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A concise route to functionalized benzofurans directly from *gem*-dibromoalkenes and phenols†

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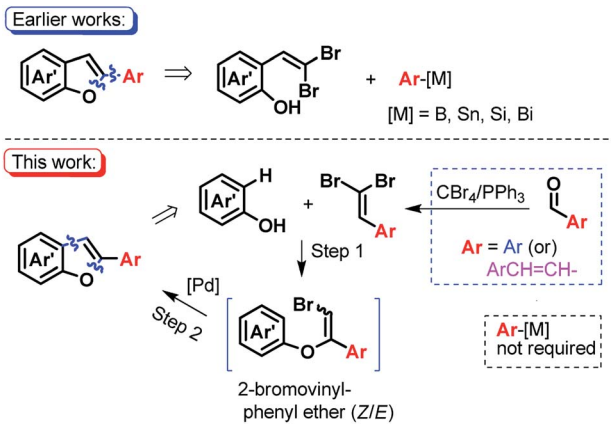
A tandem strategy for the construction of benzofuran motifs has been developed directly from *gem*-dibromoalkenes and phenols under palladium-catalyzed conditions. This flexible and novel methodology provides direct access to 2-aryl and 2-styryl benzofurans in good to high yields. This strategy is also valuable in the synthesis of benzodifurans.

Introduction

Methods involving *gem*-dibromoalkenes (1,1-dibromoalkenes) as synthetic surrogates are of immense interest with ready availability as molecular synthons in organic synthesis.[1] Reactions involving *gem*-dibromoalkenes and *o*-hydroxy-*gem*-dibromoarylalkenes in combination with triarylbismuth reagents have been reported from this laboratory for the preparation of internal alkynes[2a] and 2-arylbenzofurans[2b] respectively under palladium-catalyzed conditions. There are other applications of *gem*-dibromoalkenes[3] in organic synthesis as reviewed by Chellucci *et al.* recently.[1] To note, benzofurans are medicinal scaffolds with wide pharmacological appeal and presence in natural products.[4] Synthesis of these skeletons through sustainable approach and in one-pot operation allows minimization of waste, time and effort together with an easy execution of the target reaction protocol.[5]

Hence, we envisioned the pot-economic strategy as ideal choice for the synthesis of 2-arylbenzofuran scaffold through direct involvement of 1,1-dibromoalkene and phenol as given in Scheme 1. This approach (i) would alleviate the use of organometallic reagent as coupling partner,[3a,b] (ii) would be practicable as the proposed 1,1-dibromoalkene could be derived from aldehydes,[6] (iii) is simpler in terms of overall substrate combination and (iv) provides a wide synthetic and functional scope with 1,1-dibromoalkene as a reactant. Further, the starting materials phenols and aldehydes are routinely available. Additionally, this approach utilizes *in situ* preparation and functionalization of more reactive and not so stable 1-bromoalkyne without any isolation.

That way, the present approach is more advantageous from the fact that 1-bromoalkynes are photolabile and cannot be used/accessed as bench top chemicals.[7] The most common method of preparation of 1-bromoalkynes relies on the bromination of terminal alkynes with either CBr_4/PPh_3 (ref. 8) or Ag(I)/NBS[9] system. The proposed overall strategy is thus expected to provide an easy access to variously functionalized benzofurans with multiple practical and synthetic benefits.



Scheme 1 One-pot strategy.

Procedurally, the generation of benzofuran would thus involves (i) initial elimination,[2a] (ii) addition reaction sequence for the generation of 2-bromovinyl aryl ether and (iii) its oxidative cyclization to generate benzofuran in a one-pot operation (*vide infra*).[10] However, the overall outcome practically depends on how effectively these three steps could be converged under a viable protocol with high synthetic utility for the preparation of benzofurans.

Results and discussion

We studied our strategy with direct use of 1,1-dibromoalkene (**1a**) and phenol (**1b**) as model substrates for Step 1 to generate 2-bromovinyl phenyl ether (**1c**). This was explored using different combinations of base, solvent, temperature and reaction time conditions (Table 1).

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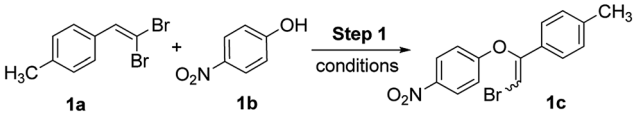
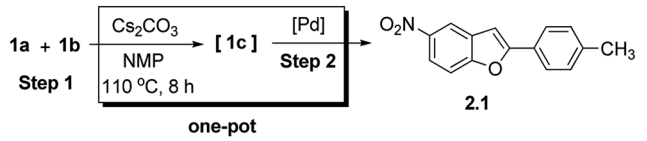
Table 1 Screening conditions[a,b]



Entry	Base (equiv.)	Solvent	Temp (°C)	Time (h)	**1c** (%)
1	K_3PO_4 (3)	DMF	90	4	16
2	K_3PO_4 (3)	DMF	110	8	70
3	K_3PO_4 (3)	NMP	110	8	75
4	KOAc (3)	NMP	110	8	32
5	K_2CO_3 (3)	NMP	110	8	57
6	Cs_2CO_3 (3)	NMP	110	8	78
7	Cs_2CO_3 (5)	NMP	110	8	87
8	Cs_2CO_3 (5)	DMA	110	8	73
9	Cs_2CO_3 (5)	DMF	110	8	67
10	Cs_2CO_3 (5)	NMP	110	6	79

[a] Conditions: 1-(2,2-dibromovinyl)-4-methylbenzene, **1a** (0.375 mmol, 1 equiv.), 4-nitrophenol, **1b** (0.375 mmol, 1 equiv.), base, solvent (3 mL), temp, time. [b] Isolated yields.

Table 2 Screening for Step 2 benzofuran formation[a,b]



Entry	Catalyst (equiv.)	Temp (°C)	Time (h)	**2.1** (%)
1	$PdCl_2$ (0.05)	130	6	54
2	$PdCl_2(PPh_3)_2$ (0.05)	130	6	45
3	$Pd(OAc)_2$ (0.05)	130	6	78
4	$Pd(OAc)_2$ (0.05)	110	6	70
5	$Pd(OAc)_2$ (0.03)	130	6	61

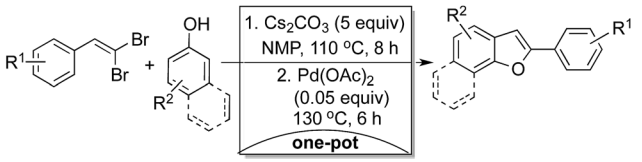
[a] Conditions: Step 1: **1a** (0.375 mmol, 1 equiv.), **1b** (0.375 mmol, 1 equiv.), Cs_2CO_3 (1.875 mmol, 5 equiv.), NMP (3 mL), 110 °C, 8 h; Step 2: [Pd] catalyst, temp, time. [b] Isolated yields refer to overall yields after two steps.

