A One-pot Synthesis of Novel Functionalized (*E*)-β-Arylvinyl Bromides from *anti*-2,3-Dibromo-3-(4-carboxyphenyl)propanoic Acid

Chunxiang Kuang[a], Yubo Jiang[a], Qing Yang[b], Wensheng Zhang[a], and Yaolin Wen[c]

[a] Department of Chemistry, Tongji University, Siping Road 1239, Shanghai 200092, China
[b] School of Pharmacy, Fudan University, Yixueyuan Road 138, Shanghai 200032, China
[c] Unilever Research China, Tianzhou Road 99, Shanghai 200233, China

Reprint requests to Prof. C. Kuang. Fax: +86-21-6598-3191. E-mail: kuangcx@mail.tongji.edu.cn or Dr. Q. Yang. Fax: +86-21-5423-7692. E-mail: yangqing68@fudan.edu.cn

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A facile one-pot synthesis of functionalized (*E*)-β-arylvinyl bromides bearing various 4-alkoxycarbonyl and 4-aryloxycarbonyl groups was achieved by debrominative decarboxylation of *anti*-2,3-dibromo-3-(4-carboxyphenyl)propanoic acid in the presence of AgOAc and subsequent esterification in the presence of dicyclohexyl carbodiimide and dimethylaminopyridine. This method gives (*E*)-β-arylvinyl bromides in high stereoselectivities and high yields, and tolerates aldehyde, ester, and nitro functional groups.

Key words: (*E*)-β-Arylvinyl Bromides, Stereoselectivity, One-pot Synthesis, Esterification

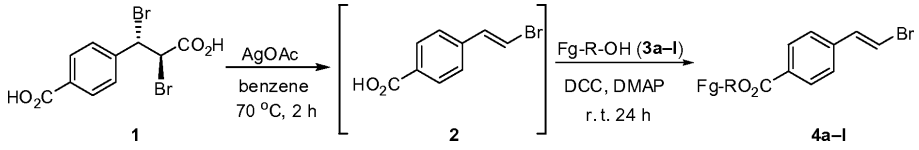
Introduction

(*E*)-β-Arylvinyl bromides are important building blocks in organic synthesis, especially as intermediates for carbon-carbon and carbon-hetero atom bond formation by transition metal-catalyzed coupling reactions [1]. The coupling products from functionalized (*E*)-β-arylvinyl bromides have found numerous applications in the preparation of pharmaceuticals, liquid crystal and natural products [2]. Although there is a necessity to incorporate functional groups in (*E*)-β-arylvinyl bromides in order to find novel functionalized compounds, synthetic methods available are limited in scope. Traditional methods for preparation of (*E*)-β-arylvinyl bromides can be classified into three major categories. The first method is the Hunsdiecker-type bromodecarboxylation [3] and the decarboxylation of cinnamic acid dibromides [2b]. The second method is the conversion of 1,1-dibromoalkenes to the corresponding (*E*)-β-arylvinyl bromides by a reduction using diethyl phosphonate [4], an organolithium reagent [5], a Grignard reagent [6], or lithium aluminum hydride [7]. The third method involves the reaction of $CHBr_3$ with aryl aldehyde mediated by $CrCl_2$ leading to the formation of (*E*)-β-arylvinyl bromides [8]. Generally, the above methods are not tolerant to reactive groups such as the aldehyde group. Hence it is extremely difficult to apply these methods in the preparation of (*E*)-β-arylvinyl bromides bearing various functional groups.

On the other hand, to find more convenient and efficient methods for the synthesis of functionalized (*E*)-β-arylvinyl bromides is our ongoing program. One of us previously reported the stereoselective synthesis of (*E*)-β-arylvinyl bromides by microwave irradiation of the corresponding *anti*-3-aryl-2,3-dibromopropanoic acids in AcOH in the presence of AgOAc [9]. Herein, we report a one-pot synthesis of novel functionalized (*E*)-β-arylvinyl bromides (**4**) having various 4-alkoxycarbonyl and 4-aryloxycarbonyl groups including aldehyde, ester or nitro moieties from *anti*-2,3-dibromo-3-(4-carboxyphenyl)propanoic acid (**1**) (Scheme 1). To the best of our knowledge, the one-pot synthesis of functionalized (*E*)-β-arylvinyl bromides from *anti*-2,3-dibromo-3-(4-carboxyphenyl) propanoic acid has not been reported.

