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SmI_2-mediated elimination reaction of Baylis–Hillman adducts controlled by temperature: a facile synthesis of trisubstituted alkenes and 1,5-hexadiene derivatives with *E*-stereoselectivity

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Abstract—Promoted by samarium diiodide, the Baylis–Hillman adducts undergo hydroxyl elimination to form trisubstituted alkenes with total (*E*)-stereoselectivity in good to excellent yields. The flexibility of this method also opens a new route to synthesize a class of 1,5-hexadiene derivatives by temperature tuning.

1. Introduction

As a class of important building block in natural products, the stereo-defined trisubstituted alkene moiety manifest their significance in the syntheses of terpenoids and insect pheromones.[1] Moreover, they are present in various biologically active molecules.[2,3] Consequently, a variety of methodologies for the syntheses of functionalized alkenes with stereo-defined trisubstituted double bonds have been well documented.[4]

The Baylis–Hillman reaction is one of the powerful carbon–carbon bond-forming method in organic synthesis.[5] The Baylis–Hillman reaction provides molecules possessing hydroxy, alkenyl, and electron-withdrawing groups in close proximity, which makes it valuable in a number of stereoselective processes.[6] Among these reactions, a few reagents such as $LiBEt_3H$ and $Pd(OAc)_2$ have been investigated towards the reduction of Baylis–Hillman adducts.[7] Though some reagents can provide good stereoselectivity, however, these reagents are generally expensive and not readily accessible. In addition, in most of the reactions Baylis–Hillman adducts must be acetylated before used as an additional step, which lower their attractiveness. Up to now, using Baylis–Hillman adducts directly in this reduction process only one report has been depicted with Low-Valent Titanium.[8] Nevertheless, the latter was also unsatisfactory in view of the low yields and the purity of products. Thus, to develop an alternative method for the reduction of Baylis–Hillman adducts with stereo-defined double bonds is still desirable.

As a powerful, versatile and ether-soluble one-electron transfer agent, SmI_2 has played an ever-increasing role in organic synthesis.[9] Among these methods, SmI_2 has proved to be a powerful tool to synthesize highly stereoselective alkenes and has been extensively developed.[10] Accordingly, we envision the possibility to synthesize stereo-defined alkenes from Baylis–Hillman adducts as direct elimination of hydroxy group promoted by SmI_2.[11] To the best of our knowledge, SmI_2-mediated reductive elimination process of Baylis–Hillman adducts has not been reported so far.

2. Results and discussion

Our first attempt was carried out by using Baylis–Hillman adducts **1d** as model substrate. When **1d** was treated with 2.2 equiv. SmI_2 in a solution of THF at room temperature, unprecedented result was observed (Table 1). Apart from the expected trisubstituted alkene **3d** with total stereoselectivity, to our surprise, we also obtained another white solid which was identified as substituted 1,5-hexadiene **2d** (Scheme 1). The *E*-configuration of **3d** was assigned on the basis of the chemical shift value of the olefinic proton in ^1H NMR spectra by comparison with reported ones.[8,12] The