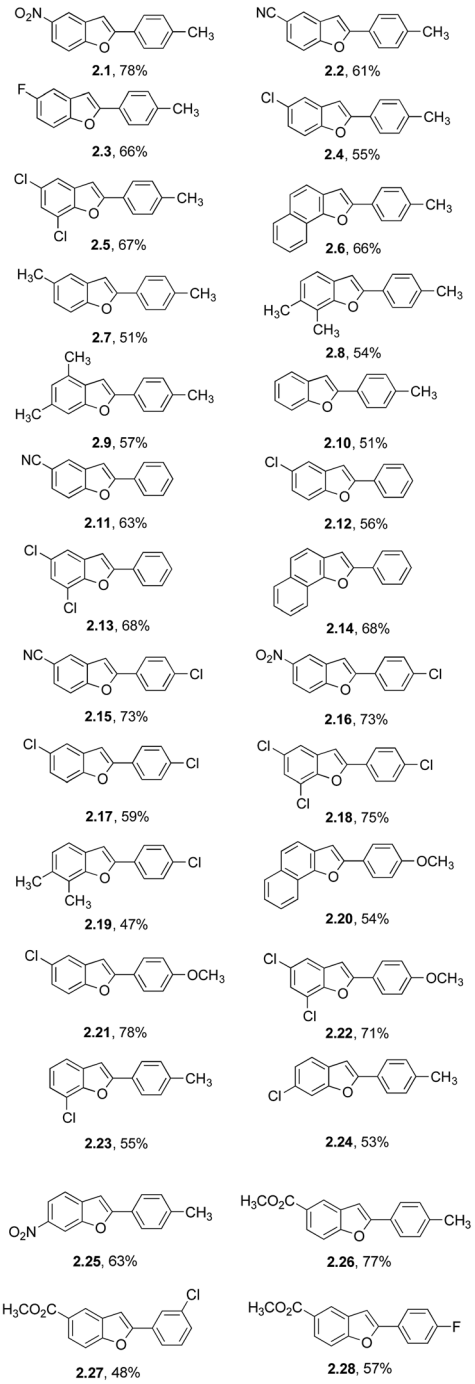
The initial examination of this reaction with K_3PO_4 base at 90 °C in DMF for 4 h afforded 2-bromovinyl phenyl ether (**1c**) in 16% yield (entry 1, Table 1). However, notable improvement was achieved with this base at 110 °C both in DMF and NMP solvents giving 70% and 75% yields respectively (entries 2 and 3, Table 1). Replacing K_3PO_4 either with KOAc or K_2CO_3 proved to be ineffective with lowered yields (entries 4 and 5, Table 1). Encouragingly, this reaction in NMP with Cs_2CO_3 (3 or 5 equiv.) demonstrated with high performance giving 78% and 87% yields (entries 6 and 7, Table 1). Further, change in solvent to either DMA or DMF resulted in lowered yields (entries 8 and 9, Table 1). Further screening with 6 h time duration furnished 79% yield (entry 10, Table 1). This investigation using different combinations of base, solvent, temperature and time conditions indicated that the formation of 2-bromovinyl phenyl ether (**1c**) is efficient with Cs_2CO_3 (5 equiv.) in NMP to give high yield (entry 7, Table 1). Considering this as optimized condition for Step 1, further attempt was made to converge the protocol for Step 1 with the proposed cyclization in Step 2 under palladium catalysis towards benzofuran formation. The underlying challenge here is in finding the compatible palladium conditions in convergence with the conditions of Step 1. Thus, the oxidative cyclization of 2-bromovinyl phenyl ether (**1c**) should be affected under palladium catalysis within the protocol limitation of Step 1.

With the above prerequisite, the screening for Step 2 was performed using different palladium catalysts under the protocol conditions of Step 1 (Table 2). This investigation initially carried out with $PdCl_2$ or $PdCl_2(PPh_3)_2$ at 130 °C furnished the desired benzofuran product **2.1** in moderate yields (entries 1 and 2, Table 2). To our satisfaction, the desired cyclization improved up to 78% using with $Pd(OAc)_2$ (entry 3, Table 2). Further check at 110 °C or with lowered amount of catalyst gave 70% (entry 4, Table 2) and 61% (entry 5, Table 2) yields respectively. It was realized that the cyclization of 2-bromovinyl phenyl ether (**1c**) could be achieved with $Pd(OAc)_2$ under the conditions of Step 1 in a two-step one-pot operation with high yield (entry 3, Table 2). It is to be highlighted that the formation of 2-bromovinyl phenyl ether (**1c**) from 1,1-dibromide (**1a**) and phenol (**1b**) was achieved efficiently with Cs_2CO_3 in NMP at 110 °C in Step 1 followed by heating 130 °C in the presence of $Pd(OAc)_2$ to afford 2-arylbenzofuran **2.1** directly in high yield through a one-pot operation (entry 3, Table 2).

This one-pot direct strategy using 1,1-dibromoalkene and phenol is synthetically more viable for the preparation of a variety of 2-arylbenzofurans. Thus, further investigation was carried out to expand the scope using different functionalized 1,1-dibromides and phenols as summarized in Table 3. The reactivity of 1-(2,2-dibromovinyl)-4-methylbenzene was tested initially with various electronically different phenols. The study with 4-nitrophenol during screening afforded 5-nitro-2-(*p*-tolyl) benzofuran, **2.1** in 78% yield. This reactivity with different phenols functionalized with 4-cyano-, 4-fluoro-, 4-chloro-, 2,4-dichloro groups afforded the corresponding benzofurans (**2.2–2.5**) in 55–67% yields. Similarly, 1-naphthol efficiently furnished benzofuran **2.6** in 66% yield. Further, electronically rich phenols substituted with 4-methyl, 2,3-dimethyl, 3,5-dimethyl groups provided benzofurans (**2.7–2.9**) in 51–57% yields. Notably, simple phenol gave benzofuran **2.10** in 51% yield. Comparable reactivity was witnessed with unsubstituted (2,2-dibromovinyl)benzene in combination with different phenols to deliver the corresponding benzofurans (**2.11–2.14**) in 56–68% yields. The study of 4-chloro and 4-methoxy substituted (2,2-dibromovinyl)benzenes demonstrated persistent reactivity and gave benzofurans (**2.15–2.22**) in 47–78% yields. Reaction with 2-chlorophenol afforded benzofuran **2.23** in 55% yield. Reactivity with 3-chloro and 3-nitro substituted phenols provided benzofurans **2.24** and **2.25** in 53% and 63% yields respectively. Further ester functionalized phenolic substrate such as methyl 4-hydroxybenzoate delivered benzofuran **2.26** in 77% high yield. The same with 3-chloro and 4-fluoro substituted (2,2-dibromovinyl)benzenes provided benzofurans **2.27** and

Table 3 Two-step one-pot synthesis of benzofurans[a,b]





[a] Conditions: Step 1: 1,1-dibromide (0.375 mmol, 1 equiv.), phenol (0.375 mmol, 1 equiv.), Cs_2CO_3 (1.875 mmol, 5 equiv.), NMP, 110 °C, 8 h; Step 2: $Pd(OAc)_2$ (0.0187 mmol, 0.05 equiv.), 130 °C, 6 h. [b] Isolated yields refer to overall yields after two steps in one-pot operation and corresponds to 0.375 mmol of product as 100% yield.

2.28 in moderate yields. Thus, moderate yields were obtained in reactions with electron rich phenols. In some of these cases, we noticed the formation of bis-phenoxy intermediates through mass spectral analysis in minor amounts.

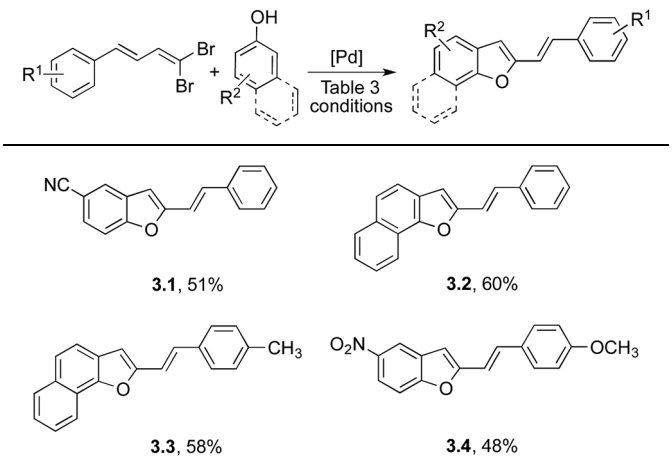
This exploration with different 1,1-dibromides and phenols demonstrated the overall synthetic potential of the developed direct strategy and was driven by electronics of both dibromides and phenols. In fact, considerable electronic influence was observed both in the Step 1 and Step 2 which led to overall moderate to good yields in one-pot operation.

Notably, some of the 2-arylbenzofuran skeletons obtained are useful intermediates with structural modifications in the preparation of natural products.[4] Additionally, benzofuran **2.21** could be modified for the synthesis of a β-amyloid aggregation inhibitor.[4f]

At this stage, it was further decided to exploit the advantage and flexibility available with our system to achieve other functionalizations at C-2 position of benzofuran employing differently functionalized 1,1-dibromides. We envisaged one such possibility with the use of 1,3-dienyldibromide to synthesize 2-styryl substituted benzofuran products (Scheme 1). In fact, synthesis of these skeletons through earlier procedures (Scheme 1) require the use of styryl based organometallic reagents which is a cumbersome in terms of preparation and other related issues.[11] Whereas, 1,3-dienyldibromides could be readily obtained from cinnamaldehydes and their direct use in comparison is expected to provide immense synthetic utility (Scheme 1). With this advantage in hand, we briefly reviewed this possibility using 1,3-dienyldibromide in the preparation of 2-styrylbenzofuran (Table 4).

