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Key structural features of *cis*-cinnamic acid as an allelochemical

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ABSTRACT

1-*O*-*cis*-cinnamoyl-β-D-glucopyranose is one of the most potent allelochemicals isolated from *Spiraea thunbergii Sieb*. It is suggested that it derives its strong inhibitory activity from *cis*-cinnamic acid, which is crucial for phytotoxicity. It was synthesized to confirm its structure and bioactivity, and also a series of *cis*-cinnamic acid analogues were prepared to elucidate the key features of *cis*-cinnamic acid for lettuce root growth inhibition. The *cis*-cyclopropyl analogue showed potent inhibitory activity while the saturated and alkyne analogues proved to be inactive, demonstrating the importance of the *cis*-double bond. Moreover, the aromatic ring could not be replaced with a saturated ring. However, the 1,3-dienylcyclohexene analogue showed strong activity. These results suggest that the geometry of the C–C double bond between the carboxyl group and the aromatic ring is essential for potent inhibitory activity. In addition, using several light sources, the photostability of the cinnamic acid derivatives and the role of the C–C double bond were also investigated.

1. Introduction

1-*O*-*cis*-Cinnamoyl-β-D-glucopyranose (**1**) (Fig. 1) was isolated from *Spiraea thunbergii* (Hiradate et al., 2004) and Spiraea prunifolia (Morita et al., 2005b) and identified as a potent allelochemical. It was found by a bioassay of the growth-inhibitory activity on root elongation of germinated seedlings of lettuce (*Lactuca sativa* L.) in 56 species of woody plants grown in Japan (Morita et al., 2001, 2005a). The assay indicated that *cis*-cinnamic acid (*cis*-**2**), the aglycone of the glycosyl ester **1**, is an essential structure for the bioactivity because *cis*-**2** inhibited lettuce root growth as effectively as **1**, while *trans*-cinnamic acid (*trans*-**2**) inhibited growth 100 times less than the *cis*-isomer (Hiradate et al., 2005). *trans*-**2** is generally considered to be physiologically inactive and antagonistic in function with regard to the effects of auxin in plants (Koepfli et al., 1938; van Overbeek et al., 1951). *cis*-**2**, on the other hand, is known as the compound that inhibits the root growth of *Avena sativa*, *Triticum aestivum*, and *Arabidopsis thaliana*, and it also induces epinastic curvature in *Solanum lycopersicum* seedlings (Koepfli et al., 1938; van Overbeek et al., 1951; Yang et al., 1999; Wong et al., 2005). Consequently, *cis*-**2** is widely considered to be an auxin agonist (Haagen and Went, 1935). Although mechanistic investigations based on molecular biology are in progress (Chen et al., 2005; Guo et al., 2011), the molecular mechanisms of these activities have not yet been described. The first chemical synthesis of the glycosyl ester **1** has already been achieved which confirmed the proposed structure and determined the optical rotation (Matsuo et al., 2011). Described herein is the synthesis of the analogues (**3–26**) to confirm the essential structural features of *cis*-**2** as an allelochemical. These *cis*-**2** analogues are expected to be new weed-killer or weed-control agents without environmental risks (Rice, 1995; Vyvyan, 2002; Macias et al., 2007). To measure the bioactivity of the *cis*-cinnamic acid analogues, the inhibitory activity against lettuce root growth was tested as described by Hiradate et al. (2005).

2. Results and discussion

2.1. Design of cis-cinnamic acid analogues

In order to identify the essential features responsible for the inhibitory activity of *cis*-cinnamic acid (*cis*-**2**), the structure of *cis*-**2** was divided into three units – carboxylic acid, *cis*-olefin and

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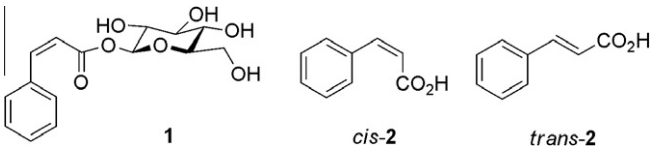


Fig. 1. Structures of 1-*O*-*cis*-cinnamoyl-β-D-glucopyranose (**1**) and *cis*- and *trans*-cinnamic acids (*cis*- and *trans*-**2**).

aromatic ring moieties. The analogues, the parts of which were individually modified, were designed as shown in Fig. 2. The analogues **3–11** are the carboxylic acid analogues, namely salt, ester, amide, alcohol, nitrile, phosphoric acid and tetrazole. The analogues *trans*-**2** and **12–15** are partially modified olefin analogues, which are the *trans*-isomer, ethyl, alkynyl, cyclopropyl, and oxiranyl analogues, respectively. Compounds **16–19** are α- and β-substituted *cis*- and *trans*-alkenyl analogues. Compounds **20–23** were designed as *cis*-cinnamic acid analogues with the cyclohexyl, cyclohexenyl or butenyl moieties replacing the phenyl ring, in order to determine the importance of the aromatic ring. As for the *E,Z*-dienyl analogues **24–26**, the spatial distances between the ring moiety and the carboxylic acid are longer than that in *cis*-**2**.

2.2. Syntheses of the cis-cinnamic acid analogues

The syntheses of *cis*-cinnamic acid (*cis*-**2**) and its *cis*-analogues **4**, **20**, **21**, **22**, **23**, **24**, **25**, and **26**, were performed mainly by the *Z*-selective olefination of the corresponding aldehydes with the Ando–Emmons reagent (Ando, 1997; Ando et al., 2000), followed by hydrolysis, as shown in Scheme 1. The glycosyl ester **1** was prepared as previously reported (Matsuo et al., 2011). The methoxymethyl ester *cis*-**5** and cyanoethyl ester *cis*-**6** were prepared *via* the esterification of *cis*-**2** with MOMCl or 2-cyanoethanol, respectively. The amide *cis*-**7** was synthesized by amidation of the corresponding acid chloride **28**, prepared by treatment of *cis*-**2** with oxalyl chloride. Reduction of *cis*-**4** with DIBAL-H provided the alcohol *cis*-**8**, and the nitrile *cis*-**9** was synthesized according to the literature (Kojima et al., 2004). The phosphoric acid *cis*-**10** was prepared *via* cross coupling of *cis*-iodostyrene (**29**) and diethyl

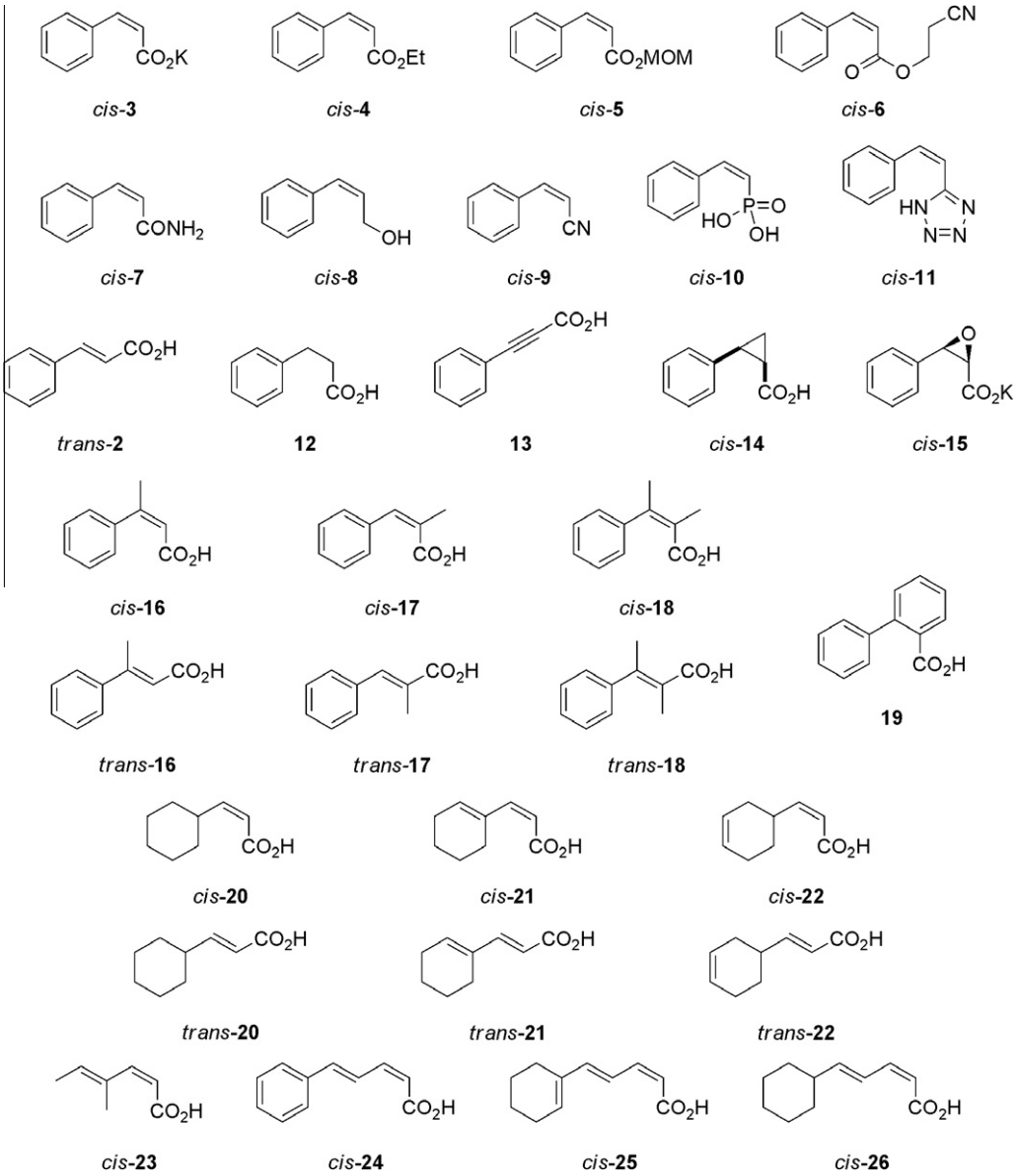
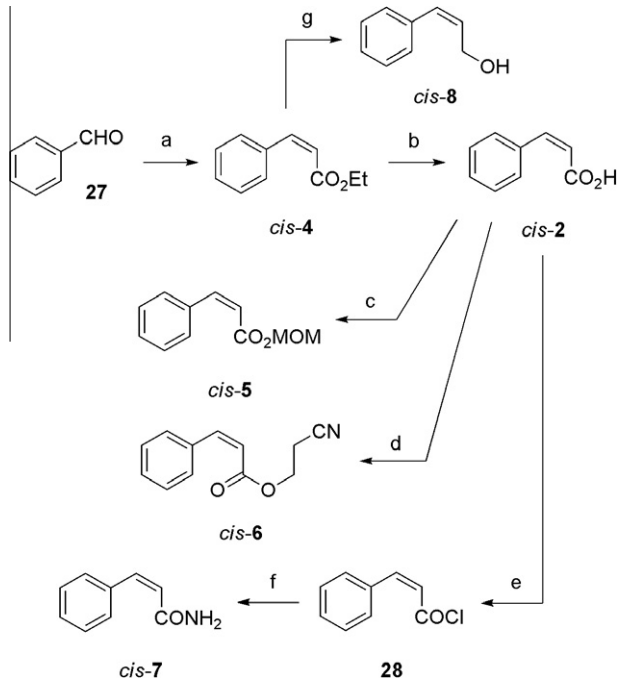
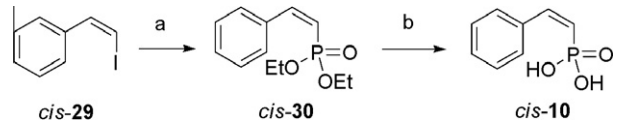


Fig. 2. Structures of the *cis*-cinnamic acid analogues.

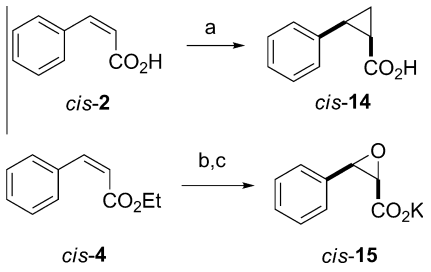


Scheme 1. Syntheses of the *cis*-cinnamic acid analogues **4–8**: (a) ethyl 2-[bis(2-isopropylphenoxy)phosphoryl]acetate, Triton B, THF, −78 °C, 94%, *Z*:*E* = 98:2, (b) 10% NaOH aq., EtOH, rt, 97%, (c) MOMCl, diisopropylethylamine, 0 °C, 99%, (d) 2-cyanoethanol, EDCI, DMAP, CH_2Cl_2, 0 °C, 91%, *Z*:*E* = 63:37, (e) $(COCl)_2$, DMF (1 drop), CH_2Cl_2, 0 °C, (f) 28% NH_4OH aq., CH_2Cl_2, 0 °C, 59% (2 steps), (g) DIBAL-H, CH_2Cl_2, −78 °C, 83%.

