Theoretical Insights into the Phosphorescence Quantum Yields of Cyclometalated (C^C*) Platinum(II) NHC Complexes: π-Conjugation Controls the Radiative and Non-Radiative Decay Processes

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Table S1. Selected bond lengths [Å], bond angles and dihedral angles [deg] at S_0 optimized geometry for **Pt-1**.

	B3LYP	PBE0	M062X	CAM-B3LYP	Exp.
Pt1-C1	1.955	1.938	1.934	1.952	1.927
Pt1-C3	2.000	1.982	1.972	1.991	2.003
Pt1-O1	2.164	2.137	2.182	2.139	2.089
Pt1-O2	2.091	2.070	2.111	2.072	2.060
O1-Pt1-O2	87.9	88.4	86.4	88.0	89.1
C1-Pt-C3	80.0	80.0	80.2	80.0	78.7
C2-N1-C1-Pt1	0.0	0.0	0.0	0.0	-0.3
N1-C1-Pt1-O1	-180.0	-180.0	180.0	-180.0	-174.1

Table S2. Selected bond lengths [Å], bond angles and dihedral angles [deg] at S_0 optimized geometry for **Pt-2**.

	B3LYP	PBE0	M062X	CAM-B3LYP	Exp.
Pt1-C1	1.953	1.936	1.932	1.950	1.927
Pt1-C3	1.998	1.980	1.970	1.989	1.973
Pt1-O1	2.165	2.138	2.183	2.141	2.094
Pt1-O2	2.094	2.072	2.113	2.075	2.047
O1-Pt1-O2	87.7	88.2	86.4	87.8	89.4
C1-Pt-C3	80.2	80.2	80.4	80.2	80.6
C2-N1-C1-Pt1	0.2	0.1	0.2	0.1	0.6
N1-C1-Pt1-O1	-180.0	-180.0	-180.0	179.9	177.9

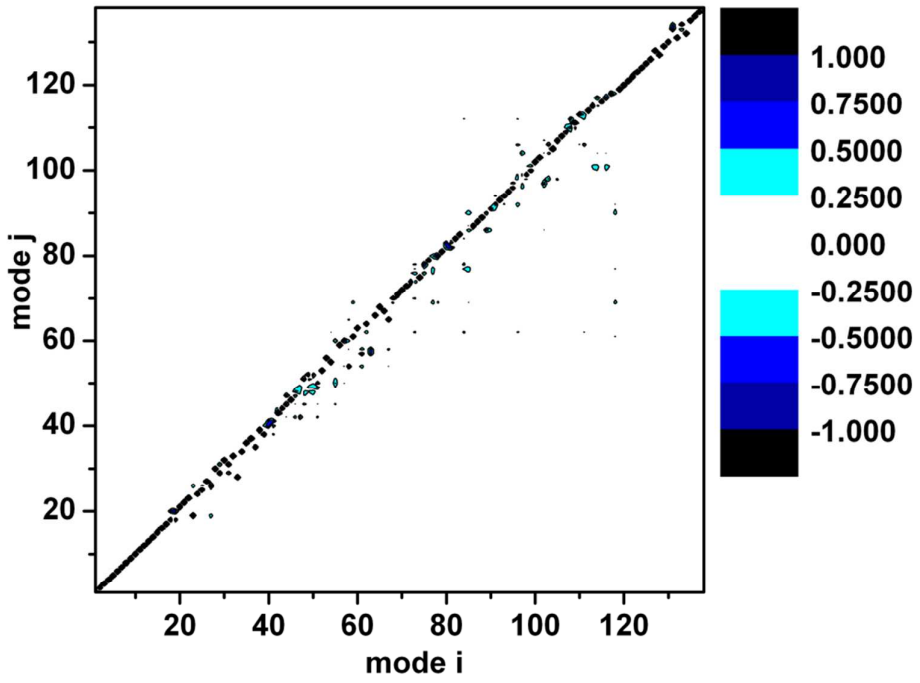


Figure S1. Duschinsky matrix for **Pt-2**.

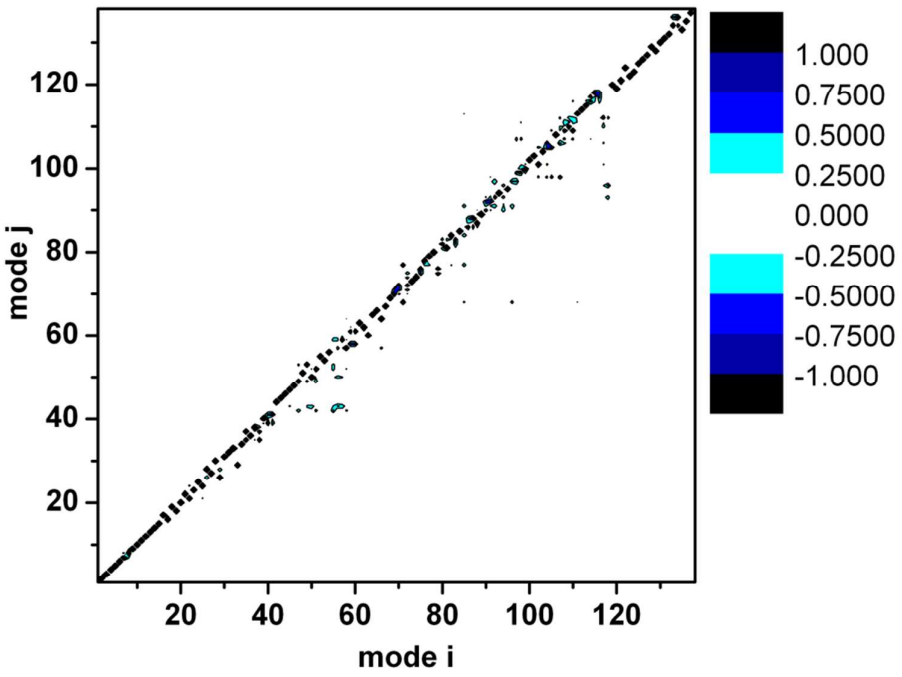


Figure S2. Duschinsky matrix for **Pt-3**.

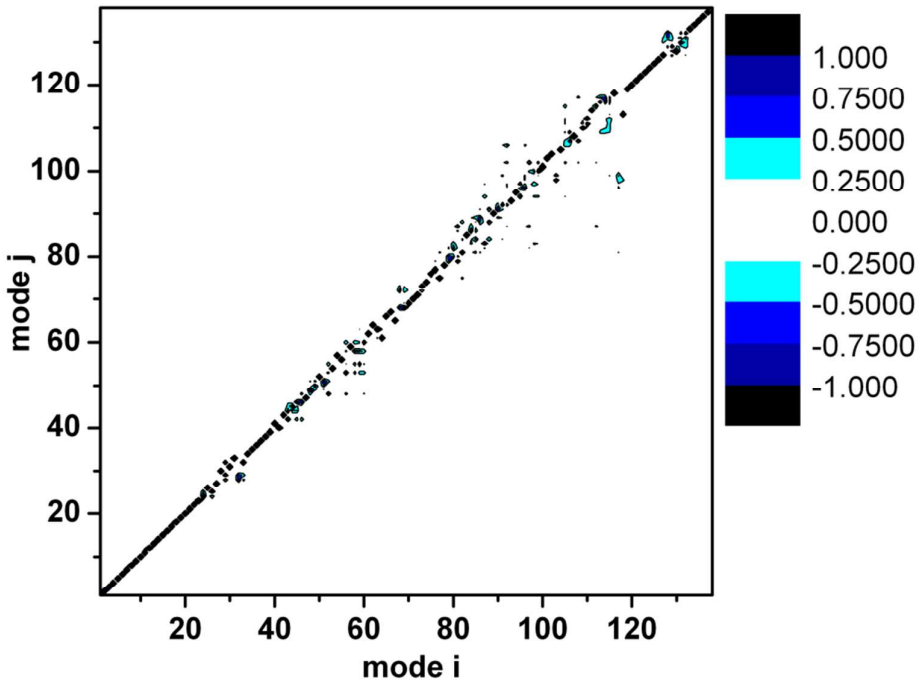


Figure S3. Duschinsky matrix for **Pt-4**.

