Electronic Supplementary Material (ESI) for Analyst.

Supporting Information For:

Biomimetic High Sensitive Detection of Carbon Dioxide by Pyrimido[1,2-a]benzimidazole derivative: Combining Experimental and Theoretical Studies

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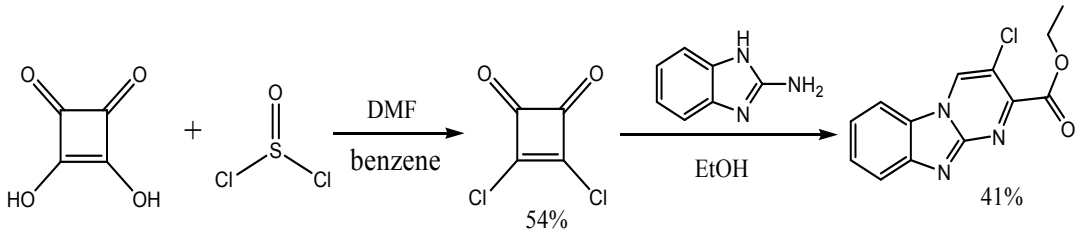
Experimental

Chemicals and reagents

All commercially available reagents and solvents were purchased from commercial suppliers and used without further purification unless otherwise stated. Absorption spectrometry was performed using Gold S54T spectrophotometer of Lengguang Company, and fluorescence spectrometry was performed using F-7000 FL Spectrophotometer of Hitachi. Melting points were determined in open capillaries. ^{1}H NMR and ^{13}C NMR spectra were recorded with a Bruker AVANCE 500 spectrometer with use of the deuterated solvoent as the lock and TMS as an internal reference. Elemental analysis was performed on Elementar Vario vario EL III. Mass spectra were acquired using a triple quadrupole mass spectrometer (6430 QqQLC/MS system; Agilent Technologies, USA) equipped with an orthogonal ESI source.The crystals for X-ray diffraction analyses were grown in dichloromethane by adding n-hexane to slow diffuse. The X-ray diffraction experiment was carried out using Bruker SMART APEX-II Single-crystal diffractometer. Tetrabutylammonium salts (F^-, AcO^-, Cl^-, Br^- and I^-) were all >98% pure and the solutions used in titrations were prepared in fresh dry acetonitrile (CH_3CN).



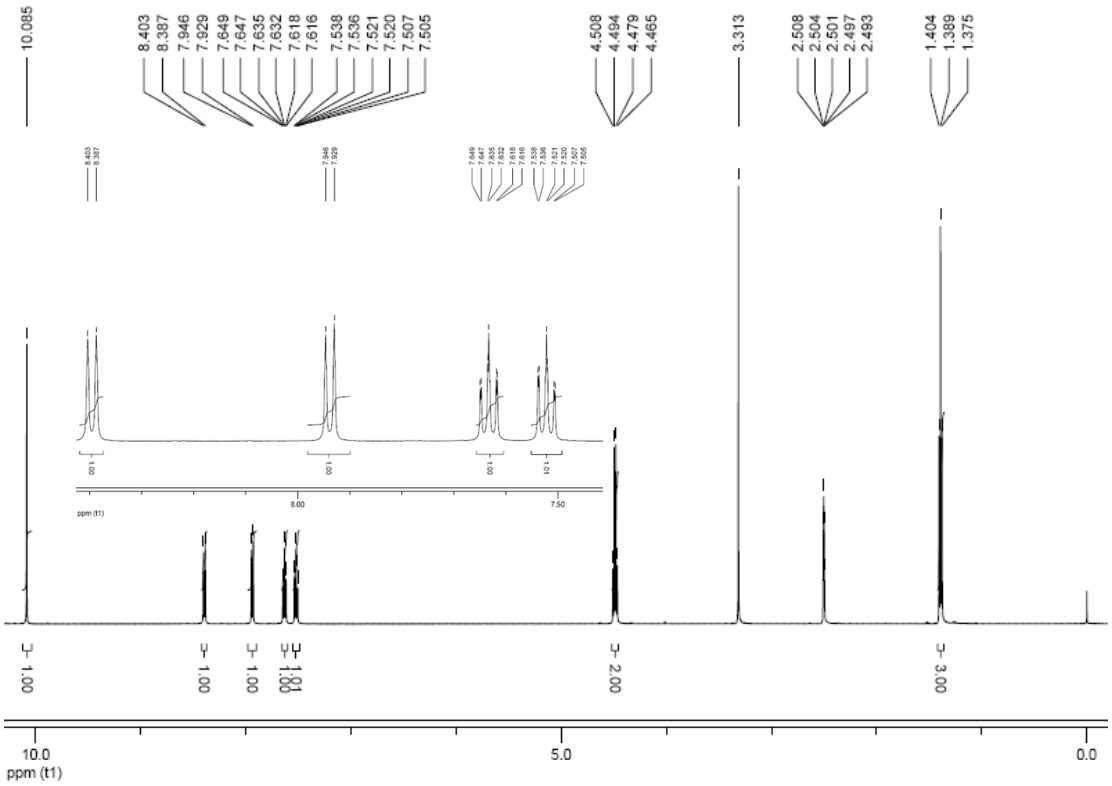
Scheme S1. The synthesis of compound **P1H**

