

## Supplementary Materials

### Ozonation of aromatic monomer compounds in water: factors determining reaction outcomes

Zhe Wang<sup>1</sup>, Wenjuan Zhang<sup>2</sup>, Zhiwei Wang<sup>3</sup>, Jing Chang<sup>2</sup>(✉)

1 School of Environmental Science and Safety Engineering, Tianjin University of Technology, Tianjin 300384, China

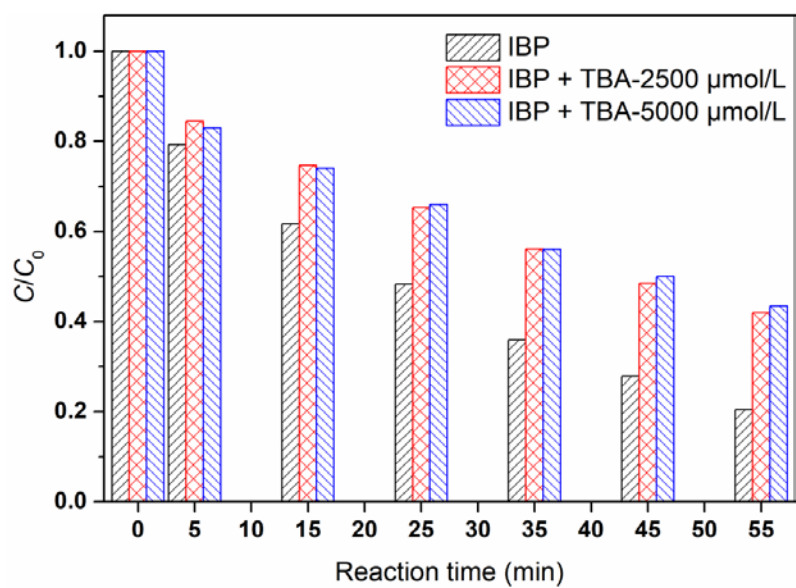
2 School of Environmental and Municipal Engineering, Tianjin Key Laboratory of Aquatic Science and Technology, Tianjin Chengjian University, Tianjin 300384, China

3 Tianjin Municipal Engineering Design & Research Institute Co., Ltd., Tianjin 300384, China

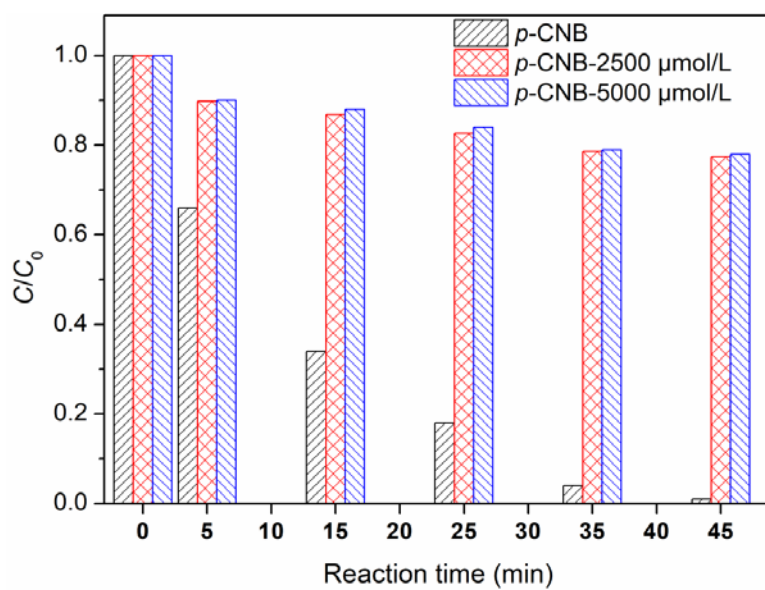
Corresponding author. [changjinghit@163.com](mailto:changjinghit@163.com) (Chang Jing), 86-18202555176