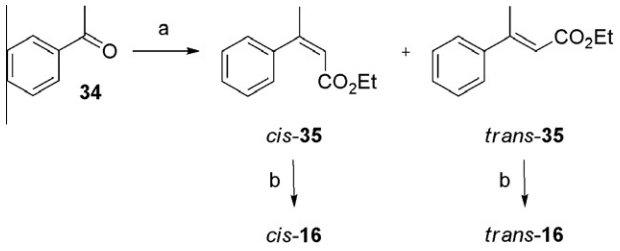


Scheme 2. Synthesis of the *cis*-cinnamic acid analogue **10**: (a) $HP(O)(OEt)_2$, $Pd(PPh_3)_4$, Et_3N, THF, 60 °C, 76%, (b) TMSBr, CH_2Cl_2, rt, 27%.

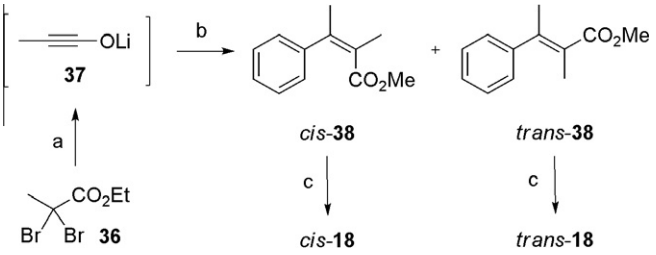
phosphonate (Kobayashi and William, 2002, 2004) (Scheme 2) (Hirao et al., 1982). The *cis*-styryl tetrazole **11** was synthesized by the Suzuki–Miyaura coupling (Yi and Yoo, 1995) of iodotetrazole and *cis*-styryl pinacolboronate **32** (Molander and Ellis, 2008), followed by deprotection of *cis*-**33** with hydrochloric acid (Scheme 3). The compounds *trans*-**2**, **12**, **13**, and **19** are all commercially available. The *cis*-cyclopropyl analogue *cis*-**14** (Kefford, 1959) was synthesized *via* a modified Simmons–Smith reaction (Furukawa et al., 1966; Lorenz et al., 2004) of *cis*-**2** (Scheme 4). The epoxide *cis*-**15** was prepared from *cis*-**4** through asymmetric epoxidation (Deng and Jacobsen, 1992) and subsequent hydrolysis. The trisubstituted olefins *cis*- and *trans*-**16**, *cis*- and *trans*-**17**, and the *trans*-analogues **20**, **21**, and **22** were synthesized *via* the Horner–Wadsworth–Emmons (Wadsworth and Emmons, 1961) or Wittig reaction, and the resulting *trans*- and *cis*-isomers were separated by silica gel column chromatography (Scheme 5). The pure com-



Scheme 4. Synthesis of the *cis*-cinnamic acid analogues **14** and **15**: (a) Et_2Zn, TFA, CH_2I_2, CH_2Cl_2, 0 °C, 62%, (b) Deng and Jacobsen, 1992, 41%, (c) KOH, EtOH-H_2O, rt, 66%.



Scheme 5. Synthesis of the cinnamic acid analogues *cis*-**16** and *trans*-**16**: (a) ethyl 2-(diethoxyphosphoryl)acetate, NaH, THF, reflux, *cis*-**35**: 14%, *trans*-**35**: 68%, (b) 10% NaOH aq., EtOH, rt.

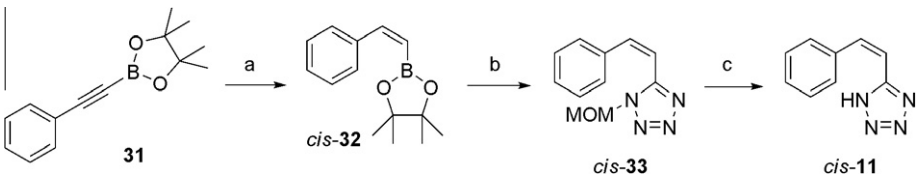


Scheme 6. Synthesis of the cinnamic acid analogues *cis*-**18** and *trans*-**18** using the ynolate: (a) ^{t}BuLi, THF, −78 °C to rt, (b) acetophenone (**34**), THF, rt, then MeI, HMPA, rt, *cis*-**38**: 20%, *trans*-**38**: 80%, (c) 10% NaOH aq., EtOH, rt.

pounds, without any geometrical isomers, were finally obtained after recrystallization. The tetrasubstituted olefins *cis*- and *trans*-**18** were prepared *via* the torquoselective olefination using the ynolate **37** (Shindo et al., 2004) (Scheme 6).

2.3. Bioassay and discussions

The growth inhibitory activity of the *cis*-cinnamic acid analogues **1–26** against root-growth of lettuce (*Lactuca sativa* cv.) was measured as described by Hiradate et al. (2005). The EC_{50} values, which indicate the effective concentration required to induce a half-maximum effect, are shown in Tables 1 and 2. The inhibitory activity of the synthetic glycosyl ester **1** was below 10^{-5} M in EC_{50} value, which was identical with the reported value and that of the



Scheme 3. Synthesis of the *cis*-cinnamic acid analogue **11**: (a) dicyclohexylborane, Et_2O, rt, then AcOH, 0 °C, 69%, (b) 5-iodo-1-(methoxymethyl)-1H-tetrazole, $Pd(PPh_3)_4$, Na_2CO_3, toluene-H_2O, reflux, 44%, *Z*:*E* = 90:10, (c) 6 M HCl, MeOH, rt, 62%.

Table 1
Inhibitory activity of *cis*-cinnamic acid analogues **1–26**. EC_{50} values are the effective concentration required to induce a half-maximum effect against root-growth of lettuce (*Lactuca sativa* cv.).

Compounds	EC_{50} (μM)	Compounds	EC_{50} (μM)
1	6.8	*cis*-14	3.9
cis-2	2.5	*cis*-15	343
cis-3	4.7	*cis*-16	1.7
cis-4	5.8	*cis*-17	5.9
cis-5	6.3	*cis*-18	15
cis-6	>500	19	123
cis-7	146	*cis*-20	>500
cis-8	>500	*cis*-21	3.6
cis-9	177	*cis*-22	72
cis-10	>500	*cis*-23	117
cis-11	>500	*cis*-24	>500
12	111	*cis*-25	>500
13	>500	*cis*-26	>500

Table 2
Inhibitory activity of the *trans*-cinnamic acid analogues. EC_{50} values are the effective concentration required to induce a half-maximum effect against root-growth of lettuce (*Lactuca sativa* cv.).

Compounds	EC_{50} (μM)	Compounds	EC_{50} (μM)
cis-**2**	2.5	*trans*-**18**	>500
trans-**2**	>500	*trans*-**20**	>500
trans-**16**	>500	*trans*-**21**	>500
trans-**17**	>500	*trans*-**22**	>500

synthetic **2**. The potassium *cis*-cinnamate (**3**), which is more soluble in water, also showed strong activity. The *trans*-cinnamic acid **2** did not exhibit any activity, as already indicated (Hiradate et al., 2005).

2.3.1. Effects of modification of the carboxylic acid

Since the *cis*-cinnamic acid ethyl ester **4** and the methoxymethyl ester **5**, which is labile to acid, showed similar levels of activity to that observed with *cis*-**2**, it is likely that the ester is metabolized to the carboxylic acid and the acid is acting as the essential moiety, a phenomenon observed in the glycoside **1**. The cyanoethyl ester *cis*-**6** can be easily removed under basic conditions; however, it had no inhibitory activity. The substitution of a variety of groups, such as amide (*cis*-**7**), alcohol (*cis*-**8**), nitrile (*cis*-**9**), phosphoric acid (*cis*-**10**) and tetrazole (*cis*-**11**), gave inactive compounds. These results indicated the importance of the carboxylic acid functionality.

2.3.2. Effects of modification of the C–C double bond

Compounds **12** and **13** turned out to be inactive. However, the cyclopropyl analogue *cis*-**14** showed activity as potent as that of **2**. These results suggest that the fixed *cis*-geometry, and not the electronic effect of the π-electrons of the C–C double bond, is critical for the inhibitory activity. Since the *cis*-double bond can be substituted by the *cis*-cyclopropane (e.g. *cis*-**14**), the conjugated 1,3-dienyl unit is not essential for good activity. However, the epoxide *cis*-**15** was not a potent inhibitor, perhaps due to the instability of the structure. The methylated tri- and tetra-substituted *cis*-cinnamic acid analogues **16**, **17**, and **18** retained their potent inhibition. The biphenyl carboxylic acid **19**, having a *cis*-geometry, showed low activity, probably due to steric hindrance. The decreased inhibitory activity of the *trans*-forms of **16**, **17**, and **18** suggested again the importance of the *cis*-form for activity.

2.3.3. Effects of modification of the aromatic ring

The compounds *cis*-**20**, *trans*-**20**, *trans*-**21**, *cis*-**22** and *trans*-**22** did not show high potency, although compound *cis*-**21** inhibited root-growth. These results suggest that the aromatic ring is not a requirement for inhibition and therefore could be substituted by the 1-cyclohexenyl group, where only the sp2-hybridized carbon at the C-1 position on the ring is necessary. The compound *cis*-**23**, which did not have a ring moiety, was inactive, indicating that the ring moiety is crucial for potent activity.

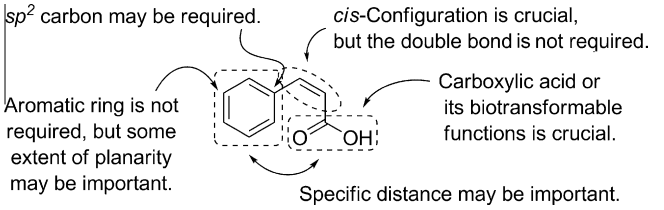


Fig. 3. Essential structural features for the phytotoxicity of the *cis*-cinnamic acid **2**.

2.3.4. Effects of the length between the carboxylic acid and the aromatic ring

Since the carbon-chain elongated compounds *cis*-**24**, *cis*-**25**, and *cis*-**26** did not show any inhibitory activity, it could be inferred that the distance between the aromatic ring and the carboxylic acid moiety plays a crucial role. The essential structural features of *cis*-**2** as an allelochemical are summarized in Fig. 3.

2.4. Photoisomerization of the cinnamic acid analogues

If the biological tests of cinnamic acid are not carried out carefully under dark conditions, the correct bioactivity cannot be obtained due to the photochemical isomerization of the cinnamic acid (Clampitt et al., 1962; Lippert and Lüder, 1962; Rontani et al., 1988; Turner et al., 1993; Wong et al., 2005; Salum et al., 2011). In order to ensure the essential bioactive moieties, the photostability of the cinnamic acid derivatives was examined with several light sources. Irradiation of *trans*-cinnamic acid (*trans*-**2**) and the glycoside *trans*-**1** was carried out in D_2O using 5-mm glass tubes under a xenon light (300 W) at 25 °C; the *Z*:*E* ratios were determined by ^1H NMR spectra. As shown in Fig. 4, the *trans*-**2** was isomerized to give the photostationary state in less than a few hours. The *Z*:*E* ratio of the photostationary state of **2** was 70:30, which is nearly consistent with that reported in the literature (Hocking, 1969). The glycoside of *trans*-cinnamic acid (*trans*-**1**) was also isomerized, but slower than the aglycone *trans*-**2**. Photochemical isomerization of *cis*-cinnamic acid (*cis*-**2**) was also carried out under the same conditions to achieve a similar

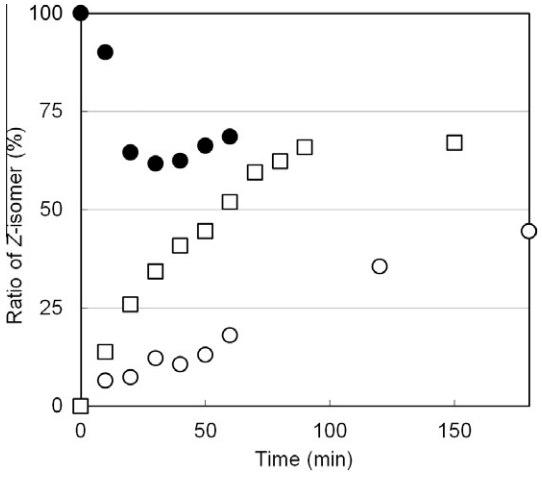


Fig. 4. Photochemical isomerization of *trans*-cinnamic acid (*trans*-**2**) (□), its glycoside (*trans*-**1**) (○), and *cis*-cinnamic acid (*cis*-**2**) (●).

