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De novo synthesis of functionalized 1,3-enynes and extended conjugated molecular systems†

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Pd-catalyzed coupling of 1,3-dienyldibromides with triarylbismuths was demonstrated for the synthesis of a diverse range of 1,3-enynes. This study provided easy access to a range of functionalized 1,3-enynes in high yields utilizing triarylbismuths in sub-stoichiometric amounts. A new and concise route was unveiled for the synthesis of extended π-conjugated molecular systems with the help of chemoselective couplings and in conjunction with Sonogashira, Heck and arylation reactions under combined catalysis.

Introduction

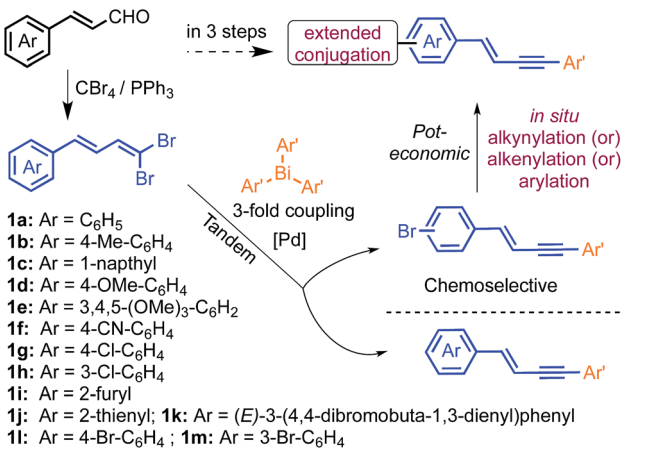
Efforts towards the synthesis of conjugated molecular skeletons are in high demand[1,2] and these systems with extended conjugation have been targets for medicinal, optical and electronic applications.[3,4] Importantly, 1,3-dienyldibromide as a molecular synthon was addressed very sparingly and an elaborate structural reactivity is conspicuously missing. There is a desperate need for an elaborate study of these reagents with broader applicability and selectivity (Scheme 1).[5] Prudently, the impact of pot-economic process[6] is enormous as this approach greatly reduces the chemical waste during the reaction process. This prompted us to explore for the synthesis of functionalized (*E*)-1,3-enynes under pot-economic tandem process.

Importantly, 1,1-dibromides are serving as novel synthons in organic synthesis.[7] In the present context, 1,3-dienyldibromides can be easily prepared from cinnamaldehydes through Ramirez olefination.[8] Accordingly, several 1,3-dienyldibromides (**1a–1m**) have been prepared (Scheme 1) for our coupling study towards 1,3-enynes using triarylbismuth reagents. Application of triarylbismuths as organometallic nucleophiles offer advantages such as atom-economic threefold reactivity and faster cross-coupling protocols under metal catalyzed conditions.[9,10] Our envisioned approach is given in Scheme 1 which involves initial tandem synthesis of 1,3-enynes followed by pot-economic *in situ* functionalizations for the synthesis of extended conjugated molecular systems under palladium-catalyzed conditions.

Results and discussion

To achieve this goal, our initial screening was explored with **1a** and tri(*p*-tolyl)Bi under palladium coupling conditions (Table 1). It was explored with $Pd(PPh_3)_4$ in DMF and different bases (entries 1–4, Table 1). Interestingly, an effective tandem coupling was obtained using Cs_2CO_3 and 2 h conditions with the formation of 1,3-enyne **2a** in 70% yield (entry 3, Table 1). Encouragingly, this yield was further improved to 84% in 3 h duration (entry 4, Table 1). Further investigation using $PdCl_2(PPh_3)_2$ and $Pd_2(dba)_3$/2 PPh_3 catalysts gave 61% and 79% yields (entries 5 and 6, Table 1). Whereas, couplings with $Pd(PPh_3)_4$ in *N*-methyl-2-pyrrolidone (NMP) and *N*,*N*-dimethylacetamide (DMA) furnished moderate yields (entries 7 and 8, Table 1). Other screenings with lowering base (entry 9, Table 1) or catalyst amount and different heating conditions furnished lowered yields (entries 10–13, Table 1). Importantly, formation of 1-bromoenyne was observed when the reaction was run without catalyst (entry 14, Table 1). This screening thus helped us to realize an efficient protocol using $Pd(PPh_3)_4$ and Cs_2CO_3 in DMF to achieve the desired tandem coupling in high product yield (entry 4, Table 1).

An elaborate structural reactivity with various functionalized dibromides has been explored in couplings with triarylbismuth



Scheme 1 Our approach towards conjugated systems.

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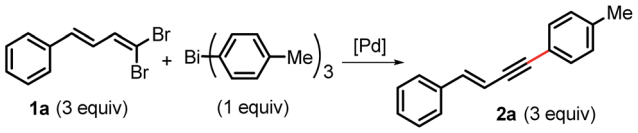
† Electronic supplementary information (ESI) available: Full experimental details with ^1H,^{13}C NMR spectra and mass spectra for all compounds. See DOI: 10.1039/c5ra01544h

Table 1 Optimization[a,b,c]



1a (3 equiv) (1 equiv) 2a (3 equiv)

Entry	Catalyst	Base	Solvent	Time (h)	2a (%)
1	$Pd(PPh_3)_4$	K_3PO_4	DMF	2	55
2	$Pd(PPh_3)_4$	K_2CO_3	DMF	2	50
3	$Pd(PPh_3)_4$	Cs_2CO_3	DMF	2	70
4	$Pd(PPh_3)_4$	Cs_2CO_3	DMF	3	84
5	$PdCl_2(PPh_3)_2$	Cs_2CO_3	DMF	3	61
6	$Pd_2(dba)_3$/2 PPh_3	Cs_2CO_3	DMF	3	79
7	$Pd(PPh_3)_4$	Cs_2CO_3	NMP	3	58
8	$Pd(PPh_3)_4$	Cs_2CO_3	DMA	3	56
9	$Pd(PPh_3)_4$	Cs_2CO_3	DMF	3	54[d]
10	$Pd(PPh_3)_4$	Cs_2CO_3	DMF	4	79
11	$Pd(PPh_3)_4$	Cs_2CO_3	DMF	3	75[e]
12	$Pd(PPh_3)_4$	Cs_2CO_3	DMF	3	49[f]
13	$Pd(PPh_3)_4$	Cs_2CO_3	DMF	3	34[g,h]
14	—	Cs_2CO_3	DMF	3	0[i]

[a] Conditions: **1a** (0.375 mmol, 3 equiv.), Bi(*p*-tolyl)$_3$ (0.125 mmol, 1 equiv.), Pd catalyst (0.0112 mmol, 0.09 equiv.), base (1.125 mmol, 9 equiv.), solvent (6 mL), 80 °C. [b] Isolated yields. [c] Biaryls as side products formed in minor amounts. [d] With 6 equiv. of base. [e] With 5 mol% catalyst. [f] At 90 °C. [g] At 60 °C. [h] GC conversion. [i] 1-Bromoenyne formed.

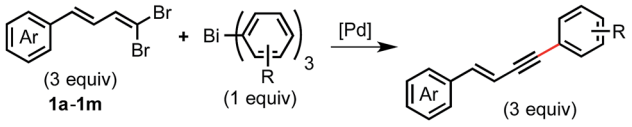
reagents (Table 2). This reactivity of different dibromides (**1a–1e**) in general afforded good to excellent yields. In fact, our tandem protocol was proved to be useful for the synthesis of a library of enynes in good to high yields.

While the electron-rich dibromides (**1b–1e**) reacted fairly well to give different enynes (**3–6**) in 61–85% yields, the corresponding reactivity with electron-deficient dibromide **1f** was proved to be moderate with the formation of **7a** in 56% yield. The reactivity of chloro substituted dibromides **1g** and **1h** was appreciable to give enynes (**8a–8h**, **9a**) in 65–77% yields. The couplings of furanyl and thienyl derived dibromides **1i** and **1j** furnished a group of heteroaryl substituted enynes (**10** and **11**) in 58–82% yields.

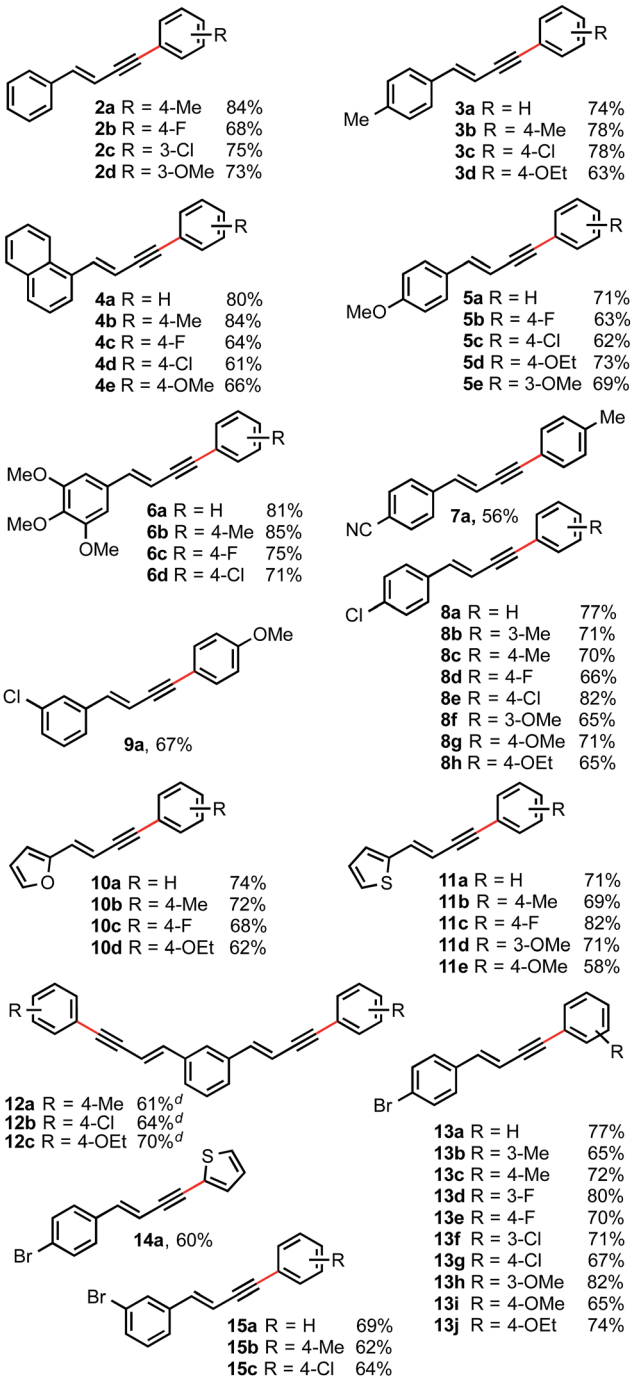
This study was extended towards tandem bis-couplings using 1,3-substituted dibromide (**1k**). This was to explore the possibility for the synthesis of bis-enynes (**12a–12c**) in one-pot operation. This approach was proved to be synthetically highly useful and corresponding bis-enynes were obtained in 61–70% yields. Further, chemoselective couplings were explored under the established coupling conditions using **1l** and **1m** possessing reactive aryl bromide. It is to be highlighted that this led to the preparation of several bromo functionalized enynes (**13–15**) in 60–82% yields. In these couplings, several aryl and heteroaryl bismuth reagents participated effectively with good to high yields.

In recent times, consecutive or sequential reactions with atom- or pot-economy are gaining popularity.[6] With the accomplishment of a wide spectrum of mono- and bis-

Table 2 Tandem synthesis of 1,3-enynes[a,b,c]



(3 equiv) **1a-1m** (1 equiv) (3 equiv)



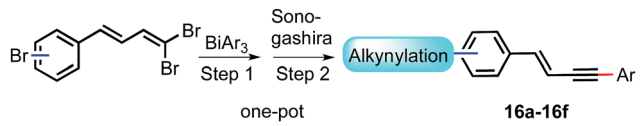
[a] Conditions: dibromide (0.375 mmol, 3 equiv.), $BiAr_3$ (0.125 mmol, 1 equiv.), $Pd(PPh_3)_4$ (0.0112 mmol, 0.09 equiv.), Cs_2CO_3 (1.125 mmol, 9 equiv.), DMF, 80 °C, 3 h. [b] Isolated yields. [c] Biaryls formed in minor amounts. [d] With additional $BiAr_3$ (0.25 mmol) and 6 h duration.

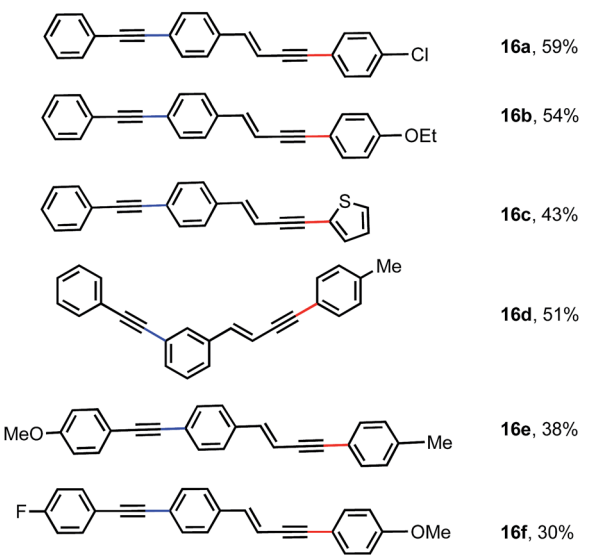
couplings, it was of interest to establish pot-economic process with *in situ* functionalizations under palladium coupling conditions.

This was to impart the overall process with greater synthetic utility in the preparation of compounds with extended π-conjugation. For this, we adopted sequential couplings involving tandem synthesis of 1,3-enynes in step 1 followed by alkynylation (Table 3), arylation (Table 4) or alkenylation (Table 5) in step 2 to synthesize a wide variety of both linear and cross-conjugated π-extended 1,3-enynes. To our delight, we could achieve this in a versatile manner with careful adaptation of reaction conditions for step 2. To start with, the strategy for the extension of molecular complexity with additional alkyne was planned with the Sonogashira coupling. In fact, the selection of a compatible condition for step 2 was cumbersome as innumerable protocol conditions are available for the Sonogashira reaction. However, we could finally explore the best option and achieved the desired extended conjugation with different alkyne functionality under compatible *in situ* reaction conditions[11] (Table 3).

