Available online at www.sciencedirect.com
SCIENCE DIRECT
Tetrahedron
Tetrahedron 61 (2005) 4043–4052

Synthesis of (*Z*)-1-bromo-1-alkenes and terminal alkynes from *anti*-2,3-dibromoalkanoic acids by microwave-induced reaction

Chunxiang Kuang,[a,*] Qing Yang,[b] Hisanori Senboku[c] and Masao Tokuda[c]

[a]*Department of Materials Chemistry, Graduate School of Engineering, Osaka University, Suita 565-0871, Japan*
[b]*Department of Biopharmaceutics, Graduate School of Pharmaceutical Sciences, The University of Tokyo, Hongo, Bunkyo-ku, Tokyo 113-0033, Japan*
[c]*Division of Molecular Chemistry, Graduate School of Engineering, Hokkaido University, Sapporo 060-8628, Japan*

Received 20 December 2004; accepted 14 February 2005

Abstract—(*Z*)-1-Bromo-1-alkenes were stereoselectively prepared in high yields in a short reaction time by microwave irradiation of the corresponding *anti*-2,3-dibromoalkanoic acids in a Et_3N/DMF system. A one-pot synthesis of terminal alkynes and enynes from 2,3-dibromoalkanoic acids were also developed by microwave-induced reaction.
© 2005 Elsevier Ltd. All rights reserved.

1. Introduction

(*Z*)-1-Bromo-1-alkenes are an important synthetic intermediate for stereospecific synthesis of substituted alkenes. A variety of methods have been reported for the stereocontrolled preparation of (*Z*)-1-bromo-1-alkenes, including Wittig-type condensation,[1] metal–halogen exchange of metalloalkenes,[2] hydroboration–protonolysis of haloalkynes,[3] palladium catalyzed hydrogenolysis of 1,1-dibromo-1-alkenes by tributyltin hydride,[4] transformation of ketones using an appropriate acetyl halide in a strongly acidic solvent,[5] SmI_2-mediated β-elimination of *O*-acetyl dihalo alcohols,[6] and debrominative decarboxylation of cinnamic and acrylic acids dibromides.[7] Debrominative decarboxylation of brominated α,β-unsaturated carboxylic acids might be one of the most useful methods for a synthesis of (*Z*)-1-bromo-1-alkenes since the starting α,β-unsaturated acids are readily available and the procedure is very simple, especially, the reaction is easy to be operated in a large scale. However, the yields are low in the case of aliphatic (*Z*)-1-bromoalkenes and (*Z*)-β-bromostyrene carrying *ortho*- and *para*-nitro-substituents even if an improved procedure using triethylamine and DMF solvent was used in these reactions.

Recently, the method of microwave irradiation to effect organic transformation has been used by organic chemists. Remarkable reductions in reaction times, clean conditions and better yields have been reported in microwave-induced reactions.[8] In a preliminary paper,[9] we reported a rapid and convenient method for a stereoselective synthesis of (*Z*)-1-bromoalkenes from the corresponding 2,3-dibromoalkanoic acids using a Et_3N/DMF system under microwave irradiation. In this paper, we describe the details of debrominative decarboxylation of 2,3-dibromoalkanoic acids, including its mechanism and its uses for the preparation of terminal alkynes and enynes in a one-pot reaction (Scheme 1).

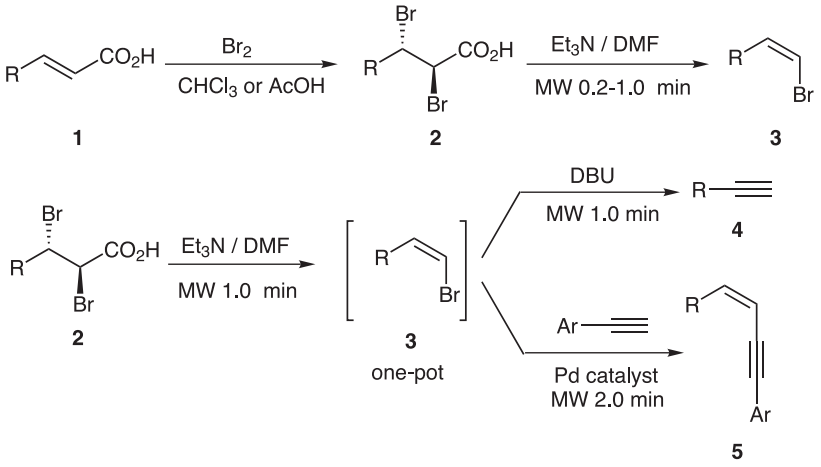
2. Results and discussion

2.1. Stereoselective synthesis of (*Z*)-1-bromo-1-alkenes

Microwave irradiation of *anti*-2,3-dibromoalkanoic acids (**2**), in DMF solution containing 1.05 equiv of triethylamine for 0.2–1.0 min, gave the corresponding (*Z*)-1-bromo-1-alkenes (**3**) in excellent yields and high (*Z*)-selectivities (Scheme 1). *anti*-2,3-Dibromoalkanoic acids (**2**) were readily obtained by bromination of the corresponding *trans*-α,β-unsaturated carboxylic acids (**1**). The yields of (*Z*)-**3** and the ratios of (*Z*) and (*E*) are summarized in Table 1. These results indicate that present reaction can be used for the synthesis of both aromatic and aliphatic (*Z*)-1-bromo-1-alkenes. Unsubstituted cinnamic acid dibromides (**2a** and **2q**) and those with electron-withdrawing group (entries 3 and 4) were converted to the corresponding (*Z*)-β-bromostyrenes (**3a**, **3q**, **3g–i**, **3k–l** and **3m–p**)in excellent

Keywords: (*Z*)-1-Bromo-1-alkenes; *anti*-2,3-Dibromoalkanoic acids; Terminal alkynes; Enynes; Microwave irradiation.
* Corresponding author. Tel.: +81 6 6879 4592; fax: +81 6 6850 5785; e-mail: kuang@ch.wani.osaka-u.ac.jp

0040–4020/$ - see front matter © 2005 Elsevier Ltd. All rights reserved.
doi:10.1016/j.tet.2005.02.043

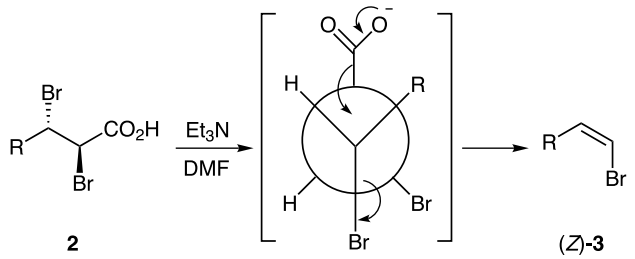


Scheme 1.

Table 1. Stereoselective synthesis of (*Z*)-1-bromo-1-alkenes

Entry	Dibromide (**2**)	Product (**3**)		MW (min)	Yield (%)[a]	*Z*/*E*[b]
1	**2a**	**3a**		0.5	95	>98/2
			EDG			
	2b	**3b**	4-CH_3	0.5	98	98/2
	2c	**3c**	4-CH_3O	0.5	95	75/25
2	**2d**	**3d**	4-*n*-$C_7H_{15}O$	0.5	96	90/10
	2e	**3e**	3,4-OCH_2O	0.5	99	95/5
	2f	**3f**	3,4,5-$(CH_3O)_3$	0.5	97	82/18
			X			
	2g	**3g**	4-Br	1.0	96	>98/2
	2h	**3h**	4-Cl	1.0	96	>98/2
	2i	**3i**	2-Cl	1.0	94	98/2
3	**2j**	**3j**	2,6-Cl_2	1.0	92	85/15
	2k	**3k**	4-F	1.0	98	>98/2
	2l	**3l**	3-F	1.0	98	>98/2
			EWG			
	2m	**3m**	4-CO_2CH_3	1.0	99	>98/2
	2n	**3n**	4-NO_2	1.0	98	>98/2
4	**2o**	**3o**	3-NO_2	1.0	99	>98/2
	2p	**3p**	2-NO_2	1.0	96	>98/2
5	**2q**	**3q**		0.5	96	>98/2
6	**2r**	**3r**		0.5	98	65/35
7	**2s**	**3s**		1.0	73	>98/2
8	**2t**	**3t**		0.2	82	>98/2
9	**2u**	**3u**		0.2	91	>98/2

[a] Isolated yields of (*Z*)- and (*E*)-1-bromo-1-alkenes.
[b] Determined by ^{1}H NMR.

