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Facile and stereoselective synthesis of (*E*)-vinyl bromides by microwave-induced reaction of 1,1-dibromoalkenes using a diethyl phosphonate/EtONa/EtOH system

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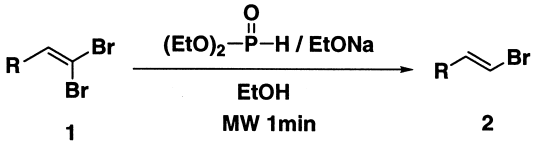
Abstract—(*E*)-Vinyl bromides were readily prepared from 1,1-dibromoalkenes by microwave irradiation within 1 min using a diethyl phosphonate/EtONa/EtOH system. This method utilizes cheap and environmentally friendly reagents, requires only a short reaction time, and gives (*E*)-vinyl bromides in high stereoselectivities and high yields.

1. Introduction

(*E*)-Vinyl bromides are extremely useful synthetic intermediates in organic synthesis. Their use as precursors of vinyl anions[1] and as coupling components in a wide range of transition metal-catalyzed coupling reactions[2] has stimulated a great deal of interests in their synthesis. Therefore, development of methods for their stereoselective synthesis is of considerable importance. There are many methods for preparation of (*E*)-vinyl bromides, but the reagents used in most cases are limited to organometallic compounds such as organoaluminium,[3] organoboron,[4] organosilicon,[5] geminal dichromium reagent,[6] organozinc reagent,[7] organolithium reagent,[7a,8] hydrozirconating reagent,[9] organotin reagent,[10] indium metal,[11] and Grignard reagent.[12] Methods using Hunsdiecker halodecarboxylation[13] and decarboxylation of cinnamic acid dibromides have also been reported.[14] In several procedures, however, these synthetic methods have several drawbacks, including complex procedures, long reaction times, low yields, limitation to arylvinyl halides carrying an electron-donating or electron-withdrawing group, and unfavorable ratios of *E*/*Z* isomers.

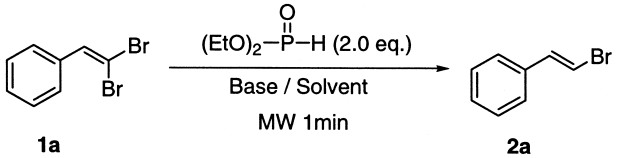


Scheme 1.

In 1981 Hirao et al. reported a procedure for the reduction of 1,1-dibromoalkenes to the corresponding (*E*)-vinyl bromides using diethyl phosphonate and triethylamine.[15] Almost two decades have passed since this initial report, and during this time little attention has been paid to this potentially valuable procedure.[16] More recently, Abbas et al.[17] have reported a procedure for the synthesis of terminal vinyl bromides from 1,1-dibromoalkenes and triethylamine by the use of DMF as a co-solvent in the Hirao reduction reaction. In the synthetic method of Abbas et al., long reaction times and use of excess dimethyl phosphonate and base were required, and the desired products were obtained in low yields.

Recently, the method of microwave irradiation to effect

Table 1. Transformation of 1,1-dibromo-2-phenylethene (**1a**) into β-bromostyrene (**2a**) under various conditions



Entry	Base (2.0 equiv.)	Solvent (5 ml)	Yield of **2a** (%)[a]	*E*/*Z*[b]
1	Et_3N	–	0	
2	Et_3N	DMF	35	94/6
3	Et_3N	CH_2Cl_2	0	
4	Et_3N	EtOH	0	
5	NaoAc	EtOH	0	
6	NaOH	EtOH	0	
7	NaH	EtOH	94	99.5/0.5
8	EtONa	EtOH	94	99.5/0.5