Table S3. Vibrational frequencies (ω_i / cm^{-1}) at the respective optimized S_0 states, Shift vector K_i (a.u.) and Huang-Rhys factor S_i of **Pt-2**.

	ω_i / (cm−1)	K_i (a.u.)	S_i
1	27.5957	9.04E-01	0.00
2	29.5173	-1.44E+00	0.00
3	44.6612	-4.21E-01	0.00
4	57.1987	5.94E-01	0.00
5	71.1400	1.85E+01	0.06
6	76.1098	-5.98E-02	0.00
7	89.5573	-3.52E-01	0.00
8	96.1000	-1.44E-01	0.00
9	109.7400	-4.67E+00	0.01
10	126.9657	-1.77E-01	0.00
11	140.1950	2.02E-02	0.00
12	162.2805	2.04E-01	0.00
13	169.0059	2.70E-02	0.00
14	182.1652	-9.60E-01	0.00
15	186.4988	-4.49E-03	0.00
16	193.4142	-1.20E-01	0.00
17	212.1466	-1.17E+01	0.07
18	246.6523	-2.58E-01	0.00
19	247.1417	-4.74E-02	0.00
20	257.3067	-8.09E+00	0.04
21	270.8135	-5.30E+00	0.02
22	280.0840	-7.69E+00	0.04
23	294.6686	9.00E+00	0.05
24	303.3143	-2.34E+01	0.38
25	321.0660	1.01E+01	0.08
26	340.9184	-3.30E+00	0.01
27	363.7803	1.37E-01	0.00
28	433.2973	-9.67E-03	0.00
29	435.1549	-7.34E-02	0.00
30	442.9538	1.01E+00	0.00
31	444.1024	6.05E-03	0.00
32	478.7032	1.14E+00	0.00
33	485.9359	2.83E-01	0.00
34	559.2082	-1.80E-02	0.00
35	567.1638	6.26E-01	0.00
36	568.5332	7.87E-03	0.00
37	571.6806	-1.01E+00	0.00
38	590.7832	1.07E+01	0.15
39	591.3343	-5.52E-02	0.00

40	607.1069	1.68E+00	0.00
41	624.7460	-1.67E+00	0.00
42	662.6982	1.39E-01	0.00
43	681.2158	2.16E+00	0.01
44	684.4504	-3.55E+00	0.02
45	686.9578	6.02E-02	0.00
46	701.4659	-2.28E-01	0.00
47	728.2703	-1.47E-03	0.00
48	749.6272	2.64E-03	0.00
49	760.5219	3.24E-02	0.00
50	763.8033	-8.94E-03	0.00
51	780.9155	1.85E-03	0.00
52	786.7176	1.30E-03	0.00
53	799.5298	3.27E+00	0.02
54	818.5850	-2.81E-02	0.00
55	842.2692	-2.38E+00	0.01
56	850.2628	2.22E-03	0.00
57	861.5233	7.90E-03	0.00
58	883.5205	5.35E-03	0.00
59	899.6946	-6.13E-01	0.00
60	927.0660	7.48E-03	0.00
61	941.1195	3.15E-01	0.00
62	949.1153	1.39E+00	0.00
63	963.1857	8.64E-03	0.00
64	967.7882	1.28E+00	0.00
65	977.8547	-5.80E-03	0.00
66	980.7524	-7.33E-02	0.00
67	991.2971	8.00E-04	0.00
68	1043.529	1.25E-01	0.00
69	1052.4970	-6.70E-03	0.00
70	1059.4190	-4.27E+00	0.04
71	1061.5260	1.48E+00	0.01
72	1063.5020	8.84E-03	0.00
73	1065.9920	4.15E-01	0.00
74	1071.8870	-1.76E-01	0.00
75	1131.0990	-2.27E-03	0.00
76	1161.7330	-3.91E+00	0.04
77	1167.0060	1.40E+00	0.01
78	1174.0030	1.12E+00	0.00
79	1174.9860	3.33E-01	0.00
80	1188.4210	-1.43E+00	0.01
81	1195.1980	2.25E-01	0.00
82	1228.2130	2.64E+00	0.02
83	1250.6590	2.84E+00	0.02

84	1254.8680	1.66E+00	0.01
85	1262.2600	-5.10E-02	0.00
86	1291.3570	6.95E-01	0.00
87	1307.7470	-3.84E-01	0.00
88	1320.870	-3.11E-01	0.00
89	1341.5690	-2.83E-02	0.00
90	1373.8350	-1.17E+00	0.00
91	1394.7570	-1.36E+00	0.01
92	1419.3430	-6.00E+00	0.12
93	1420.8800	-5.99E-02	0.00
94	1423.5450	8.99E-01	0.00
95	1439.5760	2.50E-03	0.00
96	1445.8140	4.00E+00	0.05
97	1462.4250	8.35E+00	0.23
98	1478.5600	-1.05E+01	0.37
99	1488.4790	-3.70E+00	0.05
100	1499.4460	-2.27E+00	0.02
101	1500.9580	-1.94E+00	0.01
102	1502.8000	5.11E-04	0.00
103	1505.7490	-2.11E-03	0.00
104	1506.3740	1.11E+00	0.00
105	1520.4400	-7.49E-02	0.00
106	1533.2930	-4.28E+00	0.06
107	1539.9610	1.02E+00	0.00
108	1546.4190	-1.85E-02	0.00
109	1550.0120	1.48E+00	0.01
110	1566.2540	1.21E+00	0.01
111	1573.4450	1.08E+00	0.00
112	1598.4810	-2.71E+00	0.03
113	1652.6370	-6.64E-01	0.00
114	1678.8440	1.08E-01	0.00
115	1681.7620	1.23E+01	0.58
116	1691.6270	2.48E+00	0.02
117	1698.7110	-2.56E+00	0.03
118	1707.5350	2.12E-01	0.00
119	3076.6050	-6.56E-03	0.00
120	3078.3540	1.29E-03	0.00
121	3081.7000	-3.90E-03	0.00
122	3149.9840	-1.52E-04	0.00
123	3151.1650	1.39E-04	0.00
124	3154.3960	2.89E-05	0.00
125	3183.8850	-1.65E-03	0.00
126	3186.3450	-3.51E-03	0.00
127	3199.1160	-2.75E-02	0.00

128	3205.2810	9.56E-02	0.00
129	3206.2690	-1.42E-01	0.00
130	3220.3530	-2.67E-02	0.00
131	3224.6010	1.97E-03	0.00
132	3225.1620	-2.06E-02	0.00
133	3234.2670	-1.28E-01	0.00
134	3237.3100	-1.56E-01	0.00
135	3245.5290	-1.52E-03	0.00
136	3248.5220	2.54E-02	0.00
137	3252.8720	2.12E-01	0.00
138	3285.6120	-6.55E-02	0.00

Table S4. Vibrational frequencies (ω_i / cm^{-1}) at the respective optimized S_0 states, Shift vector K_i (a.u.) and Huang-Rhys factor S_i of **Pt-3**.

