Insights into the electronic structure of non-steroidal anti-inflammatory drugs: soft X-ray study of fenoprofen, ketoprofen and methyl salicylate in the gas phase

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Supplementary Material

Table S1. Theoretical relative energy values and relative abundance at the experimental conditions of the conformers of fenoprofen and ketoprofen at the B3LYP-D3(BJ)/Def2-TZVP level of calculation.

Table S2. Theoretical molecular structures of the conformers of fenoprofen at the B3LYP-D3(BJ)/Def2-TZVP level of calculation. The principal axis system coordinates are used (Å).

Table S3. Theoretical molecular structures of the conformers of ketoprofen at the B3LYP-D3(BJ)/Def2-TZVP level of calculation. The principal axis system coordinates are used (Å).

Table S4. Complete list of experimental valence band ionization potentials of methyl salicylate compared to the theoretical vertical ionization potentials.

Table S5. Complete list of experimental valence band ionization potentials of fenoprofen compared to the theoretical vertical ionization potentials of conformer #S-FP-A1"-*anti*. *Ph1* and *Ph2* refer to the unsubstituted and substituted phenyl rings.

Table S6. Complete list of experimental valence band ionization potentials of ketoprofen compared to the theoretical vertical ionization potentials of conformer #S-KP-A1"-*anti*. *Ph1* and *Ph2* refer to the unsubstituted and substituted phenyl rings.

Figure S1. Theoretical zero point corrected relative energy values of the conformers of fenoprofen and ketoprofen at the B3LYP-D3(BJ)/Def2-TZVP level of calculation.

Figure S2a. Valence photoelectron spectra of methyl salicylate (red line), photon energy 100 eV, compared to the simulation obtained by convolution of the vertical ionization potentials with gaussian functions (σ=0.1 and 0.2 eV for the peaks with *vIP* less or more than 10 eV, respectively), using P3+ method (black line) and OVGF method (black dashed line).

Figure S2b. Theoretical molecular orbitals of MS at the B3LYP-D3(BJ)/Def2-TZVP level of calculation.

Figure S3a. Valence photoelectron spectra of fenoprofen (green line), photon energy 60 eV, compared to the simulation obtained by convolution of the vertical ionization potentials of the most stable conformer, FP#*S*-A1"-*anti*, with gaussian functions (σ=0.1 and 0.2 eV for the peaks with *vIP*

less or more than 10 eV, respectively), using P3+ method (black line) and OVGF method (black dashed line).

Figure S3b. Theoretical molecular orbitals of FP#*S*-A1"-*anti* at the B3LYP-D3(BJ)/Def2-TZVP level of calculation.

Figure S4a. Valence photoelectron spectra of ketoprofen (blue line), photon energy 100 eV, compared to the simulation obtained by convolution of the vertical ionization potentials of KP#*S*-A1"-*anti* with gaussian functions (σ=0.1 and 0.2 eV for the peaks with *vIP* less or more than 10 eV, respectively), using P3+ method (black line) and OVGF method (black dashed line).

Figure S4b. Theoretical molecular orbitals of KP#*S*-A1"-*anti* at the B3LYP-D3(BJ)/Def2-TZVP level of calculation.

Figure S5. Comparison of the valence band spectra of methyl salicylate (red line) and salicylic acid (black line).

Figure S6. Comparison of the C K edge NEXAFS spectra of methyl salicylate (red line) and salicylic acid (black line), normalized to show approximately the same intensity for peaks *a*. Note the different intensity and peak shape for peaks *e*.

Figure S7. Comparison of the O K edge NEXAFS spectra of methyl salicylate (red line) and salicylic acid (black line), normalized to show approximately the same intensity for peaks *a*. Note the different intensity and peak shape for peaks *b*.

Figure S8. Comparison of the O K edge NEXAFS spectra of fenoprofen (green line) and ketoprofen (blue line), normalized to show approximately the same intensity for peaks *a*. Note the reduced intensity of peak *b* in ketoprofen.

Table S1. Theoretical relative energy values and relative abundance at the experimental conditions of the conformers of fenoprofen and ketoprofen at the B3LYP-D3(BJ)/Def2-TZVP level of calculation.

	FP			KP		
Conformer	ΔE_e	ΔE_0	Population[a]	ΔE_e	ΔE_0	Population[b]
S-A1'-*anti*	0[c]	0[d]	1.00	67	51	0.80
S-A1"-*anti*	7	9	0.96	0[e]	0[f]	1.00
S-A2'-*anti*	31	46	0.81	58	50	0.81
S-A2"-*anti*	65	73	0.72	126	111	0.62
S-B1'-*anti*	87	86	0.68	239	200	0.42
S-B1"-*anti*	102	106	0.62	285	239	0.36
S-B2'-*anti*	92	101	0.64	114	105	0.64
S-B2"-*anti*	80	90	0.67	79	69	0.74
S-A1'-*syn*	336	363	0.20	401	411	0.17
S-A1"-*syn*	293	321	0.24	359	355	0.22
S-A2'-*syn*	385	425	0.15	380	393	0.18
S-A2"-*syn*	464	493	0.11	526	526	0.10
S-B1'-*syn*	409	437	0.14	461	462	0.14
S-B1"-*syn*	438	464	0.13	500	495	0.12
S-B2'-*syn*	490	526	0.10	585	586	0.08
S-B2"-*syn*	461	496	0.11	491	499	0.12

[a]*T*=323 K, [b]*T*=333 K, [c]E_e=-806.091782 a.u., [d]E_0=-805.835728 a.u., [e]E_e=-844.228528 a.u., [f]E_0=-843.966104 a.u.

Table S2. Theoretical molecular structures of the conformers of fenoprofen at the B3LYP-D3(BJ)/Def2-TZVP level of calculation. The principal axis system coordinates are used (Å).

	FP#*S*-B1'-*anti*	*a*	*b*	*c*
1	C	2.578395	0.261010	-0.450460
2	C	2.714171	0.522365	0.909140
3	C	3.983377	0.711302	1.440156
4	C	5.108550	0.649376	0.625357
5	C	4.957268	0.397156	-0.733274
6	C	3.693947	0.198791	-1.275417
7	O	1.346133	0.127239	-1.051891
8	C	0.341649	-0.568046	-0.419203
9	C	-0.949560	-0.086888	-0.579990
10	C	-2.025394	-0.775611	-0.024086
11	C	-1.788051	-1.940457	0.699810
12	C	-0.490929	-2.417077	0.850919
13	C	0.582858	-1.740154	0.291802
14	C	-3.444566	-0.268379	-0.222965
15	C	-3.883265	-0.337001	-1.686869
16	C	-3.540265	1.150397	0.306255
17	O	-3.424752	2.153919	-0.347597
18	O	-3.747566	1.172528	1.642413
19	H	1.836868	0.576728	1.538489
20	H	4.090506	0.916369	2.497571
21	H	6.093903	0.799761	1.045625
22	H	5.826219	0.349099	-1.376736
23	H	3.555942	-0.000063	-2.329478
24	H	-1.099476	0.829968	-1.134352
25	H	-2.617508	-2.475267	1.144092
26	H	-0.314076	-3.329270	1.406022
27	H	1.592462	-2.109093	0.403657
28	H	-4.103087	-0.884304	0.390464
29	H	-4.918409	-0.011941	-1.798064
30	H	-3.260843	0.305966	-2.306652
31	H	-3.796267	-1.361276	-2.049012
32	H	-3.748359	2.104064	1.913846

	FP#*S*-B1'-*syn*	*a*	*b*	*c*
1	C	2.592607	0.237187	-0.447801
2	C	2.698693	0.540721	0.905746
3	C	3.955158	0.759605	1.455426
4	C	5.096956	0.685474	0.665199
5	C	4.975339	0.390350	-0.687797
6	C	3.725213	0.161927	-1.248294
7	O	1.374603	0.071485	-1.069932
8	C	0.357788	-0.598105	-0.427424
9	C	-0.928140	-0.115360	-0.620206
10	C	-2.016303	-0.779272	-0.057231
11	C	-1.791935	-1.921337	0.707456
12	C	-0.499672	-2.399565	0.891338
13	C	0.584770	-1.747067	0.324302
14	C	-3.435118	-0.275172	-0.264449
15	C	-3.827191	-0.205153	-1.744885
16	C	-3.620443	1.049511	0.455253
17	O	-4.119867	1.178221	1.541605
18	O	-3.144469	2.102274	-0.251312
19	H	1.808938	0.603697	1.516524
20	H	4.038940	0.997105	2.508145
21	H	6.072150	0.858925	1.100022
22	H	5.857426	0.331714	-1.312254
23	H	3.610519	-0.070975	-2.298193
24	H	-1.060944	0.784389	-1.203939
25	H	-2.629466	-2.437168	1.158624
26	H	-0.335628	-3.293926	1.478374
27	H	1.591118	-2.116754	0.460793
28	H	-4.105482	-0.960688	0.252407

29	H	-4.855825	0.140453	-1.858336
30	H	-3.178869	0.472931	-2.296429
31	H	-3.744959	-1.197255	-2.189171
32	H	-3.273213	2.891431	0.297836

	FP#*S*-B2'-*anti*	*a*	*b*	*c*
1	C	-2.845541	0.480995	-0.213983
2	C	-3.129847	-0.834443	-0.565965
3	C	-4.443421	-1.281722	-0.514640
4	C	-5.467944	-0.425829	-0.124740
5	C	-5.170722	0.888751	0.215049
6	C	-3.859506	1.346029	0.175416
7	O	-1.573753	1.004037	-0.306626
8	C	-0.492762	0.272803	0.128080
9	C	0.698510	0.451966	-0.564783
10	C	1.854030	-0.201481	-0.152868
11	C	1.805463	-1.036287	0.963580
12	C	0.611909	-1.203956	1.652307
13	C	-0.545580	-0.552812	1.245037
14	C	3.144839	-0.026896	-0.937067
15	C	3.574477	-1.317969	-1.636124
16	C	4.228129	0.467736	0.003281
17	O	5.033766	-0.221794	0.572470
18	O	4.175667	1.808948	0.163152
19	H	-2.331208	-1.494934	-0.873800
20	H	-4.666640	-2.304644	-0.789248
21	H	-6.489270	-0.780503	-0.089096
22	H	-5.960974	1.563299	0.518168
23	H	-3.607798	2.364458	0.438233
24	H	0.706196	1.109619	-1.424042
25	H	2.701101	-1.542346	1.298319
26	H	0.580897	-1.843685	2.524852
27	H	-1.473204	-0.679536	1.784629
28	H	2.980339	0.757383	-1.676726
29	H	4.477592	-1.158497	-2.226504
30	H	3.782615	-2.099751	-0.907846
31	H	2.778840	-1.659890	-2.297956
32	H	4.858081	2.045302	0.811094

	FP#*S*-B2'-*syn*	*a*	*b*	*c*
1	C	-2.842285	0.513172	-0.155679
2	C	-3.160452	-0.726952	-0.699599
3	C	-4.482524	-1.151273	-0.693761
4	C	-5.481935	-0.345317	-0.158879
5	C	-5.151035	0.895567	0.372621
6	C	-3.830697	1.327962	0.379707
7	O	-1.560164	1.018058	-0.192653
8	C	-0.492764	0.218076	0.140817
9	C	0.708055	0.484461	-0.506510
10	C	1.854142	-0.236044	-0.188858
11	C	1.784070	-1.227783	0.790278
12	C	0.581409	-1.482884	1.434446
13	C	-0.565793	-0.765254	1.120121
14	C	3.149331	0.064886	-0.925728
15	C	3.708698	-1.159239	-1.660071
16	C	4.153602	0.684003	0.030796
17	O	4.365854	1.862828	0.136371
18	O	4.798431	-0.237510	0.785897
19	H	-2.380776	-1.347156	-1.119619
20	H	-4.732528	-2.115244	-1.117875
21	H	-6.510243	-0.681144	-0.159804
22	H	-5.921772	1.530950	0.789300
23	H	-3.552618	2.289089	0.790198
24	H	0.731240	1.263490	-1.256979
25	H	2.668343	-1.788574	1.057694
26	H	0.534469	-2.246784	2.199908

