Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/lsyc20

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Published online: 29 Oct 2009.

To cite this article: Yubo Jiang & Chunxiang Kuang (2009) Novel One-Pot Synthesis of Functionalized (Z)-2-Arylvinyl Bromides, Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry, 39:23, 4298-4308, DOI: 10.1080/00397910902906511

To link to this article: http://dx.doi.org/10.1080/00397910902906511

Synthetic Communications®, 39: 4298–4308, 2009

ISSN: 0039-7911 print/1532-2432 online
DOI: 10.1080/00397910902906511

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Novel One-Pot Synthesis of Functionalized (*Z*)-2-Arylvinyl Bromides

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Abstract: A novel and versatile one-pot synthesis of functionalized (*Z*)-2-arylvinyl bromides was developed. The new procedure involved microwave-induced debrominative decarboxylation of cinnamic acid dibromide with Et_3N and subsequent esterification in the presence of dicyclohexyl carbodiimide (DCC) and dimethyl-aminopyridine (DMAP).

Keywords: (*Z*)-2-Arylvinyl bromides, debrominative decarboxylation, esterification, one-pot synthesis

INTRODUCTION

(*Z*)-2-Arylvinyl bromides are important building blocks in organic synthesis, especially as intermediates for carbon–carbon and carbon–heteroatom bond formation by transition-metal-catalyzed coupling reactions.[1,2] The coupling products from functionalized (*Z*)-2-arylvinyl bromides have found numerous applications in the preparation of pharmaceuticals, functional polymeric material, and natural products.[3–6] Although there is a need to incorporate functional groups into (*Z*)-2-arylvinyl bromides to find novel functionalized compounds, available synthetic methods are limited in scope. Traditional methods for preparation of (*Z*)-2-arylvinyl bromides can be classified into two major categories. The first method is palladium-catalyzed hydrogenolysis of

Received November 1, 2008.
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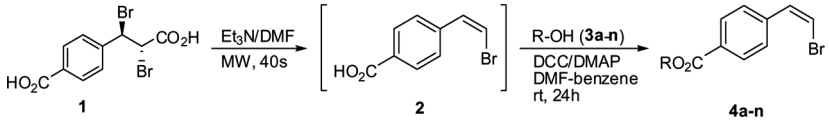


Scheme 1. One-pot synthesis of functionalized (*Z*)-2-arylvinyl bromides **4**.

1,1-dibromo-1-alkenes by tributyltin hydride.[3] The second method is the debrominative decarboxylation of cinnamic acid dibromides.[4–9] This method might be one of the most useful method for synthesis of (*Z*)-1-bromo-1-alkenes because the starting α,β-unsaturated acids are readily available and the procedure is very simple. Generally, these methods are not tolerant to reactive groups such as alkenyl, alkynyl, or aldehyde groups. Hence, it is extremely difficult to apply these methods to the preparation of (*Z*)-2-arylvinyl bromides bearing various functional groups.

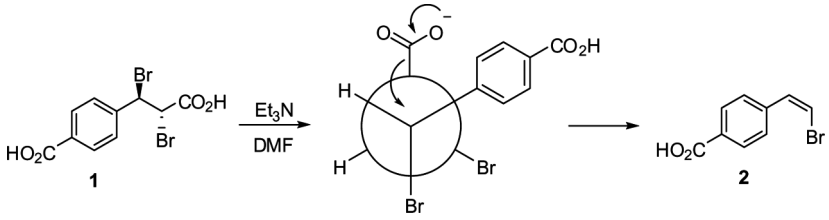
In this article, we report a novel synthetic route for preparing functionalized (*Z*)-2-arylvinyl bromides (**4**) bearing various groups from *anti*-2,3-dibromo-3-(4-carboxyphenyl)propanoic acid **1** in one pot (Scheme 1). The reaction is operationally simple and can be easily carried out. Moreover, most product molecules carry three functional groups, such as vinyl bromide, ester, and other functional groups, as compared to those already reported.

RESULTS AND DISCUSSION

The first step of this route was carried out under microwave-induced conditions and gave (*Z*)-4-(2-bromovinyl)benzoic acid **2** in dimethylformamide (DMF) with good yield and stereoselectivity. Compound **2**, carrying a carboxyl group, is a new synthon for preparation of various derivatives that are useful intermediates in organic synthesis.[1–6]

The proposed reaction pathway for the present debrominative decarboxylation is shown in Scheme 2. The reaction probably proceeds via *trans*-elimination involving simultaneous loss of carbon dioxide and bromide ion to give (Z)-vinyl bromides (Scheme 2).

