SUPPORTING INFORMATION

Photoisomerization of Ionic Liquid Ammonium Cinnamates: One-Pot Synthesis-Isolation of *Z*-Cinnamic Acids

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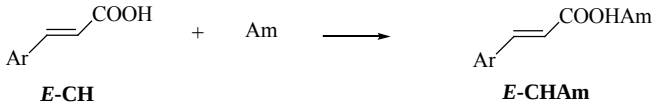
Scheme S1. Ionic liquids of *E*-cinnamic acids (*E*-CHAm)



***E*-CH** ***E*-CHAm**

ent.	amine (Am)	*E*-**1**	*E*-**2**	*E*-**3**	*E*-**4**	*E*-**5**
1	**a**	*E*-**1a**	*E*-**2a**	*E*-**3a**	*E*-**4a**	*E*-**5a**
2	**b**	*E*-**1b**	*E*-**2b**	*E*-**3b**	*E*-**4b**	*E*-**5b**
3	**c**	*E*-**1c**	*E*-**2c**	*E*-**3c**	*E*-**4c**	*E*-**5c**
4	**d**	*E*-**1d**	*E*-**2d**	*E*-**3d**	*E*-**4d**	*E*-**5d**
5	**e**	*E*-**1e**	*E*-**2e**	*E*-**3e**	*E*-**4e**	*E*-**5e**
6	**f**	*E*-**1f**	*E*-**2f**	*E*-**3f**	*E*-**4f**	*E*-**5f**
7	**g**	*E*-**1g**	*E*-**2g**	*E*-**3g**	*E*-**4g**	*E*-**5g**
8	**h**	*E*-**1h**	*E*-**2h**	*E*-**3h**	*E*-**4h**	*E*-**5h**
9	**i**	*E*-**1i**	*E*-**2i**	*E*-**3i**	*E*-**4i**	*E*-**5i**

Table S1. Results obtained by UV-irradiation of of *E*-cinnamic acids (*E*-CH) in MeCN solution . Substrate scope.

entry	*E*-cinnamic acids	products in solution yield [%] [a]	
		E-CH	Z-CH
1	*E*-**1**	67	33
2	*E*-**2**	53	47
3	*E*-**3**	79	21
4	*E*-**4**	92	8
5	*E*-**5**	59	41

[a] Determined by ^{1}H NMR spectroscopic analysis of the irradiated solution.

Table S2. Results obtained by UV-irradiation of ionic liquids of *E*-cinnamic acids (*E*-CHAm) in MeCN. Composition of the liquid fase obtained..

entry	ionic liquid	products in solution yield [%][a]		
		E-CHAm[a]	Z-CHAm[a]	aryl-alkene[a]
1	*E*-**1a**	57	37	6
2	*E*-**1b**	73	21	6
3	*E*-**1c**	55	45	-
4	*E*-**1c**	93	7	-
5	*E*-**1d**	66	34	-
6	*E*-**1f**	68	26	6
7	*E*-**1i**	60	35	5
8	*E*-**2a**	44	51	5
9	*E*-**2b**	63	34	3
10	*E*-**2b**	45	50	5
11	*E*-**2c**	78	15	7
12	*E*-**2c**	75	25	-

13	*E*-**2d**	50	46	4	
14	*E*-**2f**	29	67	4	
15	*E*-**2i**	50	46	4	
16	*E*-**3a**	57	36	7	
17	*E*-**3b**	69	31	-	
18	*E*-**3c**	21	79	-	
19	*E*-**3f**	40	60	-	
20	*E*-**4a**	93	7	-	
21	*E*-**4b**	86	14	-	
22	*E*-**4c**	94	6	-	
23	*E*-**4f**	97	3	-	
24	*E*-**5a**	58	42		-

a Determined by ^{1}H NMR spectroscopic analysis of the irradiated solution.

EXPERIMENTAL

Materials. *trans*-4-Hydroxy-3-methoxycinnamic acid (*trans*-ferulic acid; *E*-**1**), *trans*-4-hydroxy-3,5-dimethoxycinnamic acid (*trans*-sinapinic acid; *E*-**2**), *trans*-4-hydroxycinnamic acid (*trans-p*-coumaric acid; *E*-**3**) and *trans*-3,4-(methylenedioxy)cinnamic acid (*E*-**5**), were purchased from Aldrich, *trans*-cinnamic acid (*E*-**4**) was purchased from Fluka (all of them predominantly trans (*E*) 99%). Butylamine (**a**), 4-amino-1-butanol (**b**), ethanolamine (**c**), 2-phenylethylamine (**d**), diethylamine (**e**), piperidine (**f**), triethylamine (**g**), tributylamine (**h**) and n-methylpiperidine (**i**), were purchased from Aldrich. All of these chemicals were used without further purification. All organic solvents were of analytical or HPLC grade.

Instrumentation

Melting points. They were determined on a *Fisher Jones* apparatus and were not corrected.

UV/VIS Analysis. Electronic absorption spectra were recorded on a Shimadzu PC2101 spectrophotometer. Measurements were made in quartz cells of 1 cm optical-path length. The absorption spectra were recorded in MeOH or MeCN solutions at 298 K. Wavelength maxima are reported in nm.

Electron Impact Mass Spectra (EI MS). EI MS analysis were recorded on a Shimadzu QP-5000 mass spectrometer.

High Resolution Mass Spectrometry (HRMS). HRMS analysis were conducted on a micrOTOF- Q II mass spectrometer (Bruker GmbH) equipped with ESI ion source. Direct sample injection of a MeOH – $AcONH_4$ solution in negative ion mode was used. MS^2 (MS/MS) experiments were also conducted.

NMR analysis. The ^{1}H NMR spectral was recorded at 200 MHz on a Bruker AC-200 spectrometer in DMSO solution. ^{1}H and ^{13}C NMR mono- and bidimensional spectra were carried out on a Bruker AVANCE II 500 NMR spectrometer operating at 500.14 and 125.76 MHz for ^{1}H and ^{13}C, using DMSO as solvent. Tetramethyl silane was used as the internal standard. ^{1}H-^{13}C heteronuclear chemical shift correlation spectrum (HSQC) was recoded using the standard pulse sequence. A total of 32 scans were accumulated with a relaxation delay of 2 s for each of the 512 t1 experiments. Chemical shift values are reported in ppm and the coupling constants are give in Hertz.

Molecular Modeling. The ground state geometry of *Z*- and *E*-cinnamic acids and amines (Am) were fully optimized without imposing any symmetry constraints by *ab initio* and semiempirical methods. For *ab initio* DFT calculations, we used the hybrid gradient-corrected exchange functional combined with the gradient-corrected correlation functional, commonly known as B3LYP which has been shown to be quite reliable for geometries. For geometries optimization the standardized 3-21G basis set was used. We denote our B3LYP calculations by B3LYP/3-21G. For single point calculations the standarized 6-31G(d) basis set was used at B3LYP theory level (B3LYP/6-31G(d)//B3LYP/3-21G. All the a*b initio* calculations were carried out, using Gaussian 98W program.[1]

The ground-state geometry of ILs were calculated by using the semiempirical parametrized PM3 method as implemented in version of the HyperChem 7.01 for Windows program[1] (Restricted Hartree-Fock (RHF) formalism; total charge: 0; spin multiplicity: 1; convergence limit: 1e-008; iteration limit: 50; accelerate convergence: on; CI method: none; Polak-Ribiere algorithm; RMS gradient: 0.006 kcal/(Å mol); in vacuo). PM3 hasa proved to be effective in studies on aromatic molecules containing heteroatoms, compared with other methods such as MINDO/3 or MNDO.

Ionic Liquid compounds (*E*-CHAm) preparation. ***E*-CHAm** ILs were prepared by dissolving 0.3-0.1 g of acid ***E*-CH** in 10-5 mL of methanol. Subsequently, an equimolar amount of an organic base **Am** was added, the mixture was sonicated for 10 min. Then, solvent was evaporated using a vacuum evaporator. The residue obtained (viscous liquid or sirup or solid) was kep in the dark at room temperature.

***E*-CHAm** prepared were characterized by UV-absorption spectroscopy, EI MS, ^{1}H and ^{13}C NMR spectroscopy (see below).

Photolysis of *E*-CHAm in solution. A solutions of ***E*-CHAm** (0.1-0.3g) in MeCN (100-450 mL) contained in a Pyrex flask placed at 5 cm of the light source, was irradiated at 313 nm under normal atmosphere and gentle stirring with a medium-pressure Hg lamp (Hereaus TQ150) for 24 h. Sometimes a minor volume of MeOH (1-10mL) was added to made the IL ***E*-CHAm** completely soluble in MeCN. After the irradiation, the photolyzed solution showed a solid precipitate which was filtered off and washed with cold MeCN (x2, 5 mL); organic solution and washing solvent were mixtured. Sometimes this precipitation was induced (i) keeping the

solution in refrigerator at 5ºC during several hours and/or (ii) by partial evaporation of the solvent under vacuum until the appearance of few crystals or amorphous solid which induces precipitation; then solid was filtered off as usual. The solid obtained, after dissolving in DMSO was analyzed by ^{1}H NMR spectroscopy. The solvent of the mixtured organic solution was evaporated under vacuum and the solid remaining was also analyzed by ^{1}H NMR spectroscopy.

ILs photochemically prepared, ***Z*-CHAm,** were characterized by UV-absorption spectroscopy, EI MS, ^{1}H and ^{13}C NMR spectroscopy (see below).

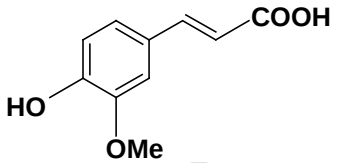
In order to get as free acid the *Z*-isomer photochemically obtained as part of the IL ***Z*-CHAm,** the IL was dissolved in water and (i) passed through an ion-exchange column chromatography (Sigma-Aldrich Dowex 50WX8-200 ion-exchange resin) or (ii) just after adjusting the pH of the water solution with HCl, extracting twice with CH_2Cl_2 and then removing the solvent by evaporation under vacuum.

cis-Cinnamic acids (***Z*-CH)** photochemically prepared were characterized by m.p., UV-absorption spectroscopy, EI MS, ^{1}H and ^{13}C NMR and HRMS (see below).

Photolysis of *trans*-cinnamic acids (*E*-CH) in solution. A solutions of ***E*-CH (**trans-cinnamic acid; $5.15x10^{-5}$ mol) in MeCN (10 mL) contained in a Pyrex flask placed at 5 cm of the light source, was irradiated at 313 nm under normal atmosphere and gentle stirring with a medium-pressure Hg lamp (Hereaus TQ150) for 24 h. After the irradiation, the photolyzed solution did not show any solid precipitate in spite of all the treatments to induce crystallization were attempted.. The solvent was evaporated under vacuum and the solid remaining was analyzed by ^{1}H NMR spectroscopy.

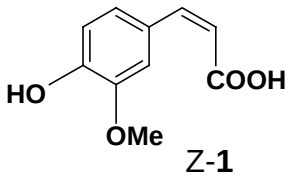
Photolysis of *Z*-1. A solution of ***Z*-1 (***cis*-FA, $5.15x10^{-5}$ mol) in MeCN (10 mL) was irradiated in same conditions that as its *E*- isomer (***E*-1)**. After irradiation, the photolyzed solutions did not show a solid precipitated in spite of all the treatments to induce crystallization were attempted. After the evaporation of the solvent under vacuum, the solid remaining was characterized by ^{1}H NMR spectroscopy as a mixture of the ***E*-1** and ***Z*-1** isomers in a molar ratio 54:46 (*E*/*Z*).

Photolyis of the IL *Z*-1c. A solution of the IL *Z*-**1c** ($4.47x10^{-4}$ mol) in MeCN-MeOH 20:1 (v:v) (315 mL) was irradiated in the same conditions than as its *E*-IL isomer (*E*-**1c**). Notice that solubility of the *Z*-IL in MeCN-MeOH is quite minor than that of the corresponding *E*-IL isomer (*E*-**1c**) ($1.66x10^{-3}$ mol in 307 mL of MeCN-MeOH 50:1 (v:v)). After irradiation, the photolyzed solutions did not show any solid precipitated in spite of all the treatments to induce crystallization were attempted. After the evaporation of the solvent under vacuum, the solid remaining was characterized by ^{1}H NMR spectroscopy as a mixture of the corresponding *E* and *Z* IL isomers (*E*-**1c** and *Z*-**1c**) in a molar ratio 49:51 (*E*/*Z*).