Appreciably, under the adopted conditions using combined catalytic approach, the final alkynylated products (**16a–16f**) were obtained with 30–59% as overall yields. This was a clear indication of the facile and amenable nature of our conditions to evolve a combined catalytic process for pot-economic *in situ* Sonogashira alkynylations towards 1,3-enyne systems with extended alkyne functionality.

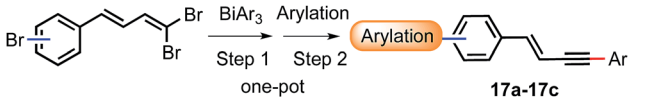
Table 3 Functionalization with Sonogashira reaction[a,b,c]

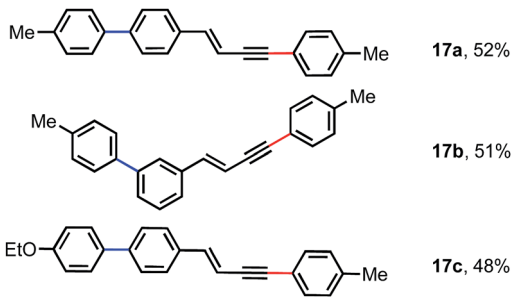




[a] Conditions for step 1: Table 2 reaction conditions followed; for step 2: $Pd(PPh_3)_4$ (0.006 mmol, 0.048 equiv.), alkyne (0.75 mmol, 6 equiv.), TBAB (0.75 mmol, 6 equiv.), NEt_3 (1.875 mmol, 15 equiv.), DMSO, 100 °C, 4 h. [b] Isolated yields. [c] Step 2 was not optimized.

Table 4 Functionalization with arylation[a,b,c]



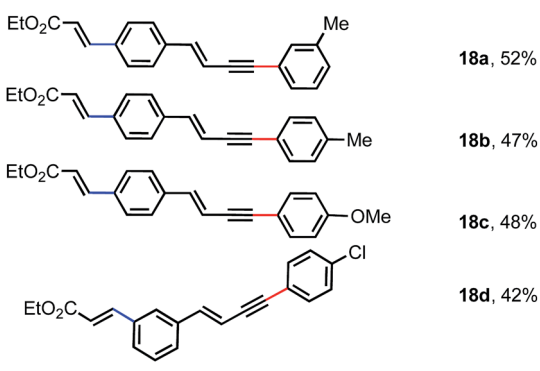


[a] Conditions for step 1: Table 2 reaction conditions followed; for step 2: $Pd(PPh_3)_4$ (0.006 mmol, 0.048 equiv.), $BiAr_3$ (0.125 mmol, 1 equiv.), Cs_2CO_3 (0.564 mmol, 4.5 equiv.), 110 °C, 4 h. [b] Isolated yields. [c] Step 2 was not optimized.

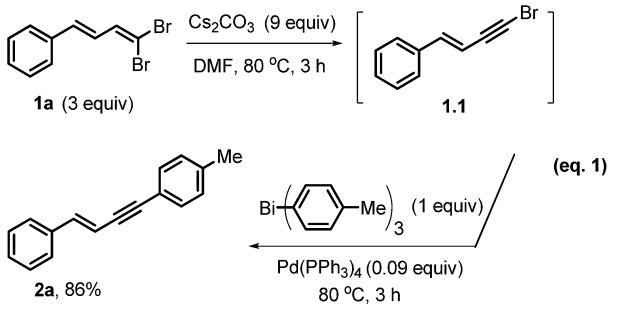
This one-pot *in situ* functionalizations under combined catalysis was extended to arylation of enynes using triarylbismuth reagents in step 2 and was given in Table 4.[12] This approach of *in situ* coupling of aryl bromide with different bismuth reagents afforded arylated 1,3-enynes **17a–17c** in 48–52% yields.

Encouraged by the compatibility witnessed above under combined catalytic approach, further attempts have been made for *in situ* Heck type alkenylations.[13] Again, it was a challenging scenario to come up with the right combination of conditions for the Heck reaction as several protocols are known.

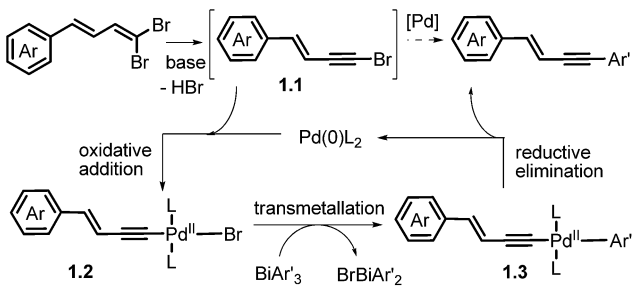
Table 5 Functionalization with Heck reaction[a,b,c]



[a] Conditions for step 1: Table 2 reaction conditions followed; for step 2: ethyl acrylate (0.562 mmol, 4.5 equiv.), $Pd(PPh_3)_4$ (0.006 mmol, 0.048 equiv.), NEt_3 (1.875 mmol, 15 equiv.), 110 °C, 4 h. [b] Isolated yields. [c] Step 2 was not optimized.



Scheme 2 A two-step control reaction.



Scheme 3 Mechanistic cycle.

Our efforts thus led to the fruitful outcome with *in situ* functionalization using ethyl acrylate in step 2 (Table 5). The combined catalytic approach thus overall furnished stereoselective (*E*)-alkenylated enynes (**18a–18d**) in 42–52% yields.

This unprecedented strategy of *in situ* functionalization of enynes under combined catalysis demonstrated a practicable and straightforward approach for the synthesis of an array of enynes with extended π-conjugation in three different ways. These processes starting from readily accessible 1,3-dienyldibromides and tailored through a complementary tandem and consecutive catalytic couplings paid rich dividends to synthesize π-conjugated extended enynes in a two-step one-pot operation.

To gain insights into the reaction mechanism a stepwise coupling was performed as given in Scheme 2. This two-step sequence furnished enyne **2a** in 86% yield after the second step. GC/GC-MS analysis of the reaction mixture after the first step indicated the formation of 1-bromo-1,3-enyne intermediate **1.1**. This was in tune with our earlier observation as 1-bromo-1,3-enyne was formed during the optimization study and in the absence of palladium catalyst (entry 14, Table 1).

This refers to the initial dehydrobromination of 1,3-dienyldibromide to give **1.1**, which in the presence of palladium cross-couples with bismuth reagent to give 1,3-enyne (Scheme 3). This process was expected to go through usual steps known for cross-coupling sequence comprising oxidative addition (**1.2**), transmetallation (**1.3**) and reductive elimination. The possibility of initial cross-coupling of bismuth reagent with 1,3-dienyldibromide followed by base mediated dehydrobromination although cannot be ruled out completely at this stage.

Conclusions

We have demonstrated a *de novo* synthesis of functionalized 1,3-enynes and its extended conjugated molecular systems from 1,3-dienyldibromides under palladium-catalyzed conditions. This one-pot tandem protocol involves the utilization of threefold reactivity of triarylbismuths and the synthesis of an array of functionalized (*E*)-1,3-enynes. The established chemoselective couplings and additional functionalizations have been carried out under combined catalysis to afford π-conjugated enynes with regulated structural features, thus proving the broad scope. The combined catalytic approach adopted with three *in situ* functionalizations employing Sonogashira, Heck or arylations demonstrates the broad applicability of the developed palladium protocol conditions in one-pot operation. Overall, the scope of different 1,3-dienyldibromides as masked enyne scaffolds was thoroughly established for the first time. This investigation thus unraveled the depth and synthetic utility of 1,3-dienyldibromides and has the potential to open up several new possibilities in this direction.

Experimental

General

The cross-coupling reactions have been performed in dry Schlenk tubes under nitrogen conditions. The dibromides (**1a–1m**) have been prepared from cinnamaldehydes.[8] General method of preparation for different cinnamaldehydes was given in the ESI.†[14,15] Solvents have been dried according to standard procedures. Purification of products was carried out by silica gel column chromatography using ethyl acetate/hexane as eluent. ^{1}H and ^{13}C NMR spectra were recorded using JEOL ECS 400 (400 MHz) and JEOL ECX 500 (500 MHz). HRMS was recorded using Electron Ionization (EI) and Electrospray Ionization (ESI) techniques with Waters CAB155 GCT Premier analyzer and Waters HAB 213 Q-TOF Premier analyzer. IR was recorded on PerkinElmer FT-IR.

Representative cross-coupling procedure for Table 2

The reaction was performed by charging dry Schlenk tube with Bi(*p*-tolyl)$_3$ (0.060 g, 0.125 mmol, 1 equiv.), **1a** (0.108 g, 0.375 mmol, 3 equiv.), Cs_2CO_3 (0.367 g, 1.125 mmol, 9 equiv.), $Pd(PPh_3)_4$ (0.013 g, 0.0112 mmol, 0.09 equiv.) and DMF (6 mL). The contents were stirred at 80 °C in an oil bath for 3 h. After the completion, it was cooled to rt and extracted with ethyl acetate (50 mL), washed with water (15 mL), brine (15 mL), dried over anhydrous $MgSO_4$ and concentrated. The crude product was purified using silica gel column chromatography using ethyl acetate/hexane as eluent. The product **2a** was obtained as pale yellow solid (0.069 g, 84%). The cross-coupled product yield calculated considering 0.375 mmol as 100% yield.

Representative cross-coupling procedure for bis-coupling (for Table 2, compounds 12a–12c)

The coupling procedure given above for Table 2 was followed with conditions involving Bi(*p*-ethoxyphenyl)$_3$ (0.215 g, 0.375 mmol, 1 equiv.), **1k** (0.187 g, 0.375 mmol, 1 equiv.),

Cs_2CO_3 (1.09 g, 3.37 mmol, 9 equiv.), $Pd(PPh_3)_4$ (0.026 g, 0.0225 mmol, 0.06 equiv.), DMF (15 mL), 80 °C, 6 h. The product **12c** was obtained as yellow solid (0.11 g, 70%).

Representative procedure for Table 3

The coupling procedure given above for Table 2 was followed for the first step with conditions involving Bi(*p*-chlorophenyl)$_3$ (0.068 g, 0.125 mmol, 1 equiv.), **1l** (0.138 g, 0.375 mmol, 3 equiv.), Cs_2CO_3 (0.367 g, 1.125 mmol, 9 equiv.), $Pd(PPh_3)_4$ (0.013 g, 0.01125 mmol, 0.09 equiv.), DMF (6 mL), 80 °C, 3 h. After the reaction is over, contents were cooled to rt and performed the second step of Sonogashira with the addition of phenylacetylene (0.077 g, 0.75 mmol, 6 equiv.), NEt_3 (0.19 g, 1.875 mmol, 15 equiv.), TBAB (0.242 g, 0.75 mmol, 6 equiv.), $Pd(PPh_3)_4$ (0.007 g, 0.0060 mmol, 0.048 equiv.), DMSO (3 mL) and stirring at 100 °C for 4 h. After workup, product **16a** was obtained as yellow solid (0.075 g, 59%).

Representative procedure for Table 4

The coupling procedure given above for Table 2 was followed for the first step with conditions involving Bi(*p*-tolyl)$_3$ (0.061 g, 0.125 mmol, 1 equiv.), **1m** (0.138 g, 0.375 mmol, 3 equiv.), Cs_2CO_3 (0.367 g, 1.125 mmol, 9 equiv.), $Pd(PPh_3)_4$ (0.013 g, 0.01125 mmol, 0.09 equiv.), DMF (6 mL), 80 °C, 3 h. After the reaction is over, contents were cooled to rt and performed the second step of arylation with the addition of Bi(*p*-tolyl)$_3$ (0.061 g, 0.125 mmol, 1 equiv.), Cs_2CO_3 (0.184 g, 0.56 mmol, 4.5 equiv.), $Pd(PPh_3)_4$ (0.007 g, 0.006 mmol, 0.048 equiv.) and stirring at 110 °C for 4 h. After workup, product **17b** was obtained as pale yellow solid (0.059 g, 51%).

Representative procedure for Table 5

The coupling procedure given above for Table 2 was followed for the first step with conditions involving Bi(*p*-methoxyphenyl)$_3$ (0.066 g, 0.125 mmol, 1 equiv.), **1l** (0.138 g, 0.375 mmol, 3 equiv.), Cs_2CO_3 (0.367 g, 1.125 mmol, 9 equiv.), $Pd(PPh_3)_4$ (0.013 g, 0.01125 mmol, 0.09 equiv.), DMF (6 mL), 80 °C, 3 h. After the reaction is over, contents were cooled to rt and performed the second step of alkenylation with the addition of ethyl acrylate (0.057 g, 0.562 mmol, 4.5 equiv.), NEt_3 (0.19 g, 1.875 mmol, 15 equiv.) and $Pd(PPh_3)_4$ (0.007 g, 0.006 mmol, 0.048 equiv.) and stirring at 110 °C for 4 h. After workup, product **18c** was obtained as bright yellow solid (0.06 g, 48%).

The analytical data for dibromides **1a–1m** and for all cross-coupled products is given below.

1a.[16] Pale yellow solid (74%); m.p. 48–50 °C, R_f = 0.70 (hexane). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.45 (d, 2H, J = 7.95 Hz, Ar-H), 7.38–7.29 (m, 3H), 7.10 (d, 1H, J = 9.8 Hz, =C*H*), 6.82–6.76 (m, 1H, =C*H*), 6.71 (d, 1H, J = 15.6 Hz, =C*H*). ^{13}C (125 MHz, $CDCl_3$): δ 137.1, 136.3, 135.7, 128.8, 128.6, 126.8, 125.2, 91.3. IR (film): 3038, 1700, 1560, 1488, 1448, 1284, 963, 853, 808, 747, 690 cm^{-1}. HRMS (EI) calcd for $C_{10}H_8Br_2$ [M$^+$] 285.8993; found 285.8994.

