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Graphical Abstract

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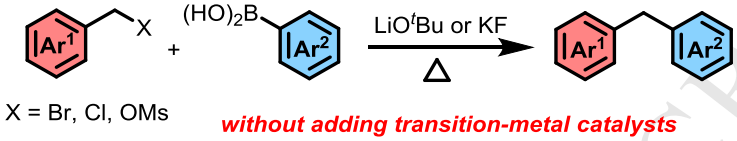

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ABSTRACT

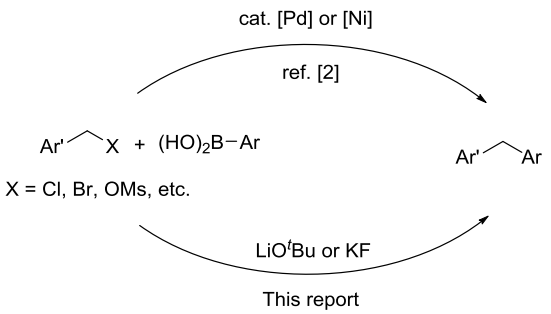
We report herein a transition-metal-free coupling reaction of arylboronic acids with benzyl halides and mesylates for the construction of $C(sp^2)$-$C(sp^3)$ bonds. A unique feature of this coupling reaction is the formation regioisomers in some cases. Mechanistic studies suggest that this reaction may proceed *via* an unprecedented Friedel–Crafts-type reaction pathway under base conditions with the assistance of boronic acid moiety.

1. Introduction

Suzuki-Miyaura cross-couplings of organoboronic acids with organohalides or pseudohalides have well-established as one of the most versatile and widely utilized reactions for the construction of C-C bonds.[1] In the past decades, the scope of Suzuki-Miyaura coupling has been significantly broadened. One of the recent advances is the Pd-catalyzed cross-coupling reaction of benzylic substrates with arylboronic acids for the synthesis of diarylmethanes,[2] which are a type of important molecules found applications in various areas.[3] For example, Molander and Elia reported the Pd-catalyzed cross-coupling of benzyl halides with potassium aryltrifluoroborates.[2d] Kumano and Yokogi developed Pd-catalyzed cross-coupling of benzyl carbonates with arylboronic acids.[2h]

On the other hand, in recent years transition-metal-free coupling reactions have attracted considerable attentions due to the obvious advantages of avoiding using precious transition metals such as palladium.[4] In 2003, a transition-metal-free Suzuki-type coupling reactions of arylboronic acid with aryl halides at 150 °C under microwave irradiation was reported by Leadbeater,[5] who later corrected that the coupling was owing to trace amount of palladium contaminants (down to a level of 50 ppb) found in commercially available Na_2CO_3 which was used as the base in their coupling reaction. In 2012, Inamoto and Doi reported a coupling reaction of aryliodides with arylboronic acids without adding any transition metal catalysts.[6] They suggested that the coupling reaction is likely a transition-metal-free process based on the results of ICP-MS analysis. In the same year, the groups of Scrivanti and Ueda-Ryu independently disclosed transition-metal-free Suzuki-type coupling of allylic bromides with arylboronic acids.[7] Later Ueda and Ryu reported transition-metal-free coupling reaction of arylpropargylic bromides with aryl- and alkenylboronic acids.[8] We report herein our study on a Suzuki-Miyaura cross-couplings of arylboronic acids and benzyl halides or mesylates under the conditions that no transition metal catalyst was added.[9] The reaction is likely a transition-metal-free process based on the mechanistic experiments and ICP-MS analysis.

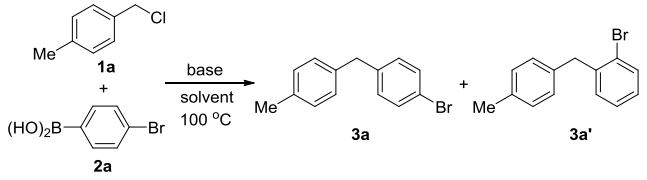
Scheme 1. Cross-coupling of Arylboronic Acids with Benzylic Halides or Pseudohalides