Results and Discussion

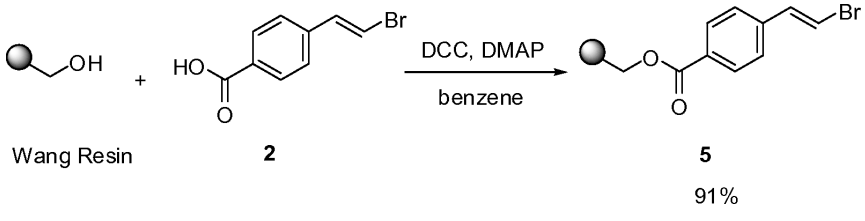
The starting dibromide **1** was easily prepared in two steps by Knoevenagel condensation of 4-formylbenzoic acid with malonic acid followed by bromination of the (*E*)-4-(2-carboxyvinyl)benzoic acid. The first step of the following one-pot reaction was carried out under conventional thermal conditions and gave (*E*)-4-(2-bromovinyl)benzoic acid (**2**) in high yield with



Fg-R = alkyl or aryl groups bearing a -CHO, -CO_2R, -NO_2 functional group

Compound	Fg-R	Compound	Fg-R
4a	C_2H_5	**4g**	5-isopropyl-2-methylphenyl
4b	*i*-C_3H_7	**4h**	4-formylphenyl
4c	*n*-C_8H_{17}	**4i**	4-(propoxycarbonyl)phenyl
4d	cyclohexyl	**4j**	4-nitrophenyl
4e	benzyl	**4k**	naphthalen-2-yl
4f	phenyl	**4l**	naphthalen-1-1yl

Scheme 1. One-pot synthesis of functionalized (*E*)-β-arylvinyl bromides.



Scheme 2. Coupling of (*E*)-4-(2-bromovinyl)benzoic acid with the Wang resin.

high stereoselectivity. Compound **2** carrying a carboxyl group is a new synthon for the preparation of various derivatives that are useful intermediates in organic synthesis. In the second step, we chose DCC/DMAP as coupling agent for the esterification of acid **2** with alcohols or phenols **3**.

It would be very convenient for a one-pot reaction to use the same solvent in two successive steps. As we previously reported, HOAc was the solvent in the preparation of (*E*)-β-arylvinyl bromides by microwave irradiation of *anti*-3-aryl-2,3-dibromopropanoic acids in the presence of AgOAc, but HOAc can not be applied in the esterification step. Recently, we found that the conversion of dibromide **1** to acid **2** could be carried out in benzene. When benzene was applied as solvent for the DCC/DMAP coupling esterification, it gave a high yield compared to other solvents such as DMF, CH_2Cl_2. Therefore, benzene was used as the common solvent for the two successive steps.

Various (*E*)-β-arylvinyl bromides were prepared by this one-pot method. The results are summarized in Scheme 1.

Isolated yields varied from 85 % to 94 %, and the *E/Z* ratio determined by ^{1}H NMR spectroscopy was over 98 : 2. These results indicate that the present reaction is very useful for the synthesis of both 4-alkoxycarbonyl- (**4a**–**e**) and 4-aryloxycarbonyl- (**4f**–**l**) (*E*)-β-arylvinyl bromides. (*E*)-β-Arylvinyl bromides carrying a naphthyl group (**4k**–**l**) were also easily prepared in excellent yields. Even if an electron-withdrawing group such as –CHO, –CO_2R, –NO_2 was present in the molecule, the reaction proceeded stereoselectively in high 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 ester **5** in high yield (Scheme 2). 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 agricultural industries. Further, ester **5** is an excellent substrate for Stille, Suzuki or Heck reactions [1].

Conclusion

In summary, we have developed a simple and efficient one-pot synthetic method for the preparation of 4-alkoxycarbonyl- and 4-aryloxy carbonyl (*E*)-β-arylvinyl bromides bearing various functional groups in high stereoselectivities and high yields. A wide range of functional groups including aldehyde, ester, and nitro groups were found to tolerate the DCC/DMAP

esterification condition. These functionalized (*E*)-β-arylvinyl bromides are important synthetic targets and widely used synthons for synthetic chemists.