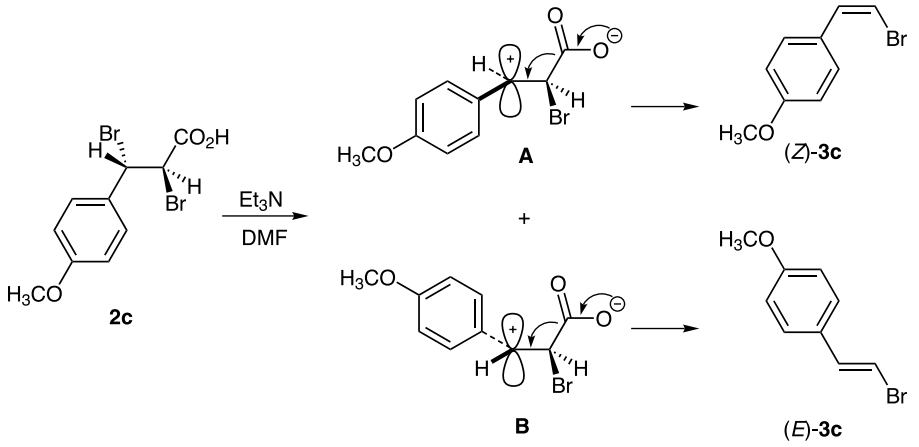


Scheme 2.

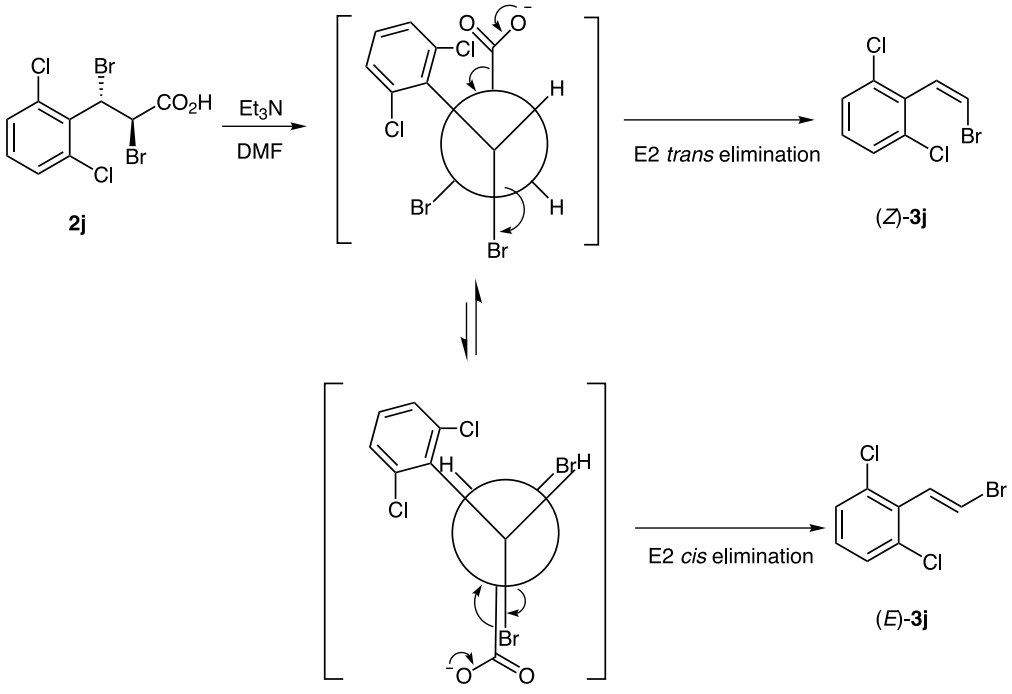
yields with high stereoselectivies. Even if weak electron-donating group such as methyl and methyenedioxy were contained in the molecules, the reaction stereoselectively proceeded in high yields (**3b** and **3e**). However, the *Z*/*E* stereoselectivity was reduced to 65–90% when the benzene ring (**3c**–**f**) was substituted with strong electron-donating group (entry 2) or there was a large steric hindrance in the *ortho* position of the benzene ring (**3j** and **3r**). The reaction of pyridyl-substituted and aliphatic *anti*-2,3-dibromoalkanoic acids gave the corresponding (*Z*)-1-bromo-1-alkenes (**3s**–**u**) with the complete *Z* selectivity and excellent yields. All of these results indicate that the yields by the present method are quite higher than those of previous procedures.

Three proposed reaction pathways for the present debrominative decarboxylations are shown in Schemes 2–4. Most of the reactions probably proceed via *trans*-elimination involving simultaneous loss of carbon dioxide and bromide ion to give (*Z*)-vinyl bromides (Scheme 2).

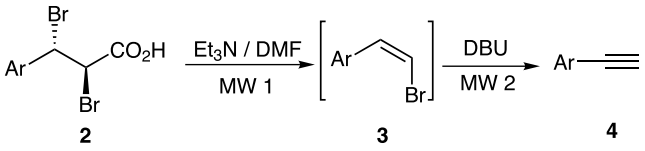
On the other hand, in the case of cinnamic acid dibromides carrying strong electron-donating group such as alkyloxyl



Scheme 3.



Scheme 4.



Scheme 5.

(**2c–f**), a unimolecular elimination process of bromide ion to give relatively stable carbocations **A** and **B** would give (*Z*)- and (*E*)-vinyl bromide, respectively, with a preferential formation of (*Z*)-isomer (Scheme 3).

When a large steric hindrance is present at the *ortho* position of the aryl ring, anion of *anti*-2,3-dibromoalkanoic acids (**2j** and **2r**) might undergo both *cis* and *trans* elimination to give *cis* and *trans* isomer, respectively (Scheme 4).

2.2. A one-pot synthesis of terminal alkynes

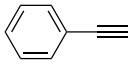
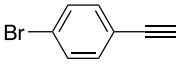
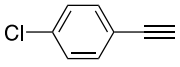
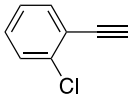
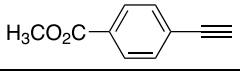
Terminal alkynes are useful and versatile intermediates in organic synthesis. In our continuous study, we have developed a new procedure for one-pot conversion of *anti*-3-aryl-2,3-dibromopropanoic acids (**2**) into terminal alkynes (**4**) in excellent yields within a few minutes under microwave irradiation (Scheme 5).

Various conditions were examined to optimize the yields of terminal alkynes. In the first step (MW1), treatment of *anti*-3-aryl-2,3-dibromopropanoic acids with triethylamine in DMF under microwave irradiation within 0.5–1.0 min resulted in (*Z*)-1-bromo-1-alkenes with high *Z*/*E* selectivity and excellent yields. No remarkable improvement of the yields and stereoselectivities of (*Z*)-1-bromo-1-alkenes was observed when the microwave irradiation was lasted for a longer time (2 min) or an excess base (3 equiv of Et_3N) was used. As to the second step (MW2), it was found that bases such as Et_3N, pyridine, DABCO, NaOH, K_2CO_3 or *t*-BuOK were not effective in this one-pot reaction. 1,8-diazabicyclo-[5.4.0]undec-7-ene (DBU) was found to be the best base in this one-pot system. It would be very convenient for this one-pot reaction to use same base in two successive steps. Unfortunately, when DBU instead of Et_3N was used in the first step, a mixture of (*Z*)- and (*E*)-vinyl bromide (approximate to 92/8) was formed, and this stereoselectivity was much lower than those using Et_3N. Since DBU did only cause an elimination of (*Z*)-vinyl bromides under these conditions, a mixture of terminal alkynes and unreacted (*E*)-vinyl bromides was obtained. Under microwave irradiation the reaction of *anti*-3-aryl-2,3-dibromopropanoic acids and triethylamine in DMF followed by addition of DBU proceeded smoothly to afford the corresponding terminal alkynes in high yields. As shown in Table 2, these terminal alkynes were obtained in high yields and in short reaction time by the microwave irradiation method. The proposed reaction pathway of the present elimination was shown in Scheme 6. However, microwave irradiation of alkyl-substituted 2,3-dibromoalkanoic acids by the same way gave the corresponding aliphatic alkynes in low yields.

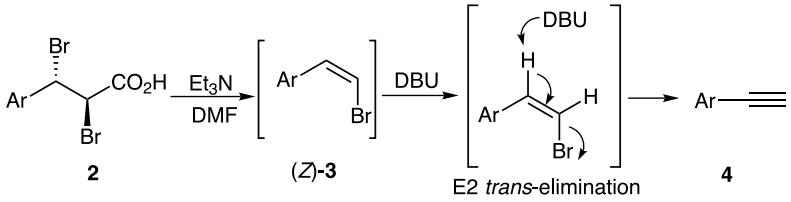
2.3. A one-pot synthesis of enynes

Furthermore, we applied this transformation to a one-pot synthesis of enynes from *anti*-2,3-dibromoalkanoic acids. Microwave irradiation of a mixture of *anti*-2,3-dibromo-3-phenylpropanoic acid (**2a**), Et_3N and DMF for 1 min and subsequent microwave irradiation of the mixture in the presence of ethynylbenzene, $Pd(PPh_3)_4$, CuI and Et_3N for

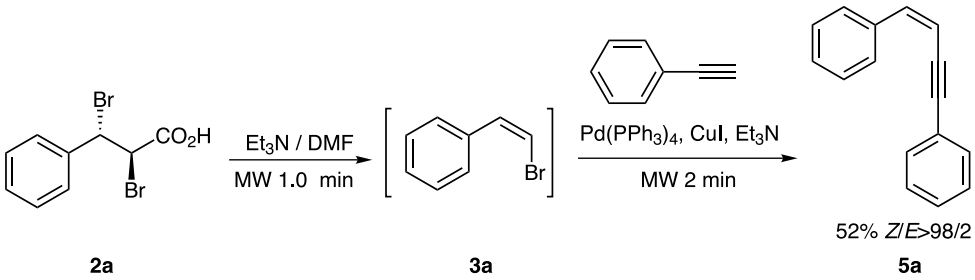
Table 2. One-pot synthesis of terminal alkynes by microwave irradiation of anti-3-aryl-2,3-dibromopropanoic acids

Entry	Dibromide (**2**)	Product (**4**)		MW1/MW2 (min)	Yield (%)[a]
1	**2a**		**4a**	0.5/1.0	88
2	**2g**		**4g**	1.0/1.0	95
3	**2h**		**4h**	1.0/1.0	93
4	**2i**		**4i**	1.0/1.0	90
5	**2m**		**4**m	1.0/1.0	99

[a] Isolated yields.