In the second step, we chose a mild reaction condition, which involved dicyclohexyl carbodiimide (DCC)–dimethyl-aminopyridine (DMAP) as coupling agent for the esterification of **2** with alcohols or phenols **3**. Otherwise, the reaction would afford poor yields as a result of the activity of the vinyl bromide group in other reaction conditions such as acid or high temperature. Benzene and a DMF–benzene mixture were found to be the best two solvents for DCC/DMAP coupling



Scheme 2. Proposed reaction pathway for the synthesis of (*Z*)-4-(2-bromovinyl)benzoic acid **2**.

esterification, whereas other solvents including DMF, CH_2Cl_2, and tetrahydrofuran (THF) afforded only poor yields.

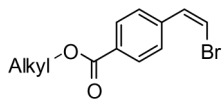
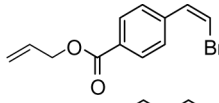
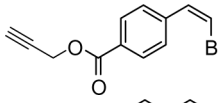
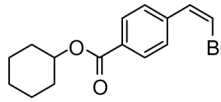
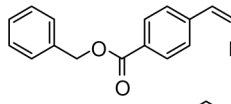
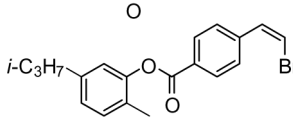
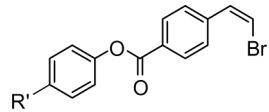
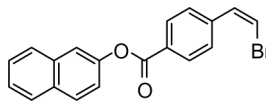
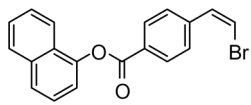
To our delight, we found that these two steps can be carried out in one pot using a DMF–benzene mixture as solvent in the second step. Various functionalized (*Z*)-2-arylvinyl bromides were prepared smoothly by this one-pot method. The results are summarized in Table 1.

These results indicated that the present reaction was very useful for the synthesis of both 4-alkoxycarbonyl (**4a**–**c**) and 4-aryloxycarbonyl-(**4h**–**n**) (*Z*)-β-arylvinyl bromides. (*Z*)-β-Arylvinyl bromides carrying functional groups such as alkenyl (**4d**), alkynyl (**4e**), and vinyl bromide (**4l**) were also easily prepared in excellent yields. Even if an electron-withdrawing group like −CHO or $-NO_2$ (**4j**–**k**) was contained in the molecule, the reaction proceeded stereoselectively in good yields.

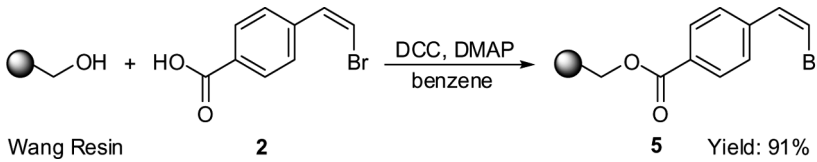
Further, acid **2** could be attached to the benzyl alcohol of Wang resin using a DCC/DMAP coupling procedure at ambient temperature to afford functionalized (*Z*)-2-arylvinyl bromide ester **5** in good yield (Scheme 3). The Wang resin–bound ester **5** carrying an active bromovinyl group can be applied to combinatorial and solid-phase organic synthesis, which are efficient techniques for the production of combinatorial libraries and are extensively used by the pharmaceutical and the agricultural industries. Moreover, **5** is an excellent substrate for Stille, Suzuki, and Heck reactions.[1]

In summary, we have developed a novel and efficient one-pot synthetic route for preparation of 4-alkoxycarbonyl and 4-aryloxycarbonyl (*Z*)-2-arylvinyl bromides bearing various functional groups in good stereoselectivities and yields. A wide range of functional groups including aldehyde, ester, nitro, olefin, alkenyl, and alkynyl groups were found to tolerate the conditions of this method. These functionalized (*Z*)-2-arylvinyl bromides are important synthetic targets and widely used synthons for synthetic chemists.