Experimental Section

Melting points were recorded using a Yanagimoto micro melting point apparatus and are uncorrected. ^{1}H and ^{13}C NMR spectra were recorded using a Bruker AM-300 spectrometer at 300 MHz (^{1}H) and at 75 MHz (^{13}C) in $CDCl_3$ with $SiMe_4$ as an internal standard. Mass spectra were obtained by EI, MALDI, and ESI methods, and HRMS was measured by the EI method. IR spectra were recorded on a Shimadzu IR-408 spectrophotometer. Elemental analyses were performed on a Flash EA1112 instrument. Organic solvents used were dried by standard methods when necessary. Commercially obtained reagents were used without further purification. All reactions were monitored by TLC with HuanghaiGF$_{254}$ silica gel coated plates. Flash column chromatography was carried out using 300 – 400 mesh silica gel at medium pressure. (*E*)-4-(2-Carboxyvinyl)benzoic acid was prepared according to a literature procedure [10].

*anti-2,3-Dibromo-3-(4-carboxyphenyl)propanoic acid (**1**)*

1 was prepared according to the previously described procedure [11]. White solid, m. p. 288 – 289 °C (HOAc). – IR (KBr): ν = 1704 (C=O), 930, 746 cm^{-1}. – ^{1}H NMR (300 MHz, [D$_6$]DMSO): δ = 5.40 (d, J = 11.9 Hz, 1H, Ar-C*H*Br-), 5.62 (d, J = 11.9 Hz, 1H, -C*H*Br-), 7.77 (d, J = 7.4 Hz, 2H of Ph), 7.93 (d, J = 7.4 Hz, 2H of Ph). – MS (EI): *m/z* (%) = 354 (23) [M+4]$^+$, 352 (47) [M+2]$^+$, 350 (24) [M]$^+$, 271 (42), 148 (100). – HRMS: *m/z* = 351.8766 (calcd. 351.8768 for $C_{10}H_8{}^{79}Br^{81}BrO_4$, [M]$^+$). – $C_{10}H_8Br_2O_4$ (351.98): calcd. C 34.12, H 2.29, Br 45.40; found C 34.18, H 2.23, Br 45.35.

*(E)-4-(2-Bromovinyl)benzoic acid (**2**)*

A mixture of *anti*-2,3-dibromo-3-(4-carboxyphenyl)propanoic acid (**1**, 1.0 mmol), AgOAc (1.2 mmol), and benzene (15 mL) was heated to 70 °C, stirred for 2 h, and cooled to r. t. Water and EtOAc were added to the reaction mixture, and the organic layer was separated. The aqueous layer was extracted with EtOAc. The combined organic layers were washed with water and brine and dried over anhydrous magnesium sulfate. Evaporation of the solvent gave the crude product, which was subjected to column chromatography (silica gel, hexane / EtOAc = 10 / 3, R_f = 0.42) to afford (*E*)-4-(2-bromovinyl)benzoic acid **2** in 96 % yield. Colorless crystals, m. p. 268 °C (hexane/EtOAc). – IR (KBr): ν =1716 (C=O), 1608, 935 cm^{-1}. – ^{1}H NMR (300 MHz, [D$_6$]DMSO): δ = 7.30 (d, J = 13.8 Hz, 1H, Br-C*H*=CH-), 7.48 (d, J = 13.8 Hz, 1H, Ar-C*H*=CH-), 7.60 (d, J = 8.4 Hz, 2H of Ph), 7.90 (d, J = 8.4 Hz, 2H of Ph). – ^{13}C NMR (75 MHz, [D$_6$]DMSO): δ = 111.34, 126.35 (2 × C), 129.72, 130.28, 136.04, 139.64, 140.77, 166.96. – MS (EI): *m/z* (%) = 228 (48) [M+2]$^+$, 226 (47) [M]$^+$, 211 (99), 209 (100), 102 (88). – HRMS: *m/z* = 225.9628 (calcd. 225.9629 for $C_9H_7{}^{79}BrO_2$, [M]$^+$). – $C_9H_7BrO_2$ (227.05): calcd. C 47.61, H 3.11, Br 35.19; found C 47.55, H 3.02, Br 35.17.