The initial benchmark was the reaction carried out with 4-methylbenzyl chloride **1a** and 4-bromophenyl boronic acid **2a** (Table 1). Our original expectation is that a carbene species may be generated by treatment of **1a** with a strong base, which may further react with **2a** to realize a transition-metal-free coupling.[10] With sodium hydride as the base and toluene as the solvent, the

coupling product **3a** was indeed observed (20% NMR yield) (Table 1, entry 1). Notably, in addition to **3a** we could also observe the formation of regioisomer **3a'** by careful inspection of the ^{1}H NMR spectra of the crude product (**3a**:**3a'** > 20:1). Inspired by this initial result, we decided to optimize the reaction conditions. No reaction occurred when sodium hydride was removed from the system (Table 1, entry 2). Changing the solvent from toluene to dioxane resulted in the formation of only trace amount of the product **3a**, while with (trifluoromethyl)benzene as the solvent the reaction was improved (Table 1, entries 2, 3). As the base plays crucial role in this reaction, we next screened various bases. K_2CO_3 and K_3PO_4 gave comparable results as NaH, while Cs_2CO_3 and Et_3N failed to afford the product **3a** (Table 1, entries 5-8). Interestingly, lithium *tert*-butoxide afforded improved result with 73% isolated yield (Table 1, entry 9). In contrast, the reaction with potassium *tert*-butoxide gave only trace product **2a**, instead S_N2 substitution product of benzyl chloride was predominant (Table 1, entry 10). With lithium *tert*-butoxide as the base, several other solvents were examined again and no improvement could be achieved (Table 1, entries 11-13). Besides, the yield diminished when the reaction temperature was changed from 100 °C to 80 °C (Table 1, entry 14). Finally, by lowing the loading of lithium *tert*-butoxide from 3.0 to 2.0 equiv, the product **3a** could be isolated in 78% yield (Table 1, entry 16).

Table 1. Optimization of the Reaction Conditions[a]

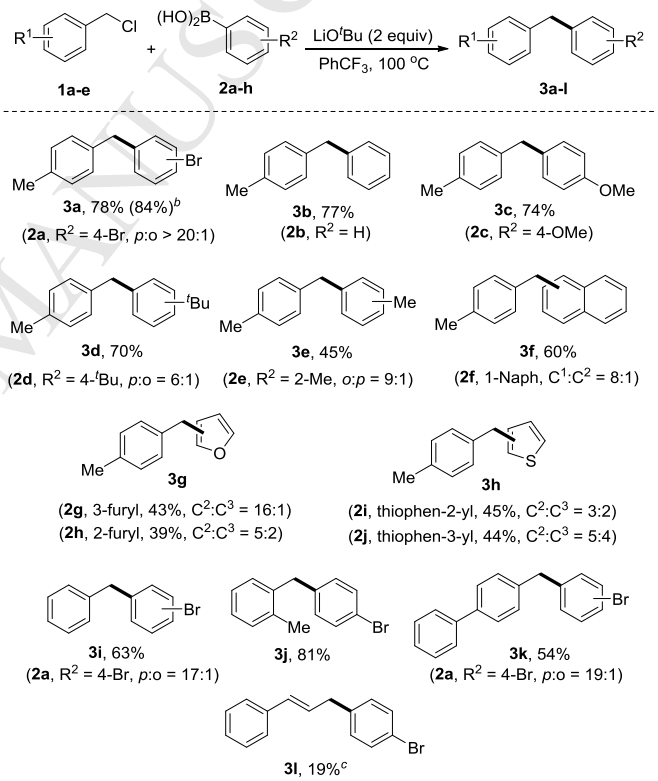


Entry	Base (equiv)	Solvent	Yield(%)[b]
1	NaH (3.0)	PhMe	20
2	--	PhMe	0
3	NaH (3.0)	dioxane	trace
4	NaH (3.0)	$PhCF_3$	43(35)[c]
5	K_2CO_3 (3.0)	$PhCF_3$	32
6	K_3PO_4 (3.0)	$PhCF_3$	46
7	Cs_2CO_3 (3.0)	$PhCF_3$	0
8	Et_3N (3.0)	$PhCF_3$	0
9	LiO^tBu (3.0)	$PhCF_3$	(73)[c]
10	KO^tBu (3.0)	$PhCF_3$	trace
11	LiO^tBu (3.0)	DMF	0
12	LiO^tBu (3.0)	DCE	(68)[c]
13	LiO^tBu (3.0)	MeCN	0
14	LiO^tBu (3.0)	$PhCF_3$	27[d]
15	LiO^tBu (3.0)	$PhCF_3$	(41)[e]
16	LiO^tBu (2.0)	$PhCF_3$	(78)[c]

[a]If not otherwise noted, the reaction was carried out with **1a** (0.25 mmol), **2a** (0.5 mmol) in solvent (1 mL) at 100 °C with the base. [b]The yields were estimated by the ^{1}H NMR with nitromethane as the internal standard. The formation of **3a'** was observed. The ratio of **3a**:**3a'** is >20:1. [c]The reaction was carried out with **1a** (0.5 mmol), **2a** (1.0 mmol) in solvent (2 mL) at 100 °C with the base. The isolated yields are indicated in the brackets. [d]The reaction was carried out at 80 °C. [e]The reaction was carried out with **1a** (0.25 mmol) and **2a** (0.37 mmol).