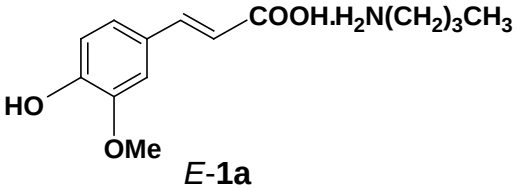
E-1

***E*-1 (*trans*-4-Hydroxy-3-methoxycinnamic acid; *trans*-Ferulic acid; t-FA).**
m.p. 168-172ºC (lit Ref.[2]: 168-172ºC, 174ºC); ^{1}H NMR (200 MHz, $(CD_3)_2SO$) δ 3.82 (s, 3H, OCH_3), 6.37 (d, *J* = 16 Hz, 1H, Hα), 6.80 (d, *J* = 8.2 Hz, 1H, HC(5)), 7.09 (dd, *J* = 8.2, 1.8 Hz, 1H, HC(6)), 7.49 (d, *J* = 16 Hz, 1H, Hβ), 7.50 (d, *J* = 16 Hz, 1H, HC(2)); ^{13}C NMR (500 MHz, $(CD_3)_2SO$) δ 55.70 (OCH_3), 111.16 (C(2)), 115.52 (C(5)), 115.64 (C(α)), 122.84 (C(6)), 125.79 (C(1)), 144.53(C(β)), 147.93 (C(3)), 149.09 (C(4)), 168.01 (COOH); UV-vis (solvent) λ_{max} (nm) (log ε): (MeCN) 319 (4.27), 295 (s); (MeOH) 320 (4.24), 295 (s); EI MS (70 eV) m/z (%): 194 (100), 179 (28), 177 (28), 151 (12), 133 (32), 107 (13), 105 (22), 95 (17), 89 (24), 77 (38), 69 (14), 51 (21), 45 (14), 41 (14).



Z-1

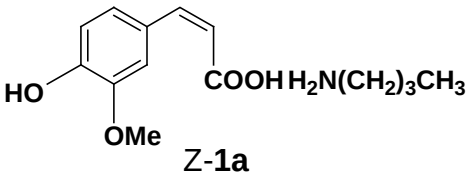
***Z*-1 (*cis*-4-Hydroxy-3-methoxycinnamic acid; *cis*-Ferulic acid; c-FA).**
m.p. 108-111ºC (lit.[3] yellow oil λmax 316 nm); ^{1}H NMR (200 MHz, $(CD_3)_2SO$) δ 3.76 (s, 3H, OCH_3), 5.74 (d, *J* = 12.6 Hz, 1H, Hα), 6.77 (dd, 2H, *J* = 12.8 Hz, Hβ and *J* = 9.0 Hz, HC(5)), 7.15 (d, *J* = 7.6, 1H, HC(6)), 7.67 (s, 1H, HC(2)), 9.50 (s, 1H, OH); ^{13}C NMR (500 MHz, $(CD_3)_2SO$) δ: 55.44 (OCH_3), 114.32 (C(2)), 114.92 (C(5)), 117.01(C(α)), 124.87 (C(6)), 126.16 (C(1)), 141.85 (C(3)), 146.06 (C(β)), 148.85 (C(4)), 167.80 (COOH); UV-vis (solvent) λ_{max} (nm) (log ε): (MeCN) 317 (4.05), 296 (s); (MeOH) 317 (4.01), 295 (s); EI MS (70 eV) m/z (%): 195 (19), 194 (100), 193 (16), 179 (27), 177 (26), 134 (12), 133 (38), 123 (12), 117 (11), 107 (18), 105 (25), 95 (15), 89 (18), 78 (15), 77 (33), 69 (10), 67 (16), 63 (19), 55 (15), 53 (15), 52 (14), 51 (28), 45 (14); HRMS negative ion mode *m/z*: $[M-H]^-$ calcd for $C_{10}H_9O_4^-$ 193.05063, found 193.05136; HRMS MS/MS negative ion mode *m/z*: (precursor ion, 193.05063) 178.02727, 134.03822, 117.03498.



E-**1a**

***E*-1a (*E*-1 + a; t-FA + butylamine)**

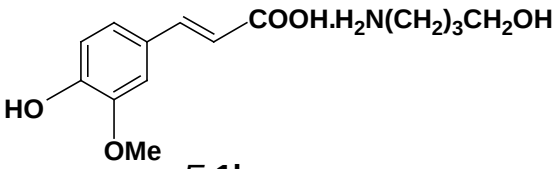
m.p. 110-113ºC; ^{1}H NMR (200 MHz, $(CD_3)_2SO$) δ 0.87 (t, 3H, $\underline{CH_3}CH_2CH_2CH_2NH_3^+$), 1.32 (m, 2H, $CH_3\underline{CH_2}CH_2CH_2NH_3^+$), 1.52 (m, 2H, $CH_3CH_2\underline{CH_2}CH_2NH_3^+$), 2.73 (t, 2H, $CH_3CH_2CH_2\underline{CH_2}NH_3^+$), 3.80 (s, 3H, OCH_3), 6.28 (d, *J* = 15.8 Hz, 1H, Hα), 6.79 (d, *J* = 7.8 Hz, 1H, HC(5)), 6.93 (d, *J* = 7.8 Hz, 1H, HC(6)), 7.11 (s, 1H, HC(2)), 7.20 (d, *J* = 15.8 Hz, 1H, Hβ); ^{13}C NMR (500 MHz, $(CD_3)_2SO$)) δ 13.63 (CH_3), 19.33 ($CH_3\underline{CH_2}$), 30.07 ($CH_3CH_2\underline{CH_2}$), 38.70 ($CH_3CH_2CH_2\underline{CH_2}NH_3^+$), 55.62 ($OCH_3$), 110.68 (C(2)), 115.61 (C(5)), 121.52 (C(6)), 122.40 (C(1)), 126.98(C(α)), 139.49 (C(β)), 147.93(C(4)), 148.22 (C(3)), 170.55 (COO^-); UV-vis (solvent) λ_{max} (nm) (log ε): (MeCN) 319 (4.25), 295 (s); (MeOH) 313 (4.20), 295 (s); EI MS (70 eV) *m/z* (%): 195 (11), 194(100), 179 (28), 177 (13), 151 (20), 148 (12), 134 (15), 133 (51), 123 (14), 117 (14), 107 (25), 106 (10), 105 (39), 95 (25), 91 (12), 89 (32), 79 (18), 78 (24), 77 (63), 67 (18), 65 (13), 63 (18), 55 (18), 53 (18), 52 (17), 51 (39), 50 (19), 45 (62), 43 (19), 42 (11), 41 (24).



Z-**1a**

***Z*-1a (*Z*-1 + a; c-FA + butylamine)**

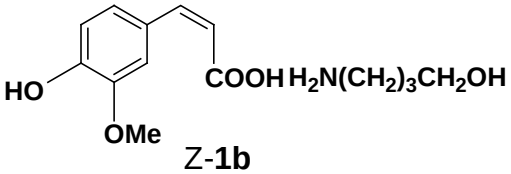
^{1}H NMR (200 MHz, $(CD_3)_2SO$) δ 0.86 (t, 3H, CH_3), 1.29 (m, 2H, $CH_3\underline{CH_2}$), 1.47 (m, 2H, $CH_3CH_2\underline{CH_2}CH_2$), 2.69 (t, 2H, $CH_3CH_2CH_2\underline{CH_2}NH_3^+$), 3.72 (s, 3H, OCH_3), 5.71 (d, *J* = 13.0 Hz, 1H, Hα), 6.10 (d, *J* = 12.8 Hz, 1H, Hβ), 6.68 (d, *J* = 8.0 Hz, 1H, HC(5)), 7.02 (d, *J* = 8.0 Hz, 1H, HC(6)), 7.66 (s, 1H, HC(2)).



E-**1b**

***E*-1b (*E*-1 + b; t-FA + 4-amino-1-butanol).**

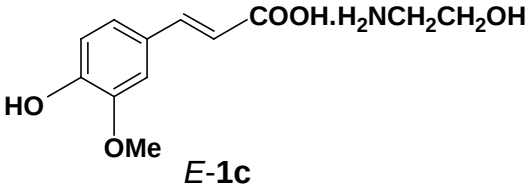
^{1}H NMR (200 MHz, $(CD_3)_2SO$) δ 1.51 (m, 4H, CH_2CH_2), 2.77 (m, 2H, $CH_2\underline{CH_2}NH_3^+$), 3.40 (m, 2H, $OH\underline{CH_2}CH_2CH_2CH_2NH_3^+$), 3.82 (s, 3H, OCH_3), 6.33 (d, *J* = 15.8 Hz, 1H, Hα), 6.78 (d, *J* = 7.8 Hz, 1H, HC(5)), 7.02 (d, *J* = 7.5 Hz, 1H, HC(6)), 7.19 (s, 1H, HC(2)), 7.35 (d, *J* = 15.8 Hz, 1H, Hβ).



Z-**1b**

***Z*-1b (*Z*-1 + b; c-FA + 4-amino-1-butanol).**

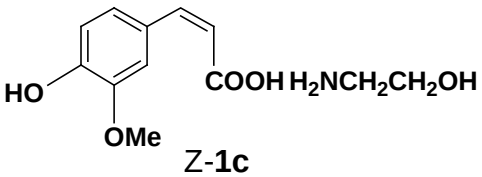
^{1}H NMR (200 MHz, $(CD_3)_2SO$) δ 1.47 (m, 4H, CH_2CH_2), 2.70 (m, 2H, $CH_2\underline{CH_2}NH_3^+$), 3.39 (m, 2H, $OH\underline{CH_2}CH_2CH_2NH_3^+$), 3.72 (s, 3H, OCH_3), 5.71 (d, *J* = 12.8 Hz, 1H, Hα), 6.12 (d, *J* = 12.8 Hz, 1H, Hβ), 6.68 (d, *J* = 8.0 Hz, 1H, HC(5)), 7.02 (d, *J* = 7.8 Hz, 1H, HC(6)), 7.67 (s, 1H, HC(2)).



E-**1c**

***E*-1c (*E*-1 + c; t-FA + ethanolamine).**

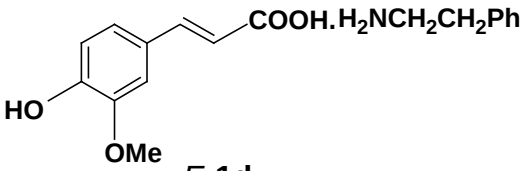
^{1}H NMR (200 MHz, $(CD_3)_2SO$) δ 2.76 (m, 2H, $\underline{CH_2}NH_3^+$), 3.52 (m, 2H, $OH\underline{CH_2}CH_2NH_3^+$), 3.79 (s, 3H, OCH_3), 6.26 (d, *J* = 16.0 Hz, 1H, Hα), 6.76 (d, *J* = 7.8 Hz, 1H, HC(5)), 6.94 (d, *J* = 7.5 Hz, 1H, HC(6)), 7.12 (s, 1H, HC(2)), 7.19 (d, *J* = 16.0 Hz, 1H, Hβ).



Z-**1c**

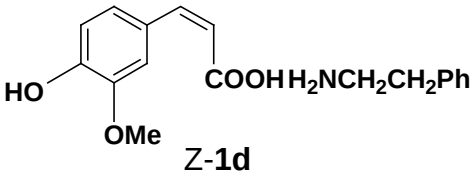
***Z*-1c (*Z*-1 + c; c-FA + ethanolamine).**

^{1}H NMR (200 MHz, $(CD_3)_2SO$) δ 2.79 (m, 2H, $\underline{CH_2}NH_3^+$), 3.55 (m, 2H, $OH\underline{CH_2}CH_2NH_3^+$), 3.73 (s, 3H, OCH_3), 5.72 (d, *J* = 12.8 Hz, 1H, Hα), 6.16 (d, *J* = 12.8 Hz, 1H, Hβ), 6.69 (d, *J* = 7.8 Hz, 1H, HC(5)), 7.01 (d, *J* = 7.4 Hz, 1H, HC(6)), 7.68 (s, 1H, HC(2)).



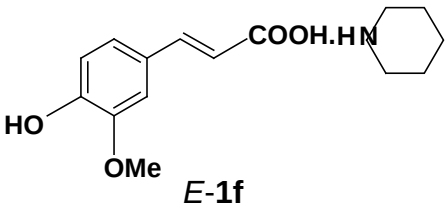
E-**1d**

***E*-1d (*E*-1 + d; t-FA + 2-phenylethylamine).**
^{1}H NMR (200 MHz, $(CD_3)_2SO$) δ 2.87 (m, 4H, Ar$\underline{CH_2CH_2}NH_3^+$), 3.80 (s, 3H, OCH_3), 6.33 (d, J = 15.8 Hz, 1H, Hα), 6.79 (d, J = 8.2 Hz, 1H, HC(5)), 6.98 (d, J = 7.6 Hz, 1H, HC(6)), 7.25 (m, 7H, $\underline{\text{Ar }}CH_2CH_2NH_3^+$, HC(2) and Hβ).