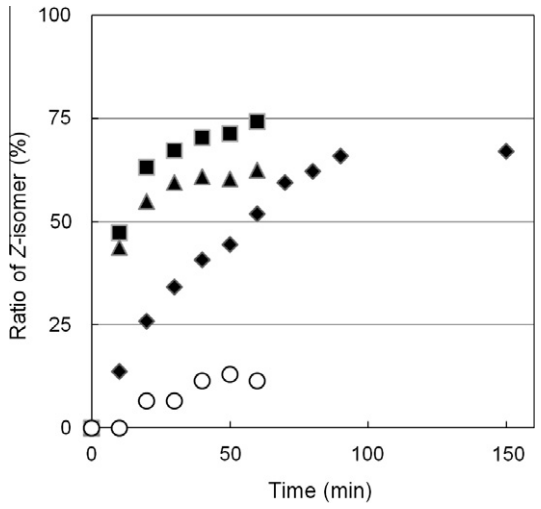


Fig. 5. Photochemical isomerization of *trans*-cinnamic acid (*trans*-**2**) (♦), and its derivatives (**16** (■), **17** (▲) and **18** (○)) by a xenon light.

photostationary state (*Z*:*E* = 70:30) within an hour (Fig. 4). The β- and α-monomethylated *trans*-cinnamic acids **16** and **17** were isomerized faster than *trans*-**2**, and the dimethylated cinnamic acid *trans*-**18** was somewhat converted by light, with the *Z*:*E* ratio of the photostationary state being 10:90 (Fig. 5).

The *cis*-**2** and *trans*-**2** compounds dissolved in water were not isomerized at all under fluorescent lighting in the laboratory, indicating that the EC_{50} values for non-isomeric *cis*-cinnamic acid had been accurately measured.

In contrast, the sunlight-irradiated isomerization of *trans*-**2** dissolved in D_2O proceeded in glass tubes. The isomerization experiments were carried out during the daytime, outdoors under cloudy conditions at ca. 10 °C. The photostationary state was achieved within a matter of hours, depending on the climate conditions, and the *E*/*Z* ratio was almost 1:1. These results indicate that *trans*-**2** might work as a plant growth inhibitor like *cis*-**2** if an aqueous solution of this essentially inactive compound is sprayed on soils in daylight. To confirm this hypothesis, a preliminary lettuce growth inhibition test using *trans*-**2** was carried out as follows: The aqueous solutions of *trans*-**2** at various concentrations were placed in glass petri dishes and were irradiated by sunlight. Then, pre-germinated lettuce seedlings were transplanted on the *trans*-**2**-treated soils and incubated in the dark in the usual manner. As shown in Fig. 6, the inhibitory activity increased as the irradiation time was lengthened until the EC_{50} value of the isomerized *trans*-**2** finally reached nearly 100 μM, in three hours. These results suggest that the inactive *trans*-**2** and its glycoside *trans*-**1**, which are not themselves poisonous to the plant, are released from the plant and converted into the active *cis*-**1** and -**2** forms by sunlight irradiation. The resulting compounds would act as allelochemicals and inhibit the growth of plants.

3. Conclusion

The *cis*-configuration of cinnamic acid is clearly essential for lettuce root-growth inhibition. The aromatic ring is thought to play the role of a planar hydrophobic moiety rather than an electronic function. In addition, it was found that the carboxylate is also essential, presumably owing to the hydrogen bonding to the target protein; however, it can be replaced by some esters, which are easily hydrolyzed in tissues. The spatial arrangement of the aromatic ring and the carboxylate is likewise important for the bioactivity. Cinnamic acids can be easily isomerized to a photostationary mixture of *cis*- and *trans*-forms by sunlight. This implies that the inactive *trans*-cinnamic acid could be used as a plant growth regulator after photoconversion. Although the mechanistic details are still unclear, these results, which partially clarified the SAR of cis-**2**, would contribute to the design of bioprobes, clarification of the bioactive mechanism, and the development of new herbicides. Further SAR study of cis-**2** along with chemical biology studies are in progress.

4. Experimental section

4.1. Materials

Optical rotations were obtained using a Horiba SEPA-300. The melting points were measured on a Yazawa micromelting point BY-1. The ^1H and ^{13}C NMR spectra were recorded using a JEOL JNM AL-400 (400 and 100 MHz), and a JNM ECA-600 spectrometer (600 and 150 MHz). Chemical shifts were reported in ppm downfield from the peak of Me_4Si (TMS) used as the internal standard. Splitting patterns are designed as "s, d, t, q, and m," indicating "singlet, doublet, triplet, quartet, and multiplet," respectively. The IR spectra were recorded on a Shimadzu FT/IR-8300 spectrometer using either a KBr disk or a NaCl cell. Mass spectra were obtained on a JEOL JMS-700 or a JEOL JMS-T100CS. High-resolution mass spectra were obtained on a JEOL JMS-700 or a JEOL JMS-T100CS. Column chromatography (CC) was performed on silica gel (Kanto Chemical Co.) whereas thin-layer chromatography (TLC) was

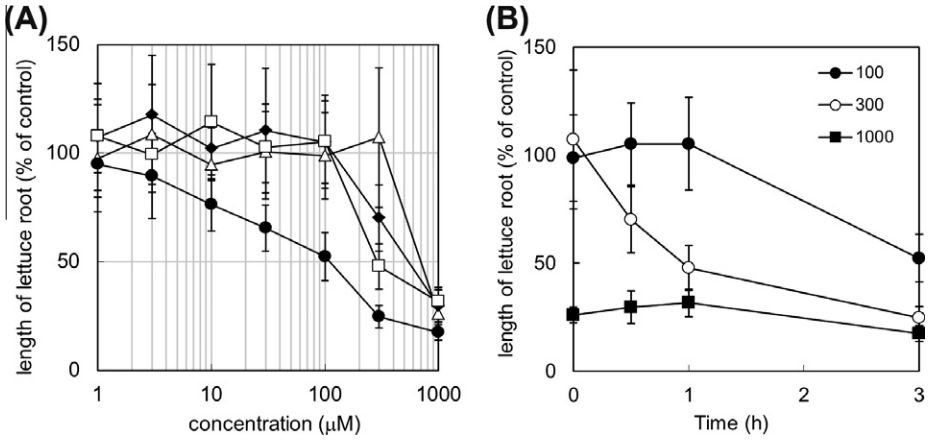


Fig. 6. Inhibitory activity of *trans*-cinnamic acid (*trans*-**2**) exposed to sunlight. (A) The effect of concentration under the conditions of various exposed time to sunlight: 0 h (△), 0.5 h (♦), 1 h (□) and 3 h (●). (B) The effect of exposed time to sunlight at various concentrations of *trans*-**2** [100 μM (●), 300 μM (○) and 1000 μM (■)].

employed pre-coated plates (0.25 mm, silica gel Merck 60 F254). Reaction mixtures were stirred magnetically. The stereochemistry was determined by NOE experiments, unless otherwise noted.

4.2. Synthesis

4.2.1. (Z)-Ethyl 3-Phenylacrylate (cis-4)

To a solution of ethyl 2-[bis(2-isopropylphenoxy)phosphoryl]acetate (3.26 g, 8.05 mmol) in tetrahydrofuran (THF) (73 mL) was added dropwise Triton B (40% in MeOH, 4.04 mL, 10.2 mmol) at −78 °C under an argon atmosphere. After 15 min of stirring, a solution of benzaldehyde (**27**) (0.777 g, 7.32 mmol) in THF (24 mL) was added dropwise to the solution. After 10 h, the mixture was quenched with saturated aqueous NH_4Cl and extracted with EtOAc. The organic layer was washed with H_2O, saturated aqueous $NaHCO_3$ and brine, dried over $MgSO_4$, filtered and concentrated *in vacuo*. The crude product was purified by silica gel CC (EtOAc/hexane, 5:95) to give *cis*-**4** (94%, 6.87 mmol, *E*:*Z* = 5:95, determined by ^1H NMR spectroscopic analysis) as a colorless oil: ^1H NMR ($CDCl_3$, 400 MHz) δ: 1.24 (t, *J* = 7.2 Hz, 3H, -CH_3), 4.17 (q, *J* = 7.2 Hz, 2H, -CH_2-), 5.95 (d, *J* = 12.8 Hz, 1H, =CH–CO_2–), 6.95 (d, *J* = 12.8 Hz, 1H, Ar–CH=), 7.32–7.38 (m, 3H, Ar–H), 7.57–7.59 (m, 2H, Ar–H); The observed characterization data were consistent with those previously reported (Ando, 1997).

4.2.2. (Z)-**3**-Phenylacrylic Acid (cis-cinnamic acid) (cis-**2**)

To a solution of *cis*-**4** (1.21 g, 6.87 mmol) in EtOH (14 mL) was added 10% NaOH (28 mL) at room temperature. After 12 h, the mixture was adjusted to pH 1.0 with 1 M HCl, and then extracted with EtOAc. The organic layer was washed with brine, dried over $MgSO_4$, filtered and concentrated *in vacuo*. The residue was purified by recrystallization (CH_2Cl_2/hexane, 5:95) to afford *cis*-**2** (0.983 g, 6.64 mmol, 97%) as colorless needles: mp 55–57 °C (CH_2Cl_2/hexane, 5:95); ^1H NMR ($CDCl_3$, 400 MHz) δ: 5.97 (d, *J* = 12.8 Hz, 1H, =CH–CO_2–), 7.07 (d, *J* = 12.8 Hz, 1H, Ar–CH=), 7.35–7.37 (m, 3H, Ar–H), 7.59–7.62 (m, 2H, Ar–H); The observed characterization data were consistent with those reported (Reed et al., 1993).

4.2.3. (Z)-Methoxymethyl 3-phenylacrylate (cis-**5**)

To a solution of *cis*-**2** (0.114 g, 0.770 mmol) in CH_2Cl_2 (11 mL) were added dropwise diisopropylethylamine (0.784 mL, 4.62 mmol) and MOMCl (methoxymethyl chloride, 0.290 mL, 3.85 mmol) at 0 °C under an argon atmosphere. After 1.5 h, the reaction was quenched with saturated aqueous $NaHCO_3$, extracted with EtOAc, and the organic layer was washed with brine, dried over $MgSO_4$, filtered and concentrated *in vacuo*. The crude product was purified by silica gel CC (EtOAc/hexane, 5:95) to afford *cis*-**5** (0.147 g, 0.764 mmol, 99%) as a colorless oil: ^1H NMR ($CDCl_3$, 400 MHz) δ: 3.38 (s, 3H, –OCH_3), 5.25 (s, 2H, –CH_2–), 5.96 (d, *J* = 12.6 Hz, 1H,=CH–CO_2–), 6.98 (d, *J* = 12.6 Hz, 1H, Ar–CH=), 7.28–7.38 (m, 3H, Ar–H), 7.57–7.64 (m, 2H, Ar–H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 57.5 (q, –OCH_3), 90.2 (t, CH_2), 119.0 (d, =*C*H–CO_2–), 127.9 (d, Ar), 129.0 (d, Ar), 129.7 (d, Ar), 134.5 (s, Ar), 144.2 (d, Ar–CH=), 165.3 (s, C=O); IR (neat) 1722 cm^{-1}; EI-MS *m/z* 192 (M^+), 147 (M^{+-}MOM); HR EI-MS *m/z* 192.0783 (M^+, calcd for $C_{11}H_{12}O_3$ 192.0786).

4.2.4. (Z)-2-Cyanoethyl 3-phenylacrylate (cis-**6**)

To a solution of *cis*-**2** (0.134 g, 0.905 mmol) in CH_2Cl_2 (11 mL) were added DMAP (4-(*N*,*N*–dimethylamino)pyridine, 22.1 mg, 18.1 μmol), 2-cyanoethanol (68.0 μL, 0.996 mmol) and EDCI (0.208 g, 1.09 mmol) at 0 °C under argon atmosphere. After 5 min, the reaction was quenched with H_2O, extracted with CH_2Cl_2, washed with saturated aqueous $NaHCO_3$ and brine, dried over $MgSO_4$, filtered and concentrated *in vacuo*. The crude product was purified by silica gel CC (EtOAc/hexane, 10:90) to afford a mixture of *cis*-**6** and *trans*-**6** (0.165 g, 0.822 mmol, 91%, *E*:*Z* = 37:63, determined by ^1H NMR analysis). A part of the mixture was further separated by HPLC (Mightysil Si 60, EtOAc/hexane, 3:97) to give only *cis*-**6** as colorless needles: mp 70–71 °C (CH_2Cl_2/hexane, 5:95); ^1H NMR ($CDCl_3$, 400 MHz) δ: 2.66 (t, *J* = 6.0 Hz, 2H, –CH_2–CN), 4.30 (t, *J* = 6.0 Hz, 2H, –CO_2–CH_2–), 5.97 (d, *J* = 12.6 Hz, 1H, =CH–CO_2–), 7.05 (d, *J* = 12.6 Hz, 1H, Ar–CH=), 7.32–7.42 (m, 3H, Ar–H), 7.59–7.62 (m, 2H, Ar–H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 17.8 (t, –*C*H_2–CN), 58.4 (t, –CO_2–*C*H_2–), 116.7 (s, –CN), 118.2 (d, =*C*H–CO_2–), 128.0 (d, Ar), 129.3 (d, Ar), 129.7 (d, Ar), 134.5 (s, Ar), 145.4 (d, Ar–CH=), 165.1 (s, C=O); IR (KBr) 2249, 1713 cm^{-1}; FAB–MS m/z 185 (M^+); Anal. calcd for $C_{12}H_{11}NO_2$: C, 71.63; H, 5.51; N, 6.96. found: C, 71.53; H, 5.54; N, 7.03.