Keywords: Baylis–Hillman adducts; Reduction; Samarium diiodide; Elimination; Self-coupling; Trisubstituted alkene; 1,5-Hexadiene derivatives; (*E*)-stereoselectivity.
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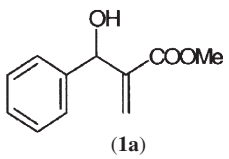
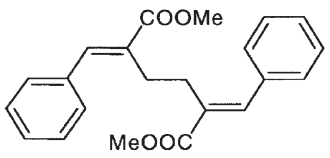
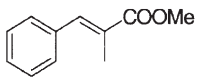
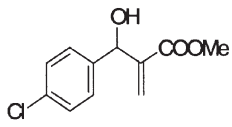
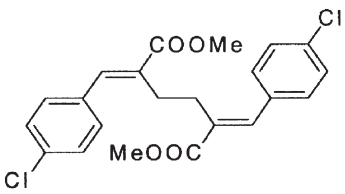
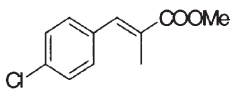
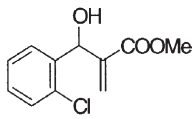
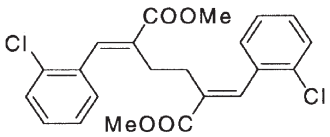
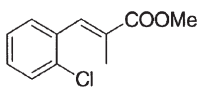
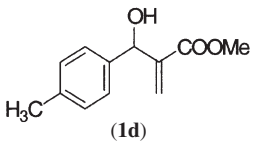
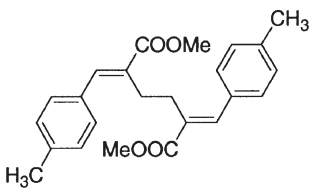
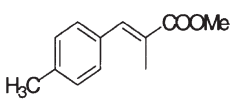
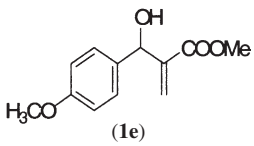
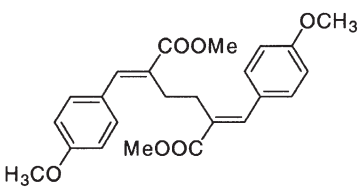
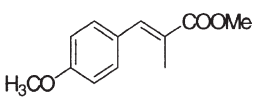
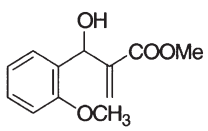
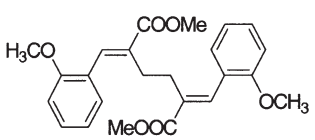
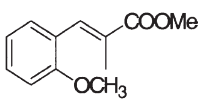
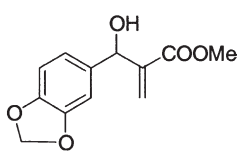
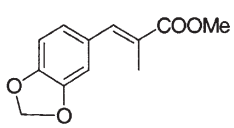
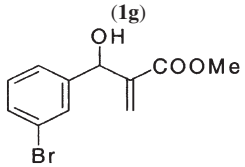
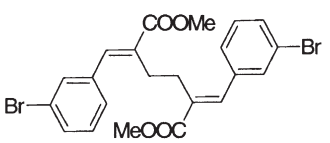
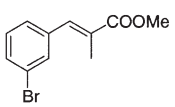
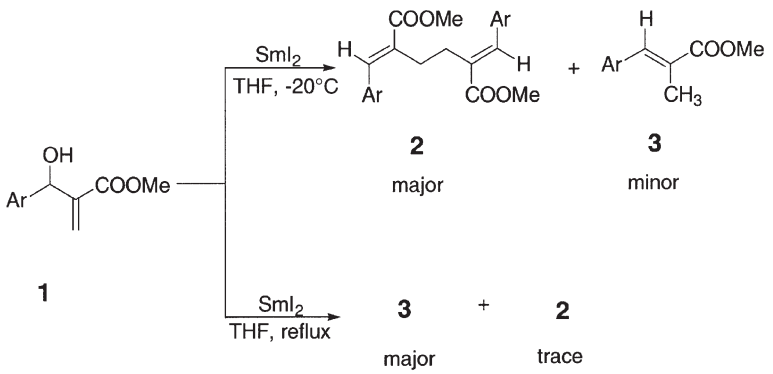
Table 1. SmI_2-mediated reductive elimination of Baylis–Hillman adducts[a]

