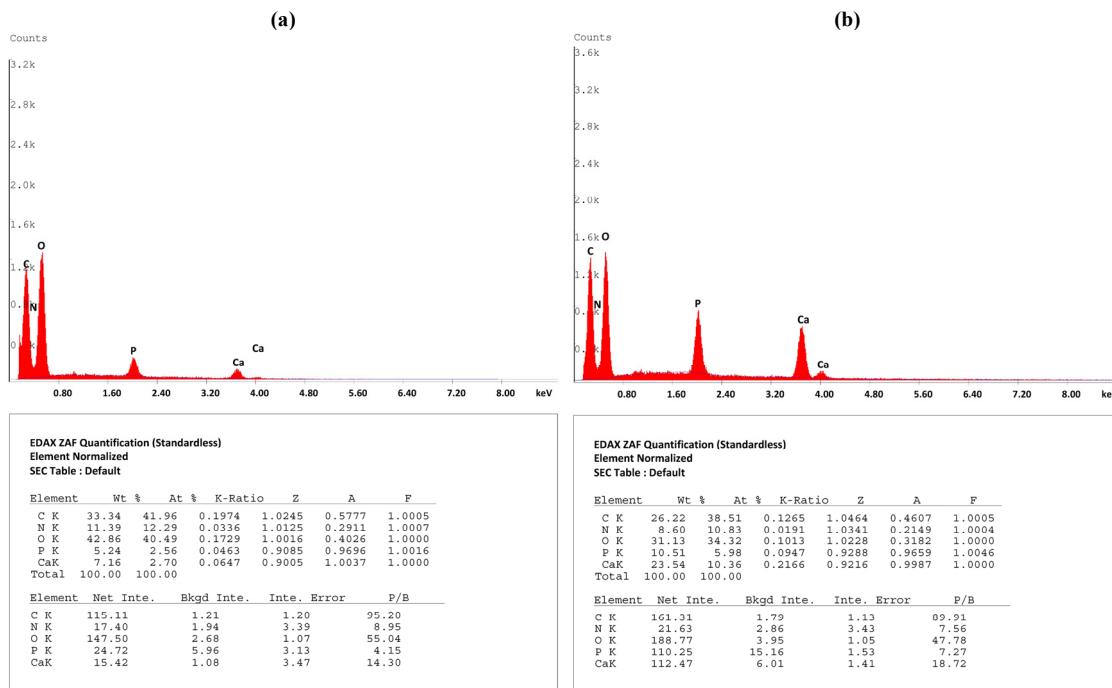


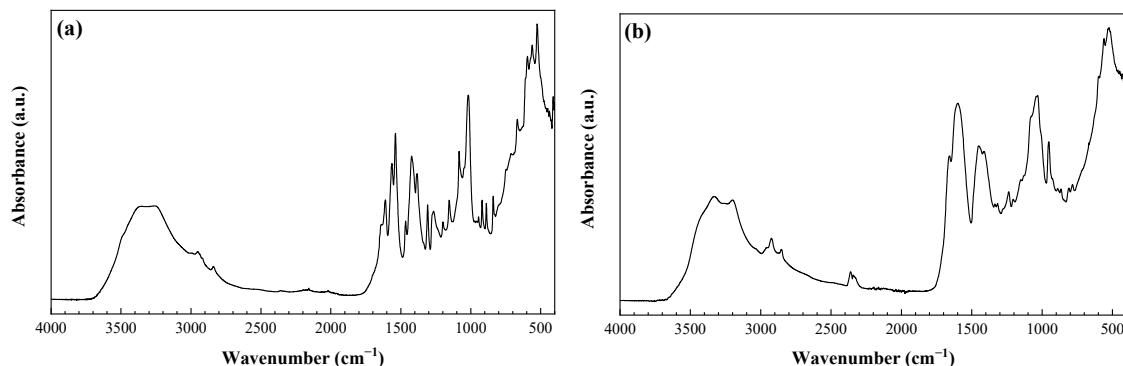
# *Uncaria tomentosa*-loaded chitosan oligomers–hydroxyapatite–carbon nitride nanocarriers for postharvest fruit protection

