# Stereoselective Synthesis of (*E*)-β-Arylvinyl Bromides by Microwave-Induced Hunsdiecker-Type Reaction

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**Abstract:** (*E*)-β-Arylvinyl bromides were readily prepared in a short reaction time (1–2 min) by microwave irradiation of the corresponding 3-arylpropenoic acids in the presence of *N*-bromosuccinimide and a catalytic amount of lithium acetate. Furthermore, two facile strategies for the efficient synthesis of (*E*)-β-bromo-4-arylethynylstyrene and (*E*)-β-bromo-4-arylstyrene have been developed by respectively combining Sonogashira and Suzuki coupling reaction with Hunsdiecker-type reaction. Formation of *cis*-α-bromo-β-lactone by microwave irradiation of *cis*-cinnamic acid with NBS provides a useful support for the mechanistic study of the present halodecarboxylation reaction.

**Key words:** (*E*)-β-arylvinyl bromides, α,β-unsaturated carboxylic acids, stereoselective synthesis, microwave irradiation, Hunsdiecker-type reaction

(*E*)-Vinyl bromides are very useful synthetic intermediates in organic synthesis. Their use as precursors of vinyl anion[1] and as coupling components in a wide range of transition metal-catalyzed coupling reaction[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 the preparation of (*E*)-vinyl bromides, but the reagents used in most cases are limited to organometallic compounds such as organoaluminum,[3] organoboron,[4] organosilicon,[5] geminal dichromium reagent,[6] organozinc reagent,[7] organolithium reagent,[8] hydrozirconating reagent,[9] organotin reagent,[10] indium metal,[11] Grignard reagent,[12] and samarium metal.[13] Methods using diethyl phosphonate,[14] lithium aluminum hydride[15] and electrochemical reduction[16] have also been reported. The Hunsdiecker-type bromodecarboxylation[17] and decarboxylation of cinnamic acid dibromides[18] have been the most frequently used methods for the synthesis of (*E*)-vinyl bromides. However, these synthetic methods have several drawbacks: use of complex reagent such as organometallic compounds, bis(collidine)halogen(I) hexafluorophosphate, and tetrabutylammonium trifluoroacetate, use of a large amount of solvent for dissolution of substrate and catalyst, long reaction time, low yields and limitation to arylvinyl bromides carrying electron-withdrawing group.

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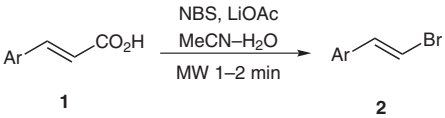
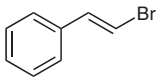
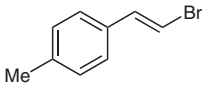
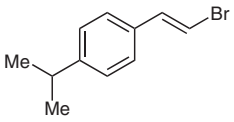
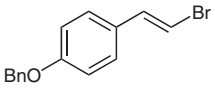
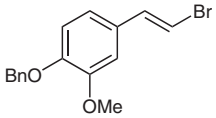
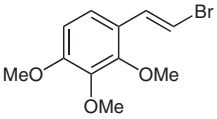
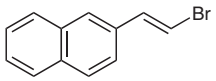
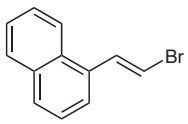
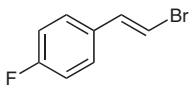
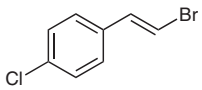
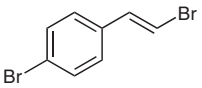
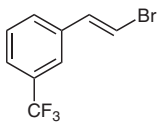
Recently, the method of microwave irradiation has been used by organic chemists to effect organic transformations. Remarkable reductions in reaction times, clean conditions and better yields have been reported in microwave-induced reactions.[19] In a preliminary paper,[20] we reported a microwave-induced Hunsdiecker-type reaction for the stereoselective synthesis of (*E*)-β-arylvinyl halides from 3-arylpropenoic acids. In this paper, we report the application of microwave-induced Hunsdiecker-type reaction to the synthesis of the various (*E*)-β-arylvinyl bromides carrying either an electron-donating or -withdrawing group. Using our optimized conditions, microwave irradiation of 3-arylpropenoic acids **1** in an acetonitrile–water (4.6:0.4) solvent containing *N*-bromosuccinimide (1.05 equiv) and catalytic amount of LiOAc (0.2 equiv) for 1–2 min gave the corresponding (*E*)-β-arylvinyl bromides **2** in good to excellent yields (Scheme 1). The results summarized in Table 1 show that the vinyl bromides **2a–h** were obtained in higher yields and in a shorter reaction time by the microwave irradiation method than by previous methods.[17h,m] By previous methods, (*E*)-β-arylvinyl bromides carrying strong electron-donating groups such as methoxy (**2f**) generally could be prepared in high yields, however, the reaction of *trans*-cinnamic acids carrying an electron-withdrawing group (**1i–l**) or unsubstituted *trans*-cinnamic acids (**1a**, **1g** and **1h**) with NBS gave (*E*)-β-arylvinyl bromides in low yields. Under previous conditions, some (*E*)-β-arylvinyl bromides even bearing an electron-donating group were still produced in moderate yields, because the electron-donating group such as methyl (**2b** and **2c**) was not strong enough. Moreover, the existence of big functional group such as benzyloxyl (**2d** and **2e**) in the molecules also resulted in unsatisfactory yields. However, these problems are circumvented by our present method. Microwave irradiation of **1i–l** gave the products **2i–l** in moderate yields; even so, these yields were higher than those obtained by previously reported methods. These results indicated that the present microwave-induced Hunsdiecker-type reac-