Scheme 6.



Scheme 7.

2 min gave the desired product **5a** in 52% yield (Scheme 7). The one-pot synthetic method is convenient for operation in comparison with a two-step strategy. The enynes could be obtained directly from *anti*-2,3-dibromo-3-arylpropanoic acid (**2**) without the isolation of (*Z*)-1-bromo-1-alkenes (**3**) which is an unstable intermediate. Furthermore, the two-step method does not have any advantage in yield over the one-pot method. By a two-step synthetic method, **3a** was obtained with a 95% isolated yield in the first step then subjected to the next coupling step. The enyne **5a** was obtained in 55% yield in the second step under the same condition as that of the one-pot method. Thus, the total yield of a two-step reaction was almost same as that of the one-pot reaction. Conjugated enynes are of great interest in organic synthesis.

3. Conclusions

In summary, we have developed a facile method for stereoselective synthesis of (*Z*)-1-bromo-1-alkenes from the corresponding *anti*-2,3-dibromoalkanoic acids using a Et_3N/DMF system, in which the use of microwave irradiation enables the preparation of (*Z*)-1-bromo-1-alkenes in high yields and high stereoselectivities within 0.2–1.0 min of reaction time. Additionally, we applied this transformation to a one-pot synthesis of terminal alkynes and enynes under microwave irradiation.

4. Experimental

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 $CDCl_3$. Chemical shifts are reported in ppm (δ) using $SiMe_4$ 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).

4.1. General procedure for the preparation of *trans*-α,β-unsaturated carboxylic acids (1)

Acids (**1a–c**, **1e–l**, **1n–s**) were commercially available. Acids (**1d**, **1m**, **1t** and **1u**) were prepared according to the procedure reported in the literature.[10–12] The physical data of **1d**, **1m**, **1t** and **1u** are shown below.

4.1.1. 4-Heptyloxy-*trans*-cinnamic acid (1d). Mp 148 °C (AcOH) (lit.[10] 148 °C); IR (nujol) 1795, 1573, 723 cm^{-1}; ^{1}H NMR ($CDCl_3$+d_6-DMSO) δ 0.89 (3H, t, J=6.6 Hz), 1.30–1.47 (8H, m), 1.78 (2H, tq, J=6.6 Hz), 3.96 (2H, t, J=6.6 Hz), 6.29 (1H, d, J=15.8 Hz), 6.88 (2H, d, J=8.6 Hz), 7.46 (2H, d, J=8.6 Hz), 7.64 (1H, d, J=15.8 Hz); ^{13}C NMR δ 13.89, 22.39, 25.75, 28.82, 28.93, 31.55, 67.92, 114.61, 115.65, 126.75, 129.52, 144.54, 160.73, 169.45.

4.1.2. 4-Methoxycarbonylcinnamic acid (1m). Mp 246–247 °C (H_2O–MeOH); IR (nujol) 1717, 1687, 1282 cm^{-1}; ^{1}H NMR ($CDCl_3$+d_6-DMSO) δ 3.92 (3H, s), 6.51 (1H, d, J=16.1 Hz), 7.60 (2H, d, J=8.2 Hz), 7.65 (1H, d, J=16.1 Hz), 8.03 (2H, d, J=8.2 Hz); ^{13}C NMR δ 51.39, 120.71, 127.04, 129.16, 130.24, 138.00, 142.01, 165.44, 167.16; EIMS *m/z* 206 (M^+, 38), 191 (20), 175 (100), 147 (32); HRMS calcd for $C_{11}H_{10}O_4$. *m/z* 206.0579. Found *m/z* 206.0579.

4.1.3. *trans*-3-Cyclohexylacrylic acid (1t). Mp 57–58 °C (hexane) (lit.[11] 58–59 °C); IR (nujol) 1774, 1695, 985 cm^{-1}; ^{1}H NMR δ 1.07–1.48 (5H, m), 1.66–1.96 (5H, m), 2.10–2.21 (1H, m), 5.77 (1H, d, J=15.8 Hz), 7.03 (1H, dd, J=15.8, J=6.6 Hz); EIMS *m/z* 154 (M^+, 26), 82 (88), 67 (100); ^{13}C NMR δ 25.60, 25.84, 31.48, 40.48, 118.27, 157.16, 172.83.

4.1.4. *trans*-Dec-2-enoic acid (1u). Bp 98 °C/0.07 mm Hg (lit.[12] 98 °C/0.07 mm Hg); IR (neat) 1774, 1695, 981 cm^{-1}; ^{1}H NMR δ 0.88 (3H, t, J=6.9 Hz), 1.28–1.64 (10H, m), 2.18–2.26 (2H, m), 5.82 (1H, d, J=15.8 Hz), 7.03–7.14 (1H, m); ^{13}C NMR δ 13.98, 22.57, 27.83, 29.00, 29.05, 31.68, 32.57, 120.61, 152.45, 172.41.

4.2. General procedure for the preparation of *anti*-2,3-dibromoalkanoic acids (2)

anti-2,3-Dibromoalkanoic acids (**2a–u**) were prepared according to the previous described procedure.[7i,7j]

4.2.1. *anti*-2,3-Dibromo-3-phenylpropanoic acid (2a). Mp 197–198 °C ($CHCl_3$) (lit.[13] 196–198 °C); ^{1}H NMR δ 4.88 (1H, d, J=11.5 Hz), 5.33 (1H, d, J=11.5 Hz), 7.38–7.43 (5H, m).

4.2.2. *anti*-2,3-Dibromo-3-(4-methylphenyl)propanoic acid (2b). Mp 191–192 °C ($CHCl_3$) (lit.[7i] 192 °C); ^{1}H NMR δ 2.35 (3H, s) 4.88 (1H, d, J=11.5 Hz), 5.32 (1H, d,

J=11.5 Hz), 7.20 (2H, d, J=8.0 Hz), 7.30 (2H, d, J=8.0 Hz).

4.2.3. *anti*-2,3-Dibromo-3-(4-methoxyphenyl)propanoic acid (2c). Mp 155–156 °C ($CHCl_3$) (lit.[7i] 155–156 °C); ^{1}H NMR δ 3.83 (3H, s), 4.86 (1H, d, J=11.9 Hz), 5.34 (1H, d, J=11.9 Hz), 6.92 (2H, d, J=8.6 Hz), 7.34 (2H, d, J=8.6 Hz).

4.2.4. *anti*-2,3-Dibromo-3-(4-heptyloxyphenyl)propanoic acid (2d). Mp 83–84 °C (hexane); IR (film) 1717, 1609, 1514 cm^{-1}; ^{1}H NMR δ 0.89 (3H, t), 1.31–1.48 (8H, m), 1.77 (2H, dd, J=6.6 Hz), 3.97 (2H, t, J=6.6 Hz), 4.88 (1H, d, J=11.5 Hz), 5.34 (1H, d, J=11.5 Hz), 6.90 (2H, d, J=8.6 Hz), 7.33 (2H, d, J=8.6 Hz); ^{13}C NMR δ 14.07, 22.59, 25.96, 29.02, 29.16, 31.75, 46.74, 50.46, 68.10, 114.79, 128.91, 129.32, 159.91, 173.35; EIMS m/z 422 (($M+2)^+$, 3), 420 (M^+, 5), 198 (50), 107 (100); HRMS calcd for $C_{16}H_{22}^{79}Br_2O_3$. m/z 419.9936. Found m/z 419.9919. Anal. Calcd for $C_{16}H_{22}Br_2O_3$: C, 45.52, H, 5.25, Br, 37.86. Found: C, 45.50, H, 5.21, Br, 37.88.

4.2.5. *anti*-2,3-Dibromo-3-(3,4-methylenedioxyphenyl)-propanoic acid (2e).[14] Mp 143–144 °C ($CHCl_3$); ^{1}H NMR δ 4.81 (1H, d, J=11.8 Hz), 5.28 (1H, d, J=11.8 Hz), 6.01 (2H, s), 6.77–6.90 (3H, m).