A. Santiago-Aliste, E. Sánchez-Hernández, L. Buzón-Durán, J. L. Marcos-Robles, J. Martín-Gil, and P. Martín-Ramos

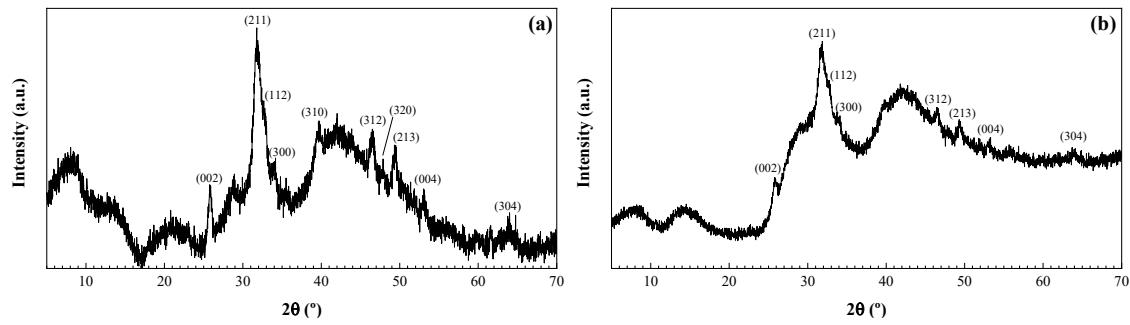
## SUPPORTING INFORMATION



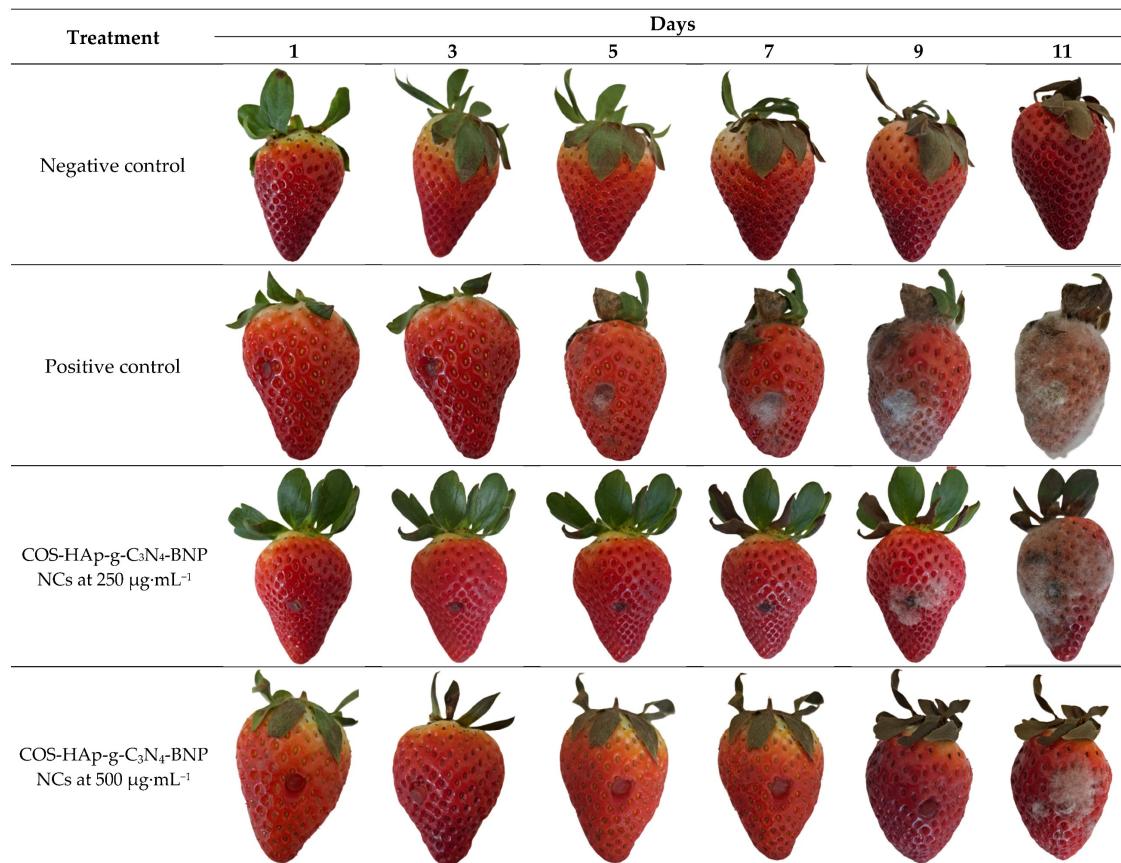
**Figure S1.** EDS multi-elemental characterization of the (a) empty nanocarriers and (b) nanocarriers loaded with *U. tomentosa* extract.



**Figure S2.** ATR-FTIR spectra of the (a) empty nanocarriers and (b) nanocarriers loaded with *U. tomentosa* extract.



**Figure S3.** X-ray powder diffraction pattern of the (a) empty nanocarriers and (b) nanocarriers loaded with *U. tomentosa* extract.



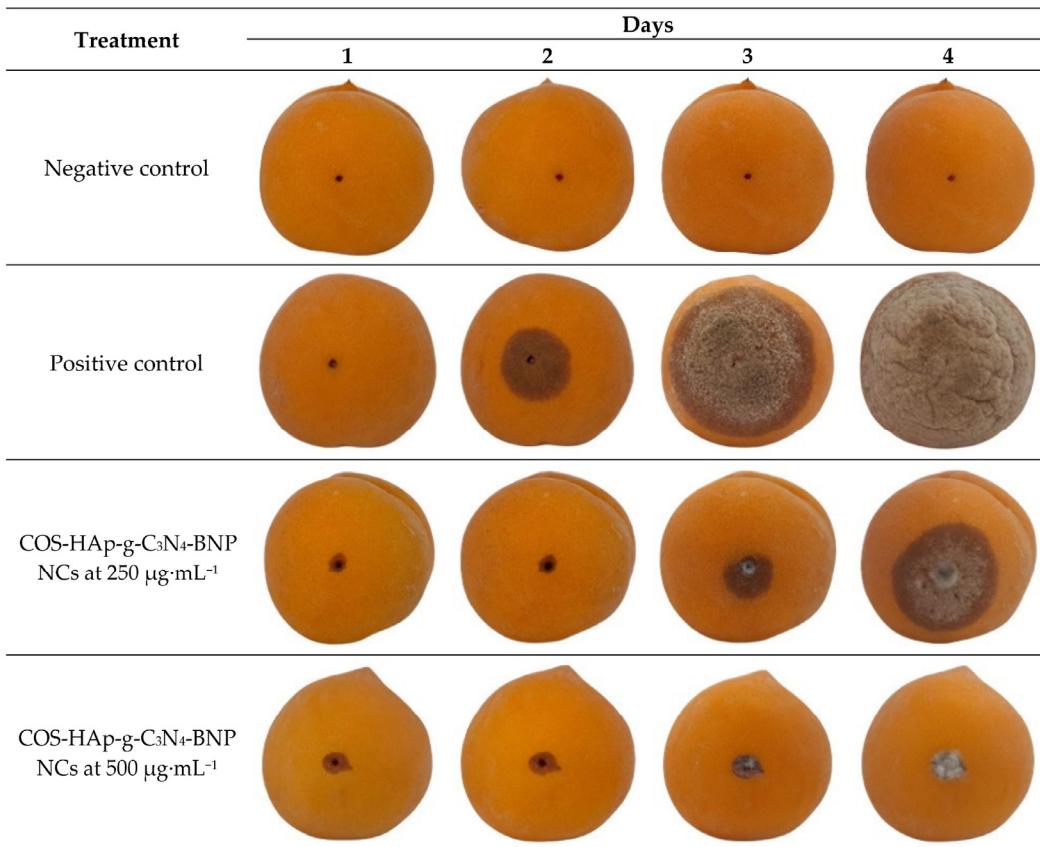
**Figure S4.** External lesions caused by *B. cinerea* on strawberries cv. “Fortuna” eleven days after artificial inoculation in the presence/absence of the NC-based treatment: (a) negative control; (b) fruits artificially inoculated with *B. cinerea* (positive control); (c) fruits treated with the COS–HAp–g–C<sub>3</sub>N<sub>4</sub> NCs loaded with the BNP at 250  $\mu\text{g}\cdot\text{mL}^{-1}$ ; (d) fruits treated with the COS–HAp–g–C<sub>3</sub>N<sub>4</sub> NCs loaded with the BNP at 500  $\mu\text{g}\cdot\text{mL}^{-1}$ . Only one replicate per treatment is shown.

