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Stereoselective synthesis of (*E*)-β-arylvinyl bromides by microwave-induced reaction of *anti*-3-aryl-2,3-dibromopropanoic acids using an AgOAc–AcOH system

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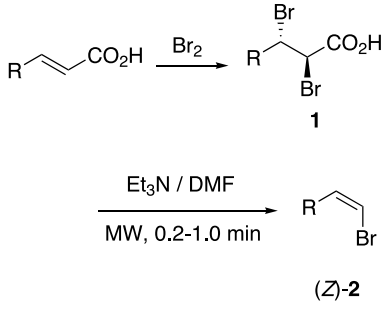
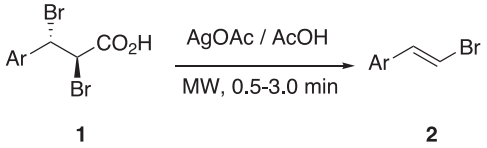
Abstract—(*E*)-β-Arylvinyl bromides were stereoselectively prepared in high yields by microwave irradiation of the corresponding *anti*-3-aryl-2,3-dibromopropanoic acids in AcOH in the presence of AgOAc for 0.5–3.0 min.

1. Introduction

(*E*)-Vinyl bromides are very useful synthetic intermediates in organic synthesis.[1] The classical Hunsdiecker reaction[2] and its modified reactions[3] and Takai procedure[4] have been frequently used for synthesis of (*E*)-β-arylvinyl bromides. Although most of these methods are useful for the synthesis of (*E*)-vinyl halides, a more convenient and efficient method for synthesis is needed to overcome the problems in these methods which involve the use of complex reagents and large amounts of solvent, long reaction times and low yields, especially in the case of cinnamic acids carrying electron-withdrawing groups or *ortho*-substituents.[3f,h–j] We recently reported that microwave irradiation of *anti*-2,3-dibromoalkanoic acids (**1**) in DMF in the presence of triethylamine for 0.2–1.0 min stereoselectively afforded (*Z*)-vinyl bromides ((*Z*)-**2**) in high yields (Scheme 1).[5] This method is very convenient and useful since the starting dibromides **1** are readily obtained by bromination of the corresponding *trans*-2-alkenoic acids. On the other hand, conventional thermal reaction of **1** under a variety of conditions also gives the corresponding (*Z*)-β-arylvinyl bromides as a major product.[6] (*E*)-β-Arylvinyl bromides are only obtained in the case of *anti*-3-aryl-2,3-dibromoalkanoic acids carrying a strongly electron-donating group at their aryl group.[7] We recently found that microwave irradiation of *anti*-3-aryl-2,3-dibromopropanoic acids (**1**, R = aryl) stereoselectively gave the corresponding (*E*)-β-arylvinyl bromides ((*E*)-**2**) by simply modifying the solvent and additive(Scheme 2). Here we report the first general method for a stereoselective synthesis of (*E*)-β-arylvinyl bromides from *anti*-3-aryl-2,3-dibromopropanoic acids by using microwave irradiation.



Scheme 1.



Scheme 2.

Microwave-induced efficient and rate accelerate technology is becoming a powerful tool in organic synthesis.[8] We have successfully used a microwave irradiation method for the synthesis of (*E*)-vinyl halides by Hunsdiecker-type reaction of 3-arylpropenoic acids[9a] and by the reaction of

Keywords: (*E*)-β-Arylvinyl bromides; *anti*-3-Aryl-2,3-dibromopropanoic acids; Silver acetate; Microwave irradiation.
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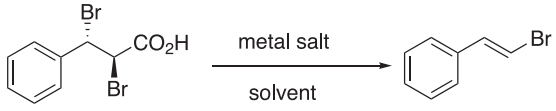
Table 1. Transformation of *anti*-2,3-dibromo-3-phenylpropanoic acid (**1a**) into (*E*)-β-bromostyrene (**2a**) under various conditions



