	-4724.55	-4725.79	-4726.89	-4727.49	-1419.48	-1421.21	-1422.71	-1423.52
28	[O-23]6: 23-R1-(23)C4	-4728.87	-4730.12	-4731.23	-4731.83	-1425.36	-1427.10	-1428.61	-1429.42
29	[O-24]7: (12)C7	-5510.38	-5511.84	-5513.14	-5513.85	-1687.08	-1689.13	-1690.90	-1691.84
30	[O-25]7: (23)C7	-5521.33	-5522.78	-5524.07	-5524.77	-1680.42	-1682.45	-1684.20	-1685.14
31	[O-26]7: (34)C7	-5519.99	-5521.44	-5522.73	-5523.44	-1678.07	-1680.11	-1681.87	-1682.81
32	[O-27]7: 2-R1-(12)C6	-5523.32	-5524.76	-5526.03	-5526.73	-1685.19	-1687.20	-1688.94	-1689.87
33	[O-28]7: 2-R1-(23)C6	-5532.93	-5534.37	-5535.65	-5536.34	-1687.73	-1689.75	-1691.48	-1692.41
34	[O-29]7: 2-R1-(34)C6	-5524.46	-5525.90	-5527.17	-5527.87	-1688.19	-1690.20	-1691.94	-1692.87
35	[O-30]7: 2-R1-(45)C6	-5527.07	-5528.49	-5529.75	-5530.44	-1683.49	-1685.49	-1687.21	-1688.13

No.	Name	Calculated value(kJ/mol)				Calculated value(J/mol)			
		H_f_698K	H_f_723K	H_f_748K	H_f_763K	S_f_698K	S_f_723K	S_f_748K	S_f_763K
36	[O-31]7: 2-R1-(56)C6	-5512.79	-5514.21	-5515.47	-5516.15	-1685.42	-1687.42	-1689.14	-1690.05
37	[O-32]7: 3-R1-(12)C6	-5513.16	-5514.59	-5515.85	-5516.54	-1692.07	-1694.08	-1695.80	-1696.73
38	[O-33]7: 3-R1-(23)C6	-5531.30	-5532.73	-5533.99	-5534.69	-1679.30	-1681.30	-1683.03	-1683.95
39	[O-34]7: 3-R1-(34)C6	-5528.10	-5529.54	-5530.81	-5531.51	-1680.56	-1682.58	-1684.32	-1685.24
40	[O-35]7: 3-R1-(45)C6	-5522.51	-5523.94	-5525.21	-5525.90	-1687.04	-1689.05	-1690.78	-1691.70
41	[O-36]7: 3-R1-(37)C6	-5520.48	-5521.91	-5523.17	-5523.87	-1686.20	-1688.20	-1689.92	-1690.85
42	[O-37]7: 3-R1-(56)C6	-5517.08	-5518.50	-5519.75	-5520.44	-1681.83	-1683.82	-1685.53	-1686.44
43	[O-38]7: 22-R1-(34)C5	-5517.66	-5519.24	-5520.67	-5521.46	-1708.97	-1711.19	-1713.13	-1714.19
44	[O-39]7: 22-R1-(45)C5	-5510.74	-5512.10	-5513.31	-5513.96	-1692.97	-1694.88	-1696.53	-1697.40
45	[O-40]7: 23-R1-(12)C5	-5525.91	-5527.31	-5528.55	-5529.23	-1669.27	-1671.23	-1672.92	-1673.82
46	[O-41]7: 23-R1-(23)C5	-5530.03	-5531.44	-5532.69	-5533.38	-1672.82	-1674.79	-1676.49	-1677.41
47	[O-42]7: 23-R1-(34)C5	-5528.45	-5529.86	-5531.10	-5531.79	-1685.47	-1687.44	-1689.15	-1690.06
48	[O-43]7: 23-R1-(45)C5	-5518.49	-5519.88	-5521.11	-5521.78	-1688.45	-1690.40	-1692.08	-1692.98
49	[O-44]7: 23-R1-(37)C5	-5524.32	-5525.73	-5526.98	-5527.66	-1685.98	-1687.95	-1689.66	-1690.56
50	[O-45]7: 24-R1-(12)C5	-5533.02	-5534.43	-5535.68	-5536.36	-1691.96	-1693.94	-1695.64	-1696.55