27	H	-1.499870	-0.962130	1.626368
28	H	2.943051	0.853141	-1.648518
29	H	4.627164	-0.906725	-2.192121
30	H	3.929072	-1.970720	-0.969388
31	H	2.975704	-1.513530	-2.385104
32	H	5.385932	0.251665	1.382886

	FP#*S*-A1'-*anti*	*a*	*b*	*c*
1	C	2.348659	0.490656	-0.306320
2	C	2.453445	0.137927	1.034952
3	C	3.348157	-0.856239	1.406869
4	C	4.138913	-1.488229	0.452832
5	C	4.030710	-1.118768	-0.882357
6	C	3.132755	-0.130737	-1.267756
7	O	1.522759	1.514441	-0.723388
8	C	0.219653	1.563858	-0.289246
9	C	-0.518208	0.419997	-0.011943
10	C	-1.851910	0.532400	0.375426
11	C	-2.437340	1.791501	0.466480
12	C	-1.691628	2.929166	0.178253
13	C	-0.361137	2.824237	-0.197060
14	C	-2.651237	-0.716306	0.712756
15	C	-2.102196	-1.437751	1.945074
16	C	-2.658912	-1.635450	-0.494414
17	O	-1.891118	-2.540738	-0.692481
18	O	-3.632770	-1.301993	-1.370743
19	H	1.838766	0.636181	1.771904
20	H	3.431707	-1.133059	2.449907
21	H	4.834695	-2.261641	0.749312
22	H	4.641900	-1.604916	-1.631608
23	H	3.030060	0.167549	-2.302164
24	H	-0.058670	-0.554042	-0.105787
25	H	-3.475123	1.881759	0.760009
26	H	-2.150314	3.906762	0.250961
27	H	0.236046	3.696946	-0.422660
28	H	-3.682571	-0.410092	0.890479
29	H	-2.715900	-2.304171	2.194654
30	H	-1.086196	-1.786140	1.767266
31	H	-2.094494	-0.756866	2.796201
32	H	-3.542675	-1.893704	-2.134434

	FP#*S*-A1'-*syn*	*a*	*b*	*c*
1	C	2.376412	0.450498	-0.316916
2	C	2.462433	0.101803	1.027117
3	C	3.356469	-0.886628	1.415964
4	C	4.165058	-1.518397	0.476872
5	C	4.075723	-1.153356	-0.861093
6	C	3.179171	-0.171059	-1.263591
7	O	1.554747	1.467284	-0.754232
8	C	0.257292	1.546350	-0.303682
9	C	-0.497493	0.417674	-0.011824
10	C	-1.824442	0.554533	0.391018
11	C	-2.384048	1.826571	0.479394
12	C	-1.622177	2.948893	0.174837
13	C	-0.297878	2.817792	-0.213979
14	C	-2.661574	-0.666061	0.737448
15	C	-2.042163	-1.504904	1.861818
16	C	-2.933829	-1.479910	-0.515558
17	O	-3.950817	-1.438477	-1.155814
18	O	-1.890357	-2.269986	-0.864010
19	H	1.835426	0.599731	1.753663
20	H	3.426033	-1.158275	2.461427
21	H	4.861000	-2.286283	0.787038
22	H	4.702125	-1.637485	-1.599078
23	H	3.092711	0.124909	-2.300191
24	H	-0.053429	-0.561966	-0.107974

25	H	-3.416452	1.937978	0.783935
26	H	-2.063091	3.934657	0.246127
27	H	0.312713	3.677837	-0.451916
28	H	-3.643335	-0.313721	1.050844
29	H	-2.672985	-2.362686	2.099839
30	H	-1.056776	-1.875066	1.585110
31	H	-1.940846	-0.891753	2.757584
32	H	-2.139252	-2.718374	-1.687254

	FP#*S*-A2'-*anti*	*a*	*b*	*c*
1	C	-2.647303	0.417034	0.026058
2	C	-2.422773	-0.591753	-0.905278
3	C	-3.275708	-1.687127	-0.937157
4	C	-4.348421	-1.775695	-0.056589
5	C	-4.566403	-0.755792	0.862326
6	C	-3.715772	0.341350	0.909943
7	O	-1.878234	1.559849	0.069712
8	C	-0.513613	1.482169	-0.085003
9	C	0.234358	0.433430	0.440722
10	C	1.618306	0.432195	0.309378
11	C	2.247387	1.488611	-0.349229
12	C	1.491829	2.534196	-0.862205
13	C	0.108869	2.538414	-0.735971
14	C	2.432883	-0.705708	0.904235
15	C	3.336935	-0.238915	2.045717
16	C	3.243049	-1.355831	-0.201873
17	O	4.396109	-1.126811	-0.458396
18	O	2.499498	-2.232353	-0.915100
19	H	-1.590358	-0.518465	-1.591093
20	H	-3.102421	-2.472694	-1.661319
21	H	-5.009755	-2.631127	-0.088774
22	H	-5.399387	-0.813965	1.550925
23	H	-3.867512	1.143831	1.618932
24	H	-0.265048	-0.380805	0.947569
25	H	3.322852	1.486958	-0.466795
26	H	1.982545	3.352037	-1.373715
27	H	-0.495071	3.342911	-1.132399
28	H	1.732995	-1.457924	1.270440
29	H	3.877750	-1.079680	2.481669
30	H	4.069766	0.482143	1.688212
31	H	2.734537	0.231800	2.822514
32	H	3.064910	-2.569342	-1.627858

	FP#*S*-A2'-*syn*	*a*	*b*	*c*
1	C	-2.632055	0.429209	0.004999
2	C	-2.399736	-0.585865	-0.917201
3	C	-3.243476	-1.688474	-0.938261
4	C	-4.315414	-1.776705	-0.056622
5	C	-4.541684	-0.750092	0.852614
6	C	-3.699360	0.354040	0.889884
7	O	-1.870842	1.578888	0.036647
8	C	-0.503409	1.508769	-0.083134
9	C	0.238639	0.454062	0.439061
10	C	1.626320	0.460586	0.340996
11	C	2.264216	1.533581	-0.281468
12	C	1.514554	2.586048	-0.789509
13	C	0.129369	2.581427	-0.696897
14	C	2.414154	-0.706223	0.916057
15	C	3.455200	-0.270279	1.952120
16	C	3.010397	-1.513082	-0.224379
17	O	2.505484	-2.489867	-0.711879
18	O	4.184314	-1.006351	-0.670566
19	H	-1.567415	-0.513584	-1.603247
20	H	-3.062403	-2.480327	-1.653451
21	H	-4.969438	-2.638030	-0.080108
22	H	-5.374104	-0.808455	1.541888

23	H	-3.856981	1.161852	1.591508
24	H	-0.267003	-0.373272	0.917155
25	H	3.340633	1.541542	-0.378771
26	H	2.012824	3.417342	-1.271301
27	H	-0.468868	3.391510	-1.090612
28	H	1.702765	-1.384929	1.385080
29	H	3.987402	-1.133561	2.354385
30	H	4.188417	0.407647	1.520079
31	H	2.955718	0.241852	2.774712
32	H	4.462969	-1.560349	-1.416435

	FP#*S*-A1"-*anti*	*a*	*b*	*c*
1	C	2.313332	-0.608872	0.020727
2	C	2.160178	0.312744	1.050443
3	C	2.996090	1.419759	1.099237
4	C	3.984094	1.601653	0.137217
5	C	4.133079	0.666988	-0.880112
6	C	3.295122	-0.439861	-0.944962
7	O	1.550839	-1.758221	-0.041397
8	C	0.182030	-1.686081	0.042567
9	C	-0.538924	-0.555193	-0.319769
10	C	-1.931089	-0.568793	-0.249955
11	C	-2.587978	-1.717747	0.178103
12	C	-1.856648	-2.848871	0.524814
13	C	-0.472389	-2.840123	0.463249
14	C	-2.721891	0.664493	-0.657553
15	C	-2.528934	1.021991	-2.132399
16	C	-2.312739	1.819372	0.237711
17	O	-1.451034	2.624276	-0.002961
18	O	-3.019057	1.833615	1.390979
19	H	1.391410	0.163782	1.795970
20	H	2.875835	2.141893	1.896224
21	H	4.632781	2.466204	0.181586
22	H	4.899743	0.800174	-1.632317
23	H	3.391512	-1.176792	-1.730624
24	H	-0.020731	0.336413	-0.642730
25	H	-3.668305	-1.728024	0.241087
26	H	-2.370501	-3.742805	0.853810
27	H	0.113600	-3.707672	0.733729
28	H	-3.774711	0.460979	-0.460592
29	H	-3.145922	1.878072	-2.408455
30	H	-1.490643	1.277629	-2.335998
31	H	-2.808501	0.172922	-2.755877
32	H	-2.671653	2.563816	1.927213

	FP#*S*-A1"-*syn*	*a*	*b*	*c*
1	C	2.311195	-0.585694	-0.080890
2	C	2.124211	0.256788	1.010463
3	C	2.961779	1.352096	1.173294
4	C	3.982390	1.604862	0.262888
5	C	4.163713	0.749565	-0.817602
6	C	3.327868	-0.345758	-0.995649
7	O	1.553598	-1.722259	-0.265431
8	C	0.196254	-1.683721	-0.040708
9	C	-0.574264	-0.578999	-0.379199
10	C	-1.951451	-0.602148	-0.170335
11	C	-2.541266	-1.743390	0.367711
12	C	-1.763053	-2.851060	0.683247
13	C	-0.390301	-2.827922	0.486241
14	C	-2.812659	0.594717	-0.539654
15	C	-2.780946	0.895533	-2.042995
16	C	-2.419345	1.790781	0.309488
17	O	-2.977960	2.132803	1.317999
18	O	-1.337966	2.446010	-0.176655
19	H	1.333080	0.054584	1.718913
20	H	2.819876	2.006248	2.024049

21	H	4.632685	2.458829	0.397284
22	H	4.956212	0.936006	-1.530754
23	H	3.451368	-1.020875	-1.831485
24	H	-0.097744	0.299766	-0.788421
25	H	-3.609463	-1.764311	0.539879
26	H	-2.228710	-3.736047	1.096972
27	H	0.234125	-3.674979	0.734548
28	H	-3.835092	0.370175	-0.238431
29	H	-3.416717	1.748999	-2.283395
30	H	-1.770494	1.118282	-2.380547
31	H	-3.144094	0.027577	-2.593600
32	H	-1.137166	3.162066	0.445931