4.2.6. *anti*-2,3-Dibromo-3-(3,4,5-trimethoxyphenyl)propanoic acid (2f). Mp 154–155 °C (benzene–hexane) (lit.[15] 153–155 °C); ^{1}H NMR δ 3.86 (3H, s), 3.88 (3H×2, s), 4.78 (1H, d, J=11.5 Hz), 5.29 (1H, d, J=11.5 Hz), 6.63 (2H, s).

4.2.7. *anti*-2,3-Dibromo-3-(4-bromophenyl)propanoic acid (2g). Mp 191–192 °C (EtOH) (lit.[7i] 192 °C); ^{1}H NMR δ 4.84 (1H, d, J=11.5 Hz), 5.28 (1H, d, J=11.5 Hz), 7.29 (2H, d, J=8.6 Hz), 7.54 (2H, d, J=8.6 Hz).

4.2.8. *anti*-2,3-Dibromo-3-(4-chlorophenyl)propanoic acid (2h). Mp 194–195 °C (acetone–hexane) (lit.[16] 194–195 °C); IR (nujol) 1719, 721 cm^{-1}; ^{1}H NMR δ 4.82 (1H, d, J=11.5 Hz), 5.30 (1H, d, J=11.5 Hz), 7.20–7.40 (4H, m).

4.2.9. *anti*-2,3-Dibromo-3-(2-chlorophenyl)propanoic acid (2i). Mp 175–176 °C (acetone–hexane) (lit.[17] 175–176 °C); ^{1}H NMR δ 4.98 (1H, d, J=11.5 Hz), 5.92 (1H, d, J=11.5 Hz), 7.28–7.51 (4H, m); ^{13}C NMR δ 44.68, 45.01, 127.68, 130.25, 130.47, 134.05, 134.84, 173.06.

4.2.10. *anti*-2,3-Dibromo-3-(2,6-dichlorophenyl)propanoic acid (2j). Mp 193–194 °C (acetone–hexane) (lit.[17] 193–194 °C); ^{1}H NMR δ 5.69 (1H, d, J=11.8 Hz), 6.37 (1H, d, J=11.8 Hz), 7.25–7.28 (1H, m), 7.35–7.41 (2H, m); EIMS m/z 376 (($M+2)^+$, 8), 374 (M^+, 5), 297 (62), 181 (64), 171 (100); HRMS calcd for $C_9H_6^{79}Br_2^{35}Cl_2O_2$. m/z 373.8111. Found m/z 373.8124.

4.2.11. *anti*-2,3-Dibromo-3-(4-fluorophenyl)propanoic acid (2k).[7i] Mp 191–192 °C ($CHCl_3$); IR (nujol) 1718, 1600, 1591, 1509 cm^{-1}; ^{1}H NMR δ 4.83 (1H, d, J=11.5 Hz), 5.32 (1H, d, J=11.5 Hz), 7.10 (2H, m), 7.40 (2H, m); ^{13}C NMR δ 47.17, 49.68, 115.11 (d, J=22.0 Hz), 129.37 (d, J=8.6 Hz), 133.39 (d, J=3.7 Hz), 161.95 (d, J=249.1 Hz), 168.64; EIMS m/z 328 (($M+2)^+$, 8), 326 (M^+, 17), 245 (43), 121 (100); HRMS calcd for $C_9H_7^{79}Br^{81}Br FO_2$. m/z 325.8777. Found m/z 325.8768.

4.2.12. *anti*-2,3-Dibromo-3-(3-fluorophenyl)propanoic acid (2l).[7i] Mp 196–197 °C ($CHCl_3$); IR (nujol) 1716, 1591, 1146 cm^{-1}; ^{1}H NMR δ 4.92 (1H, d, J=11.5 Hz), 5.38 (1H, d, J=11.5 Hz), 7.06–7.75 (4H, m); ^{13}C NMR δ 46.86, 49.32, 113.98 (d, J=22.0 Hz), 114.92 (d, J=20.7 Hz), 123.02 (d, J=3.6 Hz), 129.32 (d, J=7.3 Hz), 139.60 (d, J=7.1 Hz), 161.25 (d, J=246.5 Hz), 168.20; EIMS m/z 326 (($M+2)^+$, 35), 324 (M^+, 20), 245 (42), 121 (100); HRMS calcd for $C_9H_7^{79}Br^{81}Br FO_2$. m/z 323.8796. Found m/z 323.8796.

4.2.13. *anti*-2,3-Dibromo-3-(4-methoxycarbonylphenyl)-propanoic acid (2m). Mp 208–209 °C (acetone–hexane); IR (film) 1718, 1508, 1436 cm^{-1}; ^{1}H NMR δ 3.92 (3H, s), 4.79 (1H, d, J=11.5 Hz), 5.37 (1H, d, J=11.5 Hz), 7.48 (2H, d, J=8.2 Hz), 8.06 (2H, d, J=8.2 Hz); ^{13}C NMR δ 46.92, 49.63, 52.20, 128.10, 130.00, 130.71, 130.71, 142.64, 166.25, 169.30; EIMS m/z 366 (($M+2)^+$, 13), 364 (M^+, 10), 285 (45), 175 (100); HRMS calcd for $C_{11}H_{10}^{79}Br_2O_4$. m/z 363.8946. Found m/z 363.8942. Anal. Calcd for $C_{11}H_{10}Br_2O_4$: C, 36.10, H, 2.75, Br, 43.66. Found: C, 36.05, H, 2.78, Br, 43.70.

4.2.14. *anti*-2,3-Dibromo-3-(4-nitrophenyl)propanoic acid (2n). Mp 216–217 °C (AcOH) (lit.,[18] 216–217 °C); IR (nujol) 1715, 1515, 1366 cm^{-1}; ^{1}H NMR ($CDCl_3$+d_6-DMSO) δ 4.85 (1H, d, J=11.8 Hz), 5.43 (1H, d, J=11.8 Hz), 7.65 (2H, d, J=8.9 Hz), 8.25 (2H, d, J=8.9 Hz).

4.2.15. *anti*-2,3-Dibromo-3-(3-nitrophenyl)propanoic acid (2o). Mp 172–173 °C (AcOH) (lit.[7i] 172 °C); IR (film) 1709, 1680, 1541, 1356 cm^{-1}; ^{1}H NMR δ 4.86 (1H, d, J=11.8 Hz), 5.39 (1H, d, J=11.8 Hz), 7.61 (1H, t, J=7.9 Hz), 7.75 (1H, d, J=8.9 Hz), 8.26 (2H, dt, J=8.9, 7.9 Hz).

4.2.16. *anti*-2,3-Dibromo-3-(2-nitrophenyl)propanoic acid (2p). Mp 179–180 °C (benzene) (lit.[7i] 180 °C); IR (nujol) 1711, 1540, 1351 cm^{-1}; ^{1}H NMR ($CDCl_3$+d_6-DMSO) δ 4.89 (1H, d, J=11.8 Hz), 6.10 (1H, d, J=11.8 Hz), 7.51–7.58 (1H, m), 7.73–7.79 (2H, m), 7.91 (1H, d, J=7.9 Hz).

4.2.17. *anti*-2,3-Dibromo-3-(2-naphthyl)propanoic acid (2q). Mp 178–180 °C (EtOH) (lit.[19] 177–180 °C); ^{1}H NMR ($CDCl_3$+d_6-DMSO) δ 4.98 (1H, d, J=11.8 Hz), 5.56 (1H, d, J=11.8 Hz), 7.50–7.56 (3H, m), 7.83–7.91 (4H, m); ^{13}C NMR δ 47.06, 51.23, 123.95, 126.02, 126.28, 126.99, 127.13, 127.43, 128.28, 132.00, 132.61, 134.46, 168.98.

4.2.18. *anti*-2,3-Dibromo-3-(1-naphthyl)propanoic acid (2r). Mp 181–182 °C (CCl_4) (lit.[20] 181–182 °C); ^{1}H NMR δ 5.14 (1H, d, J=11.5 Hz), 6.29 (1H, d, J=11.5 Hz), 7.44–7.93 (6H, m), 8.16 (1H, d, J=8.6 Hz).

4.2.19. *anti*-2,3-Dibromo-3-pyridin-3-yl-propanoic acid (2s).[7j] Mp 169–170 °C ($CHCl_3$); ^{1}H NMR (d_6-DMSO+$CDCl_3$) δ 5.35 (1H, d, J=11.5 Hz), 5.82 (1H, d, J=11.5 Hz), 7.36 (1H, m), 8.48 (1H, m), 8.76 (1H, d, J=3.9 Hz), 9.06 (1H, s); ^{13}C NMR δ 44.61, 45.83, 127.49, 130.51, 141.93, 142.15, 145.44, 168.31.

