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Substituent effects of *cis*-cinnamic acid analogues as plant growh inhibitors

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ABSTRACT

1-*O*-*cis*-Cinnamoyl-β-D-glucopyranose is one of the most potent allelochemicals that has been isolated from *Spiraea thunbergii Sieb* by Hiradate et al. It derives its strong inhibitory activity from *cis*-cinnamic acid (*cis*-CA), which is crucial for phytotoxicity. By preparing and assaying a series of *cis*-CA analogues, it was previously found that the key features of *cis*-CA for lettuce root growth inhibition are a phenyl ring, *cis*-configuration of the alkene moiety, and carboxylic acid. On the basis of a structure–activity relationship study, the substituent effects on the aromatic ring of *cis*-CA were examined by systematic synthesis and the lettuce root growth inhibition assay of a series of *cis*-CA analogues having substituents on the aromatic ring. While *ortho*- and *para*-substituted analogues exhibited low potency in most cases, *meta*-substitution was not critical for potency, and analogues having a hydrophobic and sterically small substituent were more likely to be potent. Finally, several *cis*-CA analogues were found to be more potent root growth inhibitors than *cis*-CA.

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1. Introduction

1-*O*-*cis*-Cinnamoyl-β-D-glucopyranose (**1**) (Fig. 1) was isolated from *Spiraea thunbergii* (Hiradate et al., 2004) as a potent allelochemical and was found in 56 species of woody plants grown in Japan by a bioassay of growth-inhibitory activity on root elongation of the germinated seedlings of lettuce (*Lactuca sativa L.*) (Morita et al., 2001). An essential structure for the bioactivity of *cis*-cinnamic acid (*cis*-CA) (*cis*-**2**) is thought to be the aglycone of the glycosyl ester **1** because *cis*-CA inhibited lettuce root growth as effectively as **1**, while *trans*-cinnamic acid (*trans*-CA) (*trans*-**2**) inhibited growth much less than the *cis*-isomer (Hiradate et al., 2005). Generally, the *trans*-**2** isomer is considered to be physiologically inactive and a weak antagonist of auxin, a plant hormone that regulates growth in the roots and stem (Koepfli et al., 1938; van Overbeek et al., 1951; Ferro et al., 2010). On the other hand, since the *cis*-**2** isomer inhibits the root growth of *Avena sativa*, *Triticum aestivum*, and *Arabidopsis thaliana*, and 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), it is widely considered to be an auxin agonist. Although mechanistic studies based on molecular biology have been reported (Chen et al., 2005; Guo et al., 2011), the molecular mechanisms of these activities have not yet been described. Nevertheless the first chemical synthesis of the glycosyl ester **1** was previously achieved, which confirmed its proposed structure and determined its optical rotation (Matsuo et al., 2011). A structure activity relationship study of *cis*-**2** was reported, this establishing the which revealed that essential structural features for its bioactivity being the *cis*-configuration of the alkene or cyclopropane, a carboxylic acid or its esters, and a planar ring including a phenyl group (Abe et al., 2012). If additional units can be introduced in the *cis*-**2** isomer without a loss in activity, stronger bioactive compounds or functional analogues such as molecular probes for mechanistic investigations can be developed. Based on our previous reports, additional units on the *cis*-alkene moiety caused a significant loss in bioactivity, while the introduction of substituents on the aromatic ring core may be possible without a loss in bioactivity.

Describe herein are the synthesis and evaluation of the *cis*-CA analogues **3**–**58** having substituent(s) on the aromatic ring, the purpose of which was to identify substituent effects to clarify structure–activity relationship. These will be useful in the preparation of chemical probes (Fig. 2) as well as more active compounds,

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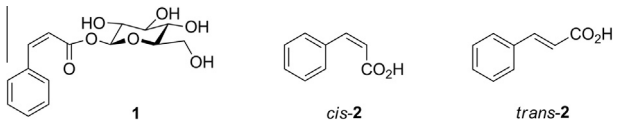


Fig. 1. Structures of 1-*O*-*cis*-cinnamoyl-β-D-glucopyranose (**1**) and *cis*- and *trans*-cinnamic acids (*cis*- and *trans*-**2**).

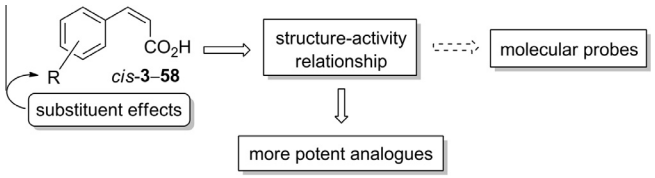


Fig. 2. An overview of this research.

leading to novel agrochemicals. To assay the bioactivity of the *cis*-CA analogues, inhibitory activity of these compounds against lettuce root growth were tested as described previously (Hiradate et al., 2005; Abe et al., 2012).

2. Results and discussion

2.1. Design and synthesis of cis-cinnamic acid analogues

A variety of *cis*-CA analogues bearing a substituent on the phenyl group at the *ortho*, *meta*, and *para* positions were systematically designed and synthesized. As a substituent, one of the alkyl, aromatic, alkoxy, halogeno, nitro, and trifluoromethyl groups were selected. Furthermore, a few multi-substituted analogues and polycyclic aromatic analogues including heteroaromatics, in place of the phenyl group, were also synthesized.

Their syntheses were mainly performed *via cis*-selective olefination of the corresponding aldehydes **59–114** with the modified Horner–Wadsworth–Emmons reaction (Ando, 1997; Ando et al., 2000), followed by hydrolysis of the ester of *cis*-olefins **115–170**, as depicted in Scheme 1.

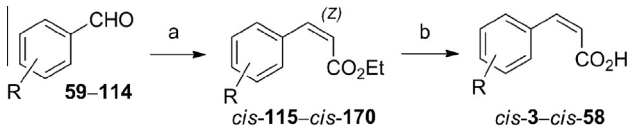
The commercially unavailable starting aldehydes **63**, **68**, **74–76**, **100**, **108** and **109** were prepared as shown in Scheme 2 (Wang et al., 2009; Li et al., 1998; Zhou and Zhao, 2009; Saitoh et al., 2009; Tasker et al., 1997).

2.2. Bioassay and discussion

The growth inhibitory activity of the *cis*-CA analogues against the root-growth of lettuce (*Lactuca sativa cv.*) was measured as described previously (Hiradate et al., 2005). EC_{50} values, which indicate the effective concentration required to induce a half-maximum effect, are shown in the Tables.

2.2.1. Effects of alkylation or alkoxylation of the aromatic ring

The *ortho*-methylated *cis*-CA analogue *cis*-**3** showed a more pronounced inhibitory activity than *cis*-CA **2** (Table 1, entry 2). However, the *meta*-methylated analogue *cis*-**4** and *para*-methylated *cis*-**5** were slightly less active. The analogues *cis*-**6**–*cis*-**13** having larger alkyl and aryl substituents, such as ethyl and phenyl groups, were markedly less active (entries 5–12). *Meta*-alkylation may have less of an effect on bioactivity than *ortho*- and *para*-alkylation, and sterically hindered substituents were more likely to reduce the activity. While the *meta*-methoxy analogue *cis*-**15** was more potent, the *para*-methoxy and *meta*-ethoxy analogues *cis*-**16** and *cis*-**17** were slightly less active and the *ortho*-methoxy one *cis*-**14** was much less active (entries 13–16). The presence of a larger alkoxyl group at the *meta* position led to inactive compounds (entries 17–19).



Scheme 1. Synthesis of the substituted *cis*-CA analogues **3**–**58**: (a) ethyl 2-[bis(2-isopropylphenoxy)phosphoryl]acetate, Triton B, THF, −78 °C, 45–99%, (b) 10% NaOH aq., EtOH, rt, 53–99%.

2.2.2. Effects of halogenation of the aromatic ring

Halogenated analogues (Table 1, entries 20–31) showed a similar level of activity to *cis*-**2**, although *cis*-**21** and *cis*-**32** were slightly less active. It was found that *meta*-substituted ones were preferred, providing compounds with EC_{50} values in the range of 1.0–2.5 μM, in which the order of activity was F < Cl < Br < I (entries 20–31). As a result, the *meta*-iodo analogue *cis*-**31** was found to be more active than *cis*-CA.

2.2.3. Effects of trifluoromethylation and nitration of the aromatic ring

While *ortho*-nitrated *cis*-**33** and *para*-nitrated *cis*-**35** were inactive, *meta*-nitrated *cis*-**34** was slightly less active than *cis*-CA **2** (Table 1, entries 32–34). It is noteworthy that *meta*-trifluoromethylated *cis*-**37** improved the activity, while *ortho*-substituted *cis*-**36** and *para*-substituted *cis*-**38** reduced it (entries 35–37). These results indicated that strong electron-withdrawing groups may markedly affect the activity.

In total, for mono-substituted *cis*-CAs, the *meta*-substitution of sterically small alkyl, alkoxy, and halogeno groups was more likely to maintain strong bioactivity, in which hydrophobic substituents were somewhat preferred. Steric factors were more important than inductive and electronic effects. On the other hand, inhibitory activity was very sensitive to *para*- and *ortho*-substitutions, and sterically bulky and strong electron withdrawing substituents showing a low Hammett σ value at these positions significantly reduced the activity.

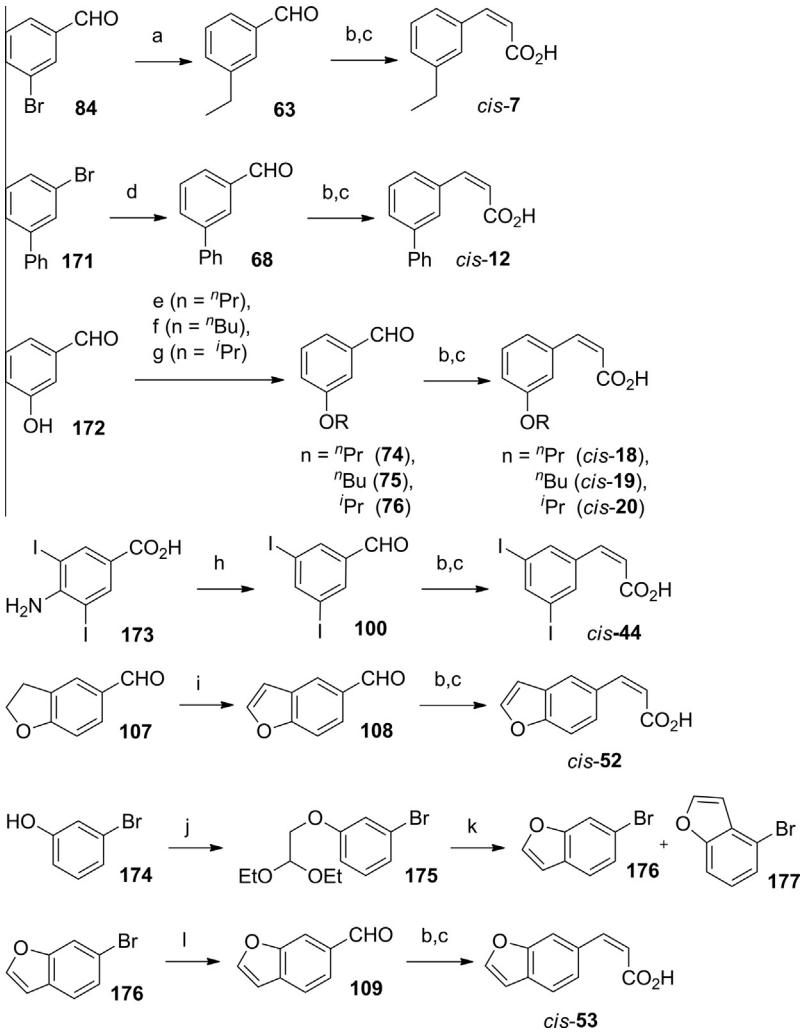
2.2.4. Effects of disubstitution of the aromatic ring

Disubstituted analogues were subjected to the inhibitory activity test (Table 1, entries 38–44). Additional *para*-methylated *cis*-**3** analogue *cis*-**39** and *para*-methoxylated *cis*-**3** analogue *cis*-**40** exhibited similar activity to *cis*-**3** (entries 38 and 39). However, the polymethoxylated *cis*-**2** analogues (*cis*-**41** and *cis*-**42**) significantly diminished the activity (entries 40 and 41). The *o*,*p*-dichloro analogue (*cis*-**43**) slightly improved activity, maybe due to higher hydrophobicity (entry 42).

If functional moieties were introduced in *cis*-**2** without a loss in inhibitory activity, a hydrophobic and relatively small substituent at the *meta*-position was preferred, regardless of its electronic properties such as the Hammet σ value.

2.2.5. Effects of the ring structure

The fused aromatic ring analogues *cis*-**46**-*cis*-**58** were examined as shown in Table 2. The 1-naphthyl, 9-phenanthryl-, 9-anthranyl-, and dibenzofuranyl analogues *cis*-**46**–*cis*-**49** markedly reduced the activity (entries 1–4). In contrast, the 2-naphthyl-, 5-benzofuranyl-, 5-(2,3-dihydro)benzofuranyl, 6-benzofuranyl, and benzothiophene-5-yl *cis*-**2** analogues *cis*-**50**–*cis*-**54** retained more potent inhibitory activity than *cis*-**2** (entries 5–9). The 5-benzofuranyl analogue *cis*-**52** also improved the activity. The potency of the 1-naphthyl analogue *cis*-**46** was markedly lower than that of the 2-naphthyl analogue *cis*-**50**. These results indicate that the "*ortho*, *meta*-disubstituted" type *cis*-CA analogues *cis*-**46**–*cis*-**49** were



Scheme 2. Preparation of commercially unavailable starting aldehydes **63**, **68**, **74**–**76**, **100**, **108**, and **109**: (a) triethylborane, $Pd(dppf)Cl_2$, CsOAc, THF, reflux, 46%, (b) ethyl 2-[bis(2-isopropylphenoxy)phosphoryl]acetate, Triton B, THF, −78 °C, (c) 10% NaOH aq., EtOH, rt, (d) ^{n}BuLi, DMF, THF, −78 °C to 0 °C, 79%, (e) K_2CO_3, 1-bromopropane, acetone, reflux, 51%, (f) K_2CO_3, 1-iodobutane, acetone, reflux, 62%, (g) K_2CO_3, 2-iodopropane, acetone, reflux, 62%, (h) Li et al. (1998), 23% (4 steps), (i) NBS, AIBN, chlorobenzene, 80 °C, 75%, (j) bromoacetaldehyde diethyl acetal, K_2CO_3, DMSO, 160 °C, 86%, (k) polyphosphoric acid (PPA), toluene, reflux, **176**: 46%, **177**: 41%, (l) ^{t}BuLi, DMF, Et_2O, −78 °C to 0 °C, 54%.

much less active than the "*meta*, *para*-disubstituted" type analogues *cis*-**50**–*cis*-**54**. The finding that the former type analogues *cis*-**46**–*cis*-**49** had lower potency and the latter type ones *cis*-**50**–*cis*-**54** had higher potency support this hypothesis. The finding that a *meta*-substituent did not decrease the activity is consistent with that of the substituent effect described in the previous section.

The 2-pyridyl analogue *cis*-**55** and 6-methoxy-2-pyridyl analogue *cis*-**56** exhibited a similar level of potency to *cis*-**2**, while the 6-methyl-2-pyridyl analogue *cis*-**57** was much less active than the corresponding analogue *cis*-**56**. The 3-pyridyl analogue *cis*-**58** was less active, which suggests critical electronic interaction between the nitrogen atom and the biomolecules.

3. Conclusion

Substituent effects on the aromatic ring of *cis*-cinnamic acid (*cis*-CA), a potent allelochemical was demonstrated. Although *para*- and *ortho*-substitution were critical for potency as an allelochemical, *meta*-substituted *cis*-CA analogues, especially those having a hydrophobic group, but not so sterically hindered substituent, were more likely to be potent. Finally, it was found that *cis*-CA analogues having *m*-iodo, *m*-methoxy, and *m*-trifluoromethyl groups were more potent than *cis*-CA (**2**).

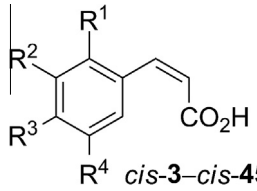
This structure–activity relationship study on *cis*-CA (**2**) will be very useful design and synthesize molecular probes for mechanistic investigations in furan and also to obtain strong inhibitors targeting new types of agrochemicals.

4. Experimental section

4.1. Materials

Optical rotations were obtained on a Horiba SEPA-300. Melting points were measured on the Yazawa micromelting point BY-1. ^{1}H- and ^{13}C-NMR spectra were recorded using JNM EX-270 (270 and 67.5 MHz), 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 internal standard. Splitting patterns are designed as "s, d, t, q, and m," indicating "singlet, doublet, triplet, quartet, and multiplet," respectively. IR spectra were recorded on a Shimadzu FT/IR-8300 spectrometer using a KBr disk or a NaCl cell. Mass spectra were obtained on JEOL JMS-700 or JEOL JMS-T100CS. High-resolution mass spectra were obtained on a JEOL JMS-700 or a JEOL JMS-

Table 1
The growth inhibitory activities of the *cis*-CA analogues **3**–**45**



cis-**3**–*cis*-**45**

Entry	(No)	R^1 (*o*-)	R^2 (*m*-)	R^3 (*p*-)	R^4 (*m*'-)	EC_{50} (μM)
1	*cis*-**2**	H	H	H	H	2.2
2	*cis*-**3**	Me	H	H	H	1.4
3	*cis*-**4**	H	Me	H	H	4.1
4	*cis*-**5**	H	H	Me	H	23
5	*cis*-**6**	Et	H	H	H	30
6	*cis*-**7**	H	Et	H	H	10
7	*cis*-**8**	H	H	Et	H	82
8	*cis*-**9**	H	H	*i*-Pr	H	218
9	*cis*-**10**	H	H	*t*-Bu	H	>500
10	*cis*-**11**	Ph	H	H	H	>500
11	*cis*-**12**	H	Ph	H	H	164
12	*cis*-**13**	H	H	Ph	H	245
13	*cis*-**14**	MeO	H	H	H	64
14	*cis*-**15**	H	MeO	H	H	1.1
15	*cis*-**16**	H	H	MeO	H	2.9
16	*cis*-**17**	H	EtO	H	H	9.3
17	*cis*-**18**	H	^{n}PrO	H	H	>500
18	*cis*-**19**	H	^{n}BuO	H	H	~270
19	*cis*-**20**	H	^{i}PrO	H	H	~260
20	*cis*-**21**	F	H	H	H	29
21	*cis*-**22**	H	F	H	H	3.2
22	*cis*-**23**	H	H	F	H	6.2
23	*cis*-**24**	Cl	H	H	H	6.9
24	*cis*-**25**	H	Cl	H	H	3.0
25	*cis*-**26**	H	H	Cl	H	2.2
26	*cis*-**27**	Br	H	H	H	4.7
27	*cis*-**28**	H	Br	H	H	2.0
28	*cis*-**29**	H	H	Br	H	4.1
29	*cis*-**30**	I	H	H	H	2.9
30	*cis*-**31**	H	I	H	H	1.8
31	*cis*-**32**	H	H	I	H	17
32	*cis*-**33**	NO_2	H	H	H	>500
33	*cis*-**34**	H	NO_2	H	H	27
34	*cis*-**35**	H	H	NO_2	H	>500
35	*cis*-**36**	CF_3	H	H	H	241
36	*cis*-**37**	H	CF_3	H	H	0.6
37	*cis*-**38**	H	H	CF_3	H	77
38	*cis*-**39**	Me	H	Me	H	5.3
39	*cis*-**40**	Me	H	MeO	H	2.0
40	*cis*-**41**	H	MeO	H	MeO	210
41	*cis*-**42**	MeO	MeO	MeO	H	123
42	*cis*-**43**	Cl	H	Cl	H	1.6
43	*cis*-**44**	H	I	H	I	8.3
44	*cis*-**45**	H	CF_3	H	CF_3	7.0

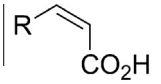
T100CS. Column chromatography (CC) was performed on silica gel (Kanto Chemical Co.). Thin-layer chromatography (TLC) was performed on pre-coated plates (0.25 mm, silica gel Merck 60 F254). Reaction mixtures were stirred magnetically. Stereochemistry was determined by NOE experiments, unless otherwise noted.