51	[O-46]7: 24-R1-(23)C5	-5534.68	-5536.08	-5537.32	-5538.00	-1671.56	-1673.53	-1675.22	-1676.12
52	[O-47]7: 33-R1-(12)C5	-5517.27	-5518.65	-5519.88	-5520.54	-1692.59	-1694.53	-1696.19	-1697.08
53	[O-48]7: 3-R2-(12)C5	-5515.28	-5516.69	-5517.93	-5518.61	-1674.28	-1676.26	-1677.96	-1678.86
54	[O-49]7: 3-R2-(23)C5	-5527.29	-5528.73	-5529.99	-5530.69	-1686.47	-1688.48	-1690.21	-1691.13
55	[O-50]7: 223-R1-(34)C4	-5533.06	-5534.63	-5536.04	-5536.82	-1719.29	-1721.49	-1723.42	-1724.45
56	[C-1]1: C1(1+)	-769.50	-769.72	-769.92	-770.03	-270.93	-271.25	-271.52	-271.66
57	[C-2]2: C2(1+)	-1598.40	-1598.78	-1599.11	-1599.28	-539.07	-539.61	-540.06	-540.29

No.	Name	Calculated value(kJ/mol)				Calculated value(J/mol)			
		H_f_698K	H_f_723K	H_f_748K	H_f_763K	S_f_698K	S_f_723K	S_f_748K	S_f_763K
58	[C-3]3: C3(1+)	-2413.70	-2414.26	-2414.73	-2414.99	-814.66	-815.44	-816.09	-816.42
59	[C-4]3: C3(2+)	-2421.94	-2422.47	-2422.91	-2423.15	-832.26	-833.00	-833.61	-833.93
60	[C-5]4: C4(1+)	-3223.80	-3224.53	-3225.16	-3225.50	-1085.13	-1086.15	-1087.02	-1087.46
61	[C-6]4: C4(2+)	-3239.09	-3239.77	-3240.35	-3240.66	-1097.63	-1098.59	-1099.38	-1099.79
62	[C-7]4: 2-R1-C3(1+)	-3229.74	-3230.44	-3231.04	-3231.36	-1096.22	-1097.21	-1098.02	-1098.45
63	[C-8]4: 2-R1-C3(2+)	-3216.17	-3216.78	-3217.29	-3217.56	-1107.92	-1108.78	-1109.48	-1109.84
64	[C-9]5: C5(1+)	-4037.99	-4038.91	-4039.69	-4040.11	-1363.47	-1364.76	-1365.82	-1366.37
65	[C-10]5: C5(2+)	-4052.64	-4053.50	-4054.23	-4054.62	-1372.31	-1373.52	-1374.51	-1375.03
66	[C-11]5: C5(3+)	-4046.83	-4047.70	-4048.43	-4048.83	-1371.34	-1372.56	-1373.56	-1374.08
67	[C-12]5: 2-R1-C4(1+)	-4040.02	-4040.91	-4041.66	-4042.06	-1374.55	-1375.79	-1376.82	-1377.35
68	[C-13]5: 2-R1-C4(2+)	-4021.72	-4022.51	-4023.17	-4023.51	-1381.04	-1382.15	-1383.04	-1383.50
69	[C-14]5: 2-R1-C4(3+)	-4050.23	-4051.08	-4051.80	-4052.18	-1375.82	-1377.01	-1377.99	-1378.50
70	[C-15]5: 2-R1-C4(4+)	-4050.33	-4051.20	-4051.95	-4052.35	-1363.88	-1365.11	-1366.13	-1366.66
71	[C-16]5: 22-R1-C3(1+)	-4027.74	-4028.56	-4029.26	-4029.64	-1370.79	-1371.95	-1372.90	-1373.39
72	[C-17]6: C6(1+)	-4860.23	-4861.30	-4862.22	-4862.71	-1644.14	-1645.65	-1646.90	-1647.55
73	[C-18]6: C6(2+)	-4864.41	-4865.44	-4866.31	-4866.78	-1638.12	-1639.56	-1640.75	-1641.37
74	[C-19]6: C6(3+)	-4843.08	-4844.12	-4845.00	-4845.47	-1635.32	-1636.78	-1637.98	-1638.60
