Structural determination of vanillin, isovanillin and ethylvanillin by means of gas electron diffraction and theoretical calculations

Toru Egawa*, Akiyo Kameyama, Hiroshi Takeuchi

Division of Chemistry, Graduate School of Science, Hokkaido University, Sapporo 060-0810, Japan

Numerical data are listed in the following tables.

Table S1: The leveled total intensities (I_T) and the backgrounds (I_B) for vanillin, isovanillin and ethylvanillin.

Table S2: Definitions of the symmetry coordinates and the corresponding scale factors, c_i, of vanillin, isovanillin and ethylvanillin expressed in terms of internal coordinates.

Table S3: Observed and calculated vibrational wavenumbers (in cm^{-1}) and assignment of the s-*cis* conformer of vanillin.

Table S4: r_a Distances and mean amplitudes of the s-*cis* conformer of vanillin and isovanillin, and the s-*cis*-*trans* conformer of ethylvanillin (in Å).

Table S5: The correlation matrices for vanillin, isovanillin and ethylvanillin.

* Corresponding author. Phone: +81-11-706-3506; Fax: +81-11-706-4924.

E-mail address: egawa@sci.hokudai.ac.jp

Table S1. The leveled total intensities (I_T) and the backgrounds (I_B) for vanillin, isovanillin and ethylvanillin [a]

a) Vanillin

s	I_T	I_B	s	I_T	I_B	s	I_T	I_B
4.668	0.8282	1.02516	14.904	1.0070	1.00623	24.792	1.0029	1.00463
4.871	0.9572	1.03252	15.102	0.9996	1.00517	24.981	0.9978	1.00530
5.073	1.1105	1.04049	15.299	0.9989	1.00412	25.170	0.9938	1.00608
5.276	1.2341	1.04819	15.497	1.0037	1.00317	25.358	0.9916	1.00677
5.478	1.3164	1.05611	15.695	1.0079	1.00224	25.547	0.9913	1.00757
5.680	1.3454	1.06386	15.892	1.0102	1.00131	25.735	0.9927	1.00848
5.883	1.3305	1.07223	16.089	1.0075	1.00038	25.923	0.9959	1.00930
6.085	1.2900	1.07924	16.286	0.9982	0.99957	26.111	1.0008	1.01022
6.287	1.2328	1.08458	16.483	0.9883	0.99887	26.298	1.0047	1.01116
6.490	1.1656	1.09214	16.680	0.9777	0.99808	26.486	1.0090	1.01211
6.692	1.0963	1.09365	16.877	0.9695	0.99739	26.673	1.0132	1.01306
6.894	1.0416	1.09049	17.073	0.9633	0.99682	26.860	1.0168	1.01413
7.096	1.0056	1.08478	17.270	0.9608	0.99625	27.046	1.0196	1.01519
7.298	0.9845	1.07979	17.466	0.9624	0.99569	27.233	1.0229	1.01627
7.499	0.9774	1.07482	17.662	0.9686	0.99524	27.419	1.0249	1.01744
7.701	0.9858	1.06988	17.858	0.9785	0.99490	27.605	1.0273	1.01862
7.903	0.9758	1.06616	18.053	0.9915	0.99456	27.791	1.0281	1.01990
8.105	0.9930	1.06056	18.249	1.0044	0.99422	27.976	1.0297	1.02118
8.306	0.9988	1.05967	18.444	1.0170	0.99399	28.161	1.0300	1.02246
8.508	1.0133	1.05730	18.640	1.0262	0.99376	28.346	1.0306	1.02393
8.709	1.0360	1.05524	18.835	1.0305	0.99363	28.531	1.0312	1.02530
8.910	1.0568	1.05309	19.029	1.0311	0.99350	28.716	1.0318	1.02676
9.112	1.0750	1.05124	19.224	1.0257	0.99346	28.900	1.0317	1.02832
9.313	1.0722	1.04960	19.419	1.0181	0.99343	29.084	1.0326	1.02986
9.514	1.0578	1.04826	19.613	1.0070	0.99349	29.268	1.0327	1.03139
9.715	1.0461	1.04671	19.807	0.9971	0.99354	29.452	1.0325	1.03312
9.916	1.0459	1.04537	20.001	0.9874	0.99359	29.635	1.0314	1.03483
10.117	1.0566	1.04361	20.195	0.9811	0.99373	29.819	1.0303	1.03652
10.317	1.0789	1.04215	20.389	0.9774	0.99397	30.002	1.0310	1.03830
10.518	1.0997	1.03999	20.582	0.9782	0.99419	30.184	1.0312	1.04017
10.718	1.1117	1.03791	20.776	0.9797	0.99441	30.367	1.0325	1.04202
10.919	1.1083	1.03551	20.969	0.9829	0.99472	30.549	1.0335	1.04396
11.119	1.0905	1.03251	21.162	0.9853	0.99492	30.731	1.0373	1.04599
11.319	1.0605	1.03089	21.355	0.9872	0.99531	30.913	1.0405	1.04800
11.519	1.0271	1.02925	21.547	0.9878	0.99569	31.094	1.0443	1.05000
11.719	0.9977	1.02760	21.740	0.9868	0.99596	31.276	1.0495	1.05218
11.919	0.9767	1.02604	21.932	0.9871	0.99642	31.457	1.0541	1.05426
12.119	0.9635	1.02456	22.124	0.9881	0.99678	31.637	1.0595	1.05642
12.319	0.9578	1.02307	22.316	0.9910	0.99722	31.818	1.0626	1.05868
12.518	0.9563	1.02157	22.508	0.9941	0.99767	31.998	1.0666	1.06094
12.718	0.9595	1.02015	22.699	0.9995	0.99821	32.178	1.0697	1.06319
12.917	0.9704	1.01872	22.890	1.0039	0.99864	32.358	1.0719	1.06553
13.116	0.9873	1.01739	23.081	1.0080	0.99917	32.538	1.0742	1.06778
13.315	1.0095	1.01604	23.272	1.0110	0.99970	32.717	1.0760	1.07013
13.514	1.0359	1.01469	23.463	1.0139	1.00023	32.896	1.0774	1.07248
13.713	1.0581	1.01343	23.653	1.0159	1.00076	33.075	1.0792	1.07485
13.912	1.0698	1.01216	23.844	1.0169	1.00139	33.253	1.0810	1.07722
14.111	1.0682	1.01090	24.034	1.0163	1.00193	33.431	1.0824	1.07960
14.309	1.0554	1.00973	24.224	1.0152	1.00257	33.609	1.0845	1.08199
14.507	1.0370	1.00856	24.413	1.0114	1.00322	33.787	1.0863	1.08440
14.706	1.0196	1.00739	24.603	1.0077	1.00387			