1b. Colourless solid (76%); m.p. 90–92 °C, R_f = 0.73 (hexane). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.35 (d, 2H, J = 7.95 Hz, Ar-H), 7.15 (d, 2H, J = 7.65 Hz, Ar-H), 7.08 (d, 1H, J = 9.45 Hz, =C*H*), 6.77–6.66 (m, 2H), 2.34 (s, 3H, –CH_3). ^{13}C (125 MHz, $CDCl_3$): δ 138.7, 137.2, 135.7, 133.5, 129.5, 126.8, 124.3, 90.5, 21.3. IR (film): 3009, 1602, 1507, 1280, 965, 802 cm^{-1}. HRMS (EI) calcd for $C_{11}H_{10}Br_2$ [M$^+$] 299.9149; found 299.9145.

1c. Yellow solid (76%); m.p. 88–90 °C, R_f = 0.58 (hexane). ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.09 (d, 1H, J = 8.55 Hz, Ar-H), 7.86 (d, 1H, J = 7.95 Hz, Ar-H), 7.83 (d, 1H, J = 8.25 Hz, Ar-H), 7.74 (d, 1H, J = 7.35 Hz, Ar-H), 7.56–7.46 (m, 4H, Ar-H), 7.27 (d, 1H, J = 9.8 Hz, =C*H*), 6.90–6.85 (m, 1H, =C*H*). ^{13}C (125 MHz, $CDCl_3$): δ 137.3, 133.7, 133.6, 132.4, 131.0, 129.0, 128.7, 127.9, 126.4, 126.0, 125.6, 123.9, 123.2, 91.7. IR (film): 3040, 1724, 1506, 1395, 1265, 963, 812, 795, 775 cm^{-1}. HRMS (EI) calcd for $C_{14}H_{10}Br_2$ [M$^+$] 335.9149; found 335.9140.

1d. Colourless solid (61%); m.p. 84–86 °C, R_f = 0.30 (EtOAc–hexane 1 : 99). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.39 (d, 2H, J = 8.85 Hz, Ar-H), 7.07–7.05 (m, 1H, Ar-H), 6.87 (d, 2H, J = 8.85 Hz), 6.66–6.65 (m, 2H), 3.82 (s, 3H, –OCH_3). ^{13}C (125 MHz, $CDCl_3$): δ 160.0, 137.3, 135.3, 129.1, 128.2, 123.2, 114.2, 89.8, 55.3. IR (film): 3022, 2970, 1725, 1602, 1507, 1287, 1255, 1025, 969, 812 cm^{-1}. HRMS (EI) calcd for $C_{11}H_{10}Br_2O$ [M$^+$] 315.9098; found 315.9095.

1e. Colourless solid (71%); m.p. 48–50 °C, R_f = 0.18 (EtOAc–hexane 1 : 99). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.07 (d, 1H, J = 8.3 Hz, Ar-H), 6.66–6.64 (m, 4H), 3.89 (s, 6H, –OCH_3), 3.86 (s, 3H, –OCH_3). ^{13}C (125 MHz, $CDCl_3$): δ 153.4, 138.7, 136.9, 135.6, 131.9, 124.6, 103.9, 91.0, 60.9, 56.1. IR (film): 2999, 2938, 1580, 1505, 1454, 1339, 1243, 1127, 1006, 961, 813 cm^{-1}. HRMS (EI) calcd for $C_{13}H_{14}Br_2O_3$ [M$^+$] 375.9310; found 375.9319.

1f. Colourless solid (90%); m.p. 126–128 °C, R_f = 0.37 (EtOAc–hexane 1 : 99). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.62 (d, 2H, J = 8.55 Hz, Ar-H), 7.52 (d, 2H, J = 8.25 Hz, Ar-H), 7.12 (d, 1H, J = 10.35 Hz, =C*H*), 6.91–6.85 (m, 1H, Ar-H), 6.70 (d, 1H, J = 15.85 Hz, =C*H*). ^{13}C (125 MHz, $CDCl_3$): δ 140.7, 136.4, 133.3, 132.5, 128.5, 127.2, 118.8, 111.5, 94.5. IR (film): 3048, 2222, 1721, 1601, 1501, 1412, 971, 809 cm^{-1}. HRMS (EI) calcd for $C_{11}H_7Br_2N$ [M$^+$] 310.8945; found 310.8943.

1g. Colourless solid (69%); m.p. 72–74 °C, R_f = 0.77 (hexane). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.38 (d, 2H, J = 8.55 Hz, Ar-H), 7.30 (d, 2H, J = 8.55 Hz, Ar-H), 7.08 (d, 1H, J = 9.75 Hz, =C*H*), 6.78–6.73 (m, 1H, =C*H*), 6.65 (d, 1H, J = 15.9 Hz, =C*H*). ^{13}C (125 MHz, $CDCl_3$): δ 136.8, 134.8, 134.2, 129.0, 127.9, 125.7, 92.0. IR (film): 3013, 1725, 1491, 1406, 1097, 968, 806 cm^{-1}. HRMS (EI) calcd for $C_{10}H_7Br_2Cl$ [M$^+$] 319.8603; found 319.8600.

1h. Yellow liquid (79%); R_f = 0.74 (hexane). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.42 (s, 1H, Ar-H), 7.32–7.25 (m, 3H, Ar-H), 7.08 (d, 1H, J = 10.4 Hz, =C*H*), 6.82–6.75 (m, 1H, =C*H*), 6.63 (d, 1H, J = 15.6 Hz, =C*H*). ^{13}C (125 MHz, $CDCl_3$): δ 138.1, 136.7, 134.8, 134.0, 130.0, 128.4, 126.6, 126.5, 125.0, 92.6. IR (film): 3063, 1703, 1595, 1476, 1281, 1079, 963, 811, 785 cm^{-1}. HRMS (EI) calcd for $C_{10}H_7Br_2Cl$ [M$^+$] 319.8603; found 319.8609.

1i.[17] Deep brown low melting solid (76%); R_f = 0.70 (hexane). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.43 (s, 1H, Ar-H), 7.02 (d, 1H, J = 10.3 Hz, =C*H*), 6.70–6.64 (m, 1H, =C*H*), 6.48 (d, 1H, J = 15.45 Hz, =C*H*), 6.42–6.40 (m, 2H). ^{13}C (125 MHz, $CDCl_3$): δ 152.3, 143.2, 136.7, 123.6, 122.5, 111.9, 110.7, 91.3. IR (film): 3116, 1622, 1540, 1475, 1262, 1152, 1014, 956, 819, 738 cm^{-1}. HRMS (EI) calcd for $C_8H_6Br_2O$ [M$^+$] 275.8785; found 275.8783.

1j. Brown solid (71%); m.p. 56–58 °C, $R_f = 0.69$ (hexane). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.26 (d, 1H, $J = 4.6$ Hz, Ar-H), 7.07 (d, 1H, $J = 3.45$ Hz, Ar-H), 7.03–6.97 (m, 2H), 6.83 (d, 1H, $J =$ 15.45 Hz, =C*H*), 6.59–6.54 (m, 1H, =C*H*). ^{13}C (125 MHz, $CDCl_3$): δ 141.6, 136.6, 128.3, 127.8, 127.5, 125.9, 124.6, 90.9. IR (film): 3086, 3028, 1797, 1602, 1423, 1292, 1204, 958, 818, 705 cm^{-1}. HRMS (EI) calcd for $C_8H_6Br_2S$ [M$^+$] 291.8557; found 291.8552.

1k. Colourless solid (67%); m.p. 116–118 °C, $R_f = 0.52$ (hexane). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.45 (s, 1H, Ar-H), 7.40 (d, 2H, $J = 7.6$ Hz, Ar-H), 7.33–7.30 (m, 1H, Ar-H), 7.10 (d, 2H, $J =$ 9.8 Hz, =C*H*), 6.82–6.77 (m, 2H, =C*H*), 6.71 (d, 2H, $J = 15.55$ Hz, =C*H*). ^{13}C (125 MHz, $CDCl_3$): δ 136.9, 136.8, 135.1, 129.2, 126.7, 125.8, 125.6, 91.9. IR (film): 3015, 2922, 1618, 1557, 1228, 969, 811, 771 cm^{-1}. HRMS (EI) calcd for $C_{14}H_{10}Br_4$ [M$^+$] 493.7516; found 493.7517.

1l. Colourless solid (81%); m.p. 90–92 °C, $R_f = 0.72$ (hexane). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.46 (d, 2H, $J = 7.95$ Hz, Ar-H), 7.31 (d, 2H, $J = 7.95$ Hz, Ar-H), 7.08 (d, 1H, $J = 10.4$ Hz, =C*H*), 6.79–6.74 (m, 1H, =C*H*), 6.64 (d, 1H, $J = 15.9$ Hz, =C*H*). ^{13}C (125 MHz, $CDCl_3$): δ 136.8, 135.2, 134.2, 131.9, 128.2, 125.8, 122.4, 92.1. IR (film): 3042, 2962, 1724, 1487, 1401, 1074, 967, 803 cm^{-1}. HRMS (EI) calcd for $C_{10}H_7Br_3$ [M$^+$] 363.8098; found 363.8098.

1m. Deep yellow liquid (81%); $R_f = 0.74$ (hexane). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.57 (s, 1H, Ar-H), 7.40 (d, 1H, $J = 7.9$ Hz, Ar-H), 7.35 (d, 1H, $J = 7.95$ Hz, Ar-H), 7.19 (t, 1H, $J = 7.8$ Hz, Ar-H), 7.08 (d, 1H, $J = 10.1$ Hz, =C*H*), 6.79–6.73 (m, 1H, =C*H*), 6.61 (d, 1H, $J = 15.55$ Hz, =C*H*). ^{13}C (125 MHz, $CDCl_3$): δ 138.4, 136.7, 133.9, 131.3, 130.2, 129.5, 126.5, 125.4, 122.9, 92.7. IR (film): 3050, 1789, 1730, 1591, 1554, 1476, 1071, 961, 890, 811, 776 cm^{-1}. HRMS (EI) calcd for $C_{10}H_7Br_3$ [M$^+$] 363.8098; found 363.8090.

2a.[18] Pale yellow solid (0.069 g, 84%); m.p. 96–98 °C, $R_f = 0.41$ (hexane). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.43 (d, 2H, $J = 7.35$ Hz, Ar-H), 7.39–7.33 (m, 4H, Ar-H), 7.30–7.27 (m, 1H, Ar-H), 7.15 (d, 2H, $J = 8.25$ Hz, Ar-H), 7.03 (d, 1H, $J = 16.15$ Hz), 6.39 (d, 1H, $J =$ 16.2 Hz), 2.37 (s, 3H, –C*H*$_3$). ^{13}C (125 MHz, $CDCl_3$): δ 140.8, 138.3, 136.4, 131.4, 129.1, 128.7, 128.5, 126.2, 120.3, 108.3, 91.9, 88.2, 21.5. IR (film): 3057, 3027, 2191, 1725, 1488, 1303, 1121, 1106, 955, 817, 748, 690 cm^{-1}. HRMS (EI) calcd for $C_{17}H_{14}$ [M$^+$] 218.1096; found 218.1098.

2b.[18] Pale yellow solid (0.056 g, 68%); m.p. 86–88 °C, $R_f = 0.47$ (hexane). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.47–7.42 (m, 4H, Ar-H), 7.37–7.34 (m, 2H, Ar-H), 7.32–7.28 (m, 1H, Ar-H), 7.06–7.01 (m, 3H), 6.37 (d, 1H, $J = 16.3$ Hz). ^{13}C (125 MHz, $CDCl_3$): δ 162.4 (d, J = 247.98 Hz), 141.3, 136.2, 133.3 (d, $J = 8.33$ Hz), 128.7, 128.6, 126.3, 119.5, 115.6 (d, $J = 21.46$ Hz), 107.9, 90.6, 88.5. IR (film): 3027, 1594, 1505, 1222, 959, 837, 750, 691 cm^{-1}. HRMS (EI) calcd for $C_{16}H_{11}F$ [M$^+$] 222.0845; found 222.0844.

2c. Yellow solid (0.067 g, 75%); m.p. 68–70 °C, $R_f = 0.56$ (hexane). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.46–7.42 (m, 3H, Ar-H), 7.37–7.26 (m, 6H, Ar-H), 7.06 (d, 1H, $J = 16.3$ Hz), 6.36 (d, 1H, $J =$ 16 Hz). ^{13}C (125 MHz, $CDCl_3$): δ 142.0, 136.1, 134.1, 131.3, 129.6, 129.5, 128.8, 128.7, 128.4, 126.4, 125.1, 107.6, 90.2, 90.0. IR (film): 3022, 2374, 2195, 1655, 1559, 1460, 1404, 1290, 1079, 951, 892, 788, 751 cm^{-1}. HRMS (EI) calcd for $C_{16}H_{11}Cl$ [M$^+$] 238.0549; found 238.0549.

2d. Yellow liquid (0.064 g, 73%); $R_f = 0.26$ (hexane). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.42 (d, 2H, $J = 7.35$ Hz, Ar-H), 7.34 (t, 2H, $J = 7.65$ Hz, Ar-H), 7.30–7.22 (m, 2H, Ar-H), 7.08–7.01 (m, 3H, Ar-H), 6.89–6.86 (m, 1H, Ar-H), 6.38 (d, 1H, $J = 16.15$ Hz), 3.81 (s, 3H, –OC*H*$_3$). ^{13}C (125 MHz, $CDCl_3$): δ 159.3, 141.4, 136.3, 129.4, 128.7, 128.6, 126.3, 124.4, 124.1, 116.2, 114.9, 108.0, 91.6, 88.7, 55.3. IR (film): 3060, 2937, 2193, 1595, 1488, 1319, 1289, 1215, 1081, 953, 779, 749, 688 cm^{-1}. HRMS (EI) calcd for $C_{17}H_{14}O$ [M$^+$] 234.1045; found 234.1048.