Amazingly, our attempt afforded 2-styrylbenzofurans in a facile manner using above established conditions. This effort also ascertained the synthetic advantage as differently

Table 4 Synthesis of 2-styrylbenzofurans[a,b]



[a] Conditions: Step 1: 1,3-dienyldibromide (0.375 mmol, 1 equiv.), phenol (0.375 mmol, 1 equiv.), Cs_2CO_3 (1.875 mmol, 5 equiv.), NMP, 110 °C, 8 h; Step 2: $Pd(OAc)_2$ (0.0187 mmol, 0.05 equiv.), 130 °C, 6 h. [b] Isolated yields refer to overall yields after two steps in one-pot corresponds to 0.375 mmol of product as 100% yield.

functionalized 2-styrylbenzofurans (**3.1–3.4**) could be obtained directly in 48–60% yields. To note, 2-styrylbenzofurans are valuable skeletons for biological and other applications.[4g,h] Given the lack of readily usable methods for the preparation of these products directly,[12] the present method is significant employing 1,3-dienyldibromides.

Further, to investigate and converge the reaction course in line with the screening carried out in Table 1 involving the isolation of the intermediate, an additional experimentation was desired with 1,3-dienyldibromide. Thus was performed directly under the conditions of Step 1 and the corresponding elimination–addition product **3c** was isolated in 73% yield (Scheme 2).

Synthesis of important skeletons like benzodifurans has always been challenging pursuit.[4i,j] Hence, it was attempted here with dibromides and resorcinols in a stepwise manner with the isolation of the intermediate structures. In this attempt the reaction of **1a** with simple resorcinol gave intermediate **4c** in 50% yield as isomeric mixture. When **4c** further subjected for cyclization under $Pd(OAc)_2/Cs_2CO_3$ conditions, it delivered benzodifuran **4.1** in 48% yield (Scheme 3). Similar attempt with 4-methoxy substituted (2,2-dibromovinyl)benzene and methyl 3,5-dihydroxybenzoate gave benzodifuran **5.1** in 52% yield involving **5c** (Scheme 3). This study in one-pot operation although failed to deliver benzodifuran, stepwise approach successfully delivered benzodifurans in moderate yields involving tandem process.

The single crystal X-ray analysis of **4.1** (Fig. 1) showed the double cyclizations C-3 and C-9 leading to benzodifuran cyclized product with bowl shaped fused tricyclic core.

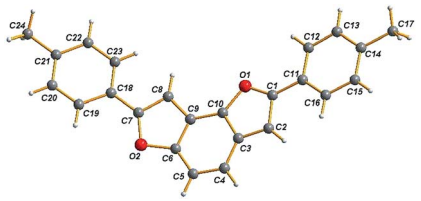


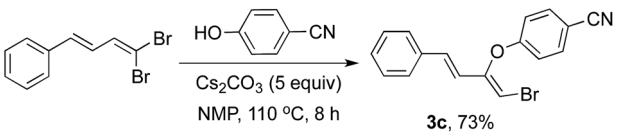
Fig. 1 X-ray structure of **4.1**.

Additional efforts to apply our protocol to gram scale reaction of dibromide **1a** in combination with methyl 4-hydroxybenzoate in a two-step one-pot operation delivered 2-arylbenzofuran **2.26** in 42% yield (Scheme 4).

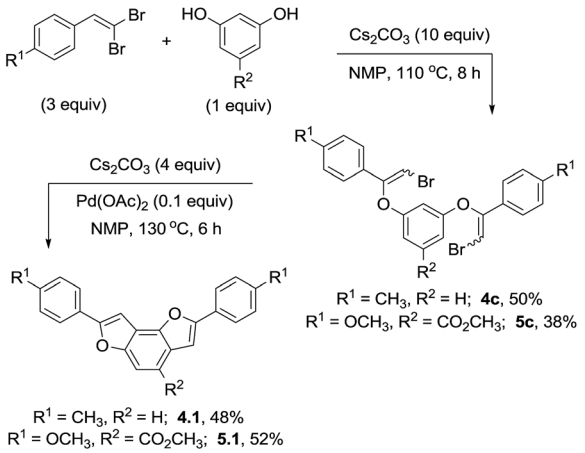
The mechanistic pathway for the formation of benzofuran from 1,1-dibromide and phenol is given Scheme 5.

During Step 1, the initial dehydrobromination of 1,1-dibromide in the presence of base would form 1-bromoalkyne (**3p**). This in turn undergoes addition reaction with phenol to afford 2-bromovinyl phenyl ether (**3q**).[10,12d,13] In Step 2, 2-bromovinyl phenyl ether (**3q**) would undergo a sequence of steps involving oxidative addition (**3r**), cyclization (**3s**) followed by reductive elimination to generate 2-substituted benzofuran in one-pot operation. The formation of 1-bromoalkyne in the presence of base was realized on our earlier studies both in the case of 1,1-dibromoalkene[2a] and 1,3-dienyldibromide.[14] Further it was evidenced by the isolation of the addition adducts **1c** (Table 1) and **3c** (Scheme 2). The second step of oxidative cyclization under palladium-catalyzed conditions is well represented in the literature towards benzofuran formation.[10,12d,13]

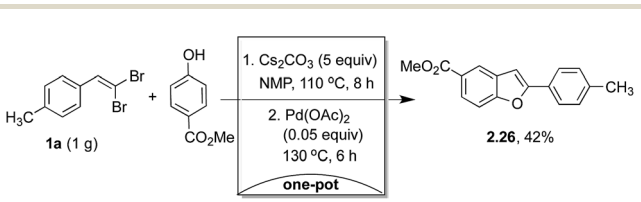
It is to be emphasized that with readily available starting materials, the present approach offers an easy access to the 2-aryl



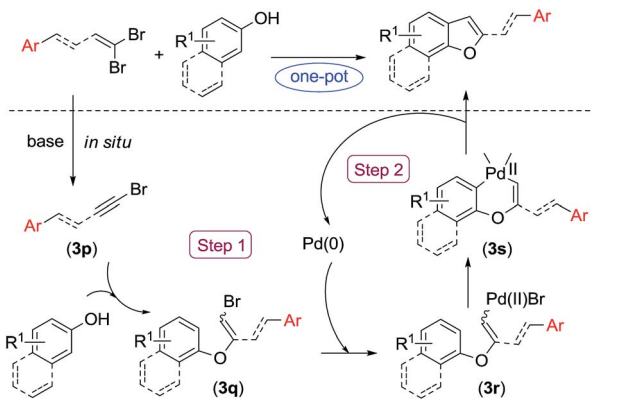
Scheme 2 Isolation of the reaction intermediate **3c**.



Scheme 3 Stepwise synthesis of benzodifurans **4.1** and **5.1**.



Scheme 4 Gram scale reaction.



Scheme 5 Mechanistic proposal.

and 2-styryl substituted benzofurans without using organometallic coupling reagents such as aryl and alkenylboronic acids. This is notable as alkenylboronic acids reagents suffer from unavoidable practical difficulties.[11,15] and our method is a devoid of these short comings in the preparation of benzofurans.

Conclusion

In conclusion, a direct tandem strategy for the construction of 2-aryl and 2-styrylbenzofuran motifs has been developed from 1,1-dibromides and phenols under palladium-catalyzed conditions. This flexible and novel methodology provides an easy access to functionalized benzofurans in a pot-economic practical way. Our study is also worthwhile to access benzodifurans in a facile manner.

Experimental

General

All reactions were conducted in Schlenk tubes under nitrogen atmosphere with dry solvents. Chromatographic purification of the products were performed using 100–200 and 230–400 mesh silica-gel with ethyl acetate/hexane as eluent. NMR spectra have been recorded using JEOL ECS 400 (400 MHz) and JEOL ECX 500 (500 MHz). HRMS measurements have been done using Electron Ionization (EI) and Electrospray Ionization (ESI) techniques with Waters CAB155 GCT Premier analyzer and Waters HAB 213 Q-TOF Premier analyzer. IR spectra were recorded with PerkinElmer FT-IR Spectrum Two and Bruker Tensor 27 spectrometer. X-ray data was recorded on Bruker SMART APEX-II CCD diffractometer. Different *gem*-dibromoalkenes were prepared according to reported procedures.[2,14] Melting points reported are uncorrected.