Entry	Substrate **1**	Temp (°C)	Time (min)	Product **2** yield (%)[b]	Product **3** yield (%)[b]
1	 (**1a**)	−20	90		
				(**2a**) 82%	(**3a**) 17%
2		Reflux	5	(**2a**) 10%	(**3a**) 80%
3	 (**1b**)	−20	90		
				(**2b**) 92%	(**3b**) 7%
4		Reflux	5	(**2b**) 11%	(**3b**) 83%
5	 (**1c**)	−20	90		
				(**2c**) 50%	(**3c**) 43%
6		Reflux	8	—[c]	(**3c**) 92%
7	 (**1d**)	−20	90		
				(**2d**) 88%	(**3d**) 11%
8		25	20	(**2d**) 40%	(**3d**) 57%
9		Reflux	10	—[c]	(**3d**) 92%
10	 (**1e**)	−20	90		
				(**2e**) 90%	(**3e**) 8%
11		Reflux	10	—[c]	(**3e**) 94%
12	 (**1f**)	−20	90		
				(**2f**) 65%	(**3f**) 30%
13		Reflux	10	(**2f**) 50%	(**3f**) 47%
14	 (**1g**)	Reflux	5	—[c]	 (**3g**) 96%
15		−20	90		
				(**2h**) 40%	(**3h**) 50%
16	(**1h**)	Reflux	10	—[c]	(**3h**) 90%

[a] All reactions were carried out with 2.2 equiv. SmI_2 in a solution of THF.
[b] All new products were characterized by ^1H NMR, ^{13}C NMR, MS, IR and element analysis.
[c] In such case, product **2** was not isolated.



Scheme 1.

corresponding 1,5-diene **2d** was also obtained simultaneously with total *E*-stereoselectivity.[13]

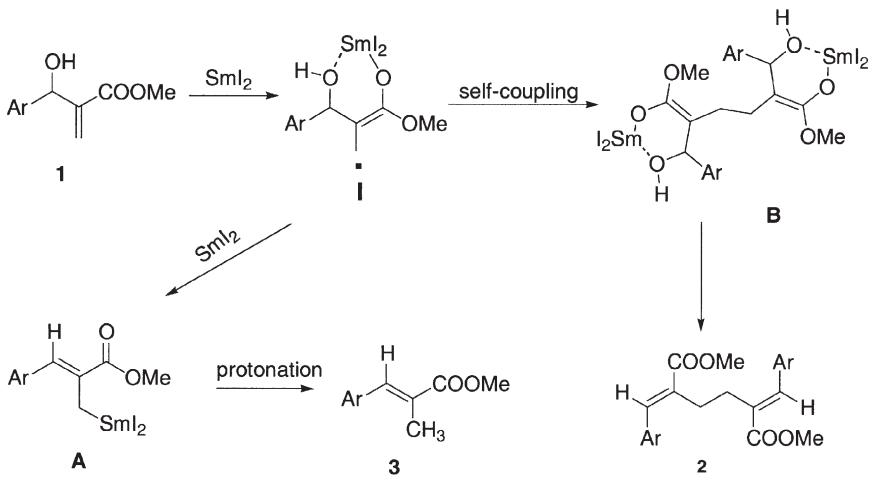
Accordingly, with a view to further investigate the reaction, the elimination processes with substrate **1d** were carried out under different temperatures and the representative results were listed in Table 1. When substrate **1d** was treated with a solution of SmI_2 at −20 °C, 1,5-diene **2d** was produced as major product in high yield (entry 7). Raising the reaction temperature resulted in the decreasing yield of **2d** and increasing yield of **3d**. Finally, when the reaction was conducted under reflux, product **3d** was afforded as the only product and no 1,5-diene **2d** was isolated (entry 9).

Encouraged by these experimental results, a variety of Baylis–Hillman adducts including electron-withdrawing and electron-donating substituents were tested in this reaction to establish the generality of the elimination reaction and the corresponding results were listed in Table 1.