4.2.5. (Z)-3-Phenylacrylamide (cis-**7**)

To a solution of *cis*-**2** (0.200 g, 1.35 mmol) in CH_2Cl_2 (2.0 mL) were added Dimethylformamide (DMF) (1 drop) and oxalyl chloride (0.240 mL, 2.80 mmol) at 0 °C under argon atmosphere. After 40 min of stirring, the mixture was concentrated *in vacuo* to afford the crude (*Z*)-3-phenylacryloyl chloride as a yellow oil. The crude product was employed directly in the following reaction. A solution of the crude (*Z*)-3-phenylacryloyl chloride in CH_2Cl_2 (0.80 ml) was poured into 28% aqueous NH_3 solution (2.0 mL) at 0 °C under an argon atmosphere. After 10 min of stirring, the mixture was extracted with CH_2Cl_2, washed with brine, dried over $MgSO_4$, filtered and concentrated *in vacuo*. The residue was purified by recrystallization (EtOAc/hexane, 10:90) to give *cis*-**7** (0.122 g, 0.830 mmol, 59% in 2 steps) as colorless needles: mp 86–87 °C; ^1H NMR ($CDCl_3$, 400 MHz) δ: 5.45 (brs, 2H, –NH_2), 5.99 (d, *J* = 12.8 Hz, 1H, =CH–CO_2–), 6.86 (d, *J* = 12.8 Hz, 1H, Ar–CH=), 7.31–7.40 (m, 3H, Ar–H), 7.48 (brd, *J* = 7.6 Hz, 2H, Ar–H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 123.8 (d, =*C*H–CO_2–), 128.6 (d, Ar), 128.8 (d, Ar), 128.9 (d, Ar), 134.8 (s, Ar), 137.6 (d, Ar–*C*H=); IR (KBr) 1667, 1618 cm^{-1}; EI-MS m/z 147 (M^+); Anal. calcd for C_9H_9NO: C, 73.45; H, 6.16; N, 9.52. found: C, 73.37; H, 6.19; N, 9.42.

4.2.6. (Z)-3-Phenylprop-2-en-1-ol (cis-**8**)

After a solution of *cis*-**4** (0.470 g, 2.67 mmol) in CH_2Cl_2 (8.9 mL) was cooled to −78 °C under an argon atmosphere, DIBAL-H (1.0 M in hexane, 6.41 mL, 6.41 mmol) was added dropwise to the solution. The mixture was stirred for 2 h, quenched with MeOH and a trace amount of H_2O at 0 °C, filtered through Celite pad, and the filtrate was washed with CH_2Cl_2 and concentrated *in vacuo*. Purification using silica gel CC (EtOAc/hexane, 20:80) yielded *cis*-**8** (0.298 g, 2.22 mmol, 83%) as a colorless oil: ^1H NMR ($CDCl_3$, 400 MHz) δ: 1.43 (brs, 1H, –OH), 4.45 (dd, *J* = 1.4, 6.4 Hz, 2H, –*C*H_2–OH), 5.88 (dt, *J* = 6.3, 12.0 Hz, 1H,=*C*H–CH_2–), 6.58 (d, *J* = 12.0 Hz, 1H, Ar–CH=), 7.20–7.38 (m, 5H, Ar–H); The observed characterization data were consistent with those reported (Denis et al., 1986).

4.2.7. (Z)-Styrylphosphonic Acid (cis-**10**)

To a degassed THF solution of (*Z*)-(2-iodovinyl)benzene (*cis*-**29**) (1.00 g, 4.34 mmol), $Pd(PPh_3)_4$ (0.745 g, 0.645 mmol) and $HP(O)(OEt)_2$ (0.527 ml, 4.12 mmol) at room temperature under an argon atmosphere, Et_3N (0.570 ml, 4.12 mmol) was added. The resulting mixture was bubbled with N_2 gas for 3 min and stirred for 24 h at 60 °C. The reaction was quenched with saturated aqueous $NaHCO_3$, extracted with EtOAc, and the organic layer was washed with brine, dried over $MgSO_4$, filtered and concentrated *in vacuo*. The crude residue was purified by silica gel CC (MeOH/$CHCl_3$, 10:90) to afford (*Z*)-diethyl styrylphosphonate (*cis*-**30**) (0.792 g, 3.30 mmol, 76%) as a brown oil; ^1H NMR ($CDCl_3$, 400 MHz) δ: 1.19 (t, *J* = 7.2 Hz, 6H, –CH_3), 3.99 (q, *J* = 7.2 Hz, 4H, –CH_2–), 5.81 (dd, *J* = 14.5, 15.8 Hz, 1H, =CH–PO_3Et_2), 7.29 (dd, *J* = 14.5, 52.0 Hz, 1H, Ar–CH=), 7.31–7.42 (m, 3H, Ar–H), 7.66–

7.71 (m, 2H, Ar–H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 16.1 (q, as a doublet, $^3J_{P-C}$ = 6.2 Hz, –CH_3), 61.7 (t, as a doublet, $^2J_{P-C}$ = 4.6 Hz, –CH_2–). 116.6 (d, as a doublet, $^1J_{P-C}$ = 185.5 Hz,=CH–PO_3Et_2), 128.1 (d, Ar), 129.3 (d, Ar), 129.5 (d, Ar), 135.2 (s, as a doublet, $^3J_{P-C}$ = 9.2 Hz, Ar), 148.3 (d, Ar–CH=); IR (neat) 1250, 1609, 2984, 3443 cm^{-1}; EI-MS *m/z* 240 (M^+); FAB-MS m/z 240 (M^+); HR EI-MS *m/z* 240.0917 (M^+, calcd for $C_{12}H_{17}O_3P$ 240.0915); Spectroscopic data were consistent with those reported in the literature (Kobayashi and William, 2002).

To a solution of *cis*-**30** (0.250 g, 1.04 mmol) in CH_2Cl_2 (2.5 mL) was added TMSBr (0.302 mL, 2.29 mmol) at room temperature under an argon atmosphere. The mixture was stirred for 1.5 h. After the solvent was removed *in vacuo*, the residue was dissolved in H_2O and the mixture was washed with Et_2O/hexane (10:90). After the mixture was concentrated *in vacuo*, the crude product was purified by recrystallization (CH_3CN) to give *cis*-**10** (51.1 mg, 0.278 mmol, 27%) as light brown plates: mp 131–133 °C; ^{1}H NMR (CD_3OD, 400 MHz) δ: 5.82 (t, *J* = 14.5 Hz, 1H, =C*H*–PO_3H_2), 7.02 (dd, *J* = 14.5, 48.4 Hz, 1H, Ar–CH=), 7.19–7.47 (m, 3H, Ar–H), 7.68–7.85 (m, 2H, Ar–H); ^{13}C NMR (CD_3OD, 100 MHz) δ: 120.5 (d, as a doublet, $^1J_{P-C}$ = 182.9 Hz, =CH_2–PO_3H_2), 129.1 (d, Ar), 130.0 (d, Ar), 130.8 (d, Ar), 137.0 (s, as a doublet, $^3J_{P-C}$ = 8.2 Hz, Ar), 147.3 (d, Ar–CH=); IR (KBr) 2855, 2299 cm^{-1}; FAB-MS m/z 185 (M^++H); HR FAB-MS *m/z* 185.0.370 (M^++H, calcd for $C_3H_{10}O_3P$ 185.0368); Anal. calcd for $C_3H_9O_3P$: C, 52.18, H, 4.93, found: C, 52.23, H, 4.88.

4.2.8. (*Z*)-5-Styryl-1*H*-tetrazole (*cis*-**11**)

To a solution of cyclohexene (0.787 mL, 7.77 mmol) in Et_2O (5.0 mL) was added dropwise BH_3-SMe_2 (0.352 mL, 3.70 mmol) at 0 °C under an argon atmosphere. After 1 h, the resulting solid was allowed to settle without stirring. The supernatant organic solution was removed by syringe, and the residual solid was dried under reduced pressure to afford dicyclohexylborane as a colorless solid, which was used without purification in the next reaction. To the dicyclohexylborane was added a solution of 4,4,5,5-tetramethyl-2-(phenylethynyl)-1,3,2-dioxaborolane (*cis*-**31**) (0.800 g, 3.51 mmol) in Et_2O (10 mL) at room temperature under an argon atmosphere. After the mixture was stirred for 1.5 h, AcOH (0.261 mL, 4.56 mmol) was added dropwise to the solution at 0 °C. After 10 min, ethanolamine (0.424 mL, 7.02 mmol) was added to the mixture. After 15 min, the resulting mixture was diluted with hexane, filtered through a plugged column, washed with EtOAc/hexane (10:90) and concentrated *in vacuo*. The crude product was purified by bulb to bulb distillation (1.5 mmHg, 150 °C) to afford (*Z*)-4,4,5,5-tetramethyl-2-styryl-1,3,2-dioxaborolane (*cis*-**32**) (0.557 g, 2.42 mmol, 69%) as a colorless oil: ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 1.29 (s, 12H, –CH_3), 5.59 (d, *J* = 15.6 Hz, 1H, =CH–BO_2–), 7.21 (d, *J* = 15.6 Hz, 1H, Ar–CH=), 7.25–7.32 (m, 3H, Ar–H), 7.49–7.57 (m, 2H, Ar–H); FAB-MS *m/z* 230 (M^+); The spectroscopic data were consistent with those reported in the literature (Molander and Ellis, 2008).

To a solution of 1*H*-tetrazole (2.10 g, 30.0 mmol) in THF (30 mL) was added Et_3N (5.40 mL, 39.0 mmol) at 0 °C under an argon atmosphere. After 30 min, MOMCl (2.87 mL, 39.0 mmol) was added to the resulting mixture. The reaction was warmed to room temperature and stirred for 5 h. The reaction was quenched with H_2O, extracted with EtOAc, and the organic layer was washed with brine, dried over $MgSO_4$, filtered and concentrated *in vacuo* to afford a mixture of 1-(methoxymethyl)-1*H*-tetrazole and 2-(methoxymethyl)-2*H*-tetrazole (2.70 g, 21.1 mmol, 70%) as a colorless oil. The mixture was used in the next step without purification. After a solution of a mixture of the protected tetrazole (1.50 g, 11.7 mmol) in THF (75 mL) was cooled to −78 °C, *n*-BuLi (2.48 M in hexane, 5.81 mL, 14.4 mmol) was added dropwise to the solution under an argon atmosphere. After 30 min, I_2 (3.66 g, 14.4 mmol) was slowly added to the solution. The reaction was stirred for 30 min at −78 °C, warmed to 0 °C and stirred for an additional 30 min. The reaction was quenched with saturated aqueous NH_4Cl, extracted with EtOAc, and the organic layer was washed with saturated aqueous $Na_2S_2O_3$ and brine, dried over $MgSO_4$, filtered and concentrated *in vacuo*. The residue was purified by bulb to bulb distillation (0.8 mmHg, 150 °C) to give 5-iodo-1-(methoxymethyl)-1*H*-tetrazole (1.10 g, 4.58 mmol, 38%) as a yellow oil: ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 3.49 (s, 3H, –OCH_3), 5.86 (s, 2H, –CH_2–); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 58.5 (q, –OCH_3), 82.6 (t, –CH_2–), 112.5 (s, tetrazole); IR (neat) 2941 cm^{-1}; EI-MS *m/z* 240 (M^+); HR EI-MS *m/z* 239.9507 (M^+, calcd for $C_3H_5N_4OI$ 239.9508).