4.2. Synthesis

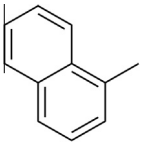
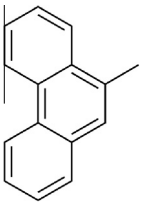
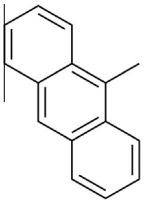
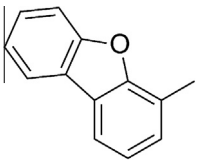
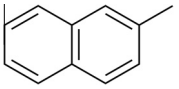
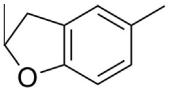
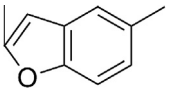
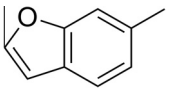
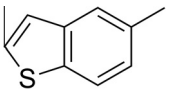
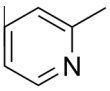
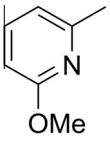
4.2.1. (Z)-3-(o-Tolyl)acrylic acid (cis-**3**) (Ando, 1997; Ando et al., 2000)

Triton B (40% in MeOH, 7.30 mL, 17.5 mmol) was added dropwise to a solution of ethyl 2-[bis(2-isopropylphenoxy) phosphoryl] acetate (5.30 g, 13.1 mmol) in THF (150 mL) at −78 °C under Ar. After 15 min of stirring, a solution of 2-methylbenzaldehyde (**59**) (1.50 g, 12.5 mmol) in THF (50 mL) was added dropwise to the solution. After 10 h of stirring, the mixture was quenched with satd. aq.

Table 2
The growth inhibitory activities of the *cis*-CA analogues **46**–**58**

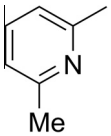
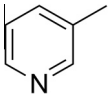


cis-**46**–*cis*-**58**

Entry	(No)	R	EC_{50} (μM)
1	*cis*-**46**		234
2	*cis*-**47**		169
3	*cis*-**48**		>500
4	*cis*-**49**		224
5	*cis*-**50**		7.7
6	*cis*-**51**		2.7
7	*cis*-**52**		1.1
8	*cis*-**53**		11.2
9	*cis*-**54**		12
10	*cis*-**55**		2.7
11	*cis*-**56**		8.7

(*continued on next page*)

Table 2 (*continued*)

Entry	(No)	R	EC_{50} (μM)
12	*cis*-**57**		155
13	*cis*-**58**		88

NH_4Cl (30 mL) and extracted with EtOAc (3 x 30 mL). The organic layer was washed successively with H_2O, satd. aq. (20 mL) $NaHCO_3$ (20 mL) and brine (20 mL), then dried ($MgSO_4$), filtered and concentrated *in vacuo*. The crude product was purified by silica gel flash CC (EtOAc/hexane, 10:90) to afford (*Z*)-ethyl 3-(*o*-tolyl)acrylate (*cis*-**115**) (2.03 g, 10.7 mmol, 85%, *Z* only, determined by ^{1}H-NMR spectrum) as a colorless oil: ^{1}H-NMR ($CDCl_3$, 270 MHz) δ: 1.15 (t, *J* = 7.0 Hz, 3H, $-CH_3$), 2.28 (s, 3H, Ar–CH_3), 4.09 (q, *J* = 7.0 Hz, 2H, $-CH_2-$), 6.02 (d, *J* = 12.2 Hz, 1H, =CH–CO_2-), 7.12 (d, *J* = 12.2 Hz, 1H, Ar–CH=), 7.14–7.22 (m, 3H, Ar–H), 7.31 (d, *J* = 7.3 Hz, 1H, Ar–H).

0.52 M NaOH (10 mL) was added to a solution of *cis*-**115** (1.50 g, 9.26 mmol) in EtOH (6.0 mL) at room temperature. The mixture was stirred for 4 h, diluted with H_2O (10 mL), and the acidity of the solution was adjusted with 1 M HCl to pH 1.0. The mixture was extracted with EtOAc (3 x 20 mL), washed with brine (20 mL), dried ($MgSO_4$), and filtered. After the solvent was removed *in vacuo*, the crude product was purified by recrystallization to give *cis*-**3** (1.35 g, 8.30 mmol, 90%) as colorless needles.: mp 96–97 °C (Toluene); ^{1}H-NMR ($CDCl_3$, 400 MHz) δ: 2.28 (s, 3H, $-CH_3$), 6.01 (d, *J* = 12.2 Hz, 1H, =CH–CO_2-), 7.12–7.25 (m, 3H, Ar–H), 7.21 (d, *J* = 12.2 Hz, 1H, Ar–CH=), 7.32 (d, *J* = 7.6 Hz, 1H, Ar–H); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ: 19.9 (q, $-CH_3$), 120.0 (d, =CH–CO_2-), 125.4 (d, Ar), 128.8 (d, Ar), 128.9 (d, Ar), 129.7 (d, Ar), 134.4 (s, Ar), 135.9 (s, Ar), 145.5 (d, Ar–CH=), 170.9 (s, C=O); IR (KBr) 1699 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, 74.02; H, 6.21.

*4.2.2. (Z)-3-(m-Tolyl)acrylic acid (cis-**4**)*

The *Z*-selective olefination of 3-methylbenzaldehyde (**60**) was performed using the procedure described above to provide (*Z*)-ethyl 3-(*m*-tolyl)acrylate (*cis*-**116**) (94%, *Z*:*E* = 98:2, determined by ^{1}H-NMR spectrum) (silica gel CC, EtOAc/hexane, 3:97) as a colorless oil: ^{1}H-NMR ($CDCl_3$, 270 MHz) δ: 1.24 (t, *J* = 7.0 Hz, 3H, $-CH_3$), 2.36 (s, 3H, Ar–CH_3), 4.18 (q, *J* = 7.0 Hz, 2H, $-CH_2-$), 5.92 (d, *J* = 12.7 Hz, 1H, =CH–CO_2-), 6.91 (d, *J* = 12.7 Hz, 1H, Ar–CH=), 7.14 (d, *J* = 7.3 Hz, 1H, Ar–H), 7.24 (t, *J* = 7.3 Hz, 1H, Ar–H), 7.37–7.40 (m, 2H, Ar–H).

Hydrolysis of *cis*-**116** was performed using the procedure described above to afford *cis*-**4** (91%) as colorless needles: mp 36–38 °C (Toluene); ^{1}H-NMR ($CDCl_3$, 400 MHz) δ: 2.36 (s, 3H, $-CH_3$), 5.95 (d, *J* = 12.8 Hz, 1H, =CH–CO_2-), 7.04 (d, *J* = 12.8 Hz, 1H, Ar–CH=), 7.16 (d, *J* = 7.6 Hz, 1H, Ar–H), 7.25 (t, *J* = 7.6 Hz, 1H, Ar–H), 7.38 (s, 1H, Ar–H), 7.42 (d, *J* = 7.6 Hz, 1H, Ar–H); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ: 21.3 (q, $-CH_3$), 118.5 (d, =CH–CO_2-), 127.0 (d, Ar), 130.1 (d, Ar), 134.3 (s, Ar), 137.6 (s, Ar), 146.0 (d, Ar–CH=), 171.7 (s, C=O); IR (KBr) 1697 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, 74.20; H, 6.10.

*4.2.3. (Z)-3-(p-Tolyl)acrylic acid (cis-**5**)*

Z-selective olefination of 4-methylbenzaldehyde (**61**) was performed using the procedure described above to provide (*Z*)-ethyl 3-(*p*-tolyl)acrylate (*cis*-**117**) (99%, *Z*:*E* = 98:2 determined by ^{1}H-NMR spectrum) (silica gel CC, EtOAc/hexane, 3:97) as a colorless oil: ^{1}H-NMR ($CDCl_3$, 270 MHz) δ: 1.26 (t, *J* = 7.1 Hz, 3H, $-CH_3$), 2.36 (s, 3H, Ar-CH_3), 4.18 (q, *J* = 7.1 Hz, 2H, $-CH_2-$), 5.90 (d, *J* = 12.7 Hz, 1H, =CH–CO_2-), 6.91 (d, *J* = 12.7 Hz, 1H, Ar–CH=), 7.18, 7.52 (d, *J* = 7.3 Hz, each 2H, Ar–H). The spectroscopic data were in agreement with those in the literature (Walter and Oestreich, 2008; Miura et al., 2009).

Hydrolysis of *cis*-**117** was performed using the procedure described above to afford *cis*-**5** (91%) as colorless needles: mp 77–79 °C (Toluene); ^{1}H-NMR ($CDCl_3$, 400 MHz) δ: 2.37 (s, 3H, $-CH_3$), 5.92 (d, *J* = 12.8 Hz, 1H, =CH–CO_2-), 7.02 (d, *J* = 12.8 Hz, 1H, Ar–CH=), 7.17, 7.55 (d, *J* = 8.4 Hz, each 2H, Ar–H); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ: 21.4 (q, $-CH_3$), 117.7 (d, =CH–CO_2-), 128.8 (d, Ar), 130.2 (d, Ar), 131.5 (s, Ar), 139.8 (s, Ar), 146.0 (d, Ar–CH=), 171.9 (s, C=O); IR (KBr) 1693 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, 6.21.

*4.2.4. (Z)-3-(2-Ethylphenyl)acrylic acid (cis-**6**)*

Z-selective olefination of 2-ethylbenzaldehyde (**62**) was performed using the procedure described above to provide (*Z*)-ethyl 3-(2-ethylphenyl)acrylate (*cis*-**118**) (72%, *Z*:*E* = 98:2, determined by ^{1}H-NMR spectrum) (silica gel CC, EtOAc/hexane, 3:97) as a colorless oil: ^{1}H-NMR ($CDCl_3$, 270 MHz) δ: 1.12 (t, *J* = 7.0 Hz, 3H, $-CH_3$), 1.19 (t, *J* = 7.3 Hz, 3H, Ar–CH_2–CH_3), 2.63 (q, *J* = 7.3 Hz, 2H, Ar–CH_2-), 4.07 (q, *J* = 7.0 Hz, 2H, $-CO_2-CH_2-$), 6.03 (d, *J* = 11.9 Hz, 1H, =CH–CO_2-), 7.15–7.30 (m, 5H, Ar–CH= and Ar–H).

Hydrolysis of *cis*-**118** was performed using the procedure described above to afford *cis*-**6** (99%) as colorless needles: mp 68–69 °C (Hexane); ^{1}H-NMR ($CDCl_3$, 400 MHz) δ: 1.18 (t, *J* = 8.0 Hz, 3H, $-CH_3$), 2.62 (q, *J* = 8.0 Hz, 2H, $-CH_2-$), 6.03 (d, *J* = 12.0 Hz, 1H, =CH–CO_2-), 7.13–7.22 (m, 2H, Ar–H and Ar–CH=), 7.28–7.31 (m, 3H, Ar–H); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ: 14.8 (q, $-CH_3$), 26.6 (t, $-CH_2-$), 120.2 (d, =CH–CO_2-), 125.3 (d, Ar), 127.9 (d, Ar), 128.9 (d, Ar), 129.2 (d, Ar), 133.8 (s, Ar), 141.8 (s, Ar), 145.5 (d, Ar–CH=), 171.5 (s, C=O); IR (KBr) 1699 cm^{-1}; ESI-MS *m*/*z* 175 (M^+–H); Anal. calcd for $C_{11}H_{12}O_2$: C, 74.98; H, 6.86. found: C, 75.01; H, 6.92.

*4.2.5. (Z)-3-(3-Ethylphenyl)acrylic acid (cis-**7**) (Wang et al., 2009)*

Triethylborane (1.00 M in THF, 2.00 mL, 2.00 mmol) was added to a suspension of 3-bromobenzaldehyde (**84**) (0.370 g, 2.00 mmol), $Pd(dppf)Cl_2$ (14.6 mg, 20.0 μmol), and CsOAc (0.384 g, 2.00 mmol) in THF (3.0 mL) under Ar., and the mixture was heated until reflux began this being maintained for 6 h. After cooling to room temperature, the mixture was diluted with Et_2O, washed with saturated aqueous $NaHCO_3$ and brine, dried (Na_2SO_4), filtered and concentrated *in vacuo*. The residue was purified by silica gel flash CC to afford 3-ethylbenzaldehyde (**63**) (0.123 g, 0.920 mmol, 46%) as a colorless oil; ^{1}H-NMR ($CDCl_3$, 400 MHz) δ: 1.28 (t, *J* = 7.2 Hz, 3H, $-CH_3$), 2.74 (q, *J* = 7.2 Hz, 2H, $-CH_2-$), 7.42–7.48, 7.69–7.72 (m, each 2H, Ar–H), 10.0 (s, 1H, –CHO); spectral data were in agreement with those in the literature (Wang et al., 2009).

The *Z*-selective olefination of **63** was performed using the procedure described above to provide (*Z*)-ethyl 3-(2-ethylphenyl)acrylate (*cis*-**119**) (72%, *Z*:*E* = 98:2, 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: 1.24 (t, *J* = 7.2 Hz, 6H, $-CH_3$), 2.65 (q, *J* = 7.2 Hz, 2H, Ar–CH_2-), 4.17 (q, *J* = 7.2 Hz, 2H, $-CO_2-CH_2-$), 5.93 (d, *J* = 12.6 Hz, 1H, =CH–CO_2-), 6.92 (d, *J* = 12.6 Hz, 1H, Ar–CH=), 7.16 (d, *J* = 7.6 Hz, 1H, Ar–H), 7.26 (t, *J* = 7.6 Hz, 1H, Ar–H), 7.39–7.42 (m, 2H, Ar–H).

Hydrolysis of *cis*-**119** was performed using the procedure described above to afford *cis*-**7** (90%) as colorless oil; ^{1}H-NMR ($CDCl_3$, 400 MHz) δ: 1.23 (t, *J* = 7.5 Hz 3H, $-CH_3$), 2.65 (q, *J* = 7.5 Hz, 2H, $-CH_2-$), 5.95 (d, *J* = 12.8 Hz, =CH–CO_2-), 7.04 (d, *J* = 12.8 Hz, 1H, Ar–CH=), 7.18 (d, *J* = 7.6 Hz, 1H, Ar–H), 7.25 (t, *J* = 7.6 Hz, 1H, Ar–H), 7.42 (s, 1H, Ar–H), 7.43 (d, *J* = 7.6 Hz, 1H, Ar–H); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ: 15.4 (q, $-CH_3$), 28.7 (t, $-CH_2-$), 118.4

(d, =CH–CO_2–), 127.3 (d, Ar), 128.0 (d, Ar), 129.0 (d, Ar), 129.5 (d, Ar), 134.4 (s, Ar), 143.9 (s, Ar), 145.9 (d, Ar–CH=), 171.3 (s, C=O); IR (KBr) 1697 cm^{-1}; ESI-MS *m*/*z* 175 (M^+−H); HR EI-MS *m*/*z* 176.0837 (M^+, calcd for $C_{11}H_{12}O_2$ 176.0837).

*4.2.6. (Z)-3-(4-Ethylphenyl)acrylic acid (cis-**8**)*

Z-selective olefination of 4-ethylbenzaldehyde (**64**) was performed using the procedure described above to provide (*Z*)-ethyl 3-(4-ethylphenyl)acrylate (*cis*-**120**) (83%, *Z*:*E* = 98:2, determined by ^{1}H-NMR spectrum) (silica gel CC, EtOAc/hexane, 3:97) as a colorless oil: ^{1}H-NMR ($CDCl_3$, 270 MHz) δ: 1.22–1.28 (m, 6H, –CH_3), 2.65 (q, *J* = 7.6 Hz, 2H, Ar–CH_2–), 4.18 (q, *J* = 7.6 Hz, 2H, –CO_2–CH_2–), 5.89 (d, *J* = 12.8 Hz, 1H, =CH–CO_2–), 6.90 (d, *J* = 12.8 Hz, 1H, Ar–CH=), 7.18, 7.55 (d, *J* = 8.4 Hz, each 2H, Ar–H).

Hydrolysis of *cis*-**120** was performed using the procedure described above to afford *cis*-**8** (99%) as colorless needles: mp 61–63 °C (Et_2O/hexane); ^{1}H-NMR ($CDCl_3$, 400 MHz) δ: 1.24 (t, *J* = 7.6 Hz, 3H, –CH_3), 2.67 (q, *J* = 7.6 Hz, 2H, –CH_2–), 5.92 (d, *J* = 12.4 Hz, 1H, =CH–CO_2–), 7.02 (d, *J* = 12.4 Hz, 1H, Ar–CH=), 7.20, 7.58 (d, *J* = 8.4 Hz, each 2H, Ar–H); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ: 15.2 (q, –CH_3), 28.7 (t, –CH_2–), 117.6 (d, =CH–CO_2–), 127.6 (d, Ar), 130.4 (d, Ar), 131.7 (s, Ar), 146.0 (d, Ar–CH=), 146.0 (s, Ar), 171.9 (s, C=O); IR (KBr) 1695 cm^{-1}; ESI-MS *m*/*z* 175 (M^+−H); Anal. calcd for $C_{11}H_{12}O_2$: C, 74.98; H, 6.86. found: C, 74.96; H, 6.89.

*4.2.7. (Z)-3-(4-Isopropylphenyl)acrylic acid (cis-**9**)*

Z-selective olefination of 4-isopropylbenzaldehyde (**65**) was performed using the procedure described above to provide (*Z*)-ethyl 3-(4-isopropylphenyl)acrylate (*cis*-**121**) (85%, *Z* only, determined by ^{1}H-NMR spectrum) (silica gel CC, EtOAc/hexane, 3:97) as a colorless oil: ^{1}H-NMR ($CDCl_3$, 270 MHz) δ: 1.24 (d, *J* = 6.8 Hz, 6H, –CH–(CH_3)$_2$), 1.26 (t, *J* = 7.0 Hz, 3H, –CH_3), 2.91 (heptet, *J* = 6.8 Hz, 1H, –CH–(CH_3)$_2$), 4.19 (q, *J* = 7.0 Hz, 2H, –CH_2–), 5.89 (d, *J* = 12.4 Hz, 1H, =CH–CO_2–), 6.90 (d, *J* = 12.4 Hz, 1H, Ar–CH=), 7.21, 7.57 (d, *J* = 8.1 Hz, each 2H, Ar–H).

Hydrolysis of *cis*-**121** was performed using the procedure described above to afford *cis*-**9** (99%) as colorless needles: mp 42–43 °C (Toluene); ^{1}H-NMR ($CDCl_3$, 400 MHz) δ: 1.25 (d, *J* = 7.2 Hz, 6H, –CH_3), 2.92 (heptet, *J* = 7.2 Hz, 1H, –CH–(CH_3)$_2$), 5.92 (d, *J* = 12.8 Hz, 1H, =CH–CO_2–), 7.02 (d, *J* = 12.8 Hz, 1H, Ar–CH=), 7.23, 7.60 (d, *J* = 8.4 Hz, each 2H, Ar–H); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ: 23.7 (q, –CH_3), 34.0 (d, –CH–(CH_3)$_2$), 117.6 (d, =CH–CO_2–), 130.4 (d, Ar), 131.8 (s, Ar), 146.0 (d, Ar–CH=), 150.6 (s, Ar), 172.0 (s, C=O); IR (KBr) 1695 cm^{-1}; ESI-MS *m*/*z* 189 (M^+−H); Anal. calcd for $C_{12}H_{14}O_2$: C, 75.76; H, 7.42. found: C, 75.81; H, 7.46.