---

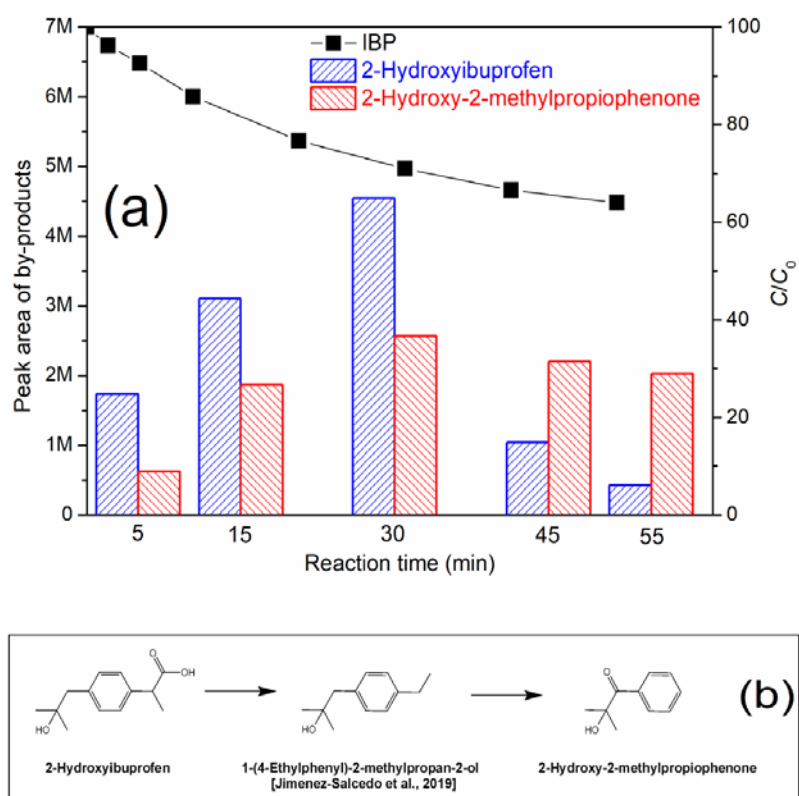
✉Corresponding author  
E-mail: [changjinghit@163.com](mailto:changjinghit@163.com)



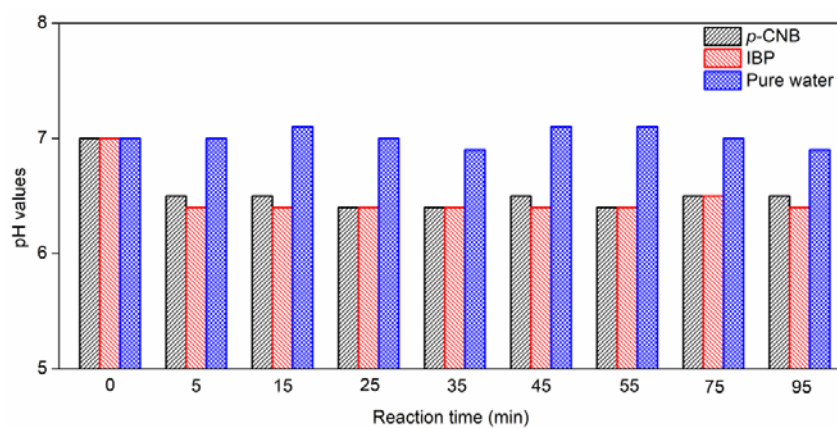
**Fig. S1** Effects of TBA concentrations on the IBP removal. Conditions:  $[\text{IBP}]_0 = 10.8 \mu\text{mol/L}$ ,  $[\text{O}_3]_0 = 0.5 \text{ mg/L}$ ,  $\text{pH} = 7.0$ ,  $T = 20 \text{ }^\circ\text{C}$ .



**Fig. S2** Effects of TBA concentrations on the *p*-CNB removal. Conditions:  $[\text{p-CNB}]_0 = 10.8 \mu\text{mol/L}$ ,  $[\text{O}_3]_0 = 0.5 \text{ mg/L}$ ,  $\text{pH} = 7.0$ ,  $T = 20 \text{ }^\circ\text{C}$ .



