

Supplementary Material

Table S1: Positions of Infrared Absorptions and Raman Scattering of Single Crystals of 4-Bromo-*Trans*-Cinnamic Acid Before and After Exposure to 165 Torr Pressure of Bromine Vapour for 1 Week.

Assignment	Infrared: 4-Bromo- <i>Trans</i> -Cinnamic Acid /cm ⁻¹	Infrared: 4-Bromo- <i>Trans</i> -Cinnamic Acid After Exposure to Bromine Vapour /cm ⁻¹	Raman: 4-Bromo- <i>Trans</i> -Cinnamic Acid /cm ⁻¹	Raman: 4-Bromo- <i>Trans</i> -Cinnamic Acid After Exposure to Bromine Vapour /cm ⁻¹
v(C-H) unsaturated (aliphatic and aromatic)	3038 br	3001 br		
v(C=O) (carboxyl)	1688 br	1725 vs		
v(C=C) (aliphatic)	1627		1652 vs	
v(C=C) (aromatic)		1596 vs,	1595 vs	1598 vs
C-H deformation (unsaturated) ^a	1510 s, 1428 s	1493 vs, 1430 vs	1458 br, 1413	1499 w, 1444 w, 1418
v(C-O) (carboxyl) ^a	1288, 1236	1270, 1215	1300, 1220	1369, 1223 s
δ(C-H) (aliphatic and aromatic) ^a	1161 s, 1094, 1013, 981, 932, 873, 825	1178, 1143 s, 1110 s, 1095, 1015 s, 906, 831 s	1188 s, 1080	1184, 1165, 1150, 1118, 1074 s, 1018, 948, 848, 833
Ring Vibration (aromatic) ^a	786, 739, 690, 639	722, 708 s	706 w, 631 w	791, 725, 695, 632 vs, 583, 519, 491, 387, 319
v(C-Br) _a		654		659 vs

a – Bands in this spectral region are difficult to assign with certainty because of coupling of vibrations and overlap of bands.

Table S2: Positions of Infrared Absorptions and Raman Scattering of Single Crystals of 4-Chloro-*Trans*-Cinnamic Acid Before and After Exposure to 165 Torr Pressure of Bromine Vapour for 1 Week.

Assignment	Infrared: 4-Chloro- <i>Trans</i> -Cinnamic Acid /cm ⁻¹	Infrared: 4-Chloro- <i>Trans</i> -Cinnamic Acid After Exposure to Bromine Vapour /cm ⁻¹	Raman: 4-Chloro- <i>Trans</i> -Cinnamic Acid /cm ⁻¹	Raman: 4-Chloro- <i>Trans</i> -Cinnamic Acid After Exposure to Bromine Vapour /cm ⁻¹
v(C-H) unsaturated (aliphatic and aromatic)	2963 br	3001 br		
v(C=O) (carboxyl)	1700 br	1725 vs		
v(C=C) (aliphatic)	1630 br		1640 vs	
v(C=C) (aromatic)	1571,	1596 vs,	1586 vs	1604 vs
C-H deformation (unsaturated) ^a	1490 s, 1406	1493 vs, 1430 vs	1444	
v(C-O) (carboxyl) ^a	1207 s	1270, 1215	1399, 1286, 1255, 1205	1225 s
δ(C-H) (aliphatic and aromatic) ^a	1176 s, 1088 s, 1012, 828	1178, 1143 s, 1110 s, 1095, 1015 s, 906, 831 s	1169 s, 1082	1099, 1079
Ring Vibration (aromatic) ^a	736, 717, 657, 635	722, 708 s	699, 627 w	792, 729, 589, 207
v(C-Br) ^a		646		659 vs

a – Bands in this spectral region are difficult to assign with certainty because of coupling of vibrations and overlap of bands.

Table S3: Positions of Infrared Absorptions and Raman Scattering of Single Crystals of 4-Fluoro-*Trans*-Cinnamic Acid Before and After Exposure to 165 Torr Pressure of Bromine Vapour for 1 Week.

Assignment	Infrared: 4-Fluoro- <i>Trans</i> -Cinnamic Acid /cm ⁻¹	Infrared: 4-Fluoro- <i>Trans</i> -Cinnamic Acid After Exposure to Bromine Vapour /cm ⁻¹	Raman: 4-Fluoro- <i>Trans</i> -Cinnamic Acid /cm ⁻¹	Raman: 4-Fluoro- <i>Trans</i> -Cinnamic Acid After Exposure to Bromine Vapour /cm ⁻¹
v(C-H) unsaturated (aliphatic and aromatic)	3038 br	3013		
v(C=O) (carboxyl)	1680 br	1721 vs		
v(C=C) (aliphatic)	1650		1663 s	
v(C=C) (aromatic)			1611 vs	1625 s
C-H deformation (unsaturated) ^a	1510 s, 1428 s	1511 s, 1436 s	1518, 1460, 1422	
v(C-O) (carboxyl) ^a	1288, 1236	1310 s, 1282, 1224	1309, 1228, 1205	1296, 1245 s
δ(C-H) (aliphatic and aromatic) ^a	1161 s, 1094, 1013, 981, 932, 873, 825	1160 s, 1106 s, 1014, 905, 841 s	1167, 872	1171, 1114, 1076, 1044, 950 br, 866
Ring Vibration (aromatic) ^a	786, 739, 690, 639	773 s, 729, 685, 633	795, 750, 646, 381, 223.	787, 750, 612, 588, 561, 466, 293, 213
v(C-Br) ^a		665		668 vs

a – Bands in this spectral region are difficult to assign with certainty because of coupling of vibrations and overlap of bands.