75	[C-20]6: 2-R1-C5(1+)	-4841.20	-4842.25	-4843.15	-4843.62	-1640.97	-1642.44	-1643.66	-1644.29
76	[C-21]6: 2-R1-C5(2+)	-4825.35	-4826.31	-4827.13	-4827.56	-1656.94	-1658.30	-1659.41	-1659.98
77	[C-22]6: 2-R1-C5(3+)	-4860.30	-4861.31	-4862.17	-4862.62	-1642.59	-1644.01	-1645.18	-1645.79
78	[C-23]6: 2-R1-C5(4+)	-4873.72	-4874.73	-4875.59	-4876.04	-1637.77	-1639.19	-1640.36	-1640.97
79	[C-24]6: 2-R1-C5(5+)	-4848.19	-4849.25	-4850.15	-4850.63	-1625.10	-1626.59	-1627.82	-1628.45

No.	Name	Calculated value(kJ/mol)				Calculated value(J/mol)			
		H_f_698K	H_f_723K	H_f_748K	H_f_763K	S_f_698K	S_f_723K	S_f_748K	S_f_763K
80	[C-25]6: 3-R1-C5(1+)	-4853.72	-4854.77	-4855.67	-4856.15	-1631.26	-1632.73	-1633.96	-1634.59
81	[C-26]6: 3-R1-C5(2+)	-4853.89	-4854.90	-4855.76	-4856.21	-1649.51	-1650.93	-1652.10	-1652.71
82	[C-27]6: 3-R1-C5(3+)	-4860.46	-4861.45	-4862.29	-4862.73	-1664.62	-1666.01	-1667.15	-1667.73
83	[C-28]6: 3-R1-C5(6+)	-4805.00	-4805.98	-4806.82	-4807.26	-1664.62	-1666.01	-1667.15	-1667.73
84	[C-29]6: 22-R1-C4(1+)	-4829.29	-4830.30	-4831.16	-4831.62	-1660.16	-1661.58	-1662.75	-1663.36
85	[C-30]6: 22-R1-C4(3+)	-4845.92	-4846.87	-4847.66	-4848.08	-1646.68	-1648.00	-1649.09	-1649.65
86	[C-31]6: 22-R1-C4(4+)	-4844.78	-4845.78	-4846.63	-4847.07	-1634.64	-1636.04	-1637.20	-1637.79
87	[C-32]6: 23-R1-C4(1+)	-4856.65	-4857.68	-4858.57	-4859.04	-1648.39	-1649.84	-1651.04	-1651.66
88	[C-33]6: 23-R1-C4(2+)	-4820.18	-4821.11	-4821.91	-4822.33	-1665.30	-1666.61	-1667.69	-1668.25
89	[C-34]7: C7(1+)	-5621.77	-5623.03	-5624.11	-5624.68	-1890.46	-1892.22	-1893.69	-1894.46
90	[C-35]7: C7(2+)	-5648.08	-5649.29	-5650.33	-5650.88	-1909.76	-1911.46	-1912.88	-1913.61
91	[C-36]7: C7(3+)	-5658.19	-5659.39	-5660.41	-5660.95	-1893.35	-1895.04	-1896.43	-1897.15
92	[C-37]7: C7(4+)	-5666.39	-5667.58	-5668.60	-5669.14	-1891.96	-1893.64	-1895.02	-1895.74
93	[C-38]7: 2-R1-C6(1+)	-5637.78	-5639.01	-5640.06	-5640.62	-1920.52	-1922.25	-1923.68	-1924.43
94	[C-39]7: 2-R1-C6(2+)	-5629.35	-5630.50	-5631.48	-5632.00	-1945.02	-1946.64	-1947.97	-1948.66
95	[C-40]7: 2-R1-C6(3+)	-5653.41	-5654.60	-5655.61	-5656.14	-1899.28	-1900.95	-1902.32	-1903.04
96	[C-41]7: 2-R1-C6(4+)	-5682.70	-5683.89	-5684.91	-5685.45	-1917.69	-1919.37	-1920.75	-1921.47
97	[C-42]7: 2-R1-C6(5+)	-5681.05	-5682.22	-5683.22	-5683.75	-1904.67	-1906.32	-1907.68	-1908.39
98	[C-43]7: 2-R1-C6(6+)	-5664.26	-5665.48	-5666.53	-5667.09	-1896.09	-1897.81	-1899.24	-1899.98