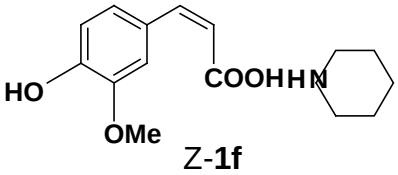
Z-**1d**

***Z*-1d (*Z*-1 + d; c-FA + 2-phenylethylamine).**
^{1}H NMR (200 MHz, $(CD_3)_2SO$ + D_2O) δ 2.87 (m, 4H, Ar$\underline{CH_2CH_2}NH_3^+$), 3.72 (s, 3H, OCH_3), 5.72 (d, J = 12.8 Hz, 1H, Hα), 6.06 (d, J = 12.8 Hz, 1H, Hβ), 6.66 (d, J = 8.2 Hz, 1H, HC(5)), 7.14(d, J = 8.2 Hz, 1H, HC(6)), 7.26 (m, 5H, $\underline{\text{Ar }}CH_2CH_2NH_3^+$), 7.62 (s, 1H, HC(2)).



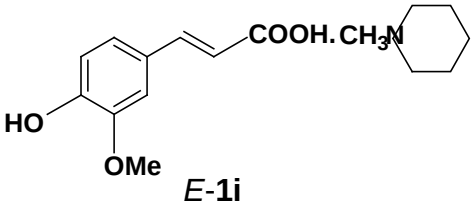
E-**1f**

***E*-1f (*E*-1 + f; t-FA + piperidine).**
^{1}H NMR (200 MHz, $(CD_3)_2SO$) δ 1.55 (m, 6H, $\underline{CH_2CH_2CH_2}HCNH^+$), 2.88 (m, 4H, $\underline{CH_2}(NH^+)\underline{CH_2}$), 3.80 (s, 3H, OCH_3), 6.28 (d, J = 15.8 Hz, 1H, Hα), 6.78 (d, J = 8.0 Hz, 1H, HC(5)), 6.93 (dd, J = 8.0, 2.0 Hz, 1H, HC(6)), 7.13 (d, J = 2.0 Hz, 1H, HC(2)), 7.22 (d, J = 16 Hz, 1H, Hβ).



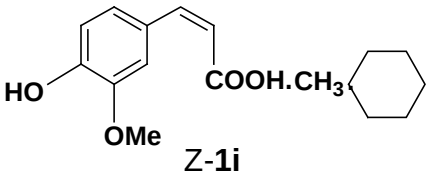
Z-**1f**

***Z*-1f (*Z*-1 + f; c-FA + piperidine).**
^{1}H NMR (200 MHz, $(CD_3)_2SO$) δ 1.54 (m, 6H, $\underline{CH_2CH_2CH_2}HCNH^+$), 2.87 (m, 4H, $\underline{CH_2}(NH^+)\underline{CH_2}$), 3.72 (s, 3H, OCH_3), 5.72 (d, J = 12.8 Hz, 1H, Hα), 6.11 (d, J = 13 Hz, 1H, Hβ), 6.66 (d, J = 7.6 Hz, 1H, HC(5)), 7.02 (d, J = 8.6 Hz, 1H, HC(6)), 7.62 (s, 1H, HC(2)).



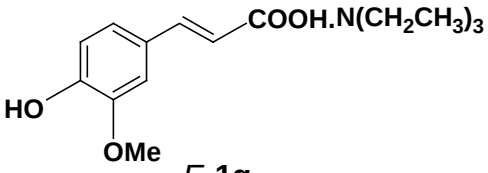
E-**1i**

***E*-1i (*E*-1 + i; t-FA + N-methylpiperidine).**
^{1}H NMR (200 MHz, $(CD_3)_2SO$) δ 1.38 (m, 2H, $H_2C(4)NH^+CH_3$), 1.52 (m, 4H, $H_2C(3)$ and $H_2C(5)$ NH^+CH_3), 2.22 (s, 3H, $^+NHCH_3$), 2.40 (m, 4H, $H_2C(2)$ and $H_2C(6)NH^+CH_3$), 3.82 (s, 3H, OCH_3), 6.37 (d, J = 16 Hz, 1H, Hα), 6.79 (d, J = 8.0 Hz, 1H, HC(5)), 7.07 (dd, J = 8.2, 1.8 Hz, 1H, HC_6), 7.27 (d, J = 1.8 Hz, 1H, HC(2)), 7.47 (d, J = 16 Hz, 1H, Hβ)



Z-**1i**

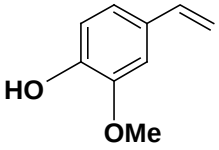
***Z*-1i (*Z*-1 + i; c-FA + N-methylpiperidine).**
^{1}H NMR (200 MHz, $(CD_3)_2SO$) δ 1.38 (m, 2H, $H_2C(4)NH^+CH_3$), 1.52 (m, 4H, $H_2C(3)$ and $H_2C(5)NH^+CH_3$), 2.22 (s, 3H, $^+NHCH_3$), 2.40 (m, 4H, $H_2C(2)$ and $H_2C(6)NH^+CH_3$), 3.75 (s, 3H, OCH_3), 5.78 (d, J = 12.8 Hz, 1H, Hα), 6.32 (d, J = 12.8 Hz, 1H, Hβ), 6.76 (d, J = 8 Hz, HC(5)), 7.07 (d, 7.64, J = 8 Hz, HC(6)), (s, 1H, HC(2)).



E-**1g**

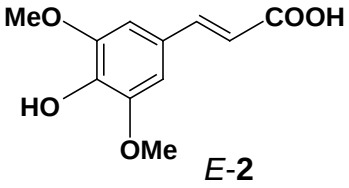
***E*-1g (*E*-1 + g; t-FA + triethylamine).**

^{1}H NMR (200 MHz, $(CD_3)_2SO$) δ 1.37 (m, 9H, $\underline{CH_3}CH_2NH^+$), 1.51 (m, 6H, $CH_3\underline{CH_2}NH^+$), 3.81 (s, 3H, OCH_3), 6.36 (d, J = 16 Hz, 1H, Hα), 6.79 (d, J = 8.2 Hz, 1H, HC(5)), 7.05 (dd, J = 8.2, 1.8 Hz, 1H, HC(6)), 7.25(d, J = 1.8 Hz, 1H, HC(2)), 7.42 (d, J = 16 Hz, 1H, Hβ).



4-Hydroxy-3-methoxyphenylethene

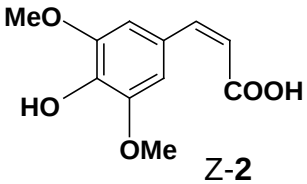
^{1}H NMR (200 MHz, $(CD_3)_2SO$) δ 3.78 (s, 3H, OCH_3), 5.06 (d, J = 10.8 Hz, 1H), 5.63 (d, J = 17.4 Hz), 6.58 (dd, J = 10.8, 17.4 Hz, 1H), 6.72 (m, 3H). [4]



E-**2**

***E*-2 (*trans*-4-Hydroxy-3,5-dimethoxycinnamic acid; *trans*-sinapinic acid; t-SA).**

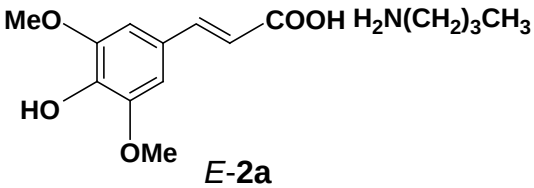
m.p. 185ºC (lit: 202ºC dec,[5]); ^{1}H NMR (200 MHz, $(CD_3)_2SO$) δ: 3.80 (s, 6H, OCH_3), 6.42 (d, J = 15.8 Hz, 1H, Hα), 6.99 (s, 2H, HC(2) and HC(6)), 7.50 (d, J = 16 Hz, 1H, Hβ); ^{13}C NMR (500 MHz, $(CD_3)_2SO$) δ: 56.13 (OCH_3), 106.12 (C(2) and C(6)), 116.12 (C(α)), 124.67 (C(1)), 138.11 (C(4)), 144.90(C(β)), 148.09 (C(3) and C(5)), 168.05 (COOH); UV-vis (solvent) λ_{max} (nm) (log ε): (MeCN) 322 (4.18); (MeOH) 322 (4.14); EI MS (70 eV) *m/z* (%): 224(100), 209 (23), 181 (13), 149 (11), 135 (11), 121 (17), 93 (12), 91 (14), 78 (11), 77 (20), 69 (13), 65 (23), 63 (11), 53 (14), 44 (17).



Z-**2**

***Z*-2 (*cis*-4-Hydroxy-3,5-dimethoxycinnamic acid; *cis*-sinapinic acid; c-SA).**

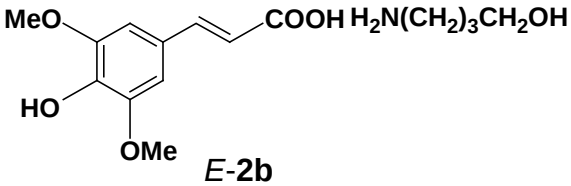
m.p. 116-118ºC; ^{1}H NMR (200 MHz, $(CD_3)_2SO$) δ 3.75 (s, 6H, OCH_3), 5.76 (d, J = 12.8 Hz, 1H, Hα), 6.76 (d, J = 12.8 Hz, 1H, Hβ), 7.23 (s, $HC_{2\text{-}6}$), 8.88 (s, 1H, OH). ^{13}C NMR (500 MHz, $(CD_3)_2SO$) δ: 55.92 (OCH_3), 117.37 (C(2) and C(6)), 124.92 (C(α)), 137.27 (C(1)), 142.06 (C(4)), 147.25(C(β)), 148.06 (C(3) and C(5)), 167.84 (COOH); UV-vis (solvent) λ_{max} (nm) (log ε): (MeCN) 319 (4.09); (MeOH) 317 (4.01); EI MS (70 eV) *m/z* (%): 225 (25), 224 (100), 209 (8), 206 (34), 181 (10), 179 (29), 163 (7), 121 (2), 65 (11), 53 (8); HRMS negative ion mode *m/z*: $[M-H]^-$ calcd for $C_{11}H_{11}O_5^-$ 223.06120, found 223.06153; HRMS MS/MS negative ion mode *m/z*: (precursor ion, 223.06120) 208.03704, 193.01351, 164.04708, 149.02391, 121.02797.



E-**2a**

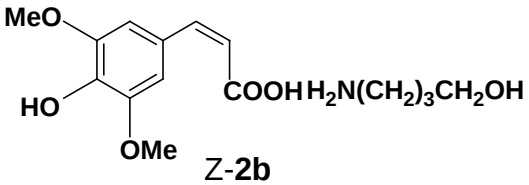
***E*-2a (*E*-2 + a; t-SA + butylamine).**

m.p. 124-127ºC; ^{1}H NMR (200 MHz, $(CD_3)_2SO$) δ 0.87 (t, 3H, CH_3), 1.31 (m, 3H, $\underline{CH_3}CH_2$), 1.45 (m, 2H, $CH_3\underline{CH_2}CH_2$), 2.68 (t, 2H, $CH_3CH_2\underline{CH_2}NH_3^+$), 3.78 (s, 6H, OCH_3), 6.33 (d, J = 15.8 Hz, 1H, Hα), 6.84 (s, 2H, HC(2) and HC(6)), 7.20 (d, J = 15.8 Hz, 1H, Hβ); ^{13}C NMR (500 MHz, $(CD_3)_2SO$) δ 13.68 (CH_3), 19.31 ($CH_3\underline{CH_2}$), 31. 34($CH_3CH_2\underline{CH_2}$), 55.98 ($CH_3CH_2CH_2\underline{CH_2}NH_4^+$), 55.99 ($OCH_3$), 105.20 (C(2) and C(6)), 122.69 (C(1)), 125.93 (C(α)), 137.00 (C(4)), 139.76 (C(β)), 148.06 (C(3) and C(5)), 169.97 (COO^-); UV-vis (solvent) λ_{max} (nm) (log ε): (MeCN) 322 (4.18); (MeOH) 310 (4.12); EI MS (70 eV) *m/z* (%): 225 (13), 224 (100), 209 (22), 181 (11), 180 (14), 149 (10), 121 (14), 91 (10), 77 (10), 65 (14), 53 (12), 44 (31);



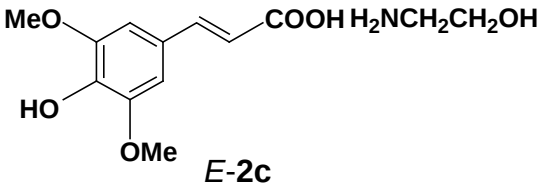
E-**2b**

***E*-2b (*E*-2 + b; t-SA + 4-amino1-1-butanol).**
^{1}H NMR (200 MHz, $(CD_3)_2SO$) δ 1.50 (m, 4H, CH_2CH_2), 2.71 (m, 2H, $CH_2\underline{CH_2}NH_3^+$), 3.17 (m, 2H, $OH\underline{CH_2}CH_2CH_2CH_2NH_3^+$), 3.79 (s, 6H, OCH_3), 6.31 (d, *J* = 16.0 Hz, 1H, Hα), 6.81 (s, 2H, HC(2) and HC(6)), 7.17 (d, *J* = 15.8 Hz, 1H, Hβ).