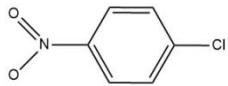
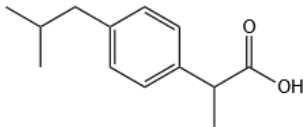
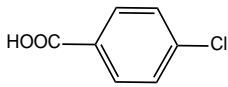
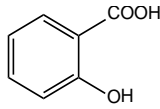
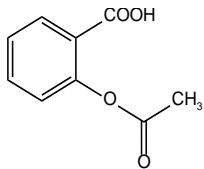
**Fig. S3** Changes of 2-hydroxyibuprofen and 2-Hydroxy-2-methylpropiophenone during the ozonation of IBP (a), and their transformation pathway proposed during  $\bullet\text{OH}$  oxidation (b). Conditions:  $[\text{IBP}]_0 = 54.0 \mu\text{mol/L}$ ,  $[\text{O}_3]_0 = 0.5 \text{ mg/L}$ ,  $\text{pH} = 5.0$ ,  $T = 20 \text{ }^\circ\text{C}$ .



**Fig. S4** Changes of pH values in the solution during the ozonation of targets. Conditions:  $[\text{AMCs}]_0 = 10.8 \mu\text{mol/L}$ ,  $[\text{O}_3]_0 = 0.5 \text{ mg/L}$ ,  $T = 20 \text{ }^\circ\text{C}$ .

Changes of pH values in the solution during the ozonation process were studied. As shown in Fig. S4, the pH values of pure water did not change significantly under 95 min of ozonation, which proved that the carbonation of water from carbon dioxide dissolution could be ignored under this condition. In comparison, when the *p*-CNB and IBP were oxidized for 5 min, the solution pH decreased from 7.0 to about 6.5, and then remained constant. It illustrated that the acid by-products formed did affect the solution pH in the first 5 min of reaction. However, maybe owing to the fact that these acid by-products were then degraded continuously, transforming to other acids, aldehydes and ketones, or even mineralized, the amount of acids did not accumulate to an extent of obviously change the solution pH. Thus, the solution pH did not drop continuously after 5 min of reaction.

**Table S1** Information regarding compounds studied

Target compounds	CAS numbers	Molecular weight	Molecular structure
<i>p</i> -Chloronitrobenzene ( <i>p</i> -CNB)	100-00-5	157.55	
Ibuprofen (IBP)	15687-27-1	206.28	
<i>p</i> -Chlorobenzoic acid ( <i>p</i> -CBA)	74-11-3	156.57	
Salicylic acid (SA)	69-72-7	138.12	
Acetylsalicylic acid (ASA)	50-78-2	180.16	

**Table S2** Bond length, bond angle, and dihedral angle of the *p*-CNB optimized.

Bond length	Value	Bond angle	Value	Dihedral angle	Value
R(1,2)	1.3838	A(2,1,6)	118.9136	D(6,1,2,3)	0.0075
R(1,6)	1.3828	A(2,1,7)	120.9671	D(6,1,2,8)	-180.0029
R(1,7)	1.0664	A(6,1,7)	120.1193	D(7,1,2,3)	180.0034
R(2,3)	1.3811	A(1,2,3)	118.9516	D(7,1,2,8)	-0.007
R(2,8)	1.0672	A(1,2,8)	120.522	D(2,1,6,5)	0.0058
R(3,4)	1.3811	A(3,2,8)	120.5263	D(2,1,6,11)	179.9945
R(3,14)	1.7966	A(2,3,4)	122.1782	D(7,1,6,5)	180.0098
R(4,5)	1.3838	A(2,3,14)	118.9115	D(7,1,6,11)	-0.0014
R(4,9)	1.0672	A(4,3,14)	118.9103	D(1,2,3,4)	-0.0109
R(5,6)	1.3829	A(3,4,5)	118.9528	D(1,2,3,14)	-180.0058
R(5,10)	1.0664	A(3,4,9)	120.525	D(8,2,3,4)	179.9995
R(6,11)	1.4479	A(5,4,9)	120.5222	D(8,2,3,14)	0.0046
R(11,12)	1.2265	A(4,5,6)	118.9127	D(2,3,4,5)	0.0008
R(11,13)	1.2265	A(4,5,10)	120.9681	D(2,3,4,9)	180.0006
		A(6,5,10)	120.1192	D(14,3,4,5)	-180.0042
		A(1,6,5)	122.0911	D(14,3,4,9)	-0.0044
		A(1,6,11)	118.9535	D(3,4,5,6)	0.0123
		A(5,6,11)	118.9554	D(3,4,5,10)	-180.0083
		A(6,11,12)	118.196	D(9,4,5,6)	180.0125
		A(6,11,13)	118.1945	D(9,4,5,10)	-0.0081