b) Isovanillin

s	I_T	I_B	s	I_T	I_B	s	I_T	I_B
4.671	0.8951	1.06056	14.912	1.0072	1.00733	24.807	1.0004	1.00307
4.873	1.0118	1.06587	15.110	1.0015	1.00641	24.996	0.9960	1.00369
5.076	1.1413	1.07080	15.308	1.0019	1.00551	25.185	0.9927	1.00434
5.279	1.2561	1.07534	15.506	1.0056	1.00472	25.374	0.9910	1.00509
5.481	1.3244	1.07989	15.704	1.0095	1.00384	25.562	0.9909	1.00586
5.684	1.3472	1.08425	15.901	1.0113	1.00307	25.750	0.9931	1.00663
5.886	1.3287	1.08902	16.099	1.0080	1.00231	25.939	0.9959	1.00752
6.089	1.2805	1.09210	16.296	0.9998	1.00156	26.126	1.0004	1.00841
6.291	1.2162	1.09320	16.493	0.9898	1.00082	26.314	1.0041	1.00941
6.493	1.1449	1.09031	16.690	0.9797	1.00018	26.502	1.0083	1.01032
6.695	1.0851	1.08562	16.887	0.9721	0.99955	26.689	1.0122	1.01143
6.898	1.0407	1.07993	17.083	0.9672	0.99893	26.876	1.0153	1.01244
7.100	1.0065	1.07363	17.280	0.9655	0.99841	27.063	1.0183	1.01355
7.302	0.9813	1.06793	17.476	0.9672	0.99789	27.249	1.0208	1.01476
7.504	0.9721	1.06431	17.672	0.9732	0.99737	27.435	1.0236	1.01596
7.706	0.9760	1.06088	17.868	0.9838	0.99695	27.622	1.0250	1.01716
7.907	0.9805	1.05754	18.064	0.9959	0.99663	27.807	1.0266	1.01845
8.109	0.9919	1.05439	18.260	1.0087	0.99630	27.993	1.0273	1.01973
8.311	0.9956	1.05122	18.455	1.0203	0.99607	28.179	1.0279	1.02110
8.513	1.0057	1.04834	18.650	1.0283	0.99584	28.364	1.0286	1.02245
8.714	1.0287	1.04554	18.846	1.0326	0.99560	28.549	1.0293	1.02379
8.916	1.0491	1.04302	19.041	1.0318	0.99545	28.733	1.0297	1.02522
9.117	1.0615	1.04059	19.236	1.0258	0.99539	28.918	1.0296	1.02663
9.318	1.0582	1.03834	19.430	1.0173	0.99521	29.102	1.0299	1.02812
9.519	1.0457	1.03627	19.625	1.0067	0.99523	29.286	1.0295	1.02949
9.720	1.0361	1.03437	19.819	0.9965	0.99524	29.470	1.0282	1.03094
9.921	1.0357	1.03266	20.013	0.9879	0.99524	29.654	1.0275	1.03238
10.122	1.0464	1.03104	20.207	0.9823	0.99533	29.837	1.0271	1.03380
10.323	1.0672	1.02959	20.401	0.9788	0.99540	30.020	1.0260	1.03530
10.524	1.0869	1.02822	20.595	0.9789	0.99546	30.203	1.0269	1.03669
10.725	1.0988	1.02694	20.788	0.9808	0.99562	30.386	1.0274	1.03806
10.925	1.0944	1.02584	20.981	0.9837	0.99576	30.568	1.0287	1.03942
11.126	1.0760	1.02473	21.174	0.9866	0.99590	30.750	1.0318	1.04087
11.326	1.0467	1.02370	21.367	0.9877	0.99613	30.932	1.0349	1.04221
11.526	1.0172	1.02266	21.560	0.9877	0.99635	31.114	1.0382	1.04354
11.726	0.9914	1.02171	21.753	0.9874	0.99656	31.295	1.0424	1.04487
11.926	0.9733	1.02085	21.945	0.9874	0.99678	31.476	1.0470	1.04620
12.126	0.9627	1.01988	22.137	0.9886	0.99709	31.657	1.0511	1.04753
12.326	0.9570	1.01900	22.329	0.9912	0.99739	31.838	1.0543	1.04897
12.526	0.9552	1.01812	22.521	0.9957	0.99770	32.018	1.0578	1.05031
12.725	0.9602	1.01723	22.712	0.9993	0.99802	32.198	1.0597	1.05177
12.925	0.9718	1.01635	22.904	1.0038	0.99833	32.378	1.0623	1.05333
13.124	0.9894	1.01546	23.095	1.0076	0.99865	32.558	1.0634	1.05492
13.323	1.0124	1.01457	23.286	1.0107	0.99908	32.737	1.0646	1.05672
13.522	1.0368	1.01369	23.477	1.0131	0.99941	32.916	1.0659	1.05854
13.721	1.0564	1.01282	23.667	1.0150	0.99986	33.095	1.0674	1.06069
13.920	1.0654	1.01185	23.858	1.0155	1.00031	33.274	1.0684	1.06306
14.119	1.0623	1.01098	24.048	1.0147	1.00078	33.452	1.0700	1.06576
14.317	1.0498	1.01003	24.238	1.0126	1.00136	33.630	1.0711	1.06879
14.516	1.0332	1.00908	24.428	1.0093	1.00185	33.808	1.0724	1.07215
14.714	1.0181	1.00825	24.617	1.0055	1.00245			

c) Ethylvanillin

s	I_T	I_B	s	I_T	I_B	s	I_T	I_B
4.468	0.8500	1.09356	14.713	1.0203	1.01063	24.615	1.0035	0.99969
4.670	0.9001	1.09856	14.911	1.0061	1.00935	24.805	0.9984	1.00044
4.873	1.0211	1.10329	15.109	0.9985	1.00808	24.994	0.9955	1.00130
5.076	1.1651	1.10754	15.307	0.9973	1.00681	25.183	0.9924	1.00207
5.278	1.2803	1.11141	15.505	1.0003	1.00565	25.372	0.9907	1.00295
5.481	1.3637	1.11521	15.702	1.0048	1.00450	25.560	0.9905	1.00384
5.683	1.3975	1.11853	15.900	1.0073	1.00335	25.748	0.9921	1.00473
5.886	1.3834	1.12199	16.097	1.0058	1.00221	25.937	0.9956	1.00574
6.088	1.3312	1.12378	16.294	0.9992	1.00118	26.124	0.9992	1.00665
6.290	1.2647	1.12420	16.492	0.9909	1.00027	26.312	1.0031	1.00767
6.493	1.1871	1.12316	16.688	0.9823	0.99926	26.500	1.0072	1.00870
6.695	1.1189	1.11956	16.885	0.9755	0.99836	26.687	1.0103	1.00974
6.897	1.0646	1.11469	17.082	0.9705	0.99757	26.874	1.0121	1.01078
7.099	1.0330	1.10945	17.278	0.9686	0.99669	27.060	1.0159	1.01183
7.301	1.0141	1.10405	17.475	0.9695	0.99601	27.247	1.0164	1.01299
7.503	1.0054	1.09867	17.671	0.9749	0.99525	27.433	1.0196	1.01415
7.705	1.0074	1.09311	17.867	0.9831	0.99460	27.619	1.0211	1.01532
7.907	1.0123	1.08998	18.062	0.9932	0.99405	27.805	1.0229	1.01648
8.109	1.0194	1.08637	18.258	1.0042	0.99340	27.991	1.0231	1.01775
8.310	1.0329	1.08277	18.454	1.0136	0.99296	28.176	1.0242	1.01902
8.512	1.0457	1.07929	18.649	1.0207	0.99253	28.362	1.0256	1.02028
8.713	1.0659	1.07582	18.844	1.0246	0.99209	28.547	1.0257	1.02154
8.915	1.0844	1.07246	19.039	1.0246	0.99176	28.731	1.0272	1.02290
9.116	1.0942	1.06911	19.234	1.0200	0.99143	28.916	1.0278	1.02435
9.317	1.0907	1.06597	19.429	1.0118	0.99119	29.100	1.0289	1.02569
9.519	1.0751	1.06282	19.623	1.0014	0.99096	29.284	1.0285	1.02713
9.720	1.0599	1.05987	19.817	0.9909	0.99082	29.468	1.0291	1.02866
9.921	1.0550	1.05702	20.012	0.9827	0.99067	29.651	1.0280	1.03017
10.122	1.0613	1.05417	20.206	0.9770	0.99062	29.835	1.0282	1.03167
10.322	1.0776	1.05150	20.399	0.9747	0.99067	30.018	1.0282	1.03327
10.523	1.0945	1.04893	20.593	0.9749	0.99060	30.201	1.0285	1.03485
10.724	1.1057	1.04645	20.786	0.9778	0.99073	30.383	1.0288	1.03651
10.924	1.1031	1.04406	20.980	0.9805	0.99085	30.566	1.0304	1.03827
11.125	1.0883	1.04175	21.173	0.9840	0.99097	30.748	1.0327	1.04001
11.325	1.0624	1.03953	21.366	0.9850	0.99117	30.930	1.0347	1.04174
11.525	1.0340	1.03739	21.558	0.9866	0.99137	31.111	1.0393	1.04356
11.725	1.0087	1.03534	21.751	0.9860	0.99165	31.293	1.0428	1.04546
11.925	0.9899	1.03338	21.943	0.9857	0.99203	31.474	1.0471	1.04736
12.125	0.9790	1.03140	22.135	0.9863	0.99230	31.655	1.0503	1.04924
12.325	0.9734	1.02950	22.327	0.9881	0.99266	31.835	1.0545	1.05122
12.525	0.9722	1.02769	22.519	0.9903	0.99312	32.016	1.0577	1.05319
12.724	0.9766	1.02597	22.711	0.9949	0.99357	32.196	1.0600	1.05526
12.924	0.9863	1.02424	22.902	0.9982	0.99402	32.376	1.0620	1.05723
13.123	1.0007	1.02260	23.093	1.0007	0.99456	32.555	1.0644	1.05929
13.322	1.0205	1.02095	23.284	1.0040	0.99510	32.735	1.0657	1.06135
13.521	1.0424	1.01938	23.475	1.0064	0.99564	32.914	1.0673	1.06342
13.720	1.0601	1.01782	23.666	1.0084	0.99627	33.093	1.0695	1.06539
13.919	1.0697	1.01634	23.856	1.0088	0.99691	33.271	1.0706	1.06737
14.118	1.0677	1.01487	24.046	1.0093	0.99755	33.450	1.0720	1.06936
14.316	1.0551	1.01339	24.236	1.0091	0.99819			
14.515	1.0368	1.01201	24.426	1.0051	0.99894			

[a] The s-values ($s = (4\pi/\lambda)\sin(\theta/2)$) are in $Å^{-1}$ units. The molecular scattering intensity, $M(s)$ is calculated as $M(s) = (I_T(s) - I_B(s)) / I_B(s)$.