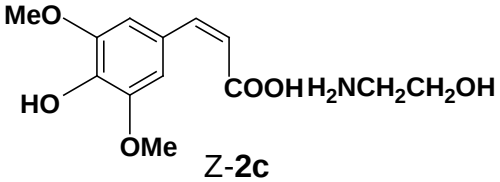
Z-**2b**

***Z*-2b (*Z*-2 + b; c-SA + 4-amino-1-butanol).**
^{1}H NMR (200 MHz, $(CD_3)_2SO$) δ 1.49 (m, 4H, CH_2CH_2), 2.78 (m, 2H, $CH_2\underline{CH_2}NH_3^+$), 3.39 (m, 2H, $OH\underline{CH_2}CH_2CH_2CH_2NH_3^+$), 3.72 (s, 6H, OCH_3), 5.73 (d, *J* = 12.8 Hz, 1H, Hα), 6.09 (d, *J* = 12.8 Hz, 1H, Hβ), 7.18 (s, 2H, HC(2) and C(6)); ^{13}C NMR (500 MHz, $(CD_3)_2SO$) δ 55.87 (OCH_3), 107.44 (C(2) and C(6)), 127.18 (C(α)), 135.44 (C(4)), 147.26 (C(β)), 148.04 (C(3) and C(5)), 171.07 (COO^-).



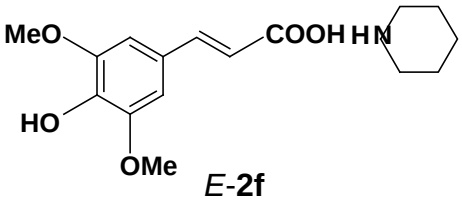
E-**2c**

***E*-2c (*E*-2 + c; t-SA + ethanolamine).**
^{1}H NMR (200 MHz, $(CD_3)_2SO$) δ 2.82 (t, 2H, $CH_2NH_3^+$), 3.58 (m, 2H, $OH\underline{CH_2}CH_2NH_3^+$), 3.78 (s, 6H, OCH_3), 6.32 (d, *J* = 15.8 Hz, 1H, Hα), 6.83 (s, HC(2) and HC(6)), 7.21 (d, *J* = 15.8 Hz, 1H, Hβ).



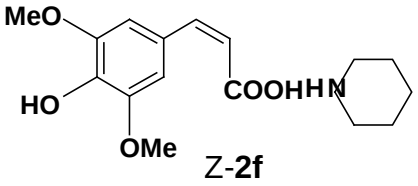
Z-**2c**

***Z*-2c (*Z*-2 + c; c-SA + ethanolamine).**
^{1}H NMR (200 MHz, $(CD_3)_2SO$) δ 2.77 (m, 2H, $CH_2NH_3^+$), 3.53 (m, 2H, $OH\underline{CH_2}CH_2NH_3^+$), 3.72 (s, 6H, OCH_3), 5.73 (d, *J* = 12.8 Hz, 1H, Hα), 6.16 (d, *J* = 12.8 Hz, 1H, Hβ), 7.18 (s, 2H, HC(2) and HC(6)).



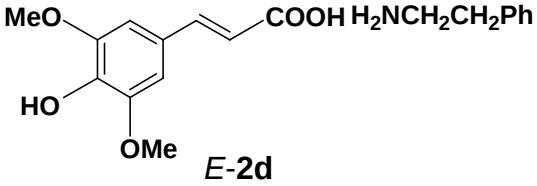
E-**2f**

***E*-2f (*E*-2 + f; t-SA + piperidine).**
^{1}H NMR (200 MHz, $(CD_3)_2SO$) δ 1.54 (m, 6H, $\underline{CH_2CH_2CH_2}HCNH_2^+$), 2.87 (m, 4H, $\underline{CH_2}(NH_2^+)\underline{CH_2}$), 3.78 (s, 6H, OCH_3), 6.33 (d, *J* = 15.8 Hz, 1H, Hα), 6.85 (s, 2H, HC(2) and C(6)), 7.23 (d, *J* = 15.8Hz, 1H, Hβ).



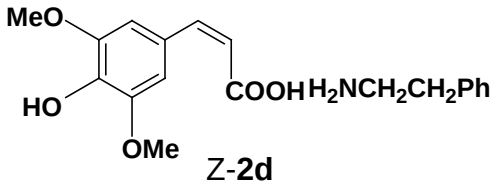
Z-**2f**

***Z*-2f (*Z*-2 + f; c-SA + piperidine).**
^{1}H NMR (200 MHz, $(CD_3)_2SO$) δ 1.56 (m, 6H, $\underline{CH_2CH_2CH_2}HCNH_2^+$), 2.90 (m, 4H, $\underline{CH_2}(NH_2^+)\underline{CH_2}$), 3.72 (s, 6H, OCH_3), 5.75 (d, *J* = 15.8 Hz, 1H, Hα), 6.17 (d, *J* = 12.8 Hz, Hβ), 7.18 (s, 2H, HC(2) and C(6)).



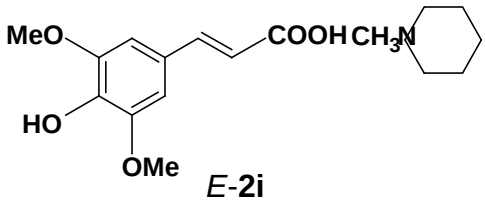
E-**2d**

***E*-2d (*E*-2 + d; t-SA + 2-phenylethylamine).**
^{1}H NMR (200 MHz, $(CD_3)_2SO$) δ 2.84 (m, 2H, $Ar\underline{CH_2}CH_2NH_3^+$), 2.90 (m, 2H, $ArCH_2\underline{CH_2}NH_3^+$), 3.79 (s, 6H, OCH_3), 6.39 (d, *J* = 15.8 Hz, 1H, Hα), 6.88 (s, 2H, HC(2) and HC(6)), 7.30 (d, *J* = 15.8 Hz, 1H, Hβ; m, 5H, $\underline{Ar}\ CH_2CH_2NH_3^+$).



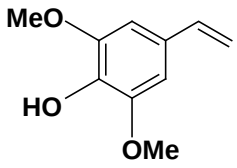
Z-**2d**

***Z*-2d (*Z*-2 + d; c-SA + 2-phenylethylamine).**
^{1}H NMR (200 MHz, $(CD_3)_2SO$) δ 2.79 (m, 2H, $Ar\underline{CH_2}CH_2NH_3^+$), 2.85 (m, 2H, $ArCH_2\underline{CH_2}NH_3^+$), 3.70 (s, 6H, OCH_3), 5.76 (d, *J* = 12.8 Hz, 1H, Hα), 6.15 (d, *J* = 12.8 Hz, 1H, Hβ), 7.24 (m, 2H, HC(2) and HC(6)), 7.30 (m, 5H, $\underline{Ar}\ CH_2CH_2NH_3^+$).

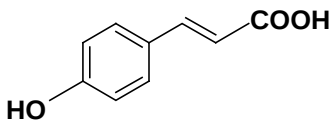


E-**2i**

***E*-2i (*E*-2 + i; t-SA + methylpiperidine).**
^{1}H NMR (200 MHz, $(CD_3)_2SO$) δ 1.37 (m, 2H, $H_2C(4)NH^+CH_3$), 1.51 (m, $H_2C(3)$ and $H_2C(5)NH^+CH_3$), 2.20 (s, 3H, $^+NH\underline{CH_3}$), 2.37 (m, 4H, $H_2C(2)$ and $H_2C(6)NH^+CH_3$), 3.80 (s, 6H, OCH_3), 6.43 (d, *J* = 15.8 Hz, 1H, Hα), 6.99 (s, 2H, HC(2) and HC(6)), 7.48 (d, *J* = 15.8, 1H, Hβ)

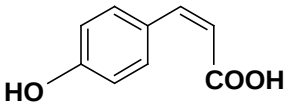


4-Hydroxy-3,5-dimethoxyphenylethene
^{1}H NMR (200 MHz, $(CD_3)_2SO$) δ 3.74 (s, 6H, OCH_3), 5.09 (d, *J* = 11.0 Hz, 1H), 5.66 (d, *J* = 17.4 Hz, 1H), 6.57 (dd, *J* = 11.0, 17.4 Hz, 1H), 6.74 (s, 2H).[6]



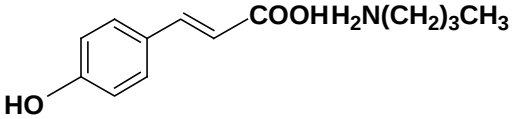
E-**3**

***E*-3 (*trans*-4-Hydroxycinnamic acid; *trans-p*-coumaric acid; t-CuA).**
m.p. 214-216ºC (lit.[9]: 210-213ºC); ^{1}H NMR (200 MHz, $(CD_3)_2SO$) δ 6.29 (d, *J* = 16.0 Hz, 1H, Hα), 6.79 (d, 2H, HC(2) and HC(6)), 7.49 (m, 3H, HC(3), H(5) and Hβ, d, *J* = 16.0 Hz), 9.98 (s, 1H, OH); ^{13}C NMR (500 MHz, $(CD_3)_2SO$) δ 115.39 (C(α)), 115.81 (C(3) and C(5)), 125.34 (C(1)), 130.16 (C(2) and C(6)), 141.25 (C(β)), 159.66 (C(4)), 168.03 (COOH); UV-vis (solvent) λ_{max} (nm) (log ε): (MeCN) 307 (4.36); (MeOH) 310 (4.34); EI MS (70 eV) *m/z* (%): 164 (100), 163 (59), 147(46), 119 (23), 118 (19), 107 (15), 91 (32), 89 (12), 65 (13), 45 (11).



Z-**3**

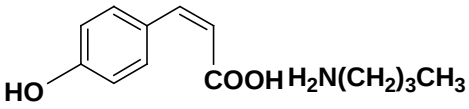
***Z*-3 (*cis*-4-Hydroxycinnamic acid; *cis-p*-coumaric acid; c-CuA).**
m.p. 123-125ºC; ^{1}H NMR (200 MHz, $(CD_3)_2SO$) δ 5.73 (d, *J* = 12.8 Hz, 1H, Hα), 6.77 (m, 3H, HC(2), HC(6) and H_β), 7.65 (d, *J* = 8.2 Hz, 2H, HC(3) and HC(5)), 9.92 (s, 1H, OH). ^{13}C NMR (500 MHz, $(CD_3)_2SO$) δ 114.87 (C(3) and C(5)), 116.95 (C(α)), 125.76 (C(1)), 132.33 (C(2) and C(6)), 141.66 (C(β)), 158.52 (C(4)), 167.66 (COOH); UV-vis (solvent) λ_{max} (nm) (log ε): (MeCN) 299 (4.16); (MeOH) 299 (4.05); EI MS (70 eV) *m/z* (%): 164 (100), 163 (59), 147(46), 119 (23), 118 (19), 107 (15), 91 (32), 89 (12), 65 (13), 45 (11); HRMS negative ion mode *m/z*: $[M-H]^-$ calcd for $C_9H_7O_3^-$ 163.04007, found 163.04018; HRMS MS/MS negative ion mode *m/z*: (precursor ion, 163.04018) 119.05019, 93,03246.



E-**3a**

***E*-3a (*E*-3 + a; t-CuA + butylamine).**
m.p. 133-136ºC; ^{1}H NMR (200 MHz, $(CD_3)_2SO$) δ 0.86 (t, 3H, $\underline{CH_3}CH_2CH_2CH_2NH_3^+$), 1.32 (m, 2H, $CH_3\underline{CH_2}CH_2CH_2NH_3^+$), 1.48 (m, 2H, $CH_3CH_2\underline{CH_2}CH_2NH_3^+$), 2.72 (t, 2H, $\underline{CH_3}CH_2CH_2\underline{CH_2}NH_3^+$), 6.22 (d, *J* = 15.8 Hz, 1H, Hα), 6.77 (d, *J* = 8.4 Hz, 2H, HC(2) and HC(6)), 7.19 (d, *J* = 15.8 Hz, 1H, Hβ), 7.35 (d, *J* = 7.0 Hz, 2H, HC(3) and HC(5)); ^{13}C NMR (500 MHz, $(CD_3)_2SO$) δ 13.58 (CH_3), 19.34 ($CH_3\underline{CH_2}$), 29.84 ($CH_3CH_2\underline{CH_2}$), 38.63 ($CH_3CH_2CH_2\underline{CH_2}NH_3^+$), 115.73 (C(3) and C(5)), 123.22 (C(1)), 126.37 (C(α)), 128.81 (C(2) and C(6)), 138.35 (C(β)), 158.84 (C(4)), 171.11 (COO^-); UV-vis (solvent) λ_{max} (nm) (log ε): (MeCN) 300 (4.34); (MeOH) 287 4.17); EI MS (70 eV) *m/z* (%): 165 (21), 164 (100), 163 (40), 147(54), 119 (39), 118 (30), 107 (24), 91 (39), 89

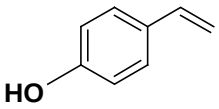
(18), 77 (11), 65 (37), 63 (30), 62 (13), 53 (12), 51 (14), 45 (17).