*4.2.8. (Z)-3-[4-(tert-Butyl)phenyl]acrylic acid (cis-**10**)*

Z-selective olefination of 4-(*tert*-butyl)benzaldehyde (**66**) was performed using the procedure described above to provide (*Z*)-ethyl 3-[4-(*tert*-butyl)phenyl]acrylate (*cis*-**122**) (94%, *Z*:*E* = 98:2, determined by ^{1}H-NMR spectrum) (silica gel CC, EtOAc/hexane, 3:97) as a colorless oil: ^{1}H-NMR ($CDCl_3$, 270 MHz) δ: 1.26 (t, *J* = 7.0 Hz, 3H, –CH_3), 1.31 (s, 9H, –C–(CH_3)$_3$), 4.18 (q, *J* = 7.0 Hz, 2H, –CH_2–), 5.89 (d, *J* = 12.4 Hz, 1H, =CH–CO_2–), 6.90 (d, *J* = 12.4 Hz, 1H, Ar–CH=), 7.37, 7.58 (d, *J* = 7.8 Hz, each 2H, Ar–H).

Hydrolysis of *cis*-**122** was performed using the procedure described above to afford *cis*-**10** (90%) as colorless needles: mp 89–90 °C (Toluene); ^{1}H-NMR ($CDCl_3$, 400 MHz) δ: 1.32 (s, 9H, –CH_3), 5.91 (d, *J* = 12.8 Hz, 1H, =CH–CO_2–), 7.02 (d, *J* = 12.8 Hz, 1H, Ar–CH=), 7.38, 7.61 (d, *J* = 8.4 Hz, each 2H, Ar–H); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ: 31.2 (q, CH_3), 34.8 (s, –C–(CH_3)$_3$), 117.6 (d, =CH–CO_2–), 125.1 (d, Ar), 130.2 (d, Ar), 131.4 (d, Ar), 145.9 (d, Ar–CH=), 171.7 (s, C=O); IR (KBr) 1693 cm^{-1}; ESI-MS *m*/*z* 203 (M^+−H); Anal. calcd for $C_{13}H_{16}O_2$: C, 76.44; H, 7.90. found: C, 76.56; H, 7.91.

*4.2.9. (Z)-3-[(1,1′-Biphenyl)-2-yl]acrylic acid (cis-**11**)*

Z-selective olefination of [1,1′-biphenyl]-2-carbaldehyde (**67**) was performed using the procedure described above to provide (*Z*)-ethyl 3-[(1,1′-biphenyl)-2-yl]acrylate (*cis*-**123**) (92%, *Z*:*E* = 99:1, determined by ^{1}H-NMR spectrum) (silica gel CC, EtOAc/hexane, 1:99) as a colorless oil: ^{1}H-NMR ($CDCl_3$, 400 MHz) δ: 1.20 (t, *J* = 7.2 Hz, 3H, .CH_3), 4.15 (q, *J* = 7.2 Hz, 2H, –CH_2–), 5.92 (d, *J* = 12.0 Hz, 1H, =CH–CO_2–), 6.85 (d, *J* = 12.0 Hz, 1H, Ar–CH=), 7.32–7.40 (m, 8H, Ar–H), 7.55 (d, *J* = 7.6 Hz, 1H, Ar–H).

Hydrolysis of *cis*-**123** was performed using the procedure described above to afford *cis*-**11** (96%) as colorless needles: mp 91–93 °C (Toluene); ^{1}H-NMR ($CDCl_3$, 400 MHz) δ: 5.91 (d, *J* = 12.4 Hz, 1H, =CH–CO_2–), 6.94 (d, *J* = 12.4 Hz, 1H, Ar–CH=), 7.30–7.42 (m, 8H), 7.59 (d, *J* = 7.6 Hz, 1H, Ar–H); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ: 119.2 (d, =CH–CO_2–), 126.8 (d, Ar), 127.5 (d, Ar), 128.1 (d, Ar), 129.1 (d, Ar), 129.4 (d, Ar), 129.8 (d, Ar), 130.2 (d, Ar), 133.3 (s, Ar), 140.4 (s, Ar), 141.4 (s, Ar), 146.8 (d, Ar–CH=), 171.8 (s, C=O); IR (KBr) 1699 cm^{-1}; ESI-MS *m*/*z* 223 (M^+−H); Anal. calcd for $C_{15}H_{12}O_2$: C, 80.34; H, 5.39. found: C, 80.42; H, 5.26.

*4.2.10. (Z)-3-[(1,1′-Biphenyl)-3-yl]acrylic acid (cis-**12**)*

n-BuLi (2.53 mL, 1.54 M in hexane, 3.90 mmol) was added to a solution of 3-bromo-1,1'-biphenyl (**171**) (0.50 mL, 3.00 mmol) in THF (8.0 mL) at −78 °C Ar., and the mixture was stirred for 20 min. DMF (0.350 mL, 4.50 mmol) was then added to the reaction mixture, and the temperature was gradually warmed to 0 °C. The reaction was quenched with H_2O and extracted with EtOAc. The organic layers were washed with brine, dried ($MgSO_4$), filtered and concentrated *in vacuo*. The crude product was purified by silica gel CC (EtOAc/hexane, 10:90) to afford (1,1′-biphenyl)-3-carbaldehyde (**68**) (0.443 g, 2.43 mmol, 79%) as a colorless oil: ^{1}H-NMR ($CDCl_3$, 400 MHz) δ: 7.39 (t, *J* = 7.2 Hz, 1H, Ar–H), 7.47 (t, *J* = 7.2 Hz, 2H, Ar–H), 7.58–7.63 (m, 3H, Ar–H), 7.86 (dd, *J* = 2.0, 7.6 Hz, 2H, Ar–H), 8.10 (s, 1H, Ar–H), 10.08 (s, 1H, –CHO).

Z-selective olefination of **68** was performed using the procedure described above to provide (*Z*)-ethyl 3-[(1,1′-biphenyl)-3-yl]acrylate (*cis*-**124**) (92%, *Z*:*E* = 95:5, determined by ^{1}H-NMR spectrum) (silica gel CC, EtOAc/hexane, 1:99) as a colorless oil: ^{1}H-NMR ($CDCl_3$, 400 MHz) δ: 1.23 (t, *J* = 7.2 Hz, 3H, –CH_3), 4.12 (q, *J* = 7.2 Hz, 2H, –CH_2–), 5.88 (d, *J* = 12.8 Hz, 1H, =CH–CO_2–), 7.15 (d, *J* = 12.8 Hz, 1H, Ar–CH=), 7.34 (t, *J* = 7.6 Hz, 1H, Ar–H), 7.43 (m, 3H, Ar–H), 7.58–7.62 (m, 4H, Ar–H), 7.84 (s, 1H, Ar–H).

Hydrolysis of *cis*-**124** was performed using the procedure described above to afford *cis*-**12** (96%) as colorless prisms: mp 105–106 °C (Toluene); ^{1}H-NMR ($CDCl_3$, 400 MHz) δ: 6.03 (d, *J* = 12.8 Hz, 1H, =CH–CO_2–), 7.14 (d, *J* = 12.8 Hz, 1H, Ar–CH=), 7.35 (t, *J* = 7.6 Hz, 1H, Ar–H), 7.43 (t, *J* = 7.6 Hz, 3H, Ar–H), 7.58–7.62 (m, 4H, Ar–H), 7.84 (s, 1H, Ar–H); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ: 119.0 (d, =CH–CO_2–), 127.2 (d, Ar), 127.4 (d, Ar), 128.1 (d, Ar), 128.5 (d, Ar), 128.7 (d, Ar), 128.8 (d, Ar), 128.9 (d, Ar), 134.8 (s, Ar), 140.7 (s, Ar), 141.1 (s, Ar), 145.7 (d, Ar–CH=), 171.1 (s, C=O); IR (KBr) 1721 cm^{-1}; ESI-MS *m*/*z* 223 (M^+−H); Anal. calcd for $C_{15}H_{12}O_2$: C, 80.34; H, 5.39. found: C, 80.08; H, 5.39.

*4.2.11. (Z)-3-[(1,1′-Biphenyl)-4-yl]acrylic acid (cis-**13**)*

Z-selective olefination of (1,1′-biphenyl)-4-carbaldehyde (**69**) was performed using the procedure described above to provide (*Z*)-ethyl 3-[(1,1′-biphenyl)-4-yl]acrylate (*cis*-**125**) (86%, *Z*:*E* = 95:5, determined by ^{1}H-NMR spectrum) (silica gel CC, EtOAc/hexane, 5:95) as a colorless oil: ^{1}H-NMR ($CDCl_3$, 270 MHz) δ: 1.28 (t, *J* = 7.3 Hz, 3H, –CH_3), 4.20 (q, *J* = 7.3 Hz, 2H, –CH_2–), 5.97 (d, *J* = 12.7 Hz, 1H, =CH–CO_2–), 6.97 (d, *J* = 12.7 Hz, 1H, Ar–CH=), 7.26 (t, *J* = 7.6 Hz, 1H, Ar–H), 7.33–7.48 (m, 2H, Ar–H), 7.57–7.62 (m, 4H, Ar–H), 7.70 (d, *J* = 6.2 Hz, 2H, Ar–H).

Hydrolysis of *cis*-**125** was performed using the procedure described above to afford *cis*-**13** (96%) as colorless needles: mp

145–146 °C (Toluene); ^{1}H-NMR ($CDCl_3$, 400 MHz) δ: 6.00 (d, J = 13.2 Hz, 1H, =CH–CO_2–), 7.09 (d, J = 13.2 Hz, 1H, Ar–CH=), 7.36 (t, J = 7.6 Hz, 1H, Ar–H), 7.45 (t, J = 7.6 Hz, 2H, Ar–H), 7.59–7.62 (m, 4H, Ar–H), 7.73 (d, J = 8.8 Hz, 2H, Ar–H); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ: 118.4 (d, =*C*H–CO_2–), 126.8 (d, Ar), 127.1 (d, Ar), 127.7 (d, Ar), 128.8 (d, Ar), 130.8 (d, Ar), 133.2 (s, Ar), 140.3 (s, Ar), 142.2 (s, Ar), 145.6 (d, Ar–*C*H=), 171.7 (s, C=O); IR (KBr) 1697 cm^{-1}; ESI-MS m/z 223 (M^+–H); Anal. calcd for $C_{15}H_{12}O_2$: C, 80.34; H, 5.39. found: C, 80.34; H, 5.39.

4.2.12. (Z)-3-(2-Methoxyphenyl)acrylic acid (cis-**14**)

Z-selective olefination of 2-methoxybenzaldehyde (**70**) was performed using the procedure described above to provide (*Z*)-ethyl 3-(2-methoxyphenyl)acrylate (*cis*-**126**) (99%, *Z* only, determined by ^{1}H-NMR spectrum) (silica gel CC, EtOAc/hexane, 10:90) as a colorless oil: ^{1}H-NMR ($CDCl_3$, 270 MHz) δ: 1.20 (t, J = 7.0 Hz, 3H, –CH_3), 3.83 (s, 3H, –OCH_3), 4.13 (q, J = 7.0 Hz, 2H, –CH_2–), 5.97 (d, J = 12.6 Hz, 1H, =CH–CO_2–), 6.87 (d, J = 7.6 Hz, 1H, Ar–H), 6.92 (t, J = 7.6 Hz, 1H, Ar–H), 7.16 (d, J = 12.6 Hz, 1H, Ar–CH=), 7.26–7.33 (m, 1H, Ar–H), 7.54 (d, J = 7.6 Hz, 1H, Ar–H); The spectroscopic data were in agreement with those in the literature (Byrne and Gilheany, 2012).

Hydrolysis of *cis*-**126** was performed using the procedure described above to afford *cis*-**14** (85%) as colorless needles: mp 90–93 °C (toluene); ^{1}H-NMR ($CDCl_3$, 400 MHz) δ: 3.75 (s, 3H, –OCH_3), 5.93 (d, J = 12.6 Hz, 1H, =CH–CO_2–), 6.81 (d, J = 8.8 Hz, 1H, Ar–H), 6.87 (m, 1H, Ar–H), 7.22 (d, J = 12.6 Hz, 1H, Ar–CH=), 7.27 (m, 1H, Ar–H), 7.52 (d, J = 7.6 Hz, 1H, Ar–H); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ: 55.1 (q, –OCH_3), 110.2 (d, Ar), 118.8 (d, Ar), 119.8 (d, =*C*H–CO_2–), 123.4 (s, Ar), 130.6 (d, Ar), 141.4 (d, Ar–CH=), 157.0 (s, Ar), 172.1 (s, C=O); IR (KBr) 1697 cm^{-1}; ESI-MS m/z 177 (M^+–H); Anal. calcd for $C_{10}H_{10}O_3$: C, 67.41; H, 5.66. found: C, 67.54; H, 5.62.

4.2.13. (Z)-3-(3-Methoxyphenyl)acrylic acid (cis-**15**)

Z-selective olefination of 3-methoxybenzaldehyde (**71**) was performed using the procedure described above to provide (*Z*)-ethyl 3-(3-methoxyphenyl)acrylate (*cis*-**127**) (88%, *Z*:*E* = 98:2, determined by ^{1}H-NMR spectrum) (silica gel CC, EtOAc/hexane, 10:90) as a colorless oil: ^{1}H-NMR ($CDCl_3$, 270 MHz) δ: 1.24 (t, J = 7.0 Hz, 3H, –CH_3), 3.80 (s, 3H, –OCH_3), 4.17 (q, J = 7.0 Hz, 2H, –CH_2–), 5.94 (d, J = 12.7 Hz, 1H, =CH–CO_2–), 6.88 (d, J = 7.8 Hz, 1H, Ar–H), 6.89 (d, J = 12.7 Hz, 1H, Ar–CH=), 7.11 (d, J = 7.8 Hz, 1H, Ar–H), 7.22–7.28 (m, 2H, Ar–H). The spectroscopic data were in agreement with those in the literature (Mueller and Jennigs, 2007).

Hydrolysis of *cis*-**127** was performed using the procedure described above to afford *cis*-**15** (90%) as colorless needles: mp 36–38 °C (toluene); ^{1}H-NMR ($CDCl_3$, 400 MHz) δ: 3.81 (s, 3H, –OCH_3), 5.97 (d, J = 12.8 Hz, 1H, =CH–CO_2–), 6.91 (d, J = 7.4 Hz, 1H, Ar–H), 7.04 (d, J = 12.8 Hz, 1H, Ar–CH=), 7.14 (d, J = 7.4 Hz, 1H, Ar–H), 7.26–7.30 (m, 2H, Ar–H); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ: 54.8 (q, –OCH_3), 114.4 (d, Ar), 115.1 (d, Ar), 122.2 (d, =*C*H–CO_2–), 128.6 (d, Ar), 135.1 (s, Ar), 145.1 (d, Ar–CH=), 158.7 (s, Ar), 171.7 (s, C=O); IR (KBr) 1699 cm^{-1}; ESI-MS m/z 177 (M^+–H); Anal. calcd for $C_{10}H_{10}O_3$: C, 67.41; H, 5.66. found: C, 67.49; H, 5.66.

4.2.14. (Z)-3-(4-Methoxyphenyl)acrylic acid (cis-**16**)

Z-selective olefination of 4-methoxybenzaldehyde (**72**) was performed using the procedure described above to provide (*Z*)-ethyl 3-(4-methoxyphenyl)acrylate (*cis*-**128**) (98%, *Z*:*E* = 98:2, determined by ^{1}H-NMR spectrum) (silica gel CC, EtOAc/hexane, 10:90) as a colorless oil: ^{1}H-NMR ($CDCl_3$, 270 MHz) δ: 1.28 (t, J = 7.2 Hz, 3H, –CH_3), 3.83 (s, 3H, –OCH_3), 4.19 (q, J = 7.2 Hz, 2H, –CH_2–), 5.82 (d, J = 12.8 Hz, 1H, =CH–CO_2–), 6.84 (d, J = 12.8 Hz, 1H, Ar–CH=), 6.87, 7.68 (d, J = 8.6 Hz, each 2H, Ar–H). The spectroscopic data were in agreement with those in the literature (Walter and Oestreich, 2008; Miura et al., 2009).

Hydrolysis of *cis*-**128** was performed using the procedure described above to afford *cis*-**16** (85%) as colorless needles: mp 77–79 °C (Toluene); ^{1}H-NMR ($CDCl_3$, 400 MHz) δ: 3.84 (s, 3H, –OCH_3), 5.85 (d, J = 12.8 Hz, 1H, =CH–CO_2–), 6.89 (d, J = 8.8 Hz, 2H, Ar–H), 6.97 (d, J = 12.8 Hz, 1H, Ar–CH=), 7.72 (d, J = 8.8 Hz, 2H, Ar–H); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ: 55.2 (q, –OCH_3), 113.5 (d, Ar), 115.9 (d, =*C*H–CO_2–), 126.9 (s, Ar), 132.6 (d, Ar), 145.9 (d, Ar–CH=), 160.6 (s, Ar), 172.1 (s, C = O); IR (KBr) 1693 cm^{-1}; ESI-MS m/z 177 (M^+–H); Anal. calcd for $C_{10}H_{10}O_3$: C, 67.41; H, 5.66. found: C, 67.41; H, 5.67.

4.2.15. (Z)-3-(3-Ethoxyphenyl)acrylic acid (cis-**17**)

Z-selective olefination of 3-ethoxybenzaldehyde (**73**) was performed using the procedure described above to provide (*Z*)-ethyl 3-(3-ethoxyphenyl)acrylate (*cis*-**129**) (78%, *Z*:*E* = 96:4, determined by ^{1}H-NMR spectrum) (silica gel CC, EtOAc/hexane, 15:85) as a colorless oil: ^{1}H-NMR ($CDCl_3$, 400 MHz) δ: 1.25 (t, J = 7.2 Hz, 3H, –CH_3), 1.41 (t, J = 6.8 Hz, 3H, –OCH_2–*C*H_3), 4.05 (q, J = 6.8 Hz, 2H, Ar–OCH_2–), 4.18 (q, J = 7.2 Hz, 2H, –CO_2–CH_2–), 5.94 (d, J = 13.2 Hz, 1H, =CH–CO_2–), 6.89–6.91 (m, 2H, Ar–CH= and Ar–H), 7.11 (d, J = 7.2 Hz, 1H, Ar–H), 7.21–7.26 (m, 2H, Ar–H).

Hydrolysis of *cis*-**129** was performed using the procedure described above to afford *cis*-**17** (93%) as colorless needles: mp 38–40 °C (Toluene/hexane, 30:70); ^{1}H-NMR ($CDCl_3$, 400 MHz) δ: 1.34 (t, J = 7.2 Hz, 3H, –CH_3), 4.05 (q, J = 7.2 Hz, 2H, –CH_2–), 5.95 (d, J = 12.6 Hz, 1H, =CH–CO_2–), 6.89 (dd, J = 2.8, 7.8 Hz, 1H, Ar–H), 7.02 (d, J = 12.6 Hz, 1H, Ar–CH=), 7.12 (d, J = 7.8 Hz, 1H, Ar–H), 7.23–7.27 (m, 2H, Ar–H); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ: 14.8 (q, –CH_3), 63.4 (t, –OCH_2–), 115.4 (d, Ar), 116.2 (d, Ar), 118.7 (d, =*C*H–CO_2–), 122.5 (d, Ar), 129.1 (d, Ar), 135.6 (s, Ar), 145.7 (d, Ar–CH=), 158.5 (s, Ar), 171.1 (s, C=O); IR (KBr) 1685 cm^{-1}; ESI-MS m/z 191 (M^+–H); HRMS (EI) calcd for $C_{11}H_{12}O_3$ 192.0786, found 192.0784.

4.2.16. (Z)-3-(3-Propoxyphenyl)acrylic acid (cis-**18**)

3-Hydroxybenzaldehyde (**172**) (1.47 g, 12.0 mmol) was added to a solution of K_2CO_3 (2.49 g, 18.0 mmol) in acetone (30 mL) at 0 °C under Ar, then the mixture was stirred for 15 min. After 1-bromopropane (2.18 mL, 24.0 mmol) was added to the solution, the resulting mixture was heated until reflux began this being maintained for 6 h. The reaction was quenched with saturated aqueous NH_4Cl (10 mL) and extracted with EtOAc (3 x 30 mL). The organic layers were washed with H_2O (20 mL) and brine (20 mL), dried ($MgSO_4$), filtered and concentrated *in vacuo*. The residue was purified by silica gel CC (EtOAc/hexane, 15:85) to afford 3-propoxybenzaldehyde (**74**) (1.00 g, 6.10 mmol, 51%) as a colorless oil: ^{1}H-NMR ($CDCl_3$, 400 MHz) δ: 1.06 (t, J = 7.0 Hz, 3H, –CH_3), 1.84 (sextet, J = 7.0 Hz, 2H, –CH_2–), 3.99 (t, J = 7.0 Hz, 2H, –OCH_2–), 7.15–7.20 (m, 1H, Ar–H), 7.37 (d, J = 2.4 Hz, 1H, Ar–H), 7.43–7.46 (m, 2H, Ar–H), 9.97 (s, 1H, –CHO).