	ω_i / (cm−1)	K_i (a.u.)	S_i
1	21.8332	2.59E-01	0.00
2	33.7916	1.53E-01	0.00
3	49.4843	-8.10E-02	0.00
4	59.4179	-1.57E-01	0.00
5	69.1696	1.63E+01	0.04
6	75.1708	6.39E-01	0.00
7	89.3385	1.36E-01	0.00
8	97.4486	-1.57E-02	0.00
9	112.2286	4.99E-02	0.00
10	123.6384	-8.38E+00	0.02
11	144.7278	-5.83E-02	0.00
12	158.7537	3.13E-02	0.00
13	170.2647	-2.11E-01	0.00
14	177.4242	2.53E+01	0.26
15	189.7311	-1.15E+00	0.00
16	215.0171	-7.14E-01	0.00
17	217.0673	2.71E+01	0.37
18	222.6195	-8.37E-01	0.00
19	224.3381	1.11E+01	0.06
20	252.2631	-4.86E+00	0.01
21	266.6393	-1.98E-01	0.00
22	275.3080	-6.90E+00	0.03
23	291.5505	9.69E+00	0.06
24	324.8794	-1.96E-01	0.00
25	356.5417	2.69E+00	0.01
26	365.0623	-7.64E-03	0.00
27	380.3052	3.58E+00	0.01
28	412.6580	1.11E-02	0.00
29	428.5693	2.98E-03	0.00
30	433.6475	-1.60E+00	0.00
31	442.6012	-1.20E+00	0.00
32	451.6779	-1.47E+00	0.00
33	485.9589	-6.60E-06	0.00
34	521.4535	1.01E+01	0.12
35	555.8240	-6.08E-03	0.00
36	562.1356	-5.64E+00	0.04
37	567.2703	-1.08E-03	0.00
38	567.8660	-4.60E-03	0.00
39	606.5671	5.86E+00	0.05

40	622.5151	2.07E+00	0.01
41	634.2523	-1.79E-01	0.00
42	678.5528	1.15E-02	0.00
43	685.4991	-5.04E-03	0.00
44	686.7594	-1.39E+00	0.00
45	703.3983	7.83E-03	0.00
46	704.0097	8.91E-02	0.00
47	732.7563	-1.41E-02	0.00
48	734.4044	1.31E+00	0.00
49	742.1015	-3.30E-03	0.00
50	759.9639	-1.40E-02	0.00
51	767.5726	-9.92E-01	0.00
52	776.2152	3.36E-03	0.00
53	785.8208	-5.13E-03	0.00
54	800.4961	-3.97E+00	0.03
55	841.4729	2.33E-03	0.00
56	861.0037	-3.01E-03	0.00
57	874.6552	4.03E-04	0.00
58	893.4789	1.46E+00	0.00
59	906.8964	1.73E-03	0.00
60	912.1821	2.87E-03	0.00
61	943.0244	-6.02E-01	0.00
62	944.1628	6.05E-01	0.00
63	962.7900	-8.67E-08	0.00
64	967.7564	-1.99E-03	0.00
65	977.7556	-2.40E-02	0.00
66	995.9332	-1.29E-01	0.00
67	999.0577	7.81E-04	0.00
68	1052.3410	-5.40E+00	0.07
69	1059.5170	-2.99E-01	0.00
70	1061.1700	1.64E-01	0.00
71	1063.6130	-2.65E-01	0.00
72	1070.9140	3.27E-01	0.00
73	1071.9420	1.81E-03	0.00
74	1073.5620	-1.96E-01	0.00
75	1120.1890	-2.18E-01	0.00
76	1161.3860	6.64E-01	0.00
77	1164.7980	4.37E-01	0.00
78	1174.8520	1.76E+00	0.01
79	1176.0690	1.91E+00	0.01
80	1191.9700	-2.76E-02	0.00
81	1195.3120	1.93E-01	0.00
82	1201.1270	-3.12E+00	0.03
83	1248.4110	1.76E+00	0.01

84	1250.6860	8.84E-02	0.00
85	1261.1490	1.21E-01	0.00
86	1292.4510	6.45E-01	0.00
87	1303.5390	8.19E-01	0.00
88	1317.6570	1.35E-01	0.00
89	1321.2860	2.29E-01	0.00
90	1372.1820	-2.10E+00	0.01
91	1397.4880	-4.46E+00	0.06
92	1416.2680	-8.02E-02	0.00
93	1419.4780	-1.07E+00	0.00
94	1421.8150	2.80E-04	0.00
95	1423.7310	5.29E-02	0.00
96	1450.1290	-7.13E-01	0.00
97	1472.4110	9.54E+00	0.31
98	1484.4140	1.32E+00	0.01
99	1488.6700	2.24E+00	0.02
100	1499.4470	4.40E-02	0.00
101	1500.9560	-3.39E-01	0.00
102	1503.2460	-1.17E-02	0.00
103	1506.3220	7.43E-03	0.00
104	1512.0020	-1.44E-01	0.00
105	1518.3150	8.28E-01	0.00
106	1531.7250	1.35E+00	0.01
107	1533.7830	8.38E+00	0.25
108	1544.4730	1.65E-01	0.00
109	1549.0620	3.29E+00	0.04
110	1560.6010	-1.12E+00	0.00
111	1587.7490	-6.15E-01	0.00
112	1598.7830	1.26E+00	0.01
113	1658.2770	3.84E+00	0.06
114	1669.8090	5.30E-02	0.00
115	1681.0610	1.89E+00	0.01
116	1684.1310	9.99E+00	0.38
117	1701.9600	3.80E+00	0.06
118	1723.6510	3.76E-01	0.00
119	3074.5080	2.03E-03	0.00
120	3078.4280	-5.64E-02	0.00
121	3081.6600	6.91E-03	0.00
122	3147.5890	-4.64E-05	0.00
123	3150.0960	-4.64E-05	0.00
124	3154.3160	-2.69E-05	0.00
125	3183.8990	-6.02E-04	0.00
126	3186.3270	1.85E-03	0.00
127	3205.8100	1.29E-02	0.00

128	3206.6620	1.28E-02	0.00
129	3209.1000	-3.42E-03	0.00
130	3210.5580	-5.16E-02	0.00
131	3226.2520	-7.15E-03	0.00
132	3227.6770	-1.88E-02	0.00
133	3232.8040	-1.92E-02	0.00
134	3239.7380	2.11E-01	0.00
135	3241.0560	1.30E-02	0.00
136	3245.3390	1.69E-01	0.00
137	3258.6240	-9.94E-02	0.00
138	3278.3030	-2.47E-01	0.00

Table S5. Vibrational frequencies (ω_i / cm^{-1}) at the respective optimized S_0 state, Shift vector K_i (a.u.) and Huang-Rhys factor S_i of **Pt-4**.

