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A new convenient access to highly functionalized (*E*)-2-arylvinyl bromides

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Abstract. Highly functionalized (*E*)-2-arylvinyl bromides were prepared in high yields through a new convenient access by acylation of (*E*)-4-(2-bromovinyl)phenol with fatty and aromatic acids at room temperature using dicyclohexyl carbodiimide (DCC) and dimethylaminopyridine (DMAP).

Keywords. (*E*)-2-Arylvinyl bromide; acylation; deacetylation.

1. Introduction

(*E*)-2-Arylvinyl bromides are important building blocks in organic synthesis, especially as intermediates for carbon–carbon and carbon–hetero atom bond formation by transition metal catalysed coupling reactions.[1,2] The coupling products from functionalized (*E*)-2-arylvinyl bromides have found numerous applications in the preparation of pharmaceuticals, functional polymeric material and natural products. Synthetic routes to these compounds are limited and mainly involve Hunsdiecker-type bromodecarboxylation of substituted *trans*-cinnamic acids with bromine sources such as NBS,[3–6] $Br^{+}(coll)_2PF_6^{-}$,[7] Br^{-}/oxidant.[8–13] However, these synthetic methods could not afford good yields and high *E*/*Z* stereoselectivities when the substrate bearing functional groups.

In this paper, we report a new convenient access to highly functionalized (*E*)-2-arylvinyl bromides **(6)** bearing various functional groups in high yields by acylation of (*E*)-4-(2-bromovinyl)phenol **(4)** with fatty acid and aromatic acid **(5)** at room temperature using dicyclohexyl carbodiimide (DCC) and dimethylaminopyridine (DMAP) (scheme 1). To the best of our knowledge, efficient synthetic method of (*E*)-2-arylvinyl bromides bearing various groups has not been reported.

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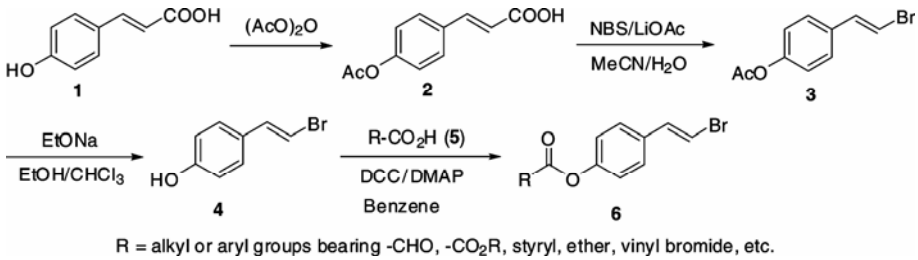
2. Experimental

2.1 *Materials and reagents*

Melting points were recorded using a A. Krüss Optronic GmbH KSPII melting-point meters and were uncorrected. IR spectra were performed on a Nexus 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 were recorded by EI, MALDI, and ESI methods. All reactions were monitored by TLC with Huanghai GF254 silica gel coated plates. Flash column chromatography was carried out using 300–400 mesh silicagel at medium pressure. *p*-Acetoxycinnamic acid **2** was prepared according to literature procedures.[14] (*E*)-4-(2-bromovinyl)phenyl acetate **3** was also prepared according to literature procedures[6] and **3** was directly converted to (*E*)-4-(2-bromovinyl)phenol **4** by selective cleavage of the acetyl protecting group in the presence of EtONa.[6] Other materials were obtained from commercial sources.

2.2 *General procedure for the synthesis of* ***6***

(*E*)-4-(2-bromovinyl)phenol (**4**, 1·0 mmol), RCO_2H (**5**, 1·1 mmol) and DMAP (1·1 mmol) in anhydrous benzene (15 mL) were stirred for 10 min. To the reaction mixture was added DCC (1·1 mmol) and stirred for 2–24 h at ambient temperature. After the completion of the reaction (monitored by TLC,



Scheme 1. Synthesis of functionalized (*E*)-2-arylvinyl bromides **6**.