	FP#*S*-A2"-*anti*	*a*	*b*	*c*
1	C	2.679040	-0.373429	-0.268993
2	C	2.717256	0.157674	1.016318
3	C	3.652288	1.138999	1.317659
4	C	4.548343	1.583473	0.351305
5	C	4.505393	1.037104	-0.926037
6	C	3.569491	0.060292	-1.242164
7	O	1.817984	-1.393015	-0.612580
8	C	0.508893	-1.359553	-0.190025
9	C	-0.218863	-0.175354	-0.129442
10	C	-1.556223	-0.199874	0.249780
11	C	-2.162647	-1.419135	0.552114
12	C	-1.430597	-2.596077	0.473609
13	C	-0.090890	-2.575186	0.108159
14	C	-2.335967	1.101731	0.349955
15	C	-2.710826	1.438147	1.794388
16	C	-3.572269	1.005142	-0.524238
17	O	-4.672412	0.687348	-0.153972
18	O	-3.294441	1.296860	-1.814554
19	H	2.023128	-0.195728	1.766139
20	H	3.684746	1.551875	2.317731
21	H	5.275622	2.346707	0.593581
22	H	5.199557	1.374752	-1.684667
23	H	3.518498	-0.374867	-2.230926
24	H	0.259818	0.761760	-0.378781
25	H	-3.206239	-1.446130	0.836009
26	H	-1.905344	-3.541041	0.703774
27	H	0.494991	-3.481817	0.045781
28	H	-1.712505	1.894860	-0.064389
29	H	-3.230896	2.395321	1.848621
30	H	-3.366345	0.675000	2.210103
31	H	-1.809250	1.494217	2.404380
32	H	-4.112893	1.165400	-2.318758

	FP#*S*-A2"-*syn*	*a*	*b*	*c*
1	C	2.666733	-0.364002	-0.287173
2	C	2.739607	0.051499	1.038385
3	C	3.663045	1.025257	1.394489
4	C	4.513537	1.575512	0.441280
5	C	4.436381	1.143965	-0.877575
6	C	3.510891	0.175918	-1.247722
7	O	1.814898	-1.371803	-0.686913
8	C	0.505484	-1.372302	-0.266635
9	C	-0.218313	-0.197756	-0.087351
10	C	-1.557422	-0.252716	0.286319
11	C	-2.168139	-1.494494	0.463037
12	C	-1.439469	-2.660197	0.268796
13	C	-0.099551	-2.609246	-0.091451
14	C	-2.321339	1.045780	0.492107
15	C	-2.904983	1.169551	1.904323
16	C	-3.372138	1.201946	-0.593256
17	O	-3.237388	1.860252	-1.590447
18	O	-4.502574	0.501364	-0.336091

19	H	2.080022	-0.384536	1.775942
20	H	3.722702	1.349104	2.425608
21	H	5.232144	2.332389	0.725766
22	H	5.094625	1.565341	-1.626223
23	H	3.432614	-0.170147	-2.269314
24	H	0.263415	0.757835	-0.241602
25	H	-3.211880	-1.550117	0.737728
26	H	-1.917898	-3.621603	0.403949
27	H	0.482698	-3.507713	-0.242693
28	H	-1.628539	1.868032	0.317805
29	H	-3.429117	2.118714	2.026091
30	H	-3.606272	0.365086	2.116763
31	H	-2.097715	1.124684	2.635658
32	H	-5.092511	0.633811	-1.094569

	FP#*S*-B1"-*anti*	*a*	*b*	*c*
1	C	2.608443	-0.544999	-0.080895
2	C	2.985776	0.334665	0.928581
3	C	4.335927	0.553421	1.168306
4	C	5.303921	-0.103337	0.416110
5	C	4.912646	-0.986960	-0.582982
6	C	3.565113	-1.208500	-0.837694
7	O	1.288053	-0.854286	-0.325026
8	C	0.336335	0.138707	-0.332312
9	C	-0.926394	-0.205020	0.129150
10	C	-1.962257	0.725209	0.087373
11	C	-1.715427	1.998144	-0.419003
12	C	-0.446472	2.333519	-0.876391
13	C	0.587740	1.409629	-0.841382
14	C	-3.339073	0.362825	0.620295
15	C	-3.330539	0.127001	2.131810
16	C	-3.847111	-0.862129	-0.117005
17	O	-3.748581	-2.000443	0.260549
18	O	-4.416046	-0.533535	-1.298540
19	H	2.230018	0.838042	1.515358
20	H	4.631373	1.236190	1.954547
21	H	6.353944	0.070148	0.609876
22	H	5.658126	-1.504773	-1.172502
23	H	3.240649	-1.890798	-1.611518
24	H	-1.089151	-1.205588	0.507123
25	H	-2.516017	2.725409	-0.458330
26	H	-0.262126	3.322949	-1.274614
27	H	1.573191	1.664600	-1.204122
28	H	-4.012684	1.185495	0.377778
29	H	-4.335763	-0.084950	2.498084
30	H	-2.694989	-0.719333	2.386390
31	H	-2.951878	1.013775	2.639987
32	H	-4.667073	-1.363645	-1.733663

	FP#*S*-B1"-*syn*	*a*	*b*	*c*
1	C	2.628821	-0.528063	-0.117477
2	C	2.985602	0.353722	0.897767
3	C	4.330806	0.571400	1.165900
4	C	5.314370	-0.087482	0.436580
5	C	4.943440	-0.972831	-0.568986
6	C	3.601823	-1.193849	-0.852005
7	O	1.315718	-0.838307	-0.394217
8	C	0.351086	0.143269	-0.355009
9	C	-0.891620	-0.221196	0.141389
10	C	-1.940001	0.696904	0.145847
11	C	-1.720352	1.978625	-0.352523
12	C	-0.470709	2.334699	-0.846650
13	C	0.573597	1.422299	-0.856391
14	C	-3.307800	0.323875	0.693282
15	C	-3.254512	-0.159084	2.147536
16	C	-3.975918	-0.679924	-0.230500

17	O	-4.804075	-0.407551	-1.058705
18	O	-3.530051	-1.944242	-0.040194
19	H	2.218981	0.860033	1.467457
20	H	4.609547	1.256192	1.956495
21	H	6.360115	0.085947	0.652158
22	H	5.700791	-1.492114	-1.141879
23	H	3.293742	-1.876865	-1.631894
24	H	-1.027117	-1.229169	0.506778
25	H	-2.529237	2.697504	-0.357362
26	H	-0.311011	3.331207	-1.237610
27	H	1.544970	1.691349	-1.246313
28	H	-3.938531	1.209797	0.632894
29	H	-4.254286	-0.396334	2.514321
30	H	-2.636502	-1.049012	2.249061
31	H	-2.833647	0.626287	2.775683
32	H	-3.979958	-2.502939	-0.693063

	FP#*S*-B2"-*anti*	*a*	*b*	*c*
1	C	-2.818583	0.196939	0.453373
2	C	-2.870641	-1.069562	-0.119758
3	C	-4.104562	-1.613703	-0.451029
4	C	-5.278175	-0.908580	-0.207098
5	C	-5.211637	0.351941	0.374971
6	C	-3.983143	0.910646	0.704008
7	O	-1.632708	0.767020	0.863579
8	C	-0.506758	0.652893	0.080696
9	C	0.705691	0.518484	0.745555
10	C	1.895810	0.467216	0.028780
11	C	1.857777	0.538651	-1.363569
12	C	0.640710	0.670373	-2.018591
13	C	-0.549897	0.734638	-1.306200
14	C	3.220920	0.354539	0.765478
15	C	4.073438	1.615603	0.613958
16	C	3.963487	-0.867950	0.259147
17	O	4.805963	-0.873787	-0.600177
18	O	3.546274	-1.996390	0.876283
19	H	-1.956589	-1.617059	-0.302756
20	H	-4.147063	-2.599615	-0.895782
21	H	-6.235917	-1.339658	-0.466072
22	H	-6.119107	0.908433	0.570518
23	H	-3.910671	1.890824	1.155297
24	H	0.702333	0.455327	1.825769
25	H	2.776726	0.483306	-1.931815
26	H	0.616202	0.730136	-3.099036
27	H	-1.497196	0.842746	-1.814994
28	H	3.000824	0.181162	1.819455
29	H	4.998278	1.530679	1.185849
30	H	4.337027	1.779651	-0.429362
31	H	3.516782	2.480840	0.973633
32	H	4.025984	-2.735893	0.470830

	FP#*S*-B2"-*syn*	*a*	*b*	*c*
1	C	-2.814396	0.093992	0.491034
2	C	-2.873909	-1.053713	-0.292631
3	C	-4.110482	-1.522087	-0.716301
4	C	-5.279386	-0.859406	-0.357247
5	C	-5.205531	0.280905	0.434002
6	C	-3.973816	0.763892	0.858022
7	O	-1.623972	0.570967	0.996988
8	C	-0.508067	0.624052	0.194670
9	C	0.715467	0.395726	0.812399
10	C	1.898983	0.499558	0.089385
11	C	1.840920	0.822581	-1.266717
12	C	0.613437	1.046688	-1.875116
13	C	-0.569926	0.955603	-1.153508
14	C	3.224619	0.258865	0.793577

15	C	4.161958	1.469364	0.715009
16	C	3.860671	-1.014774	0.264565
17	O	3.778794	-2.093379	0.789911
18	O	4.535192	-0.824574	-0.894734
19	H	-1.963080	-1.569588	-0.563163
20	H	-4.159127	-2.416315	-1.324219
21	H	-6.239490	-1.231428	-0.688909
22	H	-6.109473	0.802578	0.720629
23	H	-3.895385	1.650343	1.472597
24	H	0.726428	0.136302	1.862714
25	H	2.750243	0.888578	-1.847149
26	H	0.574464	1.302549	-2.926154
27	H	-1.524705	1.136358	-1.626300
28	H	3.008478	0.039632	1.838401
29	H	5.095696	1.272574	1.243983
30	H	4.402528	1.719481	-0.316345
31	H	3.679386	2.331951	1.174846
32	H	4.871809	-1.692283	-1.167946

Table S3. Theoretical structures of the conformers of ketoprofen at the B3LYP-D3(BJ)/Def2-TZVP level of calculation. The principal axis system coordinates are used (Å).