Table 1. One-pot synthesis of functionalized (*Z*)-2-arylvinyl bromides **4**

Entry	R-OH **3**	Product **4**		Alkyl	Yield of **4** (%)[a,b]
1	**3a**		**4a**	C_2H_5	90
	3b		**4b**	n-C_3H_7	91
	3c		**4c**	n-C_8H_{17}	87
2	**3d**		**4d**		85
3	**3e**		**4e**		88
4	**3f**		**4f**		90
5	**3g**		**4g**		92
6	**3h**		**4h**	R′	94
7	**3i**		**4i**	H	91
	3j		**4j**	CHO	89
	3k		**4k**	NO_2	81
	3l		**4l**	(*E*)-2-Bromovinyl	90
8	**3m**		**4m**		94
9	**3n**		**4n**		90

[a]Isolated yields.
[b]E/Z: > 99/1, determined by ^{1}H NMR analysis.



Scheme 3. (*Z*)-4-(2-Bromovinyl)benzoic acid linked to Wang resin.

EXPERIMENTAL

Melting points were recorded using an A. Krüss Optronic GmbH KSPII melting-point meter and are uncorrected. A Xinyi MAS-II microwave synthesizer was used for all microwave reactions. Infrared (IR) spectra were performed on a Nexus Fourier transform (FT)–IR spectrophotometer. ^{1}H and ^{13}C NMR spectra were recorded using a Bruker AM-300 spectrometer. Elemental analyses were performed with a Perkin-Elmer 2400 CHNS elemental analyzer. Mass spectra (MS) were recored by electron impact (EI), MALDI, and electrospray ionization (ESI) methods. *Anti*-2,3-dibromo-3-(4-carboxyphenyl)propanoic acid (**1**) was prepared according to a literature procedure.[5]

Preparation of (*Z*)-4-(2-Bromovinyl)benzoic Acid (2)

A mixture of *anti*-2,3-dibromo-3-(4-carboxyphenyl)-propanoic acid (**1**, 1.0 mmol), Et_3N (1.2 mmol), and DMF (5 mL) was was kept inside a microwave oven and was irradiated for 40 s at 300 W. The reaction mixture was acidified to pH 3 with 6% HCl when it was cooled to room temperature. Then, 30 mL water and 20 mL EtOAc were added to the mixture, and the organic layer was separated. The aqueous layer was extracted two times with 15 mL EtOAc. The combined organic layers were washed with water and brine and dried over anhydrous magnesium sulfate. Evaporation of the solvent gave the product (*Z*)-4-(2-bromovinyl) benzoic acid **2** in 97% yield. White solid; mp 159.7–159.8°C; IR (KBr): 1709, 924, 782 cm^{-1}; ^{1}H NMR (300 MHz, DMSO-d_6): $\delta = 6.86$ (1H, d, $J = 8.0$ Hz), 7.34 (1H, d, $J = 8.0$ Hz), 7.78 (2H, d, $J = 8.3$ Hz), 7.95 (2H, d, $J = 8.3$ Hz). Anal. calcd. for $C_9H_7BrO_2$: C, 47.61; H, 3.11; Br, 35.19. Found: C, 47.56; H, 3.04; Br, 35.18.

General Procedure for the One-Pot Synthesis of Functionalized (*Z*)-2-Arylvinyl Bromides 4a–n

A mixture of anti-2,3-dibromo-3-(4-carboxyphenyl)propanoic acid (**1**, 1.0 mmol), Et_3N (1.2 mmol), and DMF (4 mL) was kept inside a microwave oven, irradiated for 40 s at 300 W, and then cooled to room temperature. Benzene (1 mL), ROH (**3**, 1.0 mmol), and DMAP (0.2 mmol) were added to the reaction mixture and stirred for 10 min. DCC (1.1 mmol) was added to the reaction mixture and stirred for 24 h at ambient temperature. After evaporation of the solvent under reduced pressure, the crude product was purified by column chromatography

on silica gel with EtOAc–hexane to give 4-alkoxycarbonyl and 4-aryloxycarbonyl-(*Z*)-2-arylvinyl bromides **4a**–**n**.