Z-selective olefination of **74** was performed using the procedure described above to provide (*Z*)-ethyl 3-(3-propoxyphenyl)acrylate (*cis*-**130**) (92%, *Z*:*E* = 95:5, determined by ^{1}H-NMR spectrum) (silica CC, EtOAc/hexane, 15:85) as a colorless oil: ^{1}H-NMR ($CDCl_3$, 400 MHz) δ: 1.04 (t, J = 7.0 Hz, 3H, –CH_3), 1.25 (t, J = 7.6 Hz, 3H, –CO_2–CH_2–*C*H_3), 1.81 (sextet, J = 7.0 Hz, 2H, –CH_2–), 3.93 (t, J = 7.0 Hz, 2H, –OCH_2–), 4.18 (q, J = 7.6 Hz, 2H, –CO_2–CH_2–), 5.94 (d, J = 12.8 Hz, 1H, =CH–CO_2–), 6.87–6.91 (m, 2H, Ar–H and Ar–CH=), 7.11 (d, J = 7.2 Hz, 1H, Ar–H), 7.21–7.25 (m, 2H, Ar–H).

The hydrolysis of *cis*-**130** was performed using the procedure described above to afford *cis*-**18** (90%) as colorless oil: ^{1}H-NMR ($CDCl_3$, 400 MHz) δ:1.03 (t, J = 7.0 Hz, 3H, –CH_3), 1.80 (sextet, J = 7.0 Hz, 2H, –*C*H_2), 3.93, (t, J = 7.0 Hz, 2H, –OCH_2–), 5.96 (d, J = 12.8 Hz, 1H, =CH–CO_2–), 6.90 (dd, J = 2.4, 8.2 Hz, 1H, Ar–H),

7.03 (d, J = 12.8 Hz, 1H, Ar–CH=), 7.13 (d, J = 8.2 Hz, 1H, Ar–H), 7.24–7.28 (m, 2H, Ar–H); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ: 10.5 (q, $-CH_3$), 22.5 (t, $-CH_2-CH_3$), 69.5 (t, $-OCH_2-$), 115.5 (d, Ar), 116.2 (d, Ar), 118.7 (d, $=CH-CO_2-$), 122.4 (d, Ar), 129.0 (d, Ar), 135.6 (s, Ar), 145.7 (d, Ar–CH=), 158.7 (s, Ar), 171.1 (s, C=O); IR (KBr) 1686 cm^{-1}; ESI-MS m/z 205 (M^+-H); HRMS (EI) calcd for $C_{12}H_{14}O_3$ 206.0943, found 206.0938.

4.2.17. (Z)-3-(3-Butoxyphenyl)acrylic acid (cis-**19**)

172 (1.99 g, 16.3 mmol) was added to a solution of K_2CO_3 (3.39 g, 24.5 mmol) in acetone (40 mL) at 0 °C under Ar, then the reaction was stirred for 15 min. After 1-iodobutane (3.72 mL, 32.6 mmol) was added to the solution, the resulting mixture was heated until reflux began this being maintained for 5 h. The reaction was quenched with H_2O (20 mL) and extracted with EtOAc (3 x 30 mL). The organic layers were washed with H_2O (20 mL) and brine (20 mL), dried ($MgSO_4$), filtered and concentrated *in vacuo*. The residue was purified by silica gel CC (EtOAc/hexane, 5:95) to afford 3-butoxybenzaldehyde (**75**) (1.80 g, 10.1 mmol, 62%) as a yellow oil: ^{1}H-NMR ($CDCl_3$, 400 MHz) δ: 0.96 (t, J = 7.0 Hz, 3H, $-CH_3$), 1.47 (m, 2H, $-CH_2-CH_3$), 1.75 (m, 2H, $-OCH_2-CH_2-$), 3.99 (t, J = 7.0 Hz, 2H, $-OCH_2-$), 7.13–7.16 (m, 2H, Ar–H), 7.36 (s, 1H, Ar–H), 7.38–7.43 (m, 2H, Ar–H), 9.94 (s, 1H, –CHO); The spectroscopic data were in agreement with those in the literature (Lindgren et al., 2009).

Z-selective olefination of **75** was performed using the procedure described above to provide (*Z*)-ethyl 3-(3-butoxyphenyl)acrylate (*cis*-**131**) (79%, *Z*:*E* = 94:6, 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: 0.97 (t, J = 7.2 Hz, 3H, $-CH_3$), 1.25 (t, J = 7.2 Hz, 3H, $-CO_2-CH_2-CH_3$), 1.49 (sextet, J = 7.2 Hz, 2H, $-CH_2-CH_3$), 1.77 (m, 2H, $-OCH_2-CH_2-$), 3.97 (t, J = 6.8 Hz, 2H, $-OCH_2-$), 4.18 (q, J = 7.2 Hz, 2H, $-CO_2-CH_2-$), 5.94 (d, J = 12.8 Hz, 1H, $=CH-CO_2-$), 6.86–6.91 (m, 2H, Ar–H and Ar–CH=), 7.11 (d, J = 7.2 Hz, 1H, Ar–H), 7.20 (s, 1H, Ar–H), 7.25 (d, J = 7.2 Hz, 1H, Ar–H).

Hydrolysis of *cis*-**131** was performed using the procedure described above to afford *cis*-**19** (91%) as colorless needles: mp 41–42 °C (Hexane); ^{1}H-NMR ($CDCl_3$, 400 MHz) δ: 0.96 (t, J = 7.6 Hz, 3H, $-CH_3$), 1.47 (sextet, J = 7.6 Hz, 2H, $-CH_2-CH_3$), 1.79–1.72 (m, 2H, $-OCH_2-CH_2-$), 3.95 (t, J = 6.8 Hz, 2H, $-OCH_2-$), 5.95 (d, J = 12.8 Hz, 1H, $=CH-CO_2-$), 6.89 (dd, J = 2.4, 8.4 Hz, 1H, Ar–H), 7.02 (d, J = 12.8 Hz, 1H, Ar–CH=), 7.12 (d, J = 7.2 Hz, 1H, Ar–H), 7.23–7.27 (m, 2H, Ar–H); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ: 13.8 (q, $-CH_3$),19.2 (t, $-CH_2-CH_3$), 31.2 (t, $-OCH_2-CH_2-$), 67.7 (t, $-OCH_2-$), 115.4 (d, Ar), 116.2 (d, Ar), 118.7 (d, $=CH-CO_2-$), 122.4 (d, Ar), 129.0 (d, Ar), 135.5 (s, Ar), 145.7 (d, Ar–CH=), 158.7 (s, Ar), 171.4 (s, C=O); IR (KBr) 1699 cm^{-1}; ESI-MS m/z 219 (M^+-H); Anal. calcd for $C_{13}H_{16}O_3$: C, 70.98; H, 7.32. found: C, 70.98; H, 7.32.

4.2.18. (Z)-3-(3-Isopropoxyphenyl)acrylic acid (cis-**20**)

172 (1.99 g, 16.3 mmol) was added to a solution of K_2CO_3 (4.08 g, 29.5 mmol) in acetone (40 mL) at 0 °C under Ar, then the reaction was stirred for 15 min. After 2-iodopropane (3.32 mL, 32.8 mmol) was added to the solution, the resulting mixture was heated until reflux began this being maintained for 9 h. The reaction was quenched with H_2O (20 mL) and extracted with EtOAc (3 x 30 mL). The organic layers were washed with H_2O (20 mL) and brine (20 mL), dried ($MgSO_4$), filtered and concentrated *in vacuo*. The residue was purified by silica gel CC (EtOAc/hexane, 10:90) to afford 3-isopropoxybenzaldehyde (**76**) (1.61 g, 9.78 mmol, 62%) as a yellow oil: ^{1}H-NMR ($CDCl_3$, 400 MHz) δ: 1.36 (d, J = 5.6 Hz, 6H, $-CH_3$), 4.63 (heptet, J = 5.6 Hz, 1H, $-CH-(CH_3)_2$), 7.15 (m, 1H, Ar–H), 7.38 (brs, 1H, Ar–H), 7.42–7.43 (m, 2H, Ar–H), 9.97 (s, 1H, –CHO); spectral data were in agreement with those in the literature (García-Díaz et al., 2011).

Z-selective olefination of **76** was performed using the procedure described above to provide (*Z*)-ethyl 3-(3-isopropoxyphenyl)acrylate (*cis*-**132**) (82%, *Z*:*E* = 96:4, determined by ^{1}H-NMR spectrum) (silica gel CC, EtOAc/hexane, 10:90) as a colorless oil: ^{1}H-NMR ($CDCl_3$, 400 MHz) δ: 1.25 (t, J = 7.2 Hz, 3H, $-CH_3$), 1.34 (d, J = 5.6 Hz, 6H, $-CH-(CH_3)_2$), 4.18 (q, J = 7.2 Hz, 2H, $-CH_2-$), 4.56 (heptet, J = 5.6 Hz, $-CH-(CH_3)_2$), 5.93 (d, J = 12.8 Hz, 1H, $=CH-CO_2-$), 6.85 (m, 1H, Ar–H), 6.89 (d, J = 12.8 Hz, 1H, Ar–CH=), 7.10 (d, J = 7.6 Hz, 1H, Ar–H), 7.22 (s, 1H, Ar–H), 7.25 (d, J = 8.4 Hz, 1H, Ar–H).

Hydrolysis of *cis*-**132** was performed using the procedure described above to afford *cis*-**20** (99%) as colorless needles: mp 49–50 °C (hexane); ^{1}H-NMR ($CDCl_3$, 400 MHz) δ: 1.32 (d, J = 6.4 Hz, 6H, $-CH-(CH_3)_2$), 4.53 (heptet, J = 6.4 Hz, 1H, $-CH-(CH_3)_2$), 5.95 (d, J = 12.6 Hz, 1H, $=CH-CO_2-$), 6.88 (dd, J = 2.0, 8.2 Hz, 1H, Ar–H), 7.02 (d, J = 12.6 Hz, 1H, Ar–CH=), 7.10 (d, J = 8.2 Hz, 1H, Ar–H), 7.24–7.27 (m, 2H, Ar–H); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ: 22.0 (q, $-CH_3$), 70.0 (d, $-OCH-(CH_3)_2$), 116.7 (d, Ar), 117.7 (d, Ar), 118.6 (d, $=CH-CO_2-$), 122.5 (d, Ar), 129.1 (d, Ar), 135.6 (s, Ar), 145.8 (d, Ar–CH=), 157.5 (s, Ar), 171.1 (s, C=O); IR (KBr) 1694 cm^{-1}; ESI-MS m/z 205 (M^+-H); Anal. calcd for $C_{12}H_{14}O_3$: C, 69.88; H, 6.84. found: C, 69.84; H, 6.86.

4.2.19. (Z)-3-(2-Fluorophenyl)acrylic acid (cis-**21**)

Z-selective olefination of 2-fluorobenzaldehyde (**77**) was performed using the procedure described above to provide (*Z*)-ethyl 3-(2-fluorophenyl)acrylate (*cis*-**133**) (94%, *Z*:*E* = 98:2, determined by ^{1}H-NMR spectrum) (silica gel CC, EtOAc/hexane, 3:97) as a colorless oil: ^{1}H-NMR ($CDCl_3$, 270 MHz) δ: 1.29 (t, J = 7.2 Hz, 3H, $-CH_3$), 4.19 (q, J = 7.2 Hz, 2H, $-CH_2-$), 6.04 (d, J = 12.4 Hz, $=CH-CO_2-$), 7.03–7.12 (m, 2H, Ar–H), 7.28–7.32 (m, 2H, Ar–H and Ar–CH=), 7.60 (t, J = 6.8 Hz, 1H, Ar–H); spectrosopic data were in agreement with those in the literature (Houghton and Voyle, 1983).

Hydrolysis of *cis*-**133** was performed using the procedure described above to afford *cis*-**21** (77%) as colorless needles: mp 90–93 °C (toluene); ^{1}H-NMR ($CDCl_3$, 400 MHz) δ: 6.09 (d, J = 12.2 Hz, 1H, $=CH-CO_2-$), 7.04–7.14 (m, 2H, Ar–H), 7.14 (d, J = 12.2 Hz, 1H, Ar–CH=), 7.33 (m, 1H, Ar–H), 7.60 (t, J = 6.8 Hz, 1H, Ar–H); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ: 115.3 (d, as a doublet, $=CH-CO_2-$), 121.2 (d, as a doublet, Ar), 122.6 (s, as a doublet, Ar), 123.6 (d, as a doublet, Ar), 138.1 (d, as a doublet, Ar–CH=), 160.2 (s, as a doublet, Ar), 171.3 (s, C=O); IR (KBr) 1701 cm^{-1}; ESI-MS m/z 165 (M^+-H); Anal. calcd for $C_9H_7FO_2$: C, 65.06; H, 4.25. found: C, 65.02; H, 4.29.

4.2.20. (Z)-3-(3-Fluorophenyl)acrylic acid (cis-**22**)

Z-selective olefination of 3-fluorobenzaldehyde (**78**) was performed using the procedure described above to provide (*Z*)-ethyl 3-(3-fluorophenyl)acrylate (*cis*-**134**) (94%, *Z*:*E* = 98:2, determined by ^{1}H-NMR spectrum) (silica gel CC, EtOAc/hexane, 2:98) as a colorless oil: ^{1}H-NMR ($CDCl_3$, 400 MHz) δ: 1.25 (t, J = 6.8 Hz, 3H, $-CH_3$), 4.18 (q, J = 6.8 Hz, 2H, $-CH_2-$), 5.99 (d, J = 12.6 Hz, $=CH-CO_2-$), 6.90 (d, J = 12.6 Hz, 1H, Ar–CH=), 7.01–7.04 (m, 1H, Ar–H), 7.29–7.34 (m, 3H, Ar–H).

Hydrolysis of *cis*-**134** was performed using the procedure described above to afford *cis*-**22** (80%) as colorless needles: mp 40–41 °C (toluene); ^{1}H-NMR ($CDCl_3$, 400 MHz) δ: 6.02 (d, J = 12.8 Hz, 1H, $=CH-CO_2-$), 7.03 (d, J = 12.8 Hz, 1H, Ar–CH=), 7.07 (m, 1H, Ar–H), 7.31–7.34 (m, 2H, Ar–H), 7.38 (m, 1H, Ar–H); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ: 116.2 (d, as a doublet, Ar), 116.5 (d, as a doublet, Ar), 119.8 (d, $=CH-CO_2-$), 125.7 (d, as a doublet, Ar), 129.5 (d, as a doublet, Ar), 136.3 (s, as a doublet, Ar), 144.4 (d, as a doublet, Ar–CH=), 162.3 (d, as a doublet, Ar), 171.7 (s, C=O); IR (KBr) 1697 cm^{-1}; ESI-MS m/z 165 (M^+-H); Anal. calcd for $C_9H_7FO_2$: C, 65.06; H, 4.25. found: C, 65.06; H, 4.25.

*4.2.21. (Z)-3-(4-Fluorophenyl)acrylic acid (cis-**23**)*

Z-selective olefination of 4-fluorobenzaldehyde (**79**) was performed using the procedure described above to provide (*Z*)-ethyl 3-(4-fluorophenyl)acrylate (*cis*-**135**) (94%, *Z*:*E* = 98:2, determined by ^{1}H-NMR spectrum) (silica gel CC, EtOAc/hexane, 2:98) as a colorless oil: ^{1}H-NMR ($CDCl_3$, 400 MHz) δ: 1.30 (t, *J* = 7.2 Hz, 3H, $-CH_3$), 4.19 (q, *J* = 7.2 Hz, 2H, $-CH_2-$), 5.96 (d, *J* = 12.4 Hz, $=CH-CO_2-$), 6.93 (d, *J* = 12.4 Hz, 1H, Ar–CH=), 7.07 (m, 2H, Ar–H), 7.68 (dd, *J* = 2.9, 8.8 Hz, 2H, Ar–H). The spectroscopic data were in agreement with those in the literature (Mueller and Jennigs, 2007).

Hydrolysis of *cis*-**135** was performed using the procedure described above to afford *cis*-**23** (77%) as colorless needles: mp 90–93 °C (toluene); ^{1}H-NMR ($CDCl_3$, 400 MHz) δ: 5.96 (d, *J* = 12.8 Hz, 1H, $=CH-CO_2-$), 7.00–7.08 (m, 3H, Ar–CH= and Ar–H), 7.64–7.68 (m, 2H, Ar–H); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ: 115.1 (d, as a doublet, Ar), 118.3 (d, $=CH-CO_2-$), 130.3 (s, Ar), 132.3 (d, as a doublet, Ar), 145.0 (d, Ar–CH=), 163.1 (s, Ar), 171.7 (s, C=O); IR (KBr) 1686 cm^{-1}; ESI-MS *m*/*z* 165 (M^+-H); Anal. calcd for $C_9H_7FO_2$: C, 65.06; H, 4.25. found: C, 64.86; H, 4.25.

*4.2.22. (Z)-3-(2-Chlorophenyl)acrylic acid (cis-**24**)*

Z-selective olefination of 2-chlorobenzaldehyde (**80**) was performed using the procedure described above to provide (*Z*)-ethyl 3-(2-chlorophenyl)acrylate (*cis*-**136**) (90%, *Z*:*E* = 98:2, determined by ^{1}H-NMR spectrum) (silica gel CC, EtOAc/hexane, 5:95) as a colorless oil: ^{1}H-NMR ($CDCl_3$, 270 MHz) δ: 1.18 (t, *J* = 7.3 Hz, 3H, $-CH_3$), 4.11 (q, *J* = 7.3 Hz, 2H, $-CH_2-$), 6.08 (d, *J* = 12.4 Hz, 1H, $=CH-CO_2-$), 7.14 (d, *J* = 12.4 Hz, 1H, Ar–CH=), 7.23–7.29 (m, 2H, Ar–H), 7.38 (dd, *J* = 2.1, 7.0 Hz, 1H, Ar–H), 7.50 (m, 1H, Ar–H); spectroscopic data were in agreement with those in the literature (Byrne and Gilheany, 2012).

Hydrolysis of *cis*-**136** was performed using the procedure described above to afford *cis*-**24** (77%) as colorless needles: mp 136–137 °C (toluene); ^{1}H-NMR ($CDCl_3$, 400 MHz) δ: 6.08 (d, *J* = 12.8 Hz, 1H, $=CH-CO_2-$), 7.20–7.29 (m, 3H, Ar–H and Ar–CH=), 7.38, 7.50 (d, *J* = 7.2 Hz, each 1H, Ar–H); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ: 120.9 (d, $=CH-CO_2-$), 126.2 (d, Ar), 129.1 (d, Ar), 130.1 (d, Ar), 130.9 (d, Ar), 133.2 (s, Ar), 133.4 (s, Ar), 143.0 (d, Ar–CH=), 171.0 (s, C=O); IR (KBr) 1701 cm^{-1}; ESI-MS *m*/*z* 181 (M^+-H); Anal. calcd for $C_9H_7ClO_2$: C, 59.20; H, 3.86. found: C, 59.38; H, 3.85

*4.2.23. (Z)-3-(3-Chlorophenyl)acrylic acid (cis-**25**)*

Z-selective olefination of 3-chlorobenzaldehyde (**81**) was performed using the procedure described above to provide (*Z*)-ethyl 3-(3-chlorophenyl)acrylate (*cis*-**137**) (97%, *Z*:*E* = 98:2, determined by ^{1}H-NMR spectrum) (silica gel CC, EtOAc/hexane, 4:96) as a colorless oil: ^{1}H-NMR ($CDCl_3$, 270 MHz) δ: 1.25 (t, *J* = 7.3 Hz, 3H, $-CH_3$), 4.18 (q, *J* = 7.3 Hz, 2H, $-CH_2-$), 5.99 (d, *J* = 12.6 Hz, 1H, $=CH-CO_2-$), 6.89 (d, *J* = 12.6 Hz, 1H, Ar–CH=), 7.26–7.30 (m, 2H, Ar–H), 7.42 (d, *J* = 7.0 Hz, 1H, Ar–H), 7.57 (s, 1H, Ar–H).