	ω_i / (cm^{-1})	K_i (a.u.)	S_i
1	26.4294	6.01E-01	0.00
2	35.4648	5.31E-01	0.00
3	45.3137	-2.81E-01	0.00
4	58.2558	1.34E+01	0.02
5	60.3626	1.79E-01	0.00
6	76.4292	1.61E-02	0.00
7	86.3623	-1.09E-02	0.00
8	89.2498	-8.19E-02	0.00
9	125.4265	-6.67E+00	0.01
10	138.1589	6.25E-02	0.00
11	146.4239	-7.75E-02	0.00
12	152.6010	1.79E-02	0.00
13	170.8257	-1.15E-01	0.00
14	176.9710	9.14E+00	0.03
15	180.2128	-1.05E+00	0.00
16	200.2572	9.75E-01	0.00
17	203.0108	1.32E+01	0.08
18	213.9232	-1.87E+01	0.17
19	248.1172	-2.45E-01	0.00
20	252.8582	7.56E+00	0.03
21	264.1871	1.46E+01	0.13
22	280.6625	-9.86E+00	0.06
23	280.9050	-5.91E+00	0.02
24	325.3684	2.64E-02	0.00
25	338.7873	-4.63E-02	0.00
26	361.3501	-3.11E-01	0.00
27	401.2201	5.16E+00	0.02
28	430.0807	5.03E-02	0.00
29	432.0830	1.43E-03	0.00
30	440.2252	3.83E+00	0.01
31	456.4774	3.44E+00	0.01
32	481.8911	-8.23E-03	0.00
33	485.1609	-5.97E+00	0.04
34	513.5082	-8.38E+00	0.08
35	546.7553	-1.44E+00	0.00
36	553.0663	6.51E-02	0.00
37	567.3433	2.05E-03	0.00
38	586.5264	2.65E-01	0.00
39	611.1735	1.23E+00	0.00

40	621.4136	-3.73E+00	0.02
41	635.7163	-1.66E-02	0.00
42	674.2745	7.84E-03	0.00
43	683.0854	-3.46E+00	0.02
44	687.5202	1.15E-01	0.00
45	692.2352	-2.11E-01	0.00
46	706.7868	-2.83E-03	0.00
47	708.6910	-6.61E-01	0.00
48	735.4388	-3.54E-04	0.00
49	757.0587	-3.56E-02	0.00
50	759.3054	2.31E-03	0.00
51	762.4361	-1.01E-02	0.00
52	779.4534	8.98E-01	0.00
53	781.8273	1.70E-02	0.00
54	799.0338	-2.08E+00	0.01
55	808.5523	1.93E-02	0.00
56	851.4690	1.67E-03	0.00
57	855.0819	8.75E-05	0.00
58	863.3504	-4.32E-03	0.00
59	894.3340	-6.20E-01	0.00
60	911.7123	6.53E-03	0.00
61	923.2986	5.02E-03	0.00
62	946.8556	6.79E-02	0.00
63	948.8744	-8.57E-04	0.00
64	965.1305	-8.01E-05	0.00
65	966.5818	-4.58E-03	0.00
66	977.6469	-2.15E-02	0.00
67	993.3464	5.20E-02	0.00
68	1052.0360	-1.59E-01	0.00
69	1052.5110	-2.42E-01	0.00
70	1058.3770	-1.58E-04	0.00
71	1059.3360	-1.37E-02	0.00
72	1061.5570	-1.00E+00	0.00
73	1063.3520	-7.67E-01	0.00
74	1071.8640	-7.90E-04	0.00
75	1120.2890	1.33E-01	0.00
76	1144.7970	1.67E-01	0.00
77	1160.8630	-9.54E-01	0.00
78	1174.0140	1.51E-02	0.00
79	1175.8090	2.83E+00	0.02
80	1185.7370	-2.22E+00	0.01
81	1205.0660	8.83E-02	0.00
82	1218.8600	1.40E-01	0.00
83	1251.9780	-5.21E+00	0.08

84	1269.1140	1.54E+00	0.01
85	1282.0980	3.77E-02	0.00
86	1304.4920	-9.55E-01	0.00
87	1314.6080	6.48E-01	0.00
88	1316.5290	2.37E-01	0.00
89	1319.7420	-5.82E-02	0.00
90	1361.5130	-1.29E-01	0.00
91	1395.1370	2.20E-01	0.00
92	1413.6080	-2.80E+00	0.03
93	1419.4220	-1.81E-02	0.00
94	1423.4880	6.58E+00	0.14
95	1427.6850	-5.37E-02	0.00
96	1448.0350	7.54E+00	0.19
97	1462.8950	-9.19E+00	0.28
98	1479.0610	-2.64E-01	0.00
99	1484.6750	9.96E-01	0.00
100	1489.5200	-2.41E+00	0.02
101	1499.6510	7.50E-01	0.00
102	1501.1800	-1.44E-01	0.00
103	1504.4560	-3.52E-03	0.00
104	1506.5240	9.48E-03	0.00
105	1511.4230	-3.53E-02	0.00
106	1533.5230	1.03E-01	0.00
107	1535.6500	4.68E+00	0.08
108	1539.7950	-9.01E-01	0.00
109	1551.3440	8.36E+00	0.25
110	1557.6610	2.30E-01	0.00
111	1597.3290	-1.64E+00	0.01
112	1616.3750	-4.93E+00	0.09
113	1635.3220	-1.57E+00	0.01
114	1643.2930	6.84E-01	0.00
115	1673.5760	5.19E+00	0.10
116	1681.2700	-9.98E-01	0.00
117	1704.9990	6.77E+00	0.18
118	1714.7660	6.08E-01	0.00
119	3078.0520	-3.54E-04	0.00
120	3081.4810	-2.41E-03	0.00
121	3082.3560	-7.46E-03	0.00
122	3149.4890	-1.32E-04	0.00
123	3154.2260	7.63E-05	0.00
124	3160.6480	-4.24E-05	0.00
125	3183.6120	3.69E-04	0.00
126	3185.8550	-2.12E-03	0.00
127	3194.3500	1.44E-01	0.00

128	3201.0130	-1.70E-02	0.00
129	3202.3010	-8.58E-02	0.00
130	3202.3570	1.09E-01	0.00
131	3207.0910	-5.27E-02	0.00
132	3207.7100	-1.97E-01	0.00
133	3221.7940	3.44E-03	0.00
134	3223.3960	-1.31E-02	0.00
135	3235.0560	-1.77E-03	0.00
136	3244.2570	-1.20E-03	0.00
137	3321.4920	1.81E-02	0.00
138	3345.2760	1.29E-02	0.00

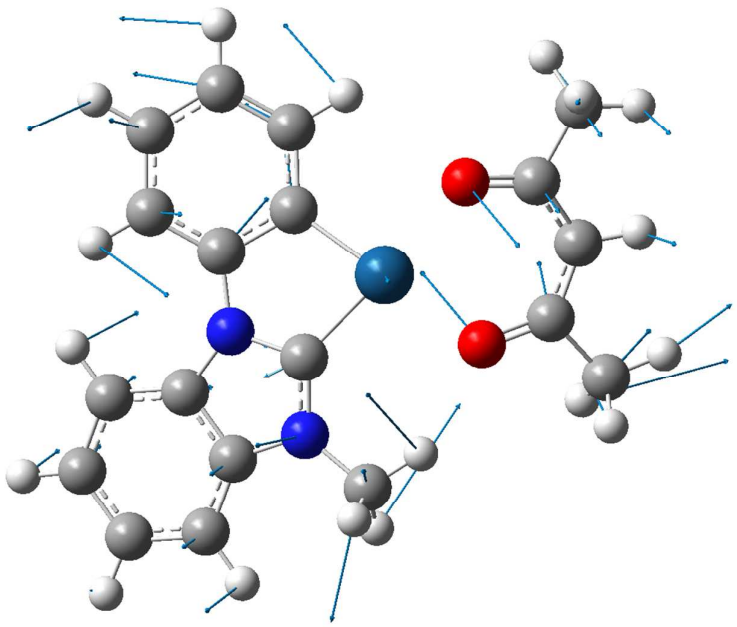


Figure S4. The vibration form of TS [T_1-^{3}MC] for **Pt-1**.