**Scheme 1**

**Table 1** Stereoselective Synthesis of (*E*)-β-Arylvinyl Bromides **2**

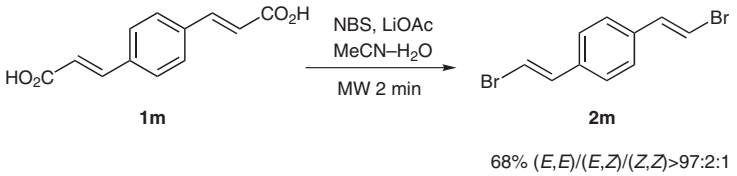
| Entry | Acid **1** | Product **2** | | MW (min) | Yield (%)[a] | *E*/*Z*[b] |
|---|---|---|---|---|---|---|
| 1 | **1a** |  | **2a** | 1 | 84 | >95:5 |
| 2 | **1b** |  | **2b** | 1 | 91 | >98:2 |
| 3 | **1c** |  | **2c** | 1 | 92 | >98:2 |
| 4 | **1d** |  | **2d** | 1 | 93 | >98:2 |
| 5 | **1e** |  | **2e** | 1 | 90 | >98:2 |
| 6 | **1f** |  | **2f** | 1 | 98 | >98:2 |
| 7 | **1g** |  | **2g** | 1 | 88 | >98:2 |
| 8 | **1h** |  | **2h** | 1 | 84 | >98:2 |
| 9 | **1i** |  | **2i** | 2 | 60 | 97:3 |
| 10 | **1j** |  | **2j** | 2 | 56 | 97:3 |
| 11 | **1k** |  | **2k** | 2 | 71 | >97:3 |
| 12 | **1l** |  | **2l** | 2 | 52 | >96:4 |

[a] Isolated yields.
[b] Determined by $^1$H NMR spectroscopy.

tion was very useful for the synthesis of (*E*)-β-arylvinyl bromides carrying either an electron-donating or -withdrawing group.

Similarly, the microwave irradiation of 4-benzenediacrylic acid (**1m**) with NBS afforded the corresponding 1,4-bis(*trans*-β-bromovinyl)benzene (**2m**) in 68% yield (Scheme 2). Compound **2m** can be used for the synthesis of conjugated polymers.[21]

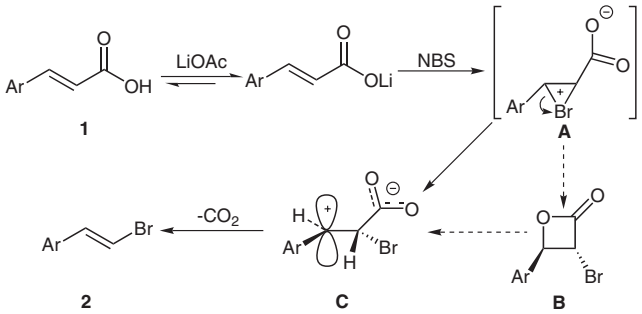
Alkynyl arenes and biarenes are very useful precursors for conducting polymers, liquid crystals, and nonlinear optical materials. For the carbon–carbon bond formation, the Sonogashira coupling and Suzuki coupling have been frequently used. (*E*)-β-Bromo-4-phenylethynylstyrene (**2n**) was prepared in two steps by coupling 4-bromocinnamic acid with ethynylbenzene followed by bromodecarboxylation of the coupling product **1n** (Scheme 3). A similar