4.2.20. *anti*-2,3-Dibromo-3-cyclohexylpropanoic acid (2t).[21] Mp 158–159 °C (hexane); ^{1}H NMR δ 1.14–1.84 (10H, m), 1.94–2.03 (1H, m), 4.36 (1H, dd, J=11.8, J=2.3 Hz), 4.53 (1H, d, J=11.8 Hz); ^{13}C NMR δ 25.39, 25.51, 25.91, 25.95, 32.05, 38.95, 45.14, 59.01, 173.78.

4.2.21. *anti*-2,3-Dibromodecanoic acid (2u). Mp 44–45 °C (hexane) (lit.[7i] 45 °C); IR (nujol) 1728, 1285 cm^{-1}; ^{1}H NMR δ 0.89 (3H, t, J=3.9 Hz), 1.22–1.48 (10H, m), 1.50–1.64 (2H, m), 4.31–4.47 (2H, m).

4.3. General procedure for the preparation of (*Z*)-1-bromo-1-alkene (3)

A mixture of *anti*-2,3-dibromoalkanoic acid (1 mmol) and triethylamine (1.05 mmol) was added to 2 ml DMF. The mixture was kept inside a microwave oven operated at 2450 MHz (TOSHIBA, ER-V11, 200 W) and was irradiated for 0.2–1.0 min without any stirring. 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. After evaporation of the solvent, the crude product was purified by column chromatography on silica gel with EtOAc–hexane to give (*Z*)-1-bromo-1-alkene (**3**). Large scale reaction using 20 mmol of *anti*-2,3-dibromoalkanoic acid was also operated in the same way.

4.3.1. (*Z*)-β-Bromostyrene (3a).[4c] Colorless oil; IR (neat) 1616, 1491, 925, 771 cm^{-1}; ^{1}H NMR δ 6.43 (1H, d, J=8.2 Hz), 7.07 (1H, d, J=8.2 Hz), 731–7.40 (3H, m), 7.66–7.69 (2H, m); ^{13}C NMR δ 106.31, 128.17, 128.26, 128.93, 132.29, 134.83; EIMS *m/z* 184((M+2)$^+$, 92), 182 (M$^+$, 97), 103 (100), 77 (42); HRMS calcd for $C_8H_7^{79}Br$. *m/z* 181.9731. Found *m/z* 181.9734.

4.3.2. (*Z*)-β-Bromo-4-methylstyrene (3b).[4c] Colorless oil; IR (neat) 1606, 1510, 947 cm^{-1}; ^{1}H NMR δ 2.36 (3H, s), 6.36 (1H, d, J=7.9 Hz), 7.02 (1H, d, J=7.9 Hz), 7.17 (2H, d, J=7.9 Hz), 7.58 (2H, d, J=7.9 Hz); ^{13}C NMR δ 21.33, 105.40, 128.89, 132.14, 138.26; EIMS *m/z* 198 ((M+2)$^+$, 8),196 (M$^+$, 8), 121 (100), 91 (44); HRMS calcd for $C_9H_9^{79}Br$. *m/z* 195.9887. Found *m/z* 195.9890.

4.3.3. (*Z*/*E*)-β-Bromo-4-methoxystyrene (3c).[22] Colorless oil; IR (neat) 1608, 1574, 1511, 927 cm^{-1}; ^{1}H NMR δ 3.80 (0.75H, s. *E*), 3.82 (2.25H, s, *Z*), 6.30 (0.75H, d, J=8.2 Hz, *Z*), 6.60 (0.25H, d, J=13.9 Hz, *E*), 6.84 (0.5H, d, J=8.9 Hz, *E*), 6.88 (0.25H, d, J=13.9 Hz, *E*), 6.90 (1.50H, d, J=8.9 Hz, *Z*), 6.99 (0.75H, d, J=8.2 Hz, *Z*), 7.22 (0.50H, d, J=8.9 Hz, *E*), 7.67 (1.50H, d, J=8.9 Hz, *Z*); ^{13}C NMR δ 55.18, 104.09, 113.54, 114.12, 127.31, 130.44, 131.59, 159.44; EIMS *m/z* 214 ((M+2)$^+$, 99), 212 (M$^+$, 100), 197 (85), 133 (68); HRMS calcd for $C_9H_9^{79}BrO$. *m/z* 211.9837. Found *m/z* 211.9835.

4.3.4. (*Z*/*E*)-β-Bromo-4-heptyloxystyrene (3d). Colorless oil; IR (neat) 1607, 1510, 924 cm^{-1}; ^{1}H NMR δ 0.89 (3H, t, J=6.9 Hz), 1.20–1.47 (8H, m), 1.78 (2H, q, J=6.9 Hz), 3.96 (2H, t, J=6.6 Hz), 6.28 (0.90H, d, J=7.9 Hz, *Z*), 6.59 (0.10H, d, J=13.9 Hz, *E*), 6.86 (0.10H, d, J=13.9 Hz, *E*),6.88 (2H, d, J=8.6 Hz), 6.98 (0.90H, d, J=7.9 Hz, *Z*), 7.65 (2H, d, J=8.6 Hz); ^{13}C NMR δ 14.05, 22.57, 25.95, 29.02, 29.16, 31.73, 67.89, 103.81, 114.03, 114.61, 127.20, 130.37, 131.59, 159.03; EIMS *m/z* 298 ((M+2)$^+$, 99), 296 (M$^+$, 100), 200 (100), 198 (98), 119 (65); HRMS calcd for $C_{15}H_{21}^{79}BrO$. *m/z* 296.0776. Found *m/z* 296.0757. Anal. Calcd for $C_{15}H_{21}BrO$: C, 60.61, H, 7.12, Br, 26.88. Found: C, 60.52, H, 7.08, Br, 26.93.

4.3.5. (*Z*)-β-Bromo-3,4-methylenedioxystyrene (3e).[14] Colorless oil; IR (neat) 1611, 1503, 1489, 965, 940 cm^{-1}; ^{1}H NMR δ 5.98 (2H, s), 6.29 (1H, d, J=7.9 Hz), 6.81 (1H, d, J=7.9 Hz), 6.95 (1H, d, J=8.2 Hz), 7.02–7.10 (1H, m), 7.38 (1H, d, J=1.3 Hz); ^{13}C NMR δ 101.16, 104.50, 108.05, 108.66, 123.78, 128.87, 131.64, 147.34, 147.45; EIMS *m/z* 228 ((M+2)$^+$, 99), 226 (M$^+$, 100), 149 (97); HRMS calcd for $C_9H_7^{79}BrO_2$. *m/z* 225.9630. Found *m/z* 225.9627.

4.3.6. (*Z*/*E*)-β-Bromo-3,4,5-trimethoxystyrene (3f).[23] Colorless oil; IR (neat) 1615, 1581, 970 cm^{-1}; ^{1}H NMR δ 3.84 (0.54H, s, *E*), 3.86 (1.08H, s, *E*), 3.87 (2.46H, s, *Z*), 3.88 (4.92H, s, *Z*), 6.37 (0.82H, d, J=8.2 Hz, *Z*), 6.51 (0.36H, s, *E*), 6.69 (0.18H, d, J=13.9 Hz, *E*), 6.97–7.05 (2.64H, m); ^{13}C NMR δ 55.99, 60.72, 103.12, 105.44, 106.20, 130.15, 131.89, 152.74; EIMS *m/z* 274 ((M+2)$^+$, 100), 272 (M$^+$, 100), 259 (96), 229 (75); HRMS calcd for $C_{11}H_{13}^{79}BrO_3$. *m/z* 272.0048. Found *m/z* 272.0044.

4.3.7. (*Z*)-β-Bromo-4-bromostyrene (3g).[7i] Colorless oil; IR (neat) 1612, 1587, 1486, 1010 cm^{-1}; ^{1}H NMR δ 6.45 (1H, d, J=8.2 Hz), 6.98 (1H, d, J=8.2 Hz), 7.48 (2H, d, J=8.6 Hz), 7.54 (2H, d, J=8.6 Hz); ^{13}C NMR δ 107.26, 122.24, 130.44, 131.21, 131.35, 133.71; EIMS *m/z* 264 ((M+4)$^+$, 8), 262 ((M+2)$^+$, 100), 260 (M$^+$, 51), 181 (31), 102 (55); HRMS calcd for $C_8H_6^{79}Br_2$. *m/z* 259.8836. Found *m/z* 259.8839.

4.3.8. (*Z*)-β-Bromo-4-chlorostyrene (3h).[16] Colorless oil; IR (neat) 1614, 1589, 1490, 1014, 946, 720 cm^{-1}; ^{1}H NMR δ 6.45 (1H, d, J=7.9 Hz), 7.12 (1H, d, J=7.9 Hz), 7.34 (2H, d, J=8.2 Hz), 7.62 (2H, d, J=8.2 Hz); ^{13}C NMR δ 107.17, 128.44, 130.22, 131.20, 133.31, 134.01; EIMS *m/z* 220 ((M+4)$^+$, 43), 218 ((M+2)$^+$, 43), 216 (M$^+$, 30), 195 (100), 139 (28), 137 (60), 102 (40), 101 (45), 75 (31); HRMS calcd for $C_8H_6^{79}Br^{35}Cl$. *m/z* 215.9341. Found *m/z* 215.9335.