3a.[19] Yellow solid (0.060 g, 74%); m.p. 72–74 °C, $R_f = 0.48$ (hexane). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.50–7.48 (m, 2H, Ar-H), 7.36–7.33 (m, 5H, Ar-H), 7.17 (d, 2H, $J = 7.95$ Hz, Ar-H), 7.04 (d, 1H, $J = 16.2$ Hz), 6.35 (d, 1H, $J = 16.2$ Hz), 2.37 (s, 3H, –C*H*$_3$). ^{13}C (125 MHz, $CDCl_3$): δ 141.2, 138.7, 133.5, 131.4, 129.4, 128.3, 128.0, 126.2, 123.5, 106.9, 91.3, 89.1, 21.3. IR (film): 3030, 2937, 1488, 1441, 959, 804, 754, 690 cm^{-1}. HRMS (EI) calcd for $C_{17}H_{14}$ [M$^+$] 218.1096; found 218.1092.

3b.[18] Pale yellow solid (0.068 g, 78%); m.p. 146–148 °C, $R_f =$ 0.41 (hexane). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.38 (d, 2H, $J = 7.95$ Hz, Ar-H), 7.33 (d, 2H, $J = 7.95$ Hz, Ar-H), 7.17–7.14 (m, 4H, Ar-H), 7.02 (d, 1H, $J = 16.2$ Hz), 6.35 (d, 1H, $J = 16.2$ Hz), 2.37 (s, 6H, –C*H*$_3$). ^{13}C (125 MHz, $CDCl_3$): δ 140.8, 138.6, 138.2, 133.6, 131.3, 129.4, 129.1, 126.2, 120.4, 107.1, 91.6, 88.4, 21.5, 21.3. IR (film): 3027, 2939, 1910, 1505, 1109, 957, 818, 802 cm^{-1}. HRMS (EI) calcd for $C_{18}H_{16}$ [M$^+$] 232.1252; found 232.1254.

3c. Yellow solid (0.074 g, 78%); m.p. 154–156 °C, $R_f = 0.50$ (hexane). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.39 (d, 2H, $J = 8.55$ Hz, Ar-H), 7.33–7.29 (m, 4H, Ar-H), 7.16 (d, 2H, $J = 8.25$ Hz, Ar-H), 7.02 (d, 1H, $J = 16.15$ Hz), 6.32 (d, 1H, $J = 16.2$ Hz), 2.36 (s, 3H, –C*H*$_3$). ^{13}C (125 MHz, $CDCl_3$): δ 141.7, 138.9, 134.0, 133.4, 132.6, 129.5, 128.6, 126.3, 122.0, 106.6, 90.2, 90.1, 21.3. IR (film): 2939, 1910, 1487, 1397, 962, 828, 804 cm^{-1}. HRMS (EI) calcd for $C_{17}H_{13}Cl$ [M$^+$] 252.0706; found 252.0701.

3d. Pale yellow solid (0.062 g, 63%); m.p. 124–126 °C, $R_f =$ 0.34 (hexane). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.40 (d, 2H, $J = 8.85$ Hz, Ar-H), 7.32 (d, 2H, $J = 7.9$ Hz, Ar-H), 7.15 (d, 2H, $J = 7.95$ Hz, Ar-H), 6.98 (d, 1H, $J = 16.2$ Hz), 6.85 (d, 2H, $J = 8.85$ Hz, Ar-H), 6.33 (d, 1H, $J = 16.15$ Hz), 4.04 (q, 2H, $J = 6.92$ Hz, –OC*H*$_2$CH$_3$), 2.36 (s, 3H, –C*H*$_3$), 1.42 (t, 3H, $J = 7.02$ Hz, –OCH$_2$C*H*$_3$). ^{13}C (125 MHz, $CDCl_3$): δ 158.9, 140.4, 138.5, 133.7, 132.9, 129.4, 126.1, 115.4, 114.5, 107.3, 91.5, 87.7, 63.5, 21.3, 14.7. IR (film): 3026, 2921, 2188, 1598, 1507, 1306, 1250, 1174, 1114, 1045, 958, 839 cm^{-1}. HRMS (EI) calcd for $C_{19}H_{18}O$ [M$^+$] 262.1358; found 262.1351.

4a. Colourless solid (0.076 g, 80%); m.p. 106–108 °C, $R_f =$ 0.44 (hexane). ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.19 (d, 1H, $J = 8.55$ Hz, Ar-H), 7.89–7.83 (m, 3H, Ar-H), 7.70 (d, 1H, $J = 7.3$ Hz, Ar-H), 7.59–7.47 (m, 5H, Ar-H), 7.40–7.34 (m, 3H, Ar-H), 6.49 (d, 1H, $J =$ 15.9 Hz). ^{13}C (125 MHz, $CDCl_3$): δ 138.3, 133.7, 133.6, 131.5, 130.8, 129.0, 128.6, 128.4, 128.2, 126.4, 126.0, 125.5, 123.5, 123.4, 123.3, 110.7, 91.5, 89.1. IR (film): 3056, 2194, 1489, 1394, 1069, 861, 755 cm^{-1}. HRMS (EI) calcd for $C_{20}H_{14}$ [M$^+$] 254.1096; found 254.1095.

4b. Yellow solid (0.084 g, 84%); m.p. 84–86 °C, $R_f = 0.44$ (hexane). ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.19 (d, 1H, $J = 8.25$ Hz,

Ar-H), 7.88–7.82 (m, 3H, Ar-H), 7.69 (d, 1H, J = 7.05 Hz, Ar-H), 7.56–7.43 (m, 5H, Ar-H), 7.17 (d, 2H, J = 8.55 Hz, Ar-H), 6.47 (d, 1H, J = 15.9 Hz), 2.38 (s, 3H, –CH_3). ^{13}C (125 MHz, $CDCl_3$): δ 138.4, 137.9, 133.8, 133.6, 131.4, 130.8, 129.1, 128.9, 128.5, 126.3, 125.9, 125.5, 123.5, 123.3, 120.2, 110.9, 91.8, 88.5, 21.5. IR (film): 3027, 2916, 1506, 1018, 970, 772, 733 cm^{-1}. HRMS (EI) calcd for $C_{21}H_{16}$ [M$^+$] 268.1252; found 268.1251.

4c. Yellow solid (0.065 g, 64%); m.p. 88–90 °C, R_f = 0.52 (hexane). ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.17 (d, 1H, J = 8.6 Hz, Ar-H), 7.87–7.82 (m, 3H, Ar-H), 7.68 (d, 1H, J = 7.2 Hz, Ar-H), 7.57–7.45 (m, 5H, Ar-H), 7.05 (t, 2H, J = 8.7 Hz, Ar-H), 6.44 (d, 1H, J = 15.9 Hz). ^{13}C (125 MHz, $CDCl_3$): δ 162.5 (d, J = 248 Hz), 138.4, 133.6, 133.4 (d, J = 8.35 Hz), 130.8, 129.0, 128.6, 126.4, 126.0, 125.5, 123.5, 123.4, 119.4, 115.7 (d, J = 21.46 Hz), 110.5, 90.4, 88.8. IR (film): 3054, 1585, 1504, 1220, 1157, 944, 833, 794 cm^{-1}. HRMS (EI) calcd for $C_{20}H_{13}F$ [M$^+$] 272.1001; found 272.1008.

4d. Pale brown solid (0.066 g, 61%); m.p. 100–102 °C, R_f = 0.48 (hexane). ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.17 (d, 1H, J = 8.25 Hz, Ar-H), 7.88–7.83 (m, 3H, Ar-H), 7.69 (d, 1H, J = 7.05 Hz, Ar-H), 7.58–7.44 (m, 5H, Ar-H), 7.34 (d, 2H, J = 8.55 Hz, Ar-H), 6.45 (d, 1H, J = 15.9 Hz). ^{13}C (125 MHz, $CDCl_3$): δ 138.7, 134.2, 133.6, 133.5, 132.7, 130.8, 129.1, 128.7, 128.6, 126.4, 126.0, 125.5, 123.4, 121.8, 110.4, 90.3, 90.1. IR (film): 3042, 2923, 2193, 1508, 1394, 1089, 1011, 971, 827 cm^{-1}. HRMS (EI) calcd for $C_{20}H_{13}Cl$ [M$^+$] 288.0706; found 288.0705.

4e. Pale brown solid (0.071 g, 66%); m.p. 86–88 °C, R_f = 0.21 (hexane). ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.18 (d, 1H, J = 8.55 Hz, Ar-H), 7.86 (d, 1H, J = 7.35 Hz, Ar-H), 7.83–7.79 (m, 2H, Ar-H), 7.68 (d, 1H, J = 7 Hz, Ar-H), 7.55–7.46 (m, 5H, Ar-H), 6.89 (d, 2H, J = 8.85 Hz, Ar-H), 6.46 (d, 1H, J = 15.9 Hz), 3.84 (s, 3H, –OCH_3). ^{13}C (125 MHz, $CDCl_3$): δ 159.6, 137.4, 133.9, 133.6, 133.0, 130.8, 128.8, 128.5, 126.3, 125.9, 125.5, 123.6, 123.3, 115.4, 114.0, 111.0, 91.6, 87.9, 55.3. IR (film): 3042, 2835, 2192, 1597, 1508, 1248, 1172, 1032, 946, 831 cm^{-1}. HRMS (EI) calcd for $C_{21}H_{16}O$ [M$^+$] 284.1201; found 284.1205.

5a.[19] Yellow solid (0.063 g, 71%); m.p. 86–88 °C, R_f = 0.29 (hexane). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.47 (dd, 2H, J = 7.8 Hz, J = 1.65 Hz, Ar-H), 7.37 (d, 2H, J = 8.85 Hz, Ar-H), 7.35–7.30 (m, 3H, Ar-H), 7.00 (d, 1H, J = 16.15 Hz), 6.88 (d, 2H, J = 8.55 Hz, Ar-H), 6.24 (d, 1H, J = 16.2 Hz), 3.82 (s, 3H, –OCH_3). ^{13}C (125 MHz, $CDCl_3$): δ 160.0, 140.8, 131.4, 129.2, 128.3, 127.9, 127.6, 123.6, 114.2, 105.6, 90.9, 89.2, 55.3. IR (film): 3055, 2908, 2191, 1573, 1510, 1441, 1261, 1177, 1032, 819, 754 cm^{-1}. HRMS (EI) calcd for $C_{17}H_{14}O$ [M$^+$] 234.1045; found 234.1044.

5b. Pale yellow solid (0.060 g, 63%); m.p. 112–114 °C, R_f = 0.25 (hexane). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.46–7.42 (m, 2H, Ar-H), 7.36 (d, 2H, J = 8.85 Hz, Ar-H), 7.02 (d, 2H, J = 8.55 Hz, Ar-H), 6.98 (d, 1H, J = 15.6 Hz), 6.88 (d, 2H, J = 8.85 Hz, Ar-H), 6.22 (d, 1H, J = 16.2 Hz), 3.83 (s, 3H, –OCH_3). ^{13}C (125 MHz, $CDCl_3$): δ 162.3 (d, J = 247.16 Hz), 160.1, 140.9, 133.2 (d, J = 7.2 Hz), 129.1, 127.6, 119.6, 115.6 (d, J = 21.58 Hz), 114.2, 105.4, 89.8, 88.9, 55.3. IR (film): 2967, 2358, 1601, 1504, 1381, 1250, 1089, 1031, 956, 836, 809 cm^{-1}. HRMS (EI) calcd for $C_{17}H_{13}FO$ [M$^+$] 252.0950; found 252.0952.

5c.[20] Pale brown solid (0.063 g, 62%); m.p. 126–128 °C, R_f = 0.30 (hexane). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.37 (t, 4H, J = 8.55 Hz, Ar-H), 7.29 (d, 2H, J = 8.55 Hz, Ar-H), 6.99 (d, 1H, J = 16.15 Hz), 6.88 (d, 2H, J = 8.55 Hz, Ar-H), 6.22 (d, 1H, J = 16.15 Hz), 3.82 (s, 3H, –OCH_3). ^{13}C (125 MHz, $CDCl_3$): δ 160.2, 141.3, 133.9, 132.6, 129.0, 128.6, 127.7, 122.1, 114.2, 105.3, 90.2, 89.8, 55.3. IR (film): 3054, 2968, 2842, 2194, 1603, 1489, 1451, 1396, 1266, 1177, 1093, 1032, 938, 829 cm^{-1}. HRMS (EI) calcd for $C_{17}H_{13}ClO$ [M$^+$] 268.0655; found 268.0652.

5d. Pale brown solid (0.076 g, 73%); m.p. 146–148 °C, R_f = 0.47 (EtOAc–hexane 1 : 99). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.39 (d, 2H, J = 8.85 Hz, Ar-H), 7.36 (d, 2H, J = 8.95 Hz, Ar-H), 6.95 (d, 1H, J = 16.2 Hz), 6.87 (d, 2H, J = 8.55 Hz, Ar-H), 6.84 (d, 2H, J = 8.55 Hz, Ar-H), 6.24 (d, 1H, J = 16.2 Hz), 4.04 (q, 2H, J = 7.02 Hz, –OCH_2CH$_3$), 3.82 (s, 3H, –OCH_3), 1.42 (t, 3H, J = 7.02 Hz, –OCH$_2$CH_3). ^{13}C (125 MHz, $CDCl_3$): δ 159.9, 158.8, 139.9, 132.8, 129.3, 127.5, 115.5, 114.4, 114.1, 105.9, 91.1, 87.8, 63.4, 55.3, 14.7. IR (film): 2982, 2933, 2187, 1602, 1505, 1255, 1174, 1030, 960, 840 cm^{-1}. HRMS (EI) calcd for $C_{19}H_{18}O_2$ [M$^+$] 278.1307; found 278.1309.