Data

(*Z*)-Ethyl-4-(2-bromovinyl)benzoate (**4a**)

Colorless oil; IR (neat): 1719, 1276, 1103, 930, 777 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): $\delta = 1.40$ (3H, t, $J = 7.5$ Hz), 4.37 (2H, q, $J = 7.5$ Hz), 6.62 (1H, d, $J = 8.1$ Hz), 7.17 (1H, d, $J = 8.1$ Hz), 7.31 (2H, d, $J = 8.3$ Hz), 8.14 (2H, d, $J = 8.3$ Hz). ^{13}C NMR (125 MHz, $CDCl_3$): $\delta = 166.2$, 139.3, 131.7, 130.0, 129.5, 128.8, 108.7, 61.0, 14.3. EI-MS: m/z (%): 256 [$(M+2)^+$, 38], 254 (M^+, 39), 228 (46), 226 (45), 211 (99), 209 (100), 181 (85), 102 (86). Anal. calcd. for $C_{11}H_{11}BrO_2$: C, 51.79; H, 4.35; Br, 31.32. Found: C, 51.72; H, 4.39; Br, 31.30.

(*Z*)-Propyl-4-(2-bromovinyl)benzoate (**4b**)

White solid, mp 87.5–88.5°C; IR (KBr): 1722, 1283, 1086, 934, 785 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): $\delta = 1.04$ (3H, t, $J = 7.5$ Hz), 1.82 (2H, m), 4.30 (2H, s, $J = 6.8$ Hz), 6.62 (1H, d, $J = 8.1$ Hz), 7.17 (1H, d, $J = 8.1$ Hz), 7.31 (2H, d, $J = 8.3$ Hz), 8.14 (2H, d, $J = 8.3$ Hz). ^{13}C NMR (125 MHz, $CDCl_3$): $\delta = 165.9$, 140.3, 131.2, 130.1, 129.1, 121.7, 109.4, 66.7, 22.1, 10.5. EI-MS: m/z (%): 270 [$(M+2)^+$, 46], 268 (M^+, 47), 228 (42), 226 (41), 211 (99), 209 (100), 181 (80), 102 (90). Anal. calcd. for $C_{12}H_{13}BrO_2$: C, 53.55; H, 4.87; Br, 29.69. Found: C, 53.64; H, 4.90; Br, 29.74.

(*Z*)-Octyl-4-(2-bromovinyl)benzoate (**4c**)

Colorless oil; IR (neat): 1714, 1271, 1103, 944, 777 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): $\delta = 0.98$–1.52 (13H, m), 1.72–1.79 (2H, m), 4.32 (2H, t, $J = 6.6$ Hz), 6.56 (1H, d, $J = 8.1$ Hz), 7.12 (1H, d, $J = 8.1$ Hz), 7.74 (2H, d, $J = 8.1$ Hz), 8.05 (2H, d, $J = 8.1$ Hz). ^{13}C NMR (125 MHz, $CDCl_3$): $\delta = 166.3$, 139.2, 131.7, 130.1, 129.4, 128.8, 108.6, 65.2, 31.8, 29.2, 29.1, 28.7, 26.0, 22.6, 14.1. EI-MS: m/z (%): 340 [$(M+2)^+$, 48], 338 (M^+, 49), 228 (45), 226 (44), 211 (99), 209 (100), 181 (80), 102 (95). Anal. calcd. for $C_{17}H_{23}BrO_2$: C, 60.18; H, 6.83; Br, 23.55. Found: C, 60.24; H, 6.89; Br, 23.58.

(*Z*)-Allyl 4-(2-bromovinyl)benzoate (**4d**)

Colorless oil; IR (neat): 3076, 1719, 1421, 1273, 1113, 942, 775 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): $\delta = 4.82–4.84$ (2H, m), 5.25–5.30 (1H, m), 5.40–5.43 (1H, m), 5.96–6.08 (1H, m) 6.53–6.56 (1H, m), 7.10 (1H, d, $J = 8.2$ Hz), 7.71–7.74 (2H, m), 8.04–8.07 (2H, m). ^{13}C NMR (125 MHz, $CDCl_3$): $\delta = 65.8$, 139.4, 132.1, 131.6, 129.5, 129.4, 128.8, 118.2, 108.7, 65.6. EI-MS: m/z (%): 268 [$(M + 2)^+$, 37], 266 (M^+, 38), 228 (41), 226 (40), 211 (99), 209 (100), 181 (85), 102 (94). Anal. calcd. for $C_{12}H_{11}BrO_2$: C, 53.96; H, 4.15; Br, 29.91. Found: C, 53.89; H, 4.29; Br, 29.88.