**Scheme 2**

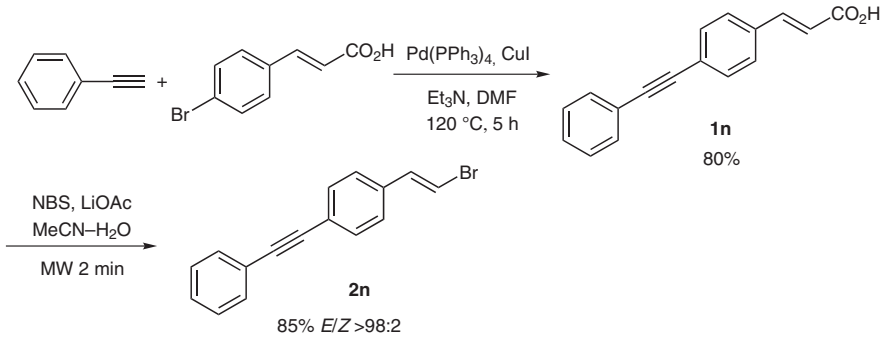
attempt involving Suzuki coupling/bromodecarboxylation led to the formation of (*E*)-β-bromo-4-anisylstyrene (**2o**) (Scheme 4). These two processes using microwave reaction as key step could provide an easy access to various substituted arylvinyl bromides.

Proposed reaction pathways of the present halodecarboxylation are shown in Scheme 5. Reaction of lithium carboxylate of **1** with NBS gives bromonium ion **A**, which is immediately converted to *trans*-α-bromo-β-lactone **B** or zwitterion **C**, which would eliminate carbon dioxide to give (*E*)-β-arylvinyl bromide **2**. The thermal decomposition of β-lactone is a well-established method for the stereoselective synthesis of substituted alkenes. These thermal reactions are reported to proceed through a transition state with a zwitterionic character.[22] The formation of *trans*-3-bromo-4-phenylbutenolide[17h,23] from the reaction of 4-phenylbut-3-enoic acid with NBS and catalytic LiOAc provides an indirect experimental support for the occurrence of intermediates **A** and **B**. However, even at low temperature, no signals for intermediate **A** and **B** were detected in the $^1$H NMR of the reaction mixture.

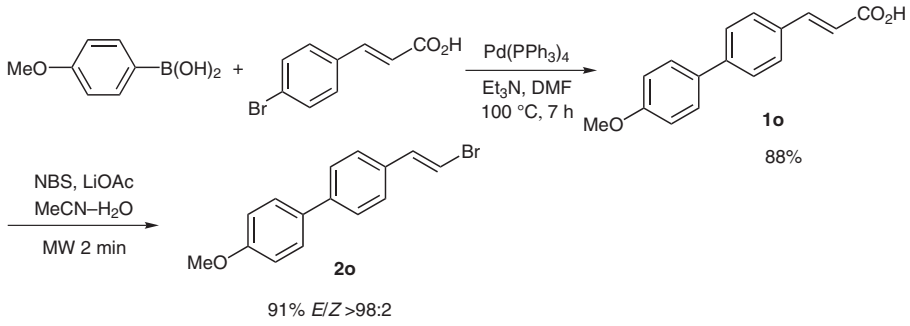



**Scheme 5**

Recently, we were induced to study the reactivity of *cis*-cinnamic acid with NBS. Much to our delight, a mixture of *cis*-3-bromo-4-phenyloxetan-2-one (**4**) and β-bromostyrene (*E*/*Z* = 74:26) were found by microwave irradiation of *cis*-cinnamic acid (**3**) with NBS (Scheme 6).[24] The coupling constant ($J$ = 5.94 Hz) observed in the $^1$H NMR of **4** clearly indicated that **4** was a *cis*-β-lactone. In the IR spectrum, the characteristic carbonyl absorption was observed at 1844 cm$^{-1}$. EI-MS spectrum showed the specific peak due to decarboxylation of the lactone ($M^+$ –

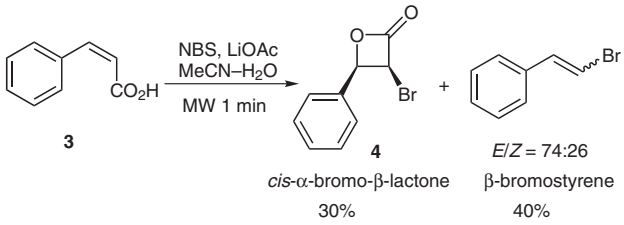



**Scheme 3**




**Scheme 4**

$CO_2$). The lability of *cis*-α-bromo-β-lactone makes it difficult to purify this compound by chromatography. The phenomenon that *cis*-α-bromo-β-lactone easily decarboxylated to the β-bromostyrene even at room temperature was observed by $^1$H NMR detection. Nishida et al. have shown that the decarboxylation rate of the *trans*-β-lactone is higher than that of *cis*-β-lactone.[25] Combining these facts together, it is not surprising to note that no signals for *trans*-α-bromo-β-lactone **B** were found in the $^1$H NMR of the reaction mixture of *trans*-cinnamic acid with NBS, even if intermediate **B** could be present.