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

Keywords: (*E*)-vinyl bromide; 1,1-dibromoalkene; diethyl phosphonate; microwave irradiation.
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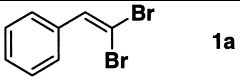
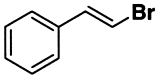
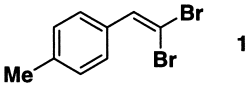
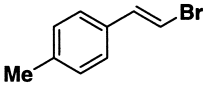
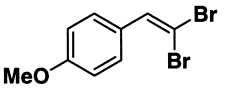
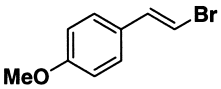
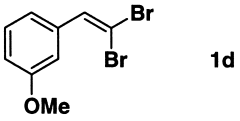
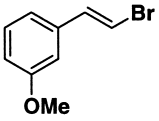
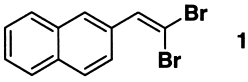
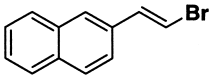
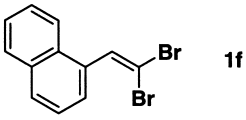
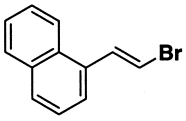
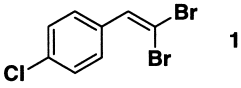
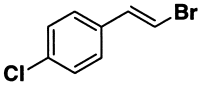
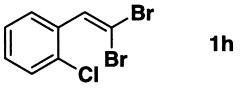
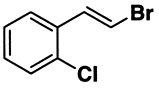
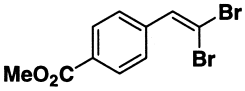
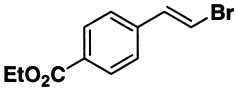
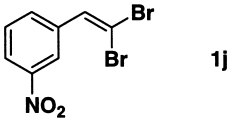
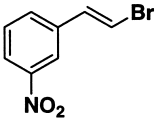
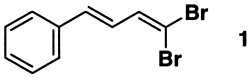
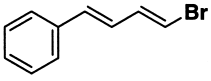
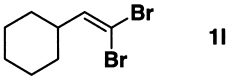
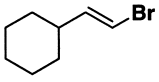
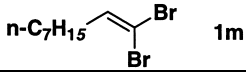
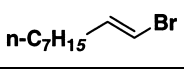
Table 2. Efficient synthesis of (*E*)-vinyl bromides (**2**) by microwave irradiation of 1,1-dibromoalkenes (**1**) in a diethyl phosphonate/EtONa/EtOH system

Entry	Dibromide	Product	Yeild of **2** (%)[a]	*E*/*Z*[b]
1	 **1a**	 **2a**	94	>99.5/0.5
2	 **1b**	 **2b**	98	98/2
3	 **1c**	 **2c**	98	94/6
4	 **1d**	 **2d**	99	96/4
5	 **1e**	 **2e**	93	>99/1
6	 **1f**	 **2f**	94	99.4/0.6
7	 **1g**	 **2g**	95	96/4
8	 **1h**	 **2h**	94	99.2/0.8
9[c]	 **1i**	 **2i**	93	>99.5/0.5
10	 **1j**	 **2j**	90	98.5/1.5
11	 **1k**	 **2k**	92	73/27
12	 **1l**	 **2l**	67	68/32
13	 **1m**	 **2m**	62	58/42

[a] Isolated yields.
[b] Isomer ratios were determined by ^{1}H NMR analysis.
[c] Ester exchange occurred in this case to give **2i** instead of methyl ester.

organic transformations has been used by organic chemists.[18] Remarkable reductions in reaction times, clean conditions and better yields have been reported in microwave-induced reactions. We have also reported microwave-induced reactions for the stereoselective synthesis of (*E*)-β-arylvinyl halides[19] and (*Z*)-vinyl bromides[20] from α,β-unsaturated carboxylic acids and their dibromides, respectively. During our recent study on the transformation of 1,1-dibromoalkenes into the corresponding (*E*)-vinyl bromides by Hirao reduction, we found that this reaction could produce high yields by microwave irradiation using a diethyl phosphonate/EtONa/EtOH system instead of diethyl phosphonate/triethylamine/DMF. Herein, we report a very simple, fast, and general method for highly efficient and stereoselective synthesis of (*E*)-vinyl bromides **2** from 1,1-dibromoalkenes **1** by the use of a diethyl phosphonate/EtONa/EtOH system and the use of microwave irradiation (Scheme 1).

2. Results and discussion

Various conditions were examined to optimize the yield and stereoselectivity of (*E*)-β-bromostyrene (**2a**). The results are summarized in Table 1. It was found that bases such as NEt_3, NaOAc, and NaOH were not effective in this reaction and that DMF and CH_2Cl_2 were less satisfactory as solvents than was EtOH. At this stage, the diethyl phosphonate/EtONa/EtOH system appears to be the best debromo reduction system. Under these conditions, (*E*)-β-bromostyrene (**2a**) was easily obtained by 1 min irradiation of **1a** in 94% yield (*E*/*Z*>99.5/0.5). It was confirmed that **2a** was obtained only in a 20% yield when a thermal reaction of **1a** using a diethyl phosphonate/EtONa/EtOH system was carried out under reflux conditions for 10 min without microwave irradiation.