Table 1. Synthesis of functionalized (*E*)-2-arylvinyl bromides.

Entry	R-CO_2H **5**		Product **6**		Time (h)	Yield of **6** (%)[a,b]
1	*n*-$C_{15}H_{31}$-CO_2H	**5a**	*n*-$C_{15}H_{31}$	**6a**	2	99
2	CO_2H	**5b**		**6b**	2	99
3	O CO_2H	**5c**	O	**6c**	24	87
4	R^1 CO_2H	**5d** R^1 = -H	R^1	**6d**	24	98
		5e -CO_2Me		**6e**	24	88
5	R^2 CO_2H	**5f** -CHO	R^2	**6f**	24	86
		5g Br		**6g**	3	93
		5h Br		**6h**	4	95
6	N CO_2H	**5i**	N	**6i**	24	97
7	N CO_2H	**5j**	N	**6j**	24	87
8	X CO_2H	**5k** X = O	X	**6k**	5	98
		5l S		**6l**	24	94

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

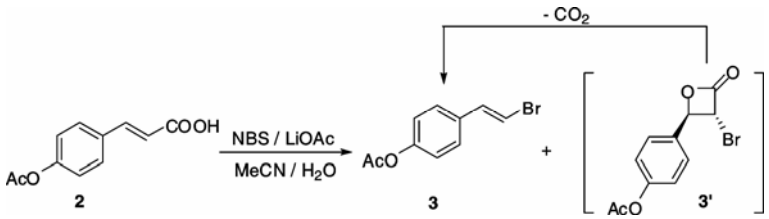
EtOAc : hexane, 1 : 2), the solvent was evaporated and the residue was subjected to column chromatography (silica gel, EtOAc-petroleum ether, 1 : 8–1 : 4) to afford functionalized 4-acyloxy-(*E*)-2-arylvinyl bromides **6a**–**l** (table 1).

3. Results and discussion

3.1 *Synthesis of (E)-4-(2-bromovinyl)phenol* **4**

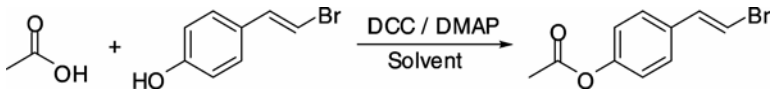
For our initial studies, *p*-hydroxy cinnamic acid (**1**) was chosen as starting material in the presence of NBS to generate (*E*)-4-(2-bromovinyl)phenol (**4**) directly, but unexpected by-product dibromide was always observed owing to the electron-donating group of hydroxyl group, and it was very difficult to separate. Thus, we attempted to acetylation of hydroxyl group before bromination in the presence of NBS and subsequent deacetylation, and (*E*)-4-(2-bromovinyl)phenol (**4**) was obtained in high yield with high stereoselectivity (scheme 1).

Interestingly, a mixture of (*E*)-4-(2-bromovinyl) phenyl acetate **3** and α-bromo-β-lactone **3′** were found in this reaction of **2** with NBS (scheme 2).



Scheme 2. Formation of (*E*)-4-(2-bromovinyl) phenyl acetate.

Table 2. Esterification condition of acetic acid with (*E*)-4-(2-bromovinyl)phenol (**4**).



Entries	CH_3CO_2H equiv.	DCC/DMAP equiv.	Solvent	Yield (%)[a,b]
1	1	1/cat.	DMF	<5
2	1	1/0·5	DMF	16
3	1	1/1	DMF	32
4	1·1	1·1/1·1	DMF	41
5	1·1	1/1	CH_2Cl_2	35
6	1·1	1·1/1·1	CH_3Cl_2	47
7	1	1·1/1	Benzene	85
8	1·1	1·1/1·1	Benzene	99
9	1·1	1·1/cat.	Benzene	23
10	1·1	1·1/1·1	Toluene	49

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

The coupling constant (J = 3·96 Hz) observed in the ^{1}H NMR of **3′** indicated that **3′** was a *trans*-*β*-lactone.[6] In the IR spectrum, the characteristic carbonyl absorption was observed at 1810 cm^{-1} (*β*-lactone C=O). In HRMS, the *m*/*z* value was found as 283·9684, compared with the calculated 283·9683. Separating *β*-lactone from this mixture by column chromatography was difficult since **3′** was unstable to elimination carbon dioxide to **3** even in room temperature as shown by ^{1}H NMR detection.