	KP#*S*-B1'-*anti*	*a*	*b*	*c*
1	C	2.682136	0.376924	-0.075752
2	C	2.832777	-0.557259	0.950868
3	C	4.094045	-0.844553	1.456409
4	C	5.214940	-0.215425	0.928527
5	C	5.071969	0.717654	-0.094786
6	C	3.812110	1.021350	-0.584873
7	C	1.342525	0.771582	-0.606082
8	C	0.225485	-0.223197	-0.599216
9	C	-1.078149	0.252584	-0.464345
10	C	-2.162833	-0.616430	-0.497321
11	C	-1.929226	-1.977177	-0.688536
12	C	-0.636330	-2.458765	-0.848770
13	C	0.442787	-1.588233	-0.794713
14	C	-3.581022	-0.090270	-0.346822
15	C	-3.962678	0.886401	-1.459577
16	C	-3.718597	0.558425	1.019008
17	O	-3.635452	1.735276	1.250807
18	O	-3.923878	-0.363209	1.988253
19	O	1.158868	1.892833	-1.042387
20	H	1.962224	-1.041967	1.370279
21	H	4.201278	-1.558047	2.263040
22	H	6.198547	-0.447064	1.316570
23	H	5.944225	1.210576	-0.504050
24	H	3.679333	1.759280	-1.364126
25	H	-1.226694	1.315349	-0.326856
26	H	-2.766939	-2.663074	-0.715165
27	H	-0.470940	-3.515248	-1.015068
28	H	1.448031	-1.963196	-0.926149
29	H	-4.254454	-0.948483	-0.359781
30	H	-4.996267	1.215485	-1.348039
31	H	-3.326184	1.768994	-1.436529
32	H	-3.851320	0.401782	-2.429457
33	H	-3.954212	0.114522	2.832180

	KP#*S*-B1'-*syn*	*a*	*b*	*c*
1	C	2.696346	0.363846	-0.064267
2	C	2.836968	-0.574568	0.959999
3	C	4.094576	-0.872873	1.468297
4	C	5.221861	-0.251497	0.944867
5	C	5.089008	0.685176	-0.076497
6	C	3.832822	1.000463	-0.568758

7	C	1.361320	0.772050	-0.595871
8	C	0.238019	-0.215002	-0.604665
9	C	-1.062967	0.272695	-0.487732
10	C	-2.155903	-0.585336	-0.531483
11	C	-1.929964	-1.949513	-0.714127
12	C	-0.639653	-2.443365	-0.856706
13	C	0.446383	-1.582471	-0.793224
14	C	-3.577284	-0.066450	-0.387482
15	C	-3.913214	1.038066	-1.395804
16	C	-3.815760	0.359191	1.051450
17	O	-4.364311	-0.313085	1.884486
18	O	-3.322296	1.589552	1.320255
19	O	1.187243	1.900337	-1.019097
20	H	1.961656	-1.053463	1.376166
21	H	4.193875	-1.589276	2.273343
22	H	6.202566	-0.492101	1.334775
23	H	5.966252	1.171859	-0.482557
24	H	3.708272	1.741536	-1.346388
25	H	-1.199371	1.336384	-0.354805
26	H	-2.773011	-2.628339	-0.748090
27	H	-0.482238	-3.501936	-1.017032
28	H	1.449658	-1.966607	-0.912183
29	H	-4.253147	-0.907653	-0.537117
30	H	-4.944293	1.372632	-1.273183
31	H	-3.260812	1.900469	-1.275511
32	H	-3.792793	0.654544	-2.409110
33	H	-3.484996	1.761510	2.260861

	KP#*S*-B2'-*anti*	*a*	*b*	*c*
1	C	-2.927215	0.365191	-0.061409
2	C	-3.162313	-0.936311	-0.508803
3	C	-4.456087	-1.439785	-0.549194
4	C	-5.521631	-0.654942	-0.125529
5	C	-5.294553	0.643924	0.321051
6	C	-4.006903	1.155264	0.340159
7	C	-1.564731	0.978294	-0.065660
8	C	-0.365999	0.113722	0.158590
9	C	0.846677	0.510991	-0.408473
10	C	2.006006	-0.223976	-0.208595
11	C	1.954031	-1.359600	0.603591
12	C	0.760293	-1.747260	1.194598
13	C	-0.402598	-1.022215	0.966716
14	C	3.303924	0.191638	-0.882138
15	C	3.750473	-0.818938	-1.941203
16	C	4.373946	0.371493	0.178799
17	O	5.132118	-0.482357	0.560366
18	O	4.366267	1.621138	0.690203
19	O	-1.430959	2.174376	-0.250313
20	H	-2.337025	-1.547080	-0.847328
21	H	-4.632017	-2.443964	-0.912364
22	H	-6.528474	-1.051753	-0.147702
23	H	-6.124250	1.257097	0.648035
24	H	-3.814334	2.169309	0.662723
25	H	0.862792	1.411360	-1.008497
26	H	2.856238	-1.929997	0.783663
27	H	0.735963	-2.617198	1.837858
28	H	-1.328197	-1.323589	1.436367
29	H	3.139497	1.165050	-1.344469
30	H	4.658002	-0.480988	-2.442908
31	H	3.957435	-1.786770	-1.487455
32	H	2.964557	-0.942502	-2.686194
33	H	5.036510	1.648145	1.391459

	KP#*S*-B2'-*syn*	*a*	*b*	*c*
1	C	2.929426	0.377657	0.046226
2	C	3.179561	-0.899459	0.551845

3	C	4.478804	-1.386625	0.612089
4	C	5.534951	-0.610609	0.150310
5	C	5.292836	0.663929	-0.354567
6	C	3.999669	1.160074	-0.393689
7	C	1.560495	0.976424	0.026329
8	C	0.370392	0.090757	-0.160155
9	C	-0.847171	0.501073	0.386837
10	C	-2.000593	-0.253660	0.223393
11	C	-1.933419	-1.426741	-0.533255
12	C	-0.735129	-1.828804	-1.104947
13	C	0.419991	-1.081434	-0.913255
14	C	-3.296038	0.200806	0.874846
15	C	-3.838711	-0.826324	1.877120
16	C	-4.320878	0.572017	-0.182881
17	O	-4.593008	1.694596	-0.514160
18	O	-4.914281	-0.511324	-0.741855
19	O	1.414948	2.177522	0.160568
20	H	2.361690	-1.502851	0.920336
21	H	4.666364	-2.371138	1.020509
22	H	6.546097	-0.995110	0.188163
23	H	6.115126	1.270474	-0.711266
24	H	3.795540	2.156318	-0.761455
25	H	-0.872579	1.428512	0.943663
26	H	-2.825692	-2.017626	-0.687901
27	H	-0.700917	-2.729198	-1.704461
28	H	1.348969	-1.395478	-1.367639
29	H	-3.092830	1.135862	1.394773
30	H	-4.757642	-0.466830	2.342463
31	H	-4.052507	-1.777917	1.393722
32	H	-3.099062	-0.995446	2.659901
33	H	-5.525759	-0.178122	-1.417146

KP#*S*-A1'-*anti*		*a*	*b*	*c*
1	C	2.376112	0.239201	-0.120949
2	C	2.179853	-0.511657	1.039813
3	C	3.011819	-1.585328	1.328466
4	C	4.033823	-1.928594	0.451886
5	C	4.236342	-1.183586	-0.706469
6	C	3.420718	-0.098638	-0.984464
7	C	1.550784	1.441166	-0.445248
8	C	0.125518	1.498370	0.004151
9	C	-0.662391	0.353821	0.108494
10	C	-2.004839	0.441476	0.471058
11	C	-2.549363	1.693531	0.737614
12	C	-1.770090	2.842222	0.635908
13	C	-0.441078	2.749172	0.259691
14	C	-2.851148	-0.815249	0.594473
15	C	-2.343992	-1.748537	1.695460
16	C	-2.871129	-1.522680	-0.748319
17	O	-2.127139	-2.406220	-1.085366
18	O	-3.822973	-1.018434	-1.564004
19	O	2.031637	2.368427	-1.070704
20	H	1.391013	-0.243215	1.728499
21	H	2.861678	-2.153966	2.236903
22	H	4.674544	-2.772854	0.671743
23	H	5.033441	-1.449028	-1.388693
24	H	3.575696	0.503338	-1.869326
25	H	-0.237513	-0.612975	-0.123887
26	H	-3.591508	1.772422	1.021831
27	H	-2.207918	3.809460	0.845674
28	H	0.175070	3.631292	0.154147
29	H	-3.874270	-0.506617	0.811542
30	H	-2.990132	-2.621538	1.793809
31	H	-1.338711	-2.100500	1.469675
32	H	-2.324364	-1.218428	2.647695
33	H	-3.742316	-1.476875	-2.415451

	KP#*S*-A1'-*syn*	*a*	*b*	*c*
1	C	2.399888	0.217285	-0.126129
2	C	2.215427	-0.515869	1.047803
3	C	3.041925	-1.593575	1.337785
4	C	4.046626	-1.958524	0.449834
5	C	4.237466	-1.231002	-0.721510
6	C	3.427536	-0.141908	-1.001101
7	C	1.581021	1.424067	-0.453494
8	C	0.159115	1.493945	0.002464
9	C	-0.630079	0.352675	0.130733
10	C	-1.970066	0.446621	0.500765
11	C	-2.509224	1.705978	0.748287
12	C	-1.729585	2.851813	0.621038
13	C	-0.403177	2.750492	0.238751
14	C	-2.838763	-0.792807	0.637067
15	C	-2.239626	-1.838113	1.585480
16	C	-3.138978	-1.361838	-0.739337
17	O	-4.167329	-1.201029	-1.340910
18	O	-2.104356	-2.073280	-1.245471
19	O	2.067025	2.342108	-1.088280
20	H	1.440477	-0.230067	1.745266
21	H	2.902554	-2.147053	2.257302
22	H	4.683887	-2.804895	0.671706
23	H	5.022014	-1.512142	-1.411980
24	H	3.575081	0.447631	-1.895604
25	H	-0.204835	-0.615124	-0.090039
26	H	-3.549222	1.791821	1.037883
27	H	-2.165313	3.822872	0.816777
28	H	0.214147	3.629365	0.114686
29	H	-3.809060	-0.477301	1.018385
30	H	-2.898195	-2.703219	1.674654
31	H	-1.270434	-2.186823	1.233806
32	H	-2.110912	-1.399700	2.575412
33	H	-2.366909	-2.362947	-2.133162

	KP#*S*-A2'-*anti*	*a*	*b*	*c*
1	C	-2.631648	0.119281	-0.000370
2	C	-2.192792	-0.997722	-0.714321
3	C	-2.958119	-2.156368	-0.740946
4	C	-4.157111	-2.214750	-0.041044
5	C	-4.601209	-1.104557	0.672002
6	C	-3.849384	0.059248	0.681535
7	C	-1.881039	1.411323	0.004719
8	C	-0.391888	1.398266	-0.126026
9	C	0.389150	0.361917	0.387017
10	C	1.776380	0.402127	0.304590
11	C	2.383311	1.487830	-0.325324
12	C	1.613556	2.525069	-0.838713
13	C	0.232329	2.490913	-0.728229
14	C	2.611776	-0.717744	0.903775
15	C	3.498734	-0.234379	2.052046
16	C	3.442885	-1.345253	-0.200039
17	O	4.578087	-1.057105	-0.475276
18	O	2.739071	-2.272045	-0.889337
19	O	-2.476334	2.467788	0.112709
20	H	-1.264579	-0.954923	-1.266807
21	H	-2.618265	-3.012686	-1.308727
22	H	-4.748022	-3.121591	-0.054463
23	H	-5.536570	-1.147990	1.214703
24	H	-4.189036	0.938393	1.211795
25	H	-0.087610	-0.477564	0.874748
26	H	3.461343	1.518110	-0.419613
27	H	2.096886	3.362836	-1.324259
28	H	-0.380172	3.298901	-1.103703
29	H	1.925517	-1.485078	1.263947

30	H	4.053120	-1.064778	2.490682
31	H	4.220028	0.501256	1.700515
32	H	2.882291	0.223049	2.825710
33	H	3.312858	-2.591507	-1.603694

	KP#*S*-A2'-*syn*	*a*	*b*	*c*
1	C	-2.607990	0.129161	-0.004431
2	C	-2.146384	-0.990042	-0.700713
3	C	-2.900211	-2.156053	-0.730259
4	C	-4.111351	-2.218911	-0.052150
5	C	-4.578809	-1.106423	0.642323
6	C	-3.837636	0.064019	0.655658
7	C	-1.868853	1.427237	0.006005
8	C	-0.377645	1.427077	-0.107664
9	C	0.406804	0.398276	0.414169
10	C	1.795463	0.446761	0.345168
11	C	2.398895	1.537632	-0.279065
12	C	1.625860	2.569885	-0.797850
13	C	0.243931	2.524901	-0.702728
14	C	2.615131	-0.692961	0.928282
15	C	3.685652	-0.223958	1.918238
16	C	3.180002	-1.521636	-0.212911
17	O	2.673686	-2.519968	-0.652764
18	O	4.322097	-1.002332	-0.721531
19	O	-2.472949	2.479767	0.104409
20	H	-1.208531	-0.945756	-1.236310
21	H	-2.540308	-3.014520	-1.281998
22	H	-4.693278	-3.131523	-0.067505
23	H	-5.523538	-1.153707	1.168254
24	H	-4.194408	0.944365	1.172504
25	H	-0.067806	-0.444986	0.897016
26	H	3.476071	1.579013	-0.367527
27	H	2.107640	3.412590	-1.276460
28	H	-0.370814	3.328474	-1.083977
29	H	1.925701	-1.365793	1.437075
30	H	4.233075	-1.074125	2.327530
31	H	4.404126	0.442887	1.445822
32	H	3.210454	0.309121	2.741882
33	H	4.583176	-1.569383	-1.463997