Treatment	Days				
	1	3	5	6	7
Negative control					
Positive control					
COS-HAp-g-C <sub>3</sub> N <sub>4</sub> -BNP NCs at 375 µg·mL <sup>-1</sup>					
COS-HAp-g-C <sub>3</sub> N <sub>4</sub> -BNP NCs at 750 µg·mL <sup>-1</sup>					

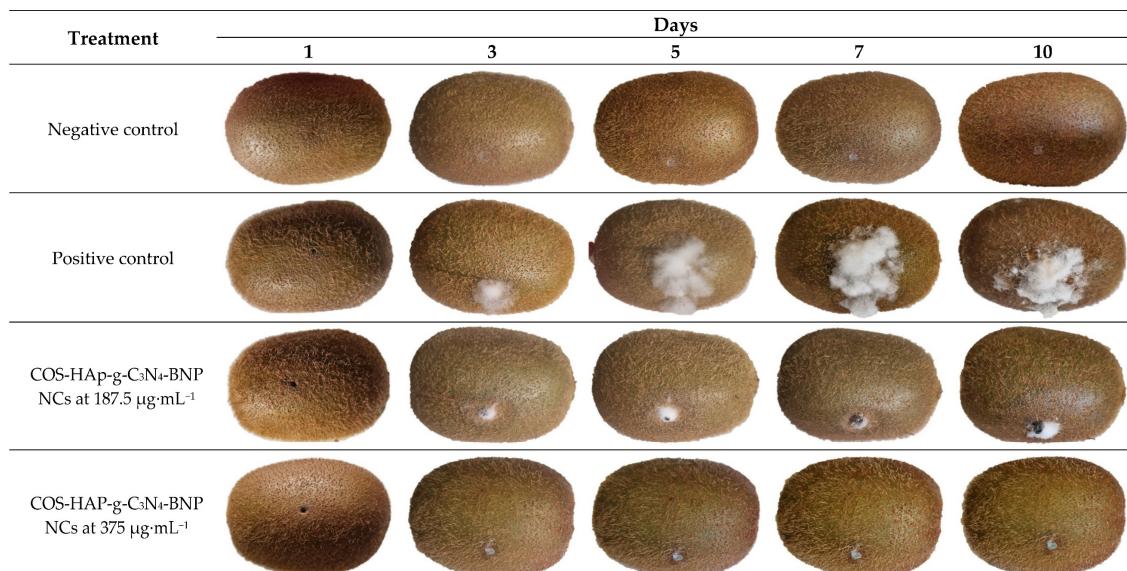
**Figure S5.** External lesions caused by *C. gloeosporioides* on mangoes cv. “Keitt” seven days after artificial inoculation in the presence/absence of the NC-based treatment: (a) negative control; (b) fruits artificially inoculated with *C. gloeosporioides* (positive control); (c) fruits treated with the COS–HAp–g–C<sub>3</sub>N<sub>4</sub> NCs loaded with the BNP at 375 µg·mL<sup>-1</sup>; (d) fruits treated with the COS–HAp–g–C<sub>3</sub>N<sub>4</sub> NCs loaded with the BNP at 750 µg·mL<sup>-1</sup>. Only one replicate per treatment is shown.

Treatment	Days					
	1	5	7	9	12	15
Negative control						
Positive control						
COS-HAp-g-C <sub>3</sub> N <sub>4</sub> -BNP NCs at 375 µg·mL <sup>-1</sup>						
COS-HAp-g-C <sub>3</sub> N <sub>4</sub> -BNP NCs at 750 µg·mL <sup>-1</sup>						

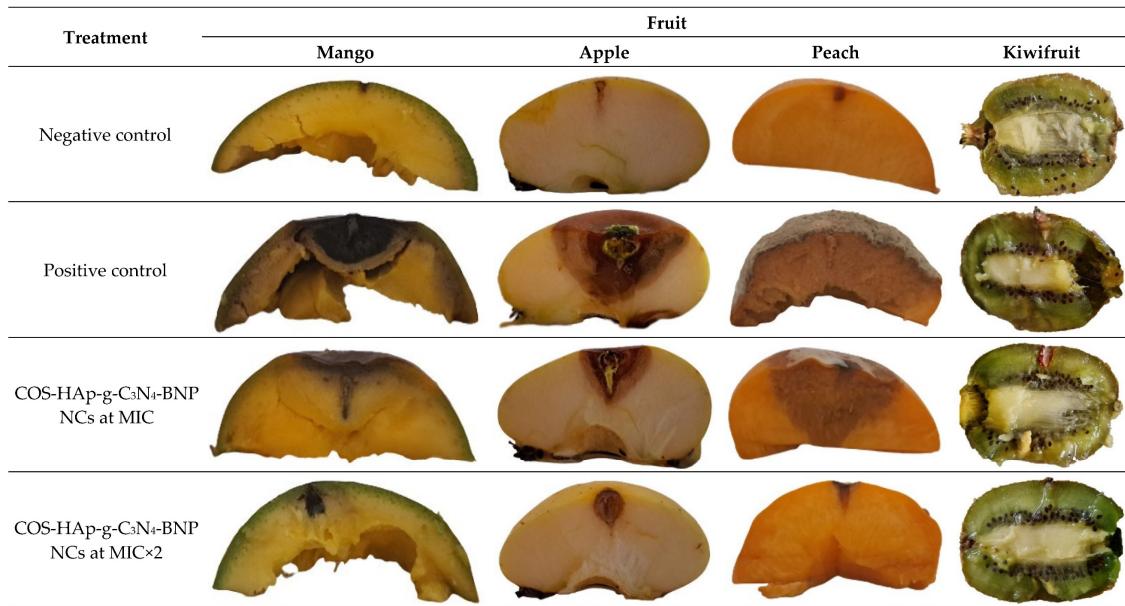
**Figure S6.** External lesions caused by *P. expansum* on apples cv. “Golden Delicious” fifteen days after artificial inoculation in the presence/absence of the NC-based treatment: (a) negative control; (b) fruits artificially inoculated with *P. expansum* (positive control); (c) fruits treated with the COS–HAp–g–C<sub>3</sub>N<sub>4</sub> NCs loaded with the BNP at 375 µg·mL<sup>-1</sup>; (d) fruits treated with the COS–HAp–g–C<sub>3</sub>N<sub>4</sub> NCs loaded with the BNP at 750 µg·mL<sup>-1</sup>. Only one replicate per treatment is shown.



**Figure S7.** External lesions caused by *M. laxa* on peaches cv. “Summer sun” four days after artificial inoculation in the presence/absence of the NC-based treatment: (a) negative control; (b) fruits artificially inoculated with *M. laxa* (positive control); (c) fruits treated with the COS–HAp–g–C<sub>3</sub>N<sub>4</sub> NCs loaded with the BNP at 250 µg·mL<sup>-1</sup>; (d) fruits treated with the COS–HAp–g–C<sub>3</sub>N<sub>4</sub> NCs loaded with the BNP at 500 µg·mL<sup>-1</sup>. Only one replicate per treatment is shown.