In the cases of **3a**, **3b**, **3e** and **3f** comparison with the ^1H NMR values in the literature has also been carried out.[14] The following experimental features are particularly noteworthy: (1) The elimination provides a novel and efficient route to synthesize a new class of 1,5-hexadiene derivatives **2** which are difficult to synthesize by other methods. Generally speaking, 1,5-diene species are valuable synthetic intermediates and not readily available.[15] (2) In all cases, the desired trisubstituted alkenes **3** are obtained in good to excellent yield under reflux with total *E*-stereoselectivity. Nevertheless, in the case of **1f**, only 47% of **3f** is yielded even reaction proceeds under reflux (entry 13). This result is somewhat intriguing. (3) The present reaction is temperature controlled to a great extent, which is especially true when *para*-substituted substrates **1** are used. In a sense, lower temperature favors the generation of 1,5-dienes **2**, while higher temperature accelerates the conversion toward the trisubstituted alkenes **3**. By temperature changing we can obtain product **2** or **3** selectively. (4) When it comes to *ortho*- and *meta*- substituted substrates, the yields of 1,5-dienes **2** are relatively lower. We have also tried these substrates below −20 °C with prolonged reaction time, however, the yields of 1,5-dienes **2** are still unsatisfactory. This may be partly due to the steric hindrance during the radical coupling process.

The observed results and the *E*-stereochemistry in this reaction may be explained with a chelation-control model.[16] As shown in Scheme 2, chelation of the oxophilic Sm^{III} center with the oxygen atom of the hydroxyl group results in a six-membered ring intermediate **I**, which increases the capability of the hydroxyl group as a leaving group.

When this elimination reaction proceeded under higher temperature, the hydroxyl group was rapidly eliminated from intermediate **I** and then reacted with another mole of



Scheme 2.

SmI_2 to form **A**. Thus, protonation of **A** stereoselectively yielded product **3** with *E*-configuration. On the other hand, when this elimination reaction was conducted under lower temperature, the leaving of hydroxyl group from intermediate **I** became much slower. Under this condition, the chance of radical intermediate **I** for self-coupling was increasing. After elimination and protonation, the intermediate **B** gave product **2** with high *E*-stereoselectivity.

3. Conclusion

In conclusion, the SmI_2-mediated elimination reaction provides a unique and valuable route to synthesize a new class of 1,5-hexadiene derivatives **2** from easily accessible Baylis–Hillman adducts. Moreover, the methodology herein described also can serve as an efficient and alternative strategy to synthesize trisubstituted alkenes **3** in good to excellent yields. It is also worth mentioning that the reaction is highly *E*-stereoselective and temperature-dependent, which adds its attractiveness.

4. Experimental

4.1. General

Tetrahydrofuran was distilled from sodium-benzophenone immediately prior to use. All the reactions in this paper were performed under a nitrogen atmosphere. All ^{1}H NMR spectra were measured in $CDCl_3$ and recorded on Brucker AC-400 (400 MHz) spectrometer with TMS as the internal standard. ^{13}C NMR spectra were measured in $CDCl_3$ and recorded on Brucker AC-100 spectrometer with TMS as the internal standard. Chemical shifts (δ) are expressed in ppm and coupling constants *J* are given in Hz. IR spectra were taken as KBr discs or thin films with a Bruck vector 22 spectrometer. EIMS were measured with a HP5989B mass spectrometer. Melting points are uncorrected. Elemental analyses were performed on an EA-1110 instrument. Metallic samarium and all solvents were purchased from commercial sources and were used without further purification. The starting materials Baylis–Hillman adducts **1** were prepared according to the literature.[17]

4.2. General procedure for the preparation of 1,5-hexadiene (2a–2f, 2h)

A solution of Baylis–Hillman adduct (1 mmol) in dry THF (3 mL) was added to the solution of SmI_2 (2.2 mmol) in THF (20 mL) at −20 °C under a nitrogen atmosphere. After being stirred for about 90 min at −20 °C (Table 1), the deep blue color of the solution changed to yellow slowly. Then, the reaction mixture was quenched with 0.1 M hydrochloric acid (5 mL) and extracted with ether (3×20 mL). The organic phase was successively washed with brine (15 mL), water (20 mL) and dried over anhydrous Na_2SO_4. The solvent was removed under reduced pressure to give the crude products, which were purified by preparative TLC using ethyl acetate and cyclohexane (1:7) as eluent.