4.3.9. (*Z*)-β-Bromo-2-chlorostyrene (3i). Colorless oil; IR (neat) 1619, 1593, 1468, 1435, 946 cm^{-1}; ^{1}H NMR δ 6.59 (1H, d, J=8.2 Hz), 7.23–7.31 (3H, m), 7.37–7.44 (1H, m), 7.80–7.84 (1H, m); ^{13}C NMR δ 109.34, 126.20, 129.38, 129.90, 130.22, 133.24, 133.46; EIMS *m/z* 220 ((M+4)$^+$, 11), 218 ((M+2)$^+$, 42), 216 (M$^+$, 32), 137 (100), 101 (52); HRMS calcd for $C_8H_6^{79}Br^{35}Cl$. *m/z* 215.9341. Found *m/z* 215.9322. Anal. Calcd for C_8H_6BrCl: C, 44.18, H, 2.78, Br, 36.74, Cl, 16.30. Found: C, 44.42, H, 2.90, Br, 36.11, Cl, 16.02.

4.3.10. (*Z*/*E*)-β-Bromo-2,6-dichlorostyrene (3j). Colorless oil; IR (film) 1698, 1558, 1429, 978 cm^{-1}; ^{1}H NMR δ 6.64 (0.15H, d, J=14.5 Hz, *E*), 6.74 (0.85H, d, J=7.6 Hz, *Z*), 6.97 (0.85H, d, J=7.6 Hz, *Z*), 7.05 (0.15H, d, J=14.5 Hz,

E); 7.15–7.30 (1H, m), 7.31–7.39 (2H, m); ^{13}C NMR δ 114.09, 127.85, 129.38, 129.47, 133.65, 134.28; EIMS *m/z* 254 ($(M+4)^+$, 18), 252 ($(M+2)^+$, 35), 250 (M^+, 24), 181 (100), 137 (52); HRMS calcd for $C_8H_5^{79}Br^{35}Cl_2$. *m/z* 249.8952. Found *m/z* 249.8954. Anal. Calcd for $C_8H_5BrCl_2$: C, 38.14, H, 2.00, Br, 31.72, Cl, 28.14. Found: C, 38.10, H, 2.02, Br, 31.75, Cl, 28.18.

4.3.11. (*Z*)-β-Bromo-4-fluorostyrene (3k).[24] Colorless oil; IR (neat) 1602, 1506, 1327, 1237 cm^{-1}; ^{1}H NMR δ 6.38 (1H, d, J=8.2 Hz), 6.97–7.07 (3H, m), 7.61–7.67 (2H, m); ^{13}C NMR δ 106.12, 115.16 (d, J=21.9 Hz), 130.75 (d, J=8.6 Hz), 130.93 (d, J=3.6 Hz), 131.14, 162.30 (d, J=249.1 Hz); EIMS *m/z* 202 ($(M+2)^+$, 92), 200 (M^+, 95), 121 (100), 101 (65); HRMS calcd for $C_8H_6^{79}BrF$. *m/z* 199.9637. Found *m/z* 199.9637.

4.3.12. (*Z*)-β-Bromo-3-fluorostyrene (3l).[24] Colorless oil; IR (neat) 1609, 1582, 950 cm^{-1}; ^{1}H NMR δ 6.47 (1H, d, J=8.2 Hz), 6.98–7.03 (2H, m), 7.27–7.49 (3H, m); ^{13}C NMR δ 107.70, 115.19 (d, J=20.8 Hz), 115.50 (d, J=21.9 Hz), 148.89 (d, J=3.7 Hz), 129.67 (d, J=8.5 Hz), 131.24 (d, J=2.4 Hz), 136.89 (d, J=7.3 Hz), 162.45 (d, J=245.4 Hz); EIMS *m/z* 202 ($(M+2)^+$, 77), 200 (M^+, 80), 121 (100), 101 (62); HRMS calcd for $C_8H_6^{79}BrF$. *m/z* 199.9637. Found *m/z* 199.9643.

4.3.13. (*Z*)-Methyl-4-(β-bromovinyl)benzoate (3m). Mp 43–44 °C (hexane); IR (film) 1722, 1609, 1565, 967 cm^{-1}; ^{1}H NMR δ 3.93 (3H, m), 7.56 (1H, d, J=8.2 Hz), 7.12 (1H, d, J=8.2 Hz), 7.74 (2H, d, J=8.6 Hz), 8.04 (2H, d, J=8.6 Hz); ^{13}C NMR δ 52.167, 108.73, 128.84, 129.47, 129.59, 131.61, 139.30, 166.68; EIMS *m/z* 242 ($(M+2)^+$, 47), 240 (M^+, 48), 209 (37), 211 (98), 209 (99), 183 (73), 181 (85), 102 (68); HRMS calcd for $C_{10}H_9^{79}BrO_2$. *m/z* 239.9786. Found *m/z* 239.9790. Anal. Calcd for $C_{10}H_9BrO_2$: C, 49.82, H, 3.76, Br, 33.14. Found: C, 49.73, H, 3.85, Br, 33.17.

4.3.14. (*Z*)-β-Bromo-4-nitrostyrene (3n).[7i] Colorless oil; IR (film) 1594, 1509, 1341, 856 cm^{-1}; ^{1}H NMR δ 6.68 (1H, d, J=8.2 Hz), 7.15 (1H, d, J=8.2 Hz), 7.83 (2H, d, J=8.9 Hz), 8.24 (2H, d, J=8.9 Hz); ^{13}C NMR δ 110.75, 123.52, 129.66, 130.65, 141.25; EIMS *m/z* 229 ($(M+2)^+$, 100), 227 (M^+, 100), 182 (60), 181 (61), 102 (81); HRMS calcd for $C_8H_6^{79}BrNO_2$. *m/z* 226.9582. Found *m/z* 226.9584.

4.3.15. (*Z*)-β-Bromo-3-nitrostyrene (3o).[7i] Colorless oil; IR (neat) 1611, 1592, 1574, 1532, 1351, 924 cm^{-1}; ^{1}H NMR δ 6.64 (1H, d, J=8.2 Hz), 7.14 (1H, d, J=8.2 Hz), 7.56 (1H, t, J=7.9 Hz), 7.98 (1H, d, J=7.9 Hz), 8.17 (1H, m), 8.55 (1H, s); ^{13}C NMR δ 109.77, 122.87, 123.59, 129.20, 130.27, 134.71, 136.42, 148.07; EIMS *m/z* 229 ($(M+2)^+$, 100), 227 (M^+, 100), 182 (80), 181 (80), 102 (71); HRMS calcd for $C_8H_6^{79}BrNO_2$. *m/z* 226.9582. Found *m/z* 226.9594.

4.3.16. (*Z*)-β-Bromo-2-nitrostyrene (3p).[7i] Colorless oil; IR (film) 1604, 1571, 1524, 1345, 960 cm^{-1}; ^{1}H NMR δ 6.62 (1H, d, J=7.9 Hz), 7.45–7.60 (2H, m), 7.62–7.71 (2H, m), 8.09–8.12 (1H, m); ^{13}C NMR δ 110.19, 124.71, 129.00, 130.19, 130.80, 131.75, 133.15, 147.38; EIMS *m/z* 148 (M^+ − Br, 46), 102 (32), 92 (100).

4.3.17. (*Z*)-2-(β-Bromovinyl)naphthalene (3q).[4c] Colorless oil; IR (film) 1615, 1592, 929 cm^{-1}; ^{1}H NMR δ 6.52 (1H, d, J=7.9 Hz), 7.23 (1H, d, J=7.9 Hz), 7.47–7.51 (2H, m), 7.80–7.85 (4H, m), 8.15 (1H, s); ^{13}C NMR δ 106.66, 126.27, 126.41, 126.47, 127.64, 127.71, 128.28, 128.57, 132.38, 132.99, 133.04, 136.90; EIMS *m/z* 234 ($(M+2)^+$, 100), 232 (M^+, 98), 153 (88), 127 (58); HRMS calcd for $C_{12}H_9^{79}Br$. *m/z* 231.9888. Found *m/z* 231.9884.

4.3.18. (*Z*/*E*)-1-(β-Bromovinyl)naphthalene (3r).[4c] Colorless oil; IR (neat) 1605, 1590, 935 cm^{-1}; ^{1}H NMR δ 6.73 (0.65H, d, J=7.9 Hz, *Z*), 6.76 (0.35H, d, J=13.5 Hz, *E*), 7.39–7.59 (4H, m), 7.70 (0.65H, d, J=7.2 Hz, *Z*), 7.79–7.92 (3H, m), 8.01–8.04 (0.35H, m, *E*); ^{13}C NMR δ 108.46 (*E*), 109.95 (*Z*), 123.61 (*E*+*Z*), 124.11 (*Z*), 124.15 (*E*), 125.08 (*Z*), 125.46 (*E*), 125.89 (*Z*), 126.03 (*E*), 126.18 (*Z*+*E*), 126.39 (*E*), 126.72 (*Z*), 128.44 (*Z*), 128.50 (*E*), 128.69 (*E*), 130.45 (*E*), 131.01 (*Z*), 131.30 (*Z*), 132.11 (*Z*), 133.42 (*Z*), 133.50 (*E*), 134.91 (*E*); EIMS *m/z* 234 ($(M+2)^+$, 92), 232 (M^+, 93), 153 (100), 126 (75); HRMS calcd for $C_{12}H_9^{79}Br$. *m/z* 231.9894. Found *m/z* 231.9893.