Synthesis of 3,4-Dichlorocyclobutene-1,2-dione

A mixture of squaric acid (1.14 g, 10 mmol), thionyl dichloride (1.8 ml, 20 mmol) and DMF (200ul) in dry benzene (10 ml) was refluxed for 6 h at 60℃. The solvent was evaporated in vacuo and hexane (20 ml) was added, then the soluble products were separated from gummy precipitates. Concentrating and cooling to give yellow crystalline which was used in the next step without further purification (0.82 g, 5.4mmol), yield 54%[1].

Synthesis of P1H

A anhydrous ethanol (30ml) solution of 2-aminobenzimidazole (798mg, 6mmol) was added into fresh 3,4-Dichlorocyclobutene-1,2-dione (750mg, 5mmol) under vigorous stirring, and the mixture was stirred at room temperature for 20min. Then the solvent was removed in vacuo and the residue purified on a column (1% methanol in chloroform as eluent) to give P1H in 41% yield (563mg, 2.08mmol) M.P. 252-253℃. ^{1}H NMR (400 MHz, DMSO-d_6) ppm 10.08 (s, 1H), 8.39 (d, J = 8.22 Hz, 1H), 7.94 (d, J = 8.26 Hz, 1H), 7.70-7.46 (m, 2H), 4.49 (q, J = 7.11 Hz, 2H), 1.46-1.32 (m, 3H). ^{13}C NMR (400 MHz, DMSO-d_6), 163.35(1C), 152.60(1C), 147.44(1C), 145.28(1C), 137.23(1C), 127.60(1C), 127.38(1C), 123.23(1C), 120.24(1C), 113.93(1C), 110.99(1C), 63.15(1C), 14.45(1C). Anal. Calcd for P1H: C, 56.64; H, 3.66; N, 15.24. Found: C, 56.60; H, 3.70; N, 15.21.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7.929
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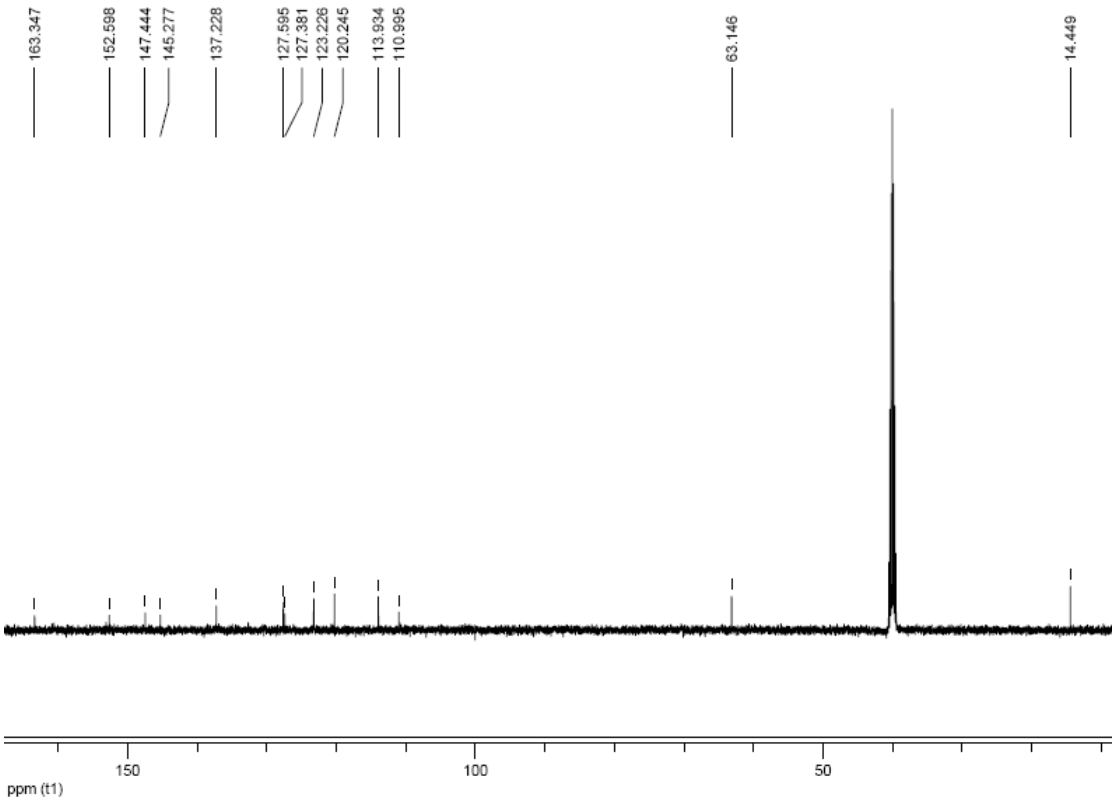
7.635
7.632
7.618
7.616
7.538
7.536
7.521
7.520
7.507
7.505
4.508
4.494
4.479
4.465
3.313
2.508
2.504
2.501
2.497
2.493
1.404
1.389
1.375
1.00
1.00
1.00
1.00
2.00
3.00
10.0
5.0
0.0
ppm (t1)


163.347
152.598
147.444
145.277
137.228
127.595
127.381
123.226
120.245
113.934
110.995
63.146
14.449
150
100
50
ppm (t1)