	A(12,11,13)	123.6095	D(4,5,6,1)	-0.0158
			D(4,5,6,11)	-180.0045
			D(10,5,6,1)	-179.9954
			D(10,5,6,11)	0.0159
			D(1,6,11,12)	179.9753
			D(1,6,11,13)	-0.035
			D(5,6,11,12)	-0.0356
			D(5,6,11,13)	-180.0459

**Table S3** Bond length, bond angle, and dihedral angle of the IBP optimized.

Bond length	Value	Bond angle	Value	Dihedral angle	Value
R(1,2)	1.5329	A(2,1,3)	110.9362	D(3,1,2,6)	56.6684
R(1,3)	1.0817	A(2,1,4)	111.1264	D(3,1,2,7)	-60.3087
R(1,4)	1.0787	A(2,1,5)	109.6331	D(3,1,2,15)	176.4872
R(1,5)	1.0803	A(3,1,4)	107.8345	D(4,1,2,6)	176.6271
R(2,6)	1.0787	A(3,1,5)	108.5435	D(4,1,2,7)	59.6501
R(2,7)	1.504	A(4,1,5)	108.6917	D(4,1,2,15)	-63.554
R(2,15)	1.5261	A(1,2,6)	109.369	D(5,1,2,6)	-63.1997
R(7,8)	1.2107	A(1,2,7)	110.9878	D(5,1,2,7)	179.8233
R(7,9)	1.3489	A(1,2,15)	112.7939	D(5,1,2,15)	56.6192
R(9,10)	0.95	A(6,2,7)	106.3067	D(1,2,7,8)	-30.4434
R(11,12)	1.3914	A(6,2,15)	107.6976	D(1,2,7,9)	150.4185
R(11,16)	1.386	A(7,2,15)	109.4267	D(6,2,7,8)	-149.2813
R(11,17)	1.0716	A(2,7,8)	126.0447	D(6,2,7,9)	31.5806
R(12,13)	1.3918	A(2,7,9)	112.6204	D(15,2,7,8)	94.6767
R(12,28)	1.5126	A(8,7,9)	121.3293	D(15,2,7,9)	-84.4614
R(13,14)	1.3856	A(7,9,10)	113.4743	D(1,2,15,14)	-114.4957
R(13,18)	1.0721	A(12,11,16)	121.3141	D(1,2,15,16)	64.0872
R(14,15)	1.3892	A(12,11,17)	119.5007	D(6,2,15,14)	6.2822
R(14,19)	1.0716	A(16,11,17)	119.1852	D(6,2,15,16)	-175.135
R(15,16)	1.3904	A(11,12,13)	117.6888	D(7,2,15,14)	121.4365