Z-**3a**

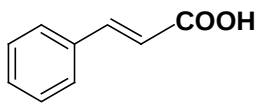
***Z*-3a (*Z*-3 + a; c-CuA + butylamine).**

^{1}H NMR (200 MHz, $(CD_3)_2SO$) δ 0.87 (t, 3H, $\underline{CH_3}CH_2CH_2CH_2NH_3^+$), 1.30 (m, 2H, $CH_3\underline{CH_2}CH_2CH_2NH_3^+$), 1.46 (m, 2H, $CH_3CH_2\underline{CH_2}CH_2NH_3^+$), 2.67 (t, 2H, $CH_3CH_2CH_2\underline{CH_2}NH_3^+$), 5.70 (d, *J* = 12.8 Hz, 1H, Hα), 6.09 (d, *J* = 12.8 Hz, 1H, Hβ), 6.66 (d, *J* = 8.6 Hz, 2H, HC(2) and HC(6)), 7.53 (d, *J* = 8.4 Hz, 2H, HC(3) and HC(5)). EI MS *m/z* (%): 165 (13), 164 (100), 163 (47), 147(81), 120 (14), 119 (60), 107 (27), 91 (50), 90 (11), 89 (25), 77 (24), 75 (10), 74 (14), 73 (14), 69 (14), 68 (12), 65 (66), 64 (15), 63 (40), 62 (19), 55 (11), 53 (12), 51 (15), 45 (16), 41 (10).



4-Hydroxyphenylethene

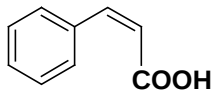
^{1}H NMR (200 MHz, $(CD_3)_2SO$) δ 5.02 (d, *J* = 10.6 Hz, 1H, CH_2), 5.57 (d, *J* = 17.2 Hz, 1H, CH_2), 6.5-6.9 (m, 2H, HC(2) and HC(6)).



E-**4**

***E*-4 (*trans*-Cinnamic acid; t-CA).**

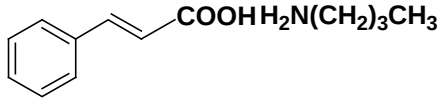
m.p. 133-135ºC,[7] honey aspect m.p. 134ºC); ^{1}H NMR (200 MHz, $(CD_3)_2SO$) δ 6.55 (d, *J* = 16 Hz, 1H, Hα), 7.42 (m, 3H, HC(3), HC(4) and HC(5)), 7.60 (d, *J* = 16 Hz, 1H, Hβ), 7.69 (m, 2H, HC(2) and HC(6)); ^{13}C NMR (500 MHz, $(CD_3)_2SO$)) δ 119.29 (C(α)), 128.24 (C(2) and C(6)), 128.95 (C(3) and C(5)), 130.26 (C(4)), 134.30 (C(1)), 144.00 (C(β)), 167.66 (COOH); UV-vis (solvent) λ_{max} (nm) (log ε): (MeCN) 273 (4.23); (MeOH) 273 (4.32); EI MS (70 eV) *m/z* (%): 147(100), 131 (27), 103 (39), 102 (29), 91 (35), 78 (17), 77 (73), 75 (16), 74 (19), 50 (17).



Z-**4**

***Z*-4 (*cis*-Cinnamic acid; c-CA).**

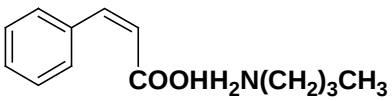
m.p. 55-57ºC (Lit.[8]); ^{1}H NMR (200 MHz, $(CD_3)_2SO$)) δ 5.97 (d, *J* = 12.8 Hz, 1H, Hα), 6.92 (d, *J* = 12.6 Hz, 1H, Hβ), 7.36 (m, 3H, HC(3), HC(4) and HC(5)), 7.60 (m, 2H, HC(2) and HC(6)); ^{13}C NMR (500 MHz, $(CD_3)_2SO$)) δ 121.10 (C(α)), 128.08 ((C(2) and C(6)), 128.80 (C(3) and C(5)), 129.50 (C(4)), 134.89 (C(1)), 140.32 (C(β)), 167.51 (COOH); UV-vis (solvent) λ_{max} (nm) (log ε): (MeCN) 269 (4.12); (MeOH) 270 (4.20); EI MS (70 eV) *m/z* (%): 149 (12), 148 (81), 147(100), 131 (34), 103 (55), 102 (32), 91 (36), 77 (71), 76 (21), 75 (18), 74 (22), 65 (13), 63 (20), 52 (12), 51 (59), 50 (30), 45 (22); HRMS negative ion mode *m/z*: $[M-H]^-$ calcd for $C_9H_7O_2^-$ 147.04515, found 147.04574. HRMS MS/MS negative ion mode *m/z*: (precursor ion, 147.04574) 119.05056, 103,05587.



E-**4a**

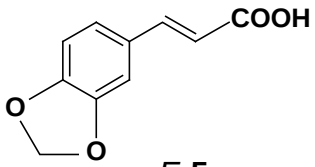
***E*-4a (*E*-4 + a; t-CA + butylamine).**

m.p. 89-92 ºC; ^{1}H NMR (200 MHz, $(CD_3)_2SO$) δ 0.86 (t, 3H, $\underline{CH_3}CH_2CH_2CH_2NH_3^+$), 1.32 (m, 2H, $CH_3\underline{CH_2}CH_2CH_2NH_3^+$), 1.52 (m, 2H, $CH_3CH_2\underline{CH_2}CH_2NH_3^+$), 2.75 (t, $CH_3CH_2CH_2\underline{CH_2}NH_3^+$), 6.45 (d, *J* = 16 Hz, 1H, Hα), 7.24 (d, *J* = 16 Hz, 1H, Hβ), 7.37 (m, 3H, HC(3), HC(4) and HC(5)), 7.45 (m, 2H, HC(2) and HC(6)); ^{13}C NMR (500 MHz, $(CD_3)_2SO$) δ 13.6 (CH_3), 19.32 ($CH_3\underline{CH_2}$), 30.09 ($CH_3CH_2\underline{CH_2}$), 38.61 ($CH_3CH_2CH_2\underline{CH_2}NH_3^+$), 127.22 (C(2) and C(6)), 127.25 (C(3) and C(5)), 128.50 (C(4)), 128.69 (C(α)), 136.07 (C(1)), 137.30 (C(β)), 170.12 (COO^-); UV-vis (solvent) λ_{max} (nm): (MeCN) 273 (4.29); (MeOH) 268 (4.26); EI MS (70 eV) *m/z* (%): 149 (8), 148 (76), 147(100), 131 (24), 103 (41), 102 (29), 91 (36), 78 (14), 77 (76), 76 (19), 75 (15), 74 (21), 73(21), 65 (11), 63 (14), 51 (47), 50 (25), 45 (12).



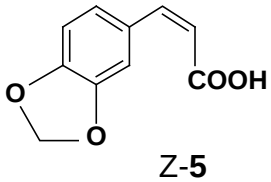
Z-**4a**

***Z*-4a (*Z*-4 + a; c-CA + butylamine).**
^{1}H NMR (200 MHz, $(CD_3)_2SO$) δ 0.86 (t, 3H, $\underline{CH_3}CH_2CH_2CH_2NH_3^+$), 1.30 (m, 2H, $CH_3\underline{CH_2}CH_2CH_2NH_3^+$), 1.47 (m, 2H, $CH_3CH_2\underline{CH_2}CH_2NH_3^+$), 2.70 (t, $CH_3CH_2CH_2\underline{CH_2}NH_3^+$), 5.91 (d, J = 12.8 Hz, 1H, Hα), 6.13 (d, J = 12.6 Hz, 1H, Hβ), 7.24 (m, 3H, HC(3), HC(4) and HC(5)), 7.62 (d, J = 7 Hz, 2H, HC(2) and HC(6)).



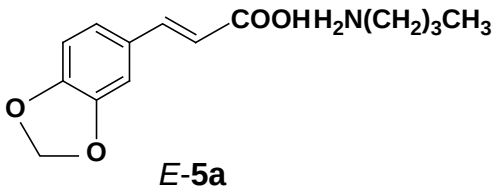
E-**5**

***E*-5 (*trans*-3,4-(methylenedioxy)cinnamic acid; t-MDOCA).**
m.p. 242-244^{0}C (dec.)[10]; ^{1}H NMR (500 MHz, $(CD_3)_2SO$) δ 6.07 (s, 4H, OCH_2), 6.39 (d, J = 15.9 Hz, 1H, Hα), 6.93 (d, J = 8.2 Hz, 1H, HC(5)), 7.15 (dd, J = 8.2, 1.7 Hz, 1H, HC(6)), 7.36 (d, J = 1.7 Hz, 1H, HC(2)), 7.50 (d, J = 15.9 Hz, 1H, Hβ); ^{13}C NMR (500 MHz, $(CD_3)_2SO$) δ 101.54 (OCH_2), 106.66 (C(5)), 108.45 (C(2)), 117.09 (C(α)), 124.62 (C(6)), 128.68 (C(1)), 143.85 (C(β)), 148.03 (C(3)), 149.14 (C(4)), 167.81 (COOH); UV-vis (solvent) λ_{max} (nm): (MeCN) 324 (4.21); (MeOH) 321 (4.18); EI MS (70 eV) *m/z* (%): 192 (100), 164(13), 149 (10), 105 (9), 75 (30), 67 (9), 51 (12).



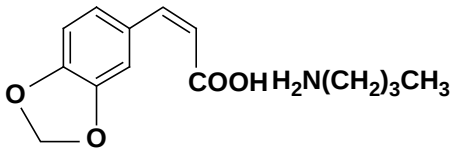
Z-**5**

***Z*-5 (*cis*-3,4-(methylenedioxy)cinnamic acid; c-MDOCA).**
m.p. 100-102 ºC; ^{1}H NMR (500 MHz, $(CD_3)_2SO$) δ 5.81 (d, J = 12.8 Hz, 1H, Hα), 6.05 (s, 2H, OCH_2), 6.80 (d, J = 12.8 Hz, 1H, Hβ), 6.92 (d, J = 8.2 Hz, 1H, HC(5)), 7.14 (dd, J = 8.0, 1.7 Hz, 1H, HC(6)), 7.52 (d, J = 1.7 Hz, 1H, HC(2)); ^{13}C NMR (500 MHz, $(CD_3)_2SO$) δ 101.82 (OCH_2), 108.40 (C(5)), 109.97 (C(2)), 119.03 (C(α)), 126.30 (C(6)), 129.27 (C(1)), 141.45 (C(β)), 147.47 (C(3)), 148.48 (C(4)), 167.98 (COOH); UV-vis (solvent) λ_{max} (nm): (MeCN) 320 (3.98); (MeOH) 312 (3.90); HRMS negative ion mode *m/z*: $[M-H]^-$ calcd for $C_{10}H_7O_4^-$ 191.03498, found 191.03556; HRMS MS/MS negative ion mode *m/z*: (precursor ion, 191.03556) 117.03389, 89,03741.



E-**5a**

***E*-5a (*E*-5 + a; t-MDOCA+ butylamine).**
^{1}H NMR (200 MHz, $(CD_3)_2SO$) δ 0.87 (t, 3H, $\underline{CH_3}CH_2CH_2CH_2NH_3^+$), 1.32 (m, 2H, $CH_3\underline{CH_2}CH_2CH_2NH_3^+$), 1.49 (m, 2H, $CH_3CH_2\underline{CH_2}CH_2NH_3^+$), 2.52 (t, 2H, $CH_3CH_2CH_2\underline{CH_2}NH_3^+$), 6.04 (s, 2H, OCH_2), 6.31 (d, J = 15.8 Hz, 1H, Hα), 6.89 (d, J = 8.0 Hz, 1H, HC(5)), 7.01 (dd, J = 8.0, 1.2 Hz, 1H, HC(6)), 7.20(s, 1H, HC(2)), 7.17 (d, J = 15.8 Hz, 1H, Hβ)



Z-**5a**

***Z*-5a (*Z*-5 + a; c-MDOCA + butylamine).**
^{1}H NMR (500 MHz, $(CD_3)_2SO$) δ 0.85 (t, 3H, $\underline{CH_3}CH_2CH_2CH_2NH_3^+$), 1.29 (m, 2H, $CH_3\underline{CH_2}CH_2CH_2NH_3^+$), 1.47 (m, 2H, $CH_3CH_2\underline{CH_2}CH_2NH_3^+$), 2.69 (t, 2H, $CH_3CH_2CH_2\underline{CH_2}NH_3^+$), 5.78 (d, J = 12.8 Hz, 1H, Hα), 5.97 (s, 2H, OCH_2), 6.06 (d, J = 12.8 Hz, 1H, Hβ), 6.80 (d, J = 8.0 Hz, 1H, HC(5)), 6.97 (dd, J = 8.0, 1.6 Hz, 1H, HC(6)), 7.61(d, J = 1.6 Hz, 1H, HC(2)); ^{13}C NMR (500 MHz, $(CD_3)_2SO$) δ 13.53 (CH_3), 19.25 ($CH_3\underline{CH_2}$), 29.88 ($CH_3CH_2\underline{CH_2}$), 38.52($CH_3CH_2CH_2\underline{CH_2}NH_3^+$), 100.78 ($OCH_2$), 107.59(C(5)), 108.69 (C(2)), 123.50 (C(6)), 126.95 (C(β)), 128.84 (C(α)) 131.28 (C(1)), 1146.23 (C(4)), 146.85 (C(3)), 171.24 (COO^-).