Table S2. Definitions of the symmetry coordinates and the corresponding scale factors, c_i, of vanillin, isovanillin and ethylvanillin expressed in terms of internal coordinates

a) Vanillin (s-*cis*)

S_i	c_i	Definitions [a]
S_1	0.920	$r(C_1\text{-}C_2) + r(C_1\text{-}C_6)$
S_2	0.920	$r(C_1\text{-}C_2) - r(C_1\text{-}C_6)$
S_3	0.950	$r(C_2\text{-}C_3)$
S_4	0.940	$r(C_5\text{-}C_6)$
S_5	0.950	$r(C_3\text{-}C_4) + r(C_4\text{-}C_5)$
S_6	0.950	$r(C_3\text{-}C_4) - r(C_4\text{-}C_5)$
S_7	0.950	$r(C_1\text{-}C_7)$
S_8	0.850	$r(C_3\text{-}O_9)$
S_9	0.950	$r(C_4\text{-}O_{11})$
S_{10}	0.900	$r(C_7\text{=}O_8)$
S_{11}	0.940	$r(O_9\text{-}C_{10})$
S_{12}	0.880	$r(C_{10}\text{-}H_{14}) + r(C_{10}\text{-}H_{15}) + r(C_{10}\text{-}H_{16})$
S_{13}	0.920	$2r(C_{10}\text{-}H_{14}) - r(C_{10}\text{-}H_{15}) - r(C_{10}\text{-}H_{16})$
S_{14}	0.920	$r(C_{10}\text{-}H_{15}) - r(C_{10}\text{-}H_{16})$
S_{15}	0.862	$r(C_2\text{-}H_{13}) + r(C_6\text{-}H_{19})$
S_{16}	0.862	$r(C_2\text{-}H_{13}) - r(C_6\text{-}H_{19})$
S_{17}	0.920	$r(C_5\text{-}H_{18})$
S_{18}	0.920	$r(C_7\text{-}H_{12})$
S_{19}	0.940	$r(O_{11}\text{-}H_{17})$
S_{20}	0.950	$4\angle(C_6\text{-}C_1\text{-}C_2) - 2\angle(C_6\text{-}C_1\text{-}C_7) - 2\angle(C_2\text{-}C_1\text{-}C_7) + 4\angle(C_3\text{-}C_4\text{-}C_5)$ $- 2\angle(C_3\text{-}C_4\text{-}O_{11}) - 2\angle(O_{11}\text{-}C_4\text{-}C_5) - 2\angle(C_1\text{-}C_2\text{-}C_3) + \angle(C_1\text{-}C_2\text{-}H_{13})$ $+ \angle(H_{13}\text{-}C_2\text{-}C_3) - 2\angle(C_2\text{-}C_3\text{-}C_4) + \angle(C_2\text{-}C_3\text{-}O_9) + \angle(C_4\text{-}C_3\text{-}O_9)$ $- 2\angle(C_4\text{-}C_5\text{-}C_6) + \angle(C_4\text{-}C_5\text{-}H_{18}) + \angle(H_{18}\text{-}C_5\text{-}C_6) - 2\angle(C_5\text{-}C_6\text{-}C_1)$ $+ \angle(C_5\text{-}C_6\text{-}H_{19}) + \angle(H_{19}\text{-}C_6\text{-}C_1)$
S_{21}	0.950	$- 2\angle(C_1\text{-}C_2\text{-}C_3) + \angle(C_1\text{-}C_2\text{-}H_{13}) + \angle(H_{13}\text{-}C_2\text{-}C_3) - 2\angle(C_2\text{-}C_3\text{-}C_4)$ $- \angle(C_2\text{-}C_3\text{-}O_9) - \angle(C_4\text{-}C_3\text{-}O_9) - 2\angle(C_4\text{-}C_5\text{-}C_6) + \angle(C_4\text{-}C_5\text{-}H_{18})$

		$+\angle(H_{18}\text{-}C_5\text{-}C_6) + 2\angle(C_5\text{-}C_6\text{-}C_1) - \angle(C_5\text{-}C_6\text{-}H_{19}) - \angle(H_{19}\text{-}C_6\text{-}C_1)$
s_{22}	0.850	$2\angle(C_6\text{-}C_1\text{-}C_2) - \angle(C_6\text{-}C_1\text{-}C_7) - \angle(C_2\text{-}C_1\text{-}C_7) - 2\angle(C_3\text{-}C_4\text{-}C_5)$ $+\angle(C_3\text{-}C_4\text{-}O_{11}) + \angle(O_{11}\text{-}C_4\text{-}C_5) - 2\angle(C_1\text{-}C_2\text{-}C_3) + \angle(C_1\text{-}C_2\text{-}H_{13})$ $+\angle(H_{13}\text{-}C_2\text{-}C_3) + 2\angle(C_2\text{-}C_3\text{-}C_4) - \angle(C_2\text{-}C_3\text{-}O_9) - \angle(C_4\text{-}C_3\text{-}O_9)$ $+2\angle(C_4\text{-}C_5\text{-}C_6) - \angle(C_4\text{-}C_5\text{-}H_{18}) - \angle(H_{18}\text{-}C_5\text{-}C_6) + 2\angle(C_5\text{-}C_6\text{-}C_1)$ $+\angle(C_5\text{-}C_6\text{-}H_{19}) + \angle(H_{19}\text{-}C_6\text{-}C_1)$
s_{23}	0.950	$\angle(O_9\text{-}C_{10}\text{-}H_{14}) + \angle(O_9\text{-}C_{10}\text{-}H_{15}) + \angle(O_9\text{-}C_{10}\text{-}H_{16}) - \angle(H_{14}\text{-}C_{10}\text{-}H_{15})$ $-\angle(H_{14}\text{-}C_{10}\text{-}H_{16}) - \angle(H_{15}\text{-}C_{10}\text{-}H_{16})$
s_{24}	0.920	$2\angle(O_9\text{-}C_{10}\text{-}H_{14}) + \angle(O_9\text{-}C_{10}\text{-}H_{15}) - \angle(O_9\text{-}C_{10}\text{-}H_{16})$
s_{25}	0.920	$\angle(O_9\text{-}C_{10}\text{-}H_{15}) - \angle(O_9\text{-}C_{10}\text{-}H_{16})$
s_{26}	0.920	$-\angle(H_{14}\text{-}C_{10}\text{-}H_{15}) - \angle(H_{14}\text{-}C_{10}\text{-}H_{16}) + 2\angle(H_{15}\text{-}C_{10}\text{-}H_{16})$
s_{27}	0.920	$\angle(H_{14}\text{-}C_{10}\text{-}H_{15}) - \angle(H_{14}\text{-}C_{10}\text{-}H_{16})$
s_{28}	0.920	$\angle(C_6\text{-}C_1\text{-}C_7) - \angle(C_2\text{-}C_1\text{-}H_7)$
s_{29}	0.950	$\angle(C_1\text{-}C_2\text{-}H_{13}) - \angle(C_3\text{-}C_2\text{-}H_{13})$
s_{30}	0.920	$\angle(C_2\text{-}C_3\text{-}O_9) - \angle(C_4\text{-}C_3\text{-}O_9)$
s_{31}	0.920	$\angle(C_3\text{-}C_4\text{-}O_{11}) - \angle(C_5\text{-}C_4\text{-}O_{11})$
s_{32}	0.950	$\angle(C_4\text{-}C_5\text{-}H_{18}) - \angle(C_6\text{-}C_5\text{-}H_{18})$
s_{33}	0.890	$\angle(C_5\text{-}C_6\text{-}H_{19}) - \angle(C_1\text{-}C_6\text{-}H_{19})$
s_{34}	0.950	$\angle(C_1\text{-}C_7\text{=}O_8) - \angle(O_8\text{=}C_7\text{-}H_{12})$
s_{35}	0.950	$\angle(C_1\text{-}C_7\text{=}O_8) + 2\angle(O_8\text{=}C_7\text{-}H_{12}) - \angle(C_1\text{-}C_7\text{-}H_{12})$
s_{36}	0.900	$\angle(C_4\text{-}O_{11}\text{-}H_{17})$
s_{37}	0.920	$\angle(C_3\text{-}O_9\text{-}C_{10})$
s_{38}	0.920	$\tau(C_1\text{-}C_2) - 2\tau(C_2\text{-}C_3) + \tau(C_3\text{-}C_4) + \tau(C_4\text{-}C_5) - 2\tau(C_5\text{-}C_6) + \tau(C_1\text{-}C_6)$
s_{39}	0.930	$-\tau(C_1\text{-}C_2) + \tau(C_2\text{-}C_3) - \tau(C_3\text{-}C_4) + \tau(C_4\text{-}C_5) - \tau(C_5\text{-}C_6) + \tau(C_1\text{-}C_6)$
s_{40}	0.920	$\tau(C_1\text{-}C_2) - \tau(C_3\text{-}C_4) + \tau(C_4\text{-}C_5) - \tau(C_1\text{-}C_6)$
s_{41}	0.920	$\tau(C_1\text{-}C_7)$
s_{42}	0.920	$\tau(O_9\text{-}C_{10})$
s_{43}	0.920	$\tau(C_3\text{-}O_9)$
s_{44}	0.920	$\tau(C_4\text{-}O_{11})$
s_{45}	0.920	$\omega(C_1\text{-}C_2\text{-}C_3\text{-}H_{13})$

s_{46}	0.950	ω (C_2-C_3-C_4-O_9)
s_{47}	0.920	ω (C_3-C_4-C_5-O_{11})
s_{48}	0.920	ω (C_4-C_5-C_6-H_{18})
s_{49}	0.920	ω (C_5-C_6-C_1-H_{19})
s_{50}	0.950	ω (C_6-C_1-C_2-C_7)
s_{51}	0.920	ω (C_1-C_7-H_{12}-O_8)

b) Isovanillin (s-*cis*)