*One-pot synthesis of functionalized (E)-β-arylvinyl bromides **4**; general procedure*

A mixture of *anti*-2,3-dibromo-3-(4-carboxyphenyl)propanoic acid (**1**, 1.0 mmol), AgOAc (1.2 mmol) and benzene (15 mL) was heated to 70 °C and stirred for 2 h, then cooled to r. t. ROH (**3**, 1.0 mmol) and DMAP (1.0 mmol) were added and the reaction mixture stirred for 10 min. DCC (1.5 mmol) was added and the reaction mixture stirred for 24 h at ambient temperature. Subsequently water (20 mL) was added to the mixture, and the product was extracted with EtOAc. The organic layer was washed with sodium bicarbonate solution and water and then dried with anhydrous sodium sulfate. After evaporation of the solvent, the crude product was purified by column chromatography on silica gel with EtOAc-hexane to give 4-alkoxycarbonyl- and 4-aryloxycarbonyl-(*E*)-β-arylvinyl bromides **4**.

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

Prepared from compound **1** and ethanol (**3a**), 224 mg (88 %). Colorless oil. – IR (neat): ν = 1714 (C=O), 1276, 1103, 935, 746 cm^{-1}. – ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.39 (t, J = 7.3 Hz, 3H, C*H*$_3$-CH$_2$-), 4.37 (q, J = 7.3 Hz, 2H, -O-C*H*$_2$-CH$_3$), 6.91 (d, J = 14.2 Hz, 1H, Br-C*H*=CH-), 7.14 (d, J = 14.2 Hz, 1H, Ar-C*H*=CH-), 7.35 (d, J = 8.6 Hz, 2H of Ph), 8.00 (d, J = 8.6 Hz, 2H of Ph). – ^{13}C NMR (75 MHz, $CDCl_3$): δ = 14.27, 61.03, 109.27, 125.88, 129.96, 130.03, 136.33, 139.91, 166.11. – MS (EI): *m/z* (%) = 256 (48) [M+2]$^+$, 254 (47) [M]$^+$, 228 (36), 226 (37), 211 (99), 209 (100), 102 (91). – HRMS: *m/z* = 253.9945 (calcd. 253.9942 for $C_{11}H_{11}{}^{79}BrO_2$, [M]$^+$).

*Isopropyl (E)-4-(2-bromovinyl)benzoate (**4b**)*

Prepared from compound **1** and propan-2-ol (**3b**), 248 mg (92 %). Colorless oil. – IR (neat): ν = 1709 (C=O), 1271, 1098, 930, 746 cm^{-1}. – ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.29 (d, J = 6.6 Hz, 6H, -CH$_3$), 5.13 – 5.21 (m, 1H, -C*H*-CH$_3$), 6.84 (d, J = 14.1 Hz, 1H, Br-C*H*=CH-), 7.06 (d, J = 14.1 Hz, 1H, Ar-C*H*=CH-), 7.28 (d, J = 8.1 Hz, 2H of Ph), 7.92 (d, J = 8.1 Hz, 2H of Ph). – ^{13}C NMR (75 MHz, $CDCl_3$): δ = 21.88, 66.44, 109.16, 125.81, 129.99, 130.37, 136.35, 139.80, 156.56. – MS (EI): *m/z* (%) = 270 (45) [M+2]$^+$, 268 (46) [M]$^+$, 228 (37), 226 (38), 211 (99), 209 (100), 102 (88). – HRMS: *m/z* = 268.0096 (calcd. 268.0098

for $C_{12}H_{13}{}^{79}BrO_2$, $[M]^+$). – $C_{12}H_{13}BrO_2$ (269.13): calcd. C 53.55, H 4.87, Br 29.69; found C 53.64, H 4.90, Br 29.74.