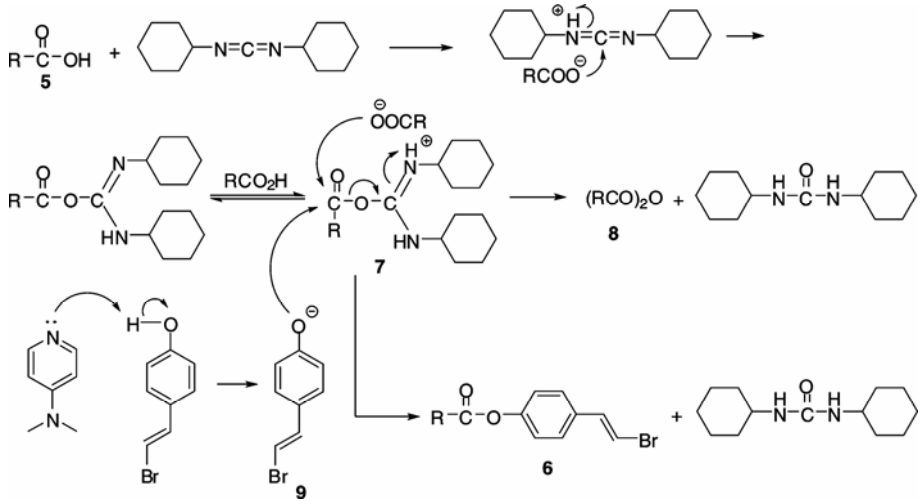
3.2 *Synthesis of functionalized (E)-2-arylvinyl bromides* **6**

The esterification of phenols using anhydrides or acyl halides as esterifying agent is one of the most routinely used transformation in organic synthesis. While this method was applied in the synthesis of 4-acyloxy-(*E*)-2-arylvinyl bromides, the yield was poor mainly due to the formation of by-product under condition of acid or high temperature. In order to avoid the formation of by-product, a mild reaction condition should be applied. We tried different activating reagents for the esterification of (*E*)-4-(2-bromovinyl)phenol (**4**) and found only DCC/DMAP offered high yields, while others such as DCC alone, DCC/HOBT, and BOP resulted in low yields (<15%).

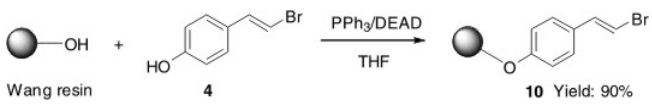
To optimize this esterification conditions, the reaction of (*E*)-4-(2-bromovinyl)phenol (**4**) with acetic acid was carried out. We tested several solvents including DMF, CH_2Cl_2, and toluene, but they afforded very low yields. As further work was carried out, we found satisfying yield when benzene and 1·1 equivalent DMAP revolved. The *E*/*Z* ratio of the products did not vary under this reaction conditions, and the geometry of the C–C double bond was retained during the reaction procedure (table 2).

The best condition for the esterification of (*E*)-4-(2-bromovinyl)phenol (**4**) was 1·1 equivalent DCC and 1.1 equivalent DMAP in benzene as solvent. When DMAP was used in catalytic amount the yield was drastically decreased (<25%, table 2, entries 1, 9). It is crucial that DCC should be added after all the other reagents had been added and stirred for ten munites. The rusults are shown in table 2.

These results indicated that the present reaction was very useful for the synthesis of both 4-alkoxy-



Scheme 3. Mechanistic hypothesis for the formation of functionalized (*E*)-2-arylvinyl bromides **6**.