1a **2a**

Entry	Metal salt (1.2 equiv)	Solvent (5 ml)	Conditions	Yield (%)[a]	*E*/*Z*[b]
1	AgOAc	AcOH	Room temperature, 1 min	40[c]	>98/2
2	AgOAc	AcOH	Room temperature, 6 h	82	98/2
3	AgOAc	AcOH	80 °C, 30 min	84	98/2
4	AgOAc	AcOH	MW 1 min	86	>98/2
5	AgOAc	DMF	MW 1 min	60	73/27
6	AgOAc	MeCN	MW 1 min	70	73/27
7	AgOAc	THF	MW 1 min	50	95/5
8	AgOTf	AcOH	MW 1 min	70	95/5
9	Ag_2O	AcOH	MW 1 min	80	92/8
10	$AgNO_2$	AcOH	MW 1 min	20	92/8
11	$AgNO_3$	AcOH	MW 1 min	0	
12	TiOAc	AcOH	MW 1 min	72	94/6
13	$Hg(OAc)_2$	AcOH	MW 1 min	0	
14	$Pb(OAc)_4$	AcOH	MW 1 min	0	

[a] Determined by ^{1}H NMR analysis.
[b] Isomer ratios were determined by ^{1}H NMR analysis.
[c] A formation of β-lactone was also observed.

1,1-dibromoalkenes with diethyl phosphonate and sodium ethoxide.[9b]

2. Results and discussion

Microwave irradiation of *anti*-3-aryl-2,3-dibromopropanoic acids carrying electron-donating or electron-withdrawing groups (**1**) in acetic acid in the presence of AgOAc gave the corresponding (*E*)-β-aryl-vinyl bromides (**2**) (Scheme 2). For example, microwave irradiation of *anti*-2,3-dibromo-3-phenylpropanoic acid (**1a**) in AcOH (5 ml) in the presence of 1.2 equiv of AgOAc for 1 min gave (*E*)-β-bromostyrene (**2a**) in 86% yield (*E*/*Z*>98/2). Various conditions were examined to optimize the yield and stereoselectivity of **2a**. The results are summarized in Table 1. The reaction of **1a** with AgOAc in acetic acid was found to give **2a** even without microwave irradiation (Table 1, entries 1–3). When microwave irradiation was applied to the reaction mixture for 1 min by using a conventional microwave oven, the reaction proceeded very rapidly and **2a** was obtained in 86% yield (entry 4). Table 1 shows that metal salts such as $AgNO_2$, $AgNO_3$, $Hg(OAc)_2$ and $Pb(OAc)_4$ were not effective in this reaction and that DMF, MeCN and THF were less satisfactory as solvents than was AcOH. At this stage, an AgOAc/AcOH system appears to be the best system for the reaction (entry 4).

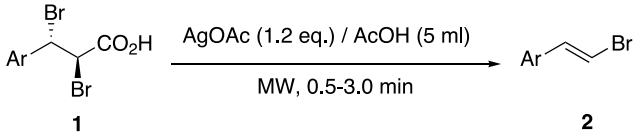
Microwave irradiation of various *anti*-3-aryl-2,3-dibromopropanoic acids **1** under the optimum conditions gave the corresponding (*E*)-β-arylvinyl bromides **2** in the yields and stereoselectivities shown in Table 2. These results indicate that *anti*-3-aryl-2,3-dibromopropanoic acids carrying electron-donating or electron-withdrawing groups at the *ortho*, *meta*, or *para* position could be converted into the corresponding (*E*)-vinyl bromides in excellent yields with high stereoselectivities by the use of a microwave irradiation method (entries 2–4 and 7–12). It is noteworthy that (*E*)-vinyl bromides carrying bromo, chloro, fluoro or methoxycarbonyl groups were obtained in 80–96% isolated yields by the present method (entries 7–12). In addition, (*E*)-β-bromostyrene carrying *ortho* chloro substituent was also obtained stereoselectively in 88% yield (entry 9). (*E*)-β-Arylvinyl bromides having 1- or 2-naphthyl groups were also obtained in high yields with high stereoselectivities (entries 5 and 6).