Representative procedure for intermediate 1c and 3c

This reaction was performed using an oven-dried Schlenk tube charged with 1-(2,2-dibromovinyl)-4-methylbenzene **1a** (0.104 g, 0.375 mmol, *p*-nitrophenol **1b** (0.52 g, 0.375 mmol, 1 equiv.), 1 equiv.), Cs_2CO_3 (0.611 g, 1.875 mmol, 5 equiv.) and NMP (3 mL) respectively under N_2 atmosphere. Reaction mixture was stirred at 110 °C in an oil bath for 8 h. It was cooled to rt and subjected to workup using ethyl acetate (50 mL), washing with water (10 mL), brine (10 mL). The organic portion was dried over anhydrous $MgSO_4$ and concentrated. The crude was purified by silica-gel column chromatography using 2% EtOAc in hexane as eluent to obtain the product **1c** as yellow viscous liquid (0.109 g, 87%). This procedure was also followed for the preparation of intermediate **3c** with (*E*)-(4,4-dibromobuta-1,3-dienyl)benzene and *p*-cyanophenol.

Representative procedure for 2-arylbenzofurans (Table 3)

This reaction was performed in an oven-dried Schlenk tube with dibromide **1a** (0.104 g, 0.375 mmol, 1 equiv.), **1b** (0.52 g, 0.375 mmol, 1 equiv.), Cs_2CO_3 (0.611 g, 1.875 mmol, 5 equiv.) and NMP (3 mL) under N_2 atmospheric conditions. Reaction mixture was stirred at 110 °C in an oil bath for 8 h. It was cooled to rt for the addition of $Pd(OAc)_2$ (0.0042 g, 0.0187 mmol, 0.05 equiv.) and reaction was further heated at 130 °C for 6 h under N_2 atmosphere conditions. It was cooled to rt and was extracted with ethyl acetate (50 mL), washed with water (10 mL), brine (10 mL), dried over anhydrous $MgSO_4$ and concentrated. The crude was subjected to silica gel column chromatography using 2% EtOAc in hexane as eluent to obtain the product 5-nitro-2-(*p*-tolyl)benzofuran (**2.1**) as brown solid (0.074 g, 78%).

Representative procedure for 2-styrylbenzofurans (Table 4)

The procedure followed above in the preparation of benzofuran **2.1** was adopted with 1,3-dienyldibromides and phenols for the synthesis of 2-styrylbenzofurans **3.1–3.4**.

Representative procedure for benzodifurans (4.1 and 5.1)

It was performed in stepwise manner in an oven-dried Schlenk tube with dibromide **1a** (0.31 g, 1.125 mmol, 3 equiv.), resorcinol (0.041 g, 0.375 mmol, 1 equiv.), Cs_2CO_3 (1.22 g, 3.75 mmol, 10 equiv.) and NMP (3 mL) under N_2 atmospheric conditions. The reaction mixture was stirred at 110 °C in an oil bath for 8 h. After usual workup and purification using silica-gel column chromatography with 5% EtOAc in hexane **4c** was obtained as viscous liquid (0.095 g, 50%). The compound **4c** (0.095 g, 0.19 mmol, 1 equiv.) was subjected for cyclization using conditions Cs_2CO_3 (0.25 g, 0.76 mmol, 4 equiv.), $Pd(OAc)_2$ (0.0042 g, 0.019 mmol, 0.10 equiv.) and NMP (2 mL) under N_2 and heated at 130 °C for 6 h in the second step. After work up and purification as above, benzodifuran **4.1** was obtained as colourless solid (0.031 g, 48%). Similarly, benzodifuran **5.1** was obtained in 52% yield from 0.142 mmol of intermediate **5c**. For analytical data of intermediates **4c** and **5c**, see ESI.†

The analytical data for intermediates **1c**, **3c**, benzofuran products **2.1–2.28**, **3.1–3.4**, **4.1** and **5.1** are given below.

1c. Yellow liquid (0.109 g, 87%); R_f = 0.38 (EtOAc–hexane 5 : 95). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.17 (d, 2H, J = 9.2 Hz, Ar–H), 7.34 (d, 2H, J = 8.24 Hz, Ar–H), 7.14 (d, 2H, J = 8 Hz, Ar–H), 7.07–7.03 (m, 2H, Ar–H), 6.58 (s, 1H, C$\underline{H}_{olefin}$), 2.32 (s, 3H, –C$\underline{H}_3$). ^{13}C (125 MHz, $CDCl_3$): δ 160.8, 152.5, 142.7, 140.1, 129.8, 129.6, 126.0, 125.4, 116.0, 95.4, 21.3. IR (film): 3093, 2923, 1610, 1590, 1517, 1343, 1238, 1111 cm^{-1}. HRMS (EI) calcd for $C_{15}H_{12}BrNO_3$ [M^+] 333.0001; found 333.0009.

3c. Yellow liquid (0.089 g, 73%); R_f = 0.40 (EtOAc–hexane 5 : 95). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.61 (d, 2H, J = 9.16 Hz, Ar–H), 7.36–7.25 (m, 5H, Ar–H), 7.08 (d, 2H, J = 9.16 Hz, Ar–H), 6.73–6.64 (m, 2H), 6.34 (s, 1H, C$\underline{H}_{olefin}$). ^{13}C (100 MHz, $CDCl_3$): δ 159.3, 151.9, 135.3, 134.2, 131.6, 128.8, 126.9, 119.7, 118.8, 116.0, 105.8, 99.9. IR (film): 3081, 2226, 1684, 1608, 1502, 1236, 1168 cm^{-1}. HRMS (EI) calcd for $C_{17}H_{12}BrNO$ [M^+] 325.0102; found 325.0105.

2.1 (ref. 10). Brown solid (0.074 g, 78%); mp 162–164 °C, R_f = 0.35 (EtOAc–hexane 2 : 98). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.48 (d, 1H, J = 2.28 Hz, Ar–H), 8.20 (dd, 1H, J = 8.9 Hz, J = 2.52 Hz, Ar–H), 7.77 (d, 2H, J = 8.24 Hz, Ar–H), 7.57 (d, 1H, J = 9.16 Hz, Ar–H), 7.29 (d, 2H, J = 8.24 Hz, Ar–H), 7.06 (s, 1H, Ar–H), 2.42 (s, 3H, –C$\underline{H}_3$). ^{13}C (100 MHz, $CDCl_3$): δ 159.5, 157.5, 144.2, 139.9, 129.7, 126.4, 125.2, 119.8, 117.0, 111.3, 100.8, 21.4. IR (film,

cm^{-1}): 2920, 1589, 1519, 1504, 1342, 886, 792, 749. HRMS (ESI) calcd for $C_{15}H_{12}NO_3$ [MH^+] 254.0817; found 254.0815.

2.2 (ref. 13). Yellow solid (0.054 g, 61%); mp 186–188 °C, R_f = 0.47 (EtOAc–hexane 5 : 95). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.88 (s, 1H, Ar–H), 7.74 (d, 2H, J = 8.24 Hz, Ar–H), 7.57–7.51 (m, 2H, Ar–H), 7.28–7.24 (m, 2H, Ar–H), 6.98 (s, 1H, Ar–H), 2.40 (s, 3H, –C$\underline{H}_3$). ^{13}C (100 MHz, $CDCl_3$): δ 158.6, 156.3, 139.8, 130.0, 129.6, 127.6, 126.5, 125.5, 125.2, 119.5, 112.1, 106.7, 99.9, 21.4. IR (film): 2923, 2225, 1589, 1463, 1032, 821, 798 cm^{-1}. HRMS (EI) calcd for $C_{16}H_{11}NO$ [M^+] 233.0841; found 233.0843.