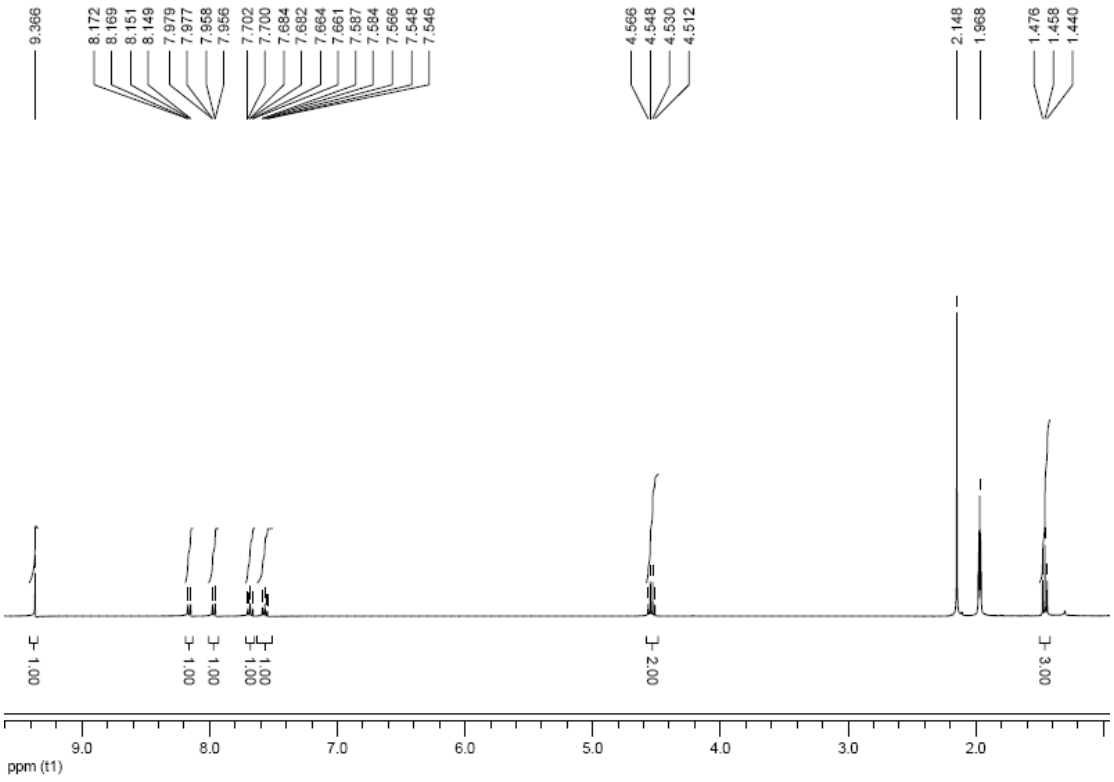


Figure S1. **(a)**The ^{1}H and ^{13}C-NMR of P1H in DMSO-d_6 and (b)The ^{1}H-NMR of P1H in CD_3CN-d_3.