We applied this transformation to a one-pot synthesis of (*E*)-vinyl bromides from substituted *trans*-cinnamic acids. For example, bromination of *trans*-4-bromocinnamic acid in AcOH at 55 °C for 2 h and subsequent microwave irradiation of the mixture in the presence of AgOAc gave the desired product **2g** in 91% yield (Scheme 3).

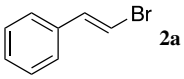
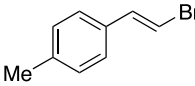
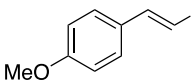
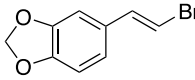
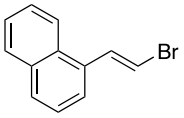
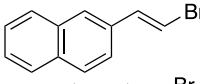
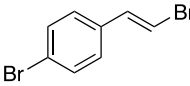
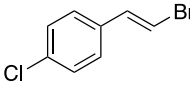
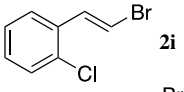
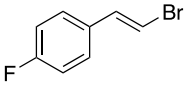
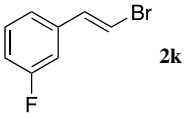
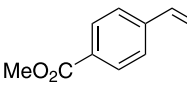
We found that microwave irradiation for only a short time of a mixture of *anti*-3-aryl-2,3-dibromopropanoic acids carrying an electron-withdrawing group and AgOAc in AcOH gave a mixture of (*E*)-β-arylvinyl bromide and β-lactone. For example, microwave irradiation of 2,3-dibromo-3-(4-methoxycarbonylphenyl)propanoic acid **1l** (1 mmol) and AgOAc in 5 ml of AcOH for only 5 s gave a mixture of methyl (*E*)-4-(β-bromovinyl)benzoate (**2l**) and *trans*-α-bromo-β-lactone (**3**) (**2l/3**=78/22) (Scheme 4). Lactone **3** could be separated by chromatography. On the other hand, in the microwave reaction of *anti*-3-aryl-2,3-dibromopropanoic acids having an electron-rich 4-methoxyl or methylenedioxyl substituent (**1c** or **1d**), no signal indicating the formation of a β-lactone intermediate was detected. The rate of decarboxylation is highly dependent on a substituent of β-lactone.[10] An electron-donating group at the aryl ring facilitates the decarboxylation, while an electron-withdrawing group retards the rate of the decarboxylation reaction.[10]

Probable reaction pathways are shown in Scheme 5. Two pathways, that is, a zwitterionic route or decarboxylation of

Table 2. Stereoselective synthesis of (*E*)-β-arylvinyl bromides **2**

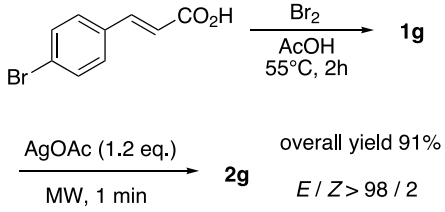


1 **2**

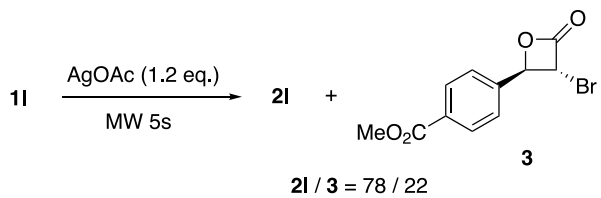
Entry	Dibromide	Product	MW (min)	Yield (%)[a]	*E*/*Z*[b]
1	**1a**	 **2a**	1.0	86	>98/2
2	**1b**	 **2b**	1.0	87	>98/2
3	**1c**	 **2c**	0.5	85	>98/2
4	**1d**	 **2d**	0.5	88	>98/2
5	**1e**	 **2e**	1.0	92	>98/2
6	**1f**	 **2f**	1.0	93	>97/3
7	**1g**	 **2g**	1.0	95	>98/2
8	**1h**	 **2h**	1.0	96	>98/2
9	**1i**	 **2i**	2.0	88	>98/2
10	**1j**	 **2j**	2.0	92	>98/2
11	**1k**	 **2k**	2.0	90	>97/3
12	**1l**	 **2l**	3.0	80	>97/3

[a] Isolated yields.
[b] Isomer ratios were determined by ^{1}H NMR analysis.