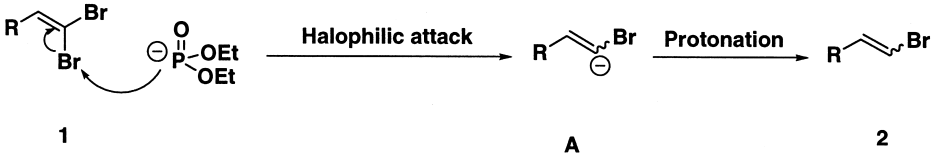
Microwave irradiation of various 1,1-dibromoalkenes **1** under the optimal conditions gave the corresponding (*E*)-vinyl bromides **2** in high yields and high stereoselectivities. The starting 1,1-dibromo-1-alkenes were easily prepared from the corresponding aldehydes with carbon tetrabromide and triphenylphosphine by the standard procedure.[21] Yields and stereoselectivites of **2** are shown in Table 2.

These results show that **2** was obtained in higher yields and in shorter reaction time by the microwave-irradiation method than by previous methods.[17] The present method could be used for the synthesis of both aromatic and aliphatic (*E*)-vinyl bromides. (*E*)-2-Aryl-1-bromo-1-alkenes carrying either an electron-donating or an electron-withdrawing group at the *ortho*, *meta*, and *para* positions (entries 2–4 and 7–10) were readily obtained in excellent yields and stereoselectivities. For example, the microwave irradiation of **1b**–**1d** with diethyl phosphonate/EtONa in EtOH for 1 min afforded **2b**–**2d** in 98–99% isolated yields. In addition, by using our microwave irradiation method, (*E*)-2-aryl-1-bromo-1-alkenes carrying electron-withdrawing groups at different positions of the aromatic ring (**2g**–**2j**) were also obtained stereoselectively in 90–95% yields (entries 7–10). (*E*)-β-Arylvinyl bromides having 1-(**2e**) or 2-naphthyl groups (**2f**) were obtained in high yields with excellent stereoselectivities. Microwave irradiation of alkyl-substituted 1,1-dibromoethenes **1l** and **1m** also gave the corresponding (*E*)-vinyl bromides **2l** and **2m** in 62 and 67% yields, respectively, with lower stereoselectivities. No remarkable improvement of the yields and stereoselectivities of **1m** was observed even if the microwave was irradiated for 2 min or if the reaction was carried out using 4 equiv. of diethyl phosphonate and EtONa. These yields of 62–67%, however, were higher than those obtained by previous methods.[17] Reduction of **1l** and **1m** with dimethyl phosphonate (4.5 equiv.) in DMF at 70°C for 16 h according to the previous method gave the corresponding vinyl bromides **2l** and **2m** in 8 and 22% yields, respectively.

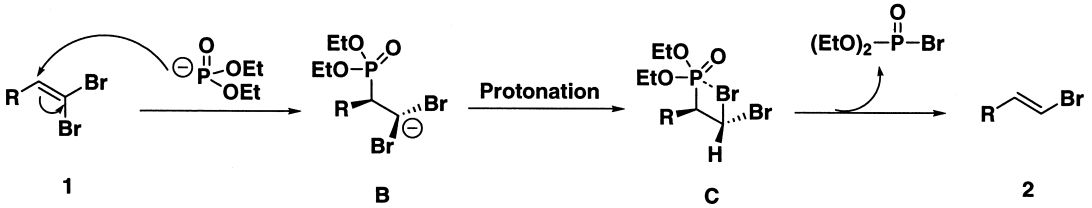
As to the reaction mechanism of Hirao reduction, halophilic attack of dialkyl phosphonate anion[22] on 1,1-dibromo-1-alkenes was suggested in the reduction of 1,1-dibromocyclopropanes (Scheme 2).[15] On the other hand, Abbas et al.[17] recently proposed two possible mechanisms that involve a vinyl anion intermediate and a Michael-type addition[23] (Schemes 2 and 3). We speculate that both of these mechanisms operate in our microwave-induced reactions. Firstly, the rection of diethyl phosphonate with a base gives $(EtO)_2PO^-$, and halophilic attack of $(EtO)_2PO^-$ to **1** would occur to give vinyl anion **A**, which would be protonated to give **2** (Scheme 2). In another pathway, Michael addition of $(EtO)_2PO^-$ to **1** would occur to give an intermediate **C**.[23] Elimination of $(EtO)_2POBr$ from **C** gives (*E*)-**2** stereoselectively (Scheme 3). In the case of alkyl-substituted 1,1-dibromoethenes, Michael addition of $(EtO)_2PO^-$ to **1** would be difficult to occur and, instead, halophilic attack to give **A** may be major pathways, which would result in lower selectivities of (*E*)-vinyl bromides.