4.2.1. 2,5-Dibenzylidene-hexanedioic acid dimethyl ester (2a). White solid, mp: 120–122 °C, ^{1}H NMR: δ 7.78 (2H, s), 7.51–7.33 (10H, m), 3.83 (6H, s), 2.86 (4H, s); ^{13}C NMR: δ 168.7, 140.3, 135.5, 132.0, 129.4, 128.5, 128.4, 52.0, 26.8; IR (KBr)/cm^{-1}: 1706, 1632, 1445; MS: *m*/*z* (%) 350 (M^+, 2.3), 175 (5.0), 115 (100); Anal. $C_{22}H_{22}O_4$. Calcd C, 75.41; H, 6.33. Found C, 75.23; H, 6.40%.

4.2.2. 2,5-Bis-(4-chloro-benzylidene)-hexanedioic acid dimethyl ester (2b). White solid, mp: 165–167 °C, ^{1}H NMR: δ 7.63 (2H, s), 7.41 (4H, d, *J*=8.0 Hz), 7.35 (4H, d, *J*=8.0 Hz), 3.78 (6H, s), 2.73 (4H, s); IR (KBr)/cm^{-1}: 1708, 1592, 1438; MS: *m*/*z* (%) 418 (M^+, 2.4), 209 (16), 149 (67), 115 (100); Anal. $C_{22}H_{20}Cl_2O_4$. Calcd C, 63.02; H, 4.81. Found C, 63.11; H, 4.72%.

4.2.3. 2,5-Bis-(2-chloro-benzylidene)-hexanedioic acid dimethyl ester (2c). White solid, mp: 143–144 °C, ^{1}H NMR: δ 7.72 (2H, s), 7.40–7.25 (8H, m), 3.67 (6H, s), 2.59 (4H, s); ^{13}C NMR: δ 167.9, 137.6, 134.2, 133.9, 133.7, 130.3, 129.5, 129.5, 126.6, 52.0, 26.9; IR (KBr)/cm^{-1}: 1702, 1588, 1435; MS: *m*/*z* (%) 418 (M^+, 1.7), 351 (59), 149 (63), 115 (100); Anal. $C_{22}H_{20}Cl_2O_4$. Calcd C, 63.02; H, 4.81. Found C, 62.91; H, 4.56%.

4.2.4. 2,5-Bis-(4-methyl-benzylidene)-hexanedioic acid dimethyl ester (2d). White solid, mp: 145–147 °C, ^{1}H NMR: δ 7.71 (2H, s), 7.41 (4H, d, *J*=8.0 Hz), 7.20 (4H, d, *J*=8.0 Hz), 3.81 (6H, s), 2.82 (4H, s), 2.38 (6H, s); ^{13}C NMR: δ 168.9, 140.3, 138.5, 132.6, 131.2, 129.6, 129.2, 51.9, 26.8, 21.3; IR (KBr)/cm^{-1}: 1703, 1608, 1435, 1066; MS: *m*/*z* (%) 378 (M^+, 2.3), 189 (20), 129 (100); Anal. $C_{24}H_{26}O_4$. Calcd C, 76.17; H, 6.92. Found C, 75.88; H, 7.00%.

4.2.5. 2,5-Bis-(4-methoxy-benzylidene)-hexanedioic acid dimethyl ester (2e). White solid, mp: 134–135 °C, ^{1}H NMR: δ 7.70 (2H, s), 7.53 (4H, d, *J*=8.0 Hz), 6.93 (4H, d, *J*=8.0 Hz), 3.85 (6H, s), 3.83 (6H, s), 2.84 (4H, s); ^{13}C NMR: δ 169.1, 159.9, 140.0, 131.5, 129.7, 127.9, 113.9, 55.3, 52.0, 26.8; IR (KBr)/cm^{-1}: 1700, 1602, 1510, 1439; MS: *m*/*z* (%) 410 (M^+, 2.1), 205 (69), 145 (100); Anal. $C_{24}H_{26}O_6$. Calcd C, 70.23; H, 6.38. Found C, 70.27; H, 6.15%.