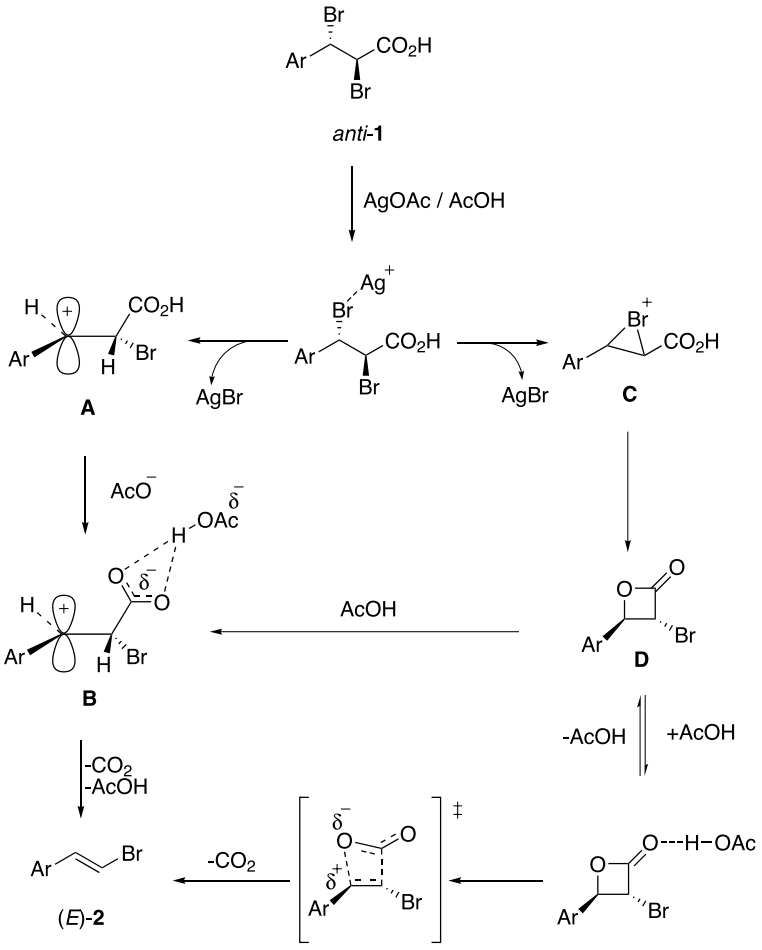
α-bromo-β-lactone, might depend on the nature of the aryl-substituent. Some of the reactions probably proceed via an electrophilic attack of Ag^+ on a bromine atom of **1** to give the zwitterionic intermediate **B**,[10c,e] which would eliminate carbon dioxide to give (*E*)-β-arylvinyl bromide ((*E*)-**2**). The reactions of *anti*-3-aryl-2,3-dibromopropanoic acids (**1c** and **1d**) undergo this mechanism. On the other hand, in some reactions, α-bromo-β-lactone (**D**) would be formed via bromonium ion (**C**), and an elimination of carbon dioxide from the lactone (**D**) would occur with a retention of



Scheme 3.



Scheme 4.



Scheme 5.

configuration to give (*E*)-**2**. In most cases, two pathways coexist; one pathway takes precedence over the other one on the basis of the electron character of the substituent. *anti*-3-Aryl-2,3-dibromopropanoic acids **1a**, **1b**,**1e** and **1f** might mainly proceed in zwitterionic route, whereas **1g**, **1h**, **1i**, **1j**, **1k** and **1l** mainly undergo α-bromo-β-lactone route. The possibility that α-bromo-β-lactone **D** can be converted to zwitterionic intermediate **B** also exists, it depends on the stability of α-bromo-β-lactone (**D**) varying from the substituents.