5e. Yellow solid (0.068 g, 69%); m.p. 88–90 °C, R_f = 0.10 (hexane). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.36 (d, 2H, J = 8.85 Hz, Ar-H), 7.25–7.21 (m, 1H, Ar-H), 7.06 (d, 1H, J = 7.6 Hz, Ar-H), 7.02–6.98 (m, 2H, Ar-H), 6.88–6.86 (m, 3H, Ar-H), 6.23 (d, 1H, J = 16.2 Hz), 3.82 (s, 3H, –OCH_3), 3.81 (s, 3H, –OCH_3). ^{13}C (125 MHz, $CDCl_3$): δ 160.1, 159.3, 141.0, 129.3, 129.1, 127.6, 124.5, 124.0, 116.1, 114.7, 114.1, 105.5, 90.9, 89.1, 55.3, 55.2. IR (film): 3031, 2958, 2192, 1600, 1510, 1249, 1175, 1032, 955, 814 cm^{-1}. HRMS (EI) calcd for $C_{18}H_{16}O_2$ [M$^+$] 264.1150; found 264.1152.

6a. Brown solid (0.089 g, 81%); m.p. 92–94 °C, R_f = 0.18 (EtOAc–hexane 1 : 99). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.47–7.46 (m, 2H, Ar-H), 7.34–7.31 (m, 3H, Ar-H), 6.96 (d, 1H, J = 16.15 Hz), 6.65 (s, 2H, Ar-H), 6.30 (d, 1H, J = 16.2 Hz), 3.89 (s, 6H, –OCH_3), 3.86 (s, 3H, –OCH_3). ^{13}C (125 MHz, $CDCl_3$): δ 153.4, 141.1, 138.7, 132.0, 131.4, 128.3, 128.2, 123.4, 107.6, 103.4, 91.8, 88.7, 60.9, 56.1. IR (film): 2989, 2935, 1579, 1505, 1418, 1343, 1240, 1127, 1005 cm^{-1}. HRMS (EI) calcd for $C_{19}H_{18}O_3$ [M$^+$] 294.1256; found 294.1255.

6b. Brown solid (0.098 g, 85%); m.p. 84–86 °C, R_f = 0.18 (EtOAc–hexane 1 : 99). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.36 (d, 2H, J = 8.25 Hz, Ar-H), 7.14 (d, 2H, J = 7.6 Hz, Ar-H), 6.94 (d, 1H, J = 16.15 Hz), 6.64 (s, 2H, Ar-H), 6.29 (d, 1H, J = 16.2 Hz), 3.88 (s, 6H, –OCH_3), 3.86 (s, 3H, –OCH_3), 2.36 (s, 3H, –CH_3). ^{13}C (125 MHz, $CDCl_3$): δ 153.4, 140.7, 138.7, 138.3, 132.1, 131.3, 129.1, 120.3, 107.7, 103.3, 92.0, 88.1, 60.9, 56.1, 21.5. IR (film): 2998, 2936, 1578, 1505, 1462, 1419, 1342, 1239, 1127, 949 cm^{-1}. HRMS (ESI) calcd for $C_{20}H_{21}O_3$ [M + H]$^+$ 309.1491; found 309.1492.

6c. Yellow solid (0.088 g, 75%); m.p. 76–78 °C, R_f = 0.29 (EtOAc–hexane 1 : 9). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.45–7.42 (m, 2H, Ar-H), 7.02 (t, 2H, J = 8.7 Hz, Ar-H), 6.95 (d, 1H, J = 16.2 Hz), 6.64 (s, 2H, Ar-H), 6.27 (d, 1H, J = 16.2 Hz), 3.88 (s, 6H, –OCH_3), 3.86 (s, 3H, –OCH_3). ^{13}C (125 MHz, $CDCl_3$): δ 162.4 (d, J = 248.36 Hz), 153.4, 141.1, 138.8, 133.3 (d, J = 8.4 Hz), 131.9, 119.5, 115.6 (d, J = 21.58 Hz), 107.3, 103.4, 90.6, 88.4, 60.9, 56.1. IR (film): 2999, 2937, 2190, 1578, 1504, 1419, 1342, 1233, 1127, 950, 812 cm^{-1}. HRMS (ESI) calcd for $C_{19}H_{18}FO_3$ [M + H]$^+$ 313.1240; found 313.1245.

6d. Yellow solid (0.088 g, 71%); m.p. 66–68 °C, R_f = 0.19 (EtOAc–hexane 1 : 99). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.38 (d, 2H,

J = 8.55 Hz, Ar-H), 7.30 (d, 2H, J = 8.85 Hz, Ar-H), 6.96 (d, 1H, J = 15.9 Hz), 6.64 (s, 2H, Ar-H), 6.27 (d, 1H, J = 16.2 Hz), 3.88 (s, 6H, –OCH_3), 3.86 (s, 3H, –OCH_3). ^{13}C (125 MHz, $CDCl_3$): δ 153.4, 141.5, 138.9, 134.1, 132.6, 131.8, 128.7, 121.9, 107.2, 103.5, 90.6, 89.7, 60.9, 56.1. IR (film): 2936, 2837, 2193, 1577, 1505, 1488, 1342, 1128, 949, 790 cm^{-1}. HRMS (ESI) calcd for $C_{19}H_{18}ClO_3$ [M + H]$^+$ 329.0944; found 329.0948.

7a. Pale yellow solid (0.051 g, 56%); m.p. 166–168 °C, R_f = 0.54 (EtOAc–hexane 1 : 99). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.62 (d, 2H, J = 8.3 Hz, Ar-H), 7.48 (d, 2H, J = 8.05 Hz, Ar-H), 7.37 (d, 2H, J = 8 Hz, Ar-H), 7.15 (d, 2H, J = 7.7 Hz, Ar-H), 6.99 (d, 1H, J = 16 Hz), 6.49 (d, 1H, J = 16.5 Hz), 2.37 (s, 3H, –CH_3). ^{13}C (125 MHz, $CDCl_3$): δ 140.7, 139.0, 138.5, 132.5, 131.5, 129.2, 126.5, 119.7, 118.8, 112.3, 111.4, 94.5, 87.5, 21.5. IR (film): 3054, 2963, 2926, 2225, 2193, 1723, 1599, 1412, 1265, 970, 950, 818, 705 cm^{-1}. HRMS (EI) calcd for $C_{18}H_{13}N$ [M$^+$] 243.1048; found 243.1047.

8a.[19] Pale yellow solid (0.068 g, 77%); m.p. 108–110 °C, R_f = 0.61 (hexane). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.49–7.47 (m, 2H, Ar-H), 7.36–7.30 (m, 7H, Ar-H), 6.99 (d, 1H, J = 16.2 Hz), 6.36 (d, 1H, J = 16.15 Hz). ^{13}C (125 MHz, $CDCl_3$): δ 139.8, 134.8, 134.3, 131.5, 128.9, 128.4, 128.3, 127.4, 123.2, 108.8, 92.3, 88.5. IR (film): 3049, 2922, 1484, 1069, 960, 809, 757, 688 cm^{-1}. HRMS (EI) calcd for $C_{16}H_{11}Cl$ [M$^+$] 238.0549; found 238.0541.

8b. Colourless solid (0.067 g, 71%); m.p. 76–78 °C, R_f = 0.53 (hexane). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.36–7.27 (m, 6H, Ar-H), 7.22 (t, 1H, J = 7.62 Hz, Ar-H), 7.14 (d, 1H, J = 7.3 Hz, Ar-H), 6.97 (d, 1H, J = 16.2 Hz), 6.35 (d, 1H, J = 16.2 Hz), 2.35 (s, 3H, –CH_3). ^{13}C (125 MHz, $CDCl_3$): δ 139.7, 138.0, 134.8, 134.2, 132.1, 129.2, 128.9, 128.6, 128.2, 127.4, 123.0, 108.9, 92.5, 88.2, 21.2. IR (film): 3033, 2919, 1490, 1404, 1092, 956, 853, 807, 786 cm^{-1}. HRMS (EI) calcd for $C_{17}H_{13}Cl$ [M$^+$] 252.0706; found 252.0709.

8c. Colourless solid (0.066 g, 70%); m.p. 164–166 °C, R_f = 0.41 (hexane). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.38–7.29 (m, 6H, Ar-H), 7.15 (d, 2H, J = 8 Hz, Ar-H), 6.96 (d, 1H, J = 16.3 Hz), 6.36 (d, 1H, J = 16.3 Hz), 2.36 (s, 3H, –CH_3). ^{13}C (125 MHz, $CDCl_3$): δ 139.4, 138.5, 134.9, 134.1, 131.4, 129.1, 128.9, 127.4, 120.1, 108.9, 92.5, 87.9, 21.5. IR (film): 3028, 2915, 2191, 1488, 1401, 1265, 1091, 959, 814, 739 cm^{-1}. HRMS (EI) calcd for $C_{17}H_{13}Cl$ [M$^+$] 252.0706; found 252.0701.

8d. Pale yellow solid (0.064 g, 66%); m.p. 128–130 °C, R_f = 0.54 (hexane). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.46–7.43 (m, 2H, Ar-H), 7.33 (q, 4H, J = 8.66 Hz, Ar-H), 7.03 (t, 2H, J = 8.55 Hz, Ar-H), 6.97 (d, 1H, J = 16.2 Hz), 6.33 (d, 1H, J = 16.15 Hz). ^{13}C (125 MHz, $CDCl_3$): δ 162.5 (d, J = 248.36 Hz), 139.9, 134.7, 134.4, 133.4 (d, J = 8.4 Hz), 128.9, 127.4, 119.3, 115.7 (d, J = 22.8 Hz), 108.6, 91.2, 88.2. IR (film): 3056, 2923, 1899, 1581, 1490, 1405, 1093, 836, 809 cm^{-1}. HRMS (EI) calcd for $C_{16}H_{10}ClF$ [M$^+$] 256.0455; found 256.0456.

8e.[18] Yellow solid (0.084 g, 82%); m.p. 158–160 °C, R_f = 0.56 (hexane). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.40–7.30 (m, 8H, Ar-H), 6.98 (d, 1H, J = 16.2 Hz), 6.33 (d, 1H, J = 16.15 Hz). ^{13}C (125 MHz, $CDCl_3$): δ 140.2, 134.6, 134.4, 134.3, 132.7, 128.9, 128.7, 127.5, 121.7, 108.4, 91.1, 89.5. IR (film): 3027, 1587, 1488, 1095, 1013, 963, 829, 811 cm^{-1}. HRMS (EI) calcd for $C_{16}H_{10}Cl_2$ [M$^+$] 272.0160; found 272.0164.

8f. Yellow solid (0.065 g, 65%); m.p. 68–70 °C, R_f = 0.30 (hexane). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.34 (d, 2H, J = 8.3 Hz, Ar-H), 7.30 (d, 2H, J = 8.6 Hz, Ar-H), 7.25–7.22 (m, 1H, Ar-H), 7.07 (d, 1H, J = 7.45 Hz, Ar-H), 6.99–6.97 (m, 2H, Ar-H), 6.88 (dd, 1H, J = 8.3 Hz, J = 2 Hz, Ar-H), 6.35 (d, 1H, J = 16.35 Hz), 3.81 (s, 3H, –OCH_3). ^{13}C (125 MHz, $CDCl_3$): δ 159.3, 139.9, 134.8, 134.3, 129.4, 128.9, 127.4, 124.2, 124.1, 116.3, 114.9, 108.7, 92.2, 88.4, 55.2. IR (film): 3032, 2938, 2194, 1724, 1592, 1489, 1218, 1088, 959, 806 cm^{-1}. HRMS (EI) calcd for $C_{17}H_{13}ClO$ [M$^+$] 268.0655; found 268.0656.

8g.[19] Yellow solid (0.072 g, 71%); m.p. 132–134 °C, R_f = 0.24 (hexane). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.41 (dd, 2H, J = 8.85 Hz, J = 1.5 Hz, Ar-H), 7.34 (d, 2H, J = 8.55 Hz, Ar-H), 7.30 (d, 2H, J = 8.25 Hz, Ar-H), 6.94 (d, 1H, J = 16.15 Hz), 6.86 (dd, 2H, J = 8.85 Hz, J = 1.2 Hz, Ar-H), 6.35 (d, 1H, J = 16.2 Hz), 3.82 (s, 3H, –OCH_3). ^{13}C (125 MHz, $CDCl_3$): δ 159.7, 139.0, 134.9, 134.0, 133.0, 128.9, 127.3, 115.3, 114.0, 109.0, 92.4, 87.3, 55.3. IR (film): 2964, 2841, 2190, 1597, 1508, 1249, 1031, 957, 837, 810 cm^{-1}. HRMS (EI) calcd for $C_{17}H_{13}ClO$ [M$^+$] 268.0655; found 268.0656.

8h. Pale yellow solid (0.069 g, 65%); m.p. 150–152 °C, R_f = 0.33 (hexane). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.39 (d, 2H, J = 8.9 Hz, Ar-H), 7.33 (d, 2H, J = 8.9 Hz, Ar-H), 7.30 (d, 2H, J = 8.55 Hz, Ar-H), 6.93 (d, 1H, J = 16.2 Hz), 6.85 (d, 2H, J = 8.85 Hz, Ar-H), 6.35 (d, 1H, J = 16.2 Hz), 4.04 (q, 2H, J = 7.03 Hz, –OCH_2CH$_3$), 1.42 (t, 3H, J = 7.02 Hz, –OCH$_2$CH_3). ^{13}C (125 MHz, $CDCl_3$): δ 159.0, 138.9, 134.9, 134.0, 132.9, 128.9, 127.3, 115.1, 114.5, 109.1, 92.5, 87.3, 63.5, 14.7. IR (film): 3030, 2934, 2189, 1598, 1509, 1288, 1251, 1174, 1088, 958, 826, 809 cm^{-1}. HRMS (EI) calcd for $C_{18}H_{15}ClO$ [M$^+$] 282.0811; found 282.0816.