S_i	c_i	Definitions [a]
S_1	0.920	$r(C_1\text{-}C_2) + r(C_1\text{-}C_6)$
S_2	0.920	$r(C_1\text{-}C_2) - r(C_1\text{-}C_6)$
S_3	0.950	$r(C_2\text{-}C_3)$
S_4	0.940	$r(C_5\text{-}C_6)$
S_5	0.950	$r(C_3\text{-}C_4) + r(C_4\text{-}C_5)$
S_6	0.950	$r(C_3\text{-}C_4) - r(C_4\text{-}C_5)$
S_7	0.950	$r(C_1\text{-}C_7)$
S_8	0.950	$r(C_3\text{-}O_9)$
S_9	0.850	$r(C_4\text{-}O_{10})$
S_{10}	0.900	$r(C_7\text{=}O_8)$
S_{11}	0.940	$r(O_{10}\text{-}C_{11})$
S_{12}	0.880	$r(C_{11}\text{-}H_{15}) + r(C_{11}\text{-}H_{16}) + r(C_{11}\text{-}H_{17})$
S_{13}	0.920	$2r(C_{11}\text{-}H_{15}) - r(C_{11}\text{-}H_{16}) - r(C_{11}\text{-}H_{17})$
S_{14}	0.920	$r(C_{11}\text{-}H_{16}) - r(C_{11}\text{-}H_{17})$
S_{15}	0.862	$r(C_2\text{-}H_{13}) + r(C_6\text{-}H_{19})$
S_{16}	0.862	$r(C_2\text{-}H_{13}) - r(C_6\text{-}H_{19})$
S_{17}	0.920	$r(C_5\text{-}H_{18})$
S_{18}	0.920	$r(C_7\text{-}H_{12})$
S_{19}	0.940	$r(O_9\text{-}H_{14})$
S_{20}	0.950	$4\angle(C_6\text{-}C_1\text{-}C_2) - 2\angle(C_6\text{-}C_1\text{-}C_7) - 2\angle(C_2\text{-}C_1\text{-}C_7) + 4\angle(C_3\text{-}C_4\text{-}C_5) - 2\angle(C_3\text{-}C_4\text{-}O_{10}) - 2\angle(O_{10}\text{-}C_4\text{-}C_5) - 2\angle(C_1\text{-}C_2\text{-}C_3) + \angle(C_1\text{-}C_2\text{-}H_{13}) + \angle(H_{13}\text{-}C_2\text{-}C_3) - 2\angle(C_2\text{-}C_3\text{-}C_4) + \angle(C_2\text{-}C_3\text{-}O_9) + \angle(C_4\text{-}C_3\text{-}O_9) - 2\angle(C_4\text{-}C_5\text{-}C_6) + \angle(C_4\text{-}C_5\text{-}H_{18}) + \angle(H_{18}\text{-}C_5\text{-}C_6) - 2\angle(C_5\text{-}C_6\text{-}C_1) + \angle(C_5\text{-}C_6\text{-}H_{19}) + \angle(H_{19}\text{-}C_6\text{-}C_1)$
S_{21}	0.950	$-2\angle(C_1\text{-}C_2\text{-}C_3) + \angle(C_1\text{-}C_2\text{-}H_{13}) + \angle(H_{13}\text{-}C_2\text{-}C_3) - 2\angle(C_2\text{-}C_3\text{-}C_4) - \angle(C_2\text{-}C_3\text{-}O_9) - \angle(C_4\text{-}C_3\text{-}O_9) - 2\angle(C_4\text{-}C_5\text{-}C_6) + \angle(C_4\text{-}C_5\text{-}H_{18}) + \angle(H_{18}\text{-}C_5\text{-}C_6) + 2\angle(C_5\text{-}C_6\text{-}C_1) - \angle(C_5\text{-}C_6\text{-}H_{19}) - \angle(H_{19}\text{-}C_6\text{-}C_1)$
S_{22}	0.850	$2\angle(C_6\text{-}C_1\text{-}C_2) - \angle(C_6\text{-}C_1\text{-}C_7) - \angle(C_2\text{-}C_1\text{-}C_7) - 2\angle(C_3\text{-}C_4\text{-}C_5)$

		$+\angle(C_3\text{-}C_4\text{-}O_{10}) +\angle(O_{10}\text{-}C_4\text{-}C_5) -2\angle(C_1\text{-}C_2\text{-}C_3) +\angle(C_1\text{-}C_2\text{-}H_{13})$ $+\angle(H_{13}\text{-}C_2\text{-}C_3) +2\angle(C_2\text{-}C_3\text{-}C_4) -\angle(C_2\text{-}C_3\text{-}O_9) -\angle(C_4\text{-}C_3\text{-}O_9)$ $+2\angle(C_4\text{-}C_5\text{-}C_6) -\angle(C_4\text{-}C_5\text{-}H_{18}) -\angle(H_{18}\text{-}C_5\text{-}C_6) +2\angle(C_5\text{-}C_6\text{-}C_1)$ $+\angle(C_5\text{-}C_6\text{-}H_{19}) +\angle(H_{19}\text{-}C_6\text{-}C_1)$
s_{23}	0.950	$\angle(O_{10}\text{-}C_{11}\text{-}H_{15}) +\angle(O_{10}\text{-}C_{11}\text{-}H_{16}) +\angle(O_{10}\text{-}C_{11}\text{-}H_{17}) -\angle(H_{15}\text{-}C_{11}\text{-}H_{16})$ $-\angle(H_{15}\text{-}C_{11}\text{-}H_{17}) -\angle(H_{16}\text{-}C_{11}\text{-}H_{17})$
s_{24}	0.920	$2\angle(O_{10}\text{-}C_{11}\text{-}H_{15}) +\angle(O_{10}\text{-}C_{11}\text{-}H_{16}) -\angle(O_{10}\text{-}C_{11}\text{-}H_{17})$
s_{25}	0.920	$\angle(O_{10}\text{-}C_{11}\text{-}H_{16}) -\angle(O_{10}\text{-}C_{11}\text{-}H_{17})$
s_{26}	0.920	$-\angle(H_{15}\text{-}C_{11}\text{-}H_{16}) -\angle(H_{15}\text{-}C_{11}\text{-}H_{17}) +2\angle(H_{11}\text{-}C_{11}\text{-}H_{17})$
s_{27}	0.920	$\angle(H_{15}\text{-}C_{11}\text{-}H_{16}) -\angle(H_{15}\text{-}C_{11}\text{-}H_{17})$
s_{28}	0.920	$\angle(C_6\text{-}C_1\text{-}C_7) -\angle(C_2\text{-}C_1\text{-}H_7)$
s_{29}	0.950	$\angle(C_1\text{-}C_2\text{-}H_{13}) -\angle(C_3\text{-}C_2\text{-}H_{13})$
s_{30}	0.920	$\angle(C_2\text{-}C_3\text{-}O_9) -\angle(C_4\text{-}C_3\text{-}O_9)$
s_{31}	0.920	$\angle(C_3\text{-}C_4\text{-}O_{10}) -\angle(C_5\text{-}C_4\text{-}O_{10})$
s_{32}	0.950	$\angle(C_4\text{-}C_5\text{-}H_{18}) -\angle(C_6\text{-}C_5\text{-}H_{18})$
s_{33}	0.890	$\angle(C_5\text{-}C_6\text{-}H_{19}) -\angle(C_1\text{-}C_6\text{-}H_{19})$
s_{34}	0.950	$\angle(C_1\text{-}C_7\text{=}O_8) -\angle(O_8\text{=}C_7\text{-}H_{12})$
s_{35}	0.950	$\angle(C_1\text{-}C_7\text{=}O_8) +2\angle(O_8\text{=}C_7\text{-}H_{12}) -\angle(C_1\text{-}C_7\text{-}H_{12})$
s_{36}	0.900	$\angle(C_3\text{-}O_9\text{-}H_{14})$
s_{37}	0.920	$\angle(C_4\text{-}O_{10}\text{-}C_{11})$
s_{38}	0.920	$\tau(C_1\text{-}C_2) -2\tau(C_2\text{-}C_3) +\tau(C_3\text{-}C_4) +\tau(C_4\text{-}C_5) -2\tau(C_5\text{-}C_6) +\tau(C_1\text{-}C_6)$
s_{39}	0.930	$-\tau(C_1\text{-}C_2) +\tau(C_2\text{-}C_3) -\tau(C_3\text{-}C_4) +\tau(C_4\text{-}C_5) -\tau(C_5\text{-}C_6) +\tau(C_1\text{-}C_6)$
s_{40}	0.920	$\tau(C_1\text{-}C_2) -\tau(C_3\text{-}C_4) +\tau(C_4\text{-}C_5) -\tau(C_1\text{-}C_6)$
s_{41}	0.920	$\tau(C_1\text{-}C_7)$
s_{42}	0.920	$\tau(O_{10}\text{-}C_{11})$
s_{43}	0.920	$\tau(C_3\text{-}O_9)$
s_{44}	0.920	$\tau(C_4\text{-}O_{10})$
s_{45}	0.920	$\omega(C_1\text{-}C_2\text{-}C_3\text{-}H_{13})$
s_{46}	0.920	$\omega(C_2\text{-}C_3\text{-}C_4\text{-}O_9)$
s_{47}	0.950	$\omega(C_3\text{-}C_4\text{-}C_5\text{-}O_{10})$