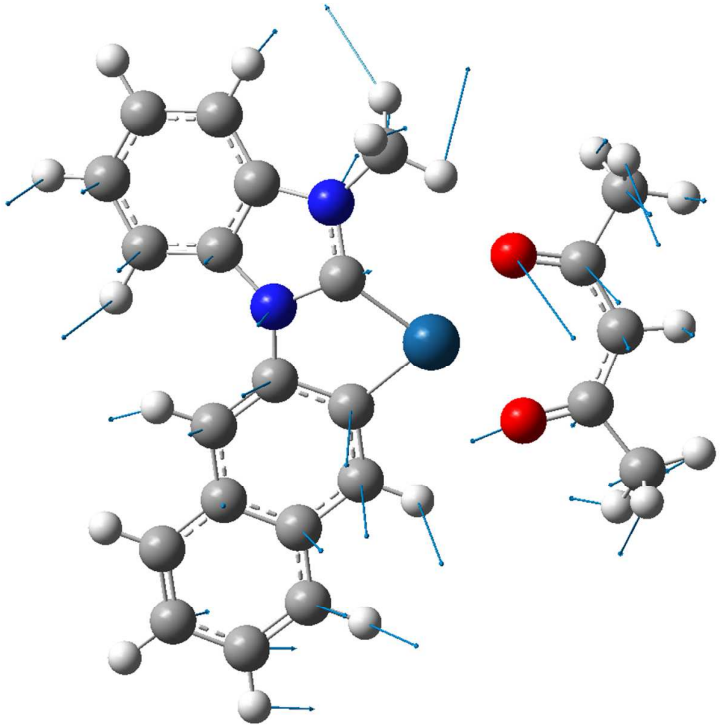


Figure S5. The vibration form of TS [T_1-^{3}MC] for **Pt-2**.

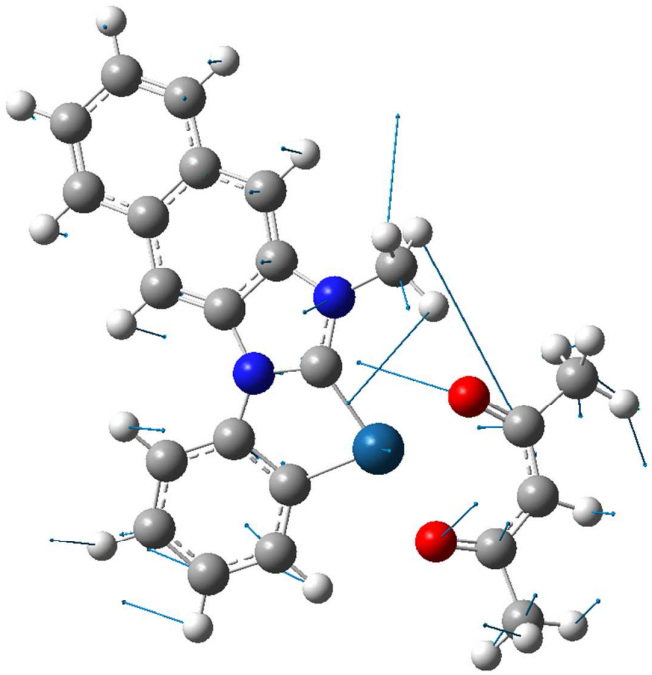


Figure S6. The vibration form of TS [T_1-^{3}MC] for **Pt-3**.

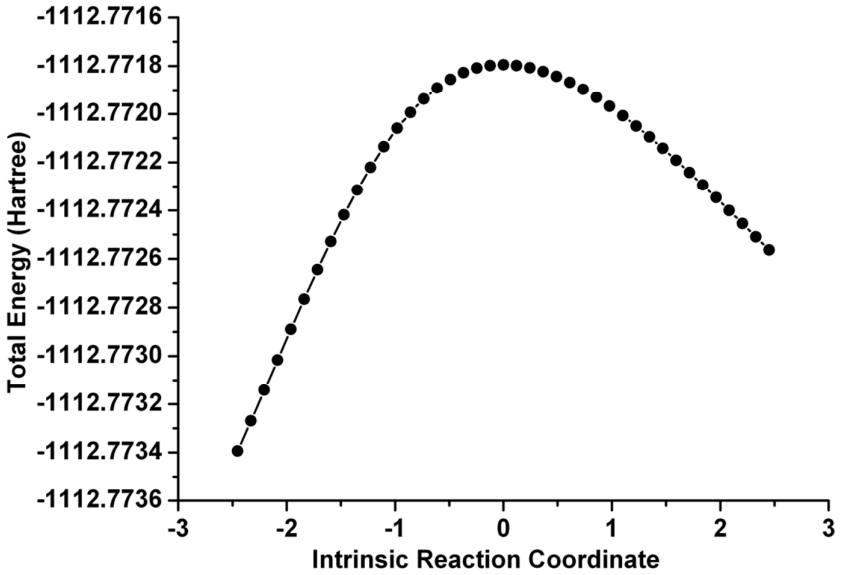


Figure S7. The curve of intrinsic reaction coordinate of TS [T_1-^{3}MC] for **Pt-1**.

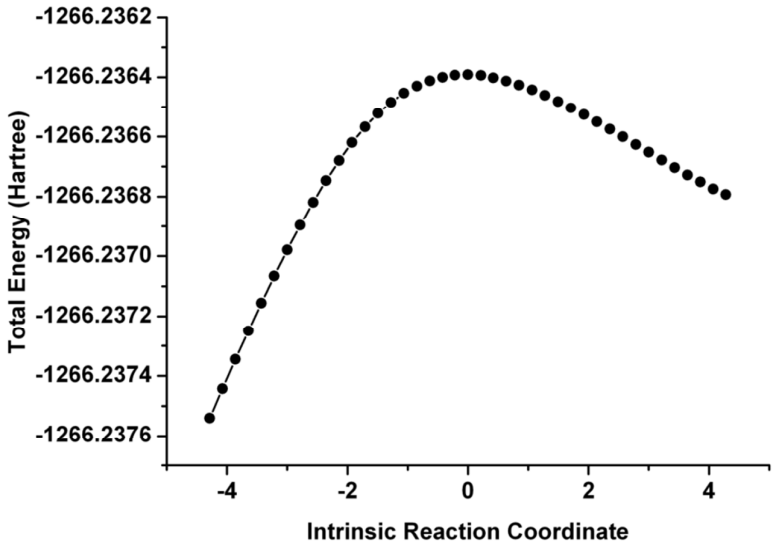


Figure S8. The curve of intrinsic reaction coordinate of TS [T_1-^{3}MC] for **Pt-2**.