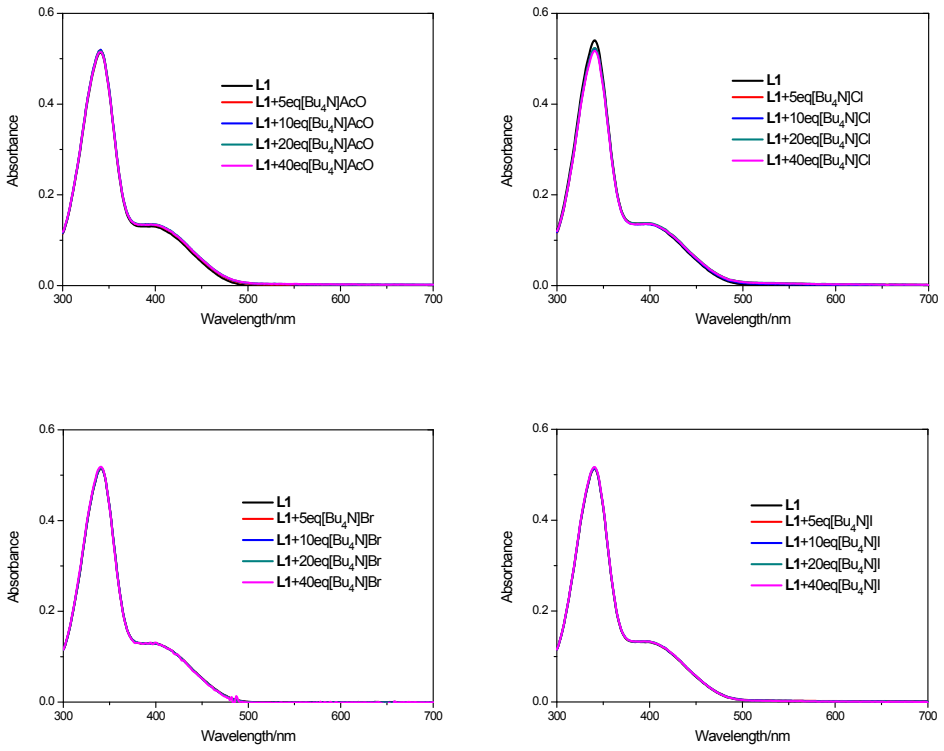


Figure S2. UV−vis spectra taken over the course of titration of receptor P1H (50μM) with $[Bu_4N]X$ in CH_3CN.