2.3. Colourless solid (0.056 g, 66%); mp 152–154 °C, R_f = 0.59 (hexane). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.74 (d, 2H, J = 8.3 Hz, Ar–H), 7.43–7.40 (m, 1H, Ar–H), 7.27–7.25 (m, 2H, Ar–H), 7.21 (dd, 1H, J = 8.5 Hz, J = 2.6 Hz, Ar–H), 6.99–6.95 (m, 1H, Ar–H), 6.92 (s, 1H, Ar–H), 2.40 (s, 3H, –C$\underline{H}_3$). ^{13}C (125 MHz, $CDCl_3$): δ 159.3 (d, J = 236.37 Hz), 157.9, 150.9, 139.0, 130.1 (d, J = 10.8 Hz), 129.5, 127.3, 124.9, 111.6, 111.5, 111.4, 106.1 (d, J = 25.2 Hz), 100.6 (J = 3.6 Hz), 21.4. IR (film): 2961, 1724, 1590, 1461, 1272, 1112, 864, 822, 796 cm^{-1}. HRMS (EI) calcd for $C_{15}H_{11}FO$ [M^+] 226.0794; found 226.0799.

2.4 (ref. 16). Colourless solid (0.050 g, 55%); mp 178–180 °C, R_f = 0.46 (hexane). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.73 (d, 2H, J = 8.05 Hz, Ar–H), 7.51 (d, 1H, J = 2 Hz, Ar–H), 7.41 (d, 1H, J = 8.6 Hz, Ar–H), 7.25 (d, 2H, J = 8 Hz, Ar–H), 7.21 (dd, 1H, J = 8.57 Hz, J = 2.27 Hz, Ar–H), 6.88 (s, 1H, Ar–H), 2.40 (s, 3H, –C$\underline{H}_3$). ^{13}C (125 MHz, $CDCl_3$): δ 157.6, 153.1, 139.1, 130.7, 129.5, 128.3, 127.2, 124.9, 124.0, 120.2, 111.9, 100.0, 21.4. IR (film): 2961, 1725, 1446, 1273, 1035, 824, 808, 796 cm^{-1}. HRMS (EI) calcd for $C_{15}H_{11}ClO$ [M^+] 242.0498; found 242.0492.

2.5 (ref. 2*b*). Colourless solid (0.070 g, 67%); mp 110–112 °C, R_f = 0.51 (hexane). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.74 (d, 2H, J = 8.05 Hz, Ar–H), 7.39 (d, 1H, J = 2 Hz, Ar–H), 7.26–7.24 (m, 3H, Ar–H), 6.88 (s, 1H, Ar–H), 2.40 (s, 3H, –C$\underline{H}_3$). ^{13}C (125 MHz, $CDCl_3$): δ 158.4, 149.0, 139.6, 131.6, 129.5, 128.5, 126.5, 125.1, 123.9, 118.8, 116.9, 100.4, 21.4. IR (film): 2960, 1724, 1575, 1505, 1443, 1277, 1169, 835, 817, 793 cm^{-1}. HRMS (EI) calcd for $C_{15}H_{10}Cl_2O$ [M^+] 276.0109; found 276.0104.

2.6. Yellow solid (0.064 g, 66%); mp 98–100 °C, R_f = 0.62 (hexane). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.40 (d, 1H, J = 8.24 Hz, Ar–H), 7.94 (d, 1H, J = 8.24 Hz, Ar–H), 7.85 (d, 2H, J = 8.24 Hz, Ar–H), 7.66 (s, 2H, Ar–H), 7.63–7.59 (m, 1H, Ar–H), 7.51–7.47 (m, 1H, Ar–H), 7.29 (d, 2H, J = 7.76 Hz, Ar–H), 7.10 (s, 1H, Ar–H), 2.43 (s, 3H, –C$\underline{H}_3$). ^{13}C (100 MHz, $CDCl_3$): δ 155.6, 150.1, 138.2, 131.3, 129.5, 128.4, 128.0, 126.3, 124.9, 124.6, 123.5, 121.3, 120.0, 119.5, 101.7, 21.4. IR (film): 3052, 1498, 915, 817, 743 cm^{-1}. HRMS (EI) calcd for $C_{19}H_{14}O$ [M]$^+$ 258.1045; found 258.1046.

2.7. Colourless solid (0.042 g, 51%); mp 144–146 °C, R_f = 0.42 (hexane). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.74 (d, 2H, J = 7.95 Hz, Ar–H), 7.38 (d, 1H, J = 8.25 Hz, Ar–H), 7.35 (s, 1H, Ar–H), 7.24 (d, 2H, J = 7.35 Hz, Ar–H), 7.07 (d, 1H, J = 7.05 Hz, Ar–H), 6.89 (s, 1H, Ar–H), 2.44 (s, 3H, –C$\underline{H}_3$), 2.39 (s, 3H, –C$\underline{H}_3$). ^{13}C (125 MHz, $CDCl_3$): δ 156.2, 153.2, 138.4, 132.2, 129.4, 127.9, 125.2, 124.8, 120.5, 110.5, 100.3, 21.36, 21.33. IR (film): 2962, 1726, 1465, 1289, 823, 800 cm^{-1}. HRMS (EI) calcd for $C_{16}H_{14}O$ [M^+] 222.1045; found 222.1043.

2.8. Pale yellow solid (0.048 g, 54%); mp 70–72 °C, R_f = 0.59 (hexane). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.75 (d, 2H, J = 8.24 Hz, Ar–H), 7.29–7.23 (m, 3H, Ar–H), 7.02 (d, 1H, J = 7.8 Hz, Ar–H), 6.90 (s, 1H, Ar–H), 2.49 (s, 3H, –C$\underline{H}_3$), 2.39 (s, 6H, –C$\underline{H}_3$). ^{13}C (125 MHz, $CDCl_3$): δ 155.3, 154.2, 138.1, 132.4, 129.4, 128.1, 126.6, 124.9, 124.6, 119.6, 117.2, 100.8, 21.3, 19.2, 11.7. IR (film): 3029, 2920, 1726, 1505, 1288, 814 cm^{-1}. HRMS (EI) calcd for $C_{17}H_{16}O$ [M^+] 236.1201; found 236.1209.

2.9. Pale yellow solid (0.050 g, 57%); mp 46–48 °C, R_f = 0.59 (hexane). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.74 (d, 2H, J = 8.05 Hz, Ar–H), 7.24 (d, 2H, J = 8 Hz, Ar–H), 7.15 (s, 1H, Ar–H), 6.93 (s, 1H, Ar–H), 6.86 (s, 1H, Ar–H), 2.50 (s, 3H, –C$\underline{H}_3$), 2.44 (s, 3H, –C$\underline{H}_3$), 2.39 (s, 3H, –C$\underline{H}_3$). ^{13}C (125 MHz, $CDCl_3$): δ 155.0, 154.9, 138.1, 134.2, 130.1, 129.4, 128.0, 126.6, 124.6, 124.5, 108.7, 99.1, 21.7, 21.3, 18.5. IR (film): 3024, 2919, 1727, 1619, 1504, 1294, 1036, 836, 820, 794 cm^{-1}. HRMS (EI) calcd for $C_{17}H_{16}O$ [M^+] 236.1201; found 236.1209.

2.10 (ref. 16). Colourless solid (0.040 g, 51%); mp 126–128 °C, R_f = 0.42 (hexane). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.76 (d, 2H, J = 8.25 Hz, Ar–H), 7.57 (d, 1H, J = 7.35 Hz, Ar–H), 7.52 (d, 1H, J = 7.3 Hz, Ar–H), 7.28–7.21 (m, 4H, Ar–H), 6.97 (s, 1H, Ar–H), 2.40 (s, 3H, –C$\underline{H}_3$). ^{13}C (125 MHz, $CDCl_3$): δ 156.1, 154.7, 138.6, 129.4, 129.3, 127.7, 124.8, 123.9, 122.8, 120.7, 111.0, 100.5, 21.4. IR (film): 2932, 1725, 1452, 1270, 801, 749, 737 cm^{-1}. HRMS (EI) calcd for $C_{15}H_{12}O$ [M^+] 208.0888; found 208.0880.

2.11 (ref. 10). Yellow solid (0.052 g, 63%); mp 138–140 °C, R_f = 0.37 (EtOAc–hexane 5 : 95). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.91 (s, 1H, Ar–H), 7.87 (d, 2H, J = 7.3 Hz, Ar–H), 7.60–7.54 (m, 2H, Ar–H), 7.48 (t, 2H, J = 7.5 Hz, Ar–H), 7.43–7.40 (m, 1H, Ar–H), 7.05 (s, 1H, Ar–H). ^{13}C (125 MHz, $CDCl_3$): δ 158.3, 156.4, 129.8, 129.5, 129.2, 128.9, 127.8, 125.7, 125.2, 119.4, 112.2, 106.8, 100.7. IR (film): 3093, 2960, 2226, 1723, 1465, 1288, 896, 825, 747, 766 cm^{-1}. HRMS (ESI) calcd for $C_{15}H_{10}NO$ [MH^+] 220.0762; found 220.0769.

