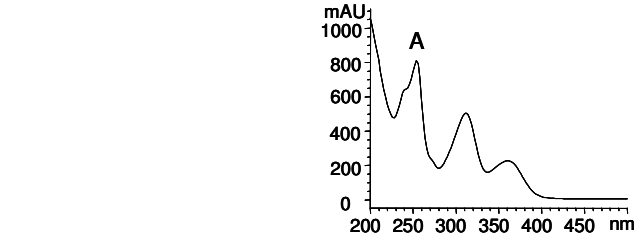

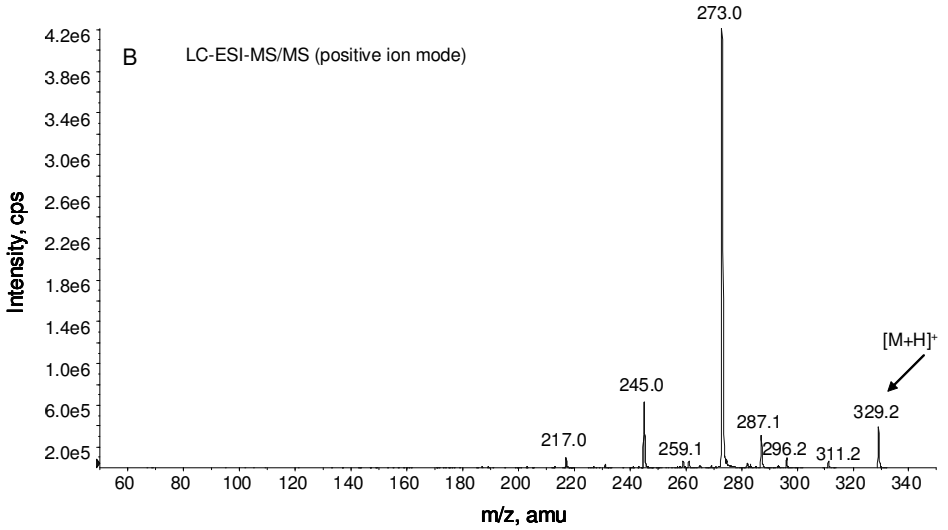

C

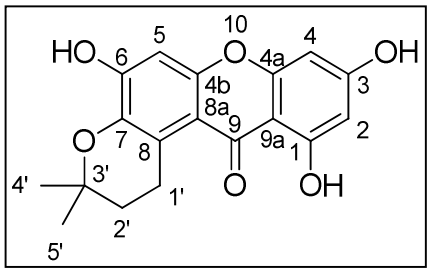

Figure S1. UV (A), MS (B), and ^{1}H and ^{13}C NMR data (C) of hyperxanthone E isolated from elicitor-treated *H. calycinum* cell cultures.

position	^{1}H (δ_H)	^{13}C (δ_C)
1	-	164.70
2	6.20 [1H, d, 2.2 Hz]	98.56
3	-	165.20
4	6.33 [1H, d, 2.2 Hz]	93.74
4a	-	158.05*
4b	-	154.22*
5	6.79 [1H, s]	101.48
6	-	154.00*
7	-	139.97
8	-	122.34
8a	-	111.30
9	-	183.13
9a	-	103.84
1'	3.48 [2H, t, 6.8 Hz]	23.17
2'	1.90 [2H, t, 6.8 Hz]	33.21
3'	-	75.33
4', 5'	1.37 [6H, s]	26.43

* These chemical shifts are interchangeable.