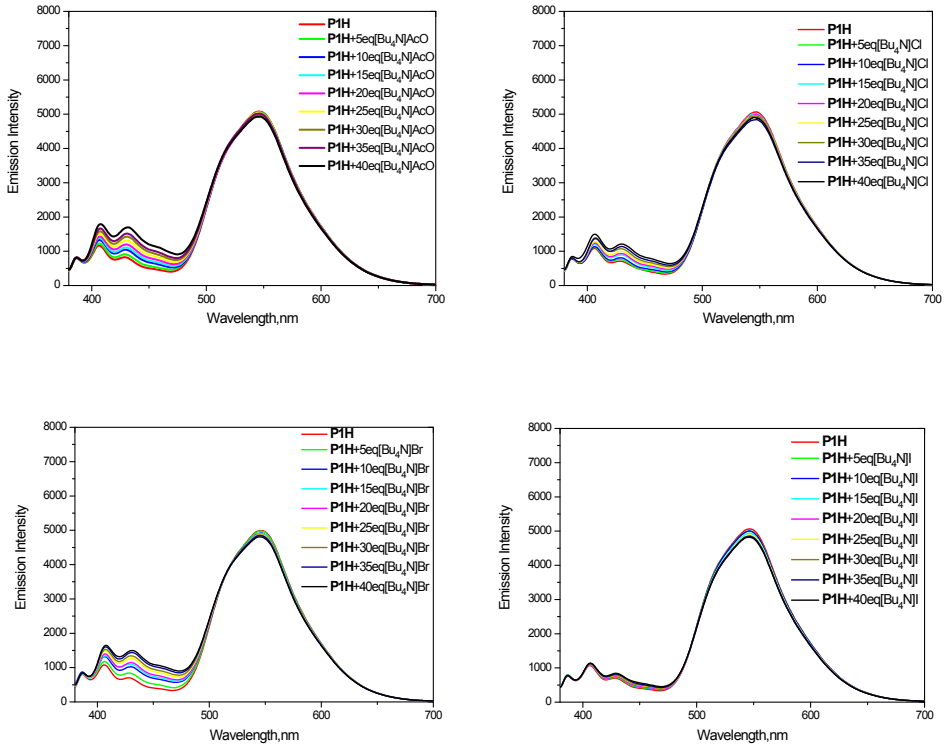


Figure S3. Emission spectra taken upon addition of $[Bu_4N]X$ to P1H (50Mm) in CH_3CN.; excitation wavelength=360 nm.

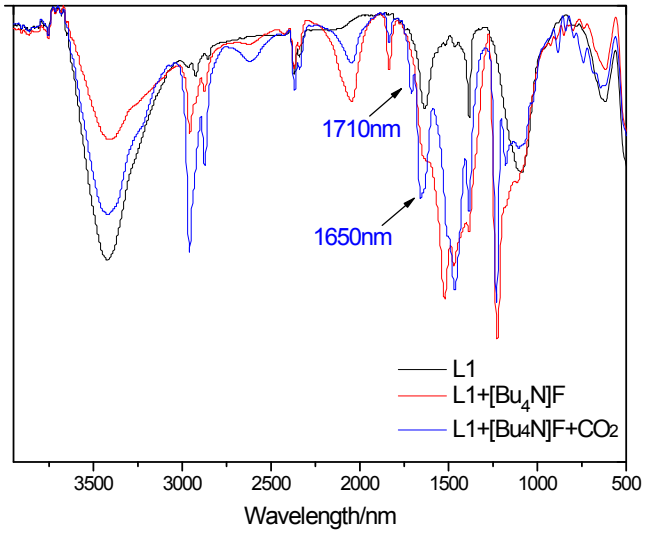


Figure S4. IR spectra taken over the course of titration of receptor P1H (4.5mM) with $[Bu_4N]F$ followed by CO_2 gas.