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

Prepared from compound **1** and octan-1-ol (**3c**), 305 mg (90 %). Colorless oil. – IR (neat): ν = 1714 (C=O), 1271, 1103, 935, 741 cm^{-1}. – ^1H NMR (300 MHz, $CDCl_3$): δ = 0.88 (t, J = 7.4 Hz, 3H, CH_3-CH_2), 1.28 – 1.95 (m, 12H, -CH_2-), 4.31 (t, J = 6.6 Hz, 2H, -OCH_2-CH_2-), 6.92 (d, J = 14.3 Hz, 1H, Br-C*H*=CH-), 7.14 (d, J = 14.3 Hz, 1H, Ar-C*H*=CH-), 7.36 (d, J = 8.2 Hz, 2H of Ph), 8.00 (d, J = 8.2 Hz, 2H of Ph). – ^{13}C NMR (75 MHz, $CDCl_3$): δ = 14.03, 22.58, 25.39, 29.13, 29.18, 31.72, 34.85, 65.18, 109.23, 125.85, 130.01, 130.08, 135.32, 139.89, 168.11. – MS (EI): *m/z* (%) = 340 (45) $[M+2]^+$, 338 (46) $[M]^+$, 228 (36), 226 (35), 211 (99), 209 (100), 102 (89). – HRMS: *m/z* = 338.0880 (calcd. 338.0882 for $C_{17}H_{23}{}^{79}BrO_2$, $[M]^+$). – $C_{17}H_{23}BrO_2$ (339.27): calcd. C 60.18, H 6.83, Br 23.55; found C 60.24, H 6.79, Br 23.58.

*Cyclohexyl(E)-4-(2-bromovinyl)benzoate (**4d**)*

Prepared from compound **1** and cyclohexanol (**3d**), 284 mg (92 %). White solid, m. p. 61 – 62 °C (hexane/EtOAc). – IR (KBr): ν = 1714 (C=O), 1270, 1103, 935, 751 cm^{-1}. – ^1H NMR (300 MHz, $CDCl_3$): δ = 1.10 – 1.86 (m, 10H, -CH_2-), 4.92 – 4.98 (m, 1H, -OC*H*-), 6.84 (d, J = 14.2 Hz, 1H, Br-C*H*=CH-), 7.07 (d, J = 14.2 Hz, 1H, Ar-C*H*=CH-), 7.28 (d, J = 8.2 Hz, 2H of Ph), 7.93 (d, J = 8.2 Hz, 2H of Ph). – ^{13}C NMR (75 MHz, $CDCl_3$): δ = 23.61, 24.64, 31.57, 73.14, 109.13, 125.82, 130.01, 130.49, 136.37, 139.78, 165.45. – MS (EI): *m/z* (%) = 310 (49) $[M+2]^+$, 308 (48) $[M]^+$, 228 (39), 226 (38), 211 (99), 209 (100), 102 (90). – HRMS: *m/z* = 308.0410 (calcd. 308.0412 for $C_{15}H_{17}{}^{79}BrO_2$, $[M]^+$). – $C_{15}H_{17}BrO_2$ (309.20): calcd. C 58.27, H 5.54, Br 25.84; found C 58.30, H 5.62, Br 25.80.

*Benzyl (E)-4-(2-bromovinyl)benzoate (**4e**)*

Prepared from compound **1** and phenylmethanol (**3e**), 285 mg (90 %). White solid, m. p. 50 – 52 °C (hexane/EtOAc). – IR (KBr): ν = 1714 (C=O), 1261, 1082, 940, 751 cm^{-1}. – ^1H NMR (300 MHz, $CDCl_3$): δ = 5.28 (s, 2H, -CH_2-Ph), 6.83 (d, J = 14.1 Hz, 1H, Br-C*H*=CH-), 7.05 (d, J = 14.1 Hz, 1H, Ar-C*H*=CH-), 7.28 – 7.38 (m, 7H, 2H of Ph, 5H of Ph), 7.95 (d, J = 8.3 Hz, 2H of Ph). – ^{13}C NMR (75 MHz, $CDCl_3$): δ = 66.75, 109.45, 125.93, 128.16, 128.26, 128.57, 129.58, 130.21, 135.90, 136.29, 140.14, 165.90. – MS (EI): *m/z* (%) = 318 (48) $[M+2]^+$, 316 (47) $[M]^+$, 228 (36), 226 (35), 211 (99), 209 (100), 102 (89). – HRMS: *m/z* = 316.0099 (calcd. 316.0098 for $C_{16}H_{13}{}^{79}BrO_2$, $[M]^+$). – $C_{16}H_{13}BrO_2$ (317.18): calcd. C 60.59, H 4.13, Br 25.19; found C 60.62, H 4.20, Br 25.22.