3. Conclusions

We have developed a simple and efficient method for the preparation of (*E*)-vinyl bromides from the corresponding 1,1-dibromoalkenes using a diethyl phosphonate/EtONa/EtOH system, in which the use of microwave irradiation enabled (*E*)-vinyl bromides to be obtained in high yields and high stereoselectivities within 1 min. Our method using microwave irradiation and a diethyl phosphonate/EtONa/EtOH system is very useful because of its high efficiency and high stereoselectivity.



Scheme 2.



Scheme 3.

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 60N (100–210 μm, Kanto Chemical Co. Ltd).

1,1-Dibromo-1-alkenes (**1a**–**1m**) were prepared according to the previously described procedures.[20,24]

4.1. General procedure for the synthesis of (*E*)-vinyl bromides (2)

A mixture of sodium ethoxide (2 mmol), diethyl phosphonate (2 mmol), 1,1-dibromo-1-alkene **1** (1 mmol) and EtOH (5 ml) in a 100 ml Erlenmeyer flask was kept in a microwave oven operated at 2450 MHz (TOSHIBA, ER-V11, 200 watts) and was irradiated for 1 min. The reaction mixture was then removed from the oven and cooled to room temperature. Evaporation of the solvent under reduced pressure gave a crude product, which was subjected to silica gel column chromatography (eluted with hexane unless otherwise noted) to afford (*E*)-vinyl bromides **2**.

4.1.1. (*E*)-β-Bromostyrene (2a).[13e,25] IR (neat) 1609, 1575, 941 cm^{-1}; ^{1}H NMR δ 6.77 (1H, d, J=13.9 Hz), 7.11 (1H, d, J=13.9 Hz), 7.27–7.32 (5H, m); ^{13}C NMR δ 106.49, 126.06, 128.23, 128.75, 135.85, 137.11; EIMS *m/z* 184 ((M+2)$^+$, 81), 182 (M$^+$, 82), 103 (100), 77 (39); HRMS Calcd for $C_8H_7{}^{79}Br$; *m/z* 181.9731. Found *m/z* 181.9729.

4.1.2. (*E*)-β-Bromo-4-methylstyrene (2b).[13e,25] Mp 46.0–46.5°C (EtOH) (lit.[25] 46.0–46.5°C); IR (nujol) 1605, 1511, 931 cm^{-1}; ^{1}H NMR 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); ^{13}C NMR δ 21.24, 105.39, 125.97, 129.45, 133.14, 137.00, 138.20; EIMS *m/z* 198 ((M+2)$^+$, 43), 196 (M$^+$, 45), 115 (100), 117 (80), 91 (44); HRMS Calcd for $C_9H_9{}^{79}Br$; *m/z* 195.9887. Found *m/z* 195.9874.

4.1.3. (*E*)-β-Bromo-4-methoxystyrene (2c).[13e,26] Column chromatography was carried out with 10% EtOAc in hexane as an eluent; mp 58–59°C (EtOH) (lit.[26] 58–59°C); IR (nujol) 1607, 1513, 950 cm^{-1}; ^{1}H NMR 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); ^{13}C NMR δ 55.28, 103.96, 114.17, 127.32, 128.75, 136.52, 159.63; EIMS *m/z* 214 ((M+2)$^+$, 99), 212 (M$^+$, 100), 199 (36), 197 (37), 171 (19), 169 (20), 133 (31), 90 (48); HRMS Calcd for $C_9H_9{}^{79}BrO$; *m/z* 211.9836. Found *m/z* 211.9835.