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Kudin, M.C. Strain, O. Farkas, J. Tomasi, V. Barone, M. Cossi, R. Cammi, B. Mennucci, C. Pomelli, C. Adamo, S. Clifford, J. Ochterski, G.A. Petersson, P.Y. Ayala, Q. Cui, K. Morokuma, D.K. Malick, A.D. Rabuck, K. Raghavachari, J.B. Foresman, J. Cioslowski, J.V. Ortiz, B.B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. Gomperts, R.L. Martin, D.J. Fox, T. Keith, M.A. Al-Laham, C.Y. Peng, A. Nanayakkara, C. Gonzalez, M. Challacombe, P.M. Gill, B. Johnson, W. Chen, M.W. Wong, J.L. Andres, C. Gonzalez, M. Head-Gordon, E.S. Replogle, J.A. Pople, Gaussian, Inc., Pittsburgh PA, 1998.

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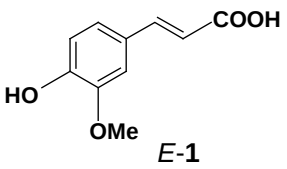
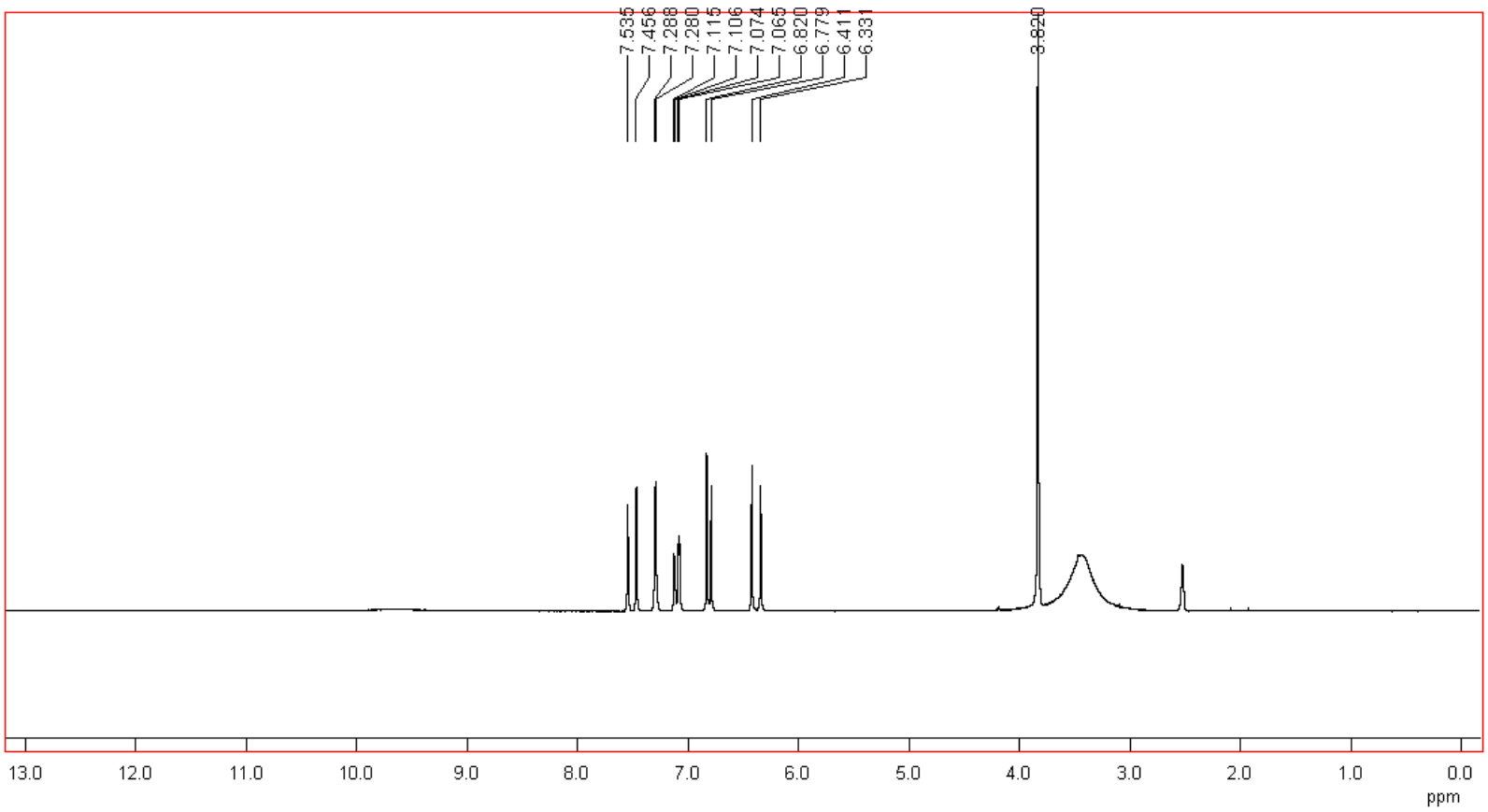
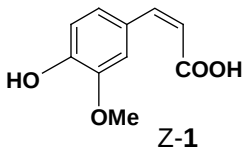


E-**1**

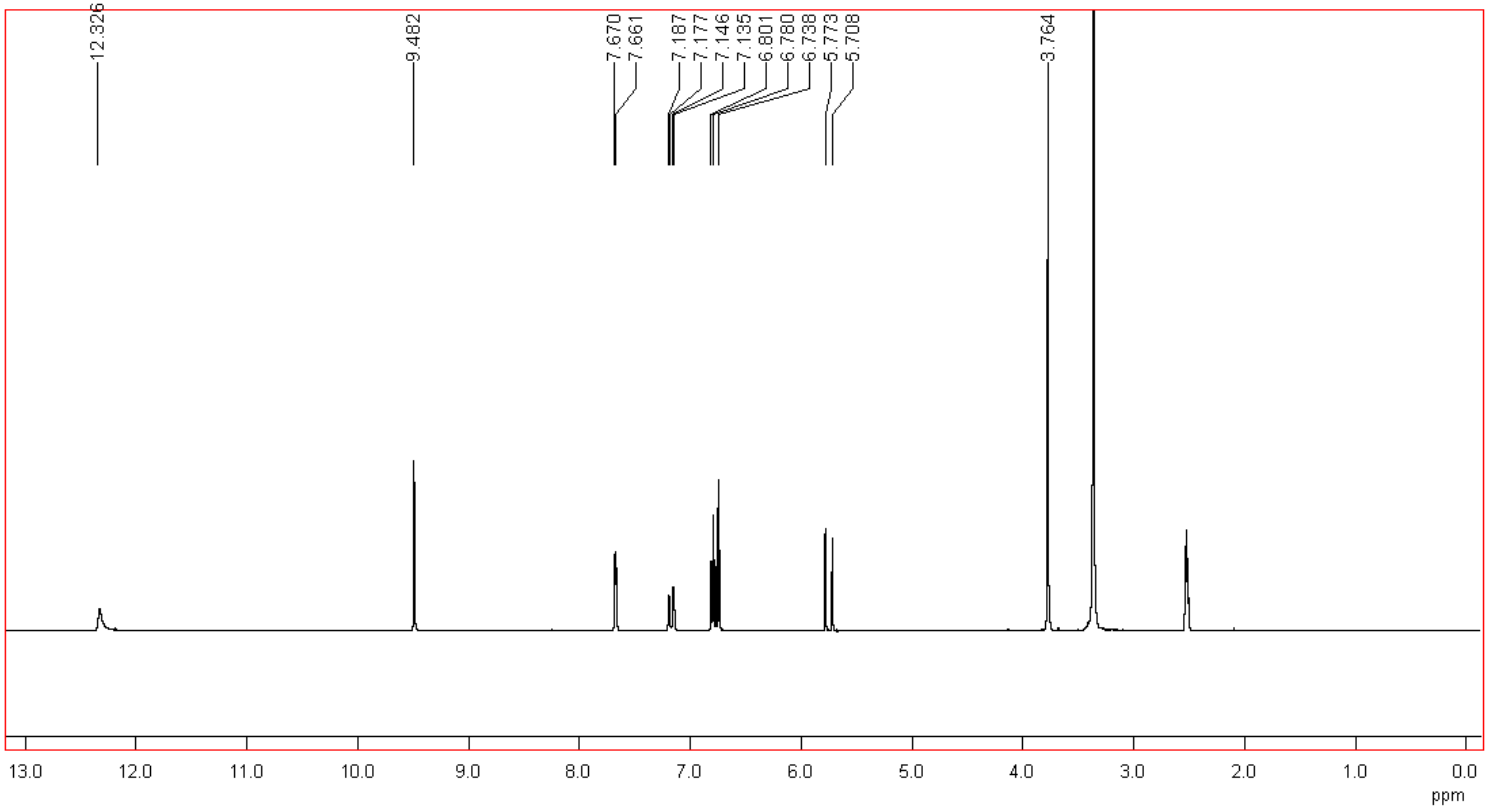
Figure S1. ^{1}H NMR spectrum of *E*-**1** (*trans*-ferulic acid). Solvent DMSO.

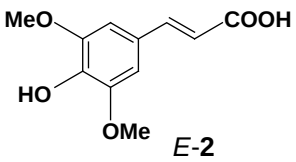




Z-**1**

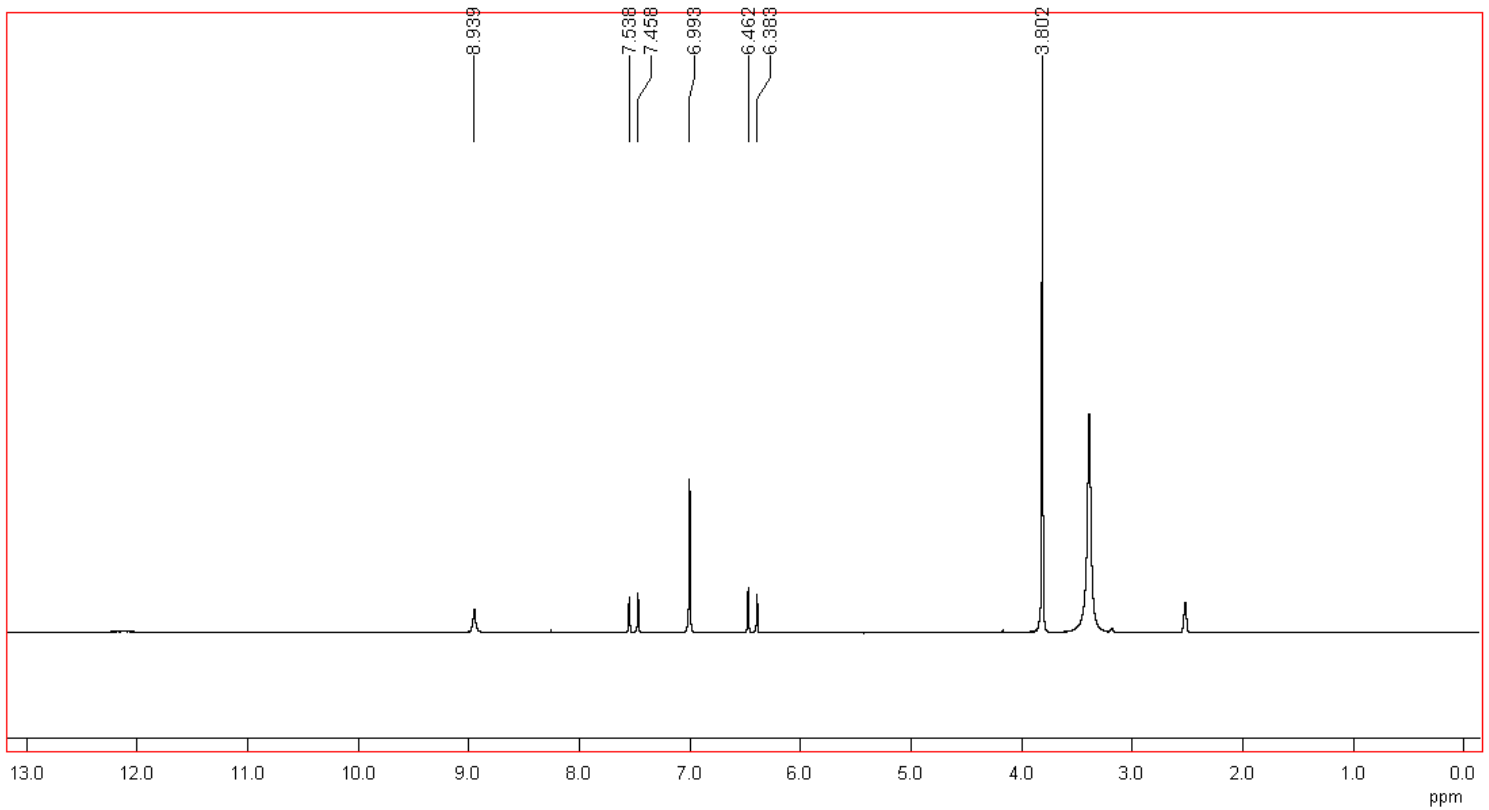
Figure S2. ^{1}H NMR spectrum of *Z*-**1** (*cis*-ferulic acid). Solvent DMSO.