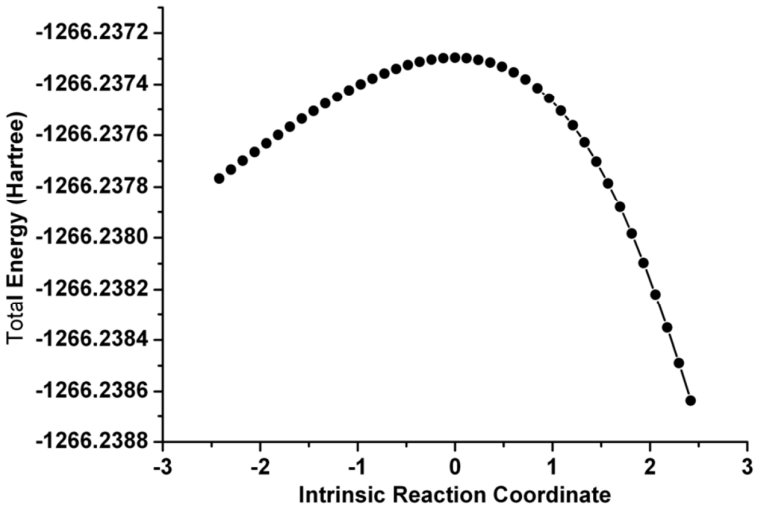
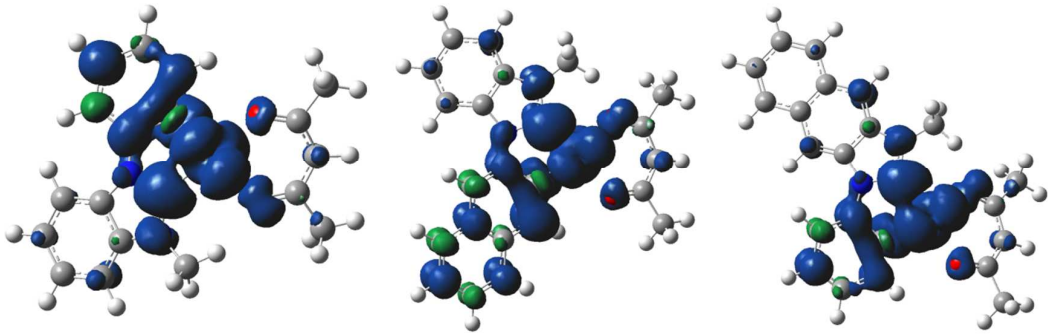
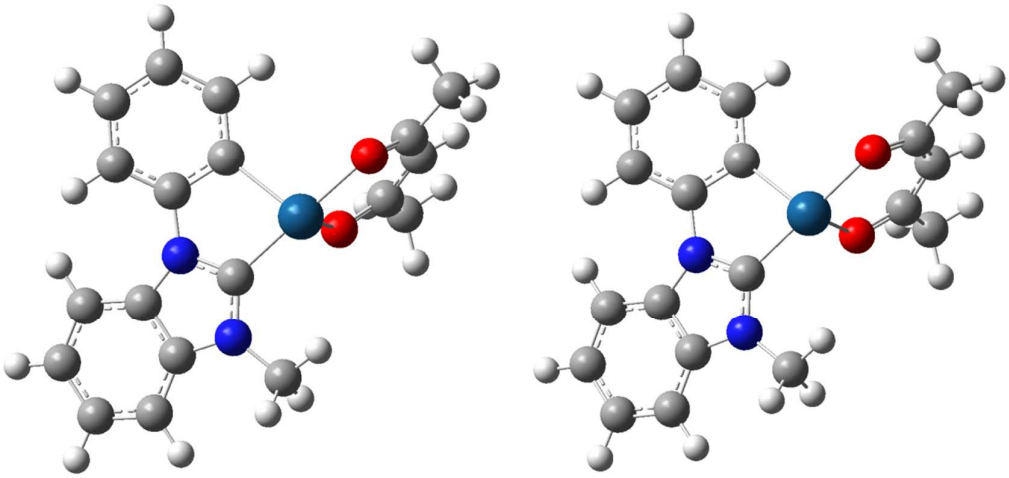


Figure S9. The curve of intrinsic reaction coordinate of TS [T_1-^{3}MC] for **Pt-3**.



Pt-1 **Pt-2** **Pt-3**

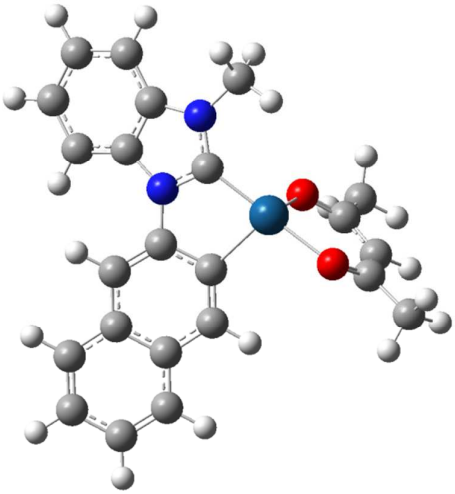
Figure S10. Spin densities computed on the TS [T_1-^{3}MC] for **Pt-1-3** complexes (isovalue = 0.002).



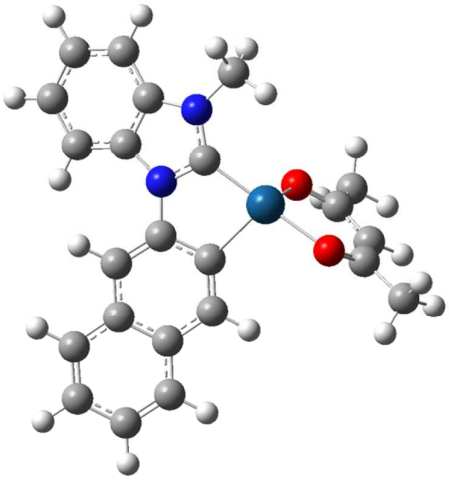
Pt1-C1=1.988 Pt1-C3=2.243
Pt1-O1=2.122 Pt1-O2=2.096
$\Phi_{C2\text{-}N1\text{-}C1\text{-}Pt1}$=-5.442
S_0^{MECP}
E= -1112.77389504a.u.

Pt1-C1=1.988 Pt1-C3=2.243
Pt1-O1=2.122 Pt1-O2=2.096
$\Phi_{O\text{-}N1\text{-}C1\text{-}N2}$=-5.442
$^3MC^{MECP}$
E= -1112.77390023a.u.

Figure S11. The structures of S_0 and ^{3}MC at MECP for **Pt-1**.