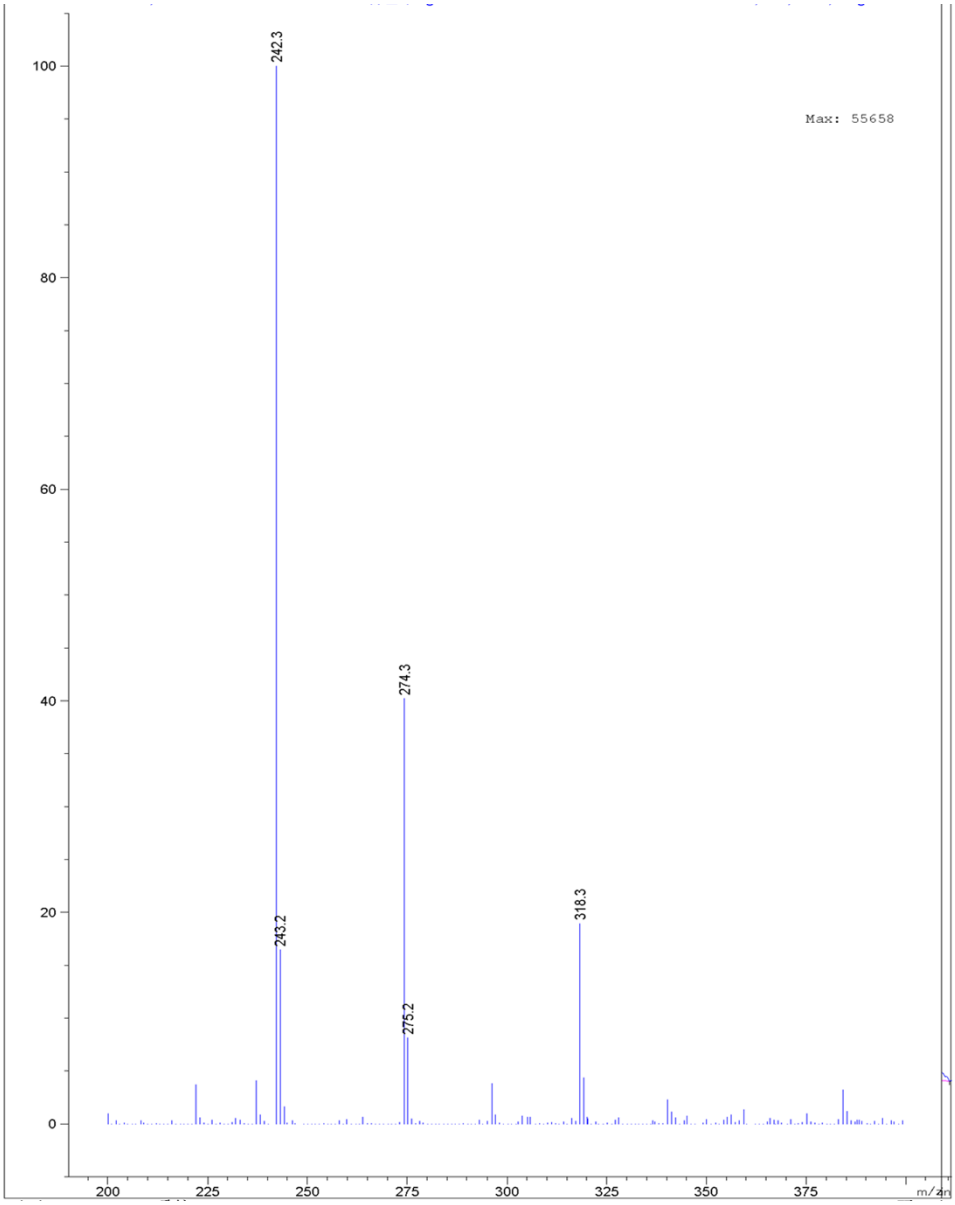


Figure S5. Mass spectrum taken upon addition of $[Bu_4N]F$ to P1H in CH_3CN and then bubbling with enough CO_2。