99	[C-44]7: 3-R1-C6(1+)	-5645.33	-5646.57	-5647.64	-5648.20	-1917.74	-1919.49	-1920.94	-1921.69
100	[C-45]7: 3-R1-C6(2+)	-5630.77	-5631.96	-5632.97	-5633.50	-1920.48	-1922.14	-1923.52	-1924.23
101	[C-46]7: 3-R1-C6(3+)	-5618.92	-5620.06	-5621.03	-5621.54	-1939.06	-1940.67	-1941.98	-1942.67

No.	Name	Calculated value(kJ/mol)				Calculated value(J/mol)			
		H_f_698K	H_f_723K	H_f_748K	H_f_763K	S_f_698K	S_f_723K	S_f_748K	S_f_763K
102	[C-47]7: 3-R1-C6(4+)	-5649.92	-5651.11	-5652.12	-5652.65	-1910.43	-1912.09	-1913.47	-1914.18
103	[C-48]7: 3-R1-C6(5+)	-5677.28	-5678.45	-5679.44	-5679.96	-1900.60	-1902.24	-1903.59	-1904.28
104	[C-49]7: 3-R1-C6(6+)	-5659.18	-5660.41	-5661.47	-5662.03	-1899.89	-1901.62	-1903.06	-1903.80
105	[C-50]7: 3-R1-C6(7+)	-5617.65	-5618.88	-5619.94	-5620.51	-1907.84	-1909.58	-1911.02	-1911.77
106	[C-51]7: 22-R1-C5(1+)	-5640.23	-5641.42	-5642.43	-5642.96	-1923.98	-1925.65	-1927.03	-1927.75
107	[C-52]7: 22-R1-C5(3+)	-5653.55	-5654.69	-5655.65	-5656.16	-1931.15	-1932.74	-1934.05	-1934.73
108	[C-53]7: 22-R1-C5(4+)	-5674.77	-5675.90	-5676.86	-5677.37	-1910.64	-1912.23	-1913.53	-1914.20
109	[C-54]7: 22-R1-C5(5+)	-5672.46	-5673.64	-5674.64	-5675.17	-1900.93	-1902.59	-1903.95	-1904.66
110	[C-55]7: 23-R1-C5(1+)	-5628.84	-5630.06	-5631.11	-5631.67	-1941.97	-1943.69	-1945.12	-1945.86
111	[C-56]7: 23-R1-C5(2+)	-5606.77	-5607.91	-5608.88	-5609.38	-1949.65	-1951.25	-1952.56	-1953.24
112	[C-57]7: 23-R1-C5(3+)	-5565.36	-5566.48	-5567.42	-5567.92	-1948.89	-1950.45	-1951.74	-1952.41
113	[C-58]7: 23-R1-C5(4+)	-5645.73	-5646.90	-5647.90	-5648.42	-1934.70	-1936.34	-1937.70	-1938.40
114	[C-59]7: 23-R1-C5(5+)	-5659.51	-5660.71	-5661.74	-5662.28	-1907.68	-1909.37	-1910.77	-1911.50
115	[C-60]7: 23-R1-C5(7+)	-5644.85	-5646.06	-5647.10	-5647.65	-1934.10	-1935.80	-1937.21	-1937.95
116	[C-61]7: 24-R1-C5(1+)	-5666.36	-5667.56	-5668.59	-5669.14	-1912.38	-1914.07	-1915.47	-1916.20
117	[C-62]7: 24-R1-C5(2+)	-5607.69	-5608.81	-5609.77	-5610.27	-1940.85	-1942.42	-1943.72	-1944.39
118	[C-63]7: 24-R1-C5(3+)	-5620.28	-5621.45	-5622.45	-5622.98	-1920.51	-1922.15	-1923.51	-1924.21
119	[C-64]7: 33-R1-C5(1+)	-5654.17	-5655.36	-5656.39	-5656.93	-1910.20	-1911.88	-1913.27	-1913.99
120	[C-65]7: 33-R1-C5(2+)	-5644.79	-5645.93	-5646.89	-5647.40	-1926.58	-1928.17	-1929.49	-1930.17
121	[C-66]7: 33-R1-C5(7+)	-5639.32	-5640.51	-5641.53	-5642.08	-1928.64	-1930.32	-1931.71	-1932.44