	KP#*S*-A1''-*anti*	*a*	*b*	*c*
1	C	-2.349219	0.219399	0.030799
2	C	-1.871013	-0.850992	0.789577
3	C	-2.599641	-2.029873	0.875249
4	C	-3.803564	-2.154833	0.193434
5	C	-4.288737	-1.091099	-0.562621
6	C	-3.571773	0.091988	-0.634091
7	C	-1.638358	1.530578	-0.051789
8	C	-0.148269	1.576904	0.075001
9	C	0.665713	0.524934	-0.339682
10	C	2.053336	0.618224	-0.255113
11	C	2.619536	1.777321	0.265469
12	C	1.815159	2.837727	0.672821
13	C	0.437910	2.744529	0.569898
14	C	2.931145	-0.535639	-0.713423
15	C	2.704610	-0.906896	-2.180275
16	C	2.655894	-1.722719	0.192590
17	O	1.785302	-2.538302	0.032724
18	O	3.492284	-1.748701	1.254061
19	O	-2.265352	2.560210	-0.224841
20	H	-0.938440	-0.760210	1.327687
21	H	-2.223050	-2.851430	1.470076
22	H	-4.365277	-3.078310	0.251911
23	H	-5.227627	-1.186663	-1.092460
24	H	-3.941560	0.934892	-1.201612
25	H	0.218904	-0.374621	-0.737641

26	H	3.696549	1.853081	0.351205
27	H	2.269797	3.736094	1.069663
28	H	-0.203419	3.562973	0.865960
29	H	3.970521	-0.244739	-0.562003
30	H	3.387485	-1.699537	-2.488716
31	H	1.687733	-1.261215	-2.338848
32	H	2.873783	-0.034917	-2.811711
33	H	3.226745	-2.499566	1.808674

	KP#*S*-A1"-*syn*	*a*	*b*	*c*
1	C	2.352302	0.203334	-0.015850
2	C	1.880979	-0.834018	-0.822954
3	C	2.598254	-2.018251	-0.930245
4	C	3.780328	-2.183346	-0.218848
5	C	4.256107	-1.153311	0.587887
6	C	3.553299	0.037305	0.678102
7	C	1.656765	1.522602	0.080273
8	C	0.171548	1.585118	-0.078483
9	C	-0.657869	0.543937	0.332929
10	C	-2.043168	0.646556	0.223634
11	C	-2.587269	1.804489	-0.325018
12	C	-1.767304	2.852806	-0.731989
13	C	-0.393298	2.751590	-0.599088
14	C	-2.956221	-0.477006	0.685107
15	C	-2.725203	-0.870468	2.149254
16	C	-2.832019	-1.662376	-0.256553
17	O	-3.629294	-1.953607	-1.107993
18	O	-1.698405	-2.375746	-0.051150
19	O	2.293640	2.539921	0.284217
20	H	0.964811	-0.708574	-1.382481
21	H	2.235530	-2.811370	-1.571134
22	H	4.333482	-3.110629	-0.295657
23	H	5.178209	-1.279693	1.140194
24	H	3.918893	0.856409	1.282118
25	H	-0.221009	-0.351342	0.749809
26	H	-3.661694	1.888661	-0.431748
27	H	-2.207614	3.748370	-1.150584
28	H	0.260282	3.561382	-0.892322
29	H	-3.984854	-0.140297	0.563324
30	H	-3.414434	-1.660490	2.450959
31	H	-1.709865	-1.227381	2.310709
32	H	-2.891804	-0.003978	2.789314
33	H	-1.694530	-3.092878	-0.704028

	KP#*S*-A2"-*anti*	*a*	*b*	*c*
1	C	2.676021	-0.150411	-0.110595
2	C	2.476025	0.752620	0.935368
3	C	3.341602	1.824531	1.110357
4	C	4.401041	2.013746	0.231264
5	C	4.606720	1.116968	-0.813463
6	C	3.757333	0.034146	-0.975201
7	C	1.815649	-1.357661	-0.298879
8	C	0.375073	-1.303613	0.096651
9	C	-0.375740	-0.130858	0.004009
10	C	-1.729622	-0.120432	0.320324
11	C	-2.331886	-1.303765	0.745930
12	C	-1.593071	-2.477627	0.836284
13	C	-0.247697	-2.483850	0.503216
14	C	-2.527889	1.169826	0.224153
15	C	-3.003145	1.659000	1.593673
16	C	-3.702845	0.950877	-0.711071
17	O	-4.809068	0.612617	-0.379072
18	O	-3.357402	1.151149	-2.001676
19	O	2.283578	-2.377833	-0.770159
20	H	1.658361	0.603144	1.626682
21	H	3.189978	2.510681	1.933458

22	H	5.069371	2.855077	0.362296
23	H	5.433641	1.261662	-1.496509
24	H	3.914890	-0.684883	-1.767423
25	H	0.094327	0.780283	-0.340856
26	H	-3.386257	-1.309231	0.991157
27	H	-2.074047	-3.390861	1.161699
28	H	0.336617	-3.392459	0.547817
29	H	-1.886351	1.922420	-0.235387
30	H	-3.535743	2.606585	1.504865
31	H	-3.677981	0.936165	2.048920
32	H	-2.146218	1.799728	2.252456
33	H	-4.136085	0.943431	-2.542230

	KP#*S*-A2"-*syn*	*a*	*b*	*c*
1	C	2.664346	-0.147461	-0.118399
2	C	2.475999	0.689660	0.983026
3	C	3.339954	1.752890	1.210562
4	C	4.385888	1.999908	0.329659
5	C	4.579805	1.169132	-0.770363
6	C	3.732390	0.094083	-0.985423
7	C	1.805825	-1.344577	-0.367646
8	C	0.369331	-1.320164	0.046158
9	C	-0.385955	-0.146818	0.038155
10	C	-1.737111	-0.158695	0.370189
11	C	-2.329867	-1.370273	0.724482
12	C	-1.586448	-2.544635	0.731741
13	C	-0.245124	-2.525900	0.383707
14	C	-2.527598	1.139013	0.341076
15	C	-3.207887	1.452182	1.679083
16	C	-3.508587	1.121055	-0.818680
17	O	-3.338839	1.675578	-1.871619
18	O	-4.617614	0.390002	-0.554025
19	O	2.271202	-2.333586	-0.903441
20	H	1.668622	0.495121	1.675244
21	H	3.197380	2.387462	2.075584
22	H	5.052423	2.835268	0.501587
23	H	5.395749	1.359196	-1.455458
24	H	3.880856	-0.574299	-1.822451
25	H	0.077707	0.785966	-0.252982
26	H	-3.380219	-1.400412	0.979881
27	H	-2.061034	-3.478159	1.004951
28	H	0.342127	-3.433501	0.364491
29	H	-1.834052	1.942465	0.096149
30	H	-3.745717	2.399942	1.627561
31	H	-3.917790	0.675609	1.957087
32	H	-2.453543	1.525959	2.462728
33	H	-5.163945	0.406931	-1.355367

	KP#*S*-B1"-*anti*	*a*	*b*	*c*
1	C	-2.709925	0.429818	-0.012463
2	C	-3.068059	-0.715596	0.701038
3	C	-4.406750	-1.016157	0.916630
4	C	-5.397089	-0.185947	0.405875
5	C	-5.047153	0.958237	-0.305865
6	C	-3.711747	1.270952	-0.502515
7	C	-1.285572	0.834470	-0.211611
8	C	-0.225952	-0.217987	-0.295823
9	C	1.055938	0.100919	0.150892
10	C	2.094961	-0.817876	0.055328
11	C	1.843731	-2.059231	-0.526548
12	C	0.575200	-2.380411	-0.992023
13	C	-0.463296	-1.468481	-0.869046
14	C	3.475881	-0.484414	0.594182
15	C	3.485759	-0.363494	2.118319
16	C	3.974177	0.793397	-0.057199
17	O	3.987657	1.882753	0.451362

18	O	4.395241	0.572388	-1.323044
19	O	-0.987426	2.010633	-0.305262
20	H	-2.300375	-1.359134	1.107527
21	H	-4.676306	-1.897230	1.484326
22	H	-6.440335	-0.426197	0.565965
23	H	-5.817887	1.607204	-0.700965
24	H	-3.420730	2.166812	-1.033691
25	H	1.226529	1.085731	0.566376
26	H	2.649555	-2.776856	-0.620004
27	H	0.397805	-3.342694	-1.454307
28	H	-1.447885	-1.715952	-1.240062
29	H	4.152959	-1.281469	0.281702
30	H	4.492090	-0.160857	2.485676
31	H	2.840358	0.450563	2.444093
32	H	3.128867	-1.291912	2.564354
33	H	4.648564	1.432679	-1.693156

	KP#*S*-B1"-*syn*	*a*	*b*	*c*
1	C	-2.734526	0.417673	-0.016805
2	C	-3.104409	-0.733813	0.680760
3	C	-4.446449	-1.044994	0.856810
4	C	-5.427975	-0.219560	0.321852
5	C	-5.066335	0.930514	-0.374290
6	C	-3.728172	1.253956	-0.531080
7	C	-1.308050	0.833524	-0.173056
8	C	-0.239946	-0.210486	-0.248110
9	C	1.033010	0.119594	0.215705
10	C	2.082239	-0.789177	0.134508
11	C	1.848218	-2.031973	-0.453759
12	C	0.589394	-2.363568	-0.937958
13	C	-0.458702	-1.461366	-0.828182
14	C	3.467310	-0.450239	0.660836
15	C	3.458398	-0.049583	2.140190
16	C	4.101095	0.604336	-0.231318
17	O	4.879055	0.373708	-1.119000
18	O	3.679506	1.854694	0.062237
19	O	-1.016279	2.013641	-0.239098
20	H	-2.343894	-1.373956	1.105696
21	H	-4.725514	-1.930836	1.412354
22	H	-6.473542	-0.468276	0.450774
23	H	-5.830232	1.575598	-0.788557
24	H	-3.429061	2.154448	-1.049783
25	H	1.186472	1.106692	0.628363
26	H	2.661400	-2.742177	-0.537614
27	H	0.427655	-3.326652	-1.404174
28	H	-1.435547	-1.716676	-1.213904
29	H	4.095486	-1.330648	0.530195
30	H	4.468613	0.171017	2.487881
31	H	2.842402	0.831278	2.309767
32	H	3.059442	-0.869864	2.737429
33	H	4.087994	2.453668	-0.582102