4.2.6. 2,5-Bis-(2-methoxy-benzylidene)-hexanedioic acid dimethyl ester (2f). White solid, mp: 132–133 °C, ^{1}H NMR: δ 7.86 (2H, s), 7.42–7.31 (4H, m), 7.00–6.90 (4H, m), 3.85 (6H, s), 3.75 (6H, s), 2.73 (4H, s); ^{13}C NMR: δ 168.7, 157.5, 136.3, 132.1, 130.0, 129.9, 124.6, 120.3, 110.4, 55.5, 51.9, 27.2; IR (KBr)/cm^{-1}: 1712, 1626, 1598, 1461; MS: *m*/*z* (%) 410 (M^+, 2.5), 205 (17), 145 (100); Anal. $C_{24}H_{26}O_6$. Calcd C, 70.23; H, 6.38. Found C, 70.09; H, 6.61%.

4.2.7. 2,5-Bis-(3-bromo-benzylidene)-hexanedioic acid dimethyl ester (2h). White solid, mp: 163–165 °C, ^{1}H NMR: δ 7.61 (2H, s), 7.51–7.24 (8H, m), 3.76 (6H, s), 2.74 (4H, s); ^{13}C NMR: δ 168.2, 138.7, 137.5, 133.1, 132.0, 131.4, 130.0, 127.7, 122.5, 52.2, 26.5; IR (KBr)/cm^{-1}: 1707, 1560, 1432; MS: *m*/*z* (%) 506 (M^+, 1.2), 174 (56), 115 (100); Anal. $C_{22}H_{20}Br_2O_4$. Calcd C, 52.00; H, 3.97. Found C, 51.87; H, 4.00%.

4.3. General procedure for the preparation of trisubstituted alkenes (3a–3h)

A solution of Baylis–Hillman adduct (1 mmol) in dry THF (3 mL) was added to the solution of SmI_2 (2.2 mmol) in

THF (20 mL) at 65 °C under a nitrogen atmosphere. After being stirred for about 10 min at 65 °C (Table 1), the deep blue color of the solution changed to yellow rapidly. Then, the reaction mixture was quenched with 0.1 M hydrochloric acid (5 mL) and extracted with ether (3×20 mL). The organic phase was successively washed with brine (15 mL), water (20 mL) and dried over anhydrous Na_2SO_4. The solvent was removed under reduced pressure to give the crude products, which were purified by preparative TLC using ethyl acetate and cyclohexane (1:7) as eluent.

4.3.1. 2-Methyl-3-phenyl-acrylic acid methyl ester (3a) (lit.[8]). Yellow oil, ^{1}H NMR: δ 7.77 (1H, s), 7.46–7.38 (5H, m), 3.89 (3H, s), 2.19 (3H, s); ^{13}C NMR: δ 169.2, 139.0, 135.9, 129.6, 128.4, 128.3, 128.3, 52.0, 14.0; IR (film)/cm^{-1}: 1709, 1606, 1512, 1435; MS: *m*/*z* (%) 176 (M^+, 48), 145 (31), 115 (100).

4.3.2. 3-(4-Chloro-phenyl)-2-methyl-acrylic acid methyl ester (3b) (lit.[8]). Yellow oil, ^{1}H NMR: δ 7.62 (1H, s), 7.36 (2H, d, *J*=8.0 Hz), 7.31 (2H, d, *J*=8.0 Hz), 3.82 (3H, s), 2.09 (3H, s); IR (film)/cm^{-1}: 1714, 1491, 1434; MS: *m*/*z* (%) 210 (M^+, 47), 150 (53), 115 (100).

4.3.3. 3-(2-Chloro-phenyl)-2-methyl-acrylic acid methyl ester (3c). Yellow oil, ^{1}H NMR: δ 7.78 (1H, s), 7.46–7.28 (4H, m), 3.86 (3H, s), 2.02 (3H, s); IR (film)/cm^{-1}: 1717, 1469, 1436; MS: *m*/*z* (%) 210 (M^+, 2.6), 175 (100), 115 (54); Anal. $C_{11}H_{11}ClO_2$. Calcd C, 62.72; H, 5.26. Found C, 62.85; H, 5.51%.