3. Conclusion

In summary, we have developed a new and efficient method for stereoselective synthesis of (*E*)-β-arylvinyl bromides from the corresponding *anti*-3-aryl-2,3-dibromopropanoic acids using an AgOAc/AcOH system, in which the use of microwave irradiation enables preparation of (*E*)-β-arylvinyl bromides in high yields and high stereoselectivities within 0.5–3.0 min of reaction time. In addition, we applied this transformation to a one-pot synthesis of (*E*)-arylvinyl bromides in high yields and high stereosectivities from substituted *trans*-cinnamic acids carrying electron-withdrawing groups. Moreover, we proved that the debrominative decarboxylation pathways including zwitterionic route and decarboxylation of α-bromo-β-lactones might depend on a nature of aryl-substituent.

4. Experimental

4.1. General

Melting points were recorded using a Yanagimoto micro melting point apparatus and were uncorrected. IR spectra were recorded using a JASCO IR-810 infrared spectrometer (between NaCl plates). ^{1}H and ^{13}C NMR spectra were recorded using a JEOL JNM-EX270 FT NMR spectrometer at 270 MHz (^{1}H) and at 67.8 MHz (^{13}C) in $CDCl_3$ with $SiMe_4$ as an internal standard. High- and low- resolution mass spectra were determined using a JEOL JMS-FABmate or JEOL JMS-700TZ spectrometer. Column chromatography was carried out on a Silica Gel 60 N (100–210 μm, Kanto Chemical Co. Ltd). New compound was further characterized by elemental analysis.

4.2. General procedure for the synthesis of (*E*)-β-arylvinyl bromides (2)

anti-2,3-Dibromo-3-arylpropanoic acid (**1a**–**l**) were prepared according to the previously described procedures.[6g,h,7a]

A mixture of *anti*-2,3-dibromo-3-arylpropanoic acid (**1**, 1 mmol), AgOAc (1.2 mmol), and AcOH (5 ml) in a 100 ml Erlenmeyer flask was kept in a microwave oven operated at 2450 MHz (TOSHIBA, ER-V11, 200 W) and was irradiated

for 0.5–3.0 min. The reaction mixture was then removed from the oven and cooled to room temperature. Water and ether were added to the reaction mixture and the organic layer was separated. Aqueous layer was extracted with ether. The combined organic layers were washed with water and brine, and dried over anhydrous magnesium sulfate. Evaporation of the solvent gave the crude product, which was subjected to column chromatography (silica gel, hexane–ether) to afford (*E*)-β-arylvinyl bromides **2**.

4.2.1. (*E*)-β-Bromostyrene (2a).[3d,11] Column chromatography was carried out with hexane as an eluent; colorless oil; IR (neat) 1609, 1575, 941 cm^{-1}; ^1H NMR ($CDCl_3$) δ 6.77 (1H, d, $J=13.9$ Hz), 7.11 (1H, d, $J=13.9$ Hz), 7.27–7.32 (5H, m).

4.2.2. (*E*)-β-Bromo-4-methylstyrene (2b).[3d,11] Column chromatography was carried out with hexane as an eluent; mp 46.0–46.5 °C (EtOH) (lit.[6g] 46.0–46.5 °C); IR (nujol) 1605, 1511, 931 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.32 (3H, s), 6.70 (1H, d, $J=13.9$ Hz), 7.06 (1H, d, $J=13.9$ Hz), 7.12 (2H, d, $J=8.3$ Hz), 7.19 (2H, d, $J=8.3$ Hz).

4.2.3. (*E*)-β-Bromo-4-methoxystyrene (2c).[3d,12] Column chromatography was carried out with 10% ether in hexane as an eluent; mp 58–59 °C (EtOH) (lit.[12] 58–59 °C); IR (nujol) 1607, 1513, 950 cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.81 (3H, s), 6.61 (1H, d, $J=13.9$ Hz), 6.85 (2H, d, $J=8.9$ Hz), 7.04 (1H, d, $J=13.9$ Hz), 7.23 (2H, d, $J=8.9$ Hz).