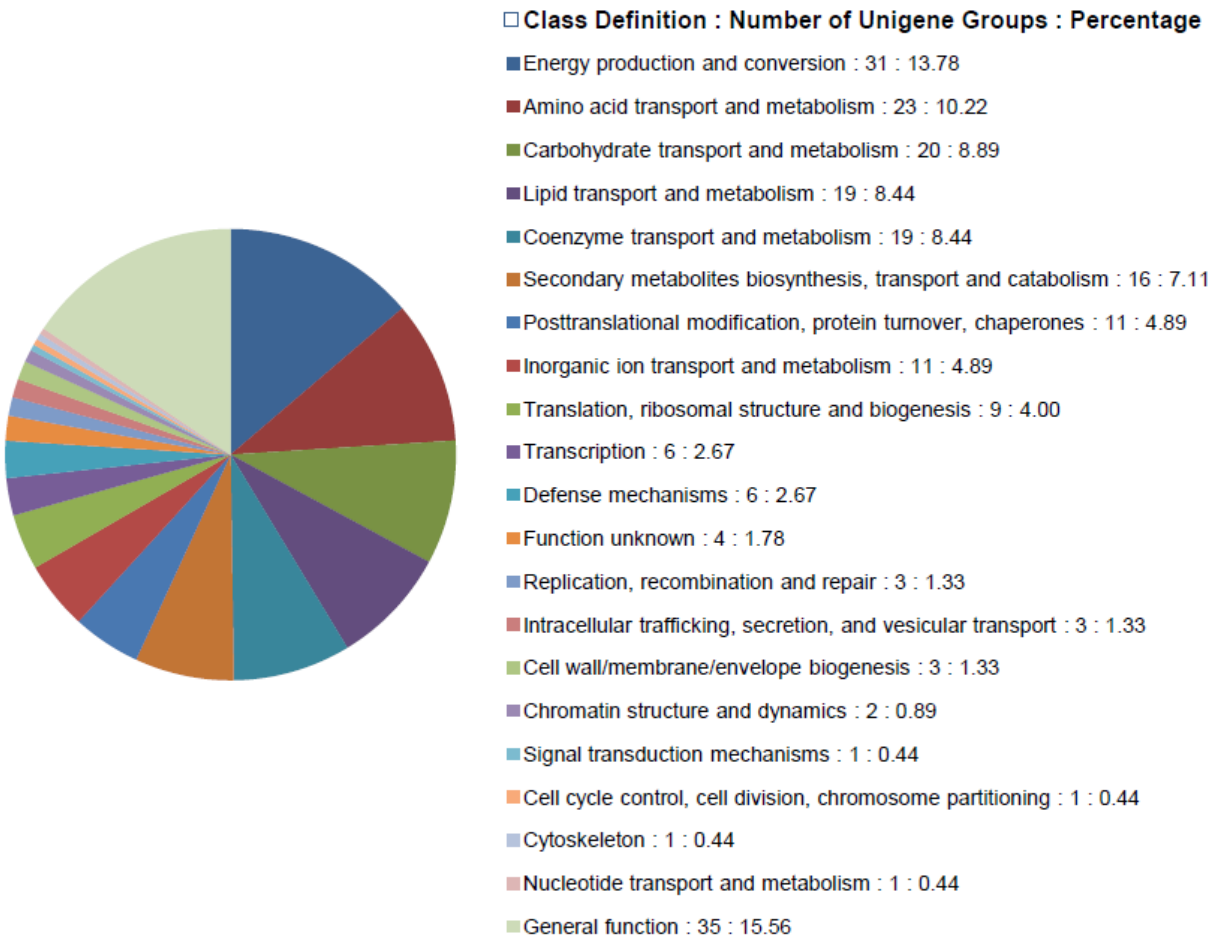

Figure S2. Proposed metabolic roles of differentially expressed unigenes from a subtracted cDNA library of *H. calycinum*.