Table S1. Crystal data and structure refinement for P1H

Empirical formula	$C_{13}H_{10}ClN_3O_2$
Formula weight	275.69
Temperature	296(2) K
Wavelength	0.71073 Å
Crystal system, space group	Orthorhombic, P b c a
Unit cell dimensions	a = 7.240(6) Å alpha = 90 deg. b = 11.439(10) Å beta = 90 deg. c = 29.79(3) Å gamma = 90 deg.
Volume	2467(4) $Å^3$
Z, Calculated density	8, 1.485 Mg/m^3
Absorption coefficient	0.311 mm^{-1}
F(000)	1136
Crystal size	0.25 x 0.20 x 0.15 mm
Theta range for data collection	2.74 to 17.19 deg.
Limiting indices	-6<=h<=5, -9<=k<=9, -24<=l<=24
Reflections collected / unique	6405 / 735 [R(int) = 0.0654]
Completeness to theta = 17.19	99.6 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.954 and 0.928
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	735 / 0 / 173
Goodness-of-fit on F^2	1.019
Final R indices [I>2sigma(I)]	R1 = 0.0300, wR2 = 0.0756
R indices (all data)	R1 = 0.0435, wR2 = 0.0823
Largest diff. peak and hole	0.161 and -0.118 e. $Å^{-3}$

Optimazed structure

TS1

1	6	0	−4. 967285	0. 193614	0. 358034
2	6	0	−5. 230085	−1. 188133	0. 362676
3	6	0	−4. 212208	−2. 112993	0. 230387
4	6	0	−2. 900775	−1. 638527	0. 091423
5	6	0	−2. 660081	−0. 245793	0. 092002
6	6	0	−3. 682197	0. 693541	0. 222024
7	1	0	−5. 796014	0. 887015	0. 462014
8	1	0	−6. 254013	−1. 532590	0. 470798
9	1	0	−4. 407590	−3. 179920	0. 230947
10	1	0	−3. 440776	1. 755646	0. 210577
11	6	0	−0. 797943	−1. 453846	−0. 149401

12	6	0	1.320271	-0.686176	-0.366428
13	6	0	0.877610	0.654209	-0.302683
14	6	0	-0.456466	0.968323	-0.148680
15	1	0	-0.682784	2.285109	-0.056429
16	7	0	-1.747007	-2.359377	-0.057160
17	7	0	-1.276777	-0.124022	-0.063376
18	7	0	0.506998	-1.711407	-0.308683
19	6	0	2.769458	-1.069803	-0.537807
20	8	0	3.171002	-1.732434	-1.459731
21	8	0	3.513817	-0.634761	0.468065
22	6	0	4.921374	-0.951491	0.406488
23	6	0	5.572321	-0.360037	1.628594
24	1	0	5.326487	-0.535426	-0.519275
25	1	0	5.029731	-2.038120	0.367597
26	1	0	6.642138	-0.582117	1.615413
27	1	0	5.446739	0.724784	1.652035
28	1	0	5.145438	-0.782336	2.541189
29	17	0	2.057969	1.924578	-0.493555
30	9	0	-2.167548	3.263479	0.095399
31	9	0	-0.185768	3.599185	0.019451

TS2

1	6	0	4.918021	0.071361	0.244433
2	6	0	5.164892	-1.306799	0.373847
3	6	0	4.139663	-2.235798	0.324035
4	6	0	2.829993	-1.770948	0.146088
5	6	0	2.605272	-0.382064	0.030795
6	6	0	3.630432	0.555055	0.067834
7	1	0	5.749552	0.767010	0.278988
8	1	0	6.186156	-1.647795	0.510708
9	1	0	4.333950	-3.299056	0.416636
10	1	0	3.431415	1.613334	-0.051781
11	6	0	0.725630	-1.566293	-0.114227
12	6	0	-1.352726	-0.723459	-0.405240
13	6	0	-0.847085	0.589730	-0.428505
14	6	0	0.490357	0.886976	-0.282986
15	7	0	1.660600	-2.482879	0.053779
16	7	0	1.233406	-0.249234	-0.131588
17	7	0	-0.589090	-1.786966	-0.258667
18	6	0	-2.816853	-1.032286	-0.582520
19	8	0	-3.268702	-1.568174	-1.562268
20	8	0	-3.522422	-0.667373	0.479286
21	6	0	-4.944533	-0.912155	0.417199
22	6	0	-5.544501	-0.426902	1.710125