	KP#*S*-B2"-*anti*	*a*	*b*	*c*
1	C	-2.894384	0.293474	0.150907
2	C	-2.946055	-1.074938	0.423293
3	C	-4.170494	-1.720482	0.536707
4	C	-5.351037	-1.009071	0.360469
5	C	-5.307002	0.355700	0.089287
6	C	-4.086534	1.005368	-0.001675
7	C	-1.606565	1.047931	0.089213
8	C	-0.369342	0.357943	-0.387969
9	C	0.860726	0.799712	0.103278
10	C	2.050874	0.237712	-0.334461
11	C	2.006124	-0.775222	-1.295585
12	C	0.790285	-1.209260	-1.803497
13	C	-0.398444	-0.652261	-1.348802

14	C	3.380874	0.744176	0.200171
15	C	4.203465	1.449756	-0.88
16	C	4.149841	-0.422460	0.791429
17	O	4.939778	-1.112881	0.201251
18	O	3.821098	-0.635108	2.084762
19	O	-1.563516	2.217811	0.424458
20	H	-2.030023	-1.629924	0.570230
21	H	-4.202601	-2.778072	0.764033
22	H	-6.304694	-1.515083	0.439108
23	H	-6.226068	0.911222	-0.044900
24	H	-4.033599	2.068976	-0.189679
25	H	0.865751	1.597403	0.834407
26	H	2.927583	-1.226985	-1.639878
27	H	0.768318	-1.985534	-2.557216
28	H	-1.342456	-0.986436	-1.755493
29	H	3.167272	1.437056	1.014174
30	H	5.132246	1.843642	-0.465990
31	H	4.459418	0.760012	-1.682920
32	H	3.628666	2.275777	-1.298656
33	H	4.312244	-1.418669	2.378882

	KP#*S*-B2"-*syn*	*a*	*b*	*c*
1	C	-2.891496	0.304913	0.136469
2	C	-2.933170	-1.040611	0.506909
3	C	-4.153128	-1.680859	0.681906
4	C	-5.339018	-0.988092	0.470639
5	C	-5.304798	0.354001	0.102153
6	C	-4.088623	0.999889	-0.051108
7	C	-1.607740	1.056586	0.002778
8	C	-0.373735	0.334659	-0.434690
9	C	0.860068	0.805078	0.018539
10	C	2.048732	0.216037	-0.389632
11	C	1.994551	-0.854758	-1.285850
12	C	0.774680	-1.318743	-1.756200
13	C	-0.410851	-0.734602	-1.328395
14	C	3.372697	0.756340	0.124965
15	C	4.280242	1.258853	-1.004614
16	C	4.051080	-0.280426	1.003147
17	O	4.024006	-0.288939	2.204870
18	O	4.697543	-1.233048	0.287694
19	O	-1.564292	2.248853	0.245620
20	H	-2.012747	-1.579995	0.681843
21	H	-4.177585	-2.719453	0.985084
22	H	-6.289282	-1.490592	0.597920
23	H	-6.228089	0.895163	-0.059012
24	H	-4.042733	2.047494	-0.315377
25	H	0.870698	1.647505	0.697440
26	H	2.909919	-1.330342	-1.610511
27	H	0.747133	-2.140093	-2.460416
28	H	-1.358054	-1.093589	-1.705595
29	H	3.150608	1.581262	0.800456
30	H	5.214407	1.655530	-0.604463
31	H	4.522743	0.461522	-1.704697
32	H	3.772835	2.054581	-1.550105
33	H	5.069735	-1.859680	0.927829

Table S4. Complete list of experimental valence band ionization potentials of methyl salicylate compared to the theoretical vertical ionization potentials. *Values obtained by fitting three Gaussian functions to the experimental peak.

		Koopmans	OVGF	P3+	Exp.	Exp. [9]	Label
no.	C_s	*MOE*/ eV	*vIP*/ eV	*vIP* /eV	*IP*/ eV	*IP*/ eV	
					23.9		XV
					22.8		XIV
					20.2		XIII
					19.0		XII
22	σ	-20.25	17.99	17.81	17.5		XI
23	σ	-19.65	17.45	17.26			
24	σ	-18.86	16.79	16.52	16.3		X
25	π–$COOCH_3$	-18.65	16.69	16.48			
26	σ	-18.35	16.22	16.09			
27	σ	-17.49	15.58	15.50	15.3	15.3	IX
28	σ	-16.82	15.02	14.92			
29	π	-16.30	14.57	14.26	14.60	14.6	VIII
30	σ	-16.14	14.63	14.54			
31	σ	-15.60	13.80	13.50	13.4*	13.4	VII
32	π	-15.20	13.96	13.69			
33	σ	-14.93	13.37	13.27	13.1*	13.0	
34	σ	-14.61	13.15	12.93	12.9*	12.61	
35	σ	-13.91	12.30	12.30	12.0	12.1	VI
36	π	-13.32	11.90	11.87	11.58	11.35	V
37	π–$COOCH_3$	-13.04	11.64	11.37	11.20		IV
38	σ (n_O)	-12.51	10.89	10.54	10.47	10.40	III
39	πPh	-9.78	9.48	9.68	9.57	9.45	II
40	$\pi Ph/OH$	-8.75	8.55	8.73	8.64	8.60	I

Table S5. Complete list of experimental valence band ionization potentials of fenoprofen compared to the theoretical vertical ionization potentials of conformer #S-FP-A1"-*anti*. *Ph1* and *Ph2* refer to the unsubstituted and substituted phenyl rings.

		Koopmans	OVGF	P3+	Exp.	Exp. [9]	Label
no.	Character	*MOE*/ eV	*vIP*/ eV	*vIP*/ eV	*IP*/ eV	*IP*/ eV	
					22.6		XIV
					21.8		XIII
					19.5		XII
					18.2		XI
35		-20.01	17.79	17.60	17.3		X
36		-19.36	17.23	17.03			
37		-19.10	16.88	16.62	16.6		IX
38		-18.81	16.74	16.56			
39		-18.32	16.31	16.11			
40		-18.03	15.74	15.54	15.4		VIII
41		-17.74	15.43	15.25			
42		-17.56	15.69	15.62			
43		-16.92	15.07	14.94	14.4	14.4	VII
44		-16.62	14.81	14.62			
45		-16.37	14.73	14.59			

46		-16.28	14.63	14.39			
47		-16.17	14.49	14.32			
48		-15.64	13.84	13.58	12.92	12.65-13.4	VI
49		-15.54	13.62	13.33			
50		-15.01	13.38	13.31			
51		-14.64	13.25	13.19			
52		-14.44	12.94	12.89			
53		-14.13	12.67	12.59			
54		-13.82	12.34	12.29	11.80	12.1	V
55		-13.77	12.29	12.24			
56		-13.71	12.26	12.22			
57		-13.34	11.88	11.76			
58		-13.17	11.90	11.77			
59		-12.85	11.36	11.28	11.02	11.0	IV
60	σ (n_O) propanoic acid moiety	-12.24	10.69	10.45	10.44	10.45	III
61	*π Ph2, Ph1*	-9.49	9.30	9.40	9.20	9.15	II
62	*π Ph1, Ph2*	-9.25	9.13	9.22			
63	*π Ph2, Ph1*	-9.21	8.97	9.11			
64	*π Ph1, Ph2*	-8.48	8.06	8.32	8.27	8.25	I

Table S6. Complete list of experimental valence band ionization potentials of ketoprofen compared to the theoretical vertical ionization potentials of conformer #S-KP-A1"-*anti*. *Ph1* and *Ph2* refer to the unsubstituted and substituted phenyl rings.

		Koopmans	OVGF	P3+	Exp.	Exp. [9]	Label
no.	Character	*MOE*/ eV	*vIP*/ eV	*vIP*/ eV	*IP*/ eV	*IP*/ eV	
					22.7		XIV
					21.6		XIII
					19.2		XII
36		-20.63	18.10	17.91	17.6		XI
37		-19.68	17.36	17.16			
38		-19.50	17.36	17.14			
39		-19.14	16.89	16.67	16.8		X
40		-18.97	16.82	16.66	16.3		IX
41		-18.12	15.97	15.83			
42		-17.69	15.40	15.27	15.07	15.0	VIII
43		-17.67	15.72	15.63			
44		-17.33	15.24	15.14			
45		-17.02	15.05	14.86			
46		-16.62	14.83	14.59	14.26	14.5	VII
47		-16.56	14.64	14.47			
48		-16.48	14.80	14.65			
49		-16.29	14.50	14.35			
50		-16.20	14.47	14.34			
51		-15.23	13.56	13.55	12.97	12.85	VI
52		-14.95	13.46	13.34			
53		-14.79	13.41	13.33			
54		-14.52	12.95	12.94			
55		-14.17	12.56	12.49	11.88	12.1	V
56		-14.02	12.47	12.40			
57		-13.94	12.42	12.43			
58		-13.73	12.23	12.21			
59		-13.58	12.04	12.05			
60		-13.37	12.13	11.99			
61		-13.24	11.90	11.86			

62	σ (n_O) propanoic acid moiety	-12.43	10.86	10.63	10.58	10.55	III
63	σ (n_O), O19	-11.49	9.65	9.29	8.98		I
64	π *Ph2, Ph2*	-9.60	9.33	9.51			
65	π *Ph1, Ph2*	-9.43	9.22	9.37	9.41	9.4	II
66	π *Ph1, Ph2*	-9.38	9.18	9.36			
67	π *Ph1, Ph2*	-9.31	9.14	9.29	8.98	9.0	I

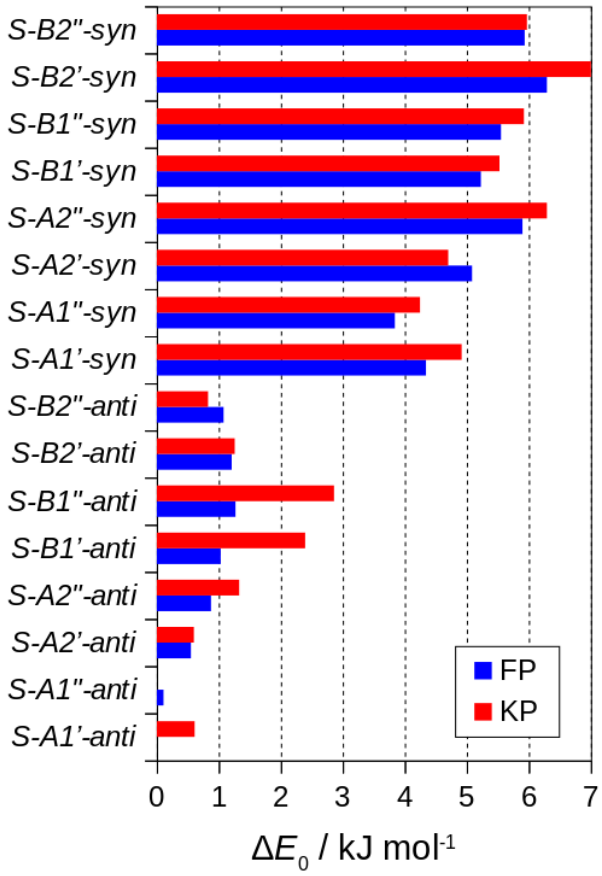


Figure S1. Theoretical zero point corrected relative energy values of the conformers of fenoprofen and ketoprofen at the B3LYP-D3(BJ)/Def2-TZVP level of calculation.