**Figure S8.** External lesions caused by *S. sclerotiorum* on kiwifruit cv. “Hayward Green” ten days after artificial inoculation in the presence/absence of the NC-based treatment: (a) negative control; (b) fruits artificially inoculated with *S. sclerotiorum* (positive control); (c) fruits treated with the COS–HAp–g–C<sub>3</sub>N<sub>4</sub> NCs loaded with the BNP at 187.5 µg·mL<sup>-1</sup>; (d) fruits treated with the COS–HAp–g–C<sub>3</sub>N<sub>4</sub> NCs loaded with the BNP at 375 µg·mL<sup>-1</sup>. Only one replicate per treatment is shown.



**Figure S9.** Internal lesions caused by *C. gloeosporioides* on mangoes, *P. expansum* on apples, *M. laxa* on peaches, and *S. sclerotiorum* on kiwifruit in the presence/absence of the NC-based treatment. Only one replicate per treatment is shown.

**Table S1.** Results of the normality and homoscedasticity tests, along with those of Kruskal-Wallis test, for the mycelial growth inhibition data presented in Figure 2 of the main document.

	<i>B. cinerea</i>	<i>C. gloeosporioides</i>	<i>P. expansum</i>	<i>M. laxa</i>	<i>S. sclerotiorum</i>
Test on the normality of the residues (p-value, two-tailed) *	<0.0001	<0.0001	<0.0001	<0.0001	<0.0001
Test for homoscedasticity of the residuals, treatment*concentration factor (p-value, two-tailed) *	<0.0001	<0.0001	<0.0001	<0.0001	<0.0001
Kruskal-Wallis test (p-value, one-tailed)	<0.0001	<0.0001	<0.0001	<0.0001	<0.0001

Since the computed p-values are lower than the significance level  $\alpha = 0.05$ , one can reject the null hypothesis (i.e., that the residuals follow a Normal distribution in the case of the Shapiro-Wilk test and that the residuals are homoscedastic in the case of Levene test)

**Table S2.** Results of the ANOVA, normality, and homoscedasticity tests for the lesion size data presented in Table 4 of the main document.

	Strawberry	Mango	Apple	Peach	Kiwifruit
Analysis of variance (Pr > F)	<0.0001	<0.0001	<0.0001	<0.0001	<0.0001
Test on the normality of the residues (p-value, two-tailed) *	0.365	0.371	0.294	0.386	0.136
Test for homoscedasticity of the residuals (p-value, two-tailed) *	0.212	0.217	0.274	0.228	0.115

Since the computed p-values are greater than the significance level  $\alpha = 0.05$ , one cannot reject the null hypothesis (i.e., that the residuals follow a Normal distribution in the case of the Shapiro-Wilk test and that the residuals are homoscedastic in the case of Levene test)

**Table S3.** Kruskal-Wallis test and multiple pairwise comparisons using the Conover-Iman procedure for *B. cinerea* mycelial growth inhibition values.

Treatment Concentration	Mean of ranks	Groups
COS-HAp-g-C <sub>3</sub> N <sub>4</sub>  1000	23.000	A
COS-HAp-g-C <sub>3</sub> N <sub>4</sub>  1500	23.000	A
COS-HAp-g-C <sub>3</sub> N <sub>4</sub>  500	23.000	A
COS-HAp-g-C <sub>3</sub> N <sub>4</sub>  750	23.000	A
COS-HAp-g-C <sub>3</sub> N <sub>4</sub> -BNP 1000	23.000	A
COS-HAp-g-C <sub>3</sub> N <sub>4</sub> -BNP 1500	23.000	A
COS-HAp-g-C <sub>3</sub> N <sub>4</sub> -BNP 250	23.000	A
COS-HAp-g-C <sub>3</sub> N <sub>4</sub> -BNP 375	23.000	A
COS-HAp-g-C <sub>3</sub> N <sub>4</sub> -BNP 500	23.000	A
COS-HAp-g-C <sub>3</sub> N <sub>4</sub> -BNP 750	23.000	A
<i>U. tomentosa</i>  1000	23.000	A
<i>U. tomentosa</i>  1500	23.000	A
<i>U. tomentosa</i>  375	23.000	A
<i>U. tomentosa</i>  500	23.000	A
<i>U. tomentosa</i>  750	23.000	A
COS-HAp-g-C <sub>3</sub> N <sub>4</sub> -BNP 187.5	47.000	B
<i>U. tomentosa</i>  250	50.000	C
<i>U. tomentosa</i>  187.5	53.000	D
<i>U. tomentosa</i>  125	56.000	E
<i>U. tomentosa</i>  93.75	59.167	F
COS-HAp-g-C <sub>3</sub> N <sub>4</sub>  375	61.833	G
COS-HAp-g-C <sub>3</sub> N <sub>4</sub> -BNP 125	65.000	H
<i>U. tomentosa</i>  62.5	68.000	I
COS-HAp-g-C <sub>3</sub> N <sub>4</sub>  250	71.000	J
COS-HAp-g-C <sub>3</sub> N <sub>4</sub> -BNP 93.75	74.000	K
COS-HAp-g-C <sub>3</sub> N <sub>4</sub> -BNP 62.5	77.000	L
COS-HAp-g-C <sub>3</sub> N <sub>4</sub>  125	86.000	M
COS-HAp-g-C <sub>3</sub> N <sub>4</sub>  187.5	86.000	M
COS-HAp-g-C <sub>3</sub> N <sub>4</sub>  62.5	86.000	M
COS-HAp-g-C <sub>3</sub> N <sub>4</sub>  93.75	86.000	M
Control 0	86.000	M

Treatments/controls labeled with the same letters are not significantly different at  $p < 0.05$ .

**Table S4.** Kruskal-Wallis test and multiple pairwise comparisons using the Conover-Iman procedure for *C. gloeosporioides* mycelial growth inhibition values.