(*Z*)-Prop-2-ynyl 4-(2-bromovinyl)benzoate (**4e**)

Colorless oil; IR (neat): 3308, 1714, 1271, 1103, 944, 777, 658 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): $\delta = 2.53$ (1H, s), 4.93 (2H, s), 6.56 (1H, d, $J = 8.2$ Hz), 7.10 (1H, d, $J = 8.2$ Hz), 7.73 (2H, d, $J = 8.4$ Hz), 8.06 (2H, d, $J = 8.4$ Hz). ^{13}C NMR (125 MHz, $CDCl_3$): $\delta = 165.3$, 139.7, 131.5, 129.7, 129.5, 128.9, 109.0, 77.6, 75.0, 52.5. EI-MS: m/z (%): 266 [$(M + 2)^+$, 45], 264 (M^+, 46), 228 (43), 226 (42), 211 (99), 209 (100), 181 (88), 102 (91). Anal. calcd. for $C_{12}H_9BrO_2$: C, 54.37; H, 3.42; Br, 30.14. Found: C, 54.41; H, 3.43; Br, 30.10.

(*Z*)-Cyclohexyl-4-(2-bromovinyl)benzoate (**4f**)

Colorless oil; IR (neat): 1714, 1276, 1103, 940, 772 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): $\delta = 0.96–1.96$ (10H, m), 5.02 (1H, m), 6.56 (1H, d, $J = 8.1$ Hz), 7.12 (1H, d, $J = 8.1$ Hz), 7.73 (2H, d, $J = 8.3$ Hz), 8.05 (2H, d, $J = 8.3$ Hz). ^{13}C NMR (125 MHz, $CDCl_3$): $\delta = 164.5$, 138.1, 130.7, 129.5, 128.4, 127.8, 107.6, 72.1, 30.6, 24.5, 22.6. EI-MS: m/z (%): 310 [$(M + 2)^+$, 47], 308 (M^+, 48), 228 (45), 226 (44), 211 (99), 209 (100), 181 (88), 102 (92). Anal. calcd. for $C_{15}H_{17}BrO_2$: C, 58.27; H, 5.54; Br, 25.84. Found: C, 58.30; H, 5.62; Br, 25.80.

(*Z*)-Benzyl-4-(2-bromovinyl)benzoate (**4g**)

Colorless oil; IR (neat): 1713, 1271, 1097, 944, 777 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): $\delta = 5.37$ (2H, s), 6.56 (1H, d, $J = 8.3$ Hz), 7.11 (1H, d, $J = 8.3$ Hz), 7.37–7.47 (5H, m), 7.73 (2H, d, $J = 8.1$ Hz), 8.08 (2H, d, $J = 8.1$ Hz). ^{13}C NMR (125 MHz, $CDCl_3$): $\delta = 166.0$, 139.4, 136.0, 131.6, 130.2, 129.6, 128.9, 128.6, 128.3, 128.2, 108.8, 66.8. EI-MS: m/z

(%): 318 [$(M+2)^+$, 48], 316 (M^+, 49), 228 (44), 226 (43), 211 (99), 209 (100), 181 (89), 102 (90). Anal. calcd. for $C_{16}H_{13}BrO_2$: C, 60.59; H, 4.13; Br, 25.19. Found: C, 60.62; H, 4.20; Br, 25.22.

(*Z*)-5-Isopropyl-2-methylphenyl-4-(2-bromovinyl)benzoate (**4h**)

Colorless oil; IR (neat): 1729, 1266, 1082, 930, 772 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): $\delta = 1.21$ (6H, d, $J = 6.9$ Hz), 2.35 (3H, s), 3.06 (1H, m), 6.61 (1H, d, $J = 8.4$ Hz), 6.95 (1H, s), 7.07 (1H, d, $J = 7.2$ Hz), 7.17 (1H, d, $J = 8.4$ Hz), 7.24 (1H, s), 7.82 (2H, d, $J = 8.3$ Hz), 8.22 (2H, $J = 8.3$ Hz). ^{13}C NMR (125 MHz, $CDCl_3$): $\delta = 165.0$, 148.1, 140.0, 137.2, 136.7, 131.6, 130.1, 129.2, 129.1, 127.2, 126.5, 122.8, 109.1, 27.3, 23.0, 20.8. EI-MS: m/z (%): 360 [$(M+2)^+$, 46], 358 (M^+, 47), 228 (43), 226 (42), 211 (99), 209 (100), 181 (85), 102 (90). Anal. calcd. for $C_{19}H_{19}BrO_2$: C, 63.52; H, 5.33; Br, 22.24. Found: C, 63.48; H, 5.38; Br, 22.38.