Hydrolysis of *cis*-**137** was performed using the procedure described above to afford *cis*-**25** (94%) as colorless needles: mp 70–71 °C (toluene); ^{1}H-NMR ($CDCl_3$, 400 MHz) δ: 6.02 (d, *J* = 12.4 Hz, 1H, $=CH-CO_2-$), 7.01 (d, *J* = 12.4 Hz, 1H, Ar–CH=), 7.34–7.29 (m, 2H, Ar–H), 7.46 (d, *J* = 7.2 Hz, 1H, Ar–H), 7.58 (s, 1H, Ar–H); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ: 120.0 (d, $=CH-CO_2-$), 127.9 (d, Ar), 129.2 (d, Ar), 129.3 (d, Ar), 129.6 (d, Ar), 133.9 (s, Ar), 136.0 (s, Ar), 144.3 (d, Ar–CH=), 171.3 (s, C=O); IR (KBr) 1699 cm^{-1}; ESI-MS *m*/*z* 181 (M^+-H); Anal. calcd for $C_9H_7ClO_2$: C, 59.20; H, 3.86. found: C, 59.13; H, 3.86.

*4.2.24. (Z)-3-(4-Chlorophenyl)acrylic acid (cis-**26**)*

Z-selective olefination of 4-chlorobenzaldehyde (**82**) was performed using the procedure described above to provide (*Z*)-ethyl 3-(4-chlorophenyl)acrylate (*cis*-**138**) (98%, *Z*:*E* = 97:3, determined by ^{1}H-NMR spectrum) (silica gel CC, EtOAc/hexane, 4:96) as a colorless oil: ^{1}H-NMR ($CDCl_3$, 270 MHz) δ: 1.26 (t, *J* = 7.3 Hz, 3H, $-CH_3$), 4.18 (q, *J* = 7.3 Hz, 2H, $-CH_2-$), 5.96 (d, *J* = 12.6 Hz, 1H, $=CH-CO_2-$), 6.88 (d, *J* = 12.6 Hz, 1H, Ar–CH=), 7.32, 7.55 (d, *J* = 7.8 Hz, each 2H, Ar–H); The spectroscopic data were in agreement with those in the literature (Walter and Oestreich, 2008).

Hydrolysis of *cis*-**138** was performed using the procedure described above to afford *cis*-**26** (89%) as colorless needles: mp 108–110 °C (toluene); ^{1}H-NMR ($CDCl_3$, 400 MHz) δ: 5.99 (d, *J* = 12.8 Hz, 1H, $=CH-CO_2-$), 7.01 (d, *J* = 12.8 Hz, 1H, Ar–CH=), 7.33, 7.56 (d, *J* = 8.6 Hz, each 2H, Ar–H); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ: 119.1 (d,$=CH-CO_2-$), 128.3 (d, Ar), 131.4 (d, Ar), 132.7 (s, Ar), 135.3 (s, Ar), 144.8 (d, Ar–CH=), 171.5 (s, C=O); IR (KBr) 1699 cm^{-1}; ESI-MS *m*/*z* 181 (M^+-H); Anal. calcd for $C_9H_7ClO_2$: C, 59.20; H, 3.86. found: C, 59.33; H, 3.86.

*4.2.25. (Z)-3-(2-Bromophenyl)acrylic acid (cis-**27**)*

Z-selective olefination of 2-bromobenzaldehyde (**83**) was performed using the procedure described above to provide (*Z*)-ethyl 3-(2-bromophenyl)acrylate (*cis*-**139**) (81%, *Z* only, determined by ^{1}H-NMR spectrum) (silica gel CC, EtOAc/hexane, 7:93) as a colorless oil: ^{1}H-NMR ($CDCl_3$, 400 MHz) δ: 1.17 (t, *J* = 7.2 Hz, 3H, $-CH_3$), 4.11 (q, *J* = 7.2 Hz, 2H, $-CH_2-$), 6.06 (d, *J* = 12.2 Hz, 1H, $=CH-CO_2-$), 7.09 (d, *J* = 12.2 Hz, 1H, Ar–CH=), 7.18 (dt, *J* = 1.6, 8.0 Hz, 1H, Ar–H), 7.26–7.30 (m, 1H, Ar–H), 7.47, 7.58 (d, *J* = 8.0 Hz, each 1H, Ar–H); spectroscopic data were in agreement with those in the literature (Byrne and Gilheany, 2012).

Hydrolysis of *cis*-**139** was performed using the procedure described above to afford *cis*-**27** (92%) as colorless needles: mp 146–147 °C (toluene); ^{1}H-NMR ($CDCl_3$, 600 MHz) δ: 6.05 (d, *J* = 12.4 Hz, 1H, $=CH-CO_2-$), 7.18 (d, *J* = 12.4 Hz, 1H, Ar–CH=), 7.19 (m, 1H, Ar–H), 7.27 (t, *J* = 7.3 Hz, 1H, Ar–H), 7.46 (dd, *J* = 1.2, 7.3 Hz, 1H, Ar–H), 7.58 (d, *J* = 7.3 Hz, 1H, Ar–H); ^{13}C-NMR ($CDCl_3$, 150 MHz) δ: 120.6 (d, $=CH-CO_2-$), 123.0 (s, Ar), 126.8 (d, Ar), 130.2 (d, Ar), 130.9 (d, Ar), 135.3 (s, Ar), 145.1 (d, Ar–CH=), 170.4 (s, C=O); IR (KBr) 1703 cm^{-1}; ESI-MS *m*/*z* 225 (M^+-H); Anal. calcd for $C_9H_7ClO_2$: C, 47.61; H, 3.11. found: C, 47.76; H, 3.11.

*4.2.26. (Z)-3-(3-Bromophenyl)acrylic acid (cis-**28**)*

Z-selective olefination of 3-bromobenzaldehyde (**84**) was performed using the procedure described above to provide (*Z*)-ethyl 3-(3-bromophenyl)acrylate (*cis*-**140**) (77%, *Z*:*E* = 98:2, determined by ^{1}H-NMR spectrum) (silica gel CC, EtOAc/hexane, 5:95) as a colorless oil: ^{1}H-NMR ($CDCl_3$, 270 MHz) δ: 1.25 (t, *J* = 7.3 Hz, 3H, $-CH_3$), 4.18 (q, *J* = 7.3 Hz, 2H, $-CH_2-$), 5.99 (d, *J* = 12.8 Hz, 1H, $=CH-CO_2-$), 6.88 (d, *J* = 12.8 Hz, 1H, Ar–CH=), 7.22 (t, *J* = 7.8 Hz, 1H, Ar–H), 7.44–7.49 (m, 2H, Ar–H), 7.72 (s, 1H, Ar–H).

Hydrolysis of *cis*-**140** was performed using the procedure described above to afford *cis*-**28** (70%) as colorless needles: mp 80–81 °C (toluene); ^{1}H-NMR ($CDCl_3$, 400 MHz) δ: 6.02 (d, *J* = 12.8 Hz, 1H, $=CH-CO_2-$), 7.00 (d, *J* = 12.8 Hz, 1H, Ar–CH=), 7.23 (t, *J* = 7.6 Hz, 1H, Ar–H), 7.48–7.52 (m, 2H, Ar–H), 7.72 (s, 1H, Ar–H); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ: 120.1 (d, $=CH-CO_2-$), 122.0 (s, Ar), 128.3 (d, Ar), 129.5 (d, Ar), 132.0 (d, Ar), 132.5 (d, Ar), 136.3 (s, Ar), 144.2 (d, Ar–CH=), 171.3 (s, C=O); IR (KBr) 1697 cm^{-1}; ESI-MS *m*/*z* 225 (M^+-H); Anal. calcd for $C_9H_7BrO_2$: C, 47.61; H, 3.11. found: C, 47.66; H, 3.04.

*4.2.27. (Z)-3-(4-Bromophenyl)acrylic acid (cis-**29**)*

Z-selective olefination of 4-bromobenzaldehyde (**85**) was performed using the procedure described above to provide (*Z*)-ethyl 3-(4-bromophenyl)acrylate (*cis*-**141**) (90%, *Z*:*E* = 97:3, determined by ^{1}H-NMR spectrum) (silica gel CC, EtOAc/hexane, 10:90) as a colorless oil: ^{1}H-NMR ($CDCl_3$, 270 MHz) δ: 1.26 (t, *J* = 7.3 Hz, 3H, $-CH_3$), 4.18 (q, *J* = 7.3 Hz, 2H, $-CH_2-$), 5.97 (d, *J* = 12.8 Hz, 1H, $=CH-CO_2-$), 6.86 (d, *J* = 12.8 Hz, 1H, Ar–CH=), 7.47 (s, 4H, Ar–H);

spectral data were in agreement with those in the literature (Pettit et al., 2009).

Hydrolysis of *cis*-**141** was performed using the procedure described above to afford *cis*-**29** (90%) as colorless needles: mp 124–127 °C (Toluene); ^{1}H-NMR ($CDCl_3$, 400 MHz) δ: 5.98 (d, J = 12.8 Hz, 1H, =CH–CO_2–), 6.99 (d, J = 12.8 Hz, 1H, Ar–CH=), 7.47 (brs, 4H, Ar–H); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ: 119.3 (d,=CH–CO_2–), 123.8 (s, Ar), 131.3 (d, Ar), 131.6 (d, Ar), 133.2 (s, Ar), 144.8 (d, Ar–CH=), 171.1 (s, C=O); IR (KBr) 1701 cm^{-1}; ESI-MS m/z 225 (M^+–H); Anal. calcd for $C_9H_7BrO_2$: C, 47.61; H, 3.11. found: C, 47.70; H, 3.13.

4.2.28. (Z)-3-(2-Iodophenyl)acrylic acid (cis-30)

The *Z*-selective olefination of 2-iodobenzaldehyde (**86**) was performed using the procedure described above to provide (*Z*)-ethyl 3-(2-iodophenyl)acrylate (*cis*-**142**) (85%, *Z*:*E* = 99:1, determined by ^{1}H-NMR spectrum) (silica gel CC, EtOAc/hexane, 6:94) as a colorless oil: ^{1}H-NMR ($CDCl_3$, 270 MHz) δ: 1.16 (t, J = 7.0 Hz, 3H, –CH_3), 4.10 (q, J = 7.0 Hz, 2H, –CH_2–), 6.02 (d, J = 12.4 Hz, 1H, =CH–CO_2–), 6.97 (d, J = 12.4 Hz, 1H, Ar–CH=), 7.06 (m, 1H, Ar–H), 7.32 (t, J = 7.6 Hz, 1H, Ar–H), 7.42 (d, J = 7.6 Hz, 1H, Ar–H), 7.85 (d, J = 7.6 Hz, 1H, Ar–H).

Hydrolysis of *cis*-**142** was performed using the procedure described above to afford *cis*-**30** (95%) as colorless needles: mp 122–124 °C (toluene); ^{1}H-NMR ($CDCl_3$, 400 MHz) δ: 6.02 (d, J = 12.2 Hz, 1H, =CH–CO_2–), 7.02 (m, 1H, Ar–H), 7.07 (d, J = 12.2 Hz, 1H, Ar–CH=), 7.32 (t, J = 7.6 Hz, 1H, Ar–H), 7.43 (d, J = 7.6 Hz, 1H, Ar–H), 7.86 (d, J = 7.6 Hz, 1H, Ar–H); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ: 98.0 (s, Ar), 120.2 (d, =CH–CO_2–), 127.6 (d, Ar), 130.0 (d, Ar), 130.2 (d, Ar), 138.5 (d, Ar), 139.0 (s, Ar), 149.0 (d, Ar–CH=), 170.8 (s, C=O); IR (KBr) 1701 cm^{-1}; ESI-MS m/z 273 (M^+–H); Anal. calcd for $C_9H_7IO_2$: C, 39.44; H, 2.57. found: C, 39.81; H, 2.57.

4.2.29. (Z)-3-(3-Iodophenyl)acrylic acid (cis-31)

Z-selective olefination of 3-iodobenzaldehyde (**87**) was performed using the procedure described above to provide (*Z*)-ethyl 3-(3-iodophenyl)acrylate (*cis*-**143**) (94%, *Z*:*E* = 98:2, determined by ^{1}H-NMR spectrum) (silica gel CC, EtOAc/hexane, 5:95) as a colorless oil: ^{1}H-NMR ($CDCl_3$, 270 MHz) δ: 1.26 (t, J = 7.2 Hz, 3H, –CH_3), 4.19 (q, J = 7.2 Hz, 2H, –CH_2–), 5.98 (d, J = 12.6 Hz, 1H, =CH–CO_2–), 6.85 (d, J = 12.6 Hz, 1H, Ar–CH=), 7.10 (t, J = 7.8 Hz, 1H, Ar–H), 7.53, 7.66 (d, J = 7.8 Hz, each 1H, Ar–H), 7.90 (s, 1H, Ar–H).

Hydrolysis of *cis*-**143** was performed using the procedure described above to afford *cis*-**31** (88%) as colorless needles: mp 102–104 °C (toluene); ^{1}H-NMR ($CDCl_3$, 400 MHz) δ: 5.99 (d, J = 12.8 Hz, 1H, =CH–CO_2–), 6.96 (d, J = 12.8 Hz, 1H, Ar–CH=), 7.09 (dd, J = 7.6, 8.4 Hz, 1H, Ar–H), 7.55 (d, J = 7.6 Hz, 1H, Ar–H), 7.66 (d, J = 8.4 Hz, 1H, Ar–H), 7.89 (s, 1H, Ar–H); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ: 93.7 (s, Ar), 120.0 (d, =CH–CO_2–), 128.9 (d, Ar), 129.7 (d, Ar), 136.4 (s, Ar), 138.0 (d, Ar), 138.4 (d, Ar), 144.1 (d, Ar–CH=), 171.0 (s, C=O); IR (KBr) 1699 cm^{-1}; ESI-MS m/z 273 (M^+–H); Anal. calcd for $C_9H_7IO_2$: C, 39.44; H, 2.57. found: C, 39.44; H, 2.57.

4.2.30. (Z)-3-(4-Iodophenyl)acrylic acid (cis-32)

Z-selective olefination of 4-iodobenzaldehyde (**88**) was performed using the procedure described above to provide (*Z*)-ethyl 3-(4-iodophenyl)acrylate (*cis*-**144**) (98%, *Z*:*E* = 98:2, determined by ^{1}H-NMR spectrum) (silica gel CC, EtOAc/hexane, 5:95) as a colorless oil: ^{1}H-NMR ($CDCl_3$, 270 MHz) δ: 1.24 (t, J = 7.3 Hz, 3H, –CH_3), 4.17 (q, J = 7.3 Hz, 2H, –CH_2–), 5.95 (d, J = 12.6 Hz, 1H, =CH–CO_2–), 6.95 (d, J = 12.6 Hz, 1H, Ar–CH=), 7.33–7.35, 7.57–7.59 (m, each 2H, Ar–H).

Hydrolysis of *cis*-**144** was performed using the procedure described above to afford *cis*-**32** (92%) as colorless needles: mp 126–129 °C (toluene); ^{1}H-NMR ($CDCl_3$, 400 MHz) δ: 5.97 (d, J = 12.8 Hz, 1H, =CH–CO_2–), 6.96 (d, J = 12.8 Hz, 1H, Ar–CH=), 7.32, 7.68 (d, J = 8.4 Hz, each 2H, Ar–H); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ: 95.8 (s, Ar), 119.4 (d,=CH–CO_2–), 131.6 (d, Ar), 133.7 (s, Ar), 137.2 (d, Ar), 144.9 (d, Ar–CH=), 171.3 (s, C=O); IR (KBr) 1699 cm^{-1}; ESI-MS m/z 273 (M^+–H); Anal. calcd for $C_9H_7IO_2$: C, 39.44; H, 2.57. found: C, 39.61; H, 2.57.

4.2.31. (Z)-3-(2-Nitrophenyl)acrylic acid (cis-33)

Z-selective olefination of 2-nitrobenzaldehyde (**89**) was performed using the procedure described above to provide (*Z*)-ethyl 3-(2-nitrophenyl)acrylate (*cis*-**145**) (82%, *Z*:*E* = 98:2, determined by ^{1}H-NMR spectrum) (silica gel CC, EtOAc/hexane, 5:95) as a colorless oil: ^{1}H-NMR ($CDCl_3$, 270 MHz) δ: 1.11 (t, J = 7.3 Hz, 3H, –CH_3), 4.03 (q, J = 7.3 Hz, 2H, –CH_2–), 6.10 (d, J = 11.8 Hz, 1H, =CH–CO_2–), 7.40 (m, 1H, Ar–H), 7.41 (d, J = 11.8 Hz, 1H, Ar–CH=), 7.50 (t, J = 7.6 Hz, 1H, Ar–H), 7.61 (d, J = 7.6 Hz, 1H, Ar–H), 8.16 (d, J = 8.4 Hz, 1H, Ar–H).

Hydrolysis of *cis*-**145** was performed using the procedure described above to afford *cis*-**33** (91%) as yellow needles: mp 147–148 °C (toluene); ^{1}H-NMR ($CDCl_3$, 400 MHz) δ: 6.07 (d, J = 12.4 Hz, 1H, =CH–CO_2–), 7.36 (d, J = 7.6 Hz, 1H, Ar–H), 7.48–7.52 (m, 2H, Ar–CH= and Ar–H), 7.59 (m, 1H, Ar–H), 8.16 (d, J = 8.4 Hz, 1H, Ar–H); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ: 120.1 (d, =CH–CO_2–), 124.4 (d, Ar), 129.3 (d, Ar), 131.0 (d, Ar), 131.9 (s, Ar), 133.3 (d, Ar), 144.0 (d, Ar–CH=), 146.6 (s, Ar), 170.8 (s, C=O); IR (KBr) 1701 cm^{-1}; ESI-MS m/z 192 (M^+–H); Anal. calcd for $C_9H_7NO_4$: C, 55.96; H, 3.65; N, 7.25. found: C, 56.05; H, 3.67; N, 7.25.

4.2.32. (Z)-3-(3-Nitrophenyl)acrylic acid (cis-34)

Z-selective olefination of 3-nitrobenzaldehyde (**90**) was performed using the procedure described above to provide (*Z*)-ethyl 3-(3-nitrophenyl)acrylate (*cis*-**146**) (66%, *Z*:*E* = 98:2, determined by ^{1}H-NMR spectrum) (silica gel CC, EtOAc/hexane, 10:90) as a colorless oil: ^{1}H-NMR ($CDCl_3$, 270 MHz) δ: 1.25 (t, J = 7.3 Hz, 3H, –CH_3), 4.19 (q, J = 7.3 Hz, 2H, –CH_2–), 6.11 (d, J = 12.4 Hz, 1H, =CH–CO_2–), 7.00 (d, J = 12.4 Hz, 1H, Ar–CH=), 7.53 (t, J = 8.1 Hz, 1H, Ar–H), 7.88, 8.19 (d, J = 8.1 Hz, each 1H, Ar–H), 8.44 (s, 1H, Ar–H).