*Phenyl (E)-4-(2-bromovinyl)benzoate (**4f**)*

Prepared from compound **1** and phenol (**3f**), 248 mg (82 %). White solid, m. p. 112 – 113 °C (hexane/EtOAc). – IR (KBr): ν = 1729 (C=O), 1261, 1072, 940, 741 cm^{-1}. – ^1H NMR (300 MHz, $CDCl_3$): δ = 6.99 (d, J = 14.1 Hz, 1H, Br-C*H*=CH-), 7.17 – 7.23 (m, 3H; 2H of Ph, 1H, Ar-C*H*=CH-), 7.30 (d, J = 7.8 Hz, 1H of Ph), 7.42 – 7.47 (m, 4H, 4H of Ph), 8.17 (d, J = 8.1 Hz, 2H of Ph). – ^{13}C NMR (75 MHz, $CDCl_3$): δ = 109.85, 121.60 (2 × C), 125.88 (3 × C), 126.08 (2 × C), 129.45 (2 × C), 130.67 (2 × C), 136.23, 140.66, 165.90. – MS (EI): *m/z* (%) = 304 (48) $[M+2]^+$, 302 (47) $[M]^+$, 228 (36), 226 (35), 211 (99), 209 (100), 102 (89). – HRMS: *m/z* = 301.9945 (calcd. 301.9942 for $C_{15}H_{11}{}^{79}BrO_2$, $[M]^+$). – $C_{15}H_{11}BrO_2$ (303.15): calcd. C 59.43, H 3.66, Br 26.36; found C 59.48, H 3.69, Br 26.40.

*5-Isopropyl-2-methylphenyl (E)-4-(2-bromovinyl) benzoate (**4g**)*

Prepared from compound **1** and 5-isopropyl-2-methylphenol (**3g**), 331 mg (92 %). Colorless oil. – IR (neat): ν = 1729 (C=O), 1261, 1082, 935, 746 cm^{-1}. – ^1H NMR (300 MHz, $CDCl_3$): δ = 1.16 (d, J = 12.9 Hz, 6H, CH_3-CH-), 2.27 (s, 3H, Ar-CH_3), 2.91 – 3.01 (q, J = 6.2 Hz, 1H, -C*H*-CH_3), 6.86 – 7.01 (m, 3H, Br-C*H*=CH-, 2H of Ph), 7.09 – 7.19 (m, 2H, Ar-C*H*=CH-, 1H of Ph), 7.37 (d, J = 8.2 Hz, 2H of Ph), 8.10 (d, J = 8.2 Hz, 2H of Ph). – ^{13}C NMR (75 MHz, $CDCl_3$): δ = 20.82, 25.42, 27.25, 109.85, 122.78, 126.16, 126.46, 127.20, 129.06, 130.65, 136.24, 136.63, 137.09, 140.64, 148.04, 164.85. – MS (EI): *m/z* (%) = 360 (48) $[M+2]^+$, 358 (47) $[M]^+$, 228 (36), 226 (35), 211 (99), 209 (100), 102 (89). – HRMS: *m/z* = 358.0569 (calcd. 358.0569 for $C_{19}H_{19}{}^{79}BrO_2$, $[M]^+$). – $C_{19}H_{19}BrO_2$ (359.26): calcd. C 63.52, H 5.33, Br 22.24; found C 63.48, H 5.38, Br 22.38.