**Scheme 6**

In conclusion, this application of microwave irradiation to the Hunsdiecker-type reaction is found to have significant advantage over existing procedure. We have developed a simple and efficient method for the preparation of β-arylvinyl bromides from the corresponding 3-aryl-propenoic acids using NBS in a high yield and with a high stereoselectivity. For the first time we have isolated and detected a new α-bromo-β-lactone by microwave irradiation of *cis*-cinnamic acid with NBS, which provide a useful support for the mechanism study of the present bromodecarboxylation reaction.

Melting points were recorded using a Yanagimoto micro melting point apparatus and were uncorrected. IR spectra were recorded using a JASCO IR-810 IR 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). Commercially available NBS, 4-bromocinnamic acid, and LiOAc were used without any further purification. Commercially available MeCN was purified by distillation. Commercially available anhyd DMF packed under $N_2$ (Kanto Chemical) was used without any further purification. $Et_3N$, CuI, $Pd(Ph_3P)_4$, phenylacetylene, and 4-anisylboronic acid are available from Aldrich. Substituted *trans*-cinnamic acids **1a**–**m** are commercially available. Acids **1n** and **1o** were prepared as described below. *cis*-Cinnamic acid (**3**) was prepared according to the procedure reported in the literature.[26]

**(*E*)-3-[(4-(2-Phenylethynyl)phenyl]prop-2-enoic Acid (1n)**

To a mixture of 4-bromocinnamic acid (5.0 mmol, 1.140 g), phenylacetylene (6.0 mmol, 613 mg), CuI (0.30 mmol, 57 mg) and $Pd(Ph_3P)_4$ (0.30 mmol, 347 mg) in anhyd degassed DMF (20 mL) was added $Et_3N$ (20.0 mmol, 2023 mg) under argon. The mixture was stirred at 120 °C in an oil bath for 5 h. After cooling to r.t., the resulting mixture was quenched with aq HCl and filtered. The precipitate was washed with $Et_2O$ and purified by column chromatography on silica gel with EtOAc–hexane to afford the crude product, which was recrystallized from AcOH to give **1n**; yield: 992 mg (80%); colorless crystals; mp 211.0–212.0 °C (AcOH).

IR (Nujol): 1701, 1677, 1627, 721 cm$^{-1}$.

$^1$H NMR ($CDCl_3$ + DMSO-$d_6$): δ = 6.44 (1 H, d, *J* = 16.0 Hz), 7.34–7.37 (3 H, m), 7.52–7.55 (6 H, m), 7.65 (1 H, d, *J* = 16.0 Hz).

$^{13}$C NMR ($CDCl_3$ + DMSO-$d_6$): δ = 89.02, 91.09, 122.06, 123.84, 128.32, 128.64, 128.86, 131.34, 131.71, 134.37, 142.85.

EIMS: *m*/*z* (%) = 248 ($M^+$, 100), 202 (45).

HRMS: *m*/*z* calcd for $C_{17}H_{12}O_2$ [$M^+$]: 248.0839; found: 248.0838.

Anal. Calcd for $C_{17}H_{12}O_2$: C, 82.24; H, 4.87. Found: C, 82.29; H, 4.83.

***trans*-4-Anisylcinnamic Acid (1o)**

To a degassed solution of 4-bromocinnamic acid (5.0 mmol, 1.140 g), 4-anisylboronic acid (6.0 mmol, 912 mg), $Pd(Ph_3P)_4$ (0.30 mmol, 347 mg) in anhyd DMF (25 mL) was added $Et_3N$ (20 mmol, 2.023 g) under argon. The mixture was stirred at 100 °C in an oil bath for 7 h. After cooling to r.t., the resulting mixture was quenched with aq HCl and filtered. The precipitate was washed with $Et_2O$ and purified by column chromatography on silica gel with EtOAc–hexane to give a crude product, which was recrystallized from acetone–$H_2O$ to yield **1o**; yield: 1.117 g (88%); colorless crystals; mp 230–231 °C (acetone–$H_2O$).

IR (Nujol): 1678, 1602, 823 cm$^{-1}$.

$^1$H NMR ($CDCl_3$ + DMSO-$d_6$): δ = 3.85 (3 H, s), 6.44 (1 H, d, *J* = 15.8 Hz), 6.98 (2 H, d, *J* = 8.5 Hz), 7.54–7.58 (6 H, m), 7.68 (1 H, d, *J* = 15.8 Hz).

$^{13}$C NMR ($CDCl_3$ + DMSO-$d_6$): δ = 54.80, 113.81, 117.88, 126.34, 127.47, 128.01, 131.91, 132.32, 141.79, 143.54, 159.01, 168.17.