(*Z*)-Phenyl-4-(2-bromovinyl)benzoate (**4i**)

White solid, mp 84.1–84.2°C; IR (KBr): 1734, 1276, 1072, 935, 772 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): $\delta = 6.61$ (1H, d, $J = 8.3$ Hz), 7.16 (1H, d, $J = 8.3$ Hz), 7.21–7.31 (3H, m), 7.42–7.47 (2H, m), 7.81 (2H, d, $J = 8.6$ Hz), 8.21 (2H, d, $J = 8.6$ Hz). ^{13}C NMR (125 MHz, $CDCl_3$): $\delta = 164.8$, 150.9, 140.0, 131.6, 130.7, 130.1, 129.5, 129.0, 125.9, 121.7, 109.2. EI-MS: m/z (%): 304 [$(M+2)^+$, 38], 302 (M^+, 39), 228 (40), 226 (39), 211 (99), 209 (100), 181 (84), 102 (88). Anal. calcd. for $C_{15}H_{11}BrO_2$: C, 59.43; H, 3.66; Br, 26.36. Found: C, 59.48; H, 3.69; Br, 26.40.

(*Z*)-4-(Formylphenyl)-4-(2-bromovinyl)benzoate (**4j**)

White solid, mp 93.2–93.4°C; IR (KBr): 1741, 1734, 1271, 1072, 940, 741 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): $\delta = 6.64$ (1H, d, $J = 8.3$ Hz), 7.18 (1H, d, $J = 8.3$ Hz), 7.43 (2H, d, $J = 8.6$ Hz), 7.84 (2H, d, $J = 8.4$ Hz), 8.00 (2H, d, $J = 8.6$ Hz), 8.22 (2H, d, $J = 8.4$ Hz), 10.04 (1H, s). ^{13}C NMR (125 MHz, $CDCl_3$): $\delta = 190.9$, 164.1, 140.5, 134.1, 131.5, 131.3, 130.9, 130.2, 129.2, 126.3, 122.5, 109.6. EI-MS: m/z (%): 332 [$(M+2)^+$, 49], 330 (M^+, 50), 228 (41), 226 (40), 211 (99), 209 (100), 181 (88), 102 (91). Anal. calcd. for $C_{16}H_{11}BrO_3$: C, 58.03; H, 3.35; Br, 24.13. Found: C, 58.10; H, 3.30; Br, 24.19.

(*Z*)-4-(Nitrophenyl)-4-(2-bromovinyl)benzoate (**4k**)

Yellow solid, mp 112.5–113.5°C; IR (KBr): 1734, 1266, 1067, 930, 772 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): $\delta = 6.57$ (1H, d, $J = 8.4$ Hz), 7.10 (1H, d, $J = 8.4$ Hz), 7.36 (2H, d, $J = 9.0$ Hz), 7.76 (2H, d, $J = 8.0$ Hz), 8.14 (2H, d, $J = 8.0$ Hz), 8.27 (2H, d, $J = 9.0$ Hz). ^{13}C NMR (125 MHz, $CDCl_3$): $\delta = 163.8$, 155.7, 145.5, 140.7, 131.4, 130.3, 129.2, 127.9, 125.3, 122.6, 109.7. EI-MS: m/z (%): 349 [$(M + 2)^+$, 47], 347 (M^+, 48), 228 (40), 226 (39), 211 (99), 209 (100), 181 (85), 102 (93). Anal. calcd. for $C_{15}H_{10}BrNO_4$: C, 51.75; H, 2.90; Br, 22.95. Found: C, 51.78; H, 2.96; Br, 22.86.

4-((*E*)-2-Bromovinyl)phenyl 4-((Z)-2-bromovinyl)benzoate (**4l**)

White solid, mp 118.5–119.5°C; IR (KBr): 1729, 1271, 1072, 935, 772 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): $\delta = 6.62$ (1H, d, $J = 8.1$ Hz), 6.77 (1H, d, $J = 8.1$ Hz), 7.10–7.18 (4H, m), 7.37 (2H, d, $J = 8.4$ Hz), 7.82 (2H, d, $J = 8.4$ Hz), 8.20 (2H, d, $J = 8.4$ Hz). ^{13}C NMR (125 MHz, $CDCl_3$): $\delta = 164.6$, 150.7, 140.1, 136.2, 133.8, 131.5, 130.1, 129.1, 127.2, 126.1, 122.1, 109.3, 106.7. EI-MS: m/z (%): 410 [$(M + 4)^+$, 10], 408 [$(M + 2)^+$, 80], 406 (M^+, 40), 228 (41), 226 (40), 211 (99), 209 (100), 181 (83), 102 (91). Anal. calcd. for $C_{17}H_{12}Br_2O_2$: C, 50.03; H, 2.96; Br, 39.16. Found: C, 50.08; H, 3.01; Br, 39.12.