122	[C-67]7: 3-R2-C5(1+)	-5661.62	-5662.85	-5663.90	-5664.46	-1904.35	-1906.07	-1907.50	-1908.25
123	[C-68]7: 3-R2-C5(2+)	-5620.20	-5621.38	-5622.38	-5622.91	-1918.92	-1920.58	-1921.95	-1922.66

No.	Name	Calculated value(kJ/mol)				Calculated value(J/mol)			
		H_f_698K	H_f_723K	H_f_748K	H_f_763K	S_f_698K	S_f_723K	S_f_748K	S_f_763K
124	[C-69]7: 3-R2-C5(3+)	-5593.88	-5595.04	-5596.03	-5596.55	-1951.72	-1953.35	-1954.70	-1955.40
125	[C-70]7: 223-R1-C4(1+)	-5626.25	-5627.42	-5628.42	-5628.95	-1934.22	-1935.87	-1937.23	-1937.93
126	[C-71]7: 223-R1-C4(3+)	-5546.49	-5547.55	-5548.44	-5548.91	-1953.86	-1955.35	-1956.56	-1957.18
127	[C-72]7: 223-R1-C4(4+)	-5620.33	-5621.50	-5622.49	-5623.02	-1938.13	-1939.77	-1941.12	-1941.82
128	[OC-1]5: (45)C5(1+)	-3830.61	-3831.35	-3831.98	-3832.31	-1244.70	-1245.74	-1246.60	-1247.05
129	[OC-2]6: (45)C6(1+)	-4651.03	-4651.93	-4652.70	-4653.10	-1501.02	-1502.28	-1503.32	-1503.86
130	[OC-3]6: (56)C6(1+)	-4646.42	-4647.30	-4648.05	-4648.45	-1497.22	-1498.46	-1499.48	-1500.01
131	[OC-4]6: (56)C6(2+)	-4653.64	-4654.49	-4655.21	-4655.59	-1506.14	-1507.33	-1508.31	-1508.81
132	[OC-5]6: 2-R1-(12)C5(5+)	-4659.90	-4660.77	-4661.51	-4661.90	-1503.27	-1504.49	-1505.50	-1506.02
133	[OC-6]6: 2-R1-(45)C5(1+)	-4645.13	-4646.02	-4646.77	-4647.17	-1513.76	-1515.01	-1516.03	-1516.56
134	[OC-7]6: 3-R1-(45)C5(1+)	-4647.05	-4647.93	-4648.69	-4649.09	-1514.59	-1515.83	-1516.86	-1517.39
135	[OC-8]7: (45)C7(1+)	-5460.95	-5462.04	-5462.97	-5463.46	-1745.72	-1747.25	-1748.51	-1749.16
136	[OC-9]7: (56)C7(1+)	-5442.28	-5443.36	-5444.28	-5444.77	-1770.82	-1772.34	-1773.60	-1774.24
137	[OC-10]7: (56)C7(2+)	-5477.81	-5478.84	-5479.73	-5480.19	-1769.00	-1770.46	-1771.66	-1772.28
138	[OC-11]7: (67)C7(1+)	-5452.29	-5453.38	-5454.30	-5454.80	-1750.75	-1752.27	-1753.53	-1754.19
139	[OC-12]7: (67)C7(2+)	-5452.09	-5453.12	-5454.00	-5454.46	-1756.50	-1757.96	-1759.15	-1759.77
140	[OC-13]7: (67)C7(3+)	-5449.76	-5450.81	-5451.69	-5452.16	-1777.85	-1779.31	-1780.52	-1781.15
141	[OC-14]7: 2-R1-(12)C6(5+)	-5489.28	-5490.29	-5491.15	-5491.60	-1774.36	-1775.78	-1776.95	-1777.55
142	[OC-15]7: 2-R1-(12)C6(6+)	-5463.90	-5464.97	-5465.87	-5466.35	-1772.83	-1774.33	-1775.56	-1776.20
143	[OC-16]7: 2-R1-(23)C6(6+)	-5470.54	-5471.61	-5472.52	-5473.00	-1755.93	-1757.43	-1758.67	-1759.31