9a. Pale yellow solid (0.068 g, 67%); m.p. 56–58 °C, R_f = 0.30 (hexane). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.42–7.38 (m, 3H, Ar-H), 7.27–7.24 (m, 3H, Ar-H), 6.91 (d, 1H, J = 16.15 Hz), 6.86 (d, 2H, J = 8.85 Hz, Ar-H), 6.37 (d, 1H, J = 16.15 Hz), 3.82 (s, 3H, –OCH_3). ^{13}C (125 MHz, $CDCl_3$): δ 159.7, 138.8, 138.3, 134.7, 133.0, 129.9, 128.3, 126.0, 124.4, 115.3, 114.0, 110.0, 92.8, 87.2, 55.3. IR (film): 2838, 2191, 1597, 1507, 1246, 1172, 954, 836, 781 cm^{-1}. HRMS (EI) calcd for $C_{17}H_{13}ClO$ [M$^+$] 268.0655; found 268.0658.

10a.[21] Deep brown liquid (0.054 g, 74%); R_f = 0.43 (hexane). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.47–7.40 (m, 3H, Ar-H), 7.35–7.31 (m, 3H, Ar-H), 6.79 (d, 1H, J = 16.2 Hz), 6.43–6.42 (m, 1H, Ar-H), 6.36 (d, 1H, J = 3.35 Hz, Ar-H), 6.29 (d, 1H, J = 15.9 Hz). ^{13}C (125 MHz, $CDCl_3$): δ 152.2, 143.0, 131.4, 128.3, 128.2, 128.1, 123.4, 111.8, 110.1, 106.1, 92.5, 88.8. IR (film): 2926, 1726, 1592, 1491, 1260, 1015, 944, 757, 690 cm^{-1}. HRMS (EI) calcd for $C_{14}H_{10}O$ [M$^+$] 194.0732; found 194.0730.

10b. Deep brown liquid (0.056 g, 72%); R_f = 0.39 (hexane). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.39 (br.s, 1H, Ar-H), 7.36 (d, 2H, J = 8.25 Hz, Ar-H), 7.13 (d, 2H, J = 8.25 Hz, Ar-H), 6.77 (d, 1H, J = 15.9 Hz), 6.42–6.41 (m, 1H, Ar-H), 6.35 (d, 1H, J = 3.05 Hz, Ar-H), 6.28 (d, 1H, J = 15.9 Hz), 2.36 (s, 3H, –CH_3). ^{13}C (125 MHz, $CDCl_3$): δ 152.3, 142.9, 138.3, 131.3, 129.1, 127.9, 120.3, 111.8, 109.8, 106.3, 92.8, 88.2, 21.5. IR (film): 2919, 2189, 1777, 1603, 1508, 1480, 1261, 1014, 943, 818, 738, 591 cm^{-1}. HRMS (EI) calcd for $C_{15}H_{12}O$ [M$^+$] 208.0888; found 208.0880.

10c. Deep brown liquid (0.053 g, 68%); $R_f = 0.42$ (hexane). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.44–7.40 (m, 3H, Ar-H), 7.02 (t, 2H, $J = 8.85$ Hz, Ar-H), 6.77 (d, 1H, $J = 15.9$ Hz), 6.43–6.41 (m, 1H, Ar-H), 6.36 (d, 1H, $J = 3.35$ Hz, Ar-H), 6.25 (d, 1H, $J = 16.2$ Hz). ^{13}C (125 MHz, $CDCl_3$): δ 162.4 (d, $J = 248.36$ Hz), 152.2, 143.1, 133.3 (d, $J = 8.4$ Hz), 128.3, 119.5, 115.6 (d, $J = 21.6$ Hz), 111.9, 110.1, 105.9, 91.4, 88.5. IR (film): 3043, 2926, 1595, 1505, 1219, 1156, 1015, 948, 837, 742 cm^{-1}. HRMS (EI) calcd for $C_{14}H_9FO$ [M$^+$] 212.0637; found 212.0631.

10d. Deep brown liquid (0.056 g, 62%); $R_f = 0.21$ (hexane). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.39–7.37 (m, 3H, Ar-H), 6.84 (dd, 2H, $J = 8.85$ Hz, $J = 1.82$ Hz, Ar-H), 6.74 (d, 1H, $J = 15.85$ Hz), 6.42–6.40 (m, 1H, Ar-H), 6.34–6.33 (m, 1H, Ar-H), 6.27 (d, 1H, $J = 15.9$ Hz), 4.04 (q, 2H, $J = 6.93$ Hz, –OCH_2CH$_3$), 1.42 (t, 3H, $J = 6.87$ Hz, –OCH$_2$CH_3). ^{13}C (125 MHz, $CDCl_3$): δ 158.9, 152.4, 142.8, 132.9, 127.4, 115.3, 114.5, 111.8, 109.6, 106.5, 92.7, 87.5, 63.5, 14.7. IR (film): 2974, 2188, 1600, 1508, 1246, 1176, 947, 738, 591 cm^{-1}. HRMS (EI) calcd for $C_{16}H_{14}O_2$ [M$^+$] 238.0994; found 238.0993.

11a.[21] Brown solid (0.056 g, 71%); m.p. 96–98 °C, $R_f = 0.51$ (hexane). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.40–7.38 (m, 2H, Ar-H), 7.26–7.24 (m, 3H, Ar-H), 7.19–7.14 (m, 1H, Ar-H), 7.07 (d, 1H, $J =$ 15.9 Hz), 6.98–6.92 (m, 2H, Ar-H), 6.13 (d, 1H, $J = 15.9$ Hz). ^{13}C (125 MHz, $CDCl_3$): δ 141.4, 134.0, 131.4, 128.3, 128.1, 127.7, 127.1, 125.5, 123.3, 107.3, 92.1, 88.6. IR (film): 3031, 1587, 1486, 937, 853, 757, 688 cm^{-1}. HRMS (EI) calcd for $C_{14}H_{10}S$ [M$^+$] 210.0503; found 210.0509.

11b. Pale brown solid (0.058 g, 69%); m.p. 100–102 °C, $R_f =$ 0.42 (hexane). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.35 (d, 2H, $J = 7.95$ Hz, Ar-H), 7.21 (d, 1H, $J = 5.2$ Hz, Ar-H), 7.14–7.01 (m, 3H, Ar-H), 7.04 (d, 1H, $J = 3.05$ Hz, Ar-H), 7.01–6.99 (m, 1H, Ar-H), 6.19 (d, 1H, $J = 15.9$ Hz), 2.36 (s, 3H, –CH_3). ^{13}C (125 MHz, $CDCl_3$): δ 141.6, 138.3, 133.6, 131.3, 129.1, 127.7, 126.9, 125.3, 120.2, 107.5, 92.3, 88.0, 21.5. IR (film): 3029, 2917, 2189, 1504, 1427, 942, 816, 700 cm^{-1}. HRMS (EI) calcd for $C_{15}H_{12}S$ [M$^+$] 224.0660; found 224.0666.

11c. Pale brown solid (0.070 g, 82%); m.p. 82–84 °C, $R_f = 0.47$ (hexane). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.44–7.42 (m, 2H, Ar-H), 7.22 (d, 1H, $J = 5.2$ Hz, Ar-H), 7.13 (d, 1H, $J = 15.9$ Hz), 7.06–6.99 (m, 4H, Ar-H), 6.17 (d, 1H, $J = 15.9$ Hz). ^{13}C (125 MHz, $CDCl_3$): δ 162.4 (d, $J = 248.36$ Hz), 141.4, 134.1, 133.3 (d, $J = 8.4$ Hz), 127.7, 127.1, 125.5, 119.4, 115.6 (d, $J = 22.78$ Hz), 107.0, 90.9, 88.3. IR (film): 2923, 1898, 1604, 1501, 1218, 1155, 948, 837, 707 cm^{-1}. HRMS (EI) calcd for $C_{14}H_9FS$ [M$^+$] 228.0409; found 228.0404.

11d. Brown liquid (0.064 g, 71%); $R_f = 0.24$ (hexane). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.25–7.21 (m, 2H, Ar-H), 7.14 (d, 1H, $J =$ 16.2 Hz), 7.06–7.04 (m, 2H, Ar-H), 7.00–6.98 (m, 2H, Ar-H), 6.87 (dd, 1H, $J = 8.25$ Hz, $J = 2.45$ Hz, Ar-H), 6.18 (d, 1H, $J = 16.2$ Hz), 3.81 (s, 3H, –OCH_3). ^{13}C (125 MHz, $CDCl_3$): δ 159.3, 141.4, 134.1, 129.4, 127.7, 127.1, 125.5, 124.3, 124.0, 116.1, 114.8, 107.2, 92.0, 88.5, 55.2. IR (film): 3071, 2999, 2935, 2191, 1593, 1573, 1488, 1426, 1045, 853, 778, 685 cm^{-1}. HRMS (EI) calcd for $C_{15}H_{12}OS$ [M$^+$] 240.0609; found 240.0602.

11e. Pale brown solid (0.052 g, 58%); m.p. 84–86 °C, $R_f = 0.24$ (hexane). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.39 (d, 2H, $J = 8.85$ Hz, Ar-H), 7.20 (d, 1H, $J = 4.85$ Hz, Ar-H), 7.09 (d, 1H, $J = 15.9$ Hz), 7.03 (d, 1H, $J = 3.04$ Hz, Ar-H), 7.00–6.98 (m, 1H, Ar-H), 6.86 (d, 2H, $J = 8.55$ Hz, Ar-H), 6.19 (d, 1H, $J = 15.85$ Hz), 3.82 (s, 3H, –OCH_3). ^{13}C (125 MHz, $CDCl_3$): δ 159.5, 141.6, 133.2, 132.9, 127.7, 126.7, 125.2, 115.4, 114.0, 107.6, 92.2, 87.4, 55.3. IR (film): 2959, 2928, 2190, 1608, 1505, 1249, 1035, 832, 703 cm^{-1}. HRMS (EI) calcd for $C_{15}H_{12}OS$ [M$^+$] 240.0609; found 240.0603.

12a. Bright yellow solid (0.082 g, 61%); m.p. 140–142 °C, $R_f =$ 0.21 (hexane). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.42 (br.s, 1H, Ar-H), 7.38–7.33 (m, 7H, Ar-H), 7.14 (d, 4H, $J = 8.25$ Hz, Ar-H), 7.01 (d, 2H, $J = 16.2$ Hz), 6.40 (d, 2H, $J = 16.2$ Hz), 2.36 (s, 6H, –CH_3). ^{13}C (125 MHz, $CDCl_3$): δ 140.3, 138.4, 136.9, 131.4, 129.1, 126.1, 124.3, 120.2, 108.9, 92.3, 88.1, 21.5. IR (film): 3026, 2917, 2193, 1508, 1262, 1106, 1021, 952, 814, 792 cm^{-1}. HRMS (ESI) calcd for $C_{28}H_{26}N$ [M + NH$_4$]$^+$ 376.2065; found 376.2067.

12b. Yellow solid (0.096 g, 64%); m.p. 158–160 °C, $R_f = 0.51$ (EtOAc–hexane 1 : 99). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.43–7.26 (m, 12H, Ar-H), 7.04 (d, 2H, $J = 16.2$ Hz), 6.39 (d, 2H, $J = 16.2$ Hz). ^{13}C (125 MHz, $CDCl_3$): δ 141.1, 136.7, 134.3, 132.7, 129.2, 128.7, 126.4, 124.4, 121.8, 108.5, 90.9, 89.6. IR (film): 2924, 2854, 2141, 1600, 1489, 1256, 1092, 1013, 828, 738 cm^{-1}. HRMS (EI) calcd for $C_{26}H_{16}Cl_2$ [M$^+$] 398.0629; found 398.0612.

12c. Yellow solid (0.110 g, 70%); m.p. 138–140 °C, $R_f = 0.40$ (EtOAc–hexane 1 : 99). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.41–7.40 (m, 5H, Ar-H), 7.34–7.31 (m, 3H, Ar-H), 6.99 (d, 2H, $J = 16.15$ Hz), 6.85 (d, 4H, $J = 8.85$ Hz, Ar-H), 6.40 (d, 2H, $J = 16.5$ Hz), 4.05 (q, 4H, $J = 6.92$ Hz, –OCH_2CH$_3$), 1.42 (t, 6H, $J = 7.02$ Hz, –OCH$_2$CH_3). ^{13}C (125 MHz, $CDCl_3$): δ 159.0, 139.9, 136.9, 133.0, 129.1, 126.0, 124.2, 115.2, 114.5, 109.0, 92.3, 87.4, 63.5, 14.7. IR (film): 2978, 2933, 2192, 1598, 1508, 1245, 838 cm^{-1}. HRMS (ESI) calcd for $C_{30}H_{27}O_2$ [M + H]$^+$ 419.2011; found 419.2017.

13a.[19] Pale yellow solid (0.081 g, 77%); m.p. 106–108 °C, $R_f =$ 0.52 (hexane). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.48–7.46 (m, 4H, Ar-H), 7.35–7.32 (m, 3H, Ar-H), 7.28 (d, 2H, $J = 8.55$ Hz, Ar-H), 6.97 (d, 1H, $J = 16.5$ Hz), 6.38 (d, 1H, $J = 16.15$ Hz). ^{13}C (125 MHz, $CDCl_3$): δ 139.8, 135.2, 131.9, 131.5, 128.3, 128.3, 127.7, 123.2, 122.5, 108.9, 92.4, 88.5. IR (film): 3027, 1484, 1441, 1072, 957, 809, 755, 690 cm^{-1}. HRMS (EI) calcd for $C_{16}H_{11}Br$ [M$^+$] 282.0044; found 282.0045.

13b. Yellow solid (0.072 g, 65%); m.p. 86–88 °C, $R_f = 0.47$ (hexane). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.46 (d, 2H, $J = 8.55$ Hz, Ar-H), 7.29–7.25 (m, 4H, Ar-H), 7.21 (t, 1H, $J = 7.62$ Hz, Ar-H), 7.13 (d, 1H, $J = 7.6$ Hz, Ar-H), 6.95 (d, 1H, $J = 16.15$ Hz), 6.36 (d, 1H, $J = 16.2$ Hz), 2.34 (s, 3H, –CH_3). ^{13}C (125 MHz, $CDCl_3$): δ 139.7, 138.0, 135.3, 132.1, 131.9, 129.2, 128.6, 128.2, 127.7, 123.0, 122.4, 109.0, 92.6, 88.2, 21.2. IR (film): 3033, 2919, 2191, 1578, 1482, 1400, 1072, 965, 805, 785 cm^{-1}. HRMS (EI) calcd for $C_{17}H_{13}Br$ [M$^+$] 296.0201; found 296.0201.