s_{48}	0.920	ω (C_4-C_5-C_6-H_{18})
s_{49}	0.920	ω (C_5-C_6-C_1-H_{19})
s_{50}	0.950	ω (C_6-C_1-C_2-C_7)
s_{51}	0.920	ω (C_1-C_7-H_{12}-O_8)

c) Ethylvanillin

S_i	c_i	Definitions [a]
s_1	0.920	$r(C_1\text{-}C_2) + r(C_1\text{-}C_6)$
s_2	0.920	$r(C_1\text{-}C_2) - r(C_1\text{-}C_6)$
s_3	0.950	$r(C_2\text{-}C_3)$
s_4	0.940	$r(C_5\text{-}C_6)$
s_5	0.950	$r(C_3\text{-}C_4) + r(C_4\text{-}C_5)$
s_6	0.950	$r(C_3\text{-}C_4) - r(C_4\text{-}C_5)$
s_7	0.950	$r(C_1\text{-}C_7)$
s_8	0.850	$r(C_3\text{-}O_9)$
s_9	0.940	$r(O_9\text{-}C_{10})$
s_{10}	0.920	$r(C_{10}\text{-}C_{11})$
s_{11}	0.950	$r(C_4\text{-}O_{12})$
s_{12}	0.900	$r(C_7\text{=}O_8)$
s_{13}	0.920	$r(C_{10}\text{-}H_{15}) + r(C_{10}\text{-}H_{16})$
s_{14}	0.920	$r(C_{10}\text{-}H_{15}) - r(C_{10}\text{-}H_{16})$
s_{15}	0.880	$r(C_{11}\text{-}H_{17}) + r(C_{11}\text{-}H_{18}) + r(C_{11}\text{-}H_{19})$
s_{16}	0.920	$2r(C_{11}\text{-}H_{17}) - r(C_{11}\text{-}H_{18}) - r(C_{11}\text{-}H_{19})$
s_{17}	0.920	$r(C_{11}\text{-}H_{18}) - r(C_{11}\text{-}H_{19})$
s_{18}	0.862	$r(C_2\text{-}H_{14}) + r(C_6\text{-}H_{22})$
s_{19}	0.862	$r(C_2\text{-}H_{14}) - r(C_6\text{-}H_{22})$
s_{20}	0.920	$r(C_7\text{-}H_{13})$
s_{21}	0.940	$r(O_{12}\text{-}H_{20})$
s_{22}	0.920	$r(C_5\text{-}H_{21})$
s_{23}	0.950	$4\angle(C_6\text{-}C_1\text{-}C_2) - 2\angle(C_6\text{-}C_1\text{-}C_7) - 2\angle(C_2\text{-}C_1\text{-}C_7) + 4\angle(C_3\text{-}C_4\text{-}C_5) - 2\angle(C_3\text{-}C_4\text{-}O_{12}) - 2\angle(O_{12}\text{-}C_4\text{-}C_5) - 2\angle(C_1\text{-}C_2\text{-}C_3) + \angle(C_1\text{-}C_2\text{-}H_{14}) + \angle(H_{14}\text{-}C_2\text{-}C_3) - 2\angle(C_2\text{-}C_3\text{-}C_4) + \angle(C_2\text{-}C_3\text{-}O_9) + \angle(C_4\text{-}C_3\text{-}O_9) - 2\angle(C_4\text{-}C_5\text{-}C_6) + \angle(C_4\text{-}C_5\text{-}H_{21}) + \angle(H_{21}\text{-}C_5\text{-}C_6) - 2\angle(C_5\text{-}C_6\text{-}C_1) + \angle(C_5\text{-}C_6\text{-}H_{22}) + \angle(H_{22}\text{-}C_6\text{-}C_1)$
s_{24}	0.920	$-2\angle(C_1\text{-}C_2\text{-}C_3) + \angle(C_1\text{-}C_2\text{-}H_{14}) + \angle(H_{14}\text{-}C_2\text{-}C_3) - 2\angle(C_2\text{-}C_3\text{-}C_4)$

		$-\angle(C_2\text{-}C_3\text{-}O_9) -\angle(C_4\text{-}C_3\text{-}O_9) -2\angle(C_4\text{-}C_5\text{-}C_6) +\angle(C_4\text{-}C_5\text{-}H_{21})$ $+\angle(H_{21}\text{-}C_5\text{-}C_6) + 2\angle(C_5\text{-}C_6\text{-}C_1) -\angle(C_5\text{-}C_6\text{-}H_{22}) -\angle(H_{22}\text{-}C_6\text{-}C_1)$
s_{25}	0.850	$2\angle(C_6\text{-}C_1\text{-}C_2) -\angle(C_6\text{-}C_1\text{-}C_7) -\angle(C_2\text{-}C_1\text{-}C_7) -2\angle(C_3\text{-}C_4\text{-}C_5)$ $+\angle(C_3\text{-}C_4\text{-}O_{12}) +\angle(O_{12}\text{-}C_4\text{-}C_5) -2\angle(C_1\text{-}C_2\text{-}C_3) +\angle(C_1\text{-}C_2\text{-}H_{14})$ $+\angle(H_{14}\text{-}C_2\text{-}C_3) +2\angle(C_2\text{-}C_3\text{-}C_4) -\angle(C_2\text{-}C_3\text{-}O_9) -\angle(C_4\text{-}C_3\text{-}O_9)$ $+2\angle(C_4\text{-}C_5\text{-}C_6) -\angle(C_4\text{-}C_5\text{-}H_{21}) -\angle(H_{21}\text{-}C_5\text{-}C_6) +2\angle(C_5\text{-}C_6\text{-}C_1)$ $+\angle(C_5\text{-}C_6\text{-}H_{22}) +\angle(H_{22}\text{-}C_6\text{-}C_1)$
s_{26}	0.920	$4\angle(H_{15}\text{-}C_{10}\text{-}H_{16}) -\angle(O_9\text{-}C_{10}\text{-}H_{15}) -\angle(O_9\text{-}C_{10}\text{-}H_{16}) -\angle(H_{15}\text{-}C_{10}\text{-}C_{11})$ $-\angle(H_{16}\text{-}C_{10}\text{-}C_{11})$
s_{27}	0.920	$\angle(O_9\text{-}C_{10}\text{-}H_{15}) +\angle(H_{15}\text{-}C_{10}\text{-}C_{11}) -\angle(O_9\text{-}C_{10}\text{-}H_{16}) -\angle(H_{16}\text{-}C_{10}\text{-}C_{11})$
s_{28}	0.920	$\angle(O_9\text{-}C_{10}\text{-}H_{15}) -\angle(H_{15}\text{-}C_{10}\text{-}C_{11}) +\angle(O_9\text{-}C_{10}\text{-}H_{16}) -\angle(H_{16}\text{-}C_{10}\text{-}C_{11})$
s_{29}	0.920	$\angle(O_9\text{-}C_{10}\text{-}H_{15}) -\angle(H_{15}\text{-}C_{10}\text{-}C_{11}) -\angle(O_9\text{-}C_{10}\text{-}H_{16}) +\angle(H_{16}\text{-}C_{10}\text{-}C_{11})$
s_{30}	0.950	$\angle(C_{10}\text{-}C_{11}\text{-}H_{17}) +\angle(C_{10}\text{-}C_{11}\text{-}H_{18}) +\angle(C_{10}\text{-}C_{11}\text{-}H_{19}) -\angle(H_{17}\text{-}C_{11}\text{-}H_{18})$ $-\angle(H_{17}\text{-}C_{11}\text{-}H_{19}) -\angle(H_{18}\text{-}C_{11}\text{-}H_{19})$
s_{31}	0.920	$2\angle(C_{10}\text{-}C_{11}\text{-}H_{17}) -\angle(C_{10}\text{-}C_{11}\text{-}H_{18}) -\angle(C_{10}\text{-}C_{11}\text{-}H_{19})$
s_{32}	0.920	$\angle(C_{10}\text{-}C_{11}\text{-}H_{18}) -\angle(C_{10}\text{-}C_{11}\text{-}H_{19})$
s_{33}	0.920	$-\angle(H_{17}\text{-}C_{11}\text{-}H_{18}) -\angle(H_{17}\text{-}C_{11}\text{-}H_{19}) +2\angle(H_{18}\text{-}C_{11}\text{-}H_{19})$
s_{34}	0.920	$\angle(H_{17}\text{-}C_{11}\text{-}H_{18}) -\angle(H_{17}\text{-}C_{11}\text{-}H_{19})$
s_{35}	0.920	$\angle(C_6\text{-}C_1\text{-}C_7) -\angle(C_2\text{-}C_1\text{-}H_7)$
s_{36}	0.950	$\angle(C_1\text{-}C_2\text{-}H_{14}) -\angle(C_3\text{-}C_2\text{-}H_{14})$
s_{37}	0.920	$\angle(C_2\text{-}C_3\text{-}O_9) -\angle(C_4\text{-}C_3\text{-}O_9)$
s_{38}	0.920	$\angle(C_3\text{-}C_4\text{-}O_{12}) -\angle(C_5\text{-}C_4\text{-}O_{12})$
s_{39}	0.950	$\angle(C_4\text{-}C_5\text{-}H_{21}) -\angle(C_6\text{-}C_5\text{-}H_{21})$
s_{40}	0.890	$\angle(C_5\text{-}C_6\text{-}H_{22}) -\angle(C_1\text{-}C_6\text{-}H_{22})$
s_{41}	0.950	$\angle(C_1\text{-}C_7\text{=}O_8) -\angle(O_8\text{=}C_7\text{-}H_{13})$
s_{42}	0.950	$-\angle(C_1\text{-}C_7\text{=}O_8) +2\angle(O_8\text{=}C_7\text{-}H_{13}) -\angle(C_1\text{-}C_7\text{-}H_{13})$
s_{43}	0.900	$\angle(C_4\text{-}O_{12}\text{-}H_{20})$
s_{44}	0.920	$\angle(C_3\text{-}O_9\text{-}C_{10})$
s_{45}	0.920	$5\angle(O_9\text{-}C_{10}\text{-}C_{11}) -\angle(H_{15}\text{-}C_{10}\text{-}H_{16}) -\angle(O_9\text{-}C_{10}\text{-}H_{15}) -\angle(H_{15}\text{-}C_{10}\text{-}C_{11})$ $-\angle(O_9\text{-}C_{10}\text{-}H_{16}) -\angle(H_{16}\text{-}C_{10}\text{-}C_{11})$