Scheme 4. (*E*)-4-(2-bromovinyl)phenol **3** linked to Wang resin.

carbonyl- and 4-aryloxycarbonyl-(*E*)-*β*-arylvinyl bromides. A wide range of functional groups such as $-CO_2R$ **(5e)**, –CHO **(5f)**, conjugate diene **(5b)**, ether **(5c)**, styryl **(5d)**, vinyl bromide **(5g–5h)** were found tolerant to this condition. Even the molecule contained heterocyclic rings such as pyridyl **(5i–5j)**, furyl **(5k)**, thienyl **(5l)**, the reaction stereoselectively proceeded in high yields. The structures of these compounds has been elucidated by elemental analysis and spectral (IR, ^{1}H NMR, ^{13}C NMR, MS) data, as shown in appendix A.

A mechanistic hypothesis for the esterification of (*E*)-4-(2-bromovinyl)phenol **(4)** with various acids is proposed in scheme 3. (*E*)-4-(2-bromovinyl)phenol is firstly converted to the corresponding anion **8** in the presence of DMAP. And then anion **8** attacks the carbonyl carbon atom of intermediate **7** generated from DCC with acid **5** to form the target molecule **6**. The key point of this mechanism is the formation of (*E*)-4-(2-bromovinyl)phenol anion **8** should be ahead of the intermediate **7**. Otherwise the acid anion will attack the carbonyl carbon atom of intermediate **7** and generate by-product **8**, leading low yields (scheme 3).

Further, (*E*)-4-(2-bromovinyl)phenol **(4)** could be attached to the benzyl alcohol of Wang resin using a PPh_3/DEAD coupling procedure at ambient temperature to afford functionalized (*E*)-2-arylvinyl bromide ether **7** in high yield (scheme 4).

The Wang resin-bound ester **10** 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. Further, **7** is an excellent substrate for Stille, Suzuki and Heck reaction.[1]

4. Conclusions

In summary, we have developed a novel and convenient synthetic route for preparing high functionalized (*E*)-2-arylvinyl bromides bearing a wide range of functional groups. These functionalized (*E*)-2-arylvinyl bromides are important synthetic targets and widely used in the preparation of pharmaceuticals, functional polymeric material and natural products.[15]

Appendix A

(E)-4-(2-Bromovinyl)phenyl palmitate **6a**: White solid, m.p. 72·5–73·0°C. IR (KBr): 1739, 1283, 1087, 935, 777 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$, δ ppm): 0·88 (3H, *t*, J = 6·3 Hz), 1·20–1·40 (24H, *m*), 1·70–1·77 (2H, *m*), 2·55 (2H, *t*, J = 7·2 Hz), 6·73 (1H, *d*, J = 14·1 Hz), 7·03–7·1 (3H, *m*), 7·31 (2H, *d*, J = 8·7 Hz). ^{13}C NMR (75 MHz, $CDCl_3$, δ ppm): 14·1, 22·7, 24·9, 29·1, 29·2, 29·4, 29·43, 29·6, 29·7,

31·9, 34·4, 106·5, 122·0, 127·1, 133·5, 136·2, 150·6, 172·1. EI–MS: *m/z* (%): 438 ($(M + 2)^+$, 18), 436 (M^+, 19), 200 (100), 198 (99). Anal. calcd. for $C_{24}H_{37}BrO_2$: C, 65·89; H, 8·53; Br, 18·27. found: C, 65·82; H, 8·58; Br, 18·32.

(2E, 4E)-4-((E)-2-Bromovinyl)phenyl hexa-2,4-dienoate **6b:** White solid, m.p. 120·4–121·4°C. IR (KBr): 1724, 1215, 1077, 935, 777 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$, δ ppm): 1·90 (3H, *d*, *J* = 4·5 Hz), 5·95 (1H, *d*, *J* = 15·6 Hz), 6·20–6·34 (2H, *m*), 6·73 (1H, *d*, *J* = 14·1 Hz), 7·09 (3H, *d*, *J* = 8·4 Hz), 7·31(2H, *d*, *J* = 8·4 Hz), 7·39–7·48 (1H, *m*). ^{13}C NMR (75 MHz, $CDCl_3$, δ ppm): 18·7, 106·5, 117·7, 122·0, 127·0, 129·7, 133·4, 136·3, 140·9, 147·2, 150·7, 165·4. EI–MS: *m/z* (%): 294 ($(M + 2)^+$, 15), 292 (M^+, 15), 200 (100), 198 (99). Anal. calcd. for $C_{14}H_{13}BrO_2$: C, 57·36; H, 4·47; Br, 27·26. found: C, 57·32; H, 4·50; Br, 27·28.