4.2.4. (*E*)-β-Bromo-3,4-methylenedioxystyrene (2d).[3h] Column chromatography was carried out with 10% ether in hexane as an eluent; mp 52.5–53.0 °C (hexane); IR (nujol) 1505, 1250, 935 cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.96 (2H, s), 6.59 (1H, d, $J=13.7$ Hz), 6.77 (2H, m), 6.81 (1H, s), 6.99 (1H, d, $J=13.7$ Hz); ^{13}C NMR ($CDCl_3$) δ 101.27, 104.51, 105.39, 108.44, 120.93, 130.27, 136.67, 147.76, 148.13; EIMS *m/z* 228 ($(M+2)^{\cdot+}$, 38), 226 (M^+, 40), 175 (100); HRMS calcd for $C_9H_7^{79}Br\,O_2$. *m/z* 225.9629. Found *m/z* 225.9635.

4.2.5. (*E*)-1-(β-Bromovinyl)naphthalene (2e).[13] The crude product was purified by silica gel column chromatography eluted with 5% ether in hexane; colorless oil; IR (neat) 1603, 1590, 935 cm^{-1}; ^1H NMR ($CDCl_3$) δ 6.76 (1H, d, $J=13.9$ Hz), 7.38–7.56 (4H, m), 7.79–7.86 (3H, m), 8.02 (1H, d, $J=8.9$ Hz).

4.2.6. (*E*)-2-(β-Bromovinyl)naphthalene (2f).[14] The crude product was purified by silica gel column chromatography eluted with 5% ether in hexane; mp 84–85 °C (EtOH); IR (nujol) 1611, 1594, 945 cm^{-1}; ^1H NMR ($CDCl_3$) δ 6.90 (1H, d, $J=13.9$ Hz), 7.26 (1H, d, $J=13.9$ Hz), 7.44–7.49 (3H, m), 7.69 (1H, d, $J=1.0$ Hz), 7.77–7.83 (3H, m).

4.2.7. (*E*)-β-Bromo-4-bromostyrene (2g).[15,16] The crude product was purified by silica gel column chromatography eluted with 10% ether in hexane; mp 67–68 °C (lit.[15] 67–68 °C); IR (nujol) 1610, 1589, 930 cm^{-1}; ^1H NMR ($CDCl_3$) δ 6.78 (1H, d, $J=14.2$ Hz), 7.04 (1H, d, $J=14.2$ Hz), 7.15 (2H, d, $J=8.3$ Hz), 7.44 (2H, d, $J=8.3$ Hz); ^{13}C NMR ($CDCl_3$) δ 107.33, 122.17, 127.55, 131.93, 134.77, 136.03; EIMS *m/z* 264 ($(M+2)^{\cdot+}$, 90), 262 (M^+, 100), 181 (78), 102 (70); HRMS calcd for $C_8H_6^{79}Br^{81}Br$. *m/z* 261.8816. Found *m/z* 261.8825.

4.2.8. (*E*)-β-Bromo-4-chlorostyrene (2h).[3d,17] The crude product was purified by silica gel column chromatography eluted with 10% ether in hexane; mp 47–48 °C (MeOH) (lit.[17] 47–48 °C); IR (nujol) 1604, 1586, 945 cm^{-1}; ^1H NMR ($CDCl_3$) δ 6.75 (1H, d, $J=13.9$ Hz), 7.05 (1H, d, $J=13.9$ Hz), 7.21 (2H, d, $J=8.6$ Hz), 7.29 (2H, d, $J=8.6$ Hz).

4.2.9. (*E*)-β-Bromo-2-chlorostyrene (2i).[3i] The crude product was purified by silica gel column chromatography eluted with 20% ether in hexane; colorless oil; IR (neat) 1605, 1470, 1440, 945 cm^{-1}; ^1H NMR ($CDCl_3$) δ 6.80 (1H, d, $J=13.9$ Hz), 7.21–7.25 (2H, m), 7.3–7.4 (2H, m), 7.47 (1H, d, $J=13.9$ Hz).