To a solution of $Pd(PPh_3)_4$ (0.285 g, 0.247 mmol) and Na_2CO_3 (0.355 g, 3.35 mmol) in toluene (80 mL) and H_2O (8.0 mL) was added a solution of 5-iodo-1-(methoxymethyl)-1*H*-tetrazole (0.418 g, 1.74 mmol) and *cis*-**32** (0.400 g, 1.74 mmol) in toluene (40 mL) at room temperature under an argon atmosphere. The mixture was heated until reflux began this being continued for 3 h, then the whole cooled to room temperature, quenched with saturated aqueous NH_4Cl and extracted with EtOAc. The combined organic phase was washed with brine, dried over $MgSO_4$, filtered and concentrated *in vacuo*. The crude product was purified by silica gel CC (EtOAc/hexane, 15:85) and following bulb to bulb distillation (0.4 mm Hg, 150 °C) to provide (*Z*)-1-(methoxymethyl)-5-styryl-1*H*-tetrazole (*cis*-**33**) (0.162 g, 0.750 mmol, 44%, *E*:*Z* = 10:90, determined by ^{1}H NMR spectrum) as a yellow oil: ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 3.46 (s, 3H, –OCH_3), 5.80 (s, 2H, –CH_2–), 6.67 (d, *J* = 12.8 Hz, 1H, Ar–CH = C*H*–), 7.09 (d, *J* = 12.8 Hz, 1H, Ar–CH=), 7.30–7.43 (m, 3H, Ar–H), 7.61 (d, *J* = 7.6 Hz, 2H, Ar–H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 58.2 (q, –OCH_3), 82.1 (t, –CH_2–), 114.3 (d, Ar–CH = *C*H–), 128.0 (d, Ar), 128.5 (d, Ar), 129.4 (d, Ar), 135.5 (s, Ar), 137.7 (d, Ar–CH=), 163.3 (s, tetrazole); IR (neat) 1643 cm^{-1}; EI-MS *m/z* 216 (M^+); HR ESI-MS *m/z* 217.1087 (M^++H, calcd for $C_{11}H_{13}N_4O$ 217.1089).

To a solution of *cis*-**33** (0.140 g, 0.648 mmol) in MeOH (15 mL) was added 6 M HCl (11 mL) at room temperature. The mixture was stirred for 12 h, diluted with H_2O, neutralized with 10% NaOH and extracted with $CHCl_3$. The combined organic layers were washed with brine, dried over $MgSO_4$, filtered and concentrated *in vacuo*. Purification over silica gel CC (Et_2O/hexane, 10:90) gave *cis*-**11** (69.0 mg, 0.401 mmol, 62%) as colorless needles: mp 114–115 °C; ^{1}H NMR (CD_3OD, 400 MHz) δ: 6.58 (d, *J* = 12.4 Hz, 1H, Ar–CH = C*H*–), 7.18 (d, *J* = 12.4 Hz, 1H, Ar–CH=), 7.31–7.35 (m, 5H, Ar–H); ^{13}C NMR (CD_3OD, 100 MHz) δ: 111.4 (d, Ar–CH = *C*H–), 129.6 (d, Ar), 130.0 (d, Ar), 130.1 (d, Ar), 136.1 (s, Ar), 141.3 (d, Ar–CH=), 153.9 (s, tetrazole); IR (KBr) 1653 cm^{-1}; FAB-MS m/z 173 (M^++H); Anal. calcd for $C_9H_8N_4$: C, 62.78; H, 4.68; N, 32.54. found: C, 62.83; H, 4.66; N, 32.50.

4.2.9. (1*RS*,2*SR*)-2-Phenylcyclopropanecarboxylic acid (*cis*-**14**)

To a solution of Et_2Zn (1.0 M in hexane, 4.08 mL, 4.08 mmol) in CH_2Cl_2 (3.0 mL) was added a solution of TFA (0.314 mL, 4.08 mmol) in CH_2Cl_2 (1.5 mL) at 0 °C under an argon atmosphere. After 20 min, a solution of CH_2I_2 (0.329 mL, 4.08 mmol) in CH_2Cl_2 (1.5 mL) was added to the mixture. After 20 min of stirring, a solution of *cis*-**2** (0.200 g, 1.36 mmol) in CH_2Cl_2 (4.0 mL) was added to the mixture. The reaction was stirred at room temperature for 5 h, quenched with saturated aqueous NH_4Cl, extracted with Et_2O, and the organic layer was dried over $MgSO_4$, filtered and concentrated *in vacuo*. The residue was purified by silica gel CC (EtOAc/hexane, 30:70) and, following recrystallization (toluene), yielded *cis*-**14** (0.137 g, 0.845 mmol, 62%) as colorless needles; mp 103–105 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 1.39 (m, 1H, *c*-Pr), 1.69 (m, 1H, *c*-Pr), 2.07 (m, 1H, –CH–CO_2–), 2.66 (dd, *J* = 8.8, 16.8 Hz, 1H, Ar–CH–), 7.13–7.38 (m, 5H, Ar–H); ^{13}C NMR ($CDCl_3$, 100 MHz) 12.0

(t, *c*-Pr), 21.3 (d, *c*-Pr), 26.5 (d, *c*-Pr), 126.8 (d, Ar), 128.0 (d, Ar), 129.3 (d, Ar), 135.9 (s, Ar), δ 176.3 (s, C=O);; IR (KBr) 1703 cm^{-1}; ESI-MS *m/z* 161 ($M^{+-}H$); Anal. calcd for $C_9H_8O_2$: C, 74.06; H, 6.21. Found: C, 73.82; H, 6.29; The spectroscopic data were in agreement with those in the literature (Concellón et al., 2007).

4.2.10. Potassium (2R,3R)-3-Phenyloxirane-2-carboxylate (cis-**15**)

The epoxidation of *cis*-**4** was performed according to the literature (Deng and Jacobsen, 1992) to give (2*R*,3*R*)-ethyl 3-phenyloxirane-2-carboxylate (41%) and its separable *trans*-form (11%) as a yellow oil: *cis*-form: $[\alpha]^{25}_{D+}$18.1 (c 2.20, $CHCl_3$); The product was not enantiomerically pure, but enantiomerically enriched; ^1H NMR ($CDCl_3$, 400 MHz) δ: 1.02 (t, *J* = 7.2 Hz, 3H, $-CH_3$), 3.82 (d, *J* = 4.8 Hz, 1H, $-CH-CO_2-$), 4.00 (m, 2H, $-CH_2-$), 4.27 (d, *J* = 4.8 Hz, 1H, Ar–CH–), 7.30–7.35 (m, 3H, Ar–H), 7.40–7.43 (m, 2H, Ar–H); The spectroscopic data were in agreement with those in the literature (Deng and Jacobsen, 1992).

To a solution of (2*R*,3*R*)-ethyl 3-phenyloxirane-2-carboxylate (120 mg, 0.625 mmol) in EtOH (5.0 mL) was added 0.52 M KOH (1.2 mL) at room temperature. The mixture was stirred for 4 h. After the solvent was removed *in vacuo*, the crude product was purified by recrystallization (^{i}PrOH) to give *cis*-**15** (84.0 mg, 0.416 mmol, 67%) as a colorless solid; ^1H NMR (CD_3OD, 400 MHz) δ: 3.67 (d, *J* = 4.8 Hz, 1H, $-CH-CO_2-$), 4.10 (d, *J* = 4.8 Hz, 1H, Ar–CH–), 7.20–7.30 (m, 3H, Ar–H), 7.45–7.47 (m, 2H, Ar–H); ^{13}C NMR (CD_3OD, 100 MHz) δ: 58.3 (d, epoxide), 60.0 (d, epoxide), 128.0 (d, Ar), 128.7 (d, Ar), 128.8 (d, Ar), 136.9 (s, Ar), 173.8 (s, C=O); IR (KBr) 1603 cm^{-1}; FAB-MS *m/z* 163 ($M^{+-}K$); The physical and spectroscopic data were consistent with those reported in the literature (Becker et al., 2005).

4.2.11. (Z)-3-Phenylbut-2-enoic acid (cis-**16**) and (E)-3-phenylbut-2-enoic acid (trans-**16**)

To a solution of NaH (60% in oil, 0.430 g, 10.8 mmol) in THF (33 mL) was added a solution of ethyl 2-(diethoxyphosphoryl)acetate (2.00 mL, 10.0 mmol) in THF (5.0 mL) at 0 °C for 30 min under an Ar atmosphere. After a solution of acetophenone (**34**) (0.650 mL, 8.30 mmol) in THF (5.0 mL) was added to the solution, the resulting mixture was refluxed for 6 h. The reaction was quenched with saturated aqueous NH_4Cl and extracted with EtOAc. The organic layers were washed with H_2O and brine, dried over $MgSO_4$, filtered and concentrated *in vacuo*. The residue was purified by silica gel CC (EtOAc/hexane, 3:97) to afford (*Z*)-ethyl 3-phenylbut-2-enoate (*cis*-**35**) (minor, 0.220 g, 1.16 mmol, 14%) and (*E*)-ethyl 3-phenylbut-2-enoate (*trans*-**35**) (major, 1.07 g, 5.62 mmol, 68%) as colorless oils: *cis*-**35**: ^1H NMR ($CDCl_3$, 400 MHz) δ: 1.08 (t, *J* = 7.2 Hz, 3H, $-CH_2-CH_3$), 2.18 (d, *J* = 1.2 Hz, 3H, Ar–C(CH_3)=), 4.00 (q, *J* = 7.2 Hz, 2H, $-CH_2-$), 5.91 (d, *J* = 1.2 Hz, 1H, $=CH-CO_2-$), 7.14–7.26 (m, 2H, Ar–H), 7.26–7.41 (m, 3H, Ar–H); The observed characterization data were consistent with those reported (Miura et al., 2009); *trans*-**35**: ^1H NMR ($CDCl_3$, 400 MHz) δ: 1.32 (t, *J* = 7.2 Hz, 3H, $-CH_2-CH_3$), 2.58 (s, 3H, Ar–C(CH_3)=), 4.22 (q, *J* = 7.2 Hz, 2H, $-CH_2-$), 6.14 (s, 1H, $=CH-CO_2-$), 7.31–7.44 (m, 3H, Ar–H), 7.44–7.58 (m, 2H, Ar–H); The physical and spectroscopic data were consistent with those reported in the literature (Miura et al., 2009).

Hydrolysis of *cis*-**35** was performed using the procedure described above to give *cis*-**16** (76%) as colorless needles: mp 125–126 °C (CH_2Cl_2/hexane, 5:95); ^1H NMR ($CDCl_3$, 400 MHz) δ 2.20 (brs, 3H, $-CH_3$), 5.91 (brs, 1H, $=CH-CO_2-$), 7.18–7.27 (m, 2H, Ar–H), 7.27–7.39 (m, 3H, Ar–H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 27.5 (q, $-CH_3$), 116.9 (d, $=CH-CO_2-$), 126.8 (d, Ar), 127.9 (d, Ar), 128.0 (d, Ar), 140.2 (s, Ar), 158.2 (s, Ar–C(CH_3)=), 171.0 (s, C=O); IR (KBr): 1695 cm^{-1}; ESI-MS *m/z* 161 ($M^{+-}H$); Anal. calcd for $C_{10}H_{10}O_2$: C, 74.06; H, 6.21. Found: C, 74.06; H, 6.15); The spectroscopic data were in agreement with those in the literature (Bellassoued et al., 2005).

Hydrolysis of *trans*-**35** was performed using the procedure described above to afford *trans*-**16** (78%) as colorless needles: mp 98–99 °C (CH_2Cl_2/hexane, 5:95); ^1H NMR ($CDCl_3$, 400 MHz) δ: 2.61 (d, *J* = 1.4 Hz, 3H, $-CH_3$), 6.18 (d, *J* = 1.4 Hz, 1H, $=CH-CO_2-$), 7.35–7.42 (m, 3H, Ar–H), 7.47–7.52 (m, 2H, Ar–H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 18.3 (q, $-CH_3$), 116.5 (d, $=CH-CO_2-$), 126.4 (d, Ar), 128.5 (d, Ar), 129.3 (d, Ar), 142.0 (s, Ar), 158.5 (s, Ar–C(CH_3)=), 172.4 (s, C=O); IR (KBr) 1678 cm^{-1}; FAB-MS *m/z* 162 (M^+); Anal. calcd for $C_{10}H_{10}O_2$: C, 74.06; H, 6.21. Found: C, 74.15; H, 6.23; The spectroscopic data were in agreement with those in the literature (Takimoto et al., 2001).