Hydrolysis of *cis*-**146** was performed using the procedure described above to afford *cis*-**34** (93%) as yellow needles: mp 157–158 °C (Toluene); ^{1}H-NMR ($CDCl_3$, 400 MHz) δ: 6.14 (d, J = 12.6 Hz, 1H,=CH–CO_2–), 7.13 (d, J = 12.6 Hz, 1H, Ar–CH=), 7.55 (t, J = 8.0 Hz, 1H, Ar–H), 7.88 (d, J = 8.0 Hz, 1H, Ar–H), 8.21 (dd, J = 1.6, 8.0 Hz, 1H, Ar–H), 8.43 (s, 1H, Ar–H); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ: 123.3 (d, =CH–CO_2–), 123.5 (d, Ar), 123.9 (d, Ar), 129.6 (d, Ar), 136.1 (d, Ar), 136.5 (s, Ar), 138.7 (d, Ar–CH=), 147.5 (s, Ar), 167.1 (s, C=O); IR (KBr) 1701 cm^{-1}; ESI-MS m/z 192 (M^+–H); Anal. calcd for $C_9H_7NO_4$: C, 55.96; H, 3.65; N, 7.25. found: C, 55.96; H, 3.65; N, 7.23.

4.2.33. (Z)-3-(4-Nitrophenyl)acrylic acid (cis-35)

Z-selective olefination of 4-nitrobenzaldehyde (**91**) was performed using the procedure described above to provide (*Z*)-ethyl 3-(4-nitrophenyl)acrylate (*cis*-**147**) (70%, *Z* only, determined by ^{1}H-NMR spectrum) (silica gel CC, EtOAc/hexane, 10:90) as a colorless oil: ^{1}H-NMR ($CDCl_3$, 270 MHz) δ: 1.25 (t, J = 7.3 Hz, 3H, –CH_3), 4.18 (q, J = 7.3 Hz, 2H, –CH_2–), 6.13 (d, J = 12.4 Hz, 1H, =CH–CO_2–), 7.01 (d, J = 12.4 Hz, 1H, Ar–CH=), 7.67, 8.21 (d, J = 8.6 Hz, each 2H, Ar–H).

Hydrolysis of *cis*-**147** was performed using the procedure described above to afford *cis*-**35** (76%) as yellow needles: mp 146–147 °C (toluene); ^{1}H-NMR ($CDCl_3$, 400 MHz) δ: 6.15 (d,

J = 12.8 Hz, 1H, =CH–CO_2–), 7.15 (d, J = 12.8 Hz, 1H, Ar–CH=), 7.66, 8.21 (d, J = 8.8 Hz, each 2H, Ar–H); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ:122.0 (d,=CH–CO_2–), 123.3 (d, Ar), 130.3 (d, Ar), 140.9 (s, Ar), 143.4 (d, Ar–CH=), 147.8 (s, Ar), 177.8 (s, C=O); IR (KBr) 1705 cm^{-1}; ESI-MS m/z 192 (M^+–H); Anal. calcd for $C_9H_7NO_4$: C, 55.96; H, 3.65; N, 7.25. found: C, 56.02; H, 3.68; N, 7.23.

*4.2.34. (Z)-3-[2-(Trifluoromethyl)phenyl]acrylic acid (cis-**36**)*

Z-selective olefination of 2-(trifluoromethyl)benzaldehyde (**92**) was performed using the procedure described above to provide (*Z*)-ethyl 3-(2-(trifluoromethyl)phenyl)acrylate (*cis*-**148**) (83%, *Z* only, determined by ^{1}H-NMR spectrum) (silica gel CC, EtOAc/hexane, 10:90) as a colorless oil: ^{1}H-NMR ($CDCl_3$, 270 MHz) δ: 1.09 (t, J = 7.0 Hz, 3H, –CH_3), 4.04 (q, J = 7.0 Hz, 2H, –CH_2–), 6.11 (d, J = 12.2 Hz, 1H, =CH–CO_2–), 7.30–7.50 (m, 4H, Ar–CH= and Ar–H), 7.66 (d, J = 7.6 Hz, 1H, Ar–H).

Hydrolysis of *cis*-**148** was performed using the procedure described above to afford *cis*-**36** (89%) as colorless needles: mp 113–114 °C (Toluene); ^{1}H-NMR ($CDCl_3$, 400 MHz) δ: 6.11 (d, J = 12.4 Hz, 1H,=CH–CO_2–), 7.37–7.44 (m, 3H, Ar–CH= and Ar–H), 7.49 (t, J = 7.2 Hz, 1H, Ar–H), 7.67 (d, J = 8.0 Hz, 1H, Ar–H); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ: 121.9 (d, =CH–CO_2–), 122.6 (a, Ar), 125.5 (d, as a quartet, Ar), 127.2 (s, as a quartet, –CF_3), 128.3 (d, Ar), 130.3 (d, Ar), 131.2 (d, Ar), 134.0 (s, as a quartet, Ar), 143.2 (d, Ar–CH=), 171.0 (s, C=O); IR (KBr) 1705 cm^{-1}; ESI–MS m/z 215 (M^+–H); Anal. calcd for $C_{10}H_7F_3O_2$: C, 55.56; H, 3.26. found: C, 55.68; H, 3.30.

*4.2.35. (Z)-3-[3-(Trifluoromethyl)phenyl]acrylic acid (cis-**37**)*

Z-selective olefination of 3-(trifluoromethyl)benzaldehyde (**93**) was performed using the procedure described above to provide (*Z*)-ethyl 3-(3-(trifluoromethyl)phenyl)acrylate (*cis*-**149**) (86%, *Z*:*E* = 98:2, determined by ^{1}H-NMR spectrum) (silica gel CC, EtOAc/hexane, 5:95) as a colorless oil: ^{1}H-NMR ($CDCl_3$, 400 MHz) δ: 1.23 (t, J = 7.2 Hz, 3H, –CH_3), 4.17 (q, J = 7.2 Hz, 2H, –CH_2–), 6.05 (d, J = 12.8 Hz, 1H, =CH–CO_2–), 6.96 (d, J = 12.8 Hz, 1H, Ar–CH=), 7.47 (dd, J = 7.6, 8.0 Hz, 1H, Ar–H), 7.58 (d, J = 7.6 Hz, 1H, Ar–H), 7.74 (d, J = 8.0 Hz, 1H, Ar–H), 7.80 (s, 1H, Ar–H).

Hydrolysis of *cis*-**149** was performed using the procedure described above to afford *cis*-**37** (90%) as colorless needles: mp 56–57 °C (Toluene); ^{1}H-NMR ($CDCl_3$, 400 MHz) δ: 6.07 (d, J = 12.6 Hz, 1H, =CH–CO_2–), 7.10 (d, J = 12.6 Hz, 1H, Ar–CH=), 7.48 (dd, J = 7.6, 8.0 Hz, 1H, Ar–H), 7.60 (d, J = 7.6 Hz, 1H, Ar–H), 7.77 (d, J = 8.0 Hz, 1H, Ar–H), 7.83 (s, 1H, Ar–H); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ: 120.5 (d, =CH–CO_2–), 122.5 (s, Ar), 125.8 (d, as a quartet, Ar), 126.6 (d, as a quartet, Ar), 128.5 (d, Ar), 130.5 (s, as a quartet, –CF_3), 132.9 (d, Ar), 135.6 (s, Ar), 144.3 (d, Ar–CH=), 170.8 (s, C=O); IR (KBr) 1701 cm^{-1}; ESI-MS m/z 215 (M^+–H); Anal. calcd for $C_{10}H_7F_3O_2$: C, 55.56; H, 3.26. found: C, 55.47; H, 3.26.

*4.2.36. (Z)-3-[4-(Trifluoromethyl)phenyl]acrylic acid (cis-**38**)*

The *Z*-selective olefination of 4-(trifluoromethyl)benzaldehyde (**94**) was performed using the procedure described above to provide (*Z*)-ethyl 3-(4-(trifluoromethyl)phenyl)acrylate (*cis*-**150**) (90%, *Z*:*E* = 95:5, determined by ^{1}H-NMR spectrum) (silica gel CC, EtOAc/hexane, 10:90) as a colorless oil: ^{1}H-NMR ($CDCl_3$, 270 MHz) δ: 1.24 (t, J = 7.0 Hz, 3H, –CH_3), 4.17 (q, J = 7.0 Hz, 2H, –CH_2–), 6.06 (d, J = 12.7 Hz, 1H, =CH–CO_2–), 6.98 (d, J = 12.7 Hz, 1H, Ar–CH=), 7.60, 7.64 (d, J = 8.9 Hz, each 2H, Ar–H).

Hydrolysis of *cis*-**150** was performed using the procedure described above to afford *cis*-**38** (87%) as colorless needles: mp 90–93 °C (toluene); ^{1}H-NMR ($CDCl_3$, 400 MHz) δ: 6.09 (d, J = 12.6 Hz, 1H, =CH–CO_2–), 7.11 (d, J = 12.6 Hz, 1H, Ar–CH=), 7.61, 7.66 (d, J = 8.8 Hz, each 2H, Ar–H); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ: 120.8 (d, =CH–CO_2–), 122.5 (s, Ar), 125.0 (d, as a quartet, Ar), 129.9 (d, Ar), 130.9 (s, as a quartet, –CF_3), 137.9 (s, Ar), 144.3 (d, Ar–CH=), 171.1 (s, C=O); IR (KBr) 1701 cm^{-1}; ESI-MS m/z 215 (M^+–H); Anal. calcd for $C_{10}H_7F_3O_2$: C, 55.56; H, 3.26. found: C, 55.65; H, 3.33.

*4.2.37. (Z)-3-(2,4-Dimethylphenyl)acrylic acid (cis-**39**)*

Z-selective olefination of 2,4-dimethylbenzaldehyde (**95**) was performed using the procedure described above to provide (*Z*)-ethyl 3-(2,4-dimethylphenyl)acrylate (*cis*-**151**) (94%, *Z* only, determined by ^{1}H-NMR spectrum) (silica gel CC, EtOAc/hexane, 10:90) as a colorless oil: ^{1}H-NMR ($CDCl_3$, 270 MHz) δ: 1.18 (t, J = 7.0 Hz, 3H, –CH_3), 2.25, 2.31 (s, each 3H, Ar–CH_3), 4.10 (q, J = 7.0 Hz, 2H, –CH_2–), 5.97 (d, J = 12.2 Hz, 1H, =CH–CO_2–), 6.95–6.99 (m, 2H, Ar–H), 7.08 (d, J = 12.2 Hz, 1H, Ar–CH=), 7.26 (d, J = 7.8 Hz, 1H, Ar–H).

Hydrolysis of *cis*-**151** was performed using the procedure described above to afford *cis*-**39** (96%) as colorless needles: mp 91–94 °C (toluene); ^{1}H-NMR ($CDCl_3$, 400 MHz) δ: 2.25, 2,31 (s, each 3H, –CH_3), 5.96 (d, J = 12.4 Hz, 1H,=CH–CO_2–), 6.95 (d, J = 7.8 Hz, 1H, Ar–H), 6.99 (s, 1H, Ar–H), 7.18 (d, J = 12.4 Hz, 1H, Ar–CH=), 7.27 (d, J = 7.8 Hz, 1H, Ar–H); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ: 19.8 (q, –CH_3), 21.2 (q, –CH_3), 119.3 (d,=CH–CO_2–), 126.1 (d, Ar), 129.1 (d, Ar), 130.6 (d, Ar), 131.3 (s, Ar), 136.0 (s, Ar), 138.9 (s, Ar), 145.4 (d, Ar–CH=), 171.2 (s, C=O); IR (KBr) 1697 cm^{-1}; ESI-MS m/z 175 (M^+–H); Anal. calcd for $C_{11}H_{12}O_2$: C, 74.98; H, 6.86. found: C, 75.03; H, 6.68.

*4.2.38. (Z)-3-(4-Methoxy-2-methylphenyl)acrylic acid (cis-**40**)*

Z-selective olefination of 4-methoxy-2-methylbenzaldehyde (**96**) was performed using the procedure described above to provide (*Z*)-ethyl 3-(4-methoxy-2-methylphenyl)acrylate (*cis*-**152**) (86%, *Z*:*E* = 98:2, 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: 1.20 (t, J = 7.6 Hz, 3H, –CH_3), 2.28 (s, 3H, Ar–CH_3), 3.80 (s, 3H, –OCH_3), 4.12 (q, J = 7.6 Hz, 2H, –CH_2–), 5.93 (d, J = 12.2 Hz, 1H, =CH–CO_2–), 6.70–6.72 (m, 2H, Ar–H), 7.05 (d, J = 12.2 Hz, 1H, Ar–CH=), 7.42 (d, J = 8.4 Hz, 1H, Ar–H).

Hydrolysis of *cis*-**152** was performed using the procedure described above to afford *cis*-**40** (96%) as colorless needles: mp 145–146 °C (toluene); ^{1}H-NMR ($CDCl_3$, 400 MHz) δ: 2.29 (s, 3H, –CH_3), 3.80 (s, 3H, –OCH_3), 5.92 (d, J = 12.4 Hz, 1H, =CH–CO_2–), 6.69–6.72 (m, 2H, Ar–H), 7.16 (d, J = 12.4 Hz, 1H, Ar–CH=), 7.44 (d, J = 8.8 Hz, 1H, Ar–H); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ: 20.2 (q, –CH_3), 55.2 (q, –OCH_3), 110.7 (d, Ar), 115.3 (d, Ar), 118.2 (d, =CH–CO_2–), 126.5 (d, Ar), 131.1 (s, Ar), 138.3 (s, Ar), 144.9 (s, Ar), 160.1 (d, Ar–CH=), 171.7 (s, C=O); IR (KBr) 1695 cm^{-1}; ESI-MS m/z 191 (M^+–H); Anal. calcd for $C_{11}H_{12}O_3$: C, 68.74; H, 6.29. found: C, 68.78; H, 6.31.

*4.2.39. (Z)-3-(3,5-Dimethoxyphenyl)acrylic acid (cis-**41**)*

Z-selective olefination of 3,5-dimethoxybenzaldehyde (**97**) was performed using the procedure described above to provide (*Z*)-ethyl 3-(3,5-dimethoxyphenyl)acrylate (*cis*-**153**) (94%, *Z* only, determined by ^{1}H-NMR spectrum) (silica gel CC, EtOAc/hexane, 10:90) as a colorless oil: ^{1}H-NMR ($CDCl_3$, 400 MHz) δ: 1.25 (t, J = 6.8 Hz, 3H, –CH_3), 3.78 (s, 6H, –OCH_3), 4.17 (q, J = 6.8 Hz, 2H, –CH_2–), 5.94 (d, J = 12.8 Hz, 1H, =CH–CO_2–), 6.45 (s, 1H, Ar–H), 6.78 (s, 2H, Ar–H), 6.84 (d, J = 12.8 Hz, 1H, Ar–CH=).

Hydrolysis of *cis*-**153** was performed using the procedure described above to afford *cis*-**41** (97%) as colorless needles: mp 99–100 °C (toluene); ^{1}H-NMR ($CDCl_3$, 400 MHz) δ: 3.77 (s, 6H, –OCH_3), 5.95 (d, J = 12.6 Hz, 1H, =CH–CO_2–), 6.47 (s, 1H, Ar–H), 6.79 (s, 2H, Ar–H), 6.97 (d, J = 12.6 Hz, 1H, Ar–CH=); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ: 55.3 (q, –OCH_3), 102.0 (d, Ar), 107.8 (d, Ar), 119.0 (d,=CH–CO_2–), 136.0 (s, Ar), 145.5 (d, Ar–CH=), 160.3 (s, Ar), 171.4 (s, C=O); IR (KBr) 1705 cm^{-1}; ESI-MS m/z 207 (M^+–H); Anal. calcd for $C_{11}H_{12}O_4$: C, 63.45; H, 5.81. found: C, 63.22; H, 5.79.

*4.2.40. (Z)-3-(2,3,4-Trimethoxyphenyl)acrylic acid (cis-**42**)*

Z-selective olefination of 2,3,4-trimethoxybenzaldehyde (**98**) was performed using the procedure described above to provide (*Z*)-ethyl 3-(2,3,4-trimethoxyphenyl)acrylate (*cis*-**154**) (92%, *Z* only, determined by ^{1}H-NMR spectrum) (silica gel CC, EtOAc/hexane, 5:95) as a colorless oil: ^{1}H-NMR ($CDCl_3$, 270 MHz) δ: 1.25 (t, *J* = 7.0 Hz, 3H, $-CH_3$), 3.87 (s, 6H, $-OCH_3$), 3.88 (s, 3H, $-OCH_3$), 4.16 (q, *J* = 7.0 Hz, 2H, $-CH_2-$), 5.91 (d, *J* = 12.6 Hz, 1H, $=CH-CO_2-$), 6.66 (d, *J* = 8.8 Hz, 1H, Ar–H), 7.09 (d, *J* = 12.6 Hz, 1H, Ar–CH=), 7.51 (d, *J* = 8.8 Hz, 1H, Ar–H).

Hydrolysis of *cis*-**154** was performed using the procedure described above to afford *cis*-**42** (93%) as colorless needles: mp 96–98 °C (Toluene); ^{1}H-NMR ($CDCl_3$, 400 MHz) δ: 3.86 (s, 3H, $-OCH_3$), 3.88 (s, 6H, $-OCH_3$), 5.92 (d, *J* = 12.8 Hz, 1H, $=CH-CO_2-$), 6.65 (d, *J* = 8.8 Hz, 1H, Ar–H), 7.15 (d, *J* = 12.8 Hz, 1H, Ar–CH=), 7.51 (d, *J* = 8.8 Hz, 1H, Ar–H); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ: 56.0 (q, $-OCH_3$), 60.9 (q, $-OCH_3$), 61.4 (q, $-OCH_3$), 106.7 (d, Ar), 117.6 (d,$=CH-CO_2-$), 121.3 (s, Ar), 126.0 (d, Ar), 140.7 (d, Ar–CH=), 141.6 (s, Ar), 152.6 (s, Ar), 155.0 (s, Ar), 171.4 (s, C=O); IR (KBr) 1695 cm^{-1}; ESI-MS *m*/*z* 237 (M^+-H); Anal. calcd for $C_{12}H_{14}O_5$: C, 60.50; H, 5.92. found: C, 60.53; H, 5.92.

*4.2.41. (Z)-3-(2,4-Dichlorophenyl)acrylic acid (cis-**43**)*

Z-selective olefination of 2,4-dichlorobenzaldehyde (**99**) was performed using the procedure described above to provide (*Z*)-ethyl 3-(2,4-dichlorophenyl)acrylate (*cis*-**155**) (85%, *Z*:*E* = 98:2, determined by ^{1}H-NMR spectrum) (silica gel CC, EtOAc/hexane, 3:97) as a colorless oil: ^{1}H-NMR ($CDCl_3$, 270 MHz) δ: 1.21 (t, *J* = 7.0 Hz, 3H, $-CH_3$), 4.13 (q, *J* = 7.0 Hz, 2H, $-CH_2-$), 6.09 (d, *J* = 12.2 Hz, 1H, $=CH-CO_2-$), 7.05 (d, *J* = 12.2 Hz, 1H, Ar–CH=), 7.22 (dd, *J* = 2.2, 8.4 Hz, 1H, Ar–H), 7.41 (d, *J* = 2.2 Hz, 1H, Ar–H), 7.48 (d, *J* = 8.4 Hz, 1H, Ar–H).

The hydrolysis of *cis*-**155** was performed using the procedure described above to afford *cis*-**43** (91%) as colorless needles: mp 137–138 °C (Toluene); ^{1}H-NMR ($CDCl_3$, 400 MHz) δ: 6.09 (d, *J* = 12.0 Hz, 1H, $=CH-CO_2-$), 7.17 (d, *J* = 12.0 Hz, 1H, Ar–CH=), 7.21 (dd, *J* = 1.8, 8.3 Hz, 1H, Ar–H), 7.41 (d, *J* = 1.8 Hz, 1H, Ar–H), 7.46 (d, *J* = 8.3 Hz, 1H, Ar–H); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ: 121.3 (d, $=CH-CO_2-$), 126.6 (d, Ar), 129.0 (d, Ar), 131.8 (d, Ar), 131.9 (s, Ar), 134.0 (s, Ar), 135.4 (s, Ar), 141.9 (d, Ar–CH=), 169.9 (s, C=O); IR (KBr) 1710 cm^{-1}; ESI-MS *m*/*z* 215 (M^+-H); Anal. calcd for $C_9H_6Cl_6O_2$: C, 49.80; H, 2.79. found: C, 49.93; H, 2.80.