(E)-4-(2-Bromovinyl)phenyl 2-phenoxyacetate **6c**: White solid, m.p. 204·5–205·5°C. IR (KBr): 1729, 1240, 1092, 935, 746 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$, δ ppm): 4·89 (2H, *s*), 6·75 (1H, *d*, *J* = 14·1 Hz), 6·91–7·15 (6H, *m*), 7·23–7·36 (4H, *m*). ^{13}C NMR (75 MHz, $CDCl_3$, δ ppm): 64·5, 108·2, 114·4, 120·9, 121·4, 122·0, 127·5, 129·4, 129·5, 133·64, 135·8, 157·4, 157·7, 167·6. EI–MS: *m/z* (%): 334 ($(M + 2)^+$, 19), 332 (M^+, 20), 200 (100), 198 (99). Anal. calcd. for $C_{16}H_{13}BrO_3$: C, 57·68; H, 3·93; Br, 23·98. found: C, 57·74; H, 3·96; Br, 23·96.

4-((E)-2-Bromovinyl)phenyl cinnamate **6d**: White solid, m.p. 151·5–152·0°C. IR (KBr): 1714, 1276, 1103, 935, 746 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$, δ ppm): 6·63 (1H, *d*, *J* = 8·1 Hz), 6·76 (1H, *d*, *J* = 8·4 Hz), 7·09–7·16 (3H, *m*), 7·35 (2H, *d*, *J* = 8·4 Hz), 7·42–7·45 (3H, *m*), 7·58–7·60 (2H, *m*), 7·88 (1H, *d*, *J* = 13·8 Hz). ^{13}C NMR (75 MHz, $CDCl_3$, δ ppm): 106·6, 117·0, 122·0, 127·1, 128·3, 129·0, 130·8, 133·6, 134·1, 136·2, 134·1, 136·2, 146·8, 150·6, 165·2. EI–MS: *m/z* (%): 330 ($(M + 2)^+$, 20), 328 (M^+, 21), 200 (100), 198 (99). Anal. calcd. for $C_{17}H_{13}BrO_2$: C, 62·03; H, 3·98; Br, 24·27. found: C, 62·07; H, 3·41; Br, 24·30.

Methyl-4-((E)-3-(4-((E)-2-bromovinyl)phenoxy)-3-oxoprop-1-enyl)benzoate **6e**: White solid, m.p. 164·2–164·9°C. IR (KBr): 1729, 1291, 1153, 940, 767 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$, δ ppm): 3·95 (3H, *s*), 6·68–6·78 (2H, *m*), 7·09–7·37 (5H, *m*), 7·65–7·67 (2H, *m*), 7·89 (1H, *d*, *J* = 15·0 Hz), 8·10 (2H, *d*, *J* = 8·1 Hz). ^{13}C NMR (75 MHz, $CDCl_3$, δ ppm): 52·3, 106·1, 119·5, 121·9, 127·1, 128·1, 130·2, 131·8, 133·8, 136·2, 138·2, 145·3, 150·5, 164·3, 165·9. EI–MS: *m/z* (%): 388 ($(M + 2)^+$, 20), 386 (M^+, 20), 200 (100), 198 (99). Anal. calcd. for $C_{19}H_{15}BrO_4$: C, 58·93; H, 3·90; Br, 20·64. found: C, 58·90; H, 3·88; Br, 20·68.