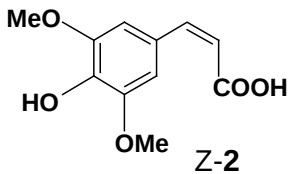




E-**2**

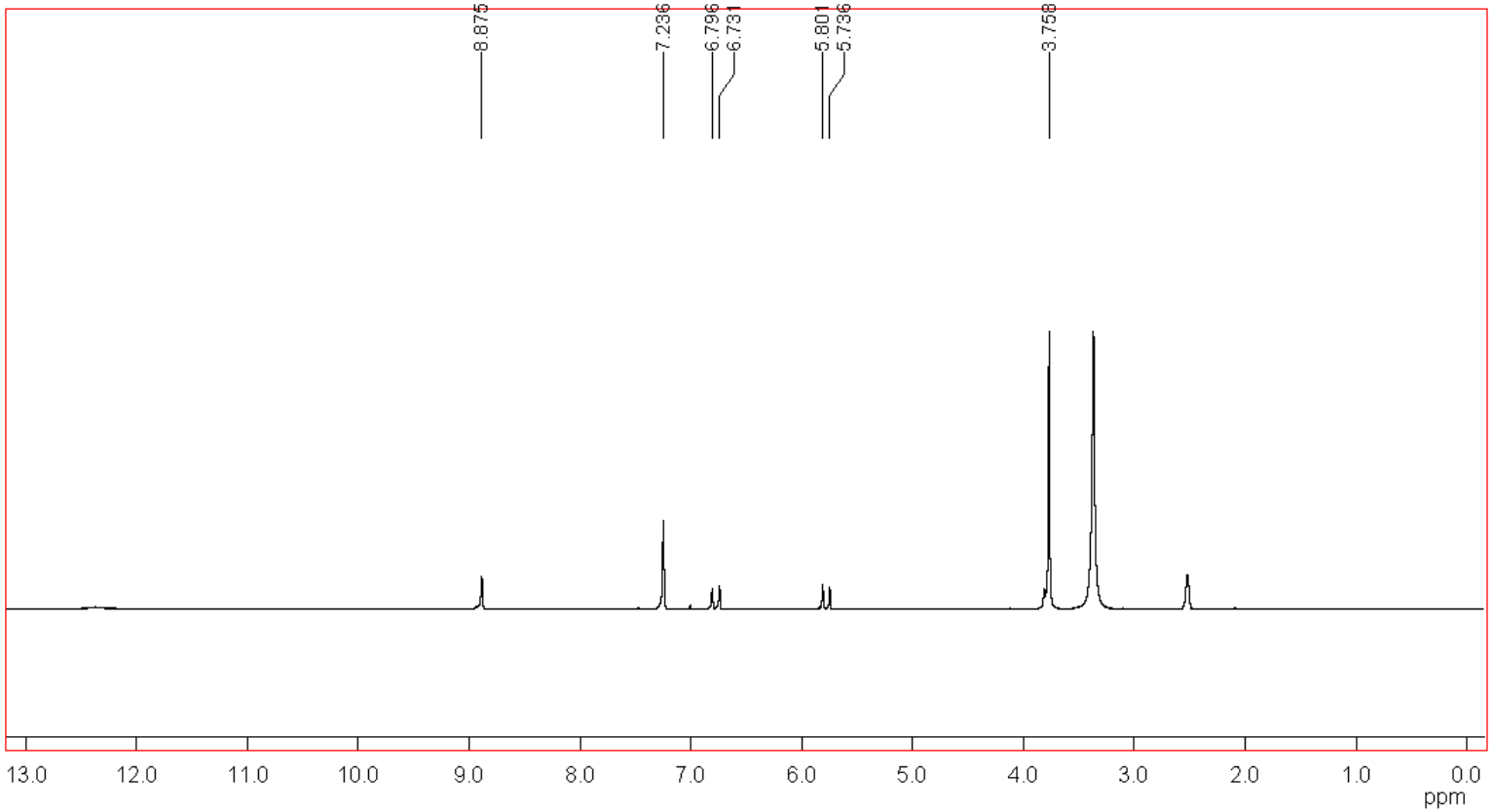
Figure S3. ^{1}H NMR spectrum of *E*-**2** (*trans*-sinapinic acid). Solvent DMSO.

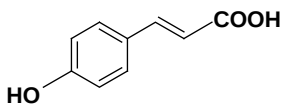




Z-**2**

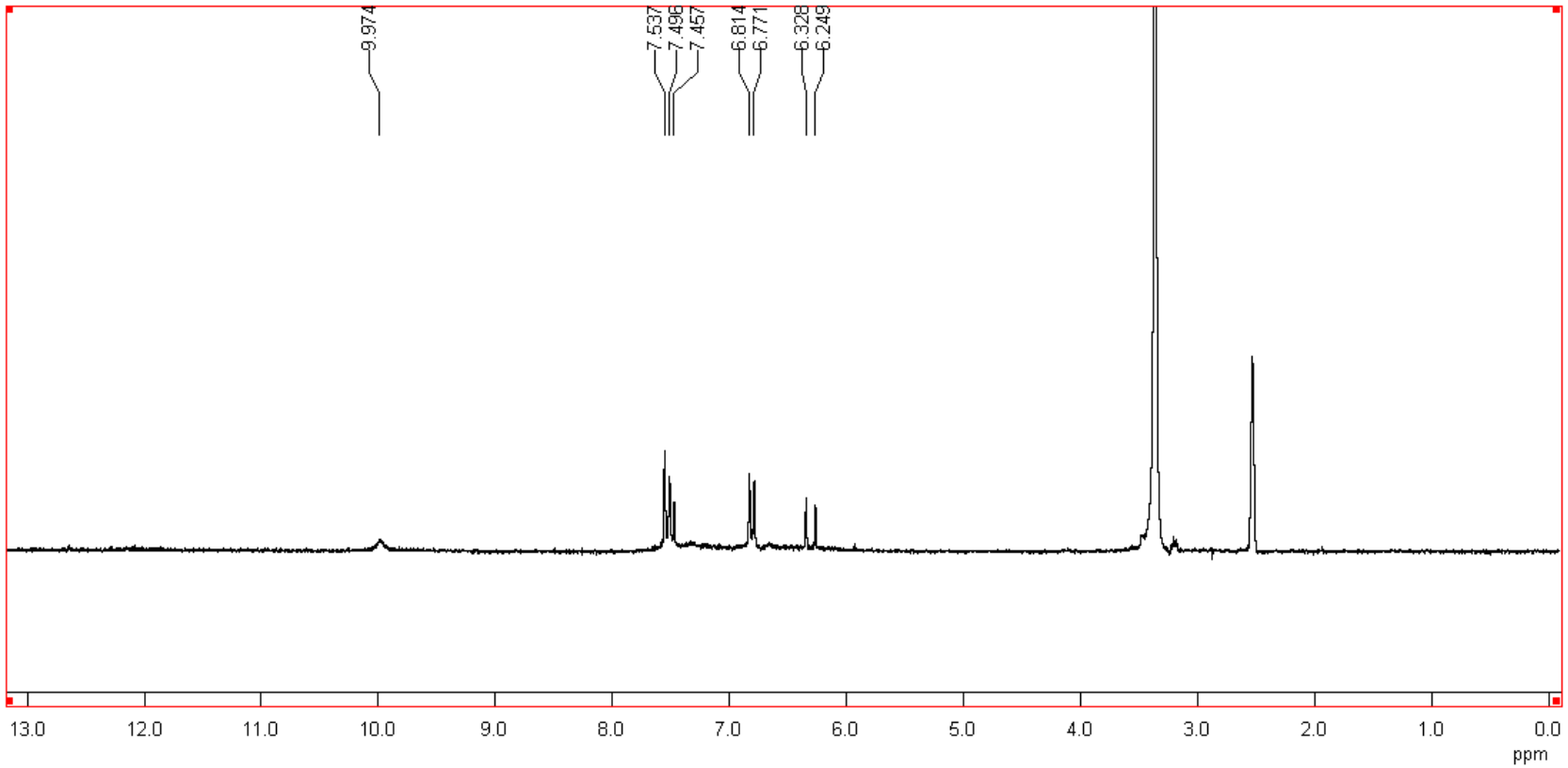
Figure S4. ^{1}H NMR spectrum of *Z*-**2** (cis-sinapinic acid). Solvent DMSO.

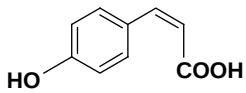




E-**3**

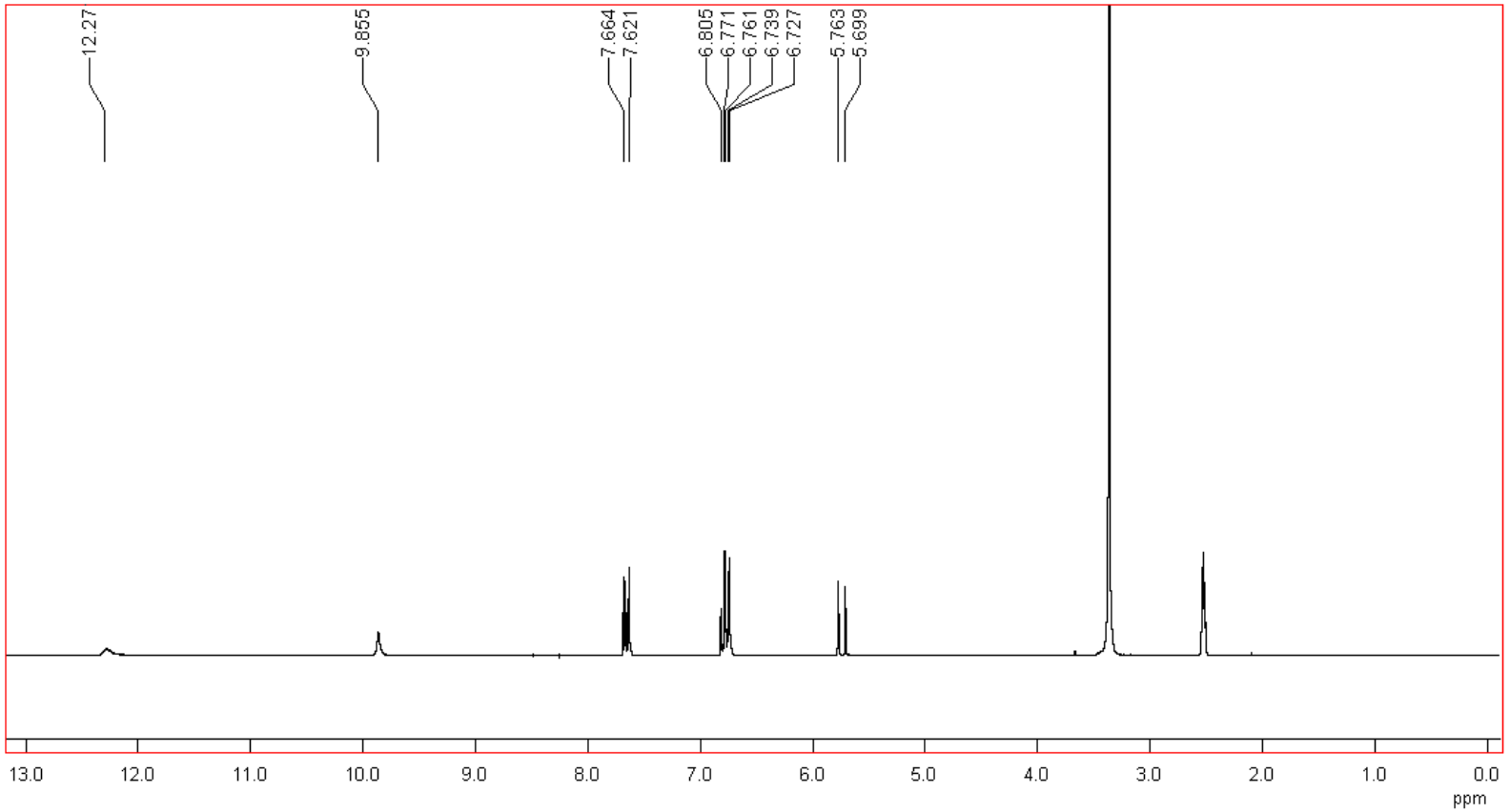
Figure S5. ^{1}H NMR spectrum of *E*-**3** (*trans*-p-coumaric acid). Solvent DMSO.