*4.2.42. (Z)-3-(3,5-Diiodophenyl)acrylic acid (cis-**44**) (Li et al., 1998; Zhou and Zhao, 2009)*

The methyl esterification of 4-amino-3,5-diiodobenzoic acid (**173**), deamination with isopentyl nitrite, DIBAL-H reduction, and PCC oxidation, using procedures according to the literature (Li et al., 1998), produced 3,5-diiodobenzaldehyde (**100**) (23% in 4 steps) as colorless needles: ^{1}H-NMR ($CDCl_3$, 270 MHz) δ: 8.15 (s, 2H, Ar–H), 8.30 (s, 1H, Ar–H), 9.83 (s, 1H, –CHO).

Z-selective olefination of **100** was performed using the procedure described above to provide (*Z*)-ethyl 3-(3,5-diiodophenyl)acrylate (*cis*-**156**) (88%, *Z*:*E* = 96:4, determined by ^{1}H-NMR spectrum) (silica gel CC, EtOAc/hexane, 3:97) as a colorless oil: ^{1}H-NMR ($CDCl_3$, 270 MHz) δ: 1.26 (t, *J* = 6.8 Hz, 3H, $-CH_3$), 4.18 (q, *J* = 6.8 Hz, 2H, $-CH_2-$), 6.00 (d, *J* = 12.8 Hz, 1H, $=CH-CO_2-$), 6.75 (d, *J* = 12.8 Hz, 1H, Ar–CH=), 7.82 (s, 2H, Ar–H), 8.00 (s, 1H, Ar–H).

Hydrolysis of *cis*-**156** was performed using the procedure described above to afford *cis*-**44** (95%) as colorless needles: mp 170–172 °C (CH_2Cl_2/hexane, 20:80); ^{1}H-NMR ($CDCl_3$, 400 MHz) δ: 6.02 (d, *J* = 12.6 Hz, 1H, $=CH-CO_2-$), 6.88 (d, *J* = 12.6 Hz, 1H, Ar–CH=), 7.84 (s, 2H, Ar–H), 8.01 (s, 1H, Ar–H); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ: 94.1 (s, Ar), 121.1 (d, $=CH-CO_2-$), 137.5 (d, Ar), 128.0 (s, Ar), 142.3 (d, Ar), 145.3 (d, Ar–CH=), 169.8 (s, C=O); IR (KBr) 1688 cm^{-1}; ESI-MS *m*/*z* 399 (M^+-H); Anal. calcd for $C_9H_6Cl_6O_2$: C, 27.03; H, 1.51. found: C, 27.28.; H, 1.49.

*4.2.43. (Z)-3-[3,5-Bis(trifluoromethyl)phenyl]acrylic acid (cis-**45**)*

Z-selective olefination of 3,5-bis(trifluoromethyl)benzaldehyde (**101**) was performed using the procedure described above to provide (*Z*)-ethyl 3-(3,5-bis(trifluoromethyl)phenyl)acrylate (*cis*-**157**) (85%, *Z*:*E* = 93:7, determined by ^{1}H-NMR spectrum) (silica gel CC, EtOAc/hexane, 5:95) as a colorless oil: ^{1}H-NMR ($CDCl_3$, 400 MHz) δ: 1.23 (t, *J* = 7.2 Hz, 3H, $-CH_3$), 4.18 (q, *J* = 7.2 Hz, 2H, $-CH_2-$), 6.15 (d, *J* = 12.8 Hz, 1H, $=CH-CO_2-$), 6.99 (d, *J* = 12.8 Hz, 1H, Ar–CH=), 7.83 (s, 1H, Ar–H), 7.99 (s, 2H, Ar–H).

Hydrolysis of *cis*-**157** was performed using the procedure described above to afford *cis*-**45** (93%) as colorless needles: mp 102–103 °C (CH_2Cl_2/hexane, 20:80); ^{1}H-NMR ($CDCl_3$, 400 MHz) δ: 6.18 (d, *J* = 12.4 Hz, 1H, $=CH-CO_2-$), 7.14 (d, *J* = 12.4 Hz, 1H, Ar–CH=), 7.85 (s, 1H, Ar–H), 8.00 (s, 2H, Ar–H); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ: 122.3 (d, $=CH-CO_2-$), 122.6 (d, as a quartet, Ar), 123.1 (s, as a quartet, $-CF_3$), 129.7 (d, Ar), 131.4 (s, as a quartet, Ar), 136.2 (s, Ar), 142.8 (d, Ar–CH=), 170.4 (s, C=O); IR (KBr) 1709 cm^{-1}; ESI-MS *m*/*z* 283 (M^+-H); Anal. calcd for $C_{11}H_6F_6O_2$: C, 46.50; H, 2.13. found: C, 45.59; H, 2.04.

*4.2.44. (Z)-3-(Naphthalen-1-yl)acrylic acid (cis-**46**)*

Z-selective olefination of 1-naphthaldehyde (**102**) was performed using the procedure described above to provide (*Z*)-ethyl 3-(naphthalen-1-yl)acrylate (*cis*-**158**) (93%, *Z*:*E* = 99:1, determined by ^{1}H-NMR spectrum) (silica gel CC, EtOAc/hexane, 10:90) as a colorless oil: ^{1}H-NMR ($CDCl_3$, 400 MHz) δ: 1.01 (t, *J* = 7.2 Hz, 3H, $-CH_3$), 4.00 (q, *J* = 7.2 Hz, 2H, $-CH_2-$), 6.24 (d, *J* = 12.2 Hz, 1H, $=CH-CO_2-$), 7.43–7.52 (m, 4H, Ar–H), 7.56 (d, *J* = 12.2 Hz, 1H, Ar–CH=), 7.82–7.91 (m, 3H, Ar–H). The spectroscopic data were in agreement with those in the literature (Oyamada and Kitamura, 2007).

Hydrolysis of *cis*-**158** was performed using the procedure described above to afford *cis*-**46** (91%) as colorless needles: mp 163–164 °C (Toluene); ^{1}H-NMR ($CDCl_3$, 400 MHz) δ: 6.20 (d, *J* = 12.6 Hz, 1H, $=CH-CO_2-$), 7.42 (t, *J* = 7.6 Hz, 1H, Ar–H), 7.47–7.52 (m, 3H, Ar–H), 7.65 (d, *J* = 12.6 Hz, 1H, Ar–CH=), 7.81–7.86 (m, 3H, Ar–H); The physical and spectral data were consistent with those reported in the literature (Oyamada and Kitamura, 2007).

4.2.45. (Z)-3-(Phenanthren-9-yl)acrylic acid (cis-47)

Z-selective olefination of phenanthrene-9-carbaldehyde (**103**) was performed using the procedure described above to provide (*Z*)-ethyl 3-(phenanthren-9-yl)acrylate (*cis*-**159**) (85%, *Z* only, determined by ^{1}H-NMR spectrum) (silica gel CC, EtOAc/hexane, 5:95) as a colorless oil: ^{1}H-NMR ($CDCl_3$, 270 MHz) δ: 0.95 (t, *J* = 7.3 Hz, 3H, $-CH_3$), 4.00 (q, *J* = 7.3 Hz, 2H, $-CH_2-$), 6.30 (d, *J* = 11.9 Hz, 1H, $=CH-CO_2-$), 7.54–7.68 (m, 5H, Ar–H and Ar–CH=), 7.76 (s, 1H, Ar–H), 7.86, 7.96 (d, *J* = 7.6 Hz, each 1H, Ar–H), 8.67, 8.73 (d, *J* = 7.9 Hz, each 1H, Ar–H).

Hydrolysis of *cis*-**159** was performed using the procedure described above to afford *cis*-**47** (77%) as colorless needles: mp 218–219 °C (toluene); ^{1}H-NMR (DMSO-d_6, 270 MHz) δ: 6.30 (d, *J* = 11.9 Hz, 1H, $=CH-CO_2-$), 7.58–7.76 (m, 6H, Ar–CH = and Ar–H), 7.96 (d, *J* = 7.6 Hz, 2H, Ar–H), 8.85 (m, 2H, Ar–H); ^{13}C-NMR (DMSO-d_6, 100 MHz) δ: 122.8 (d,$=CH-CO_2-$), 123.3 (d, Ar), 124.3 (d, Ar), 125.2 (d, Ar), 126.6 (d, Ar), 126.8 (d, Ar), 126.9 (d, Ar), 127.0 (d, Ar), 127.1 (d, Ar), 128.7 (d, Ar), 129.6 (s, Ar), 129.7 (s, Ar), 129.7 (s, Ar), 130.8 (s, Ar), 132.0 (s, Ar), 140.6 (d, Ar–CH=), 166.9 (s, C=O); IR (KBr) 1684 cm^{-1}; ESI-MS *m*/*z* 247 (M^+-H); Anal. calcd for $C_{17}H_{12}O_2$: C, 82.24; H, 4.87. found: C, 82.07; H, 4.93.

*4.2.46. (Z)-3-(Anthracen-9-yl)acrylic acid (cis-**48**)*

Z-selective olefination of anthracene-9-carbaldehyde (**104**) was performed using the procedure described above to provide (*Z*)-ethyl 3-(anthracen-9-yl)acrylate (*cis*-**160**) (45%, *Z* only, determined by ^{1}H-NMR spectrum) (silica gel CC, EtOAc/hexane, 3:97) as a colorless oil: ^{1}H-NMR ($CDCl_3$, 270 MHz) δ: 0.55 (t, *J* = 7.3 Hz, 3H, $-CH_3$), 3.71 (q, *J* = 7.3 Hz, 2H, $-CH_2-$), 6.61 (d, *J* = 12.2 Hz, 1H, $=CH-CO_2-$), 7.43–7.47 (m, 4H, Ar–H), 7.77 (d, *J* = 12.2 Hz, 1H, Ar–CH=), 7.99–8.06 (m, 4H, Ar–H), 8.42 (s, 1H, Ar–H).

Hydrolysis of *cis*-**160** was performed using the procedure described above to afford *cis*-**48** (85%) as yellow needles: mp 261–263 °C (Toluene); ^{1}H-NMR (DMSO-d_6, 270 MHz) δ: 6.61 (d, *J* = 12.2 Hz, 1H, $=CH-CO_2-$), 7.49–7.53 (m, 4H, Ar–H), 7.79 (d, *J* = 12.2 Hz, 1H, Ar–CH=), 7.99–8.02, 8.07–8.11 (m, each 2H, Ar–H), 8.55 (s, 1H, Ar–H); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ: 125.3 (d), 125.5 (d), 125.8 (d, Ar), 126.3 (d, Ar), 126.9 (d, Ar), 127.9 (s, Ar), 128.6 (d, Ar), 130.8 (s, Ar), 131.5 (s, Ar), 140.4 (d, Ar–CH=), 166.2 (s, C=O); IR (KBr) 1701 cm^{-1}; ESI-MS *m*/*z* 247 (M^+-H); Anal. calcd for $C_{17}H_{12}O_2$: C, 82.24; H, 4.87. found: C, 82.00; H, 4.91.

*4.2.47. (Z)-3-(Dibenzo[b,d]furan-4-yl)acrylic acid (cis-**49**)*

Z-selective olefination of dibenzo[*b*,*d*]furan-4-carbaldehyde (**105**) was performed using the procedure described above to provide (*Z*)-ethyl 3-(dibenzo[*b*,*d*]furan-4-yl)acrylate (*cis*-**161**) (60%, *Z*:*E* = 98:2, determined by ^{1}H-NMR spectrum) (silica gel CC, EtOAc/hexane, 5:95) as a colorless oil: ^{1}H-NMR ($CDCl_3$, 270 MHz) δ: 1.15 (t, *J* = 7.3 Hz, 3H, $-CH_3$), 4.14 (q, *J* = 7.3 Hz, 2H, $-CH_2-$), 6.20 (d, *J* = 12.7 Hz, 1H, $=CH-CO_2-$), 7.30–7.39 (m, 2H, Ar–H), 7.39 (d, *J* = 12.7 Hz, 1H, Ar–CH=), 7.46 (t, *J* = 7.6 Hz, 1H, Ar–H), 7.57, 7.82 (d, *J* = 7.6 Hz, each 1H, Ar–H), 7.92–7.96 (m, 2H, Ar–H).

Hydrolysis of *cis*-**161** was performed using the procedure described above to afford *cis*-**49** (82%) as colorless needles: mp 160–163 °C (toluene); ^{1}H-NMR ($CDCl_3$, 270 MHz) δ: 6.18 (d, *J* = 12.6 Hz, 1H, $=CH-CO_2-$), 7.29–7.36 (m, 2H, Ar–H), 7.45 (t, *J* = 7.6 Hz, 1H, Ar–H), 7.50 (d, *J* = 12.6 Hz, 1H, Ar–CH=), 7.56, 7.78 (d, *J* = 7.6 Hz, each 1H, Ar–H), 7.91–7.95 (m, 2H, Ar–H); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ: 111.7 (d, $=CH-CO_2-$), 120.1 (s, Ar), 121.2 (d, Ar), 121.5 (d, Ar), 122.7 (d, Ar), 123.3 (d, Ar), 123.5 (s, Ar), 123.5 (s, Ar), 123.9 (d, Ar), 127.7 (s, Ar), 127.7 (d, Ar), 133.8 (s, Ar), 153.2 (d, Ar–CH=), 155.3 (s, Ar), 167.3 (s, C=O); IR (KBr) 1699 cm^{-1}; ESI-MS *m*/*z* 237 (M^+-H); Anal. calcd for $C_{15}H_{10}O_3$: C, 75.62; H, 4.23. found: C, 75.62; H, 4.23.

*4.2.48. (Z)-3-(Naphthalen-2-yl)acrylic acid (cis-**50**)*

Z-selective olefination of 2-naphthaldehyde (**106**) was performed using the procedure described above to provide (*Z*)-ethyl 3-(naphthalen-2-yl)acrylate (*cis*-**162**) (83%, *Z*:*E* = 99:1, determined by ^{1}H-NMR spectrum) (silica gel CC, EtOAc/hexane, 3:97) as a colorless oil: ^{1}H-NMR ($CDCl_3$, 270 MHz) δ: 1.25 (t, *J* = 7.3 Hz, 3H, $-CH_3$), 4.20 (q, *J* = 7.3 Hz, 2H, $-CH_2-$), 6.02 (d, *J* = 12.7 Hz, 1H, $=CH-CO_2-$), 7.10 (d, *J* = 12.7 Hz, 1H, Ar–CH=), 7.46–7.50 (m, 2H, Ar–H), 7.73 (dd, *J* = 1.6, 8.6 Hz, 1H, Ar–H), 7.79–7.86 (m, 3H, Ar–H), 8.03 (s, 1H, Ar–H).

Hydrolysis of *cis*-**162** was performed using the procedure described above to afford *cis*-**50** (91%) as colorless needles: mp 135–137 °C (Toluene); ^{1}H-NMR ($CDCl_3$, 400 MHz) δ: 6.05 (d, *J* = 12.7 Hz, 1H, $=CH-CO_2-$), 7.23 (d, *J* = 12.7 Hz, 1H, Ar–CH=), 7.51–7.47 (m, 2H, Ar–H), 7.85–7.76 (m, 4H, Ar–H), 8.05 (s, 1H, Ar–H); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ: 118.7 (d,$=CH-CO_2-$), 126.3 (d, Ar), 127.0 (d, Ar), 127.0 (d, Ar), 127.5 (d, Ar), 127.6 (d, Ar), 128.6 (d, Ar), 130.4 (d, Ar), 131.9 (s, Ar), 132.8 (s, Ar), 133.6 (s, Ar), 145.9 (d, Ar–CH=), 171.7 (s, C=O); IR (KBr) 1697 cm^{-1}; ESI-MS *m*/*z* 197 (M^+-H); Anal. calcd for $C_{13}H_{10}O_2$: C, 78.77; H, 5.09. found: C, 78.69; H, 5.11.

*4.2.49. (Z)-3-(2,3-Dihydrobenzofuran-5-yl)acrylic acid (cis-**51**)*

Z-selective olefination of 2,3-dihydrobenzofuran-5-carbaldehyde (**107**) was performed using the procedure described above to provide (*Z*)-ethyl 3-(2,3-dihydrobenzofuran-5-yl)acrylate (*cis*-**163**) (78%, *Z*:*E* = 93:7, 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: 1.26 (t, *J* = 7.4 Hz, 3H, $-CH_3$), 3.22 (t, *J* = 8.8 Hz, 2H, dihydrofuran-H), 4.19 (q, *J* = 7.4 Hz, 2H, $-CH_2-$), 4.60 (t, *J* = 8.8 Hz, 2H, dihydrofuran-H), 5.78 (d, *J* = 12.8 Hz, 1H, $=CH-CO_2-$), 6.75 (d, *J* = 8.4 Hz, 1H, Ar–H), 6.82 (d, *J* = 12.8 Hz, 1H, Ar–CH=), 7.42 (d, *J* = 8.4 Hz, 1H, Ar–H), 7.79 (s, 1H, Ar–H).

Hydrolysis of *cis*-**163** was performed using the procedure described above to afford *cis*-**51** (98%) as colorless needles: mp 123–125 °C (CH_2Cl_2/hexane, 20:80); ^{1}H-NMR ($CDCl_3$, 400 MHz) δ: 3.22 (t, *J* = 8.8 Hz, 2H, dihydrofuran-H), 4.61 (t, *J* = 8.8 Hz, 2H, dihydrofuran-H), 5.81 (d, *J* = 12.8 Hz, 1H, $=CH-CO_2-$), 6.77 (d, *J* = 8.4 Hz, 1H, Ar–H), 6.94 (d, *J* = 12.8 Hz, 1H, Ar–CH=), 7.74 (d, *J* = 8.4 Hz, 1H, Ar–H), 7.75 (s, 1H, Ar–H); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ: 29.3 (t, dihydrofuran), 71.8 (t, dihydrofuran), 108.9 (d, Ar), 115.2 (d, $=CH-CO_2-$), 127.0 (s, Ar), 127.1 (s, Ar), 127.5 (d, Ar), 132.3 (d, Ar), 146.3 (d, Ar–CH=), 161.6 (s, Ar), 171.7 (s, C=O); IR (KBr) 1692 cm^{-1}; ESI-MS *m*/*z* 189 (M^+-H); Anal. calcd for $C_{11}H_{10}O_3$: C, 69.46; H, 5.30. found: C, 69.65; H, 5.26.

*4.2.50. (Z)-3-(Benzofuran-5-yl)acrylic acid (cis-**52**) (Saitoh et al., 2009)*

NBS (0.656 g, 3.69 mmol) and AIBN (8.10 mg, 49.2 μmol) were added to a solution of **107** (0.364 g, 2.46 mmol) in chlorobenzene (7.3 mL) at room temperature under an argon atmosphere. After stirring for 1 h at 80 °C, the mixture was cooled to room temperature and diluted with EtOAc. The organic layers were washed with saturated aqueous $NaHCO_3$ and brine, dried (Na_2SO_4), filtered, and concentrated *in vacuo*. The residue was purified by silica gel CC (EtOAc/hexane, 3:97) to afford benzofuran-5-carbaldehyde (**108**) (0.268 g, 1.84 mmol, 75%) as a colorless oil: ^{1}H-NMR ($CDCl_3$, 400 MHz) δ: 6.82 (d, *J* = 2.0 Hz, 1H, furan-H), 7.54 (d, *J* = 8.8 Hz, 1H, Ar–H), 7.65 (d, *J* = 2.0 Hz, 1H, furan-H), 7.79 (d, *J* = 8.8 Hz, 1H, Ar–H), 8.07 (s, 1H, Ar–H), 9.99 (s, 1H, –CHO); spectroscopic data were consistent with those reported in the literature (van Otterlo et al., 2005).

Z-selective olefination of **108** was performed using the procedure described above to provide (*Z*)-ethyl 3-(benzofuran-5-yl)acrylate (*cis*-**164**) (96%, *Z*:*E* = 97:3, 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: 1.25 (t, *J* = 7.6 Hz, 3H, $-CH_3$), 4.13 (q, *J* = 7.6 Hz, 2H, $-CH_2-$), 5.93 (d, *J* = 12.6 Hz, 1H, $=CH-CO_2-$), 6.76 (d, *J* = 2.0 Hz, 1H, furan-H), 7.01 (d, *J* = 12.6 Hz, 1H, Ar–CH=), 7.46 (d, *J* = 8.8 Hz, 1H, Ar–H), 7.56 (d, *J* = 8.8 Hz, 1H, Ar–H), 7.60 (d, *J* = 2.0 Hz, 1H, furan-H), 7.99 (s, 1H, Ar–H).