(E)-4-(2-Bromovinyl)phenyl-4-formylbenzoate **6f**: White solid, m.p. 129·0–130·0°C. IR (KBr): 1734, 1266, 1067, 935, 756 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$, δ ppm): 6·79 (1H, *d*, *J* = 13·7 Hz), 7·13 (1H, *d*, *J* = 13·7 Hz), 7·21 (2H, *d*, *J* = 8·7 Hz), 7·39 (2H, *d*, *J* = 8·7 Hz), 8·04 (2H, *d*, *J* = 8·3 Hz), 8·37 (2H, *d*, *J* = 8·3 Hz), 10·16 (1H, *s*). ^{13}C NMR (75 MHz, $CDCl_3$, δ ppm): 107·0, 121·3, 121·9, 127·2, 129·6, 130·8, 134·1, 136·1, 139·7, 150·5, 164·5, 191·4. EI–MS: *m/z* (%): 332 ($(M + 2)^+$, 17), 330 (M^+, 18), 200 (100), 198 (99). Anal. calcd. for $C_{16}H_{11}BrO_3$: C, 58·03; H, 3·35; Br, 24·13. found: C, 58·06; H, 3·32; Br, 24·18.

4-((E)-2-Bromovinyl)phenyl 4-((Z)-2-bromovinyl) benzoate **6g**: Light yellow solid, m.p. 118·5–119·0°C. IR (KBr) 1724, 1261, 1072, 935, 772 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$, δ ppm): 6·62 (1H, *d*, *J* = 8·1 Hz), 6·77 (1H, *d*, *J* = 14·1 Hz), 7·10–7·21 (4H, *m*), 7·37 (2H, *d*, *J* = 8·4 Hz), 7·81 (2H, *d*, *J* = 8·4 Hz), 8·20 (2H, *d*, *J* = 8·4 Hz). ^{13}C NMR (75 MHz, $CDCl_3$, δ ppm): 106·7, 109·3, 122·1, 126·1, 127·2, 129·1, 130·1, 131·5, 133·8, 136·2, 140·1, 150·7, 164·6. EI–MS: *m/z* (%): 408 ($(M + 2)^+$, 16), 406 (M^+, 16), 200 (100), 198 (99). Anal. calcd. for $C_{17}H_{12}Br_2O_2$: C, 50·03; H, 2·96; Br, 39·16. found: C, 50·04; H, 3·02; Br, 39·21.

4-((E)-2-Bromovinyl)phenyl 4-((E)-2-bromovinyl) benzoate **6h**: White solid, m.p. 136·5–137·5°C. IR (KBr) 1724, 1271, 1072, 935, 746 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$, δ ppm): 6·77 (1H, *d*, *J* = 14·0 Hz), 6·99 (1H, *d*, *J* = 14·0 Hz), 7·10–7·20 (4H, *m*), 7·35–7·45 (4H, *m*), 8·15 (2H, *d*, *J* = 8·7 Hz). ^{13}C NMR (75 MHz, $CDCl_3$, δ ppm): 106·8, 110·1, 122·1, 126·2, 127·2, 128·7, 130·7, 133·8, 136·2, 138·2, 140·8, 150·7, 164·5. EI–MS: *m/z* (%): 408 ($(M + 2)^+$, 16), 406 (M^+, 17), 200 (100), 198 (99). Anal. calcd. for $C_{17}H_{12}Br_2O_2$: C, 50·03; H, 2·96; Br, 39·16. found: C, 50·05; H, 3·01; Br, 39·20.