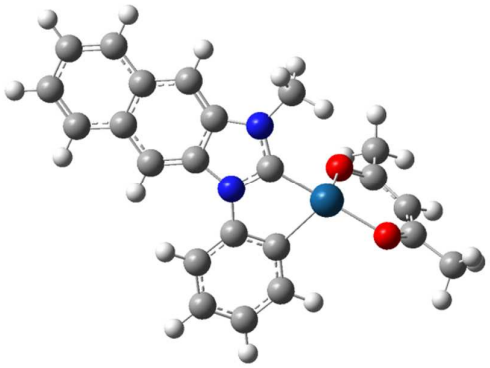


Pt1-C1=1.985 Pt1-C3=2.239
Pt1-O1=2.120 Pt1-O2=2.095
$\Phi_{C2\text{-}N1\text{-}C1\text{-}Pt1}$=6.049
S_0^{MECP}
E= -1266.23991464a.u.

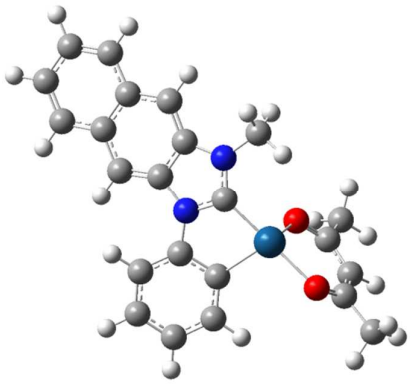


Pt1-C1=1.985 Pt1-C3=2.239
Pt1-O1=2.120 Pt1-O2=2.095
$\Phi_{C2\text{-}N1\text{-}C1\text{-}Pt1}$=6.049
$^3MC^{MECP}$
E= -1266.23991351a.u.

Figure S12. The structures of S_0 and ^{3}MC at MECP for **Pt-2**.

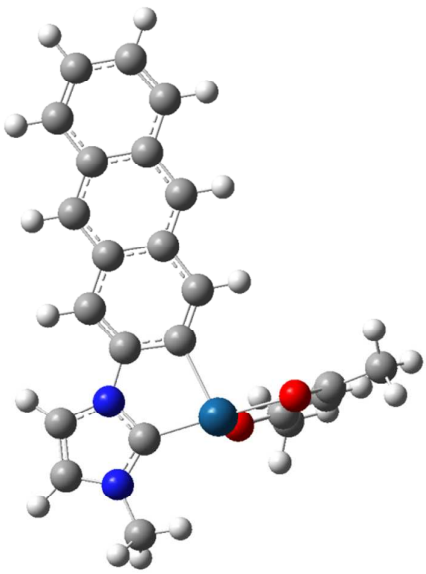


Pt1-C1=1.984 Pt1-C3=2.250
Pt1-O1=2.119 Pt1-O2=2.095
$\Phi_{C2\text{-}N1\text{-}C1\text{-}Pt1}$=4.134
S_0^{MECP}
E= -1266.23639424a.u.

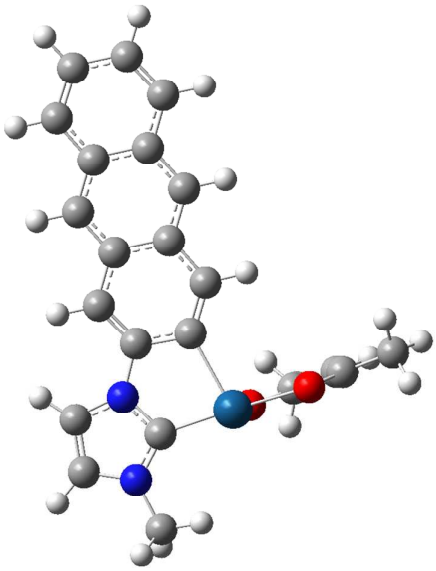


Pt1-C1=1.984 Pt1-C3=2.250
Pt1-O1=2.119 Pt1-O2=2.095
$\Phi_{C2\text{-}N1\text{-}C1\text{-}Pt1}$=4.134
$^3MC^{MECP}$
E= -1266.23638019a.u.

Figure S13. The structures of S_0 and ^{3}MC at MECP for **Pt-3**.



Pt1-C1=1.992 Pt1-C3=2.242
Pt1-O1=2.123 Pt1-O2=2.100
$\Phi_{C2\text{-}N1\text{-}C1\text{-}Pt1}$=-3.523
S_0^{MECP}
E= -1266.22663885a.u.



Pt1-C1=1.992 Pt1-C3=2.242
Pt1-O1=2.123 Pt1-O2=2.100
$\Phi_{C2\text{-}N1\text{-}C1\text{-}Pt1}$=-3.523
$^3MC^{MECP}$
E= -1266.22661456 a.u.

Figure S14. The structures of S_0 and ^{3}MC at MECP for **Pt-4**.

Table S6. Cartesian coordinates of the structures for **Pt-1** reported in the main text.

	S_0		
78	0.843903	0.047278	0.000105
6	-0.072546	1.804722	-0.000033
6	0.535046	3.057928	-0.000093
6	-1.478577	1.765282	0.000070
6	-0.233571	4.223933	-0.000024
1	1.619506	3.115097	-0.000181
6	-2.260980	2.911942	0.000198
6	-1.622396	4.152192	0.000138
1	-3.343397	2.867576	0.000392
1	-2.220096	5.059430	0.000231
6	-1.003838	-0.537091	0.000165
7	-1.968378	0.435603	0.000101
7	-1.648925	-1.724491	0.000049
8	1.812726	-1.857020	0.000234
6	3.839065	0.337076	-0.000470
6	3.070369	-2.040784	0.000082
6	4.057779	-1.046905	-0.000297
1	5.089415	-1.379639	-0.000442
6	5.026565	1.264839	-0.000884
1	5.979444	0.730948	-0.001053
1	4.977674	1.914010	-0.882000
1	4.978116	1.914237	0.880091
6	3.495050	-3.488223	0.000428

1	3.080714	-3.988262	0.883028
1	3.079180	-3.989167	-0.880926
1	4.580572	-3.609675	-0.000419
8	2.714946	0.932394	-0.000304
1	0.257491	5.193957	-0.000074
6	-3.233363	-0.132296	-0.000122
6	-3.020478	-1.521541	-0.000124
6	-4.529754	0.378498	-0.000353
6	-4.068722	-2.432572	-0.000304
6	-5.581382	-0.533250	-0.000543
1	-4.731943	1.441490	-0.000426
6	-5.359852	-1.915067	-0.000509
1	-3.887369	-3.502818	-0.000299
1	-6.600366	-0.157751	-0.000731
1	-6.207455	-2.593703	-0.000657
6	-1.029816	-3.031559	0.000120
1	0.053501	-2.906006	0.000293
1	-1.339172	-3.586513	0.892058
1	-1.338877	-3.586478	-0.891943

T_1

78	0.881439	0.040279	0.349496
6	-0.029744	1.794618	0.164200
6	0.576620	3.048712	0.171334
6	-1.426619	1.748071	0.002689
6	-0.184264	4.210309	0.018167

1	1.652720	3.108913	0.305610
6	-2.200409	2.888865	-0.152469
6	-1.562617	4.130815	-0.143944
1	-3.275230	2.841293	-0.278806
1	-2.154902	5.033685	-0.263476
6	-0.966541	-0.551633	0.183481
7	-1.918828	0.417095	0.019158
7	-1.610421	-1.737385	0.189437
8	1.841503	-1.841502	0.500103
6	3.808288	0.387134	-0.019514
6	2.992404	-2.052677	-0.085079
6	3.931552	-1.004268	-0.297974
1	4.900704	-1.317013	-0.683354
6	4.945378	1.332088	-0.256622
1	5.806357	0.833365	-0.712475
1	4.635336	2.152124	-0.918240
1	5.274975	1.792796	0.685100
6	3.320305	-3.472556	-0.431890
1	3.291380	-4.112676	0.461306
1	2.586588	-3.883040	-1.139995
1	4.312184	-3.566446	-0.884999
8	2.743333	0.896109	0.540866
1	0.304201	5.181472	0.027291
6	-3.179463	-0.152344	-0.077759
6	-2.973968	-1.538472	0.032885