Treatment Concentration	Mean of ranks	Groups
COS-HAp-g-C <sub>3</sub> N <sub>4</sub>  1000	17.000	A
COS-HAp-g-C <sub>3</sub> N <sub>4</sub>  1500	17.000	A
COS-HAp-g-C <sub>3</sub> N <sub>4</sub>  500	17.000	A
COS-HAp-g-C <sub>3</sub> N <sub>4</sub>  750	17.000	A
COS-HAp-g-C <sub>3</sub> N <sub>4</sub> -BNP 1000	17.000	A
COS-HAp-g-C <sub>3</sub> N <sub>4</sub> -BNP 1500	17.000	A
COS-HAp-g-C <sub>3</sub> N <sub>4</sub> -BNP 375	17.000	A
COS-HAp-g-C <sub>3</sub> N <sub>4</sub> -BNP 500	17.000	A
COS-HAp-g-C <sub>3</sub> N <sub>4</sub> -BNP 750	17.000	A
<i>U. tomentosa</i>  1000	17.000	A
<i>U. tomentosa</i>  1500	17.000	A
COS-HAp-g-C <sub>3</sub> N <sub>4</sub>  375	35.000	B
COS-HAp-g-C <sub>3</sub> N <sub>4</sub> -BNP 250	38.000	B C
<i>U. tomentosa</i>  750	41.000	C D
COS-HAp-g-C <sub>3</sub> N <sub>4</sub> -BNP 187.5	44.000	D E
<i>U. tomentosa</i>  500	47.167	E F
COS-HAp-g-C <sub>3</sub> N <sub>4</sub>  250	49.833	F G
COS-HAp-g-C <sub>3</sub> N <sub>4</sub>  187.5	54.833	G H
<i>U. tomentosa</i>  375	54.833	G H
COS-HAp-g-C <sub>3</sub> N <sub>4</sub> -BNP 125	59.333	H I
COS-HAp-g-C <sub>3</sub> N <sub>4</sub>  125	63.167	I J
<i>U. tomentosa</i>  250	64.333	I J
COS-HAp-g-C <sub>3</sub> N <sub>4</sub> -BNP 93.75	68.333	J K
<i>U. tomentosa</i>  125	71.167	K
<i>U. tomentosa</i>  187.5	72.000	K
COS-HAp-g-C <sub>3</sub> N <sub>4</sub>  62.5	84.500	L
COS-HAp-g-C <sub>3</sub> N <sub>4</sub>  93.75	84.500	L
COS-HAp-g-C <sub>3</sub> N <sub>4</sub> -BNP 62.5	84.500	L
Control 0	84.500	L
<i>U. tomentosa</i>  62.5	84.500	L
<i>U. tomentosa</i>  93.75	84.500	L

Treatments/controls labeled with the same letters are not significantly different at  $p < 0.05$ .

**Table S5.** Kruskal-Wallis test and multiple pairwise comparisons using the Conover-Iman procedure for *M. laxa* mycelial growth inhibition values.

Treatment Concentration	Mean of ranks	Groups
COS-HAp-g-C <sub>3</sub> N <sub>4</sub>  1000	15.500	A
COS-HAp-g-C <sub>3</sub> N <sub>4</sub>  1500	15.500	A
COS-HAp-g-C <sub>3</sub> N <sub>4</sub>  750	15.500	A
COS-HAp-g-C <sub>3</sub> N <sub>4</sub> -BNP 1000	15.500	A
COS-HAp-g-C <sub>3</sub> N <sub>4</sub> -BNP 1500	15.500	A
COS-HAp-g-C <sub>3</sub> N <sub>4</sub> -BNP 250	15.500	A
COS-HAp-g-C <sub>3</sub> N <sub>4</sub> -BNP 375	15.500	A
COS-HAp-g-C <sub>3</sub> N <sub>4</sub> -BNP 500	15.500	A
COS-HAp-g-C <sub>3</sub> N <sub>4</sub> -BNP 750	15.500	A
<i>U. tomentosa</i>  1500	15.500	A
COS-HAp-g-C <sub>3</sub> N <sub>4</sub>  500	32.333	B
<i>U. tomentosa</i>  1000	34.667	B C
<i>U. tomentosa</i>  750	38.333	C D
COS-HAp-g-C <sub>3</sub> N <sub>4</sub> -BNP 187.5	41.000	D E
COS-HAp-g-C <sub>3</sub> N <sub>4</sub>  375	43.833	D E
COS-HAp-g-C <sub>3</sub> N <sub>4</sub> -BNP 125	46.833	E F
<i>U. tomentosa</i>  500	50.000	F G
COS-HAp-g-C <sub>3</sub> N <sub>4</sub>  250	53.000	G H
<i>U. tomentosa</i>  375	56.000	H I
COS-HAp-g-C <sub>3</sub> N <sub>4</sub>  187.5	59.667	I J
COS-HAp-g-C <sub>3</sub> N <sub>4</sub> -BNP 93.75	65.167	J K
<i>U. tomentosa</i>  250	65.167	J K
COS-HAp-g-C <sub>3</sub> N <sub>4</sub>  125	69.667	K
COS-HAp-g-C <sub>3</sub> N <sub>4</sub> -BNP 62.5	69.667	K
<i>U. tomentosa</i>  187.5	69.667	K
<i>U. tomentosa</i>  125	77.000	L
COS-HAp-g-C <sub>3</sub> N <sub>4</sub>  62.5	86.000	M
COS-HAp-g-C <sub>3</sub> N <sub>4</sub>  93.75	86.000	M
Control 0	86.000	M
<i>U. tomentosa</i>  62.5	86.000	M
<i>U. tomentosa</i>  93.75	86.000	M

Treatments/controls labeled with the same letters are not significantly different at  $p < 0.05$ .

**Table S6.** Kruskal-Wallis test and multiple pairwise comparisons using the Conover-Iman procedure for *P. expansum* mycelial growth inhibition values.