2.12 (ref. 16). Colourless solid (0.048 g, 56%); mp 146–148 °C, R_f = 0.60 (hexane). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.84 (d, 2H, J = 7.32 Hz, Ar–H), 7.53 (d, 1H, J = 2.28 Hz, Ar–H), 7.47–7.35 (m, 4H, Ar–H), 7.25–7.21 (m, 1H, Ar–H), 6.94 (s, 1H, Ar–H). ^{13}C (125 MHz, $CDCl_3$): δ 157.3, 153.2, 130.5, 129.9, 128.9, 128.8, 128.4, 125.0, 124.3, 120.4, 112.1, 100.7. IR (film): 2961, 1723, 1638, 1451, 1275, 810, 763 cm^{-1}. HRMS (EI) calcd for $C_{14}H_9ClO$ [M^+] 228.0342; found 228.0343.

2.13 (ref. 10). Colourless solid (0.067 g, 68%); mp 120–122 °C, R_f = 0.59 (hexane). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.86 (d, 2H, J = 8.05 Hz, Ar–H), 7.48–7.38 (m, 4H, Ar–H), 7.27–7.25 (m, 1H, Ar–H), 6.96 (s, 1H, Ar–H). ^{13}C (125 MHz, $CDCl_3$): δ 158.1, 149.2, 131.5, 129.4, 129.3, 128.9, 128.7, 125.2, 124.2, 119.0, 117.1, 101.2. IR (film): 3087, 1720, 1577, 1455, 1176, 909, 839, 757 cm^{-1}. HRMS (EI) calcd for $C_{14}H_8Cl_2O$ [M^+] 261.9952; found 261.9953.

2.14 (ref. 17). Yellow solid (0.063 g, 68%); mp 84–86 °C, R_f = 0.57 (hexane). ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.41 (d, 1H, J = 8.3 Hz, Ar–H), 7.97–7.93 (m, 3H, Ar–H), 7.67–7.60 (m, 3H, Ar–H), 7.51–7.47 (m, 3H, Ar–H), 7.38–7.35 (m, 1H, Ar–H), 7.16 (s, 1H, Ar–H). ^{13}C (125 MHz, $CDCl_3$): δ 155.3, 150.3, 131.4, 130.7, 128.8, 128.4, 128.2, 126.3, 125.0, 124.8, 124.6, 123.6, 121.3, 120.0,

119.5, 102.4. IR (film): 3059, 2959, 1724, 1487, 1286, 1121, 1072, 818, 744, 689 cm^{-1}. HRMS (EI) calcd for $C_{18}H_{12}O$ [M^+] 244.0888; found 240.0887.

2.15. Yellow solid (0.069 g, 73%); mp 174–176 °C, R_f = 0.38 (EtOAc–hexane 5 : 95). ^1H NMR (500 MHz, $CDCl_3$): δ 7.90 (s, 1H, Ar–H), 7.78 (d, 2H, J = 8.6 Hz, Ar–H), 7.58–7.54 (m, 2H, Ar–H), 7.44 (d, 2H, J = 8.05 Hz, Ar–H), 7.02 (s, 1H, Ar–H). ^{13}C (125 MHz, $CDCl_3$): δ 157.1, 156.4, 135.4, 129.7, 129.2, 128.1, 127.7, 126.4, 125.8, 119.3, 112.3, 107.0, 101.1. IR (film): 2960, 2225, 1723, 1486, 1461, 1269, 1090, 810, 793 cm^{-1}. HRMS (EI) calcd for $C_{15}H_8ClNO$ [M^+] 253.0294; found 253.0290.

2.16 (ref. 10). Yellow solid (0.075 g, 73%); mp 178–180 °C, R_f = 0.27 (EtOAc–hexane 2 : 98). ^1H NMR (500 MHz, $CDCl_3$): δ 8.51 (s, 1H, Ar–H), 8.23 (d, 1H, J = 9.2 Hz, Ar–H), 7.81 (d, 2H, J = 8 Hz, Ar–H), 7.59 (d, 1H, J = 9.2 Hz, Ar–H), 7.47 (d, 2H, J = 8 Hz, Ar–H), 7.12 (s, 1H, Ar–H). ^{13}C (125 MHz, $CDCl_3$): δ 158.1, 157.6, 144.4, 135.6, 129.5, 129.3, 127.7, 126.5, 120.3, 117.4, 111.5, 102.0. IR (film): 3099, 2961, 1722, 1588, 1520, 1486, 1348, 1268, 1090, 793 cm^{-1}. HRMS (EI) calcd for $C_{14}H_8ClNO_3$ [M^+] 273.0193; found 273.0197.

2.17 (ref. 2*b*). Colourless solid (0.058 g, 59%); mp 154–156 °C, R_f = 0.67 (hexane). ^1H NMR (500 MHz, $CDCl_3$): δ 7.76 (d, 2H, J = 8.55 Hz, Ar–H), 7.53 (s, 1H, Ar–H), 7.41 (d, 3H, J = 7.45 Hz, Ar–H), 7.25–7.23 (m, 1H, Ar–H), 6.93 (s, 1H, Ar–H). ^{13}C (100 MHz, $CDCl_3$): δ 156.2, 153.2, 134.8, 130.4, 129.1, 128.6, 128.4, 126.2, 124.7, 120.5, 112.1, 101.2. IR (film): 2961, 1724, 1444, 1273, 828, 811, 800 cm^{-1}. HRMS (EI) calcd for $C_{14}H_8Cl_2O$ [M^+] 261.9952; found 261.9955.

2.18 (ref. 2*b*). Colourless solid (0.084 g, 75%); mp 136–138 °C, R_f = 0.57 (hexane). ^1H NMR (500 MHz, $CDCl_3$): δ 7.79 (d, 2H, J = 8.6 Hz, Ar–H), 7.44–7.42 (m, 3H, Ar–H), 7.28 (d, 1H, J = 2 Hz, Ar–H), 6.95 (s, 1H, Ar–H). ^{13}C (100 MHz, $CDCl_3$): δ 157.0, 149.3, 135.3, 131.3, 129.2, 128.8, 127.8, 126.4, 124.6, 119.1, 117.2, 101.6. IR (film): 2961, 1724, 1577, 1446, 1284, 824, 787, 734 cm^{-1}. HRMS (EI) calcd for $C_{14}H_7Cl_3O$ [M^+] 295.9562; found 295.9569.

2.19. Pale yellow solid (0.045 g, 47%); mp 68–70 °C, R_f = 0.55 (hexane). ^1H NMR (500 MHz, $CDCl_3$): δ 7.78 (d, 2H, J = 8.75 Hz, Ar–H), 7.40 (d, 2H, J = 8.6 Hz, Ar–H), 7.29 (d, 1H, J = 8.05 Hz, Ar–H), 7.05 (d, 1H, J = 8 Hz, Ar–H), 6.95 (s, 1H, Ar–H), 2.49 (s, 3H, –C$\underline{H}_3$), 2.40 (s, 3H, –C$\underline{H}_3$). ^{13}C (125 MHz, $CDCl_3$): δ 154.4, 153.9, 133.8, 133.0, 129.3, 128.9, 126.3, 125.9, 125.1, 119.8, 117.5, 102.0, 19.3, 11.7. IR (film): 3037, 2921, 1725, 1481, 1090, 814, 750 cm^{-1}. HRMS (EI) calcd for $C_{16}H_{13}ClO$ [M^+] 256.0655; found 256.0650.