(E)-4-(2-Bromovinyl)phenyl nicotinate **6i**: Light yellow solid, m.p. 126·0–127·0°C. IR (KBr): 1734,

1276, 1076, 935, 777 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$, δ ppm): 6·79 (1H, *d*, *J* = 14·3 Hz), 7·13 (1H, *d*, *J* = 14·3 Hz), 7·21 (2H, *d*, *J* = 8·1 Hz), 7·38 (2H, *d*, *J* = 8·1 Hz), 7·46–7·50 (1H, *t*), 8·45 (1H, *d*, *J* = 8·1 Hz), 8·87 (1H, *d*, *J* = 5·1 Hz), 9·40 (1H, *s*). ^{13}C NMR (75 MHz, $CDCl_3$, δ ppm): 107·0, 122·0, 123·5, 125·4, 127·2, 134·1, 136·1, 137·6, 150·3, 151·3, 154·0, 163·7. EI–MS: *m/z* (%): 305 $((M + 2)^+$, 21), 303 (M^+, 22), 200 (100), 198 (99). Anal. calcd. for $C_{14}H_{10}BrNO_2$: C, 55·29; H, 3·31; Br, 26·27. found: C, 55·34; H, 3·33; Br, 26·21.

(E)-4-(2-Bromovinyl)phenyl isonicotinate **6j**: Light yellow solid, m.p. 124·0–124·6°C. IR (KBr): 1734, 1271, 1087, 935, 746 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$, δ ppm): 6·79 (1H, *d*, *J* = 14·3 Hz), 7·13 (1H, *d*, *J* = 14·3 Hz), 7·20 (2H, *d*, *J* = 8·3 Hz), 7·38 (2H, *d*, *J* = 8·3 Hz), 7·50 (2H, *d*, *J* = 5·7 Hz), 8·87 (2H, *d*, *J* = 5·7 Hz). ^{13}C NMR (75 MHz, $CDCl_3$, δ ppm): 107·1, 121·8, 123·2, 127·3, 134·2, 136·0, 136·6, 150·2, 150·8, 163·6. EI–MS: *m/z* (%): 305 $((M + 2)^+$, 20), 303 (M^+, 21), 200 (100), 198 (99). Anal. calcd. for $C_{14}H_{10}BrNO_2$: C, 55·29; H, 3·31; Br, 26·27. found: C, 55·35; H, 3·34; Br, 26·20.

(E)-4-(2-Bromovinyl)phenyl furan-2-carboxylate **6k**: White solid, m.p. 100·5–101·0°C. IR (KBr): 1734, 1275, 1092, 930, 762 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$, δ ppm): 6·60–6·61 (1H, *m*), 6·76 (1H, *d*, *J* = 14·1 Hz), 7·11 (1H, *d*, *J* = 14·1 Hz), 7·19 (2H, *d*, *J* = 8·4 Hz), 7·34–7·40 (3H, *q*), 7·69 (1H, *s*). ^{13}C NMR (75 MHz, $CDCl_3$, δ ppm): 106·8, 112·2, 119·6, 121·9, 127·2, 133·9, 136·1, 143·8, 147·3, 150·0, 156·6. EI–MS: *m/z* (%): 294 $((M + 2)^+$, 15), 292 (M^+, 15), 200 (100), 198 (99). Anal. calcd. for $C_{13}H_9BrO_3$: C, 53·27; H, 3·09; Br, 27·26. found: C, 53·33; H, 3·02; Br, 27·23.

(E)-4-(2-Bromovinyl)phenyl thiophene-2-carboxylate **6l**: Yellow solid, m.p. 114·9–115·5°C. IR (KBr): 1719, 1272, 1080, 935, 767 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$, δ ppm): 6·77 (1H, d, *J* = 14·3 Hz), 7·12 (1H, *d*, *J* = 14·3 Hz), 7·17–7·21 (3H, *m*), 7·36 (2H, *d*, *J* = 8·1 Hz), 7·67 (1H, *m*), 7·98–7·99 (1H, *m*). ^{13}C NMR (75 MHz, $CDCl_3$, δ ppm): 106·8, 121·7, 127·1, 128·1, 129·6, 132·0, 133·7, 134·8, 136·2, 150·4, 160·4. EI–MS: *m/z* (%): 310 $((M + 2)^+$, 14), 308 (M^+, 15), 200 (100), 198 (99). Anal. calcd. for $C_{13}H_9BrO_2S$: C, 50·50; H, 2·93; Br, 25·84. found: C, 50·45; H, 2·95; Br, 25·85.

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