4.2.12. (Z)-2-Methyl-3-phenylacrylic acid (cis-**17**) and (E)-2-Methyl-3-phenylacrylic acid (trans-**17**)

The *E*-selective olefination of **27** using ethyl 2-(triphenylphosphoranylidene)propanoate was performed using the procedure described above to provide (*E*)-ethyl 2-methyl-3-phenylacrylate (quant., *E* only) (silica gel column chromatography, EtOAc/hexane, 3:97) as a colorless oil: ^1H NMR ($CDCl_3$, 400 MHz) δ: 1.35 (t, *J* = 7.6 Hz, 3H, $-CH_2-CH_3$), 2.12 (brs, 3H, $=C(CH_3)-CO_2-$), 4.28 (q, *J* = 7.6 Hz, 2H, $-CH_2-$), 7.22–7.51 (m, 5H, Ar–H), 7.69 (d, *J* = 1.2 Hz, 1H, Ar–CH=); The spectral data were in agreement with those in the literature (Maji et al., 2010).

A solution of (*E*)-ethyl 2-methyl-3-phenylacrylate (0.300 g, 1.58 mmol) in CH_2Cl_2 (0.32 mL) was irradiated with a xenon light (300 W) at room temperature for 4 h. After the removal of the solvent, purification over silica gel CC (EtOAc/hexane, 3:97) gave (*Z*)-ethyl 2-methyl-3-phenylacrylate (minor, 46.8 mg, 0.246 mmol, 16%) and the recovered *E*-form (major, 0.249 g, 1.31 mmol, 83%) as a colorless oil: *Z*-form: ^1H NMR ($CDCl_3$, 400 MHz) δ: 1.11 (t, *J* = 7.4 Hz, 3H, $-CH_2-CH_3$), 2.10 (brs, 3H, $=C(CH_3)-CO_2-$), 4.11 (q, *J* = 7.4 Hz, 2H, $-CH_2-$), 6.71 (brs, 1H, Ar–CH=), 7.18–7.41 (m, 5H, Ar–H); The spectroscopic data were in agreement with those in the literature (Maji et al., 2010).

Hydrolysis of (*Z*)-ethyl 2-methyl-3-phenylacrylate was performed using the procedure described above to afford *cis*-**17** (70%) as colorless needles: mp 82–83 °C (CH_2Cl_2/hexane, 5:95); ^1H NMR ($CDCl_3$, 400 MHz) δ: 2.12 (d, *J* = 1.4 Hz, 3H, $-CH_3$), 6.86 (q, *J* = 1.4 Hz, 1H, Ar–CH=), 7.20–7.36 (m, 5H, Ar–H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 21.5 (q, $-CH_3$), 128.0 (d, Ar), 128.1 (s, $=C(CH_3)-CO_2-$), 128.3 (d, Ar), 128.4 (d, Ar), 135.9 (s, Ar), 137.7 (d, Ar–CH=), 172.5 (s, C=O); IR (KBr) 1684 cm^{-1}; EI-MS *m/z* 162 (M^+); HR EI-MS *m/z* 162.0679 (M^+, calcd for $C_{10}H_{10}O_2$ 162.0681); Anal. calcd for $C_{10}H_{10}O_2$: C, 74.06; H, 6.21. Found: C, 73.76; H, 6.27; The spectroscopic data were in agreement with those in the literature (Rudler and Durand-Réville, 2001).

Hydrolysis of (*E*)-ethyl 2-methyl-3-phenylacrylate was performed using the procedure described above to afford *trans*-**17** (quant.) as colorless needles: mp 80–82 °C (CH_2Cl_2/hexane, 5:95); ^1H NMR ($CDCl_3$, 400 MHz) δ: 2.16 (d, *J* = 1.2 Hz, 3H, $-CH_3$), 7.24–7.48 (m, 5H, Ar–H), 7.84 (q, *J* = 1.2 Hz, 1H, Ar–CH=); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 13.7 (q, $-CH_3$), 127.5 (s, $=C(CH_3)-CO_2-$), 128.5 (d, Ar), 128.7 (d, Ar), 129.8 (d, Ar), 135.6 (s, Ar), 141.1 (d, Ar–CH=), 174.0 (s, C=O); IR (KBr) 1670 cm^{-1}; EI-MS *m/z* 162 (M^+); HR EI-MS *m/z* 162.0675 (M+, calcd for $C_{10}H_{10}O_2$ 162.0681); Anal. calcd for $C_{10}H_{10}O_2$: C, 74.06; H, 6.21. Found: C, 74.08; H, 6.27; The spectroscopic data were in agreement with those in the literature (Rudler and Durand-Réville, 2001).

4.2.13. (Z)-2-Methyl-3-phenylbut-2-enoic Acid (cis-**18**) and (E)-2-Methyl-3-phenylbut-2-enoic Acid (trans-**18**)

The olefination of **34** using the ynolate was performed according to the literature (Shindo et al., 2004) to give the (*Z*)-methyl 2-methyl-3-phenylbut-2-enoate (*cis*-**38**) (minor, 20%) and the (*E*)-methyl 2-methyl-3-phenylbut-2-enoate (*trans*-**38**) (major, 80%) (silica gel CC, EtOAc/hexane, 3:97) as colorless oils: *cis*-**38**:

^{1}H NMR ($CDCl_3$, 400 MHz) δ: 2.04 (s, 3H, =C(CH_3)–CO_2–), 2.10 (s, 3H, Ar–C(CH_3)=), 3.39 (s, 3H, –OCH_3), 7.10–7.15 (m, 2H, Ar–H), 7.24–7.43 (m, 3H, Ar–H); *trans*-**38**: ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 1.76 (d, J = 1.6 Hz, 3H, =C(CH_3)–CO_2–), 2.27 (d, J = 1.6 Hz, 3H, Ar–C(CH_3)=), 3.80 (s, 3H, –OCH_3), 7.10–7.19 (m, 2H, Ar–H), 7.24–7.43 (m, 3H, Ar–H); The physical and spectroscopic data were consistent with those reported in the literature (Shindo et al., 2004).

Hydrolysis of *cis*-**38** was performed using the procedure described above to afford *cis*-**18** (58%) as colorless needles: mp 110–111 °C (CH_2Cl_2/hexane, 5:95); ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 2.04 (s, 3H, =C(CH_3)–CO_2–), 2.11 (s, 3H, Ar–C(CH_3)=), 7.12–7.16 (m, 2H, Ar–H), 7.25–7.32 (m, 3H, Ar–H); ^{13}C NMR ($CDCl_3$, 150 MHz) δ 16.3 (q, =C(*C*H$_3$)–CO_2–), 22.7 (q, Ar–C(*C*H$_3$)=), 124.6 (s, =*C*(CH_3)–CO_2–), 126.8 (d, Ar), 127.2 (d, Ar), 128.1 (d, Ar), 143.7 (s, Ar), 146.3 (s, Ar–*C*(CH_3)=), 173.6 (s, C=O); IR (KBr) 1686 cm^{-1}; EI-MS *m/z* 176 (M^+); ESI-MS *m/z* 175 (M^+–H); HR EI-MS *m/z* 176.0843 (M^+, calcd for $C_{11}H_{12}O_2$ 176.0837); Anal. calcd for $C_{11}H_{12}O_2$: C, 74.98; H, 6.86. Found: C, 74.73; H, 6.98.

Hydrolysis of *trans*-**38** was performed using the procedure described above to afford *trans*-**18** (62%) as colorless needles; mp 101–103 °C (CH_2Cl_2/hexane, 5:95); ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 1.80 (d, J = 1.2 Hz, 3H, =C(CH_3)–CO_2–), 2.38 (d, J = 1.2 Hz, 3H, Ar–C(CH_3)=), 7.13–7.17 (m, 2H, Ar–H), 7.24–7.41 (m, 3H, Ar–H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 17.3 (q, =C(*C*H$_3$)–CO_2–), 23.7 (q, Ar–C(*C*H$_3$)=), 123.7 (s, =*C*(CH_3)–CO_2–), 127.0 (d, Ar), 127.2 (d, Ar), 128.4 (d, Ar), 143.8 (s, Ar), 150.2 (s, Ar–*C*(CH_3)=), 174.8 (s, C=O); IR (KBr) 1684 cm^{-1}; EI-MS *m/z* 176 (M^+); ESI-MS *m/z* 175 (M^+–H); HR EI-MS *m/z* 176.0834 (M^+, calcd for $C_{11}H_{12}O_2$ 176.0837); Anal. calcd for $C_{11}H_{12}O_2$: C, 74.98; H, 6.86. Found: C, 74.89; H, 6.86.

4.2.14. (*Z*)-3-Cyclohexylacrylic acid (*cis*-**20**)

The *Z*-selective olefination of cyclohexanecarboxaldehyde was performed using the procedure described above to provide the (*Z*)-ethyl 3-cyclohexylacrylate (62%, *Z* only) (silica gel CC, EtOAc/hexane, 3:97) as a colorless oil: ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.01–1.42 (m, 5H, *c*-Hex-H), 1.29 (t, J = 7.2 Hz, 3H, –CH_3), 1.63–1.80 (m, 5H, *c*-Hex-H), 3.29 (m, 1H, *c*-Hex-H), 4.16 (q, J = 7.2 Hz, 2H, –CH_2–), 5.65 (d, J = 11.6 Hz, 1H, =*C*H–CO_2–), 6.02 (dd, J = 9.2, 11.6 Hz, 1H, *c*-Hex-C*H*=); The spectroscopic data were in agreement with those in the literature (Miura et al., 2009).

Hydrolysis of (*Z*)-ethyl 3-cyclohexylacrylate was performed using the procedure described above to afford *cis*-**20** (88%) as colorless needles: mp 41–42 °C (hexane); ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 1.04–1.46 (m, 5H, *c*-Hex-H), 1.63–1.82 (m, 5H, *c*-Hex-H), 3.30 (m, 1H, *c*-Hex-H), 5.68 (d, J = 11.2 Hz, 1H, =CH–CO_2–), 6.16 (dd, J = 9.9, 11.2 Hz, 1H, *c*-Hex-CH=); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 25.4 (t, *c*-Hex), 25.9 (t, *c*-Hex), 32.2 (t, *c*-Hex), 37.4 (d, *c*-Hex), 116.5 (d,=CH–CO_2–), 158.1 (d, *c*-Hex-CH=), 171.2 (s, C=O); IR (KBr) 1701 cm^{-1}; EI-MS *m/z* 154 (M^+); FAB-MS *m/z* 154 (M^+); HR EI-MS *m/z* 154.0992 (M^+, calcd for $C_9H_{14}O_2$ 154.0994); Anal. calcd for $C_9H_{14}O_2$: C, 70.10; H, 9.15. Found: C, 70.14; H, 9.23; The spectroscopic data were in agreement with those in the literature (Vuagonoux-d' and Alexakis, 2007).

4.2.15. (*E*)-3-Cyclohexylacrylic acid (*trans*-**20**)

The *E*-selective olefination of cyclohexanecarboxaldehyde was performed using the previously described procedure (Alhamadsheh et al., 2007) to provide (*E*)-ethyl 3-cyclohexylacrylate (78%, *E* only) (silica gel CC, EtOAc/hexane, 3:97) as a colorless oil: ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 1.05–1.26 (m, 5H, *c*-Hex-H), 1.29 (t, J = 7.2 Hz, 3H, –CH_3), 1.72–1.82 (m, 5H, *c*-Hex-H), 2.12 (m, 1H, *c*-Hex-H), 4.18 (q, J = 7.2 Hz, 2H, –CH_2–), 5.76 (d, J = 16.2 Hz, 1H, =CH–CO_2–), 6.91 (dd, J = 6.8, 16.2 Hz, 1H, *c*-Hex-CH=); The physical and spectroscopic data were consistent with those reported in the literature (Ando, 1997).

The hydrolysis of (*E*)-ethyl 3-cyclohexylacrylate, using the procedure described above, afforded *trans*-**20** (78%) as colorless needles: mp 46–47 °C (hexane); ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 1.09–1.38 (m, 5H, *c*-Hex-H), 1.63–1.85 (m, 5H, *c*-Hex-H), 2.18 (m, 1H, *c*-Hex-H), 5.78 (d, J = 16.0 Hz, 1H, =CH–CO_2–), 7.01 (dd, J = 6.8 Hz, 16.0 Hz, 1H, *c*-Hex-CH=); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 25.7 (t, *c*-Hex), 25.9 (t, *c*-Hex), 31.6 (t, *c*-Hex), 40.5 (d, *c*-Hex), 118.0 (d, =*C*H–CO_2–), 157.1 (d, *c*-Hex-CH=), 171.3 (s, C=O); IR (KBr): 1686 cm^{-1}; EI-MS *m/z* 154 (M^+); FAB-MS *m/z* 154 (M^+); HR FAB-MS *m/z* 154.0995 (M^+, calcd for $C_9H_{14}O_2$ 154.0994); Anal. calcd for $C_9H_{14}O_2$: C, 70.10; H, 9.15. Found: C, 70.01; H, 9.18; The spectroscopic data were in agreement with those in the literature (Alhamadsheh et al., 2007).