2.20. Colourless solid (0.056 g, 54%); mp 110–112 °C, R_f = 0.29 (hexane) .^1H NMR (400 MHz, $CDCl_3$): δ 8.38 (d, 1H, J = 8.2 Hz, Ar–H), 7.94–7.87 (m, 3H, Ar–H), 7.65–7.58 (m, 3H, Ar–H), 7.49–7.46 (m, 1H, Ar–H), 7.03–7.00 (m, 3H, Ar–H), 3.88 (s, 3H, –OC$\underline{H}_3$). ^{13}C (100 MHz, $CDCl_3$): δ 159.7, 155.4, 149.9, 131.2, 128.4, 126.2, 126.1, 125.0, 124.7, 123.6, 123.4, 121.3, 119.9, 119.4, 114.3, 100.8, 55.3. IR (film): 2926, 1500, 1252, 1032, 814, 748 cm^{-1}. HRMS (EI) calcd for $C_{19}H_{14}O_2$ [M]$^+$ 274.0994; found 274.0985.

2.21 (ref. 16). Colourless solid (0.076 g, 78%); mp 172–174 °C, R_f = 0.47 (EtOAc–hexane 2 : 98). ^1H NMR (400 MHz, $CDCl_3$): δ 7.77 (d, 2H, J = 9.16 Hz, Ar–H), 7.50 (d, 1H, J = 1.84 Hz, Ar–H), 7.40 (d, 1H, J = 8.68 Hz, Ar–H), 7.19 (dd, 1H, J = 8.68 Hz, J = 1.84 Hz, Ar–H), 6.98 (d, 2H, J = 8.68 Hz, Ar–H), 6.81 (s, 1H, Ar–H), 3.86 (s, 3H, –OC$\underline{H}_3$). ^{13}C (100 MHz, $CDCl_3$): δ 160.3, 157.5, 153.0, 130.8, 128.3, 126.5, 123.8, 122.7, 120.0, 114.3, 111.9, 99.1, 55.3. IR (film): 2964, 1724, 1505, 1271, 1040, 832, 796 cm^{-1}. HRMS (EI) calcd for $C_{15}H_{11}ClO_2$ [M^+] 258.0448; found 258.0445.

2.22. Colourless solid (0.078 g, 71%); mp 166–168 °C, R_f = 0.43 (EtOAc–hexane 2 : 98). ^1H NMR (500 MHz, $CDCl_3$): δ 7.79 (d, 2H, J = 6.85 Hz, Ar–H), 7.39 (s, 1H, Ar–H), 7.25–7.23 (m, 1H, Ar–H), 6.97 (d, 2H, J = 7.45 Hz, Ar–H), 6.81 (s, 1H, Ar–H), 3.86 (s, 3H, –OC$\underline{H}_3$). ^{13}C (125 MHz, $CDCl_3$): δ 160.6, 158.3, 149.0, 131.8, 128.5, 126.8, 123.7, 122.1, 118.7, 116.9, 114.3, 99.5, 55.4. IR (film): 2967, 1720, 1610, 1505, 1445, 1255, 824, 792 cm^{-1}. HRMS (EI) calcd for $C_{15}H_{10}Cl_2O_2$ [M^+] 292.0058; found 292.0050.

2.23. Colourless solid (0.050 g, 55%); mp 74–76 °C, R_f = 0.73 (hexane). ^1H NMR (400 MHz, $CDCl_3$): δ 7.78 (d, 2H, J = 8.68 Hz, Ar–H), 7.44 (d, 1H, J = 7.8 Hz, Ar–H), 7.25 (d, 3H, J = 8.68 Hz, Ar–H), 7.17–7.12 (m, 1H, Ar–H), 6.97 (s, 1H, Ar–H), 2.40 (s, 3H, –C$\underline{H}_3$). ^{13}C (100 MHz, $CDCl_3$): δ 157.0, 150.5, 139.1, 130.9, 129.5, 127.1, 125.1, 124.1, 123.7, 119.2, 116.5, 100.9, 21.4. IR (film): 3033, 1589, 1471, 1193, 1034, 905, 805, 734 cm^{-1}. HRMS (EI) calcd for $C_{15}H_{11}ClO$ [M^+] 242.0498; found 242.0497.

2.24. Colourless solid (0.048 g, 53%); mp 136–138 °C, R_f = 0.75 (hexane). ^1H NMR (400 MHz, $CDCl_3$): δ 7.72 (d, 2H, J = 8.24 Hz, Ar–H), 7.51 (s, 1H, Ar–H), 7.45 (d, 1H, J = 8.24 Hz, Ar–H), 7.26–7.24 (d, 2H, Ar–H), 7.19 (dd, 1H, J = 8.44 Hz, J = 1.62 Hz, Ar–H), 6.91 (s, 1H, Ar–H), 2.39 (s, 3H, –C$\underline{H}_3$). ^{13}C (100 MHz, $CDCl_3$): δ 157.0, 154.8, 138.9, 129.5, 128.0, 127.3, 124.9, 123.6, 121.1, 111.6, 100.2, 21.4. IR (film): 3092, 1582, 1503, 1423, 1030, 925, 816 cm^{-1}. HRMS (EI) calcd for $C_{15}H_{11}ClO$ [M^+] 242.0498; found 242.0495.

2.25 (ref. 13). Brown solid (0.060 g, 63%); mp 132–134 °C, R_f = 0.57 (EtOAc–hexane 1 : 9).^1H NMR (400 MHz, $CDCl_3$): δ 8.40 (s, 1H, Ar–H), 8.17 (dd, 1H, J = 8.72 Hz, J = 1.82 Hz, Ar–H), 7.79 (d, 2H, J = 8.24 Hz, Ar–H), 7.62 (d, 1H, J = 8.72 Hz, Ar–H), 7.30 (d, 2H, J = 8.24 Hz, Ar–H), 7.05 (s, 1H, Ar–H), 2.43 (s, 3H, –C$\underline{H}_3$). ^{13}C (100 MHz, $CDCl_3$): δ 161.7, 153.3, 144.5, 140.4, 135.4, 129.7, 126.4, 125.5, 120.2, 118.9, 107.5, 100.6, 21.5. IR (film): 3025, 1600, 1516, 1502, 1345, 915, 874, 816, 730 cm^{-1}. HRMS (EI) calcd for $C_{15}H_{11}NO_3$ [M^+] 253.0739; found 253.0731.

2.26. Brown solid (0.077 g, 77%); mp 136–138 °C, R_f = 0.57 (EtOAc–hexane 1 : 9).^1H NMR (400 MHz, $CDCl_3$): δ 8.28 (s, 1H, Ar–H), 7.98 (dd, 1H, J = 8.48 Hz, J = 1.6 Hz, Ar–H), 7.74 (d, 2H J = 8.24 Hz, Ar–H), 7.51 (d, 1H, J = 8.68 Hz, Ar–H), 7.25 (d, 2H J = 7.76 Hz, Ar–H), 6.99 (s, 1H, Ar–H), 3.93 (s, 3H, –$CO_2C\underline{H}_3$), 2.39 (s, 3H, C$\underline{H}_3$). ^{13}C (100 MHz, $CDCl_3$): δ 167.3, 157.6, 157.3, 139.1, 129.5, 129.4, 127.1, 125.8, 125.2, 125.0, 123.0, 110.9, 100.7, 52.1, 21.4. IR (film): 2952, 1720, 1307, 1244, 1090, 907, 800, 770 cm^{-1}. HRMS (EI) calcd for $C_{17}H_{14}O_3$ [M^+] 266.0943; found 266.0949.

2.27. Pale yellow solid (0.052 g, 48%); mp 146–148 °C, R_f = 0.52 (EtOAc–hexane 1 : 9). ^1H NMR (400 MHz, $CDCl_3$): δ 8.32 (d, 1H, J = 1.4 Hz, Ar–H), 8.03 (dd, 1H, J = 8.94 Hz, J = 1.62 Hz, Ar–H), 7.85 (t, 1H, J = 1.6 Hz, Ar–H), 7.74–7.72 (m, 1H, Ar–H), 7.54 (d, 1H, J = 8.68 Hz, Ar–H), 7.41–7.33 (m, 2H, Ar–H), 7.09 (s, 1H, Ar–H), 3.95 (s, 3H, –$CO_2C\underline{H}_3$). ^{13}C (100 MHz, $CDCl_3$): δ 167.1, 157.4, 155.7, 135.0, 131.5, 130.1, 128.9, 126.5, 125.5, 125.0,

123.5, 123.1, 111.1, 102.6, 52.1. IR (film): 3108, 1718, 1432, 1276, 912, 821, 762 cm^{-1}. HRMS (EI) calcd for $C_{16}H_{11}ClO_3$ $[M^+]$ 286.0397; found 286.0394.