Treatment Concentration	Mean of ranks	Groups
COS-HAp-g-C <sub>3</sub> N <sub>4</sub>  1000	12.500	A
COS-HAp-g-C <sub>3</sub> N <sub>4</sub>  1500	12.500	A
COS-HAp-g-C <sub>3</sub> N <sub>4</sub> -BNP 1000	12.500	A
COS-HAp-g-C <sub>3</sub> N <sub>4</sub> -BNP 1500	12.500	A
COS-HAp-g-C <sub>3</sub> N <sub>4</sub> -BNP 375	12.500	A
COS-HAp-g-C <sub>3</sub> N <sub>4</sub> -BNP 500	12.500	A
COS-HAp-g-C <sub>3</sub> N <sub>4</sub> -BNP 750	12.500	A
<i>U. tomentosa</i>  1500	12.500	A
COS-HAp-g-C <sub>3</sub> N <sub>4</sub> -BNP 250	26.000	B
<i>U. tomentosa</i>  1000	29.667	B C
COS-HAp-g-C <sub>3</sub> N <sub>4</sub>  750	31.667	B C
<i>U. tomentosa</i>  750	36.667	B C D
<i>U. tomentosa</i>  500	38.500	C D
COS-HAp-g-C <sub>3</sub> N <sub>4</sub>  500	39.833	C D E
COS-HAp-g-C <sub>3</sub> N <sub>4</sub>  375	47.000	D E F
<i>U. tomentosa</i>  375	47.000	D E F
COS-HAp-g-C <sub>3</sub> N <sub>4</sub> -BNP 187.5	50.667	E F G
COS-HAp-g-C <sub>3</sub> N <sub>4</sub>  250	51.167	F G
COS-HAp-g-C <sub>3</sub> N <sub>4</sub>  187.5	56.167	F G H
<i>U. tomentosa</i>  250	57.333	F G H
<i>U. tomentosa</i>  187.5	60.667	G H
<i>U. tomentosa</i>  125	66.000	H I
COS-HAp-g-C <sub>3</sub> N <sub>4</sub>  125	67.000	H I
COS-HAp-g-C <sub>3</sub> N <sub>4</sub>  93.75	74.333	I J
COS-HAp-g-C <sub>3</sub> N <sub>4</sub> -BNP 125	79.333	J
COS-HAp-g-C <sub>3</sub> N <sub>4</sub>  62.5	83.000	J
COS-HAp-g-C <sub>3</sub> N <sub>4</sub> -BNP 62.5	83.000	J
COS-HAp-g-C <sub>3</sub> N <sub>4</sub> -BNP 93.75	83.000	J
Control 0	83.000	J
<i>U. tomentosa</i>  62.5	83.000	J
<i>U. tomentosa</i>  93.75	83.000	J

Treatments/controls labeled with the same letters are not significantly different at  $p < 0.05$ .

**Table S7.** Kruskal-Wallis test and multiple pairwise comparisons using the Conover-Iman procedure for *S. sclerotiorum* mycelial growth inhibition values.

Treatment concentration	Mean of ranks	Groups
COS-HAp-g-C <sub>3</sub> N <sub>4</sub>  1000	23.000	A
COS-HAp-g-C <sub>3</sub> N <sub>4</sub>  1500	23.000	A
COS-HAp-g-C <sub>3</sub> N <sub>4</sub>  500	23.000	A
COS-HAp-g-C <sub>3</sub> N <sub>4</sub>  750	23.000	A
COS-HAp-g-C <sub>3</sub> N <sub>4</sub> -BNP 1000	23.000	A
COS-HAp-g-C <sub>3</sub> N <sub>4</sub> -BNP 1500	23.000	A
COS-HAp-g-C <sub>3</sub> N <sub>4</sub> -BNP 187.5	23.000	A
COS-HAp-g-C <sub>3</sub> N <sub>4</sub> -BNP 250	23.000	A
COS-HAp-g-C <sub>3</sub> N <sub>4</sub> -BNP 375	23.000	A
COS-HAp-g-C <sub>3</sub> N <sub>4</sub> -BNP 500	23.000	A
COS-HAp-g-C <sub>3</sub> N <sub>4</sub> -BNP 750	23.000	A
<i>U. tomentosa</i>  1000	23.000	A
<i>U. tomentosa</i>  1500	23.000	A
<i>U. tomentosa</i>  500	23.000	A
<i>U. tomentosa</i>  750	23.000	A
COS-HAp-g-C <sub>3</sub> N <sub>4</sub>  375	47.000	B
<i>U. tomentosa</i>  375	50.000	C
COS-HAp-g-C <sub>3</sub> N <sub>4</sub> -BNP 125	53.000	D
<i>U. tomentosa</i>  250	56.000	E
COS-HAp-g-C <sub>3</sub> N <sub>4</sub>  125	75.500	F
COS-HAp-g-C <sub>3</sub> N <sub>4</sub>  187.5	75.500	F
COS-HAp-g-C <sub>3</sub> N <sub>4</sub>  250	75.500	F
COS-HAp-g-C <sub>3</sub> N <sub>4</sub>  62.5	75.500	F
COS-HAp-g-C <sub>3</sub> N <sub>4</sub>  93.75	75.500	F
COS-HAp-g-C <sub>3</sub> N <sub>4</sub> -BNP 62.5	75.500	F
COS-HAp-g-C <sub>3</sub> N <sub>4</sub> -BNP 93.75	75.500	F
Control 0	75.500	F
<i>U. tomentosa</i>  125	75.500	F
<i>U. tomentosa</i>  187.5	75.500	F
<i>U. tomentosa</i>  62.5	75.500	F
<i>U. tomentosa</i>  93.75	75.500	F

Treatments/controls labeled with the same letters are not significantly different at  $p < 0.05$ .

**Table S8.** Nanocarriers reported in the literature for the control of *Botrytis cinerea*, *Colletotrichum* spp., *Monilinia* spp., *Penicillium* spp., and *Sclerotinia sclerotiorum*.