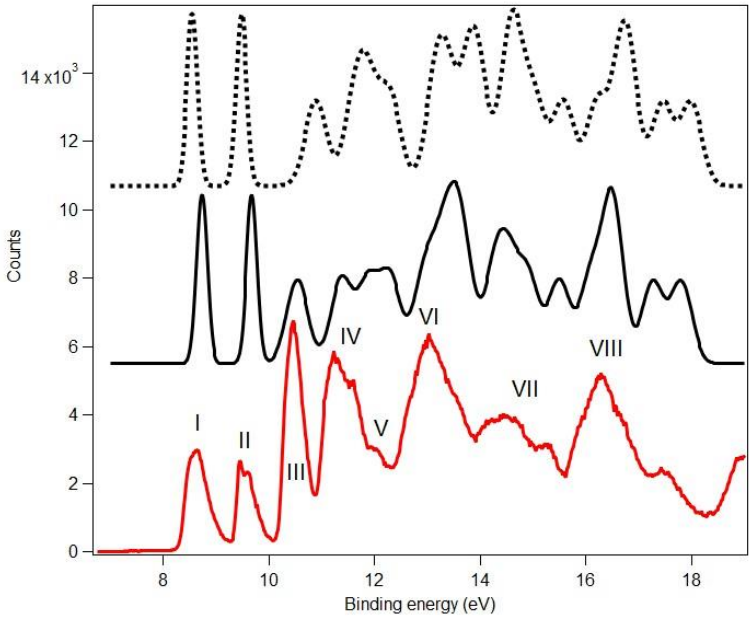
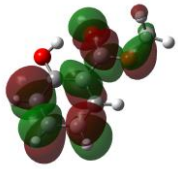
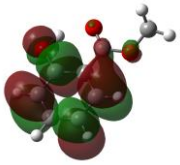
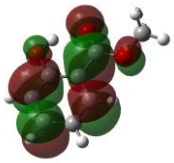
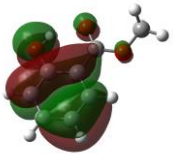
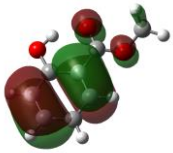
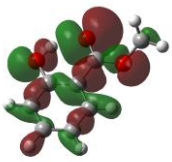
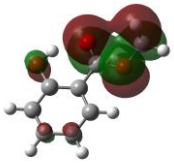
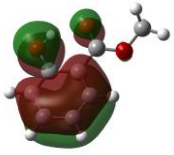
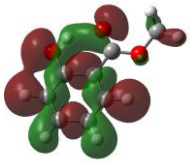
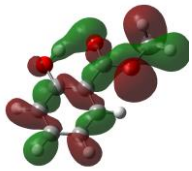
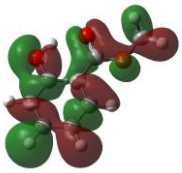
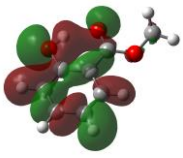
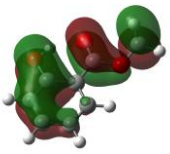
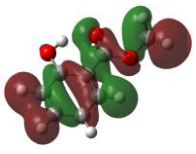
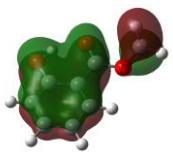


Figure S2a. Valence photoelectron spectra of methyl salicylate (red line), photon energy 100 eV, compared to the simulation obtained by convolution of the vertical ionization potentials with gaussian functions (σ=0.1 and 0.2 eV for the peaks with *vIP* less or more than 10 eV, respectively), using P3+ method (black line) and OVGF method (black dashed line).

				
LUMO+2 43	LUMO+1 42	LUMO 41	HOMO 40	HOMO-1 39
				
HOMO-2 38	MO 37	MO 36	MO 35	MO 34
				
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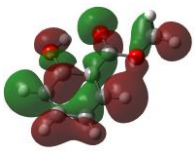
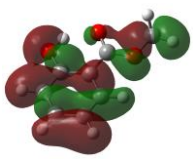
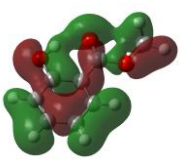
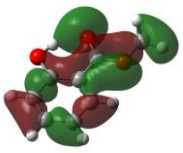
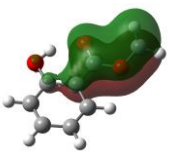
				
MO 28	MO 27	MO 26	MO 25	MO 24

Figure S2b. Theoretical molecular orbitals of MS at the B3LYP-D3(BJ)/Def2-TZVP level of calculation.

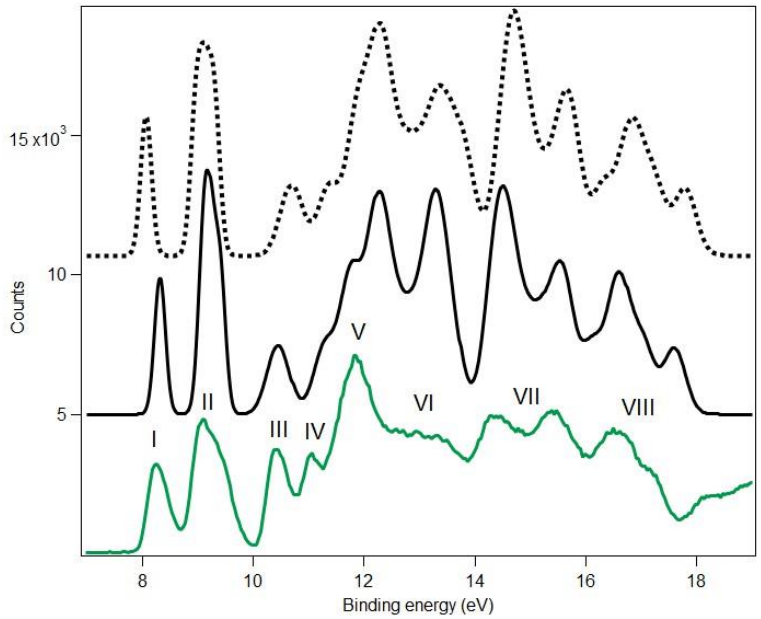
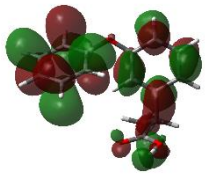
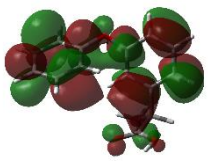
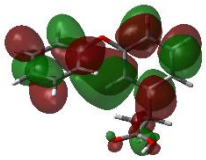
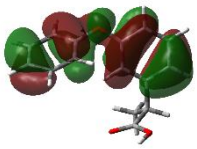
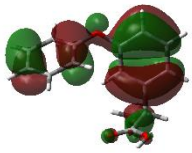


Figure S3a. Valence photoelectron spectra of fenoprofen (green line), photon energy 60 eV, compared to the simulation obtained by convolution of the vertical ionization potentials of the most stable conformer, FP#S-A1"-*anti*, with gaussian functions (σ=0.1 and 0.2 eV for the peaks with *vIP* less or more than 10 eV, respectively), using P3+ method (black line) and OVGF method (black dashed line).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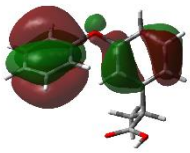
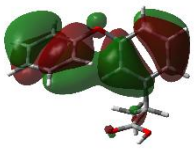
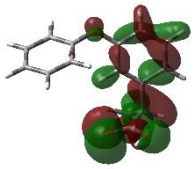
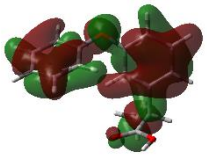
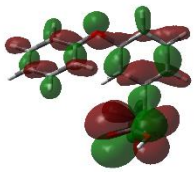
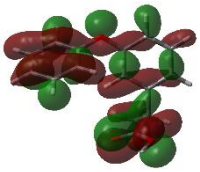
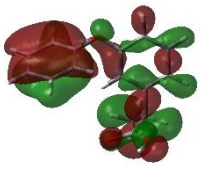
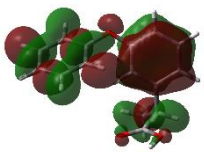
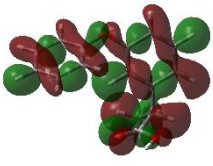
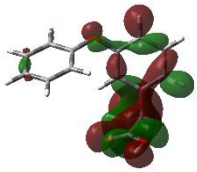
				
HOMO-2 62	HOMO-3 61	HOMO-4 60	MO 59	MO 58
				
MO 57	MO 56	MO 55	MO 54	MO 51

Figure S3b. Theoretical molecular orbitals of FP#*S*-A1"-*anti* at the B3LYP-D3(BJ)/Def2-TZVP level of calculation.

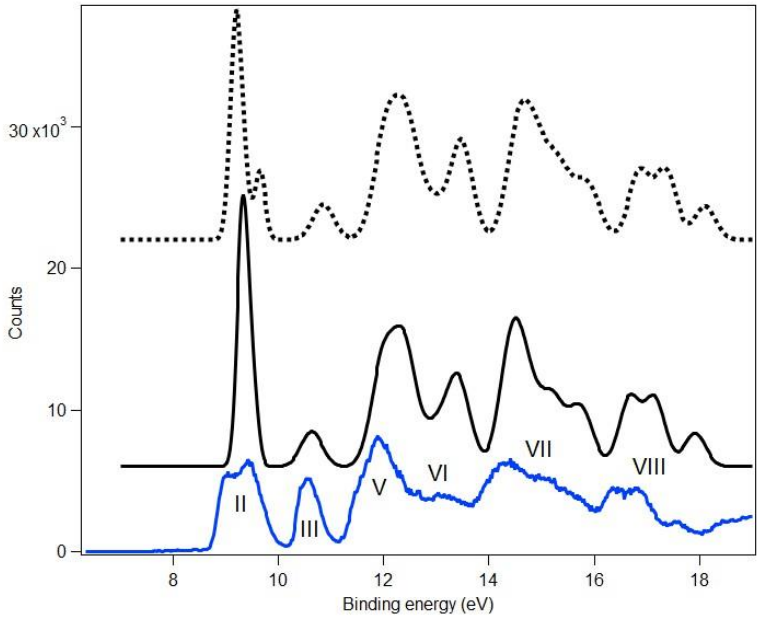


Figure S4a. Valence photoelectron spectra of ketoprofen (blue line), photon energy 100 eV, compared to the simulation obtained by convolution of the vertical ionization potentials of KP#*S*-A1''-*anti* with gaussian functions (σ=0.1 and 0.2 eV for the peaks with *vIP* less or more than 10 eV, respectively), using P3+ method (black line) and OVGF method (black dashed line).

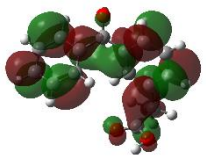
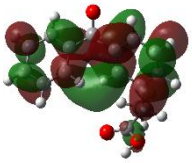
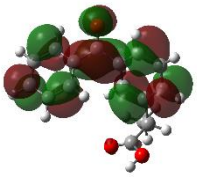
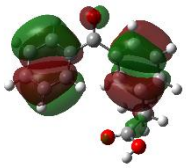
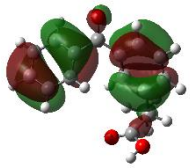
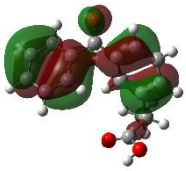
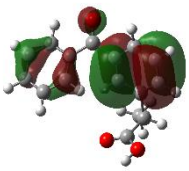
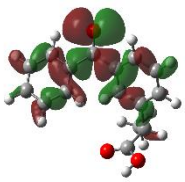
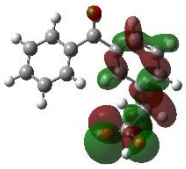
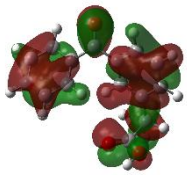
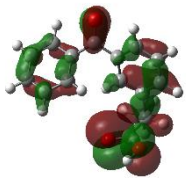
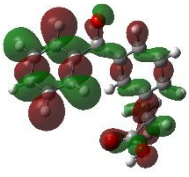
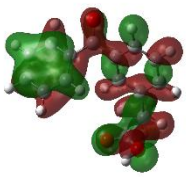
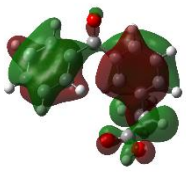
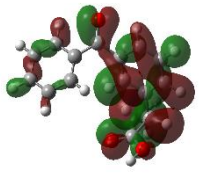
				
LUMO+2 70	LUMO+1 69	LUMO 68	HOMO 67	HOMO-1 66
				
HOMO-2 65	HOMO-3 64	HOMO-4 63	MO 62	MO 61
				
MO 60	MO 59	MO 58	MO 57	MO 56

Figure S4b. Theoretical molecular orbitals of KP#*S*-A1''-*anti* at the B3LYP-D3(BJ)/Def2-TZVP level of calculation.