EIMS: *m*/*z* (%) = 254 ($M^+$, 100), 239 (35), 211 (18).

HRMS: *m*/*z* calcd for $C_{16}H_{14}O_3$ [$M^+$]: 254.0943; found: 254.0932.

Anal. Calcd for $C_{16}H_{14}O_3$: C, 75.58; H, 5.55. Found: C, 75.63; H, 5.48.

**(*E*)-β-Arylvinyl Bromides 2; General Procedure**

A mixture of substituted *trans*-cinnamic acid **1** (5 mmol), LiOAc (1 mmol), and NBS (935 mg, 5.25 mmol) was added to a mixture of MeCN–$H_2O$ (5 mL, 4.6:0.4). The mixture was kept inside a microwave oven operating at 2450 MHz (Toshiba, ER-V11, 200 watt) and was irradiated for 1–2 min. The reaction mixture was removed from the oven, and cooled to r.t. Evaporation of the solvent under reduced pressure gave the crude product, which was subjected to column chromatography (silica gel, EtOAc–hexane) to afford (*E*)-β-arylvinyl bromides **2**. In the case of acids **1d**, **1e**, **1g**, **1h**, **1m**, **1n** and **1o**, the reaction scale was 1.0 mmol.

**(*E*)-β-Bromostyrene (2a)[27]**

Yield: 764 mg (84%); colorless oil.

IR (neat): 1609, 1575, 941 cm$^{-1}$.

$^1$H NMR (270 MHz, $CDCl_3$): δ = 6.77 (1 H, d, *J* = 13.9 Hz), 7.11 (1 H, d, *J* = 13.9 Hz), 7.27–7.32 (5 H, m).

$^{13}$C NMR (67.5 MHz, $CDCl_3$): 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: *m*/*z* calcd for $C_8H_7{}^{79}Br$ [$M^+$]: 181.9731; found: 181.9729.

**(*E*)-β-Bromo-4-methylstyrene (2b)[27]**

Yield: 892 mg (91%); colorless crystals; mp 46.0–46.5 °C (EtOH) (Lit.[27] mp 46.0–46.5 °C).

IR (Nujol): 1605, 1511, 931 $cm^{-1}$.

$^1H$ NMR (270 MHz, $CDCl_3$): δ = 2.32 (3 H, s), 6.70 (1 H, d, *J* = 13.9 Hz), 7.06 (1 H, d, *J* = 13.9 Hz), 7.12 (2 H, d, *J* = 8.3 Hz), 7.19 (2 H, d, *J* = 8.3 Hz).

$^{13}C$ NMR (67.5 MHz, $CDCl_3$): 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), 117 (100), 115 (80), 91 (44).

HRMS: *m*/z calcd for $C_9H_9{}^{79}Br$ [M$^+$]: 195.9887; found: 195.9874.

**(*E*)-β-Bromo-4-isopropylstyrene (2c)[15]**
Yield: 1.031 g (92%); colorless oil.

IR (neat): 1610, 1578, 1513, 1223, 933 $cm^{-1}$.

$^1H$ NMR (270 MHz, $CDCl_3$): δ = 1.23 (6 H, d, *J* = 6.9 Hz), 2.87 (1 H, q, *J* = 6.9 Hz), 6.69 (1 H, d, *J* = 13.9 Hz), 7.06 (1 H, d, *J* = 13.9 Hz), 7.16 (2 H, d, *J* = 8.6 Hz), 7.21 (2 H, d, *J* = 8.6 Hz).

$^{13}C$ NMR (67.5 MHz, $CDCl_3$): δ = 23.79, 33.87, 105.46, 126.07, 126.81, 133.51, 136.98, 149.14.

EIMS: *m*/*z* (%) = 226 [(M + 2)$^+$, 54], 224 (M$^+$, 57), 209 (100), 130 (46).

HRMS: *m*/*z* calcd for $C_{11}H_{13}{}^{79}Br$ [M$^+$]: 224.0200; found: 224.0201.

**(*E*)-β-Bromo-4-benzyloxystyrene (2d)**
Yield: 268 mg (93%); colorless crystals; mp 77–78 °C.

IR (film): 1509, 1458, 955, 695 $cm^{-1}$.

$^1H$ NMR (270 MHz, $CDCl_3$): δ = 5.06 (2 H, s), 6.61 (1 H, d, *J* = 13.9 Hz), 6.92 (2 H, d, *J* = 8.9 Hz), 7.03 (1 H, d, *J* = 13.9 Hz), 7.23 (2 H, d, *J* = 8.9 Hz), 7.34–7.41 (5 H, m).