S_{46}	0.920	$\tau(C_1\text{-}C_2) - 2\tau(C_2\text{-}C_3) + \tau(C_3\text{-}C_4) + \tau(C_4\text{-}C_5) - 2\tau(C_5\text{-}C_6) + \tau(C_1\text{-}C_6)$
S_{47}	0.930	$-\tau(C_1\text{-}C_2) + \tau(C_2\text{-}C_3) - \tau(C_3\text{-}C_4) + \tau(C_4\text{-}C_5) - \tau(C_5\text{-}C_6) + \tau(C_1\text{-}C_6)$
S_{48}	0.920	$\tau(C_1\text{-}C_2) - \tau(C_3\text{-}C_4) + \tau(C_4\text{-}C_5) - \tau(C_1\text{-}C_6)$
S_{49}	0.920	$\tau(C_1\text{-}C_7)$
S_{50}	0.920	$\tau(C_3\text{-}O_9)$
S_{51}	0.920	$\tau(O_9\text{-}C_{10})$
S_{52}	0.920	$\tau(C_{10}\text{-}C_{11})$
S_{53}	0.920	$\tau(C_4\text{-}O_{12})$
S_{54}	0.920	$\omega(C_1\text{-}C_2\text{-}C_3\text{-}H_{14})$
S_{55}	0.950	$\omega(C_2\text{-}C_3\text{-}C_4\text{-}O_9)$
S_{56}	0.920	$\omega(C_3\text{-}C_4\text{-}C_5\text{-}O_{12})$
S_{57}	0.920	$\omega(C_4\text{-}C_5\text{-}C_6\text{-}H_{21})$
S_{58}	0.920	$\omega(C_5\text{-}C_6\text{-}C_1\text{-}H_{22})$
S_{59}	0.950	$\omega(C_6\text{-}C_1\text{-}C_2\text{-}C_7)$
S_{60}	0.920	$\omega(C_1\text{-}C_7\text{-}H_{13}\text{-}O_8)$

[a] Normalization factors are omitted. Abbreviations used: *r*, stretching; $\angle$, bending; τ, torsion; ω, out of plane bending. See Fig. 1 for the atom numberings.

Table S3. Observed and calculated vibrational wavenumbers (in cm^{-1}) and assignment of the s-*cis* conformer of vanillin

ν_{obs} [a]	ν_{calc}	PED [b]					
3639	3639	s_{19}(100)					
3075	3086	s_{17}(100)					
	3027	s_{12}(97)					
3013	2997	s_{15}(50)	s_{16}(48)				
2969	2971	s_{14}(100)					
2943	2960	s_{15}(51)	s_{16}(50)				
2847	2845	s_{12}(98)					
	2780	s_{18}(101)					
1698	1700	s_{2}(89)	s_{7}(17)				
1682 [c]							
1608	1606	s_{1} (29)	s_{2} (15)	s_{3} (15)	s_{4} (11)		
1600	1593	s_{1} (34)	s_{2} (23)				
1509	1507	s_{1} (27)	s_{2} (16)	s_{3} (15)	s_{4} (14)	s_{5} (12)	
1466	1459	s_{1} (48)	s_{23}(47)				
1455	1453	s_{1} (41)	s_{3} (39)				
	1440	s_{25}(96)					
1436	1427	s_{1} (18)	s_{2} (14)	s_{3} (13)			
1401	1403	s_{1} (49)	s_{2} (28)	s_{3} (18)	s_{4} (11)		
1379	1370	s_{1} (27)	s_{2} (24)	s_{3} (24)	s_{4} (18)	s_{6} (11)	
1291	1290	s_{1} (33)	s_{2} (19)	s_{4} (16)	s_{5} (14)		
1281 [c]							
1268	1265	s_{2} (35)	s_{3} (18)	s_{4} (11)			
1248 [c]							
1207	1222	s_{1} (19)	s_{4} (17)	s_{6} (15)	s_{7} (13)	s_{8} (13)	s_{9} (10)
1186	1184	s_{3} (32)	s_{5} (13)	s_{6} (12)	s_{8} (11)		
1175	1164	s_{1} (35)	s_{2} (16)	s_{6} (13)			
1149	1140	s_{1} (17)	s_{2} (16)	s_{4} (16)	s_{7} (14)	s_{8} (13)	
1120	1131	s_{25}(93)					
1113	1100	s_{1} (34)	s_{4} (18)	s_{6} (14)	s_{8} (13)		
1034	1022	s_{1} (50)	s_{5} (20)	s_{8} (11)			
	985	s_{39}(88)					
	938	s_{1} (27)	s_{2} (12)	s_{4} (12)			

	905	s_{38}(45)	s_{39}(39)	s_{45}(28)	s_{48}(14)	
872	864	s_{38}(83)	s_{39}(13)			
	798	s_{40}(44)	s_{47}(36)			
	793	s_1 (23)	s_3 (22)	s_4 (16)		
	715	s_1 (29)	s_3 (14)	s_5 (14)	s_6 (13)	
	682	s_{39}(44)	s_{45}(40)	s_{46}(18)		
627	614	s_1 (18)	s_2 (15)	s_3 (10)		
589	576	s_{39}(36)	s_{40}(17)	s_{42}(13)	s_{46}(10)	
	530	s_1 (29)	s_3 (26)	s_5 (20)		
	525	s_1 (28)	s_6 (12)	s_7 (12)		
480	481	s_{44}(96)				
	448	s_{38}(34)	s_{40}(22)	s_{41}(22)		
	404	s_1 (39)	s_3 (14)	s_4 (14)		
	368	s_{38}(14)	s_{39}(13)	s_{41}(12)	s_{42}(11)	s_{43}(11)
	328	s_4 (36)	s_5 (17)	s_7 (14)		
	247	s_{38}(69)	s_{39}(12)	s_{41}(10)		
	239	s_3 (24)	s_{20}(23)	s_{28}(19)	s_{30}(14)	
	199	s_{38}(55)	s_{39}(24)			
	183	s_{38}(28)	s_{39}(25)	s_{40}(20)		
	149	s_1 (46)	s_2 (20)	s_3 (11)		
	101	s_{38}(46)	s_{40}(27)	s_{41}(25)	s_{42}(16)	
	77	s_{40}(121)	s_{41}(40)			

[a] Ref. [15]

[b] Potential energy distribution (%). The values less than 10% are not shown. See Table S2 for the definitions of the coordinates.

[c] Assigned to the s-*trans* conformer.