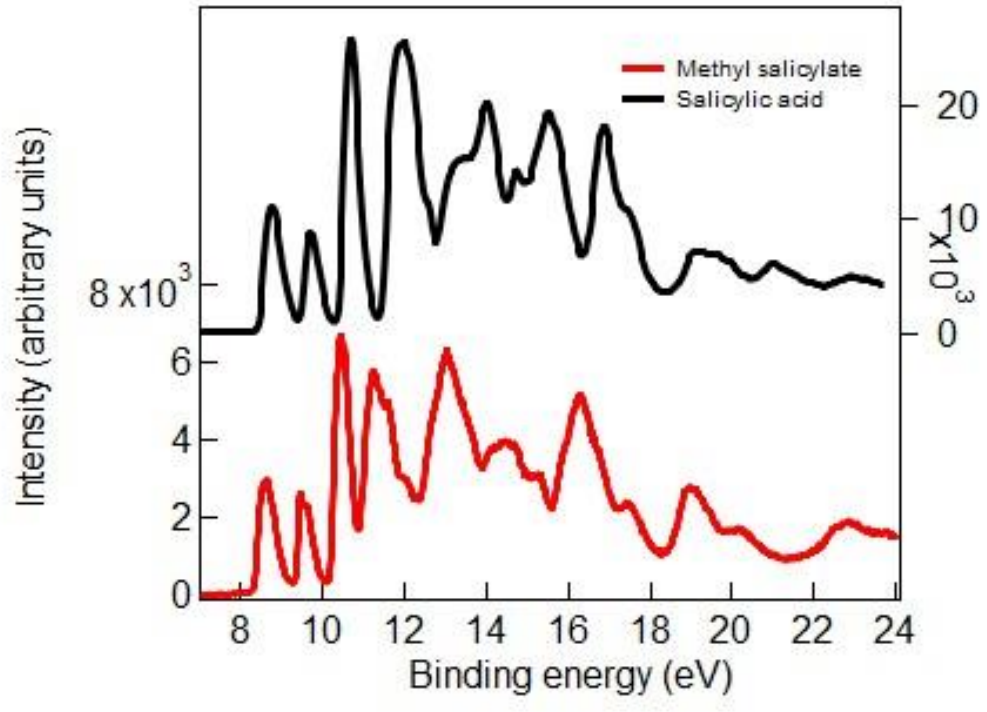


Figure S5. Comparison of the valence band spectra of methyl salicylate (red line) and salicylic acid (black line). The data for salicylic acid is from A. Hill, H. Sa'adeh, D. Cameron, F. Wang, A. B. Trofimov, E. Y. Larionova, R. Richter, K. C. Prince, *J. Phys. Chem. A*, 2021, 125 (45), 9877-9891. https://doi.org/10.1021/acs.jpca.1c07523

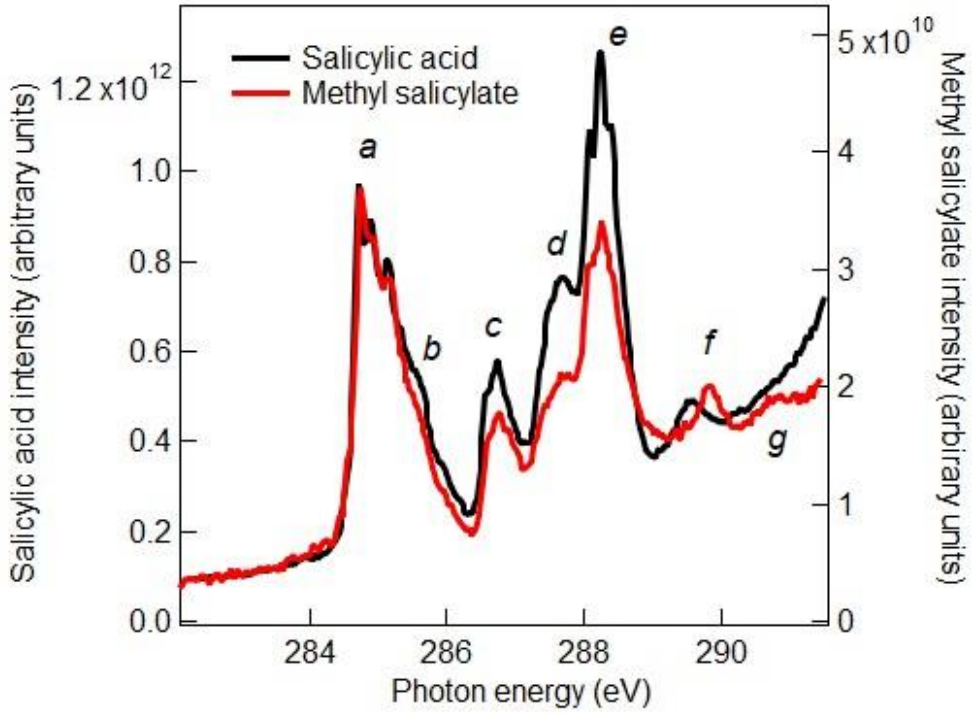


Figure S6. Comparison of the C K edge NEXAFS spectra of methyl salicylate (red line) and salicylic acid (black line), normalized to show approximately the same intensity for peaks *a*. Note the different intensity and peak shape for peaks *e*. The data for salicylic acid is from A. Hill, H. Sa'adeh, D. Cameron, F. Wang, A. B. Trofimov, E. Y. Larionova, R. Richter, K. C. Prince, J. Phys. Chem. A, 2021, 125 (45), 9877-9891. https://doi.org/10.1021/acs.jpca.1c07523

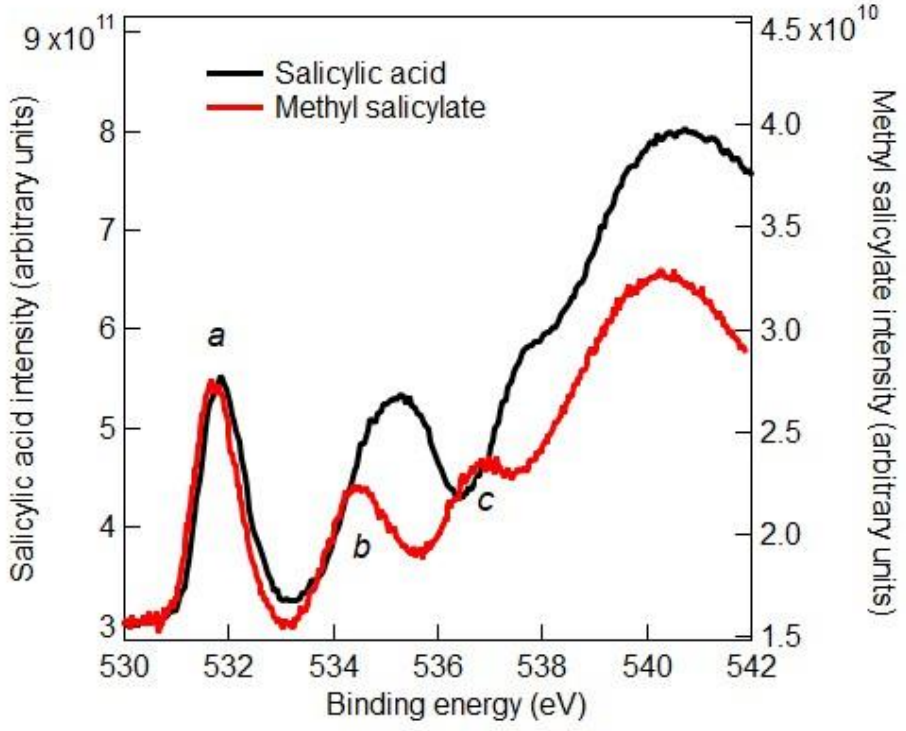


Figure S7. Comparison of the O K edge NEXAFS spectra of methyl salicylate (red line) and salicylic acid (black line), normalized to show approximately the same intensity for peaks *a*. Note the different intensity and peak shape for peaks *b*. The data for salicylic acid is from A. Hill, H. Sa'adeh, D. Cameron, F. Wang, A. B. Trofimov, E. Y. Larionova, R. Richter, K. C. Prince, J. Phys. Chem. A, 2021, 125 (45), 9877-9891. https://doi.org/10.1021/acs.jpca.1c07523

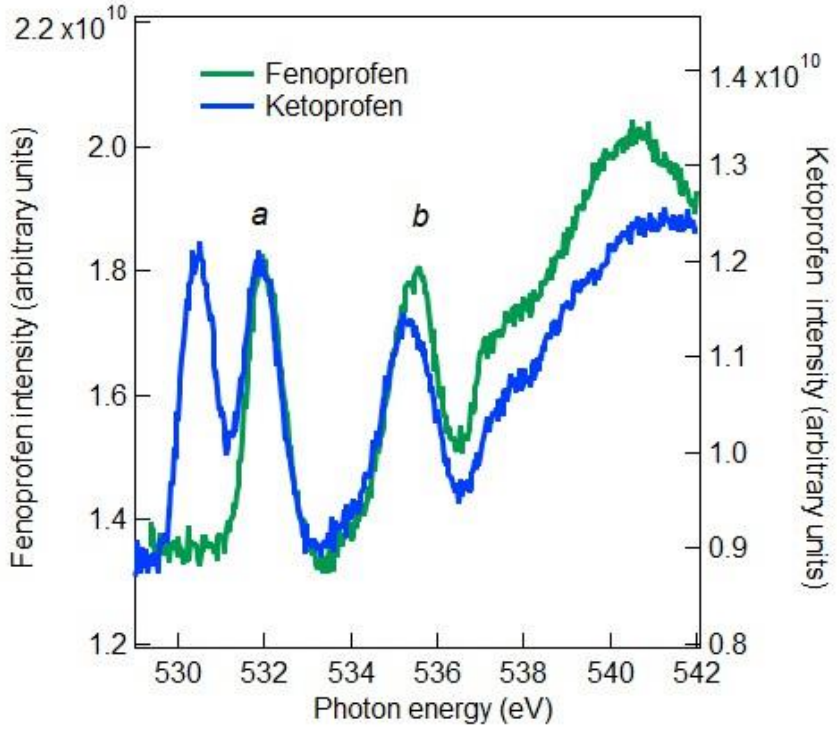


Figure S8. Comparison of the O K edge NEXAFS spectra of fenoprofen (green line) and ketoprofen (blue line), normalized to show approximately the same intensity for peaks *a*. Note the reduced intensity of peak *b* in ketoprofen.