4.2.16. (*Z*)-3-(Cyclohex-1-en-1-yl)acrylic Acid (*cis*-**21**)

The *Z*-selective olefination of cyclohex-1-enecarboxaldehyde was performed using the procedure described above to provide (*Z*)-ethyl 3-(cyclohex-1-en-1-yl)acrylate (53%, *Z* only) (silica gel CC, EtOAc/hexane, 5:95) as a colorless oil: ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 1.29 (t, J = 7.2 Hz, 3H, -CH_3), 1.54–1.73 (m, 4H, *c*-Hexene-H), 2.15–2.22 (m, 2H, *c*-Hexene-H), 2.22–2.35 (m, 2H, *c*-Hexene-H), 4.17 (q, J = 7.2 Hz, 2H, –CH_2–), 5.59 (d, J = 12.8 Hz, 1H, =CH–CO_2–), 6.01 (brs, 1H, *c*-Hexene-H), 6.32 (d, J = 12.8 Hz, 1H, *c*-Hexene-CH=); FAB-MS *m/z* 180 (M^+).

The hydrolysis of (*Z*)-ethyl 3-(cyclohex-1-en-1-yl)acrylate was performed using the procedure described above to afford *cis*-**21** (85%) as colorless needles: mp 62–64 °C (CH_2Cl_2/hexane, 5:95); ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 1.59–1.64 (m, 4H, *c*-Hexene-H), 2.16–2.26 (m, 2H, *c*-Hexene-H), 2.26–2.32 (m, 2H, *c*-Hexene-H), 5.63 (d, J = 12.4 Hz, 1H, =CH–CO_2–), 6,08 (brs, 1H, *c*-Hexene-H), 6.45 (d, J = 12.4 Hz, 1H, *c*-Hexene-CH=); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 21.6 (t, *c*-Hexene), 22.5 (t, *c*-Hexene), 26.4 (t, *c*-Hexene), 27.0 (t, *c*-Hexene), 114.9 (d, =*C*H–CO_2–), 135.4 (s, *c*-Hexene), 137.2 (d, *c*-Hexene-CH=), 147.4 (d, *c*-Hexene), 172.2 (s, C=O); IR (KBr) 1684 cm^{-1}; EI-MS *m/z* 152 (M^+); FAB-MS *m/z* 152 (M^+); HR EI-MS *m/z* 152.0832 (M^+, calcd for $C_9H_{12}O_2$ 152.0837); Anal. calcd for $C_{10}H_{11}O_2$: C, 71.03; H, 7.95. Found: C, 71.05; H, 8.00.

4.2.17. (*E*)-3-(Cyclohex-1-en-1-yl)acrylic Acid (*trans*-**21**)

The *E*-selective olefination of cyclohex-1-enecarboxaldehyde was performed according to the literature (Piva and Comesse, 2000) to give (*E*)-ethyl 3-(cyclohex-1-en-1-yl)acrylate (53%, *E* only) (silica gel CC, EtOAc/hexane, 3:97) as a colorless oil: ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 1.29 (t, J = 7.2 Hz, 3H, -CH_3), 1.49–1.78 (m, 4H, *c*-Hexene-H), 2.04–2.25 (m, 4H, *c*-Hexene-H), 4.20 (q, J = 7.2 Hz, 2H, –CH_2–), 5.77 (d, J = 15.8 Hz, 1H, =CH–CO_2–), 6.16 (s, 1H, *c*-Hexene-H), 7.28 (d, J = 15.8 Hz, 1H, *c*-Hexene-CH=); The physical and spectroscopic data were consistent with those reported in the literature (Piva and Comesse, 2000).

The hydrolysis of (*E*)-ethyl 3-(cyclohex-1-en-1-yl)acrylate, using the procedure described above, afforded *trans*-**21** (quant.) as colorless needles: mp 116–117 °C (CH_2Cl_2/hexane, 5:95); ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 1.54–1.75 (m, 4H, *c*-Hexene-H), 2.14–2.25 (m, 4H, *c*-Hexene-H), 5.77 (d, J = 16.4 Hz, 1H, =CH–CO_2–), 6.23 (m, 1H, *c*-Hexene-H), 7.36 (d, J = 16.4 Hz, 1H, *c*-Hexene-CH=); ^{13}C NMR($CDCl_3$, 100 MHz) δ: 21.9 (t, *c*-Hexene), 22.0 (t, *c*-Hexene), 24.1 (t, *c*-Hexene), 26.5 (t, *c*-Hexene), 113.7 (d, =*C*H–CO_2–), 134.9 (s, *c*-Hexene), 140.3 (d, *c*-Hexene-CH=), 150.4 (d, *c*-Hexene), 173.3 (s, C=O); IR (KBr) 1684 cm^{-1}; FAB-MS *m/z* 152 (M^+); Anal. calcd for $C_{10}H_{11}O_2$: C, 71.03; H, 7.95. Found: C, 70.94; H, 7.93; The spectroscopic data were in agreement with those in the literature. (Chackalamannil et al., 1999).

4.2.18. (*Z*)-3-(Cyclohex-3-en-1-yl)acrylic Acid (*cis*-**22**)

The *Z*-selective olefination of cyclohex-3-enecarboxaldehyde was performed using the procedure described above to provide

(*Z*)-ethyl 3-(cyclohex-3-en-1-yl)acrylate (59%, *Z* only) (silica gel CC, EtOAc/hexane, 3:97) as a colorless oil: ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 1.29 (t, J = 7.2 Hz, 3H, $-CH_3$), 1.46 (m, 1H, *c*-Hexene-H), 1.72–1.92 (m, 2H, *c*-Hexene-H), 2.00–2.29 (m, 3H, *c*-Hexene-H), 3.58 (m, 1H, *c*-Hexene-H), 4.17 (q, J = 7.2 Hz, 2H, $-CH_2-$), 5.62–5.81 (m, 2H, *c*-Hexene-H), 5.72 (d, J = 11.6 Hz, 1H, $=CH-CO_2-$), 6.11 (dd, J = 10.0, 11.6 Hz, 1H, *c*-Hexene-CH=).

The hydrolysis of (*Z*)-ethyl 3-(cyclohex-3-en-1-yl)acrylate was performed using the procedure described above to afford *cis*-**22** (78%) as colorless needles: mp 64–65 °C (CH_2Cl_2/hexane, 5:95); ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 1.47 (m, 1H, *c*-Hexene-H), 1.72–1.95 (m, 2H, *c*-Hexene-H), 1.99–2.29 (m, 3H, *c*-Hexene-H), 3.59 (m, 1H, *c*-Hexene-H), 5.62–5.83 (m, 2H, *c*-Hexene-H), 5.75 (d, J = 11.6 Hz, 1H, $=CH-CO_2-$), 6.26 (dd, J = 10.2, 11.6 Hz, 1H, *c*-Hexene-CH=); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 24.0 (t, *c*-Hexene), 28.0 (t, *c*-Hexene), 30.4 (t, *c*-Hexene), 33.2 (d, *c*-Hexene), 117.7 (d, $=CH-CO_2-$), 125.3 (d, *c*-Hexene), 127.0 (d, *c*-Hexene), 157.3 (d, *c*-Hexene-CH=), 171.5 (s, C=O); IR (KBr) 1686 cm^{-1}; EI-MS *m/z* 152 (M^+); HR EI-MS *m/z* 152.0835 (M^+, calced for $C_9H_{12}O_2$ 152.0837); Anal. calcd for $C_9H_{12}O_2$: C, 71.03; H, 7.95. Found: C, 70.99; H, 7.78.

*4.2.19. (E)-3-(Cyclohex-3-en-1-yl)acrylic Acid (trans-**22**)*

The *E*-selective olefination of cyclohex-3-enecarboxaldehyde was performed using the procedure described above to provide (*E*)-ethyl 3-(cyclohex-3-en-1-yl)acrylate (89%, *E* only) (silica gel CC, EtOAc/hexane, 3:97) as a colorless oil: ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 1.29 (t, J = 7.2 Hz, 3H, -CH_3), 1.47 (m, 1H, *c*-Hexene-H), 1.83 (m, 1H, *c*-Hexene-H), 1.93 (m, 1H, *c*-Hexene-H), 2.03–2.25 (m, 3H, *c*-Hexene-H), 2.44 (m, 1H, *c*-Hexene-H), 4.19 (q, J = 7.2 Hz, 2H, $-CH_2-$), 5.63–5.76 (m, 2H, *c*-Hexene-H), 5.82 (dd, J = 1.4, 16.2 Hz, 1H, $=CH-CO_2-$), 6.98 (dd, J = 7.4, 16.2 Hz, 1H, *c*-Hexene-CH=)

Hydrolysis of (*E*)-ethyl 3-(cyclohex-3-en-1-yl)acrylate was performed by using the procedure described above to give *trans*-**22** (72%) as colorless needles: mp 43–44 °C (CH_2Cl_2/hexane, 5:95); H NMR ($CDCl_3$, 400 MHz) δ: 1.49 (m, 1H, *c*-Hexene-H), 1.78–2.01 (m, 2H, *c*-Hexene-H), 2.03–2.28 (m, 3H, *c*-Hexene-H), 2.48 (m, 1H, *c*-Hexene-H), 5.62–5.78 (m, 2H, *c*-Hexene-H), 5.84 (dd, J = 1.0, 16.0 Hz, 1H, $=CH-CO_2-$), 7.10 (dd, J = 7.0, 16.0 Hz, 1H, *c*-Hexene-CH=); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 24.3 (t, *c*-Hexene), 27.4 (t, *c*-Hexene), 29.9 (t, *c*-Hexene), 36.5 (d, *c*-Hexene), 118.9 (d, $=CH-CO_2-$), 125.1 (d, *c*-Hexene), 127.0 (d, *c*-Hexene), 156.1 (d, *c*-Hexene-CH=), 172.0 (s, C=O); IR (KBr) 1690 cm^{-1}; EI-MS *m/z* 152 (M^+); HR EI-MS *m/z* 152.0842 (M^+, calcd for $C_9H_{12}O_2$ 152.0837); Anal. calcd for $C_9H_{12}O_2$: C, 71.03; H, 7.95. Found: C, 71.05; H, 7.98.

*4.2.20. (2Z,4E)-4-Methylhexa-2,4-dienoic Acid (cis-**23**)*

The *Z*-selective olefination of (*E*)-2-methylbut-2-enal (tiglic aldehyde) was performed using the procedure described above to provide (2*Z*,4*E*)-ethyl 4-methylhexa-2,4-dienoate (31%, 2*E*:2*Z* = 14:86, determined by analysis of the ^{1}H NMR spectrum) (silica gel column chromatography, EtOAc/hexane, 3:97) as a colorless oil: ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 1.30 (t, J = 7.2 Hz, 3H, $-CH_2-CH_3$), 1.74 (d, J = 6.8 Hz, 3H, $C(CH_3)H=$), 1.87 (s, 3H, $C(CH_3)H=C(CH_3)-$), 4.23 (q, J = 7.2 Hz, 2H, $-CH_2-$), 5.60 (d, J = 12.8 Hz, 1H, $=CH-CO_2-$), 5.81 (q, J = 6.8 Hz, 1H, $C(CH_3)H=$), 6.38 (d, J = 12.8 Hz, 1H, $-CH=CH-CO_2-$).

Hydrolysis of (2*Z*,4*E*)-ethyl 4-methylhexa-2,4-dienoate was performed using the procedure described above to yield *cis*-**23** (85%) (silica gel CC, EtOAc/hexane, 10:90) as a colorless oil: ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 1.76 (d, J = 6.8 Hz, 3H, $C(CH_3)H=$), 1.88 (s, 3H, $C(CH_3)H=C(CH_3)-$), 5.63 (d, J = 12.6 Hz, 1H, $=CH-CO_2-$), 5,88 (q, J = 6.8 Hz, 1H, $C(CH_3)H=$), 6.53 (d, J = 12.6 Hz, 1H, $-CH=CH-CO_2-$); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 14.3 (q, $C(CH_3)-H=C(CH_3)-$), 14.9 (q, $C(CH_3)H=$), 115.2 (d,$=CH-CO_2-$), 133.7 (s, $C(CH_3)H=C(CH_3)-$), 134.3 (d, $C(CH_3)H=$), 148.7 (d, $-CH=CH-CO_2-$), 171.9 (s, C=O); IR (neat) 1694 cm^{-1}; EI-MS *m/z* 126 (M^+), 111 (M^+-Me); HR EI-MS *m/z* 126.0681 (M^+, calcd for $C_7H_{10}O_2$ 126.0681).