*4-(Formylphenyl) (E)-4-(2-bromovinyl)benzoate (**4h**)*

Prepared from compound **1** and 4-hydroxybenzaldehyde (**3h**), 308 mg (93 %). White solid, m. p. 163 – 164 °C (hexane/EtOAc). – IR (KBr): ν = 1741 (C=O), 1734 (C=O), 1271, 1072, 940, 741 cm^{-1}. – ^1H NMR (300 MHz, $CDCl_3$): δ = 7.01 (d, J = 14.2 Hz, 1H, Br-C*H*=CH-), 7.20 (d, J = 14.2 Hz, 1H, Ar-C*H*=CH-), 7.40 – 7.47 (m, 4H of Ph), 7.99 (d, J = 8.4 Hz, 2H of Ph), 8.17 (d, J = 8.1Hz, 2H of Ph), 10.04 (s, 1H, -C*H*O). – ^{13}C NMR (75 MHz, $CDCl_3$): δ = 110.27, 122.43, 126.20, 128.27, 130.78, 131.22, 134.06, 136.10, 141.10, 155.54, 164.01, 190.82. – MS (EI): *m/z* (%) = 332 (90) $[M+2]^+$, 330 (92) $[M]^+$, 228 (36), 226 (35), 211 (99), 209 (100), 102 (89). – HRMS: *m/z* = 329.9888 (calcd. for $C_{16}H_{11}{}^{79}BrO_3$, $[M]^+$). – $C_{16}H_{11}BrO_3$ (331.16): calcd. C 58.03, H 3.35, Br 24.13; found C 58.10, H 3.30, Br 24.19.

*Propyl (E)-4-(4-(2-bromovinyl)benzoyloxy)benzoate (**4i**)*

Prepared from compound **1** and propyl 4-hydroxybenzoate (**3i**), 358 mg (92 %). White solid, m. p. 100 – 101 °C (hexane/EtOAc). – IR (KBr): ν = 1738 (C=O), 1719 (C=O), 1281, 1072, 940, 762 cm^{-1}. – ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.04 (t, J = 7.5 Hz, 3H, CH_3-CH_2-), 1.75 – 1.84 (m, 2H, CH_3-CH_2-OCH_2-), 4.30 (t, J = 6.6 Hz, 2H, -OCH_2-), 7.00 (d, J = 14.2 Hz, 1H, Br-CH=CH-), 7.20 (d, J = 14.2 Hz, 1H, Ar-CH=CH-), 7.27 – 7.46 (m, 4H, 4H of Ph), 8.13 – 8.18 (m, 4H, 4H of Ph). – ^{13}C NMR (75 MHz, $CDCl_3$): δ = 10.46, 22.06, 66.63, 110.15, 121.61, 126.15, 128.15, 128.49, 130.75, 131.13, 136.13, 140.93, 154.38, 164.12, 165.82. – MS (EI): *m/z* (%) = 390 (90) $[M+2]^+$, 388 (88) $[M]^+$, 228 (40), 226 (38), 211 (99), 209 (100), 102 (85). – HRMS: *m/z* = 388.0313 (calcd. 388.0310 for $C_{19}H_{17}{}^{79}BrO_4$, $[M]^+$). – $C_{19}H_{17}BrO_4$ (389.24): calcd. C 58.63, H 4.40, Br 20.53; found C 58.58, H 4.47, Br 20.42.

*4-(Nitrophenyl) (E)-4-(2-bromovinyl)benzoate (**4j**)*

Prepared from compound **1** and 4-nitrophenol (**3j**), 327 mg (94 %). Yellow solid, m. p. 161 – 162 °C (hexane/EtOAc). – IR (KBr): ν = 1729 (C=O), 1255, 1057, 940, 746 cm^{-1}. – ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.02 (d, J = 14.2 Hz, 1H, Br-CH=CH-), 7.20 (d, J = 14.2 Hz, 1H, Ar-CH=CH-), 7.40 – 7.48 (m, 4H, 4H of Ph), 8.16 (d, J = 8.8 Hz, 2H of Ph), 8.34 (d, J = 8.8 Hz, 2H of Ph). – ^{13}C NMR (75 MHz, $CDCl_3$): δ = 110.49, 122.51, 125.22, 126.25, 127.88, 130.84, 136.04, 141.32, 145.41, 155.58, 163.71. – MS (EI): *m/z* (%) = 349 (46) $[M+2]^+$, 347 (48) $[M]^+$, 228 (36), 226 (35), 211 (99), 209 (100), 102 (89). – HRMS: *m/z* = 346.9795 (calcd. 346.9793 for $C_{15}H_{10}{}^{79}BrNO_4$, $[M]^+$). – $C_{15}H_{10}BrNO_4$ (348.15): calcd. C 51.75, H 2.90, Br 22.95; found C 51.78, H 2.96, Br 22.86.