144	[OC-17]7: 2-R1-(45)C6(1+)	-5466.07	-5467.14	-5468.04	-5468.52	-1783.10	-1784.59	-1785.82	-1786.46
145	[OC-18]7: 2-R1-(56)C6(1+)	-5461.88	-5462.94	-5463.85	-5464.33	-1783.32	-1784.81	-1786.04	-1786.68

No.	Name	Calculated value(kJ/mol)				Calculated value(J/mol)			
		H_f_698K	H_f_723K	H_f_748K	H_f_763K	S_f_698K	S_f_723K	S_f_748K	S_f_763K
146	[OC-19]7: 2-R1-(56)C6(2+)	-5338.97	-5339.95	-5340.79	-5341.22	-1790.96	-1792.34	-1793.47	-1794.05
147	[OC-20]7: 3-R1-(12)C6(5+)	-5468.88	-5469.88	-5470.72	-5471.17	-1766.42	-1767.82	-1768.96	-1769.56
148	[OC-21]7: 3-R1-(12)C6(6+)	-5460.14	-5461.20	-5462.09	-5462.57	-1762.57	-1764.05	-1765.27	-1765.90
149	[OC-22]7: 3-R1-(23)C6(6+)	-5470.21	-5471.28	-5472.19	-5472.68	-1749.83	-1751.33	-1752.57	-1753.21
150	[OC-23]7: 3-R1-(45)C6(1+)	-5440.99	-5442.06	-5442.97	-5443.46	-1770.53	-1772.03	-1773.27	-1773.92
151	[OC-24]7: 3-R1-(37)C6(6+)	-5462.99	-5464.06	-5464.97	-5465.45	-1755.71	-1757.22	-1758.46	-1759.10
152	[OC-25]7: 3-R1-(56)C6(1+)	-5446.15	-5447.21	-5448.11	-5448.59	-1786.19	-1787.69	-1788.91	-1789.54
153	[OC-26]7: 3-R1-(56)C6(2+)	-5436.57	-5437.60	-5438.49	-5438.95	-1791.76	-1793.21	-1794.42	-1795.04
154	[OC-27]7: 3-R1-(56)C6(7+)	-5425.50	-5426.57	-5427.49	-5427.98	-1786.41	-1787.91	-1789.16	-1789.81
155	[OC-28]7: 22-R1-(45)C5(1+)	-5443.89	-5444.92	-5445.79	-5446.25	-1779.22	-1780.66	-1781.85	-1782.46
156	[OC-29]7: 23-R1-(12)C5(5+)	-5479.41	-5480.44	-5481.32	-5481.78	-1780.60	-1782.05	-1783.25	-1783.86
157	[OC-30]7: 23-R1-(45)C5(1+)	-5437.20	-5438.23	-5439.11	-5439.57	-1769.94	-1771.38	-1772.58	-1773.19
158	[OC-31]7: 24-R1-(45)C5(1+)	-5460.84	-5461.89	-5462.78	-5463.25	-1782.71	-1784.19	-1785.40	-1786.03
159	[OC-32]7: 33-R1-(45)C5(1+)	-5463.43	-5464.45	-5465.31	-5465.77	-1770.98	-1772.42	-1773.59	-1774.19
160	[OC-33]7: 3-R2-(45)C5(1+)	-5461.62	-5462.68	-5463.58	-5464.06	-1773.02	-1774.51	-1775.74	-1776.37
161	[N5C-1]5: 5N(1+)	-3894.55	-3895.34	-3896.02	-3896.38	-1273.95	-1275.06	-1275.99	-1276.46
162	[N5C-2]6: C1,5N(1+)	-4715.64	-4716.55	-4717.33	-4717.75	-1545.16	-1546.45	-1547.51	-1548.06
163	[N5C-3]6: C1,5N(2+)	-4699.62	-4700.60	-4701.43	-4701.88	-1549.07	-1550.44	-1551.58	-1552.17
164	[N5C-4]6: C1,5N(3+)	-4699.68	-4700.65	-4701.49	-4701.94	-1549.19	-1550.56	-1551.69	-1552.29
165	[N5C-5]6: C1,5N(6+)	-4695.62	-4696.63	-4697.50	-4697.97	-1552.05	-1553.48	-1554.66	-1555.28
166	[N5C-6]7: C2,5N(1+)	-5504.46	-5505.54	-5506.45	-5506.94	-1819.26	-1820.78	-1822.03	-1822.68