$^{13}C$ NMR (67.5 MHz, $CDCl_3$): δ = 69.97, 104.11, 115.07, 127.33, 127.42, 128.03, 128.59, 128.95, 136.47, 136.64, 158.79.

EIMS: *m*/*z* (%) = 290 [(M + 2)$^+$, 5], 288 (M$^+$, 5), 91 (100).

HRMS: *m*/*z* calcd for $C_{15}H_{13}{}^{79}BrO$ [M$^+$]: 288.0150; found: 288.0149.

Anal. Calcd for $C_{15}H_{13}BrO$: C, 62.30; H, 4.53; Br, 27.63. Found: C, 62.11; H, 4.63; Br, 27.45.

**(*E*)-β-Bromo-4-benzyloxy-3-methoxystyrene (2e)**
Yield: 286 mg (90%); colorless crystals; mp 104–105 °C (hexane).

IR (Nujol): 1612, 1508, 1277, 1155, 720 $cm^{-1}$.

$^1H$ NMR (270 MHz, $CDCl_3$): δ = 3.88 (3 H, s), 5.14 (2 H, s), 6.52 (1 H, d, *J* = 13.9 Hz), 6.84 (3 H, m), 6.97 (1 H, d, *J* = 13.9 Hz), 7.30–7.46 (5 H, m).

$^{13}C$ NMR (67.5 MHz, $CDCl_3$): δ = 56.01, 71.12, 104.22, 111.46, 111.69, 119.89, 127.29, 127.97, 128.60, 128.89, 136.69, 136.83, 148.26, 150.00.

EIMS: *m*/*z* (%) = 320 [(M + 2)$^+$, 48], 318 (M$^+$, 50), 91 (100).

HRMS: *m*/*z* calcd for $C_{16}H_{15}{}^{79}BrO_2$ [M$^+$]: 318.0256; found: 318.0244.

Anal. Calcd for $C_{16}H_{15}BrO_2$: C, 60.21; H, 4.74; Br, 25.03. Found: C, 60.05; H, 4.61; Br, 25.01.

**(*E*)-β-Bromo-2,3,4-trimethoxystyrene (2f)**
Yield: 1.333 g (98%); colorless crystals; mp 66–67 °C (hexane).

IR (film): 1595, 1494, 944, 669 $cm^{-1}$.

$^1H$ NMR (270 MHz, $CDCl_3$): δ = 3.86 (3 H, s), 3.87 (3 H, s), 3.88 (3 H, s), 6.63 (1 H, d, *J* = 8.6 Hz), 6.77 (1 H, d, *J* = 13.9 Hz), 6.98 (1 H, d, *J* = 8.6 Hz), 7.20 (1 H, d, *J* = 13.9 Hz).

$^{13}C$ NMR (67.5 MHz, $CDCl_3$): δ = 55.97, 60.84, 60.95, 106.02, 107.51, 121.70, 122.84, 132.18, 142.37, 151.19, 153.74.

EIMS: *m*/*z* (%) = 274 [(M + 2)$^+$, 48], 272 (M$^+$, 50), 193 (42), 178 (100).

HRMS: *m*/*z* calcd for $C_{11}H_{13}{}^{79}BrO_3$ [M$^+$]: 272.0048; found: 272.0047.

Anal. Calcd for $C_{11}H_{13}BrO_3$: C, 48.37; H, 4.80; Br, 29.26. Found: C, 48.18; H, 4.71; Br, 29.10.

**(*E*)-2-(β-Bromovinyl)naphthalene (2g)[12]**
Yield: 204 mg (88%); colorless crystals; mp 84–85 °C (EtOH).

IR (Nujol): 1611, 1594, 945 $cm^{-1}$.

$^1H$ NMR (270 MHz, $CDCl_3$): δ = 6.90 (1 H, d, *J* = 13.9 Hz), 7.26 (1 H, d, *J* = 13.9 Hz), 7.44–7.49 (3 H, m), 7.69 (1 H, d, *J* = 1.0 Hz), 7.77–7.83 (3 H, m).

$^{13}C$ NMR (67.5 MHz, $CDCl_3$): 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: *m*/*z* calcd for $C_{12}H_9{}^{79}Br$ [M$^+$]: 231.9887; found: 231.9907.

**(*E*)-1-(β-Bromovinyl)naphthalene (2h)[11]**
Yield: 195 mg (84%); colorless oil.

IR (neat): 1603, 1590, 935 $cm^{-1}$.

$^1H$ NMR (270 MHz, $CDCl_3$): δ = 6.76 (1 H, d, *J* = 13.9 Hz), 7.38–7.56 (4 H, m), 7.79–7.86 (3 H, m), 8.02 (1 H, d, *J* = 13.9 Hz).