R(16,20)	1.0711	A(11,12,28)	121.5589	D(7,2,15,16)	-59.9806
R(21,22)	1.532	A(13,12,28)	120.7523	D(2,7,9,10)	176.7229
R(21,24)	1.0808	A(12,13,14)	121.1648	D(8,7,9,10)	-2.4612
R(21,25)	1.0829	A(12,13,18)	119.6409	D(16,11,12,13)	0.2127
R(21,26)	1.0848	A(14,13,18)	119.1942	D(16,11,12,28)	-179.8029
R(22,23)	1.0856	A(13,14,15)	120.8778	D(17,11,12,13)	-179.7475
R(22,27)	1.5333	A(13,14,19)	119.4371	D(17,11,12,28)	0.2369
R(22,28)	1.5456	A(15,14,19)	119.685	D(12,11,16,15)	-0.0376
R(27,29)	1.0831	A(2,15,14)	120.5001	D(12,11,16,20)	179.6784
R(27,30)	1.0844	A(2,15,16)	121.2237	D(17,11,16,15)	179.9227
R(27,31)	1.0827	A(14,15,16)	118.2616	D(17,11,16,20)	-0.3613
R(28,32)	1.0841	A(11,16,15)	120.6915	D(11,12,13,14)	-0.4203
R(28,33)	1.0841	A(11,16,20)	119.3618	D(11,12,13,18)	179.4441
		A(15,16,20)	119.9461	D(28,12,13,14)	179.5951
		A(22,21,24)	111.667	D(28,12,13,18)	-0.5405
		A(22,21,25)	110.693	D(11,12,28,22)	106.4476
		A(22,21,26)	110.7762	D(11,12,28,32)	-16.0033
		A(24,21,25)	107.84	D(11,12,28,33)	-131.8943
		A(24,21,26)	107.9968	D(13,12,28,22)	-73.5685
		A(25,21,26)	107.7159	D(13,12,28,32)	163.9807
		A(21,22,23)	107.9455	D(13,12,28,33)	48.0896
		A(21,22,27)	110.8357	D(12,13,14,15)	0.458

A(21,22,28)	112.1167	D(12,13,14,19)	-179.647
A(23,22,27)	107.9432	D(18,13,14,15)	-179.407
A(23,22,28)	107.7318	D(18,13,14,19)	0.488
A(27,22,28)	110.1042	D(13,14,15,2)	178.3568
A(22,27,29)	111.3776	D(13,14,15,16)	-0.2673
A(22,27,30)	110.8899	D(19,14,15,2)	-1.5379
A(22,27,31)	110.9941	D(19,14,15,16)	179.8379
A(29,27,30)	107.8435	D(2,15,16,11)	-178.5535
A(29,27,31)	107.8337	D(2,15,16,20)	1.7322
A(30,27,31)	107.7461	D(14,15,16,11)	0.0602
A(12,28,22)	114.8712	D(14,15,16,20)	-179.6541
A(12,28,32)	109.4332	D(24,21,22,23)	-59.5041
A(12,28,33)	108.8861	D(24,21,22,27)	-177.5217
A(22,28,32)	108.6114	D(24,21,22,28)	58.9975
A(22,28,33)	108.3247	D(25,21,22,23)	60.658
A(32,28,33)	106.375	D(25,21,22,27)	-57.3596
		D(25,21,22,28)	179.1596
		D(26,21,22,23)	-179.9217
		D(26,21,22,27)	62.0606
		D(26,21,22,28)	-61.4202
		D(21,22,27,29)	177.2506
		D(21,22,27,30)	-62.6429

---

	D(21,22,27,31)	57.0863
	D(23,22,27,29)	59.2315
	D(23,22,27,30)	179.338
	D(23,22,27,31)	-60.9328
	D(28,22,27,29)	-58.119
	D(28,22,27,30)	61.9875
	D(28,22,27,31)	-178.2833
	D(21,22,28,12)	-63.7622
	D(21,22,28,32)	59.1305
	D(21,22,28,33)	174.275
	D(23,22,28,12)	54.8657
	D(23,22,28,32)	177.7583
	D(23,22,28,33)	-67.0971
	D(27,22,28,12)	172.3473
	D(27,22,28,32)	-64.76
	D(27,22,28,33)	50.3845