*4.2.21. (2Z,4E)-5-Phenylpenta-2,4-dienoic Acid (cis-**24**)*

The *Z*-selective olefination of cinnamaldehyde was performed using the procedure described above to provide (2*Z*,4*E*)-ethyl 5-phenylpenta-2,4-dienoate (74%, 2*E*:2*Z* = 23:77, determined by ^{1}H NMR spectrum) (silica gel CC, EtOAc/hexane, 3:97) as a colorless oil: ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 1.33 (t, J = 7.4 Hz, 3H, $-CH_3$), 4.23 (q, J = 7.4 Hz, 2H, $-CH_2-$), 5.72 (d, J = 11.2 Hz, 1H,=$CH-CO_2-$), 6.74 (dd, J = 11.2, 11.6 Hz, 1H, $-CH=CH-CO_2-$), 6.81 (d, J = 16.4 Hz, 1H, Ar–$CH=CH-$), 7.22–7.43 (m, 3H, Ar–H), 7.47–7.60 (m, 2H, Ar–H), 8.16 (dd, J = 11.6, 16.4 Hz, 1H, Ar–$CH=CH-$); FAB-MS *m/z* 202 (M^+); The spectroscopic data were in agreement with those in the literature. (Miura et al., 2009).

The hydrolysis of (2*Z*,4*E*)-ethyl 5-phenylpenta-2,4-dienoate was performed using the procedure described above to give *cis*-**24** (94%) as colorless needles: mp 134–136 °C (CH_2Cl_2/hexane, 5:95); ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 5.77 (d, J = 11.2 Hz, 1H,=$CH-CO_2-$), 6.86 (dd, J = 11.2, 11.6 Hz, 1H, $-CH=CH-CO_2-$), 6.88 (d, J = 16.4 Hz, 1H, Ar–CH=), 7.28–7.43 (m, 3H, Ar–H), 7.40–7.49 (m, 2H, Ar–H), 8.10 (dd, J = 11.6, 16.4 Hz, 1H, Ar–$CH=CH-$); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 116.5 (d, $=CH-CO_2-$), 124.8 (d, Ar–$CH=CH-$), 127.7 (d, Ar), 128.8 (d, Ar), 129.2 (d, Ar), 136.1 (s, Ar), 142.5 (d, Ar–CH=), 147.1 (d, $-CH=CH-CO_2-$), 172.1 (s, C=O); IR (KBr) 1690 cm^{-1}; ESI-MS *m/z* 173 (M^+-H); Anal. calcd for $C_{11}H_{10}O_2$: C, 75.83; H, 5.79. Found: C, 75.53; H, 5.79; The spectroscopic data were in agreement with those in the literature (Concepcion et al., 1995).

*4.2.22. (2Z,4E)-5-(Cyclohex-1-en-1-yl)penta-2,4-dienoic Acid (cis-**25**)*

DIBAL-H (1.03 M in hexane, 21.9 mL, 22.6 mmol) was added to a solution of (*E*)-ethyl 3-(cyclohex-1-en-1-yl)acrylate (1.94 g, 10.8 mol) in THF (43 mL) at −78 °C under an argon atmosphere. The mixture was stirred for 2 h, quenched with saturated aqueous NH_4Cl and extracted with CH_2Cl_2. The combined organic layers were washed with H_2O and brine, dried over $MgSO_4$, filtered and concentrated *in vacuo*. The crude (*E*)-3-(cyclohex-1-en-1-yl)prop-2-en-1-ol was immediately employed in the next reaction. To a solution of crude (*E*)-3-(cyclohex-1-en-1-yl)prop-2-en-1-ol in CH_2Cl_2 (30 mL) were added Na_2CO_3 (3.70 g, 35.1 mmol) and MnO_2 (3.00 g, 34.5 mmol) at room temperature under an argon atmosphere. The mixture was stirred for 6 h, filtered through a Celite pad, washed with CH_2Cl_2 and concentrated *in vacuo*. Purification using silica gel CC (EtOAc/hexane, 10:90) provided (*E*)-3-(cyclohex-1-en-1-yl)acrylaldehyde (1.35 g, 9.91 mmol, 92% in 2 steps) as a colorless oil: ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 1.57–1.90 (m, 4H, *c*-Hexene-H), 2.13–2.23 (m, 2H, *c*-Hexene-H), 2.23–2.42 (m, 2H, *c*-Hexene-H), 6.08 (dd, J = 8.2, 15.8 Hz, 1H, $=CH-CHO$), 6.31 (brs, 1H, *c*-Hexene-H), 7.09 (d, J = 16.0 Hz, 1H, *c*-Hexene-CH=), 9.56 (d, J = 8.2 Hz, 1H, CHO); The spectroscopic data were in agreement with those in the literature (Trost and Livingston, 2008).

The *Z*-selective olefination of (*E*)-3-(cyclohex-1-en-1-yl)acrylaldehyde was performed using the procedure described above to provide (2*Z*,4*E*)-ethyl 5-(cyclohex-1-en-1-yl)penta-2,4-dienoate (60%, 2*E*:2*Z* = 25:75, determined by ^{1}H NMR spectrum) (silica gel CC, EtOAc/hexane, 3:97) as a colorless oil: ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 1.30 (t, J = 7.4 Hz, 3H, $-CH_3$), 1.53–1.78 (m, 4H, *c*-Hexene-H), 2.13–2.35 (m, 4H, *c*-Hexene-H), 4.19 (q, J = 7.4 Hz, 2H, $-CH_2-$), 5,60 (d, J = 11.2 Hz, 1H, $=CH-CO_2-$), 5.98 (brs, 1H, *c*-Hexene-H), 6.47 (d, J = 15.4 Hz, 1H, *c*-Hexene-C*H*=), 6.63 (dd, J = 11.2, 11.6 Hz, 1H, $-CH=CH-CO_2-$), 7.45 (dd, J = 11.6, 15.4 Hz, 1H, *c*-Hexene-CH=C*H*–).

The hydrolysis of (2*Z*,4*E*)-ethyl 5-(cyclohex-1-en-1-yl)penta-2,4-dienoate was performed by using the procedure described above to afford *cis*-**25** (89%) as colorless needles: mp 125–126 °C (hexane); ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 1.52–1.81 (m, 4H, *c*-Hexene-H), 2.14–2.33 (m, 4H, *c*-Hexene-H), 5,63 (d, *J* = 11.2 Hz, 1H, =CH–CO_2–), 6.02 (brs, 1H, *c*-Hexene-H), 6.51 (d, *J* = 15.8 Hz, 1H, *c*-Hexene-CH=), 6.73 (dd, *J* = 11.2, 11.6 Hz, 1H, –*CH*=CH–CO_2–), 7.39 (dd, *J* = 11.6, 15.8 Hz, 1H, *c*-Hexene-CH=C*H*–); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 22.19 (t, *c*-Hexene), 22.21 (t, *c*-Hexene), 24.5 (t, *c*-Hexene), 26.4 (t, *c*-Hexene), 114.8 (d, =*C*H–CO_2–), 121.7 (d, *c*-Hexene-CH=*C*H_2–), 135.9 (d, *c*-Hexene-*C*H=), 136.4 (s, *c*-Hexene), 146.6 (d, –*C*H=CH–CO_2–), 148.1 (d, *c*-Hexene), 172.4 (s, C=O); IR (KBr): 1684 cm^{-1}; EI-MS *m/z* 178 (M^+); FAB-MS *m/z* 178 (M^+); HR EI-MS *m/z* 178.0992 (M^+, calcd for $C_{11}H_{14}O_2$ 178.0994); Anal. calcd for $C_{11}H_{14}O_2$: C, 74.13; H, 7.92. Found: C, 73.99; H, 7.91.

4.2.23. (2*Z*,4*E*)-5-Cyclohexylpenta-2,4-dienoic Acid (cis-**26**)

The DIBAL-H reduction of (*E*)-ethyl 3-cyclohexylacrylate and subsequent MnO_2 oxidation were performed using the procedure described above to give (*E*)-3-cyclohexylacrylaldehyde (79% yield in 2 steps) (silica gel CC, EtOAc/hexane, 10:90) as a colorless oil: ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 1.07–1.43 (m, 5H, *c*-Hex-H), 1.62–1.87 (m, 5H, *c*-Hex-H), 2.28 (m, 1H, *c*-Hex-H), 6.07 (dd, *J* = 7.6, 16.4 Hz, 1H, =*CH*–CHO), 6.78 (dd, *J* = 6.8, 16.4 Hz, 1H, *c*-Hex-CH=), 9.50 (d, *J* = 7.6 Hz, 1H, –CHO); The spectroscopic data were in agreement with those in the literature (Stiller et al., 2011).

The *Z*-selective olefination of (*E*)-3-cyclohexylacrylaldehyde was performed using the procedure described above to provide (2*Z*,4*E*)-ethyl 5-cyclohexylpenta-2,4-dienoate (64%, 2*Z* only) (silica gel CC, EtOAc/hexane, 3:97) as a colorless oil: ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 1.07–1.38 (m, 5H, *c*-Hex-H), 1.30 (t, *J* = 7.2 Hz, 3H, -CH_3), 1.59–1.86 (m, 5H, *c*-Hex-H), 2.13 (m, 1H, *c*-Hex-H), 4.18 (q, *J* = 7.2 Hz, 2H, –CH_2–), 5,57 (d, *J* = 11.2 Hz, 1H, =CH–CO_2–), 6.01 (dd, *J* = 6.8, 15.6 Hz, 1H, *c*-Hex-CH=), 6.54 (dd, *J* = 11.2, 11.6 Hz, 1H, –*CH*=CH–CO_2–), 7.34 (dd, *J* = 11.6, 15.6 Hz, 1H, *c*-Hex-CH=C*H*–); FAB-MS *m/z* 208 (M^+).

Hydrolysis of the (2*Z*,4*E*)-ethyl 5-cyclohexylpenta-2,4-dienoate was performed using the procedure described above to give *cis*-**26** (78%) as colorless needles: mp 57–58 °C (hexane); ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 1.08–1.39 (m, 5H, *c*-Hex-H), 1.59–1.85 (m, 5H, *c*-Hex-H), 2.16 (m, 1H, *c*-Hex-H), 5,59 (d, *J* = 11.2 Hz, 1H, =CH–CO_2–), 6.06 (dd, *J* = 7.6, 15.6 Hz, 1H, *c*-Hex-CH=), 6.65 (dd, *J* = 11.2, 11.8 Hz, 1H, –*CH*=CH–CO_2–), 7.32 (dd, *J* = 11.8, 15.6 Hz, 1H, *c*-Hex-CH=C*H*–); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 25.8 (t, *c*-Hex), 26.0 (t, *c*-Hex), 32.3 (t, *c*-Hex), 41.3 (d, *c*-Hex), 114.5 (d, =*C*H–CO_2–), 124.6 (d, *c*-Hex-CH=*C*H–), 148.1 (d, *c*-Hex-*C*H=), 152.5 (d, –*C*H=CH–CO_2–), 171.2 (s, C=O) IR (KBr): 1686 cm^{-1}; EI-MS *m/z* 180 (M^+); FAB-MS *m/z* 180 (M^+); HR EI-MS *m/z* 180.1153 (M^+, calcd for $C_{11}H_{16}O_2$ 180.1150); Anal. calcd for $C_{11}H_{16}O_2$: C, 73.03; H, 8.95. Found: C, 73.23; H, 8.79.

4.3. Measurement of phytotoxic activities against lettuce root growth

The phytotoxic activity was measured according to the method described by Hiradate et al. (2004). A filter paper was placed in a glass petri dish. The test compound was dissolved in water at various concentrations and a portion of each test solution was added on the filter paper in the petri dish for each treatment. Fifteen pregerminated (25 °C in the dark) seedlings of lettuce (*Lactuca sativa* cv. Great Lakes 366) were used as a replicate for each treatment. The seedlings were incubated for 48 h at 25 °C in the dark, and the inhibitory activity of each test solution on root elongation was determined by measuring the length of each root and comparing it with that of the untreated control (using only distilled water). An EC_{50} value, which indicates the effective concentration required to induce a half-maximum effect, was calculated from a dose response curve of the phytotoxicity for each compound by applying a statistical model, probit model (Bliss, 1934), using the computer program, SPSS 13.0J.

4.4. Photoisomerization of cinnamic acid and its analogues by a xenon light

A solution of cinnamic acid in D_2O (5 mM) was irradiated in a glass tube placed at 3 cm from a xenon light (300 W) at 25 °C. The *Z*:*E* ratios of the cinnamic acids were determined by ^{1}H NMR spectra every 10 min until the achievement of the photostationary states.

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