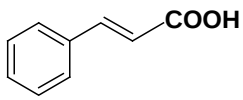




Z-**3**

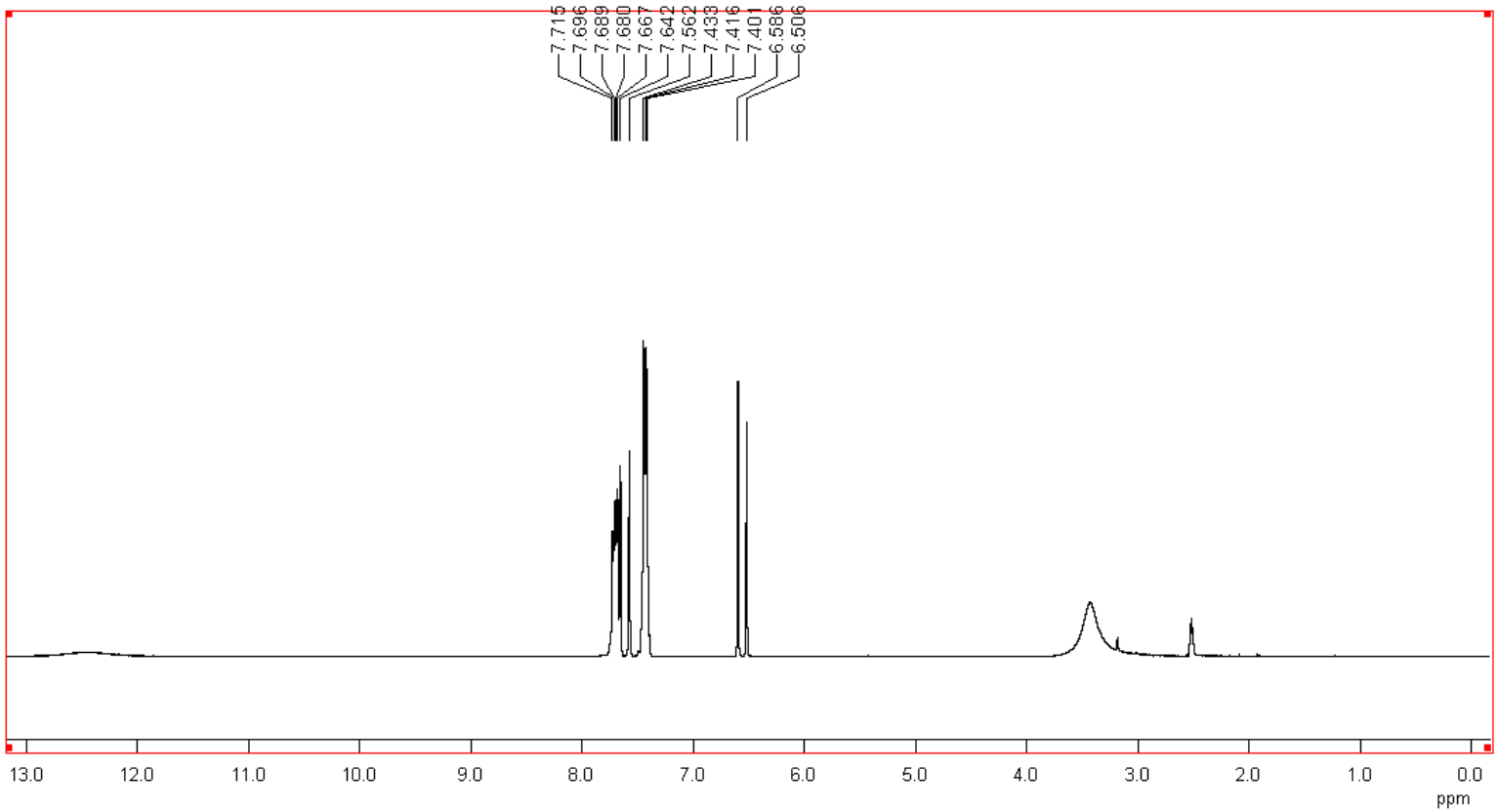
Figure S6. ^{1}H NMR spectrum of *Z*-**3** (*cis*-p-coumaric acid). Solvent DMSO.

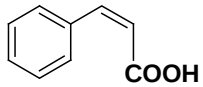




E-**4**

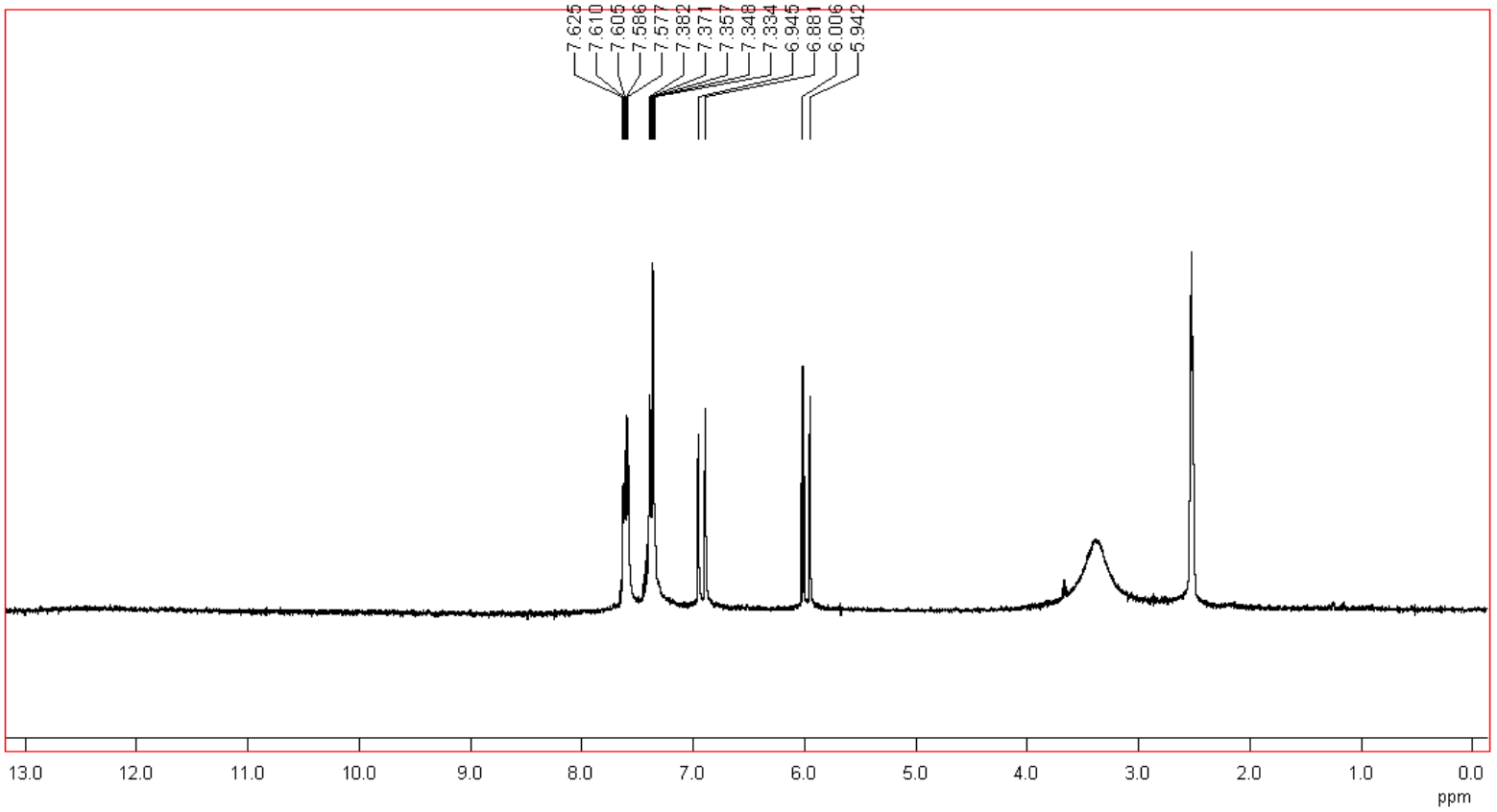
Figure S7. ^{1}H NMR spectrum of *E*-**4** (*trans*-cinnamic acid). Solvent DMSO.

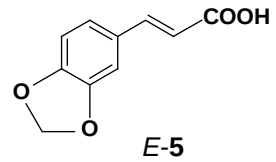




Z-**4**

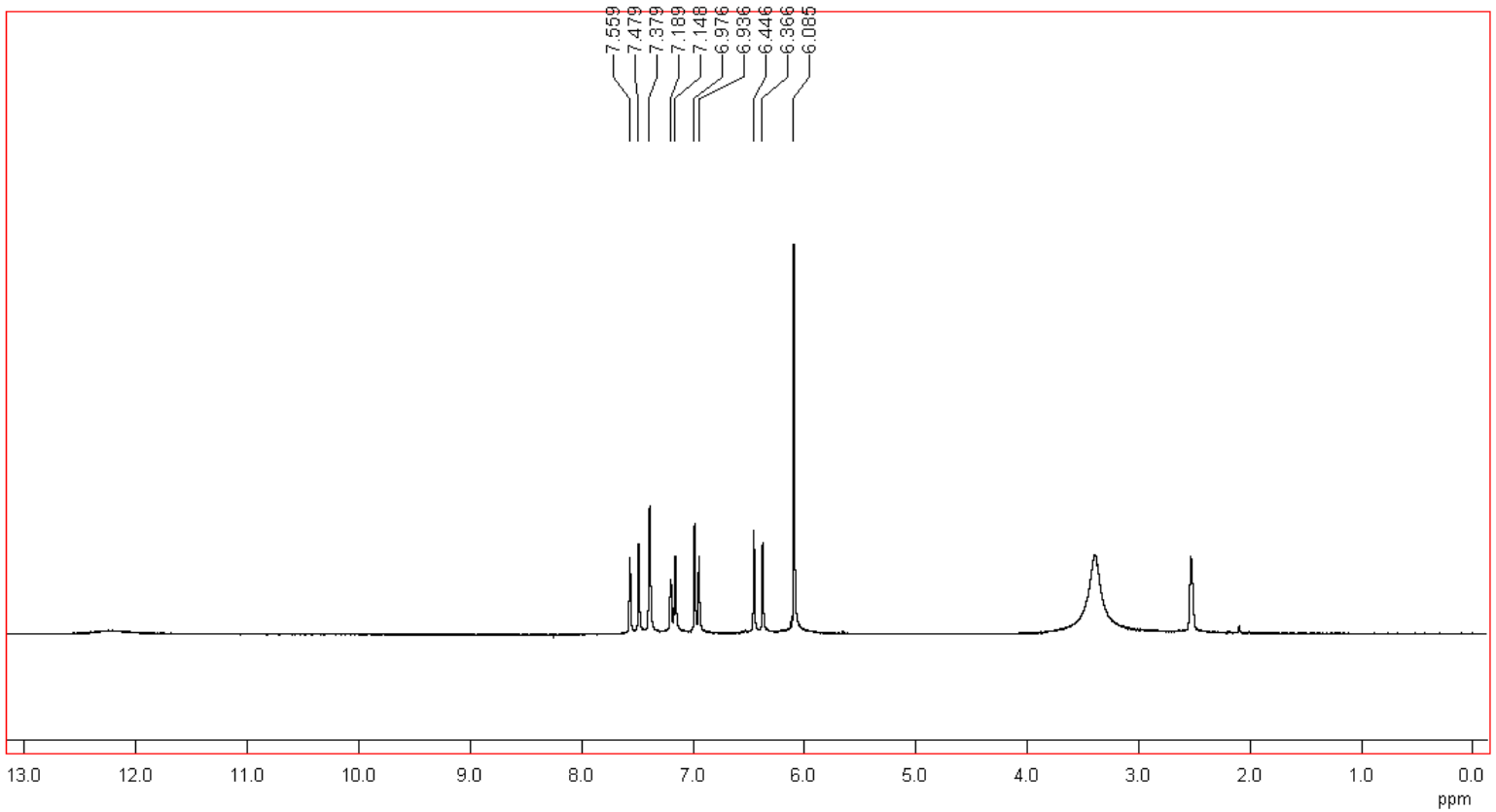
Figure S8. ^{1}H NMR spectrum of *Z*-**4** (*cis*-cinnamic acid). Solvent DMSO.

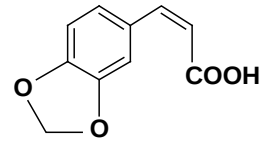




E-**5**

Figure S9. ^{1}H NMR spectrum of *E*-**5** (*trans*-3,4-(methylenedioxy)cinnamic acid). Solvent DMSO.





Z-**5**

Figure S10. ^{1}H NMR spectrum of *Z*-**5** (*cis*-3,4-(methylenedioxy)cinnamic acid). Solvent DMSO.