---

**Table S4** Orbital coefficients of *p*-CNB.

Atomic r	Atomic orbital i	$FED_{r,i}^{HOMO}$	$FED_{r,i}^{LOMO}$	$\sum_i (FED_{r,i}^{HOMO})^2 + \sum_i (FED_{r,i}^{LOMO})^2$
C1	1S	-0.00001	0.00001	0.081
	2S	-0.00001	0.00001	
	2PX	0.00003	0	
	2PY	-0.00001	-0.00003	
	2PZ	0.04477	0.08031	
	3S	0.00003	-0.00004	
	3PX	0.00004	0	
	3PY	-0.00001	-0.00005	
	3PZ	0.07378	0.12536	
	4S	0.00002	-0.00022	
	4PX	-0.00002	-0.00016	
	4PY	-0.00007	-0.00017	
	4PZ	0.0604	0.21954	
	C2	1S	0	
2S		0.00001	0	
2PX		-0.00002	0	
2PY		0.00001	0	
2PZ		-0.08362	0.02014	
3S		-0.00002	0	
3PX		-0.00003	0	
3PY		0.00001	-0.00001	
3PZ		-0.13582	0.03025	
4S		-0.00004	-0.00005	
4PX		-0.00004	-0.00004	
4PY		0.00003	0.00006	
4PZ		-0.13138	0.05453	
C3		1S	0	0
	2S	0	0	
	2PX	0.00001	0	
	2PY	0.00001	0.00001	
	2PZ	-0.1264	-0.10195	
	3S	0.00001	0.00001	
	3PX	0.00001	0	
	3PY	0.00001	0.00001	
	3PZ	-0.20317	-0.16297	
	4S	-0.00003	0.00004	
	4PX	-0.00001	0.00001	
	4PY	0.00002	0.00007	
	4PZ	-0.16534	-0.24044	

			0.179
C4	1S	0	0
	2S	-0.00001	0.00001
	2PX	0.00003	-0.00001
	2PY	0.00001	0
	2PZ	-0.08362	0.02014
	3S	0.00002	-0.00002
	3PX	0.00005	-0.00002
	3PY	0.00001	0
	3PZ	-0.13583	0.03025
	4S	0.00014	-0.00008
	4PX	0.00008	-0.00001
	4PY	0	0.00008
	4PZ	-0.13139	0.05453
C5	1S	0	-0.00001
	2S	0.00001	-0.00001
	2PX	-0.00002	0.00001
	2PY	-0.00001	-0.00003
	2PZ	0.04476	0.0803
	3S	-0.00001	0.00003
	3PX	-0.00004	0.00002
	3PY	-0.00001	-0.00006
	3PZ	0.07376	0.12535
	4S	-0.00018	0.00042
	4PX	0.00007	0.00009
	4PY	0.00003	-0.0003
	4PZ	0.06039	0.21953
C6	1S	0	0
	2S	0	0
	2PX	0.00002	-0.00001
	2PY	-0.00005	0.00002
	2PZ	0.13061	-0.0643
	3S	-0.00002	-0.00001
	3PX	0.00004	-0.00003
	3PY	-0.00009	0.00003
	3PZ	0.21945	-0.10794
	4S	0.00011	-0.00008
	4PX	-0.00004	0.00009
	4PY	-0.00006	-0.00041
	4PZ	0.20275	-0.20078

**Table S5** Orbital coefficients of IBP.

Atomic r	Atomic orbital i	$FED_{r,i}^{HOMO}$	$2\sum_i (FED_{r,i}^{HOMO})^2$
C1	1S	-0.00838	0.046
	2S	-0.01369	
	2PX	0.02934	
	2PY	0.02081	
	2PZ	0.01783	
	3S	0.03846	
	3PX	0.04709	
	3PY	0.03771	
	3PZ	0.0328	
	4S	0.1051	
	4PX	0.0221	
	4PY	0.03962	
	4PZ	0.04556	
C2	1S	0.00072	0.021
	2S	0.00117	
	2PX	-0.00174	
	2PY	-0.03861	
	2PZ	-0.00626	
	3S	-0.00042	
	3PX	-0.00179	
	3PY	-0.06289	
	3PZ	-0.00782	
	4S	-0.06423	
	4PX	0.02021	
	4PY	-0.02684	
	4PZ	-0.00253	
C7	1S	0.01075	
	2S	0.01779	
	2PX	-0.0131	
	2PY	0.03227	
	2PZ	-0.007	
	3S	-0.05847	
	3PX	-0.02199	
	3PY	0.0514	
	3PZ	-0.02026	
	4S	-0.05506	
	4PX	-0.01287	
	4PY	0.01325	
	4PZ	-0.03404	