4.3.4. 2-Methyl-3-*p*-tolyl-acrylic acid methyl ester (3d). Yellow oil, ^{1}H NMR: δ 7.66 (1H, s), 7.30 (2H, d, *J*=8.0 Hz), 7.19 (2H, d, *J*=8.0 Hz), 3.80 (3H, s), 2.36 (3H, s), 2.11 (3H, s); IR (film)/cm^{-1}: 1711, 1632, 1435; MS: *m*/*z* (%) 190 (M^+, 100), 159 (48), 115 (57); Anal. $C_{12}H_{14}O_2$. Calcd C, 75.76; H, 7.42. Found C, 75.89; H, 7.31%.

4.3.5. 3-(4-Methoxy-phenyl)-2-methyl-acrylic acid methyl ester (3e) (lit.[8]). Yellow oil, ^{1}H NMR: δ 7.65 (1H, s), 7.38 (2H, d, *J*=8.0 Hz), 6.92 (2H, d, *J*=8.0 Hz), 3.82 (3H, s), 3.80 (3H, s), 2.14 (3H, s); ^{13}C NMR: δ 169.4, 159.7, 138.7, 131.5, 128.4, 126.0, 113.8, 55.3, 52.0, 14.1; IR (film)/cm^{-1}: 1709, 1606, 1512, 1435; MS: *m*/*z* (%) 206 (M^+, 100), 146 (89), 103 (57).

4.3.6. 3-(2-Methoxy-phenyl)-2-methyl-acrylic acid methyl ester (3f) (lit.[8]). Yellow oil, ^{1}H NMR: δ 7.84 (1H, s), 7.34–6.90 (4H, m), 3.86 (3H, s), 3.81 (3H, s), 2.06 (3H, s); IR (film)/cm^{-1}: 1711, 1598, 1436; MS: *m*/*z* (%) 206 (M^+, 53), 175 (100), 131 (92), 115 (23).

4.3.7. 3-Benzo[1,3]dioxol-5-yl-2-methyl-acrylic acid methyl ester (3g). White solid, mp: 75–76 °C, ^{1}H NMR: δ 7.59 (1H, s), 6.93–6.82 (3H, m), 5.99 (2H, s), 3.80 (3H, s), 2.11 (3H, s); ^{13}C NMR: δ 169.3, 147.7, 147.6, 138.7, 129.9, 126.6, 124.7, 109.6, 108.4, 101.3, 52.1, 14.2; IR (KBr)/cm^{-1}: 1691, 1600, 1501, 1449; MS: *m*/*z* (%) 220 (M^+, 99), 160 (100), 131 (40), 103 (30); Anal. $C_{12}H_{12}O_4$. Calcd C, 65.45; H, 5.49. Found C, 65.32; H, 5.70%.

4.3.8. 3-(3-Bromo-phenyl)-2-methyl-acrylic acid methyl ester (3h). Yellow oil, ^{1}H NMR: δ 7.60 (1H, s), 7.52–7.28 (4H, m), 3.82 (3H, s), 2.10 (3H, s); IR (film)/cm^{-1}: 1715, 1469, 1435; MS: *m*/*z* (%) 254 (M^+, 22), 196 (31), 115 (100); Anal. $C_{11}H_{11}BrO_2$. Calcd C, 51.79; H, 4.35. Found C, 52.01; H, 4.47%.

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13. The symmetrical structure of **2d** can be easily recognized from ^{1}H NMR and ^{13}C NMR. Furthurmore, the chemical shift value of olefinic proton in ^{1}H NMR and the allylic methylene carbon in ^{13}C NMR are quite in analog with **3d**. The *E*-stereochemistry of **2d** can be easily explained according to the following mechanism proposed (Scheme 2).
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