13c.[19] Pale yellow solid (0.080 g, 72%); m.p. 178–180 °C, $R_f =$ 0.54 (hexane). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.46 (d, 2H, $J = 8.25$ Hz, Ar-H), 7.37 (d, 2H, $J = 7.95$ Hz, Ar-H), 7.28 (d, 2H, $J = 8.25$ Hz, Ar-H), 7.14 (d, 2H, $J = 8.25$ Hz, Ar-H), 6.94 (d, 1H, $J = 16.2$ Hz), 6.37 (d, 1H, $J = 16.2$ Hz), 2.36 (s, 3H, –CH_3). ^{13}C (125 MHz, $CDCl_3$): δ 139.4, 138.5, 135.3, 131.8, 131.4, 129.1, 127.6, 122.3, 120.1, 109.1, 92.6, 87.9, 21.5. IR (film): 3028, 2937, 1400, 958, 819, 807 cm^{-1}. HRMS (EI) calcd for $C_{17}H_{13}Br$ [M$^+$] 296.0201; found 296.0207.

13d. Colourless solid (0.090 g, 80%); m.p. 90–92 °C, $R_f = 0.53$ (hexane). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.47 (d, 2H, $J = 8.3$ Hz, Ar-H), 7.31–7.23 (m, 4H, Ar-H), 7.16–7.15 (m, 1H, Ar-H), 7.04–7.00 (m, 1H, Ar-H), 6.97 (d, 1H, $J = 16.35$ Hz), 6.34 (d, 1H, $J = 16.05$ Hz). ^{13}C (125 MHz, $CDCl_3$): δ 162.3 (d, $J = 244.76$ Hz), 140.6, 135.0, 131.9, 129.9 (d, $J = 8.4$ Hz), 127.7, 127.4, 125.0 (d, $J = 9.6$ Hz), 122.7, 118.2 (d, $J = 21.6$ Hz), 115.6 (d, $J = 21.6$ Hz), 108.4, 90.9, 89.4. IR (film): 3033, 2922, 1575, 1482, 1432, 1400, 1263, 1151, 1074, 946, 807 cm^{-1}. HRMS (EI) calcd for $C_{16}H_{10}BrF$ [M$^+$] 299.9950; found 299.9955.

13e. Yellow solid (0.079 g, 70%); m.p. 122–124 °C, $R_f = 0.52$ (hexane). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.48–7.43 (m, 4H, Ar-H), 7.28 (d, 2H, $J = 8.55$ Hz, Ar-H), 7.03 (t, 2H, $J = 8.4$ Hz, Ar-H), 6.95 (d, 1H, $J = 16.5$ Hz), 6.35 (d, 1H, $J = 16.15$ Hz). ^{13}C (125 MHz, $CDCl_3$): δ 162.5 (d, $J = 248.36$ Hz), 139.9, 135.1, 133.4 (d, $J = 8.4$ Hz), 131.9, 127.7, 122.5, 119.3, 115.7 (d, $J = 21.6$ Hz), 108.7, 91.2, 88.2. IR (film): 3065, 1505, 1221, 964, 836, 807 cm^{-1}. HRMS (EI) calcd for $C_{16}H_{10}BrF$ [M$^+$] 299.9950; found 299.9953.

13f. Yellow solid (0.084 g, 71%); m.p. 88–90 °C, $R_f = 0.49$ (hexane). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.47–7.44 (m, 3H, Ar-H), 7.34–7.32 (m, 1H, Ar-H), 7.30–7.23 (m, 4H, Ar-H), 6.97 (d, 1H, $J = 16.35$ Hz), 6.34 (d, 1H, $J = 16.35$ Hz). ^{13}C (125 MHz, $CDCl_3$): δ 140.6, 135.0, 134.2, 131.9, 131.3, 129.6, 129.5, 128.5, 127.8, 124.9, 122.7, 108.4, 90.8, 89.7. IR (film): 3033, 2923, 2195, 1615, 1587, 1471, 1303, 1072, 1008, 948, 799, 779 cm^{-1}. HRMS (EI) calcd for $C_{16}H_{10}BrCl$ [M$^+$] 315.9654; found 315.9653.

13g. Yellow solid (0.080 g, 67%); m.p. 162–164 °C, $R_f = 0.59$ (hexane). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.47 (d, 2H, $J = 8.6$ Hz, Ar-H), 7.39 (d, 2H, $J = 8.6$ Hz, Ar-H), 7.31–7.26 (m, 4H, Ar-H), 6.96 (d, 1H, $J = 16$ Hz), 6.35 (d, 1H, $J = 16.3$ Hz). ^{13}C (125 MHz, $CDCl_3$): δ 140.3, 135.0, 134.3, 132.7, 131.9, 128.7, 127.7, 122.6, 121.7, 108.5, 91.2, 89.5. IR (film): 3027, 1583, 1486, 1396, 1090, 963, 830, 809 cm^{-1}. HRMS (EI) calcd for $C_{16}H_{10}BrCl$ [M$^+$] 315.9654; found 315.9655.

13h. Yellow solid (0.096 g, 82%); m.p. 70–72 °C, $R_f = 0.23$ (hexane). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.46 (d, 2H, $J = 8.6$ Hz, Ar-H), 7.27 (d, 2H, $J = 8.55$ Hz, Ar-H), 7.25–7.22 (m, 1H, Ar-H), 7.06 (dd, 1H, $J = 7.75$ Hz, $J = 1.15$ Hz, Ar-H), 7.00–6.99 (m, 1H, Ar-H), 6.96 (d, 1H, $J = 16.3$ Hz), 6.89–6.87 (m, 1H, Ar-H), 6.36 (d, 1H, $J = 16.3$ Hz), 3.81 (s, 3H, –OCH_3). ^{13}C (125 MHz, $CDCl_3$): δ 159.3, 140.0, 135.2, 131.9, 129.4, 127.7, 124.2, 124.1, 122.5, 116.2, 115.0, 108.8, 92.3, 88.3, 55.2. IR (film): 3008, 2938, 2190, 1580, 1460, 1324, 1218, 1073, 964, 807, 786 cm^{-1}. HRMS (EI) calcd for $C_{17}H_{13}BrO$ [M$^+$] 312.0150; found 312.0152.

13i. Yellow solid (0.076 g, 65%); m.p. 154–156 °C, $R_f = 0.32$ (hexane). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.45 (d, 2H, $J = 8.55$ Hz, Ar-H), 7.40 (d, 2H, $J = 8.9$ Hz, Ar-H), 7.26 (d, 2H, $J = 8.6$ Hz, Ar-H), 6.91 (d, 1H, $J = 16.05$ Hz), 6.86 (d, 2H, $J = 8.9$ Hz, Ar-H), 6.36 (d, 1H, $J = 16.35$ Hz), 3.81 (s, 3H, –OCH_3). ^{13}C (125 MHz, $CDCl_3$): δ 159.6, 139.0, 135.4, 133.0, 131.8, 127.6, 122.2, 115.3, 114.0, 109.2, 92.5, 87.3, 55.3. IR (film): 2932, 2838, 2190, 1595, 1507, 1485, 1291, 1249, 1173, 1007, 955, 836, 807 cm^{-1}. HRMS (EI) calcd for $C_{17}H_{13}BrO$ [M$^+$] 312.0150; found 312.0153.

13j. Pale yellow solid (0.091 g, 74%); m.p. 162–164 °C, $R_f = 0.36$ (hexane). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.45 (d, 2H, $J = 8.55$ Hz, Ar-H), 7.39 (d, 2H, $J = 8.25$ Hz, Ar-H), 7.26 (d, 2H, $J = 8.55$ Hz, Ar-H), 6.91 (d, 1H, $J = 16.2$ Hz), 6.84 (d, 2H, $J = 8.25$ Hz, Ar-H), 6.36 (d, 1H, $J = 16.2$ Hz), 4.04 (q, 2H, $J = 6.92$ Hz, –OCH_2CH$_3$), 1.41 (t, 3H, $J = 6.85$ Hz, –OCH$_2$CH_3). ^{13}C (125 MHz, $CDCl_3$): δ 159.1, 138.9, 135.4, 132.9, 131.8, 127.6, 122.2, 115.1, 114.5, 109.2, 92.6, 87.3, 63.5, 14.7. IR (film): 3028, 2188, 1724, 1598, 1508, 1394, 1288, 1250, 1174, 1114, 1045, 958, 807 cm^{-1}. HRMS (EI) calcd for $C_{18}H_{15}BrO$ [M$^+$] 326.0306; found 326.0303.

14a. Pale yellow solid (0.065 g, 60%); m.p. 94–96 °C, $R_f = 0.51$ (hexane). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.45 (d, 2H, $J = 8.72$ Hz, Ar-H), 7.27–7.22 (m, 4H, Ar-H), 7.00–6.91 (m, 2H, Ar-H), 6.36 (d, 1H, $J = 16.48$ Hz). ^{13}C (100 MHz, $CDCl_3$): δ 139.7, 135.1, 131.9, 127.7, 127.5, 127.2, 123.3, 122.6, 108.5, 92.4, 85.6. IR (film): 3098, 2184, 1582, 1485, 1421, 1400, 1072, 956, 853, 807 cm^{-1}. HRMS (EI) calcd for $C_{14}H_9BrS$ [M$^+$] 287.9608; found 287.9601.

15a. Pale brown solid (0.073 g, 69%); m.p. 54–56 °C, $R_f = 0.43$ (hexane). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.57 (br.s, 1H, Ar-H), 7.50–7.48 (m, 2H, Ar-H), 7.42 (d, 1H, $J = 7.75$ Hz, Ar-H), 7.35–7.33 (m, 4H, Ar-H), 7.21 (t, 1H, $J = 7.87$ Hz, Ar-H), 6.95 (d, 1H, $J = 16.05$ Hz), 6.39 (d, 1H, $J = 16.3$ Hz). ^{13}C (125 MHz, $CDCl_3$): δ 139.5, 138.4, 131.5, 131.3, 130.2, 129.0, 128.3, 124.8, 123.1, 122.9, 109.7, 92.6, 88.3. IR (film): 3057, 2195, 1589, 1561, 1489, 1473, 1422, 1071, 949, 776, 756 cm^{-1}. HRMS (EI) calcd for $C_{16}H_{11}Br$ [M$^+$] 282.0044; found 282.0045.

15b. Pale yellow solid (0.069 g, 62%); m.p. 66–68 °C, $R_f = 0.50$ (hexane). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.55 (s, 1H, Ar-H), 7.41–7.36 (m, 3H, Ar-H), 7.33 (d, 1H, $J = 7.7$ Hz, Ar-H), 7.20 (t, 1H, $J = 7.72$ Hz, Ar-H), 7.14 (d, 2H, $J = 7.7$ Hz, Ar-H), 6.92 (d, 1H, $J = 16.35$ Hz), 6.38 (d, 1H, $J = 16.35$ Hz), 2.36 (s, 3H, –CH_3). ^{13}C (125 MHz, $CDCl_3$): δ 139.0, 138.6, 138.5, 131.4, 131.2, 130.2, 129.1, 129.0, 124.8, 122.9, 120.0, 109.9, 92.9, 87.7, 21.5. IR (film): 3028, 2918, 2190, 1587, 1558, 1377, 1072, 954, 820, 782, 682 cm^{-1}. HRMS (EI) calcd for $C_{17}H_{13}Br$ [M$^+$] 296.0201; found 296.0208.

15c. Yellow solid (0.076 g, 64%); m.p. 76–78 °C, $R_f = 0.55$ (hexane). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.56 (s, 1H, Ar-H), 7.43–7.19 (m, 7H, Ar-H), 6.95 (d, 1H, $J = 16.15$ Hz), 6.36 (d, 1H, $J = 16.2$ Hz). ^{13}C (125 MHz, $CDCl_3$): δ 139.9, 138.2, 134.4, 132.7, 131.5, 130.2, 129.1, 128.7, 124.9, 122.9, 121.6, 109.4, 91.4, 89.3. IR (film): 2923, 2852, 1587, 1488, 1095, 993, 828, 787 cm^{-1}. HRMS (EI) calcd for $C_{16}H_{10}BrCl$ [M$^+$] 315.9654; found 315.9656.

16a. Pale yellow solid (0.075 g, 59%); m.p. 186–188 °C, $R_f = 0.25$ (hexane). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.55–7.49 (m, 4H, Ar-H), 7.40 (d, 4H, $J = 8.48$ Hz, Ar-H), 7.36–7.30 (m, 5H, Ar-H), 7.02 (d, 1H, $J = 16.24$ Hz), 6.39 (d, 1H, $J = 16.04$ Hz). ^{13}C (100 MHz, $CDCl_3$): δ 140.8, 135.9, 134.3, 132.7, 131.9, 131.6, 128.7, 128.3, 126.2, 123.5, 123.1, 121.8, 108.6, 91.4, 90.9, 89.8, 89.2. IR (film): 3081, 1913, 1488, 1441, 1397, 1099, 950, 833, 817, 754, 692 cm^{-1}. HRMS (EI) calcd for $C_{24}H_{15}Cl$ [M$^+$] 338.0862; found 338.0862.

16b. Yellow solid (0.071 g, 54%); m.p. 154–156 °C, $R_f = 0.40$ (EtOAc–hexane 1 : 99). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.54–7.48 (m, 4H, Ar-H), 7.42–7.34 (m, 7H, Ar-H), 6.98 (d, 1H, $J = 16.52$ Hz), 6.85 (d, 2H, $J = 8.72$ Hz, Ar-H), 6.41 (d, 1H, $J = 16.04$ Hz), 4.04 (q, 2H, $J = 7.02$ Hz, –OCH_2CH$_3$), 1.42 (t, 3H, $J = 6.88$ Hz, –OCH$_2$CH_3). ^{13}C (100 MHz, $CDCl_3$): δ 159.0, 139.5, 136.3, 133.0, 131.9, 131.6, 128.3, 126.1, 123.1, 123.0, 115.1, 114.5, 109.3, 92.9, 90.7, 89.3, 87.5, 63.5, 14.7. IR (film): 2979, 1594, 1506, 1248,

1174, 1114, 1046, 946, 839, 816, 752 cm^{-1}. HRMS (EI) calcd for $C_{26}H_{20}O$ [M^+] 348.1514; found 348.1518.