6	-4.466698	0.354540	-0.245476
6	-4.020513	-2.450310	-0.018163
6	-5.516086	-0.557856	-0.296601
1	-4.663834	1.414825	-0.333446
6	-5.301988	-1.936665	-0.185326
1	-3.844561	-3.517851	0.069277
1	-6.527974	-0.185538	-0.426003
1	-6.148159	-2.615538	-0.229986
6	-0.996097	-3.037975	0.349366
1	0.080734	-2.901573	0.466264
1	-1.408606	-3.533631	1.234114
1	-1.198665	-3.652535	-0.533978
	TS		
78	0.848308	0.124815	0.476605
6	-0.083276	1.785493	-0.082336
6	0.514611	3.045175	-0.287762
6	-1.503660	1.733036	0.065833
6	-0.257133	4.194690	-0.324348
1	1.593074	3.101065	-0.404700
6	-2.276001	2.891823	0.072326
6	-1.647996	4.114118	-0.144443
1	-3.341475	2.855716	0.274001
1	-2.245654	5.021639	-0.155020
6	-1.027932	-0.500720	0.627889
7	-1.985608	0.447627	0.277806

7	-1.656553	-1.712690	0.519980
8	1.713645	-1.750243	-0.046270
6	3.880496	0.338710	0.149170
6	2.934096	-1.918890	-0.391903
6	3.964031	-0.980271	-0.346800
1	4.939355	-1.313017	-0.682767
6	5.142500	1.162397	0.219519
1	6.001151	0.661784	-0.233774
1	4.976398	2.122744	-0.279353
1	5.370836	1.380417	1.268926
6	3.238155	-3.313941	-0.878104
1	3.016469	-4.032952	-0.081505
1	2.581535	-3.553290	-1.721539
1	4.279359	-3.434205	-1.185495
8	2.841386	0.916815	0.573453
1	0.208640	5.161636	-0.494603
6	-3.205638	-0.160756	0.008977
6	-2.987537	-1.540557	0.183186
6	-4.449172	0.320284	-0.379440
6	-4.014451	-2.463095	0.026342
6	-5.477696	-0.609621	-0.551915
1	-4.625018	1.374857	-0.554961
6	-5.268002	-1.972998	-0.343149
1	-3.848911	-3.524605	0.181280
1	-6.460445	-0.258117	-0.851765

1	-6.092290	-2.668167	-0.473145
6	-1.075000	-2.975916	0.902181
1	0.009942	-2.875241	0.894763
1	-1.419633	-3.280842	1.898240
1	-1.359225	-3.743126	0.175252
	^{3}MC		
78	0.805399	-0.045343	1.098092
6	0.038382	1.648305	0.024710
6	0.671769	2.834736	-0.326174
6	-1.356618	1.587196	-0.100729
6	-0.063316	3.928619	-0.792337
1	1.752996	2.914412	-0.233836
6	-2.112735	2.676758	-0.520118
6	-1.449648	3.850054	-0.879410
1	-3.196711	2.647626	-0.538505
1	-2.027531	4.706570	-1.215553
6	-1.094335	-0.538688	0.932462
7	-1.920775	0.337215	0.287846
7	-1.800884	-1.672339	1.131938
8	1.481066	-1.380040	-0.507002
6	3.792716	0.135034	0.771163
6	2.695371	-1.421880	-0.875721
6	3.791831	-0.739919	-0.327288
1	4.751940	-0.924663	-0.795177
6	5.105005	0.722581	1.227305

1	5.944728	0.424189	0.595773
1	5.028704	1.815075	1.236357
1	5.301551	0.406789	2.257903
6	2.938693	-2.342359	-2.049996
1	2.603159	-3.353055	-1.794231
1	2.335293	-2.006933	-2.900236
1	3.989647	-2.376992	-2.345958
8	2.791273	0.500219	1.459246
1	0.446255	4.845931	-1.078172
6	-3.158064	-0.249780	0.055669
6	-3.077311	-1.539792	0.609624
6	-4.320357	0.163425	-0.592759
6	-4.141867	-2.431710	0.568860
6	-5.385879	-0.730654	-0.637651
1	-4.399313	1.132484	-1.068145
6	-5.305558	-2.003484	-0.060924
1	-4.064774	-3.424132	1.002053
1	-6.301220	-0.430446	-1.138989
1	-6.160396	-2.670864	-0.114513
6	-1.291106	-2.855558	1.782872
1	-0.298826	-2.616649	2.172342
1	-1.952400	-3.145976	2.605698
1	-1.211502	-3.680806	1.068318

MECP

78	0.83724512	-0.08905047	1.15729161

6	0.08402557	1.58138839	-0.13639244
6	0.69228801	2.77186654	-0.52125581
6	-1.31642271	1.54455174	-0.12757434
6	-0.07042029	3.88630668	-0.88341687
1	1.77867869	2.83974997	-0.54232385
6	-2.09760112	2.65567435	-0.43175214
6	-1.45995227	3.83099313	-0.82603564
1	-3.17765795	2.63587556	-0.32439932
1	-2.05566501	4.70625013	-1.06976095
6	-1.08347270	-0.56519490	0.97197716
7	-1.88427245	0.30424036	0.29496809
7	-1.80774981	-1.68627174	1.18023673
8	1.43628535	-1.28151734	-0.49221731
6	3.80478795	0.11866383	0.83416609
6	2.65372573	-1.33329697	-0.86923192
6	3.76750890	-0.70044476	-0.31006081
1	4.71379716	-0.87708824	-0.80757341
6	5.12861228	0.69047506	1.27335009
1	5.95684025	0.37827031	0.63367229
1	5.06711965	1.78433170	1.27263083
1	5.33059944	0.38210402	2.30457839
6	2.85643169	-2.21899785	-2.07512343
1	2.52480814	-3.23513759	-1.83675575
1	2.23050817	-1.85797876	-2.89737780
1	3.89883089	-2.25038373	-2.39984994

8	2.82453592	0.43449884	1.56863103
1	0.42132548	4.80403062	-1.19765253
6	-3.12354984	-0.27139389	0.04897089
6	-3.07267166	-1.54989257	0.63066717
6	-4.25885551	0.14475538	-0.64427581
6	-4.15080599	-2.42623074	0.58221235
6	-5.33480438	-0.73514818	-0.70010404
1	-4.30278794	1.10363404	-1.14530012
6	-5.28920067	-1.99458164	-0.08934423
1	-4.10449802	-3.40958441	1.03953263
1	-6.23066395	-0.43719400	-1.23654061
1	-6.15199650	-2.65064013	-0.15222222
6	-1.31489202	-2.86509193	1.85203301
1	-0.33835022	-2.61611656	2.27375691
1	-2.00291838	-3.16046116	2.65072600
1	-1.20409298	-3.69080678	1.14194739