*Naphthalen-2-yl (E)-4-(2-bromovinyl)benzoate (**4k**)*

Prepared from compound **1** and naphthalen-2-ol (**3k**), 325 mg (92 %). White solid, m. p. 147 – 148 °C (hexane/EtOAc). – IR (KBr): ν = 1724 (C=O), 1528, 1348, 1276, 1067, 940, 746 cm^{-1}. – ^{1}H NMR (300 MHz, $CDCl_3$): δ = 6.93 (d, J = 13.6 Hz, 1H, Br-CH=CH-), 7.13 (d, J = 13.6 Hz, 1H, Ar-CH=CH-), 7.29 (d, J = 9.0 Hz, 1H, Ar-H), 7.38 – 7.47 (m, 4H, Ar-H), 7.62 (s, 1H, Ar-H), 7.75 – 7.89 (m, 3H, 3H of Ph), 8.14 (d, J = 8.1 Hz, 2H of Ph). – ^{13}C NMR (75 MHz, $CDCl_3$): δ = 109.90, 118.61, 121.10, 125.71, 126.12, 126.56, 127.63, 127.75, 129.01, 129.43, 130.72, 131.48, 133.76, 136.24, 140.73, 148.49, 165.90. – MS (EI): *m/z* (%) = 354 (88) $[M+2]^+$, 352 (90) $[M]^+$, 228 (40), 226 (39), 211 (99), 209 (100), 102 (92). – HRMS: *m/z* = 352.0096 (calcd. 352.0098 for $C_{19}H_{13}{}^{79}BrO_2$, $[M]^+$). – $C_{19}H_{13}BrO_2$ (353.21): calcd. C 64.61, H 3.71, Br 22.62; found C 64.70, H 3.75, Br 22.58.

*Naphthalen-1-yl (E)-4-(2-bromovinyl)benzoate (**4l**)*

Prepared from compound **1** and naphthalen-1-ol (**3l**), 300 mg (85 %). White solid, m. p.118 – 119 °C (hexane/EtOAc). – IR (KBr): ν = 1729 (C=O), 1255, 1057, 940, 762 cm^{-1}. – ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.02 (d, J = 14.4 Hz, 1H, Br-CH=CH-), 7.23 (d, J = 14.4 Hz, 1H, Ar-CH=CH-), 7.37 (d, J = 7.8 Hz, 1H, Ar-H), 7.48 – 7.56 (m, 5H, Ar-H), 7.80 (d, 1H, J = 8.1 Hz), 7.91 (d, J = 8.7 Hz, 2H, Ar-H), 8.30 (d, J = 8.1 Hz, 2H of Ph). – ^{13}C NMR (75 MHz, $CDCl_3$): δ = 110.01, 118.17, 121.15, 125.42, 126.09, 126.24, 126.48, 126.89, 128.04, 128.84, 130.83, 134.67, 136.23, 140.88, 146.73, 164.69. – MS (EI): *m/z* (%) = 354 (48) $[M+2]^+$, 352 (49) $[M]^+$, 228 (38), 226 (37), 211 (99), 209 (100), 102 (90). – HRMS: *m/z* = 352.0096 (calcd. 352.0098 for $C_{19}H_{13}{}^{79}BrO_2$, $[M]^+$). – $C_{19}H_{13}BrO_2$ (353.21): calcd. C 64.61, H 3.71, Br 22.62; found C 64.71, H 3.74, Br 22.66.

*Preparation of (E)-4-(2-bromovinyl)benzoic acid linked to Wang resin (**5**)*

Wang resin (5 mmol, 1.0 mmol g^{-1}) was swollen in a minimal amount of benzene, and (*E*)-4-(2-bromovinyl)benzoic acid (**2**, 15 mmol), DCC (15 mmol), 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 MeOH. The resin was dried under reduced pressure for 24 h. The loading of the resin was estimated by IR analysis (ν(C=O) = 1734 cm^{-1}). The coupling yield was determined by cleaving 100 mg of the resin with a solution of 20 % TFA in CH_2Cl_2 for 20 min at ambient temperature. The solvent mixture was evaporated and the residue recrystallized to provide **2** in 91 % yield. Compound **2** was identical with authentic samples.

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