Table S4. r_a Distances and mean amplitudes of the s-*cis* conformer of vanillin and isovanillin, and the s-*cis*-*trans* conformer of ethylvanillin (in Å)

a) Vanillin (s-*cis*)

atom pair [a]	r_a	l_{calc}	l_{obs} [b]	group
C_1–C_2	1.403	0.047	0.050 (2)	1
C_1···C_3	2.395	0.057	0.056 (4)	2
C_1···C_4	2.779	0.063	0.069 (9)	3
C_1···C_5	2.410	0.057	0.055	2
C_1–C_6	1.394	0.046	0.050	1
C_1–C_7	1.469	0.050	0.053	1
C_1···O_8	2.313	0.060	0.058	2
C_1···O_9	3.697	0.064	0.077 (11)	4
C_1···C_{10}	4.318	0.108	0.117 (16)	5
C_1···O_{11}	4.132	0.066	0.076	5
C_2–C_3	1.383	0.045	0.049	1
C_2···C_4	2.428	0.058	0.056	2
C_2···C_5	2.803	0.065	0.071	3
C_2···C_6	2.428	0.058	0.056	2
C_2···C_7	2.517	0.070	0.068	2
C_2···O_8	2.817	0.111	0.117	3
C_2···O_9	2.462	0.061	0.059	2
C_2···C_{10}	2.935	0.106	0.112	3
C_2···O_{11}	3.650	0.063	0.076	4
C_2–H_{13}	1.096	0.078	0.081	1
C_3–C_4	1.411	0.047	0.050	1
C_3···C_5	2.416	0.058	0.056	2
C_3···C_6	2.777	0.064	0.070	3
C_3···C_7	3.757	0.069	0.082	4
C_3···O_8	4.184	0.112	0.121	5
C_3–O_9	1.372	0.048	0.051	1
C_3···C_{10}	2.419	0.069	0.067	2
C_3···O_{11}	2.386	0.062	0.060	2
C_4–C_5	1.388	0.046	0.049	1
C_4···C_6	2.405	0.057	0.055	2
C_4···C_7	4.238	0.070	0.080	5

$C_4 \cdots O_8$	4.970	0.091	0.150 (53)	6
$C_4 \cdots O_9$	2.308	0.062	0.060	2
$C_4 \cdots C_{10}$	3.618	0.069	0.083	4
$C_4 – O_{11}$	1.359	0.045	0.048	1
$C_5 – C_6$	1.392	0.046	0.049	1
$C_5 \cdots C_7$	3.718	0.069	0.082	4
$C_5 \cdots O_8$	4.700	0.070	0.128	6
$C_5 \cdots O_9$	3.595	0.065	0.078	4
$C_5 \cdots C_{10}$	4.800	0.077	0.135	6
$C_5 \cdots O_{11}$	2.392	0.063	0.061	2
$C_5 – H_{18}$	1.097	0.077	0.080	1
$C_6 \cdots C_7$	2.432	0.070	0.068	2
$C_6 \cdots O_8$	3.523	0.066	0.079	4
$C_6 \cdots O_9$	4.135	0.068	0.078	5
$C_6 \cdots C_{10}$	5.082	0.094	0.153	6
$C_6 \cdots O_{11}$	3.651	0.064	0.077	4
$C_6 – H_{19}$	1.099	0.078	0.082	1
$C_7 = O_8$	1.212	0.038	0.042	1
$C_7 \cdots O_9$	4.964	0.082	0.140	6
$C_7 \cdots C_{10}$	5.329	0.141	0.199	6
$C_7 \cdots O_{11}$	5.589	0.074	0.132	6
$C_7 – H_{12}$	1.121	0.081	0.084	1
$O_8 \cdots O_9$	5.188	0.140	0.198	6
$O_8 \cdots C_{10}$	5.241	0.202	0.261	6
$O_8 \cdots O_{11}$	6.295	0.098	0.156	6
$O_9 – C_{10}$	1.426	0.049	0.053	1
$O_9 \cdots O_{11}$	2.589	0.100	0.106	3
$C_{10} \cdots O_{11}$	3.964	0.108	0.117	5
$C_{10} – H_{14}$	1.100	0.078	0.081	1
$C_{10} – H_{15,\ 16}$	1.106	0.079	0.082	1
$O_{11} – H_{17}$	0.985	0.070	0.073	1

b) Isovanillin (s-*cis*)

atom pair [a]	r_a	l_{calc}	l_{obs} [b]	group
C_1–C_2	1.405	0.047	0.045 (2)	1
C_1···C_3	2.401	0.058	0.051 (9)	2
C_1···C_4	2.813	0.065	0.070 (11)	3
C_1···C_5	2.419	0.058	0.052	2
C_1–C_6	1.399	0.047	0.044	1
C_1–C_7	1.477	0.051	0.049	1
C_1···O_8	2.347	0.062	0.055	2
C_1···O_9	3.614	0.066	0.083 (11)	4
C_1···O_{10}	4.168	0.070	0.070	
C_1···C_{11}	5.137	0.098	0.098	
C_2–C_3	1.387	0.045	0.043	1
C_2···C_4	2.449	0.058	0.052	2
C_2···C_5	2.799	0.067	0.072	3
C_2···C_6	2.428	0.059	0.052	2
C_2···C_7	2.546	0.072	0.066	2
C_2···O_8	2.900	0.119	0.124	3
C_2···O_9	2.333	0.064	0.058	2
C_2···O_{10}	3.632	0.066	0.083	4
C_2···C_{11}	4.846	0.079	0.079	
C_2–H_{13}	1.103	0.078	0.076	1
C_3–C_4	1.416	0.047	0.045	1
C_3···C_5	2.404	0.059	0.052	2
C_3···C_6	2.775	0.065	0.070	3
C_3···C_7	3.783	0.071	0.088	4
C_3···O_8	4.267	0.119	0.119	
C_3–O_9	1.356	0.046	0.043	1
C_3···O_{10}	2.339	0.063	0.057	2
C_3···C_{11}	3.647	0.072	0.089	4
C_4–C_5	1.396	0.046	0.044	1
C_4···C_6	2.431	0.058	0.052	2
C_4···C_7	4.277	0.073	0.073	
C_4···O_8	5.054	0.097	0.097	
C_4···O_9	2.412	0.064	0.057	2

C_4–O_{10}	1.367	0.048	0.046	1
C_4···C_{11}	2.437	0.071	0.064	2
C_5–C_6	1.400	0.046	0.044	1
C_5···C_7	3.721	0.072	0.089	4
C_5···O_8	4.734	0.073	0.073	
C_5···O_9	3.652	0.065	0.083	4
C_5···O_{10}	2.477	0.063	0.056	2
C_5···C_{11}	3.002	0.110	0.115	3
C_5–H_{18}	1.101	0.077	0.075	1
C_6···C_7	2.424	0.073	0.067	2
C_6···O_8	3.537	0.068	0.085	4
C_6···O_9	4.124	0.069	0.069	
C_6···O_{10}	3.725	0.065	0.083	4
C_6···C_{11}	4.380	0.112	0.112	
C_6–H_{19}	1.105	0.078	0.076	1
C_7=O_8	1.219	0.038	0.036	1
C_7···O_9	4.869	0.088	0.088	
C_7···O_{10}	5.631	0.077	0.077	
C_7···C_{11}	6.559	0.107	0.107	
C_7–H_{12}	1.128	0.081	0.079	1
O_8···O_9	5.115	0.154	0.154	
O_8···O_{10}	6.366	0.107	0.107	
O_8···C_{11}	7.418	0.112	0.112	
O_9···O_{10}	2.683	0.105	0.110	3
O_9···C_{11}	4.046	0.113	0.113	
O_9–H_{14}	0.990	0.070	0.068	1
O_{10}–C_{11}	1.420	0.050	0.048	1
C_{11}–H_{15}	1.106	0.078	0.076	1
C_{11}–$H_{16,\ 17}$	1.111	0.079	0.077	1

c) Ethylvanillin (s-*cis*-*trans*)

atom pair [a]	r_a	l_{calc}	l_{obs} [b]	group
C_1–C_2	1.403	0.047	0.051 (3)	1
C_1···C_3	2.389	0.058	0.058 (5)	2
C_1···C_4	2.808	0.064	0.068 (11)	3
C_1···C_5	2.403	0.058	0.058	2
C_1–C_6	1.394	0.047	0.050	1
C_1–C_7	1.469	0.050	0.054	1
C_1···O_8	2.403	0.060	0.060	2
C_1···O_9	3.668	0.065	0.076 (15)	4
C_1···C_{10}	4.115	0.110	0.110	
C_1···C_{11}	5.529	0.103	0.103	
C_1···O_{12}	4.152	0.067	0.067	
C_2–C_3	1.384	0.045	0.049	1
C_2···C_4	2.450	0.058	0.058	2
C_2···C_5	2.787	0.066	0.070	3
C_2···C_6	2.426	0.058	0.058	2
C_2···C_7	2.504	0.071	0.071	2
C_2···O_8	2.955	0.114	0.118	3
C_2···O_9	2.425	0.061	0.061	2
C_2···C_{10}	2.730	0.108	0.112	3
C_2···C_{11}	4.160	0.105	0.105	
C_2···O_{12}	3.659	0.064	0.075	4
C_2–H_{14}	1.095	0.078	0.081	1
C_3–C_4	1.411	0.047	0.051	1
C_3···C_5	2.384	0.058	0.058	2
C_3···C_6	2.763	0.065	0.069	3
C_3···C_7	3.746	0.070	0.082	4
C_3···O_8	4.319	0.115	0.115	
C_3–O_9	1.363	0.048	0.052	1
C_3···C_{10}	2.322	0.071	0.071	2
C_3···C_{11}	3.510	0.077	0.089	4
C_3···O_{12}	2.383	0.062	0.062	2
C_4–C_5	1.388	0.046	0.049	1
C_4···C_6	2.428	0.057	0.057	2