Phytopathogen	Type of Nanocarrier	Active Ingredient Encapsulated	Encapsulation Efficiency	Type of Bioassay	Activity	Ref.
Quaternary ammonium salt modified-mesoporous silica NPs modified with carboxylatopillar[5]arene capping	Berberine hydrochloride	n.a.	In vitro, ex-situ, and in vivo	In vitro: 36.20 and 48.36% at 60 and 120 $\mu\text{g}\cdot\text{mL}^{-1}$ , respectively. Ex-situ (detached tomato leaves): 45.47 and 52.71% at 60 and 120 $\mu\text{g}\cdot\text{mL}^{-1}$ , respectively, after 54 h. In vivo (potted tomato leaves): high inhibition.	[1]	
Poly (lactic-co-glycolic acid) NPs	Pterostilbene	37-75%	In vitro	In vitro: 25% at 20 $\mu\text{g}\cdot\text{mL}^{-1}$ after 72 h.	[2]	
$\beta$ -Glucans and/or soy lecithin	Resveratrol	67-94%	In vitro	In vitro: 50-70% inhibition at 100 $\mu\text{g}\cdot\text{mL}^{-1}$	[3]	
$\beta$ -Cyclodextrin (CD) inclusion compounds dispersed in a low-density polyethylene (LDPE) film	Carvacrol and trans-cinnamaldehyde	61-92%	In vitro	In vitro: 31.4 and 10.9% fungicidal activity for LDPE doped with 1 wt% of $\beta$ -CD-carvacrol or $\beta$ -CD-cinnamaldehyde, respectively.	[4]	
Chitosan NPs	D-limonene	89.4-92.3%	In vivo	In vivo: activation of plant ( <i>Arabidopsis thaliana</i> ) immune response @ chitosan 250 $\mu\text{g}\cdot\text{mL}^{-1}$ and D-limonene 5 $\text{mg}\cdot\text{mL}^{-1}$ dose.	[5]	
Mesoporous silica NPs	Eugenol (encapsulated) and Ag <sup>+</sup> (coordinated to polydopamine as a coating)	n.a.	In vitro, ex-situ, and in vivo	In vitro: 47.92% and 71.38% inhibition at 30 and 60 $\mu\text{g}\cdot\text{mL}^{-1}$ , respectively. Ex situ (detached tomato leaves): 72.59% and 82.63% at 60 and 120 $\mu\text{g}\cdot\text{mL}^{-1}$ , respectively. In vivo (potted tomato leaves): high protection at both doses.	[6]	
Casein NPs	Eugenol	67.1-90.4%	In vitro and ex-situ	In vitro: MIC = 40.2 $\mu\text{g}\cdot\text{mL}^{-1}$ of eugenol. Ex-situ (pear fruit): 23 and 45% disease incidence after 8 and 12 days, respectively.	[7]	
ZnO@OAm nanorod-based nanocapsules	Geraniol	33-78%	In vitro and in vivo	In vitro: EC <sub>50</sub> = 150 $\mu\text{g}\cdot\text{mL}^{-1}$ for 1:3 ZnO:geraniol ratio. In vivo (tomato and cucumber plants): disease index of 3 (vs. 6 for control) in cucumber and 4 (vs. 7 for control) in tomato after 96 h	[8]	
Chitosan-pea protein	EO from <i>Hyssopus officinalis</i>	n.a.	In vitro and ex-situ	In vitro: 85% inhibition at 2 $\text{mg}\cdot\text{mL}^{-1}$ . Ex-situ (strawberry fruits): 12.2% infection on day 8 at 2 $\text{mg}\cdot\text{mL}^{-1}$ ; 0.8 disease severity (vs. 4.3 for control) on day 9.	[9]	
Chitosan NPs	EO from <i>Pistacia atlantica</i> hulls	43.3-61.5%	In vitro and ex-situ	In vitro: MIC = 20 $\mu\text{g}\cdot\text{mL}^{-1}$ . Ex-situ (strawberry fruits): 23.4% infection on the 10th day at 20 $\mu\text{g}\cdot\text{mL}^{-1}$ .	[10]	
Poly (vinyl alcohol)/chitosan nanospheres	EO from <i>Salvia officinalis</i>	66.1-73.3%	In vitro	In vitro: MIC = 0.16-0.40 $\mu\text{L}\cdot\text{mL}^{-1}$ for 0.25%, 0.5%, and 1% v/v of sage EO	[11]	
Chitosan	EO from <i>Zataria multiflora</i>	3.2-45%	In vitro and ex-situ	In vitro: MIC = 1500 $\mu\text{g}\cdot\text{mL}^{-1}$ . Ex-situ (strawberry fruits): 16.67% infection rate on day 9 at 1500 $\mu\text{g}\cdot\text{mL}^{-1}$ ; 1.5 disease severity (vs. 4.9 for control).	[12]	
Cyclodextrin-based nanosponges	1-methylcyclopropene *	n.a.	Ex-situ	Ex-situ (cut flowers): 40% inhibition at 0.25 $\mu\text{L}\cdot\text{L}^{-1}$ after 11 days.	[13]	
Chitosan-gum arabic-coated liposomes	5I-1H-indole *	92%	In vitro and ex-situ	In vitro: MIC = 25 $\mu\text{g}\cdot\text{mL}^{-1}$ . Ex-situ (strawberries, Kyoho Japanese grapes, and tangerines): high protection at 200 $\mu\text{g mL}^{-1}$ .	[14]	
ZIF-67 NPs	Boscalid *	18% loading ratio	In vitro and in vivo	In vitro: EC <sub>90</sub> = 17.6 $\mu\text{g}\cdot\text{mL}^{-1}$ . In vivo (citrus leaves): full inhibition at lower dose than non-encapsulated Boscalid.	[15]	