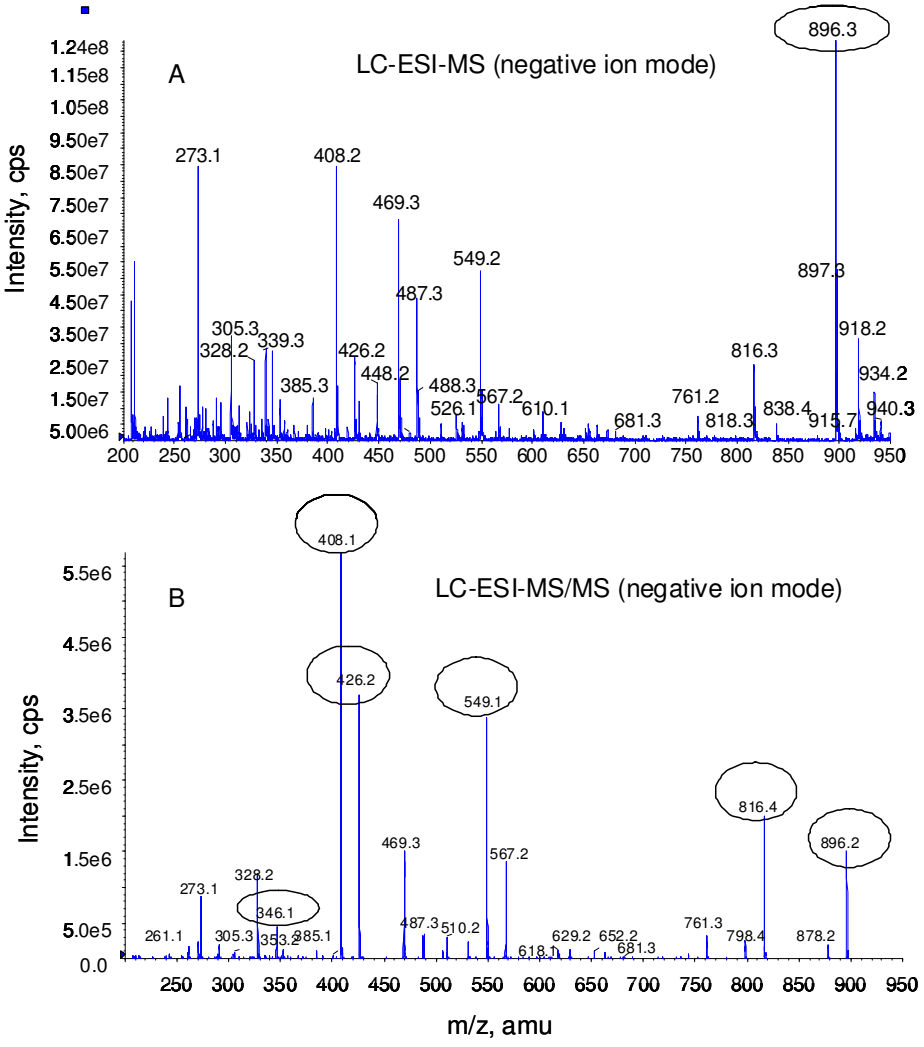

Figure S3. LC-ESI-MS analysis of CNL-formed cinnamoyl-CoA represented in the mass spectrum A by the molecular ion $[M-H]^-$ at *m/z* 896.3. This singly charged cinnamoyl-CoA ion was selected for further fragmentation and the product ions were recorded in negative ion mode (B). MS/MS analysis showed characteristic fragments of CoA and phosphoadenosine-containing compounds, such as $[AMP-H]^-$ at *m/z* 346.3, $[ADP-H]^-$ at *m/z* 426.2, and $[ADP-H_2O-H]^-$ at *m/z* 408.2, together with fragments containing parts of the cinnamoyl moiety, such as $[M-H_2PO_3]^-$ at *m/z* 816.2 and $[M-AMP-H]^-$ at *m/z* 549.2.