(*Z*)-Naphthalen-2-yl-4-(2-bromovinyl)benzoate (**4m**)

White solid, mp 126.4–126.9°C; IR (KBr): 1734, 1266, 1067, 925 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): $\delta = 6.62$ (1H, d, $J = 8.3$ Hz), 7.17 (1H, d, $J = 8.3$ Hz), 7.35–7.38 (1H, m), 7.47–7.54 (2H, m), 7.70 (1H, d, $J = 2.4$ Hz), 7.82–7.93 (5H, m), 8.26 (2H, d, $J = 8.7$ Hz). ^{13}C NMR (125 MHz, $CDCl_3$): $\delta = 164.9$, 148.6, 140.1, 133.8, 131.6, 131.5, 130.1, 129.5, 129.1, 127.8, 127.7, 126.6, 125.8, 121.2, 118.7, 110.7, 109.2. EI-MS: m/z (%): 354 [$(M + 2)^+$, 51], 352 (M^+, 52), 228 (40), 226 (39), 211 (99), 209 (100), 181 (83), 102 (90). Anal. calcd. for $C_{19}H_{13}BrO_2$: C, 64.61; H, 3.71; Br, 22.62. Found: C, 64.70; H, 3.75; Br, 22.58.

(*Z*)-Naphthalen-1-yl-4-(2-bromovinyl)benzoate (**4n**)

White solid, mp 82.0–83.0°C; IR (KBr): 1719, 1261, 925, 767 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): $\delta = 6.64$ (1H, d, $J = 8.1$ Hz), 7.19 (1H, d, $J = 8.1$ Hz), 7.38 (1H, d, $J = 7.2$ Hz), 7.50–7.55 (3H, m), 7.79–7.95 (5H, m), 8.34 (2H, d, $J = 8.1$ Hz). ^{13}C NMR (125 MHz, $CDCl_3$):

δ = 164.8, 146.8, 140.2, 134.7, 131.6, 130.2, 129.2, 128.8, 128.1, 126.9, 126.5, 126.1, 125.5, 121.2, 118.2, 109.3. EI-MS: m/z (%): 354 [$(M+2)^+$, 49], 352 (M^+, 50), 228 (38), 226 (37), 211 (99), 209 (100), 181 (81), 102 (95). Anal. calcd. for $C_{19}H_{13}BrO_2$: C, 64.61; H, 3.71; Br, 22.62. Found: C, 64.71; H, 3.74; Br, 22.66.

Preparation of (*Z*)-4-(2-Bromovinyl)benzoic Acid Linked to Wang Resin (5)

The Wang resin (5 mmol, 1.0 mmol/g) was swollen in a minimal amount of benzene, and (*Z*)-4-(2-bromovinyl)benzoic acid (**2**, 15 mmol), DCC (15 mmol), and DMAP (1 mmol) in benzene (30 mL) were added sequentially to the resin. The resulting mixture was reacted for 24 h. The resin was filtered and washed consecutively with benzene, CH_2Cl_2, and methanol (MeOH). The resin was then dried under reduced pressure for 24 h. The loading of the resin was estimated by IR analysis ($\nu_{C=O}$: 1736 cm^{-1}). The coupling yield was determined by cleaving 100 mg of the resin with a solution of 20% trifluoroacetic acid (TFA) in CH_2Cl_2 for 20 min at ambient temperature. The solvent mixture was evaporated to provide **2** in 90% yield. Compound **2** was identical with authentic samples.

ACKNOWLEDGMENTS

The work was supported by the Natural Science Foundation of Shanghai, China (No. 06ZR14085), the Key Projects of Shanghai in Biomedical (No. 08431902700), and by the Scientific Research Foundation for the Returned Overseas Chinese Scholars, State Education Ministry. We thank the Instrumental Analysis Center, Tongji University, China, for assistance.

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