167	[N5C-7]7: C2,5N(2+)	-5490.41	-5491.54	-5492.52	-5493.04	-1832.62	-1834.22	-1835.54	-1836.23

No.	Name	Calculated value(kJ/mol)				Calculated value(J/mol)			
		H_f_698K	H_f_723K	H_f_748K	H_f_763K	S_f_698K	S_f_723K	S_f_748K	S_f_763K
168	[N5C-8]7: C2,5N(3+)	-5527.64	-5528.78	-5529.76	-5530.27	-1806.12	-1807.72	-1809.05	-1809.73
169	[N5C-9]7: C2,5N(6+)	-5544.28	-5545.43	-5546.40	-5546.93	-1809.27	-1810.88	-1812.21	-1812.90
170	[N5C-10]7: C1,1-R1-5N(2+)	-5456.41	-5457.53	-5458.49	-5459.00	-1837.30	-1838.88	-1840.18	-1840.86
171	[N5C-11]7: C1,1-R1-5N(3+)	-5531.70	-5532.79	-5533.71	-5534.20	-1812.13	-1813.65	-1814.90	-1815.55
172	[N5C-12]7: C1,1-R1-5N(6+)	-5521.26	-5522.40	-5523.39	-5523.91	-1815.23	-1816.83	-1818.17	-1818.87
173	[N5C-13]7: C1,2-R1-5N(1+)	-5466.08	-5467.14	-5468.04	-5468.51	-1838.29	-1839.77	-1841.00	-1841.63
174	[N5C-14]7: C1,2-R1-5N(3+)	-5510.91	-5512.01	-5512.94	-5513.43	-1819.50	-1821.04	-1822.31	-1822.97
175	[N5C-15]7: C1,2-R1-5N(4+)	-5528.28	-5529.40	-5530.35	-5530.86	-1812.65	-1814.22	-1815.52	-1816.20
176	[N5C-16]7: C1,2-R1-5N(6+)	-5542.57	-5543.72	-5544.71	-5545.23	-1801.79	-1803.41	-1804.75	-1805.45
177	[N5C-17]7: C1,3-R1-5N(1+)	-5541.28	-5542.34	-5543.24	-5543.72	-1815.95	-1817.45	-1818.67	-1819.31
178	[N5C-18]7: C1,3-R1-5N(2+)	-5485.32	-5486.44	-5487.40	-5487.91	-1815.60	-1817.17	-1818.48	-1819.17
179	[N5C-19]7: C1,3-R1-5N(4+)	-5505.23	-5506.34	-5507.29	-5507.80	-1829.15	-1830.73	-1832.02	-1832.69
180	[N5C-20]7: C1,3-R1-5N(6+)	-5532.04	-5533.21	-5534.22	-5534.76	-1793.42	-1795.07	-1796.44	-1797.16
181	[NC-1]6: N1(1+)	-4699.11	-4700.12	-4700.98	-4701.44	-1555.53	-1556.94	-1558.11	-1558.72
182	[NC-2]7: C1,N1(1+)	-5512.26	-5513.38	-5514.34	-5514.85	-1843.86	-1845.44	-1846.74	-1847.42
183	[NC-3]7: C1,N1(2+)	-5525.91	-5527.07	-5528.06	-5528.59	-1821.74	-1823.38	-1824.73	-1825.44
184	[NC-4]7: C1,N1(3+)	-5518.49	-5519.64	-5520.64	-5521.17	-1827.28	-1828.91	-1830.26	-1830.96
185	[NC-5]7: C1,N1(4+)	-5519.74	-5520.92	-5521.94	-5522.49	-1813.59	-1815.26	-1816.64	-1817.37
186	[NC-6]7: C1,N1(7+)	-5534.65	-5535.86	-5536.91	-5537.46	-1808.63	-1810.34	-1811.75	-1812.49

Reference

1. W. N. Zhang, Y. C. Zhi, J. D. Huang, X. Q. Wu, S. Zeng, S. T. Xu, A. M. Zheng, Y. X. Wei and Z. M. Liu, *Acs Catalysis*, 2019, **9**, 7373-7379.
2. M. Gao, H. Li, J. Yu, M. Ye and Z. Liu, *AIChE Journal*, 2022, DOI: 10.1002/aic.17881, e17881.