Table SI. *Accession numbers of amino acid sequences used for phylogenetic reconstruction*

Sequence	**Accession No.**
Capsicum annuum 4CL	AAG43823
Nicotiana tabacum 4CL1	O24145
Solanum tuberosum 4CL1	P31684
Solanum tuberosum 4CL2	P31685
Nicotiana tabacum 4CL	AAB18638
Nicotiana tabacum 4CL2	O24146
Vanilla planifolia 4CL	O24540
Petroselinum crispum 4CL1	P14913
Scutellaria baicalensis 4CL	BAD90936
Salvia miltiorrhiza 4CL2	AAP68991
Arabidopsis thaliana 4CL1	NP_001077697
Arabidopsis thaliana 4CL2	NP_188761
Ruta graveolens 4CL2	ABY60843
Populus trichocarpa x *deltoids* 4 CL3	AAK58908
Sorbus aucuparia 4CL1	ADF30254
Rubus idaeus 4CL1	AAF91310
Medicago truncatula 4CL	XP_003637266
Glycine max 4CL1	NP_001236418
Amorpha fruticosa 4CL	AAL35216
Sorbus aucuparia 4CL2	ADE96996
Rubus idaeus 4CL2	AAF91309
Populus trichocarpa x *deltoids* 4CL2	AAC39365
Populus trichocarpa x *deltoids* 4CL1	AAC39366
Salvia miltiorrhiza 4CL1	AAP68990
Physcomitrella patens 4CL1 [a]	ABY21312
Physcomitrella patens 4CL4 [a]	ABY21315
Physcomitrella patens 4CL2 [a]	ABY21313
Physcomitrella patens 4CL3 [a]	ABY21314
Selaginella moellendorffii 4CL [b]	EFJ29005
Pinus radiate 4CL [c]	ACF35279
Pinus taeda 4CL [c]	AAB42383
Pinus massoniana 4CL [c]	ACO40513
Nothotsuga longibracteata 4CL [c]	AAF74016
Tsuga Canadensis 4CL [c]	AAF74019
Abies beshanzuensis 4CL [c]	AAF74014
Larix gmelinii var. Olgensis 4CL [c]	AAQ05330
Pseudotsuga menziesii 4CL [c]	AAQ05340
Picea wilsonii 4CL [c]	ADC97166
Lolium perenne 4CL1	AAF37732
Arabidopsis thaliana 4CL3	NP_849844
Ruta graveolens 4CL1	ABY60842
Lithospermum erythrorhizon 4CL	BAA08366

Sequence (continued)	**Accession No.**
Agastache rugosa 4CL	AAT02218
Glycine max 4CL2	NP_001236236
Glycine max 4CL4	CAC36095
Glycine max 4CL3	AAC97389
Camellia sinensis 4CL	ABA40922
Populus trichocarpa x *deltoids* 4CL4	AAK58909
Gossypium hirsutum 4CL2	ACZ06243
Rubus idaeus 4CL3	AAF91308
Sorbus aucuparia 4CL3	ADE96997
Prunus avium 4CL	ADZ54779
Oryza sativa 4CL	CAA36850
Neosinocalamus affinis 4CL	ACA09448
Lolium perenne 4CL2	AAF37733
Lolium perenne 4CL3	AAF37734
Panicum virgatum 4CL1	ACD02135
Cenchrus purpureus 4CL	AEW12812
Zea mays 4CL	AAS67644
Medicago truncatula OSBZL1	XP_003600627
Hypericum calycinum CNL	AFS60176
Petunia hybrida CNL	AEO52693
Arabidopsis thaliana CNL	Q9SS01
Brassica rapa subsp. Pekinensis BZL	ACR10278
Clarkia breweri BZL/CNL	AEO52695
Medicago truncatula OSBZL2	XP_003610946
Medicago truncatula OSBZL3	XP_003610948
Medicago truncatula OSBZL4	XP_003629166
Medicago truncatula OSBZL5	XP_003609738
Medicago truncatula OSBZL6	XP_003616111
Glycine max OSBZL1	XP_003518357
Glycine max OSBZL2	XP_003544347
Medicago truncatula OSBZL7	XP_003616110
Medicago truncatula OSBZL8	XP_003616108
Arabidopsis lyrata fatty acid CL	XP_002880289

[a]moss, [b]pteridophyte, [c]gymnosperm.