4.1.4. (*E*)-β-Bromo-3-methoxystyrene (2d).[10a,27] The crude product was purified by silica gel column chromatography eluted with 10% EtOAc in hexane; IR (neat) 1612, 1577, 938 cm^{-1}; ^{1}H NMR δ 3.80 (3H, s), 6.76 (1H, d, J=13.9 Hz), 6.82 (1H, s), 6.84–6.90 (2H, m), 7.07 (1H, d, J=13.9 Hz), 7.21–7.26 (1H, m); ^{13}C NMR δ 55.17, 106.83, 111.48, 113.75, 118.62, 129.72, 137.00, 137.14, 159.78; EIMS *m/z* 214 ((M+2)$^+$, 99), 212 (M$^+$, 100), 133 (72), 118 (33), 90 (41), 89 (39), 63 (37); HRMS Calcd for $C_9H_9{}^{79}BrO$; *m/z* 211.9836. Found *m/z* 211.9828.

4.1.5. (*E*)-2-(β-Bromovinyl)naphthalene (2e).[12] The crude product was purified by silica gel column chromatography eluted with 5% EtOAc in hexane; mp 84–85°C (EtOH); IR (nujol) 1611, 1594, 945 cm^{-1}; ^{1}H NMR 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); ^{13}C NMR δ 106.84, 122.90, 126.28, 126.35, 126.60, 127.74, 128.08, 128.55, 133.12, 133.33, 133.44, 137.25; EIMS *m/z* 234 ((M+2)$^+$, 85), 232 (M$^+$, 86), 153 (95), 152 (100), 127 (20), 76 (27); HRMS Calcd for $C_{12}H_9{}^{79}Br$; *m/z* 231.9887. Found *m/z* 231.9907.

4.1.6. (*E*)-1-(β-Bromovinyl)naphthalene (2f).[11] The crude product was purified by silica gel column chromatography eluted with 5% EtOAc in hexane; IR (neat) 1603, 1590, 935 cm^{-1}; ^{1}H NMR 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); ^{13}C NMR δ 108.46, 123.67, 124.19, 125.50, 126.07, 126.22, 126.42, 128.50, 128.73, 130.49, 133.50, 134.95; EIMS *m/z* 234 ((M+2)$^+$, 13), 232 (M$^+$, 13), 153 (93), 152 (100), 126 (17), 76 (12); HRMS Calcd for $C_{12}H_9{}^{79}Br$; *m/z* 231.9887. Found *m/z* 231.9891.

4.1.7. (*E*)-β-Bromo-4-chlorostyrene (2g).[13e,28] The crude product was purified by silica gel column chromatography eluted with 10% EtOAc in hexane; mp 47–48°C (MeOH) (lit.[28] 47–48°C); IR (nujol) 1604, 1586, 945 cm^{-1}; ^{1}H NMR 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); ^{13}C NMR δ 107.19, 127.26, 129.00, 134.03, 134.36, 135.98; EIMS *m/z* 220 ((M+4)$^+$, 23), 218 ((M+2)$^+$, 100), 216 (M$^+$, 77), 139 (32), 137 (98), 102 (57), 101 (63), 75 (36); HRMS Calcd for $C_8H_6{}^{79}Br{}^{35}Cl$; *m/z* 215.9341. Found *m/z* 215.9343.

4.1.8. (*E*)-β-Bromo-2-chlorostyrene (2h).[13k] The crude product was purified by silica gel column chromatography eluted with 10% EtOAc in hexane; IR (neat) 1605, 1470, 1440, 945 cm^{-1}; ^{1}H NMR 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); ^{13}C NMR δ 109.18, 126.90, 127.00, 129.33, 129.90, 132.44, 133.73, 134.09; EIMS *m/z* 220 ((M+4)$^+$, 26), 218 ((M+2)$^+$, 100), 216 (M$^+$, 74), 139 (35), 137 (98), 102 (26), 101 (41), 75 (22); HRMS Calcd for $C_8H_6{}^{79}Br{}^{35}Cl$; *m/z* 215.9341. Found *m/z* 215.9344.

4.1.9. (*E*)-4-(β-Bromovinyl)benzoic acid ethyl ester (2i).[10a] The crude product was purified by silica gel column chromatography eluted with 30% EtOAc in hexane; IR (neat) 1719, 1606, 937 cm^{-1}; ^{1}H NMR δ 1.39 (3H, t, J=7.3 Hz), 4.37 (2H, q, J=7.3 Hz), 6.91 (1H, d, J=14.2 Hz), 7.14 (1H, d, J=14.2 Hz), 7.35 (2H, d, J=8.6 Hz), 8.00 (2H, d, J=8.6 Hz); ^{13}C NMR δ 14.27, 61.03, 109.27, 125.88, 129.96, 130.03, 136.33, 139.91, 166.11; EIMS *m/z* 256 ((M+2)$^+$, 47), 254 (M$^+$, 48), 228 (36), 226 (37), 211 (99), 209 (100), 102 (90); HRMS Calcd for $C_{11}H_{11}{}^{79}BrO_2$; *m/z* 253.9942. Found *m/z* 253.9943.