16c. Pale yellow solid (0.050 g, 43%); m.p. 162–164 °C, R_f = 0.27 (hexane). ^1H NMR (400 MHz, $CDCl_3$): δ 7.53–7.48 (m, 4H, Ar-H), 7.39–7.23 (m, 7H, Ar-H), 7.02–6.97 (m, 2H, Ar-H), 6.39 (d, 1H, J = 16.48 Hz). ^{13}C (100 MHz, $CDCl_3$): δ 140.3, 136.0, 131.9, 131.6, 128.3, 127.4, 127.2, 126.2, 123.4, 123.1, 108.6, 92.7, 90.9, 89.3, 85.8. IR (film): 3080, 1440, 1192, 962, 948, 815 cm^{-1}. HRMS (EI) calcd for $C_{22}H_{14}S$ [M^+] 310.0816; found 310.0815.

16d. Colourless solid (0.061 g, 51%); m.p. 128–130 °C, R_f = 0.25 (hexane). ^1H NMR (400 MHz, $CDCl_3$): δ 7.59 (br.s, 1H, Ar-H), 7.57–7.54 (m, 2H, Ar-H), 7.45 (d, 1H, J = 7.56 Hz, Ar-H), 7.40–7.31 (m, 7H, Ar-H), 7.15 (d, 2H, J = 8 Hz, Ar-H), 6.99 (d, 1H, J = 16.24 Hz), 6.42 (d, 1H, J = 16.28 Hz), 2.37 (s, 3H, –CH_3). ^{13}C (100 MHz, $CDCl_3$): δ 139.8, 138.5, 136.6, 131.6, 131.4, 129.3, 129.1, 128.7, 128.3, 126.0, 123.7, 123.0, 120.1, 109.2, 92.5, 89.7, 88.9, 88.0, 21.5. IR (film): 3024, 1598, 1508, 1491, 1441, 956, 817, 794, 754, 687 cm^{-1}. HRMS (EI) calcd for $C_{25}H_{18}$ [M^+] 318.1409; found 318.1407.

16e. Yellow solid (0.050 g, 38%); m.p. 168–170 °C, R_f = 0.32 (EtOAc–hexane 2 : 98). ^1H NMR (400 MHz, $CDCl_3$): δ 7.47 (d, 4H, J = 9.16 Hz, Ar-H), 7.39–7.36 (m, 4H, Ar-H), 7.14 (d, 2H, J = 8.24 Hz, Ar-H), 6.99 (d, 1H, J = 16 Hz), 6.89–6.86 (m, 2H, Ar-H), 6.39 (d, 1H, J = 16.48 Hz), 3.83 (s, 3H, –OCH_3), 2.36 (s, 3H, –CH_3). ^{13}C (100 MHz, $CDCl_3$): δ 159.7, 140.1, 138.4, 135.9, 133.0, 131.7, 131.4, 129.1, 126.1, 123.6, 120.2, 115.2, 114.0, 108.9, 92.8, 90.8, 88.2, 88.1, 55.3, 21.5. IR (film): 2921, 2212, 1605, 1508, 1246, 833, 817 cm^{-1}. HRMS (EI) calcd for $C_{26}H_{20}O$ [M^+] 348.1514; found 348.1528.

16f. Bright yellow solid (0.040 g, 30%); m.p. 176–178 °C, R_f = 0.30 (EtOAc–hexane 2 : 98). ^1H NMR (400 MHz, $CDCl_3$): δ 7.53–7.47 (m, 4H, Ar-H), 7.43–7.38 (m, 4H, Ar-H), 7.05 (t, 2H, J = 8.82 Hz, Ar-H), 6.98 (d, 1H, J = 16.28 Hz), 6.87 (d, 2H, J = 8.92 Hz, Ar-H), 6.40 (d, 1H, J = 16.28 Hz), 3.83 (s, 3H, –OCH_3). ^{13}C (100 MHz, $CDCl_3$): δ 162.5 (d, J = 251 Hz), 159.6, 139.5, 136.4, 133.5 (d, J = 7.67 Hz), 133.0, 131.8, 126.1, 122.9, 119.2, 115.6 (d, J = 22.03 Hz), 115.3, 114.0, 109.3, 92.8, 89.6, 89.0, 87.6, 55.3. IR (film): 2923, 2851, 2189, 1597, 1508, 839, 816 cm^{-1}. HRMS (EI) calcd for $C_{25}H_{17}FO$ [M^+] 352.1263; found 352.1277.

17a. Pale yellow solid (0.060 g, 52%); m.p. 194–196 °C, R_f = 0.22 (hexane). ^1H NMR (400 MHz, $CDCl_3$): δ 7.56 (d, 2H, J = 8.24 Hz, Ar-H), 7.50–7.46 (m, 4H, Ar-H), 7.37 (d, 2H, J = 8.28 Hz, Ar-H), 7.25–7.23 (m, 2H, Ar-H), 7.13 (d, 2H, J = 8 Hz, Ar-H), 7.04 (d, 1H, J = 16.24 Hz), 6.40 (d, 1H, J = 16 Hz), 2.39 (s, 3H, –CH_3), 2.35 (s, 3H, –CH_3). ^{13}C (100 MHz, $CDCl_3$): δ 141.2, 140.4, 138.3, 137.5, 137.3, 135.1, 131.4, 129.5, 129.1, 127.1, 126.7, 126.6, 120.3, 108.0, 92.1, 88.4, 21.5, 21.1. IR (film): 2917, 1494, 1400, 948, 803 cm^{-1}. HRMS (EI) calcd for $C_{24}H_{20}$ [M^+] 308.1565; found 308.1563.

17b. Pale yellow solid (0.059 g, 51%); m.p. 108–110 °C, R_f = 0.26 (hexane). ^1H NMR (400 MHz, $CDCl_3$): δ 7.61 (br.s, 1H, Ar-H), 7.51 (d, 3H, J = 8.04 Hz, Ar-H), 7.41–7.39 (m, 4H, Ar-H), 7.28 (d, 2H, J = 7.8 Hz, Ar-H), 7.16 (d, 2H, J = 7.8 Hz, Ar-H), 7.10 (d, 1H, J = 16.04 Hz), 6.46 (d, 1H, J = 16.04 Hz), 2.42 (s, 3H, –CH_3), 2.38 (s, 3H, –CH_3). ^{13}C (100 MHz, $CDCl_3$): δ 141.6, 140.8, 138.3, 137.9, 137.3, 136.8, 131.4, 129.5, 129.1, 127.2, 126.9, 124.9, 124.7, 120.3, 108.6, 92.1, 88.2, 21.5, 21.1. IR (film): 2920, 2190, 1595, 1508, 953, 817, 786 cm^{-1}. HRMS (EI) calcd for $C_{24}H_{20}$ [M^+] 308.1565; found 308.1562.

17c. Yellow solid (0.061 g, 48%); m.p. 200–202 °C, R_f = 0.45 (EtOAc–hexane 2 : 98). ^1H NMR (400 MHz, $CDCl_3$): δ 7.54–7.52 (m, 4H, Ar-H), 7.46 (d, 2H, J = 8.24 Hz, Ar-H), 7.38 (d, 2H, J = 7.8 Hz, Ar-H), 7.14 (d, 2H, J = 7.76 Hz, Ar-H), 7.05 (d, 1H, J = 16.48 Hz), 6.97 (d, 2H, J = 8.68 Hz, Ar-H), 6.40 (d, 1H, J = 16.48 Hz), 4.08 (q, 2H, J = 7.01 Hz, –OCH_2CH$_3$), 2.36 (s, 3H, CH_3), 1.44 (t, 3H, J = 7.08 Hz, –OCH$_2$CH_3). ^{13}C (100 MHz, $CDCl_3$): δ 158.7, 140.9, 140.5, 138.3, 134.7, 132.7, 131.4, 129.1, 127.9, 126.8, 126.7, 120.3, 114.8, 107.8, 92.0, 88.4, 63.5, 21.5, 14.8. IR (film): 2927, 2977, 1604, 1499, 1246, 821 cm^{-1}. HRMS (EI) calcd for $C_{25}H_{22}O$ [M^+] 338.1671; found 338.1671.

18a. Yellow solid (0.062 g, 52%); m.p. 80–82 °C, R_f = 0.33 (EtOAc–hexane 1 : 99). ^1H NMR (400 MHz, $CDCl_3$): δ 7.66 (d, 1H, J = 15.8 Hz), 7.50 (d, 2H, J = 8.28 Hz, Ar-H), 7.43 (d, 2H, J = 8.48 Hz, Ar-H), 7.30–7.20 (m, 3H, Ar-H), 7.14 (d, 1H, J = 7.56 Hz, Ar-H), 7.01 (d, 1H, J = 16.24 Hz), 6.44 (d, 2H, J = 15.36 Hz), 4.27 (q, 2H, J = 7.17 Hz, –OCH_2CH$_3$), 2.34 (s, 3H, –CH_3), 1.34 (t, 3H, J = 7.1 Hz, –OCH$_2$CH_3). ^{13}C (100 MHz, $CDCl_3$): δ 166.9, 143.7, 140.0, 138.2, 138.0, 134.5, 132.1, 129.3, 128.6, 128.4, 128.2, 126.6, 122.9, 118.3, 109.6, 93.1, 88.4, 60.5, 21.2, 14.3. IR (film): 3029, 2979, 1710, 1633, 1599, 1308, 1175, 1038, 957, 811, 784 cm^{-1}. HRMS (EI) calcd for $C_{22}H_{20}O_2$ [M^+] 316.1463; found 316.1460.

18b. Bright yellow solid (0.056 g, 47%); m.p. 122–124 °C, R_f = 0.33 (EtOAc–hexane 1 : 99). ^1H NMR (400 MHz, $CDCl_3$): δ 7.66 (d, 1H, J = 16.04 Hz), 7.49 (d, 2H, J = 8.24 Hz, Ar-H), 7.42 (d, 2H, J = 8.2 Hz, Ar-H), 7.37 (d, 2H, J = 8.24 Hz, Ar-H), 7.14 (d, 2H, J = 8.24 Hz, Ar-H), 7.00 (d, 1H, J = 16 Hz), 6.43 (d, 2H, J = 16.04 Hz), 4.27 (q, 2H, J = 7.17 Hz, –OCH_2CH$_3$), 2.36 (s, 3H, CH_3), 1.34 (t, 3H, J = 7.32 Hz, –OCH$_2$CH_3). ^{13}C (100 MHz, $CDCl_3$): δ 166.9, 143.8, 139.8, 138.6, 138.2, 134.5, 131.4, 129.1, 128.4, 126.6, 120.1, 118.2, 109.7, 93.2, 88.1, 60.5, 21.5, 14.3. IR (film): 2985, 1707, 1633, 1176, 963, 816 cm^{-1}. HRMS (EI) calcd for $C_{22}H_{20}O_2$ [M^+] 316.1463; found 316.1461.

18c. Bright yellow solid (0.060 g, 48%); m.p. 138–140 °C, R_f = 0.18 (EtOAc–hexane 1 : 99). ^1H NMR (400 MHz, $CDCl_3$): δ 7.66 (d, 1H, J = 16.04 Hz), 7.49 (d, 2H, J = 8.24 Hz, Ar-H), 7.41 (d, 4H, J = 8.92 Hz, Ar-H), 6.98 (d, 1H, J = 16.04 Hz), 6.86 (d, 2H, J = 8.92 Hz, Ar-H), 6.43 (d, 2H, J = 16.04 Hz), 4.27 (q, 2H, J = 7.1 Hz, –OCH_2CH$_3$), 3.82 (s, 3H, –OCH_3), 1.34 (t, 3H, J = 7.1 Hz, –OCH$_2$CH_3). ^{13}C (100 MHz, $CDCl_3$): δ 167.0, 159.7, 143.8, 139.3, 138.3, 134.4, 133.0, 128.4, 126.6, 118.2, 115.3, 114.0, 109.8, 93.1, 87.6, 60.5, 55.3, 14.3. IR (film): 2936, 2189, 1708, 1629, 1507, 1309, 1178, 1032, 836, 816 cm^{-1}. HRMS (EI) calcd for $C_{22}H_{20}O_3$ [M^+] 332.1412; found 332.1410.

18d. Yellow solid (0.053 g, 42%); m.p. 120–122 °C, R_f = 0.30 (EtOAc–hexane 1 : 99). ^1H NMR (400 MHz, $CDCl_3$): δ 7.66 (d, 1H, J = 16.04 Hz), 7.50 (d, 2H, J = 8.48 Hz, Ar-H), 7.44–7.39 (m, 4H, Ar-H), 7.31 (d, 2H, J = 8.48 Hz, Ar-H), 7.02 (d, 1H, J = 16.24 Hz), 6.44 (d, 1H, J = 16.04 Hz), 6.41 (d, 1H, J = 16.04 Hz), 4.27 (q, 2H, J = 7.18 Hz, –OCH_2CH$_3$), 1.34 (t, 3H, J = 7.1 Hz, –OCH$_2$CH_3). ^{13}C (100 MHz, $CDCl_3$): δ 166.9, 143.7, 140.6, 138.0, 134.7, 134.3, 132.7, 128.8, 128.7, 128.5, 126.7, 121.7, 118.4, 109.1, 91.7, 89.7, 60.6, 14.3. IR (film): 2981, 1712, 1636, 1489, 1263, 1093, 965, 828 cm^{-1}. HRMS (EI) calcd for $C_{21}H_{17}ClO_2$ [M^+] 336.0917; found 336.0915.

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