Hydrolysis of *cis*-**164** was performed using the procedure described above to afford *cis*-**52** (96%) as colorless needles: mp 82–83 °C (CH_2Cl_2/hexane, 10:90); ^{1}H-NMR ($CDCl_3$, 400 MHz) δ: 5.97 (d, *J* = 12.8 Hz, 1H, $=CH-CO_2-$), 6.79 (d, *J* = 2.0 Hz, 1H, furan-H), 7.16 (d, *J* = 12.8 Hz, 1H, Ar–CH=), 7.48, 7.59 (d, *J* = 8.6 Hz, each 1H, Ar–H), 7.63 (d, *J* = 2.0 Hz, 1H, furan-H), 7.98 (s, 1H, Ar–H); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ: 106.9 (d, furan), 111.0 (d, Ar), 117.5 (d,$=CH-CO_2-$), 123.5 (d, Ar), 127.0 (d, furan), 127.3 (s, Ar), 129.2 (s, Ar), 145.6 (d, Ar–CH=), 146.3 (d, Ar), 155.3 (s, Ar), 171.4 (s, C=O); IR (KBr) 1715 cm^{-1}; ESI-MS *m*/*z* 187 (M^+-H); Anal. calcd for $C_{11}H_8O_3$: C, 70.21; H, 4.29. found: C, 69.57; H, 4.19.

*4.2.51. (Z)-3-(Benzofuran-6-yl)acrylic acid (cis-**53**) (Tasker et al., 1997)*

Potassium carbonate (8.82 g, 63.8 mmol) was added to a solution of 3-bromophenol (**174**) (10.0 g, 58.0 mmol) and bromoacetaldehyde diethyl acetal (11.1 g, 56.1 mmol) in DMSO (58 mL) at

room temperature under Ar. After the mixture was stirred for 12 h at 160 °C, H_2O and EtOAc were added to the reaction. The mixture was extracted with EtOAc, washed with brine, dried ($MgSO_4$), filtered and concentrated *in vacuo*. The crude product was purified by silica gel CC (EtOAc/hexane, 5:95) to give 1-bromo-3-(2,2-diethoxyethoxy)benzene (**175**) (14.4 g, 50.1 mmol, 86%) as a colorless oil: ^{1}H-NMR ($CDCl_3$, 400 MHz) δ: 1.25 (t, *J* = 6.8 Hz, 6H, –CH_3), 3.59–3.67, 3.72–3.80 (m, each 2H, –OCH_2–), 3.98 (d, *J* = 5.0 Hz, 2H, ArO–CH_2–), 4.82 (t, *J* = 5.0 Hz, –*CH*–$(OEt)_2$), 6.85–6.87 (m, 1H, Ar–H), 7.07–7.15 (m, 3H, Ar–H).

Polyphosphoric acid (PPA) (0.743 g, 6.83 mmol) was added to a solution of **175** (0.656 g, 2.28 mmol) in toluene (4.6 mL) at room temperature under Ar. The mixture was headed until reflux began, this being maintained for 4 h, then cooled to room temperature, quenched with cooled H_2O and extracted with EtOAc. The organic layers were washed with brine, dried ($MgSO_4$), filtered and concentrated *in vacuo*. The crude product was purified by silica gel CC (EtOAc/hexane, 2:98) to give 6-bromobenzofuran (**176**) (major, 0.206 g, 1.05 mmol, 46%) and 4-bromobenzofuran (**177**) (minor, 0.183 g, 0.935 mmol, 41%) as colorless oils: **176**: ^{1}H-NMR ($CDCl_3$, 400 MHz) δ: ^{1}H-NMR ($CDCl_3$, 400 MHz) δ: 6.75 (d, *J* = 1.6 Hz, 1H, furan-H), 7.36 (dd, *J* = 1.2, 8.4 Hz, 1H, Ar–H), 7.46 (d, *J* = 8.4 Hz, 1H, Ar–H), 7.60 (d, *J* = 1.6 Hz, 1H, furan-H), 7.69 (s, 1H, Ar–H); **177**: ^{1}H-NMR ($CDCl_3$, 400 MHz) δ: 6.82 (d, *J* = 2.4 Hz, 1H, furan-H), 7.17 (dd, *J* = 7.6, 8.4 Hz, Ar–H), 7.40 (d, *J* = 7.6 Hz, 1H, Ar–H), 7.45 (d, *J* = 8.4 Hz, 1H, Ar–H), 7.66 (d, *J* = 2.4 Hz, 1H, furan-H).^{t}BuLi (0.652 mL, 1.59 M in pentane, 1.00 mmol) was added to a solution of **176** (99.0 mg, 0.502 mmol) in Et_2O (2.5 mL) at −78 °C under Ar. After 5 min of stirring, DMF (0.117 mL, 1.51 mmol) was added to the reaction. The mixture was warmed to 0 °C and then stirred for 30 min. The mixture was diluted with Et_2O, washed with H_2O, 1 M HCl and brine, dried over Na_2SO_4, filtered and concentrated *in vacuo*. The crude product was purified by silica gel CC (EtOAc/hexane, 5:95) to give benzofuran-6-carbaldehyde (**109**) (51.0 mg, 0.271 mmol, 54%) as a colorless oil: ^{1}H-NMR ($CDCl_3$, 400 MHz) δ: 6.87 (d, *J* = 2.2 Hz, 1H, furan-H), 7.73 (d, *J* = 7.6 Hz, 1H, Ar–H), 7.80 (dd, *J* = 1.6, 7.6 Hz, 1H, Ar–H), 7.83 (d, *J* = 2.2 Hz, 1H, furan-H), 8.02 (s, 1H, Ar–H), 10.08 (s, 1H, –CHO); spectroscopic data were consistent with those reported in the literature (Coleman et al., 2004).

Z-selective olefination of **109** was performed using the procedure described above to provide (*Z*)-ethyl 3-(benzofuran-6-yl)acrylate (*cis*-**165**) (82%, *Z*:*E* = 94:6, 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: 1.27 (t, *J* = 7.2 Hz, 3H, –CH_3), 4.21 (q, *J* = 7.2 Hz, 2H, –CH_2–), 5.95 (d, *J* = 12.8 Hz, 1H, =CH–CO_2–), 6.76 (d, *J* = 2.0 Hz, 1H, furan-H), 7.02 (d, *J* = 12.8 Hz, 1H, Ar–CH=), 7.45 (d, *J* = 8.0 Hz, 1H, Ar–H), 7.55 (d, *J* = 8.0 Hz, 1H, Ar–H), 7.66 (d, *J* = 2.0 Hz, 1H, furan-H), 7.96 (s, 1H, Ar–H).

Hydrolysis of *cis*-**165** was performed using the procedure described above to afford *cis*-**53** (99%) as colorless needles: mp 98–100 °C (Et_2O/hexane, 10:90); ^{1}H-NMR ($CDCl_3$, 400 MHz) δ: 5.98 (d, *J* = 12.8 Hz, 1H, =CH–CO_2–), 6.77 (d, *J* = 2.0 Hz, 1H, furan-H), 7.15 (d, *J* = 12.8 Hz, 1H, Ar-CH=), 7.47 (d, *J* = 8.4 Hz, 1H, Ar–H), 7.56 (d, *J* = 8.4 Hz, 1H, Ar–H), 7.67 (d, *J* = 2.0 Hz, 1H, furan–H), 7.98 (s, 1H, Ar–H); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ: 106.7 (d, furan), 113.2 (d, Ar), 117.7 (d,=*C*H–CO_2–), 120.5 (d, Ar), 125.6 (d, Ar), 128.8 (s, Ar), 130.7 (s, Ar), 146.0 (d), 146.7 (d), 170.5 (s, C=O); IR (KBr) 1688 cm^{-1}; ESI-MS *m*/*z* 211 ($[M + Na]^+$); Anal. calcd for $C_{11}H_3O_3$: C, 70.21; H, 4.29. found: C, 69.98; H, 4.23.

*4.2.52. (Z)-3-(Benzo[b]thiophen-5-yl)acrylic acid (cis-**54**)*

Z-selective olefination of benzo[*b*]thiophene-5-carbaldehyde (**110**) was performed using the procedure described above to provide (*Z*)-ethyl 3-(benzo[*b*]thiophen-5-yl)acrylate (*cis*-**166**) (89%, *Z*:*E* = 94:6, determined by ^{1}H-NMR spectrum) (silica gel CC, EtOAc/hexane, 5:95) as a colorless oil: ^{1}H-NMR ($CDCl_3$, 400 MHz) δ: 1.24 (t, *J* = 6.8 Hz, 3H, –CH_3), 4.19 (q, *J* = 6.8 Hz, 2H, –CH_2–), 5.97 (d, *J* = 12.6 Hz, 1H,=CH–CO_2–), 7.03 (d, *J* = 12.6 Hz, 1H, Ar–CH=), 7.32 (d, *J* = 5.8 Hz, 1H, thiophene-H), 7.41 (d, *J* = 5.8 Hz, 1H, thiophene-H), 7.59, 7.82 (d, *J* = 8.6 Hz, each 1H, Ar–H), 8.11 (s, 1H, Ar–H).

Hydrolysis of *cis*-**166** was performed using the procedure described above to afford *cis*-**54** (96%) as colorless needles: mp 125–126 °C (CH_2Cl_2/hexane, 10:90); ^{1}H-NMR ($CDCl_3$, 400 MHz) δ: 5.99 (d, *J* = 12.8 Hz, 1H,=CH–CO_2–), 7.18 (d, *J* = 12.8 Hz, 1H, Ar–CH=), 7.33, 7.45 (d, *J* = 5.4 Hz, each 1H, thiophene–H), 7.62, 7.84 (d, *J* = 8.4 Hz, each 1H, Ar–H), 8.09 (s, 1H, Ar–H); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ: 118.1 (d,=*C*H–CO_2–), 122.0 (d), 124.2 (d), 125.6 (d), 126.0 (d), 127.1 (d), 130.6 (s, Ar), 139.4 (s, Ar), 140.8 (s, Ar), 146.2 (d, Ar–CH=), 171.1 (s, C=O); IR (KBr) 1684 cm^{-1}; ESI-MS *m*/*z* 203 (M^+–H); Anal. calcd for $C_{11}H_8O_2S$: C, 64.69; H, 3.95. found: C, 64.48; H, 3.95.

*4.2.53. (Z)-3-(Pyridin-2-yl)acrylic acid (cis-**55**)*

Z-selective olefination of picolinaldehyde (**111**) was performed using the procedure described above to provide (*Z*)-ethyl 3-(pyridin-2-yl)acrylate (*cis*-**167**) (78%, *Z*:*E* = 92:8, determined by ^{1}H-NMR spectrum) (silica gel CC, EtOAc/hexane, 10:90) as a colorless oil: ^{1}H-NMR ($CDCl_3$, 400 MHz) δ: 1.26 (t, *J* = 7.2 Hz, 3H, –CH_3), 4.21 (q, *J* = 7.2 Hz, 2H, –CH_2–), 6.14 (d, *J* = 12.8 Hz, 1H, =CH–CO_2–), 6.95 (d, *J* = 12.8 Hz, 1H, Ar–CH=), 7.22 (m, 1H, Py–H), 7.64–7.70 (m, 2H, Py–H), 8.59 (d, *J* = 4.8 Hz, 1H, Py–H); spectroscopic data were consistent with those reported in the literature (Tsukada et al., 1998; Beveridge and Arndtsen, 2010).

Hydrolysis of *cis*-**167** was performed using the procedure described above to afford *cis*-**55** (89%) as colorless needles: mp 107–108 °C (Toluene); ^{1}H-NMR ($CDCl_3$, 400 MHz) δ: 6.32 (d, *J* = 13.6 Hz, 1H, =CH–CO_2–), 6.86 (d, *J* = 13.6 Hz, 1H, Py–CH=), 7.53–7.48 (m, 2H, Py–H), 8.61 (dt, *J* = 1.6, 7.6 Hz, 1H, Py-H), 8.61 (d, *J* = 4.8 Hz, 1H, Py–H); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ: 124.7 (d,=*C*H–CO_2–), 127.4 (d, Py), 130.1 (d, Py), 135.1 (d, Py), 139.9 (d, Py), 146.0 (d, Py–CH=), 151.3 (s, Py), 166.7 (s, C=O); IR (KBr) 1695 cm^{-1}; ESI-MS *m*/*z* 148 (M^+–H); Anal. calcd for $C_8H_7NO_2$: C, 64.42; H, 4.73; N, 9.39. found: C, 64.42; H, 4.65; N, 9.44.

*4.2.54. (Z)-3-(6-Methoxypyridin-2-yl)acrylic acid (cis-**56**)*

Z-selective olefination of 6-methoxypicolinaldehyde (**112**) was performed using the procedure described above to provide (*Z*)-ethyl 3-(6-methoxypyridin-2-yl)acrylate (*cis*-**168**) (83%, *Z*:*E* = 99:1, 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: 1.27 (t, *J* = 7.2 Hz, 3H, –CH_3), 3.89 (s, 3H, –OCH_3), 4.24 (q, *J* = 7.2 Hz, 2H, –CH_2–), 6.35 (d, *J* = 12.8 Hz, 1H, =CH-CO_2–), 6.66 (d, *J* = 8.4 Hz, 1H, Py–H), 6.72 (d, *J* = 12.8 Hz, 1H, Ar–CH=), 7.05 (d, *J* = 7.2 Hz, 1H, Py–H), 7.54 (t, *J* = 7.2, 8.4 Hz, 1H, Py–H).

Hydrolysis of *cis*-**168** was performed using the procedure described above to afford *cis*-**56** (91%) as colorless needles: mp 107–108 °C (toluene); ^{1}H-NMR ($CDCl_3$, 400 MHz) δ: 4.06 (s, 3H, –OCH_3) 6.20 (d, *J* = 13.4 Hz, 1H, =CH–CO_2–), 6.76 (d, *J* = 13.4 Hz, 1H, Py–CH=), 6.91 (d, *J* = 8.8 Hz, 1H, Py–H), 7.04 (d, *J* = 7.6 Hz, 1H, Py–H), 7.78 (dd, *J* = 7.6, 8.8 Hz, 1H, Py–H); ^{13}C-NMR (CD_3OD, 100 MHz) δ: 55.9 (q, –OCH_3), 114.1 (d, Py), 122.1 (d, =*C*H–CO_2–), 126.6 (d, Py), 138.1 (d, Py), 143.5 (d, Py–CH=), 149.8 (s, Py), 164.2 (s, Py), 170.0 (s, C=O); IR (KBr) 1701 cm^{-1}; ESI-MS *m*/*z* 178 (M^+–H); Anal. calcd for $C_9H_9NO_3$: C, 60.33; H, 5.06; N, 7.82. found: C, 58.50; H, 5.06; N, 7.82.

*4.2.55. (Z)-3-(6-Methylpyridin-2-yl)acrylic acid (cis-**57**)*

Z-selective olefination of 6-methylpicolinaldehyde (**113**) was performed using the procedure described above to provide (*Z*)-

ethyl 3-(6-methylpyridin-2-yl)acrylate (*cis*-**169**) (83%, *Z* only, determined by ^{1}H-NMR spectrum) (silica gel CC, EtOAc/hexane, 15:85) as a colorless oil: ^{1}H-NMR ($CDCl_3$, 400 MHz) δ: 1.26 (t, *J* = 7.2 Hz, 3H, –CH_3), 2.53 (s, 3H, Py–CH_3), 4.22 (q, *J* = 7.2 Hz, 2H, –CH_2–), 6.11 (d, *J* = 12.8 Hz, 1H, =CH–CO_2–), 6.90 (d, *J* = 12.8 Hz, 1H, Ar–CH=), 7.07, 7.40 (d, *J* = 7.6 Hz, each 1H, Py–H), 7.56 (t, *J* = 7.6 Hz, 1H, Py–H).

Hydrolysis of *cis*-**169** was performed using the procedure described above to afford *cis*-**57** (85%) as colorless needles: mp 131–132 °C (EtOAc); ^{1}H-NMR (CD_3OD, 270 MHz) δ: 2.66 (s, 3H, –CH_3), 6.31 (d, *J* = 13.0 Hz, 1H, =CH–CO_2–), 6.77 (d, *J* = 13.0 Hz, 1H, Py–CH=), 7.32–7.28 (m, 2H, Py–H), 7.85 (t, *J* = 7.8 Hz, 1H, Py–H); ^{13}C-NMR (CD_3OD, 100 MHz) δ: 21.7 (q, –CH_3), 126.5 (d, =CH–CO_2–), 127.1 (d, Py), 130.8 (d, Py), 136.6 (d, Py), 142.7 (d, Py–CH=), 150.9 (s, Py), 156.9 (s, Py), 170.5 (s, C=O); IR (KBr) 1695 cm^{-1}; ESI-MS *m*/*z* 162 (M^+–H); Anal. calcd for $C_9H_9NO_2$: C, 66.25; H, 5.56; N, 8.58. found: C, 66.28; H, 5.58; N, 8.58.

4.2.56. (*Z*)-3-(Pyridin-3-yl)acrylic acid (*cis*-**58**)

Z-selective olefination of nicotinaldehyde (**114**) was performed using the procedure described above to provide (*Z*)-ethyl 3-(pyridin-3-yl)acrylate (*cis*-**170**) (93%, *Z*:*E* = 96:4, determined by ^{1}H-NMR spectrum) (silica gel CC, EtOAc/hexane, 15:85) as a colorless oil: ^{1}H-NMR ($CDCl_3$, 270 MHz) δ: 1.25 (t, *J* = 7.3 Hz, 3H, –CH_3), 4.18 (q, *J* = 7.3 Hz, 2H, –CH_2–), 6.08 (d, *J* = 12.6 Hz, 1H, =CH–CO_2–), 6.93 (d, *J* = 12.6 Hz, 1H, Ar–CH=), 7.31 (m, 1H, Py–H), 8.08 (d, *J* = 7.8 Hz, 1H, Py–H), 8.54 (d, *J* = 4.6 Hz, 1H, Py–H), 8.65 (s, 1H, Py–H).

Hydrolysis of *cis*-**170** was performed using the procedure described above to afford *cis*-**58** (53%) as colorless needles: mp 154–156 °C (toluene); ^{1}H-NMR (CD_3OD, 400 MHz) δ: 6.14 (d, *J* = 12.8 Hz, 1H, =CH–CO_2–), 7.01 (d, *J* = 12.8 Hz, 1H, Py–CH=), 7.43 (dd, *J* = 4.8, 8.2 Hz, 1H, Py–H), 8.11 (dd, *J* = 1.6, 8.2 Hz, 1H, Py–H), 8.45 (dd, *J* = 1.6, 4.8 Hz 1H, Py–H), 8.68 (d, *J* = 1.6 Hz, 1H, Py–H); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ: 124.4 (d, =CH–CO_2–), 124.7 (d, Py), 133.3 (s, Py), 139.0 (d, Py), 139.3 (d, Py), 149.3 (d, Py–CH=), 150.6 (d, Py), 169.0 (s, C=O); IR (KBr) 1706 cm^{-1}; ESI-MS *m*/*z* 148 (M^+–H); Anal. calcd for $C_8H_7NO_2$: C, 64.42; H, 4.73; N, 9.39. found: C, 64.32; H, 4.81; N, 9.32.

4.3. Measurement of phytotoxic activities against lettuce root growth

Phytotoxic activity was measured according to the method described by Hiradate et al. (2004). Filter paper was placed in a glass petri dish. The test compound was dissolved in H_2O at various concentrations and a portion of each test solution was added on to the filter paper in the petri dish for each treatment. Fifteen pre-germinated (25 °C in the dark) seedlings of lettuce (*Lactuca sativa* cv. Great Lakes 366) were used as a replicate for each treatment. 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 13.0 J.

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