4.1.10. (*E*)-β-Bromo-3-nitrostyrene (2j).[27,29] The crude product was purified by silica gel column chromatography eluted with 40% EtOAc in hexane; mp 70–71°C; IR (nujol) 1616, 1524, 1352, 937 cm^{-1}; ^1H NMR δ 6.99 (1H, d, J=14.2 Hz), 7.18 (1H, d, J=14.2 Hz), 7.52 (1H, t, J=7.6 Hz), 7.62 (1H, dd, J=1.3 and 7.6 Hz), 8.7 (1H, d, J=1.7 Hz), 8.3–8.7 (1H, m); ^{13}C NMR δ 110.10, 120.68, 122.79, 129.79, 131.81, 134.99, 137.47, 148.80; EIMS *m/z* 229 ($(M+2)^+$, 45), 227 (M^+, 48), 183 (15), 181 (16), 102 (100); HRMS Calcd for $C_8H_6{}^{79}BrNO_2$; *m/z* 226.9581. Found *m/z* 226.9571.

4.1.11. (*E*/*Z*)-1-Bromo-4-phenylbuta-1,3-diene (2k).[13i] IR (nujol) 1691, 1448, 974, 741 cm^{-1}; ^1H NMR δ 6.23 (0.27H, d, J=6.9 Hz, (*Z*)), 6.42 (0.73H, d, J=13.2 Hz, (*E*)), 6.5–6.8 (2H, m), 6.87 (0.73H, dd, J=10.2 and 13.5 Hz, (*E*)), 7.11 (0.27H, ddd, J=1.0, 9.9 and 13.5 Hz, (*Z*)), 7.2–7.5 (5H, m); EIMS *m/z* 210 ($(M+2)^+$, 3), 208 (M^+, 3), 129 (75), 128 (100), 102 (26); HRMS Calcd for $C_{10}H_9{}^{79}Br$; *m/z* 207.9887. Found *m/z* 207.9893.

4.1.12. (*E*/*Z*)-1-Bromo-2-cyclohexylethene (2l).[5,30] IR (neat) 1619, 942, 707 cm^{-1}; ^1H NMR δ 1.0–1.4 (5H, m), 1.6–1.8 (5H, m), 1.9–2.1 (0.68H, m, *E*), 2.4–2.6 (0.32H, m), 5.92 (0.32H, m, *Z*), 5.92 (0.32H, dd, J=6.9 and 8.9 Hz, *Z*), 5.99 (0.68H, dd, J=1.0 and 13.5 Hz, *E*), 6.04 (0.32H, dd, J=1.0 and 6.9 Hz, *Z*), 6.14 (0.68H, dd, J=7.3 and 13.5 Hz, *E*); ^{13}C NMR δ 25.54 (*Z*), 25.72 (*E*), 25.88 (*E* and *Z*), 31.55 (*Z*), 32.24 (*E*), 38.79 (*Z*), 41.76 (*E*), 103.08 (*E*), 105.42 (*Z*), 140.14 (*Z*), 143.69 (*E*); EIMS *m/z* 190 ($(M+2)^+$, 7), 188 (M^+, 8), 109 (100), 67 (94); HRMS Calcd for $C_8H_{13}{}^{79}Br$; *m/z* 188.0200. Found *m/z* 188.0194.

4.1.13. (*E*/*Z*)-1-Bromonon-1-ene (2m).[31] IR (neat) 1623, 940, 721 cm^{-1}; ^1H NMR δ 0.85–0.95 (3H, m), 1.2–1.5 (10H, m), 1.99–2.07 (1.16H, m, *E*), 2.15–2.22 (0.84H, m, *Z*), 6.00 (0.58H, J=1.3 and 13.5 Hz, *E*), 6.02–6.23 (1.42H, m); EIMS *m/z* 206 ($(M+2)^+$, 20), 204 (M^+, 21), 123 (56), 83 (61), 81 (71), 69 (100), 43 (96), 41 (77); HRMS Calcd for $C_9H_{17}{}^{79}Br$; *m/z* 204.0513. Found *m/z* 204.0500.

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