	Imidazolate framework-8	Dazomet *	4.4% loading content	In vitro and in vivo	In vitro: EC <sub>50</sub> = 7.9 µg·mL <sup>-1</sup> . In vivo (potted cucumber leaves): 75% efficacy after 10 days, higher than that of dazomet (52%).	[16]
<i>B. cinerea</i> , <i>S. sclerotiorum</i>	Fenhexamid and polyhexamethylene biguanide NPs	Fenhexamid *	n.a.	In vitro and in vivo	In vitro: EC <sub>50</sub> = 3.26 and 0.18 µg·mL <sup>-1</sup> for <i>B. cinerea</i> and <i>S. sclerotiorum</i> , respectively. In vivo (tomato and rape for <i>B. cinerea</i> and <i>S. sclerotiorum</i> , resp.): some protection in both cases at 1700 µg·mL <sup>-1</sup>	[17]
	rGO-decorated Cu <sub>2-x</sub> Se NCs, coated with chitosan	Captan *	36%	In vitro and in vivo	In vitro: EC <sub>50</sub> = 200 µg·mL <sup>-1</sup> at neutral pH. In vivo (chili leaves): 25% disease incidence (vs. 55% for control) after 10 days	[18]
<i>C. capsici</i>	Glucose oxidase-N-succinyl chitosan nanospheres	Empty	-	In vitro and in vivo	In vitro: EC <sub>50</sub> = 211.2 µg·mL <sup>-1</sup> . Ex-situ (mango fruits): high protection at 125 µg·mL <sup>-1</sup> for 7 days.	[19]
	Chitosan-agar	EO from <i>Cymbopogon citratus</i>	83%	In vitro and in vivo	In vitro: MIC = 1370 µg·mL <sup>-1</sup> . In vivo (Topito chili plants): high protection for 30-40 EO (non-nano) capsules dosage.	[20]
<i>C. gloeosporioides</i>	Polyvinyl alcohol nanofibers	EOs from <i>Thymus vulgaris</i> and <i>Piper betel</i>	40–76%	In vitro and ex-situ	In vitro: ENF containing 300 µg·mL <sup>-1</sup> of blended EOs showed 24 mm inhibition zone on 6th day of incubation. Ex-situ (sapota fruits): 40% disease incidence (vs. 100% for control).	[21]
	Benzoylated lignin sulfonates-based NCs	Difenoconazole *	n.a.	In vitro	In vitro: EC <sub>50</sub> = 0.36 µg·mL <sup>-1</sup> ; 75% inhibition at 4 µg·mL <sup>-1</sup> . In vivo (strawberry leaves): 82% inhibition after 14 days.	[22]
<i>C. gossypii</i>	Chitosan-lactide copolymer	Pyraclostrobin *	45-92%	In vitro	In vitro: 85.1% inhibition at 15 µg·mL <sup>-1</sup> .	[23]
<i>C. higginsianum</i>	Poly (lactic acid) microspheres	Azoxystrobin *	78.5-92.7%	In vitro	In vitro: EC <sub>50</sub> = 2-21.3 µg·mL <sup>-1</sup> depending on microsphere size.	[24]
<i>C. nymphaeae</i>	Copper NPs	EOs from <i>Thymus daenensis</i> and <i>Anethum graveolens</i>	n.a.	In vitro	In vitro: EC <sub>50</sub> = 51.3 and 42.3 µg·mL <sup>-1</sup> for dill and thyme EOs encapsulated in Cu NPs, respectively.	[25]
<i>M. fructicola</i>	Zein casein NPs	Natamycin *	55-84%	In vitro and ex-situ	In vitro: MIC = 80 µg·mL <sup>-1</sup> , similar to non-encapsulated natamycin. Ex-situ (peach fruit): higher protection than non-encapsulated natamycin.	[26]
<i>P. citrinum</i>	<i>Azadirachta indica</i> oil nanoemulsion in Tween 20 and water	-	-	In vitro	In vitro: 25 mm inhibition zone at 3% w/v, comparable to positive control.	[27]
<i>P. fellutenum</i>	Chitosan	EO from <i>Cymbopogon nardus</i>	46.7-81.6%	In vitro	In vitro: MIC = 0.16 µL·mL <sup>-1</sup> .	[28]
<i>P. italicum</i> , <i>P. chrysogenum</i> , <i>P. spinulosum</i>	Chitosan nanomatrix	EO from <i>Coriandrum sativum</i>	26.5-78%	In vitro	In vitro: MICs not specified, but higher efficacy was attained for the encapsulated EO in all cases.	[29]
	Curcumin NPs	-	-	In vitro	In vitro: no activity (MIC > 1000 µg·mL <sup>-1</sup> )	[30]
<i>P. notatum</i>	Chitosan	EO from <i>Cymbopogon communatus</i>	19.8-44.8%	In vitro	In vitro: 56.5% inhibition at 5 mg·mL <sup>-1</sup> .	[31]
<i>P. chrysogenum</i>	Carbomer (Carbopol Aqua SF1) nanogels, with and without poly(diallyldimethylammonium chloride) surface functionalization	Zinc bis(dimethylidithiocarbamate) (Ziram) * and 3-iodo-2-	-	In vitro	In vitro: no inhibition for Ziram-loaded NCs; full inhibition for carbopol 0.1 wt% + IPBC 0.02-0.04 wt% when the NC suspensions were applied in the bulk and the surface of the growth media	[32]

propynyl-N-butylcarbamate (IPBC)*						
<i>P. digitatum</i> , <i>P. italicum</i>	Mesoporous silica-chitosan NPs	Prochloraz *	25.4%	In vivo and ex situ	In vivo (citrus trees): 12.7% infection rate at 400 µg·mL <sup>-1</sup> (pre-harvest treatment). Ex-situ (citrus fruit, postharvest treatment): disease severity = 3 after 10 days (vs. 5 for control).	[33]
<i>Penicillium</i> spp.	Rod-like hollow silica (hSiO <sub>2</sub> ) with tannic acid-Cu complexes capping	Dinotefuran *	n.a.	In vitro	In vitro: 26.4 and 67.1% inhibition at 100 and 200 µg·mL <sup>-1</sup> , respectively.	[34]
	Mesoporous selenium functionalized with trimethylammoniumpillar[5]arene and methyl orange	Carbendazim *	23.5% loading rate	In vitro and in vivo	In vitro: EC <sub>50</sub> = 0.41 µg·mL <sup>-1</sup> . In vivo (oilseed rape plants): 30.64% lesion area (vs. full infection in control) after 72 h.	[35]
	Disulfide-bridged mesoporous organosilica nanoparticles with calcium carbonate as the capping agent	Prochloraz *	8.9% loading ratio	In vitro and in vivo	In vitro: EC <sub>50</sub> = 0.142 µg·mL <sup>-1</sup> . In vivo (potted rapeseed plants): 36.1% efficacy after 7 days.	[36]
<i>S. sclerotiorum</i>	Starch-doped porous CaCO <sub>3</sub> with tannic acid-Cu complexes capping	Prochloraz *	15.2% loading capacity	In vitro and in vivo	In vitro: EC <sub>50</sub> = 0.144 µg·mL <sup>-1</sup> . In vivo (potted oilseed rape leaves): 56.8% control effect after 7 days for 100 µg·mL <sup>-1</sup> .	[37]
	Hollow mesoporous silica with tannic acid-Cu as a capping agent	Prochloraz *	17.7% loading	In vitro	In vitro: EC <sub>50</sub> = 0.131 µg·mL <sup>-1</sup> ; 91.05% inhibition at 0.8 µg·mL <sup>-1</sup> .	[38]
	Phosphonium ionic liquid-porous hollow silica microcapsules coated with pectin	Prochloraz *	35.95%	In vitro and in vivo	In vitro: 97.9% control efficacy at 0.1 µg·mL <sup>-1</sup> of encapsulated PRO. In vivo (rapeseed leaves): 97% efficacy after 9 days (vs. 5.8% for non-encapsulated PRO).	[39]
	Zeolitic imidazolate framework-8 NPs	Prochloraz * + 2,4-dinitrobenzaldehyde (pH-jump reagent)	n.a.	In vitro and in vivo	In vitro: EC <sub>50</sub> = 0.122 µg·mL <sup>-1</sup> . In vivo (oilseed rape plants): 51.2% efficacy after 14 days.	[40]
	Graphene oxide	Pyraclostrobin *	87.04%	In vitro and in vivo	In vitro: 97% inhibition at 200 µg·mL <sup>-1</sup> . In vivo (oilseed rape plants): 62.32% control efficacy at 200 µg·mL <sup>-1</sup> after 7 days.	[41]

EC<sub>50</sub>: half maximal effective concentration; EO: essential oil; MIC: minimum inhibitory concentration; NC: nanocarrier; NP: nanoparticle; n.a.: no activity; \* Conventional fungicides.

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