Table S4: Positions of Infrared Absorptions and Raman Scattering of Single Crystals of 2-Fluoro-*Trans*-Cinnamic Acid Before and After Exposure to 165 Torr Pressure of Bromine Vapour for 1 Week.

Assignment	Infrared: 2-Fluoro- <i>Trans</i> -Cinnamic Acid /cm ⁻¹	Infrared: 2-Fluoro- <i>Trans</i> -Cinnamic Acid After Exposure to Bromine Vapour /cm ⁻¹	Raman: 2-Fluoro- <i>Trans</i> -Cinnamic Acid /cm ⁻¹	Raman: 2-Fluoro- <i>Trans</i> -Cinnamic Acid After Exposure to Bromine Vapour /cm ⁻¹
v(C-H) unsaturated (aliphatic and aromatic)	2980 br	2979 br		
v(C=O) (carboxyl)	1679	1723 br		
v(C=C) (aliphatic)	1652		1652 s	
v(C=C) (aromatic)	1583,	1589	1624 s	1626 s
C-H deformation (unsaturated) ^a	1486 s, 1456 s, 1430	1469	1462	1506
v(C-O) (carboxyl) ^a	1290, 1229, 1208	1370, 1271 br	1295, 1239	1295, 1245 s, 1202
δ(C-H) (aliphatic and aromatic) ^a	1187, 1145, 1093 vs, 1033 s, 988, 932, 877	1148, 1105 s, 1064, 1031 s, 915	1042, 889 w, 804	1170, 1115, 1075, 1044, 950, 866
Ring Vibration (aromatic) ^a	797 s, 759, 695	798, 759, 738, 687	687 w, 570, 506, 309 w, 243	787, 748, 612, 587, 561, 466, 291, 211
v(C-Br) ^a		661		668 vs

a – Bands in this spectral region are difficult to assign with certainty because of coupling of vibrations and overlap of bands.

Table S5: Positions of Infrared Absorptions and Raman Scattering of Single Crystals of 3-Fluoro-*Trans*-Cinnamic Acid Before and After Exposure to 165 Torr Pressure of Bromine Vapour for 1 Week.

Assignment	Infrared: 3-Fluoro- <i>Trans</i> -Cinnamic Acid /cm ⁻¹	Infrared: 3-Fluoro- <i>Trans</i> -Cinnamic Acid After Exposure to Bromine Vapour /cm ⁻¹	Raman: 3-Fluoro- <i>Trans</i> -Cinnamic Acid /cm ⁻¹	Raman: 3-Fluoro- <i>Trans</i> -Cinnamic Acid After Exposure to Bromine Vapour /cm ⁻¹
v(C-H) unsaturated (aliphatic and aromatic)	2974 br	3004		
v(C=O) (carboxyl)	1684	1722 vs		
v(C=C) (aliphatic)	1658		1654 vs	
v(C=C) (aromatic)		1592 vs	1602 s	1622
C-H deformation (unsaturated) ^a	1491, 1442 s, 1419	1490 vs, 1433		
v(C-O) (carboxyl) ^a	1295	1258	1299, 1274, 1215	1265
δ(C-H) (aliphatic and aromatic) ^a	1142 s, 1079, 986, 861 s	1177, 1146 s, 1074, 921, 871	1182, 1002	1012
Ring Vibration (aromatic) ^a	783 s, 732 s, 697 s, 667	796 s, 766, 730, 615 vs	897 w	797, 770, 708, 587, 281
v(C-Br) ^a		699 vs		690

a – Bands in this spectral region are difficult to assign with certainty because of coupling of vibrations and overlap of bands.

Table S6: ^1H NMR Peak Positions Derivatives of *Trans*-Cinnamic Acid and Their Reaction Products with Bromine Vapour

4-Bromo-*Trans*-Cinnamic Acid δ_{H} (DMSO) 6.57 (d, 2H), 7.61 (m, 5H).

4-Bromo-*Trans*-Cinnamic Acid After Exposure to Bromine Vapour δ_{H} (DMSO) 5.34 (d, 1H), 5.58 (d, 1H), 7.61 (m, 5H).

4-Chloro-*Trans*-Cinnamic Acid δ_{H} (DMSO) 6.56 (d, 2H), 7.46, 7.55, 7.72 (m, 5H).

4-Chloro-*Trans*-Cinnamic Acid After Exposure to Bromine Vapour δ_{H} (DMSO) 5.35 (d, 1H), 5.59 (d, 1H), 7.46, 7.70 (m, 5H).

4-Fluoro-*Trans*-Cinnamic Acid δ_{H} (DMSO) 6.50 (d, 2H), 7.29, 7.58, 7.76 (m, 5H).

4-Fluoro-*Trans*-Cinnamic Acid After Exposure to Bromine Vapour δ_{H} (DMSO) 5.35 (d, 1H), 5.60 (d, 1H), 7.22, 7.73 (m, 5H).

2-Fluoro-*Trans*-Cinnamic Acid δ_{H} (DMSO) 6.61 (d, 2H), 7.33, 7.47, 7.62, 7.84 (m, 5H).

2-Fluoro-*Trans*-Cinnamic Acid After Exposure to Bromine Vapour δ_{H} (DMSO) 5.32 (d, 1H), 5.62 (d, 1H), 7.28, 7.63 (m, 5H).

3-Fluoro-*Trans*-Cinnamic Acid δ_{H} (DMSO) 6.61 (d, 2H), 7.24, 7.47, 7.59 (m, 5H).

3-Fluoro-*Trans*-Cinnamic Acid After Exposure to Bromine Vapour δ_{H} (DMSO) 5.33 (d, 1H), 5.56 (d, 1H), 7.21, 7.59 (m, 5H).