4.3.19. (*Z*)-3-(β-Bromovinyl)pyridine (3s).[4c] Colorless oil; IR (neat) 1617, 1567, 954 cm^{-1}; ^{1}H NMR δ 6.57 (1H, d, J=8.2 Hz), 7.05 (1H, d, J=8.2 Hz), 7.28 (1H, dd, J=7.9, 4.3 Hz), 8.13 (1H, d, J=7.9 Hz), 8.53 (1H, d, J=4.3 Hz), 8.76 (1H, s); ^{13}C NMR δ 109.21, 123.07, 129.14, 130.96, 135.50, 149.07, 150.27; EIMS *m/z* 185 ($(M+2)^+$, 96), 183 (M^+, 94), 104 (100), 77 (41); HRMS calcd for $C_7H_6^{79}BrN$. *m/z* 182.9684. Found *m/z* 182.9682.

4.3.20. (*Z*)-1-Bromo-2-cyclohexylethene (3t).[4c] Colorless oil; IR (neat) 1412, 1261, 929, 701 cm^{-1}; ^{1}H NMR δ 1.05–1.43 (5H, m), 1.61–1.73 (5H, m), 5.92 (1H, dd, J=6.9, 8.9 Hz), 6.04 (1H, dd, J=1.0 Hz, 6.9 Hz); ^{13}C NMR δ 25.55, 25.91, 31.57, 38.82, 105.42, 140.16; EIMS *m/z* 190 ($(M+2)^+$, 7), 188 (M^+, 8), 109 (100), 67 (94); HRMS calcd for $C_8H_{13}^{79}Br$. *m/z* 188.0201. Found *m/z* 188.0190.

4.3.21. (*Z*)-1-Bromonon-1-ene (3u).[7i] Colorless oil; IR (neat) 1623, 939 cm^{-1}; ^{1}H NMR δ 0.88 (3H, t, J=6.6 Hz), 1.21–1.44 (10H, m), 2.18 (2H, q, J=6.9 Hz), 6.04–6.15 (2H, m); ^{13}C NMR δ 14.09, 22.64, 28.14, 29.09, 29.68, 31.79, 107.49, 135.04; EIMS *m/z* 206 ($(M+2)^+$, 30), 204 (M^+, 31), 119 (20), 69 (82), 43 (100); HRMS calcd for $C_9H_{17}^{79}Br$. *m/z* 204.0514. Found *m/z* 204.0522.

4.4. General procedure for the one-pot synthesis of terminal alkynes (4)

A mixture of *anti*-3-aryl-2,3-dibromopropanoic acids (**2**, 1.0 mmol) and triethylamine (1.05 mmol) was added to 2 ml DMF. The mixture was kept inside a microwave oven operated at 2450 MHz (TOSHIBA, ER-V11, 200 W) and was irradiated for 0.5–1.0 min without any stirring. The reaction mixture was then removed from the oven and cooled to room temperature. DBU (2.0 mmol) was added to the reaction mixture and the mixture was also irradiated for 1.0 min without any stirring. 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. After evaporation of the

solvent, the crude product was purified by column chromatography on silica gel with EtOAc–hexane to give terminal alkynes (**4**).

4.4.1. Ethynylbenzene (4a).[25] Colorless oil; IR (neat) 3290, 2108, 1599, 1575, 1489, 1445, 1071, 1026 cm^{-1}; ^1H NMR δ 3.05 (1H, s), 7.27–7.31 (3H, m), 7.46–7.49 (2H, m); ^{13}C NMR δ 77.18, 83.59, 122.06, 128.24, 128.71, 132.05.

4.4.2. 4-Bromo-1-ethynylbenzene (4g).[26] Mp 63.5–64.5 °C (hexane); IR (nujol) 3312, 2110, 1485, 1071, 825 cm^{-1}; ^1H NMR δ 3.12 (1H, s), 7.35 (2H, d, $J=8.5$ Hz), 7.46 (2H, d, $J=8.5$ Hz); ^{13}C NMR δ 78.33, 82.55, 121.04, 123.12, 131.59, 133.54; EIMS *m/z* 182 ($(M+2)^+$, 90), 180 (M^+, 100), 101 (92), 75 (52); HRMS calcd for $C_8H_5^{79}Br$. *m/z* 179.9575. Found *m/z* 179.9575.

4.4.3. 4-Chloro-1-ethynylbenzene (4h).[27] Mp 45–46 °C (hexane); IR (nujol) 3272, 2110 cm^{-1}; ^1H NMR δ 3.10 (1H, s), 7.29 (2H, d, $J=8.5$ Hz), 7.41 (2H, d, $J=8.5$ Hz); ^{13}C NMR δ 78.15, 82.49, 120.57, 128.65, 133.33, 134.90; EIMS *m/z* 138 ($(M+2)^+$, 38), 136 (M^+, 100), 101 (40), 75 (37); HRMS calcd for C_8H_5Cl. *m/z* 136.0080. Found *m/z* 136.0077.

4.4.4. 2-Chloro-1-ethynylbenzene (4i).[28] Colorless oil; IR (neat) 3312, 2114, 1485, 1071, 825 cm^{-1}; ^1H NMR δ 3.12 (1H, s), 7.35 (2H, d, $J=8.5$ Hz), 7.46 (2H, d, $J=8.5$ Hz); ^{13}C NMR δ 78.33, 82.55, 121.04, 123.12, 131.59, 133.54; EIMS *m/z* 138 ($(M+2)^+$, 35), 136 (M^+, 100), 101 (38), 75 (34); HRMS calcd for C_8H_5Cl. *m/z* 136.0080. Found *m/z* 136.0078.

4.4.5. Methyl 4-ethynylbenzoate (4m).[29] Mp 94–95 °C (hexane–EtOAc); IR (nujol) 2106, 1733, 1275 cm^{-1}; ^1H NMR δ 3.23 (1H, s), 3.92 (3H, s), 7.55 (2H, d, $J=8.5$ Hz), 7.98 (2H, d, $J=8.5$ Hz); ^{13}C NMR δ 52.25, 80.00, 82.77, 126.73, 129.43, 130.11, 132.05, 166.39; EIMS *m/z* 160 (M^+, 53), 129 (100), 101 (52); HRMS calcd for $C_{10}H_8O_2$. *m/z* 160.0524. Found *m/z* 160.0508.

4.5. General procedure for the one-pot synthesis of enyne (5a)

A mixture of *anti*-2,3-dibromo-3-phenylpropanoic acid (**2a**, 1.0 mmol) and triethylamine (1.05 mmol) was added to 2 ml DMF. The mixture was kept inside a microwave oven operated at 2450 MHz (TOSHIBA, ER-V11, 200 W) and was irradiated for 1.0 min without any stirring. The reaction mixture was then removed from the oven and cooled to room temperature. A mixture of ethynylbenzene (1.2 mmol), $Pd(PPh_3)_4$ (0.05 mmol), CuI (1.2 mmol) and Et_3N (2.0 mmol) was added to the reaction mixture and the mixture was kept inside a microwave oven and was irradiated for 2.0 min. 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. After evaporation of the solvent, the crude product was purified by column chromatography on silica gel with EtOAc–hexane to give (*Z*)-1,4-diphenyl-1-buten-3-yne (**5a**).

4.5.1. (*Z*)-1,4-diphenyl-1-buten-3-yne (5a).[30] Colorless oil; IR (neat) 3061, 3022, 2185, 1595, 1449 cm^{-1}; ^1H NMR δ 5.91 (1H, d, $J=12.0$ Hz), 6.69 (1H, d, $J=12.0$ Hz), 7.28–7.43 (10H, m); ^{13}C NMR δ 138.65, 136.53, 131.48, 128.75, 128.48, 128.38, 128.32, 128.28, 123.43, 107.36, 95.83, 88.23; EIMS *m/z* 204 (M^+, 31), 119 (20), 69 (82), 43 (100); HRMS calcd for $C_{16}H_{12}$. *m/z* 204.0939. Found *m/z* 204.0938.

Acknowledgements

This work was supported by a Grant-in-Aid for Exploratory Research (No. 13875171) from Japan Society for the Promotion of Science. We would like to thank S. Oka, M. Kiuchi, Y. Takihata and N. Hazama (Center for Instrumental Analysis, Hokkaido University) for their assistance in measurement of mass spectra.