$C_4 \cdots C_7$	4.268	0.071	0.071	
$C_4 \cdots O_8$	5.111	0.093	0.093	
$C_4 \cdots O_9$	2.311	0.062	0.062	2
$C_4 \cdots C_{10}$	3.561	0.071	0.083	4
$C_4 \cdots C_{11}$	4.505	0.101	0.101	
$C_4 – O_{12}$	1.350	0.045	0.049	1
$C_5 – C_6$	1.392	0.046	0.049	1
$C_5 \cdots C_7$	3.725	0.070	0.082	4
$C_5 \cdots O_8$	4.775	0.071	0.071	
$C_5 \cdots O_9$	3.574	0.065	0.077	4
$C_5 \cdots C_{10}$	4.679	0.079	0.079	
$C_5 \cdots C_{11}$	5.770	0.094	0.094	
$C_5 \cdots O_{12}$	2.410	0.063	0.063	2
$C_5 – H_{21}$	1.096	0.077	0.080	1
$C_6 \cdots C_7$	2.448	0.071	0.071	2
$C_6 \cdots O_8$	3.583	0.067	0.078	4
$C_6 \cdots O_9$	4.116	0.069	0.069	
$C_6 \cdots C_{10}$	4.918	0.096	0.096	
$C_6 \cdots C_{11}$	6.214	0.091	0.091	
$C_6 \cdots O_{12}$	3.675	0.065	0.076	4
$C_6 – H_{22}$	1.098	0.078	0.082	1
$C_7 = O_8$	1.204	0.038	0.042	1
$C_7 \cdots O_9$	4.917	0.084	0.084	
$C_7 \cdots C_{10}$	5.079	0.145	0.145	
$C_7 \cdots C_{11}$	6.532	0.148	0.148	
$C_7 \cdots O_{12}$	5.609	0.075	0.075	
$C_7 – H_{13}$	1.120	0.081	0.084	1
$O_8 \cdots O_9$	5.293	0.144	0.144	
$O_8 \cdots C_{10}$	5.147	0.208	0.208	
$O_8 \cdots C_{11}$	6.580	0.226	0.226	
$O_8 \cdots O_{12}$	6.428	0.100	0.100	
$O_9 – C_{10}$	1.425	0.051	0.054	1
$O_9 \cdots C_{11}$	2.266	0.077	0.077	2
$O_9 \cdots O_{12}$	2.606	0.102	0.106	3
$C_{10} – C_{11}$	1.492	0.052	0.056	1
$C_{10} \cdots O_{12}$	3.978	0.110	0.110	

C_{10}–$H_{15,\ 16}$	1.107	0.079	0.082	1
$C_{11}\cdots O_{12}$	4.520	0.168	0.168	
C_{11}–H_{17}	1.103	0.078	0.082	1
C_{11}–$H_{18,\ 19}$	1.102	0.078	0.082	1
O_{12}–H_{20}	0.984	0.070	0.073	1

[a] See Fig. 1 for the atom numberings. Non-bonded C···H, O···H and H···H pairs are not listed although they were included in the data analysis.

[b] Numbers in parentheses are estimated error limits (3σ) referring to the last significant digit.

Table S5. The correlation matrices for vanillin, isovanillin and ethylvanillin [a]

a) Vanillin

	k	r_1	r_2	r_3	r_4	θ_1	θ_2	θ_3	θ_4	θ_5
k	1.00									
r_1	0.48	1.00								
r_2	-0.53	-0.94	1.00							
r_3	-0.65	-0.33	0.47	1.00						
r_4	-0.53	-0.34	0.43	0.56	1.00					
θ_1	0.16	0.50	-0.39	-0.07	-0.15	1.00				
θ_2	0.32	0.34	-0.33	-0.20	-0.22	-0.11	1.00			
θ_3	-0.10	-0.27	0.22	-0.03	0.22	-0.15	-0.46	1.00		
θ_4	0.58	0.71	-0.71	-0.37	-0.23	0.29	0.24	-0.02	1.00	
θ_5	0.51	0.36	-0.44	-0.36	-0.17	0.15	0.39	-0.04	0.72	1.00
l_1	0.60	-0.18	0.11	-0.57	-0.34	-0.14	0.08	0.09	0.06	0.20
l_2	0.30	-0.05	-0.02	-0.14	0.03	-0.41	-0.16	0.61	0.39	0.23
l_3	-0.04	-0.01	0.02	0.04	0.03	-0.20	-0.32	0.16	0.07	-0.21
l_4	-0.00	-0.01	0.04	0.02	-0.00	0.13	-0.17	0.04	0.02	-0.10
l_5	0.31	0.12	-0.13	-0.12	0.01	0.04	-0.11	0.34	0.50	0.41
l_6	-0.03	-0.01	0.02	0.04	0.01	-0.06	-0.27	0.08	-0.03	-0.24

	l_1	l_2	l_3	l_4	l_5	l_6
l_1	1.00					
l_2	0.26	1.00				
l_3	-0.04	0.36	1.00			
l_4	0.01	0.01	0.07	1.00		
l_5	0.17	0.49	0.10	0.08	1.00	
l_6	-0.03	0.12	0.19	-0.02	0.04	1.00

b) Isovanillin

	k	r_1	r_2	r_3	r_4	θ_1	θ_2	θ_3	θ_4	θ_5
k	1.00									
r_1	0.37	1.00								
r_2	-0.43	-0.93	1.00							
r_3	-0.64	-0.30	0.46	1.00						
r_4	-0.54	-0.36	0.46	0.60	1.00					
θ_1	0.16	0.07	-0.12	-0.16	-0.07	1.00				
θ_2	0.44	0.59	-0.54	-0.28	-0.28	0.16	1.00			
θ_3	0.23	-0.17	0.05	-0.25	-0.01	0.21	0.18	1.00		
θ_4	0.17	-0.02	-0.01	-0.09	-0.10	-0.21	0.52	0.19	1.00	
θ_5	0.25	-0.04	-0.08	-0.23	-0.11	0.28	0.42	0.14	0.43	1.00
l_1	0.48	-0.45	0.38	-0.43	-0.21	0.07	-0.10	0.31	0.13	0.19
l_2	0.32	-0.09	0.01	-0.20	-0.08	0.79	0.25	0.65	0.13	0.28
l_3	-0.17	-0.46	0.42	0.13	0.13	0.01	-0.21	0.06	0.32	0.04
l_4	0.21	-0.17	0.12	-0.09	-0.01	0.36	0.14	0.41	0.23	0.24

	l_1	l_2	l_3	l_4
l_1	1.00			
l_2	0.29	1.00		
l_3	0.20	0.15	1.00	
l_4	0.27	0.53	0.16	1.00

c) Ethylvanillin

	k	c	r_1	r_2	r_3	r_4	r_5	θ_1	θ_2	θ_3
k	1.00									
c	-0.07	1.00								
r_1	0.56	-0.06	1.00							
r_2	-0.56	0.10	-0.96	1.00						
r_3	0.34	0.06	0.46	-0.36	1.00					
r_4	-0.43	0.05	-0.20	0.32	0.30	1.00				
r_5	-0.53	0.04	-0.44	0.50	-0.10	0.46	1.00			
θ_1	0.06	0.05	-0.04	0.08	0.08	0.06	0.02	1.00		
θ_2	0.26	-0.29	0.53	-0.45	0.32	0.09	-0.17	-0.06	1.00	
θ_3	0.13	0.09	-0.37	0.31	-0.16	-0.25	0.07	0.36	-0.32	1.00
θ_4	0.61	0.15	0.72	-0.67	0.44	-0.17	-0.30	0.15	0.23	0.16
θ_5	0.39	0.42	0.40	-0.41	0.25	-0.15	-0.15	-0.12	0.04	0.14
θ_6	-0.17	0.27	0.07	-0.11	-0.24	-0.06	0.04	0.09	0.02	-0.16
l_1	-0.01	0.05	-0.63	0.59	-0.67	-0.40	0.04	0.03	-0.42	0.45
l_2	0.41	0.16	0.06	-0.02	0.21	-0.05	-0.03	0.52	-0.08	0.51
l_3	0.13	0.17	0.11	-0.07	0.11	0.02	-0.03	0.30	-0.14	0.12
l_4	0.29	0.38	0.00	0.03	0.19	-0.01	0.01	0.37	-0.25	0.50

	θ_4	θ_5	θ_6	l_1	l_2	l_3	l_4
θ_4	1.00						
θ_5	0.67	1.00					
θ_6	-0.03	-0.03	1.00				
l_1	-0.39	-0.19	-0.02	1.00			
l_2	0.58	0.49	0.10	0.08	1.00		
l_3	0.36	0.25	0.01	-0.05	0.45	1.00	
l_4	0.52	0.49	-0.01	0.08	0.69	0.34	1.00

[a] See Tables 5 to 7 for the definitions of the structural parameters. k is the index of resolution. C is the abundance of the (s-*cis*-*trans* + s-*trans*-*trans*) conformers of ethylvanillin. l_1 to l_6 are the mean amplitudes for the groups 1 to 6, respectively (see Table S4).