			0.026
C11	1S	-0.0003	
	2S	-0.0005	
	2PX	-0.00656	
	2PY	-0.06773	
	2PZ	-0.02162	
	3S	0.0017	
	3PX	-0.00993	
	3PY	-0.10886	
	3PZ	-0.0351	
	4S	-0.00261	
	4PX	-0.01003	
	4PY	-0.10692	
	4PZ	-0.04202	
C12	1S	0.00017	
	2S	0.00026	
	2PX	-0.0116	
	2PY	-0.1341	
	2PZ	-0.04032	
	3S	-0.00023	
	3PX	-0.01915	
	3PY	-0.21771	
	3PZ	-0.06613	
	4S	-0.01256	
	4PX	-0.0356	
	4PY	-0.20274	
	4PZ	-0.05601	
C13	1S	-0.00063	
	2S	-0.00105	
	2PX	-0.00733	
	2PY	-0.08051	
	2PZ	-0.02508	
	3S	0.00349	
	3PX	-0.01162	
	3PY	-0.13002	
	3PZ	-0.04007	
	4S	-0.0069	
	4PX	-0.01128	
	4PY	-0.12862	
	4PZ	-0.03624	
C14	1S	0.00046	

	2S	0.00074	
	2PX	0.0064	
	2PY	0.06102	
	2PZ	0.01931	
	3S	-0.00156	
	3PX	0.01011	
	3PY	0.09874	
	3PZ	0.031	
	4S	0.00041	
	4PX	0.01478	
	4PY	0.09629	
	4PZ	0.02611	
			0.050
	1S	-0.00009	
	2S	-0.00007	
	2PX	0.01044	
	2PY	0.13587	
	2PZ	0.04078	
	3S	-0.00098	
C15	3PX	0.01916	
	3PY	0.22033	
	3PZ	0.0665	
	4S	-0.00637	
	4PX	-0.00126	
	4PY	0.20893	
	4PZ	0.06822	
			0.244
	1S	0.00034	
	2S	0.00056	
	2PX	0.0073	
	2PY	0.07317	
	2PZ	0.02394	
	3S	-0.00159	
C16	3PX	0.01202	
	3PY	0.11859	
	3PZ	0.03836	
	4S	0.0047	
	4PX	0.01422	
	4PY	0.11049	
	4PZ	0.04966	
			0.073
	1S	-0.00009	
C21	2S	-0.0003	
	2PX	-0.01086	

	2PY	0.0172	
	2PZ	0.00138	
	3S	0.00287	
	3PX	-0.01986	
	3PY	0.02726	
	3PZ	0.00116	
	4S	-0.01053	
	4PX	-0.01867	
	4PY	0.04317	
	4PZ	0.00696	
			0.008
	1S	-0.00946	
	2S	-0.01528	
	2PX	-0.03315	
	2PY	-0.04102	
	2PZ	-0.01785	
	3S	0.03938	
C22	3PX	-0.05482	
	3PY	-0.06768	
	3PZ	-0.02992	
	4S	0.13721	
	4PX	-0.01842	
	4PY	-0.06489	
	4PZ	-0.04852	
			0.078
	1S	0.00161	
	2S	0.00258	
	2PX	0.01753	
	2PY	0.0038	
	2PZ	0.00278	
	3S	-0.00642	
C27	3PX	0.03043	
	3PY	0.00406	
	3PZ	0.00388	
	4S	-0.04245	
	4PX	0.04262	
	4PY	0.00085	
	4PZ	0.00967	
			0.010
	1S	-0.00158	
	2S	-0.00259	
C28	2PX	0.00583	
	2PY	0.04647	
	2PZ	0.01232	

---

3S	0.01012
3PX	0.01047
3PY	0.06702
3PZ	0.01863
4S	-0.00619
4PX	-0.02965
4PY	0.0508
4PZ	0.01242

0.022

---