References and notes

1. (a) Smithers, R. H. *J. Org. Chem.* **1978**, *43*, 2833–2838. (b) Matsumoto, M.; Kuroda, K. *Tetrahedron Lett.* **1980**, *21*, 4021–4024. (c) Stork, G.; Zhao, K. *Tetrahedron Lett.* **1989**, *30*, 2173–2174. (d) Zhang, X.-P.; Schlosser, M. *Tetrahedron Lett.* **1993**, *34*, 1925–1928.
2. (a) Zweifel, G.; Whitney, C. C. *J. Am. Chem. Soc.* **1967**, *89*, 2753–2754. (b) Brown, H. C.; Hanaoka, T.; Ravindran, N. *J. Am. Chem. Soc.* **1973**, *95*, 6456–6457. (c) Levy, A. B.; Talley, P.; Dunford, J. A. *Tetrahedron Lett.* **1977**, *40*, 3545–3548. (d) Miller, R. B.; McGarvey, G. *J. Org. Chem.* **1978**, *43*, 4424–4431. (e) Brown, H. C.; Bhat, N. G. *Tetrahedron Lett.* **1988**, *29*, 21–24. (f) Chabaud, L.; Landais, Y. *Tetrahedron Lett.* **2003**, *44*, 6995–6998.
3. (a) Hara, S.; Kato, T.; Suzuki, A. *Synthesis* **1983**, 1005–1006. (b) Brown, H. C.; Blue, C. D.; Nelson, D. J.; Bhat, N. G. *J. Org. Chem.* **1989**, *54*, 6064–6067. (c) Brown, H. C.; Subrahmanyam, C.; Hanaoka, T.; Ravindran, N.; Bowman, D. H.; Misumi, S.; Unni, M. K.; Somayaji, V.; Bhat, N. G. *J. Org. Chem.* **1989**, *54*, 6068–6075.
4. (a) Uenishi, J.; Kawahama, R.; Shiga, Y.; Yonemitsu, O. *Tetrahedron Lett.* **1996**, *37*, 6759–6762. (b) Uenishi, J.; Kawahama, R.; Yonemitsu, O.; Tsuji, J. *J. Org. Chem.* **1996**, *61*, 5716–5717. (c) Uenishi, J.; Kawahama, R.; Yonemitsu, O.; Tsuji, J. *J. Org. Chem.* **1998**, *63*, 8965–8975. (d) Uenishi, J.; Kawahama, R.; Yonemitsu, O.; Wada, A.; Ito, M. *Angew. Chem., Int. Ed.* **1998**, *37*, 320–323. (e) Defretin, J.; Saez, J.; Franck, X.; Hocquemiller, R.; Figadère, B. *Tetrahedron Lett.* **1999**, *40*, 4041–4044. (f) Tietze, L. F.; Petersen, S. *Eur. J. Org. Chem.* **2000**, 1827–1830. (g) Bosanc, T.; Wilcox, C. S. *Tetrahedron Lett.* **2001**, *42*, 4309–4312. (h) Rahman, S. N. A.; Sonoda, M.; Itahashi, K.; Tobe, Y. *Org. Lett.* **2003**, *5*, 3411–3414.
5. Moughamir, K.; Mezguedi, B.; Atmani, A.; Mestdagh, H.; Rolando, C. *Tetrahedron Lett.* **1999**, *40*, 59–62.
6. Concellón, J. M.; Bernad, P. L.; P.-Andrés, J. A. *Angew. Chem., Int. Ed.* **1999**, *38*, 2384–2386.
7. (a) Grovenstein, J. E.; Lee, D. E. *J. Am. Chem. Soc.* **1953**, *75*, 2639–2644. (b) Cristol, S. J.; Norris, W. P. *J. Am. Chem. Soc.* **1953**, *75*, 2645–2646. (c) Paquette, L. A.; Fristad, W. E.; Dime, D. S.; Bailey, T. R. *J. Org. Chem.* **1980**, *45*, 3017–3028.

(d) Murahashi, S.; Naota, T.; Tanigawa, Y. In *Organic Syntheses*; Wiley: New York, 1990; Collect Vol. VII; pp 172–175. (e) Fuller, C. E.; Walker, D. G. *J. Org. Chem.* **1991**, *56*, 4066–4067. (f) Mori, K.; Brevet, J.-L. *Synthesis* **1991**, 1125–1129. (g) Pinhey, J. T.; Stoermer, M. J. *J. Chem. Soc., Perkin Trans. 1* **1991**, 2455–2460. (h) Brevet, J.-C.; Mori, K. *Synthesis* **1992**, 1007–1012. (i) Matveeva, E. D.; Erin, A. S.; Kurz, A. L. *Russ. J. Org. Chem.* **1997**, *33*, 1065–1067. (j) Kim, S. H.; Wei, H.-X.; Willis, S.; Li, G. *Synth. Commun.* **1999**, *29*, 4179–4185.

8. For reviews, see (a) Abramovitch, R. A. *Org. Prep. Proc. Int.* **1991**, *23*, 683–711. (b) Caddick, S. *Tetrahedron* **1995**, *51*, 10403–10432. (c) Loupy, A.; Petit, A.; Hamelin, J.; Texier-Boullet, F.; Jacquault, P.; Mathé, D. *Synthesis* **1998**, 1213–1234. (d) Lidström, P.; Tierney, J.; Wathey, B.; Westman, J. *Tetrahedron* **2001**, *57*, 9225–9283. (e) Kidwai, M. *Pure Appl. Chem.* **2001**, *73*, 147–151. (f) Larhed, M.; Moberg, C.; Hallberg, A. *Acc. Chem. Res.* **2002**, *35*, 717–727. (g) Hter, M. N.; Ondruschka, B.; Bonrath, W.; Gun, A. *Green Chem.* **2004**, *6*, 128–141.
9. Kuang, C.; Senboku, H.; Tokuda, M. *Tetrahedron Lett.* **2001**, *42*, 3893–3896.
10. (a) Gray, G. W.; Jones, B. *J. Chem. Soc.* **1954**, 1467–1470. (b) Nakai, H.; Konno, M.; Kosuge, S.; Sakuyama, S.; Toda, M.; Arai, Y.; Obata, T.; Katsube, N.; Miyamoto, T.; Okegawa, T.; Kawasaki, A. *J. Med. Chem.* **1988**, *31*, 84–91.
11. Larock, R. C. *J. Org. Chem.* **1975**, *40*, 3237–3242.
12. Song, J.; Hesse, M. *Tetrahedron* **1993**, *49*, 6797–6804.
13. Barnes, R. A.; Neto, A. C. *J. Org. Chem.* **1970**, *35*, 4259.
14. Overman, L. E.; Shim, J. *J. Org. Chem.* **1993**, *58*, 4662–4672.
15. Kato, M.; Kido, F.; Wu, M.; Yoshikoshi, A. *Bull. Chem. Soc. Jpn.* **1974**, *47*, 1516–1521.
16. Loar, M. K.; Stille, J. K. *J. Am. Chem. Soc.* **1981**, *103*, 4174–4181.
17. Frank, P. D.; John, H. C. N. US 3470151, 1969.
18. Grob, C. A.; Pfaendler, H. R. *Helv. Chim. Acta* **1971**, *54*, 2060–2068.
19. Jensen, S.; Kjer, A.; Linholt, S. C. *Acta Chem. Scand.* **1952**, *6*, 180–188.
20. Al-Arab, M. M. *J. Chem. Eng. Data* **1985**, *30*, 493–495.
21. Sircar, S. S. G. *J. Chem. Soc.* **1928**, 54–57.
22. Vassilikogiannakis, G.; Hatzimarinaki, M.; Orfanopoulos, M. *J. Org. Chem.* **2000**, *65*, 8180–8187.
23. Herz, H.-G.; Queiroz, M. J. R. P.; Maas, G. *Synthesis* **1999**, 1013–1016.
24. Happer, D. A. R.; Steenson, B. E. *J. Chem. Soc., Perkin Trans. 2* **1988**, 19–24.
25. (a) Wang, Z.; Yin, J.; Campagna, S.; Pesti, J. A.; Fortunak, J. M. *J. Org. Chem.* **1999**, *64*, 6918–6920. (b) Wang, Z.; Campagna, S.; Yang, K.; Xu, G.; Pierce, M. E.; Fortunak, J. M.; Confalone, P. N. *J. Org. Chem.* **2000**, *65*, 1889–1891.
26. Pearson, D. L.; Tour, J. M. *J. Org. Chem.* **1997**, *62*, 1376–1387.
27. Roth, G. J.; Liepold, B.; Müller, S. G.; Bestmann, H. J. *Synthesis* **2004**, 59–62.
28. Villieras, J.; Perriot, P.; Normant, J. F. *Synthesis* **1975**, 458–460.
29. Negishi, E.; Kotora, M.; Xu, C. *J. Org. Chem.* **1997**, *62*, 8957–8960.
30. Galli, C.; Gentili, P.; Rappoport, Z. *J. Org. Chem.* **1994**, *59*, 6786–6795.