$^{13}C$ NMR (67.5 MHz, $CDCl_3$): 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: *m*/*z* calcd for $C_{12}H_9{}^{79}Br$ [M$^+$]: 231.9887; found: 231.9907.

**(*E*)-β-Bromo-4-fluorostyrene (2i)[28]**
Yield: 600 mg (60%); colorless oil.

IR (neat): 1602, 1589, 946 $cm^{-1}$.

$^1H$ NMR (270 MHz, $CDCl_3$): δ = 6.67 (1 H, d, *J* = 13.9 Hz), 6.95–7.03 (2 H, m), 7.04 (1 H, d, *J* = 13.9 Hz), 7.21–7.25 (2 H, m).

$^{13}C$ NMR (67.5 MHz, $CDCl_3$): 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)$^+$, 28], 200 (M$^+$, 27), 202 (28), 149 (100).

HRMS: *m*/*z* calcd for $C_8H_6{}^{79}BrF$ [M$^+$]: 199.9637; found: 199.9629.

**(*E*)-β-Bromo-4-chlorostyrene (2j)[29]**
Yield: 605 mg (56%); colorless crystals; mp 47–48 °C (MeOH) (Lit.[29] mp 47–48 °C).

IR (Nujol): 1604, 1586, 945 $cm^{-1}$.

$^1H$ NMR (270 MHz, $CDCl_3$): δ = 6.75 (1 H, d, *J* = 13.9 Hz), 7.05 (1 H, d, *J* = 13.9 Hz), 7.21 (2 H, d, *J* = 8.6 Hz), 7.29 (2 H, d, *J* = 8.6 Hz).

$^{13}C$ NMR (67.5 MHz, $CDCl_3$): 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: *m*/*z* calcd for $C_8H_6{}^{79}Br^{35}Cl$ [M$^+$]: 215.9341; found: 215.9343.

**(*E*)-β-Bromo-4-bromostyrene (2k)[30]**
Yield: 930 mg (71%); colorless crystals; mp 67–68 °C (Lit.[30] mp 67–68 °C).

IR (Nujol): 1610, 1589, 930 $cm^{-1}$.

$^1H$ NMR (270 MHz, $CDCl_3$): δ = 6.78 (1 H, d, *J* = 14.2 Hz), 7.04 (1 H, d, *J* = 14.2 Hz), 7.15 (2 H, d, *J* = 8.3 Hz), 7.44 (2 H, d, *J* = 8.3 Hz).

$^{13}C$ NMR (67.5 MHz, $CDCl_3$): δ = 107.33, 122.17, 127.55, 131.93, 134.77, 136.03.

EIMS: *m*/*z* (%) = 264 [$(M + 2)^+$, 90], 262 ($M^+$, 100), 181 (78), 102 (70).

HRMS: *m*/*z* calcd for $C_8H_6{}^{79}Br^{81}Br$ [$M^+$]: 261.8816; found: 261.8825.

**(*E*)-β-Bromo-3-trifluoromethylstyrene (2l)[31]**
Yield: 650 mg (60%); colorless oil.

IR (neat): 1613, 1591, 939 $cm^{-1}$.

$^1H$ NMR (270 MHz, $CDCl_3$): δ = 6.86 (1 H, d, *J* = 14.0 Hz), 7.12 (1 H, d, *J* = 14.0 Hz), 7.40–7.90 (4 H, m).

$^{13}C$ NMR (67.5 MHz, $CDCl_3$): δ = 108.68, 122.74 (d, *J* = 3.7 Hz), 124.77 (d, *J* = 3.7 Hz), 126.79 (q, *J* = 272.2 Hz), 129.22 (d, *J* = 8.5 Hz), 131.25 (d, *J* = 33.0 Hz), 135.81, 136.58.

EIMS: *m*/*z* (%) = 252 [$(M + 2)^+$, 86], 250 ($M^+$, 88), 171 (92), 120 (100).

HRMS: *m*/*z* calcd for $C_9H_6{}^{79}BrF_3$ [$M^+$]: 249.9604; found: 249.9596.

**(*E*,*E*)-1,4-Bis(β-bromovinyl)benzene (2m)[32]**
Yield: 195 mg (68%); colorless crystals; mp 139–140 °C (benzene) (Lit.[32] mp 138–140 °C).

IR (Nujol): 1624, 940, 770 $cm^{-1}$.

$^1H$ NMR (270 MHz, $CDCl_3$): δ = 6.79 (2 H, d, *J* = 14.0 Hz), 7.06 (2 H, d, *J* = 14.0 Hz), 7.25 (4 H, s).

$^{13}C$ NMR (67.5 MHz, $CDCl_3$): δ = 107.07, 126.48, 135.73, 136.54.