23	1	0	-5.105113	-1.982222	0.265116
24	1	0	-5.347640	-0.381233	-0.448850
25	1	0	-6.623600	-0.598272	1.698767
26	1	0	-5.120814	-0.963139	2.562398
27	1	0	-5.367919	0.642570	1.845809
28	17	0	-1.977957	1.919296	-0.699440
29	6	0	1.134208	3.154218	0.271813
30	8	0	1.708733	3.497524	-0.688134
31	8	0	0.652173	3.169335	1.337602

P1-COOH

1	6	0	4.877264	0.042694	0.917819
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3	6	0	4.159994	-2.142307	0.199113
4	6	0	2.885356	-1.597712	-0.045655
5	6	0	2.638112	-0.215165	0.159370
6	6	0	3.604189	0.615322	0.656524
7	1	0	5.655655	0.690088	1.304306
8	1	0	6.142012	-1.687607	0.889794
9	1	0	4.331435	-3.199231	0.034047
10	1	0	3.444501	1.669292	0.823157
11	6	0	0.795081	-1.318521	-0.451277
12	6	0	-1.346641	-0.595043	-0.449247
13	6	0	-0.952082	0.704593	-0.184431
14	6	0	0.430209	1.046146	-0.150793
15	7	0	1.780754	-2.249740	-0.435325
16	7	0	1.265102	-0.062307	-0.168603
17	7	0	-0.484067	-1.607031	-0.669257
18	6	0	-2.785350	-1.007837	-0.602431
19	8	0	-3.191894	-1.571663	-1.585113
20	8	0	-3.504853	-0.722329	0.470538
21	6	0	-4.905312	-1.080207	0.415800
22	6	0	-5.525836	-0.681580	1.727937
23	1	0	-4.977999	-2.155031	0.234252
24	1	0	-5.358350	-0.559411	-0.431233
25	1	0	-6.587032	-0.941634	1.721505
26	1	0	-5.049441	-1.204881	2.560059
27	1	0	-5.436952	0.394606	1.892466
28	17	0	-2.159753	1.939589	-0.002861
29	6	0	1.047658	2.362651	-0.354069
30	8	0	2.159322	2.481632	-0.828705
31	8	0	0.371248	3.462291	-0.001055
32	1	0	-0.502448	3.246262	0.353894

TS3

1	6	0	4.930369	-0.088734	0.015339
2	6	0	5.173497	-1.450460	0.271397
3	6	0	4.138620	-2.360046	0.369823
4	6	0	2.827763	-1.891494	0.213801
5	6	0	2.600498	-0.516369	-0.020063
6	6	0	3.644143	0.398374	-0.137682
7	1	0	5.768327	0.594638	-0.067244
8	1	0	6.197480	-1.790480	0.385361
9	1	0	4.320258	-3.413186	0.553001
10	1	0	3.467668	1.447185	-0.326686
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24	1	0	-5.391965	-0.691397	-0.550281
25	1	0	-6.709706	-0.458202	1.569485
26	1	0	-5.220603	-0.592832	2.518862
27	1	0	-5.479291	0.811543	1.462921
28	17	0	-2.042140	1.639811	-0.918686
29	6	0	0.949665	2.726238	0.575895
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31	8	0	-0.212996	3.026280	1.052038
32	1	0	-0.925981	2.895238	0.395528
33	8	0	0.951495	3.212890	-1.008243
34	1	0	0.934762	2.269813	-1.343607
35	1	0	1.795749	3.642814	-1.227380

[1] Masatomi Ohno, Yoshihiko Yamamoto, Yuhichi Shirasaki and Shoji Eguchi. J. CHEM. SOC. PERKIN TRANS. 1993.