2.28. Pale yellow solid (0.058 g, 57%); mp 154–156 °C, R_f = 0.52 (EtOAc–hexane 1 : 9). ^1H NMR (400 MHz, $CDCl_3$): δ 8.30 (s, 1H, Ar–H), 8.00 (dd, 1H, J = 8.7 Hz, J = 1.82 Hz, Ar–H), 7.85–7.82 (m, 2H, Ar–H), 7.52 (d, 1H, J = 8.72 Hz, Ar–H), 7.15 (t, 2H, J = 8.7 Hz, Ar–H), 6.99 (s, 1H, Ar–H), 3.95 (s, 3H, $-CO_2C\underline{H}_3$). ^{13}C (100 MHz, $CDCl_3$): δ 167.2, 163.1 (d, J = 250.05 Hz), 157.3, 156.4, 129.2, 126.9 (d, J = 8.62 Hz), 126.2, 126.1, 125.4, 123.2, 116.0 (d, J = 22.99 Hz), 110.9, 101.2, 52.1. IR (film): 3115, 1719, 1615, 1507, 1301, 1231, 816, 762 cm^{-1}. HRMS (EI) calcd for $C_{16}H_{11}FO_3$ $[M^+]$ 270.0692; found 270.0691.

3.1. Yellow solid (0.047 g, 51%); mp 134–136 °C, R_f = 0.31 (EtOAc–hexane 5 : 95). ^1H NMR (500 MHz, $CDCl_3$): δ 7.85 (s, 1H, Ar–H), 7.55–7.54 (m, 4H, Ar–H), 7.41–7.36 (m, 3H), 7.34–7.31 (m, 1H, Ar–H), 7.00 (d, 1H, J = 16.2 Hz, $C\underline{H}_{olefin}$), 6.70 (s, 1H, Ar–H). ^{13}C (125 MHz, $CDCl_3$): δ 157.3, 156.4, 135.9, 132.4, 129.8, 128.9, 128.8, 128.1, 126.9, 125.5, 119.4, 115.3, 111.9, 106.8, 104.1. IR (film): 3029, 2226, 1723, 1590, 1464, 1269, 812, 755, 696 cm^{-1}. HRMS (EI) calcd for $C_{17}H_{11}NO$ $[M^+]$ 245.0841; found 245.0842.

3.2. Yellow solid (0.061 g, 60%); mp 94–96 °C, R_f = 0.55 (hexane). ^1H NMR (400 MHz, $CDCl_3$): δ 8.40 (d, 1H, J = 8.24 Hz, Ar–H), 7.92 (d, 1H, J = 8.24 Hz, Ar–H), 7.66–7.57 (m, 5H, Ar–H), 7.51–7.47 (m, 1H, Ar–H), 7.44–7.38 (m, 3H, Ar–H), 7.32–7.28 (m, 1H, Ar–H), 7.09 (d, 1H, J = 16 Hz, $-C\underline{H}_{olefin}$), 6.83 (s, 1H, Ar–H). ^{13}C (100 MHz, $CDCl_3$): δ 154.6, 150.3, 136.7, 131.6, 129.3, 128.8, 128.4, 128.0, 126.6, 126.3, 125.1, 124.7, 123.6, 121.1, 120.1, 119.4, 116.6, 106.2. IR (film): 3057, 2925, 1638, 1386, 1084, 951, 815, 746, 685 cm^{-1}. HRMS (EI) calcd for $C_{20}H_{14}O$ $[M^+]$ 270.1045; found 270.1042.

3.3. Yellow solid (0.062 g, 58%); mp 120–122 °C, R_f = 0.50 (hexane). ^1H NMR (400 MHz, $CDCl_3$): δ 8.39 (d, 1H, J = 8.24 Hz, Ar–H), 7.92 (d, 1H, J = 8.24 Hz, Ar–H), 7.65–7.59 (m, 3H, Ar–H), 7.51–7.47 (m, 3H, Ar–H), 7.40 (d, 1H, J = 16.48 Hz, $-C\underline{H}_{olefin}$), 7.21 (d, 2H, J = 7.76 Hz, Ar–H), 7.05 (d, 1H, J = 16.48 Hz, $-C\underline{H}_{olefin}$), 6.79 (s, 1H, Ar–H), 2.39 (s, 3H, $-C\underline{H}_3$). ^{13}C (100 MHz, $CDCl_3$): δ 154.8, 150.2, 138.0, 133.9, 131.5, 129.5, 129.3, 128.4, 126.5, 126.3, 125.0, 124.7, 123.5, 121.1, 120.1, 119.4, 115.6, 105.7, 21.3. IR (film): 3052, 2919, 1636, 1519, 1386, 1083, 961, 947, 818, 744 cm^{-1}. HRMS (EI) calcd for $C_{21}H_{16}O$ $[M^+]$ 284.1201; found 284.1209.

3.4. Yellow solid (0.053 g, 48%); mp 184–186 °C, R_f = 0.25 (EtOAc–hexane 5 : 95). ^1H NMR (400 MHz, $CDCl_3$): δ 8.43 (d, 1H, J = 2.52 Hz, Ar–H), 8.18 (dd, 1H, J = 9.02 Hz, J = 2.4 Hz, Ar–H), 7.53–7.48 (m, 3H, Ar–H), 7.35 (d, 1H, J = 16.48 Hz, $-C\underline{H}_{olefin}$), 6.93 (d, 2H, J = 8.92 Hz, Ar–H), 6.87 (d, 1H, J = 16.48 Hz, $-CH_{olefin}$), 6.72 (s, 1H, Ar–H), 3.85 (s, 3H, $-OC\underline{H}_3$). ^{13}C (125 MHz, $CDCl_3$): δ 160.4, 158.8, 157.7, 144.3, 132.4, 129.8, 128.7, 128.5, 120.2, 116.9, 114.4, 113.2, 111.0, 104.1, 55.5. IR (film): 3094, 2924, 1602, 1526, 1510, 1346, 1175, 817 cm^{-1}. HRMS (EI) calcd for $C_{17}H_{13}NO_4$ $[M^+]$ 295.0845; found 295.0842.

4.1. Colourless solid (0.031 g, 48%); mp 204–206 °C, R_f = 0.66 (hexane). ^1H NMR (400 MHz, $CDCl_3$): δ 7.79 (t, 4H, J = 8 Hz, Ar–H), 7.43 (s, 2H, Ar–H), 7.28–7.25 (m, 5H, Ar–H), 7.04 (s, 1H, Ar–H), 2.40 (s, 6H, $-C\underline{H}_3$). ^{13}C (100 MHz, $CDCl_3$): δ 156.1, 155.4, 153.9, 147.1, 138.6, 138.1, 129.5, 129.4, 128.1, 127.7, 124.8, 124.5, 124.0, 116.1, 114.9, 107.2, 101.3, 97.0, 21.4, 21.3. IR (film): 2922, 2853, 1504, 1244, 1032, 911, 807 cm^{-1}. HRMS (EI) calcd for $C_{24}H_{18}O_2$ $[M^+]$ 338.1307; found 338.1309.

5.1. Yellow solid (0.032 g, 52%); mp 152–154 °C, R_f = 0.24 (EtOAc–hexane 1 : 9). ^1H NMR (400 MHz, $CDCl_3$): δ 8.14 (s, 1H, Ar–H), 7.88–7.84 (m, 4H, Ar–H), 7.60 (s, 1H, Ar–H), 7.19 (s, 1H, Ar–H), 7.00 (dd, 4H, J = 8.92 Hz, J = 1.6 Hz, Ar–H), 4.02 (s, 3H, $-CO_2C\underline{H}_3$), 3.88 (s, 6H, $-OC\underline{H}_3$). ^{13}C (100 MHz, $CDCl_3$): δ 167.3, 160.6, 160.0, 159.0, 156.5, 152.5, 146.7, 126.8, 126.4, 125.1, 123.3, 122.6, 119.2, 116.7, 114.4, 114.3, 109.6, 101.7, 96.1, 55.4, 51.9. IR (KBr): 3011, 2392, 1693, 1647, 1556, 1099, 696 cm^{-1}. HRMS (EI) calcd for $C_{26}H_{20}O_6$ $[M^+]$ 428.1260; found 428.1266.

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