EIMS: *m*/*z* (%) = 290 [$(M + 4)^+$, 48], 288 [$(M + 2)^+$, 100], 286 ($M^+$, 52), 207 (36), 128 (72).

HRMS: *m*/*z* calcd for $C_{10}H_8{}^{79}Br_2$ [$M^+$]: 285.8992; found: 285.8984.

**(*E*)-β-Bromo-4-phenylethynylstyrene (2n)**
Yield: 240 mg (85%); colorless crystals; mp 135–136 °C (EtOH).

IR (film): 1507, 1440, 941, 693 $cm^{-1}$.

$^1H$ NMR (270 MHz, $CDCl_3$): δ = 6.82 (1 H, d, *J* = 14.0 Hz), 7.10 (1 H, d, *J* = 14.0 Hz), 7.26–7.37 (5 H, m), 7.47–7.55 (4 H, m).

$^{13}C$ NMR (67.5 MHz, $CDCl_3$): δ = 89.10, 90.61, 107.54, 123.09, 125.99, 128.37, 131.57, 131.99, 135.62, 136.56.

EIMS: *m*/*z* (%) = 284 [$(M + 2)^+$, 98], 282 ($M^+$, 100), 202 (80), 101(29).

HRMS: *m*/*z* calcd for $C_{16}H_{11}{}^{79}Br$ [$M^+$]: 282.0044; found: 282.0058.

Anal. Calcd for $C_{16}H_{11}Br$: C, 67.87; H, 3.92; Br, 28.22. Found: C, 67.68; H, 3.74; Br, 28.15.

**(*E*)-β-Bromo-4-anisylstyrene (2o)**
Yield: 254 mg (91%); colorless crystals; mp 94–95 °C (hexane).

IR (Nujol): 1610, 1497, 762 $cm^{-1}$.

$^1H$ NMR (270 MHz, $CDCl_3$): δ = 3.85 (3 H, s), 6.79 (1 H, d, *J* = 13.9 Hz), 6.97 (2 H, d, *J* = 8.6 Hz), 7.13 (1 H, d, *J* = 13.9 Hz), 7.34 (2 H, d, *J* = 8.3 Hz), 7.52 (2 H, d, *J* = 8.6 Hz), 7.53 (2 H, d, *J* = 8.9 Hz).

$^{13}C$ NMR (67.5 MHz, $CDCl_3$): δ = 55.34, 106.14, 114.17, 114.26, 126.48, 126.72, 126.93, 127.94, 128.14, 128.69, 132.86, 134.25, 136.78, 140.62, 159.33.

EIMS: *m*/*z* (%) = 290 [$(M + 2)^+$, 8], 288 ($M^+$, 8), 184 (100).

HRMS: *m*/*z* calcd for $C_{15}H_{13}{}^{79}BrO$ [$M^+$]: 288.0149; found: 288.0148.

Anal. Calcd for $C_{15}H_{13}BrO$: C, 62.30; H, 4.53; Br, 27.63. Found: C, 62.24; H, 4.55; Br, 27.61.

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(23) (a) Microwave irradiation of 4-phenylbut-3-enoic acid (162 mg, 1 mmol) in MeCN–$H_2O$ (4.6 mL:0.4 mL) solvent containing NBS (187 mg, 1.05 mmol) and catalytic amount of LiOAc (13 mg, 0.2 mmol) for 1 min gave the corresponding *trans*-3-bromo-4-phenylbutenolide in 85% yield. The physical data of *trans*-3-bromo-4-phenylbutenolide are as follows: colorless oil; IR (Nujol): 1810 $cm^{-1}$ (γ-lactone C=O); $^1H$ NMR (270 MHz, $CDCl_3$): δ = 2.96 (1 H, dd, *J* = 18.1, 6.6 Hz), 3.23 (1 H, dd, *J* = 18.1, 7.6 Hz), 4.24 (1 H, m, *J* = 6.6, 7.6 Hz), 5.64 (1 H, d, *J* = 5.3 Hz), 7.35–7.44 (5 H, m); $^{13}C$ NMR (67.5 MHz, $CDCl_3$): δ = 38.73, 45.63, 87.75, 125.46, 128.97, 129.29, 135.74, 172.99; EIMS: *m*/*z* (%) = 242 [$(M + 2)^+$, 24], 240 ($M^+$, 25), 161 (45), 107 (100); HRMS: *m*/*z* calcd for $C_{10}H_9{}^{79}BrO_2$ [$M^+$]: 239.9785; found: 239.9762. (b) For early studies by other reaction, see: Crich, D.; Beckwith, A. L. J.; Filzene, G. F.; Longmore, R. W. *J. Am Chem. Soc.* **1996**, *118*, 7422.
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