4.2.10. (*E*)-β-Bromo-4-fluorostyrene (2j).[16] The crude product was purified by silica gel column chromatography eluted with 5% ether in hexane; colorless oil; IR (neat) 1602, 1589, 946 cm^{-1}; ^1H NMR ($CDCl_3$) δ 6.67 (1H, d, $J=13.9$ Hz), 6.95–7.03 (2H, m), 7.04 (1H, d, $J=13.9$ Hz), 7.21–7.25 (2H, m); ^{13}C NMR ($CDCl_3$) δ 106.07 (d, $J=2.5$ Hz), 115.76 (d, $J=20.7$ Hz), 127.68 (d, $J=8.5$ Hz), 132.10 (d, $J=3.7$ Hz), 135.93, 162.56 (d, $J=247.8$ Hz); EIMS *m/z* 202 ($(M+2)^{\cdot+}$, 28), 200 (M^+, 27), 202 (28), 149 (100); HRMS calcd for $C_8H_6^{79}BrF$. *m/z* 199.9637. Found *m/z* 199.9629.

4.2.11. (*E*)-β-Bromo-3-fluorostyrene (2k).[16] The crude product was purified by silica gel column chromatography eluted with 5% ether in hexane; colorless oil; IR (neat) 1611, 1582, 937 cm^{-1}; ^1H NMR ($CDCl_3$) δ 6.77 (1H, d, $J=13.9$ Hz), 6.93–7.06 (4H, m), 7.10–7.30 (1H, m); ^{13}C NMR ($CDCl_3$) δ 108.03, 112.64 (d, $J=23.2$ Hz), 115.11 (d, $J=22.0$ Hz), 167.45 (d, $J=2.5$ Hz), 130.26 (d, $J=8.5$ Hz), 136.06 (d, $J=2.4$ Hz), 137.96 (d, $J=7.3$ Hz), 162.98 (d, $J=246.6$ Hz); EIMS *m/z* 202 ($(M+2)^{\cdot+}$, 28), 200 (M^+, 27), 202 (28), 149 (100); HRMS calcd for $C_8H_6^{79}BrF$. *m/z* 199.9637. Found *m/z* 199.9642.

4.2.12. (*E*)-4-(β-Bromovinyl)benzoic acid methyl ester (2l).[16] The crude product was purified by silica gel column chromatography eluted with 25% ether in hexane; mp 60–61 °C (hexane); IR (nujol) 1732, 1607, 1584, 936 cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.92 (3H, s), 6.92 (1H, d, $J=14.0$ Hz), 7.13 (1H, d, $J=14.0$ Hz), 7.36 (2H, d, $J=8.3$ Hz), 7.98 (2H, d, $J=8.3$ Hz); ^{13}C NMR ($CDCl_3$) δ 52.17, 109.38, 125.95, 129.63, 130.10, 136.32, 140.05, 166.61; EIMS *m/z* 242 ($(M+2)^{\cdot+}$, 100), 240 (M^+, 100), 211 (100), 181 (75), 102 (70); HRMS calcd for $C_{10}H_9^{81}BrO_2$. *m/z* 241.9765. Found *m/z* 241.9774.

4.2.13. 4-(3-Bromo-4-oxo-oxetan-2-yl)-benzoic acid methyl ester (3). The crude product was purified by silica gel column chromatography eluted with 50% ether in hexane; Yield: 20%; mp 85–86 °C (hexane/ether=6/4); IR (nujol) 1850 (γ CO), 1725 cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.95 (3H, s), 4.99 (1H, d, $J=3.96$ Hz), 5.64 (1H, d, $J=3.96$ Hz), 7.50 (2H, d, $J=8.4$ Hz), 8.12 (2H, d, $J=8.4$ Hz); ^{13}C NMR ($CDCl_3$) δ 46.72, 52.45, 80.29, 125.31, 130.45, 131.68, 139.20, 163.57, 166.15; EIMS *m/z* 286 ($(M+2)^{\cdot+}$, 47), 284 (M^+, 46), 255 (25), 240 (M^+-CO_2, 46), 209 (80), 122

(100); HRMS calcd for $C_{11}H_9^{79}BrO_4$. *m/z* 283.9657. Found *m/z* 283.9684. Anal. Calcd for $C_{11}H_9BrO_4$: C, 46.34, H, 3.18, Br, 28.03. Found: C, 46.48, H, 3.23, Br, 27.76.

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