With the optimized the reaction conditions, we proceeded to examine the substrate scope of the reaction. As shown in Scheme 2, the reaction with a series of substituted arylboronic acids worked smoothly to afford the corresponding cross-coupling products. The reaction also worked with heterocyclic boronic acids (**3g, 3h**). In addition to the anticipated coupling products, the formation of minor regioisomers was observed in many cases, but the ratio varied considerably. For example, the reactions of 4-methylbenzyl chloride with 4-anisylboronic acid afforded **3c** as the only product. However, the reactions with 4-*tert*-butylphenylboronic acid and 2-tolylboronic acid gave two isomeric products in each case, with ratio of 6:1 (**3d**) and 9:1 (**3e**) respectively. In the case of 3-furylboronic acid and 2-furylboronic acid both reactions gave the product with benzylation at C2-position as the major one. Similar results were observed in the reaction of 2 and 3-thienylboronic acid (**3h**). The reaction of cinnamyl bromide with 4-bromophenylboronic acid also afforded the corresponding coupling product **3l**, but with low yield.

Scheme 2. *Reaction of Benzyl Chlorides with Arylboronic Acids*[a]

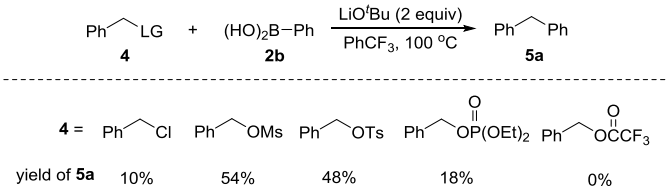


[a]*Reaction conditions: The solution of* **1** *(0.5 mmol),* **2** *(1.0 mmol) and LiO^tBu (1.0 mmol) in $PhCF_3$ (2 mL) was stirred at 100 °C for 10-24 h. All the yields refer to isolated products. Isomeric ratio was determined by ^{1}H NMR spectra.* [b]*The yield in bracket refers to the reaction with 4-methylbenzyl bromide.* [c]*The reaction was with cinnamyl bromide.*

Notably, the reaction of benzyl chloride with phenylboronic **2b** *under the optimized reaction conditions gave the coupling product* **5a** *in only 10% yield (Scheme 3). We then proceeded to examine the reaction with various benzyl alcohol derivatives. Compared with benzyl chloride, benzyl mesylate and tosylate showed high reactivity and gave the coupling product in improved yields. However, the reaction with benzyl trifluoroacetate failed to give the coupling product. With benzyl mesylate as the substrate, the reaction can be further optimized by changing LiO^tBu to KF, the solvent from $PhCF_3$ to DCE, and lowering the reaction temperature from 100 °C to 80 °C. Under*

such conditions, the coupling product **5a** *could be obtained in 77% isolated yield.*

Scheme 3. *Comparison of the Reactivity of Benzyl Chloride with Benzyl Alcohol Derivatives*[a]

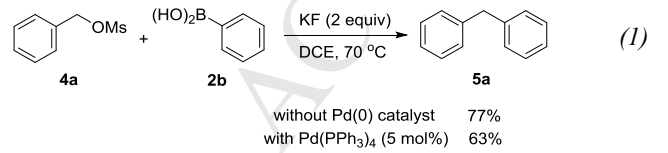


[a]*Reaction was carried out with* **4** *(0.25 mmol),* **2k** **(***0.5 mmol), LiO*[t]*Bu (0.5 mmol) in PhCF₃ (1 mL) at 100* [o]*C for 10 h.*

*Under the modified conditions, a series of arylboronic acids and benzyl mesylates were subjected to the reaction. As shown in Scheme 4, the reaction with a series of benzyl mesylates worked smoothly to afford the corresponding coupling products. Notably, the reaction also worked well with ortho-substituted mesylates, indicating that the reaction does not significantly affected by steric effects (***5k-r***). It should be noted that benzyl mesylate bearing electron withdrawing group such as nitro, ester also gave satisfactory results with modified reaction conditions (LiO*[t]*Bu, 100* [o]*C) (***5z, 6a** *and* **6b***).*

*Different from metal-catalyzed coupling reaction, the reaction with 3-iodobenzyl mesylate gave the products with iodine remained intact (***5t-v***). The reaction with allyl phosphate and propargyl mesylate also afforded the desired products with excellent yields (***6c** *and* **6d***). The reaction with phenethyl mesylate gave the coupling products, albeit with a lower yield (***6e***). Interestingly, the reaction of benzyl mesylates and arylboronic acid showed different regioselectivity as compared with the reaction with benzyl halides in the cases that regio-isomers were formed in the reaction. For the reactions with benzyl chlorides, the benzylation took place in ipso- and meta-position of the boron, while the benzylation took place in suit- or ortho-position of the boron when using benzyl mesylates or phosphates as the substrates.*

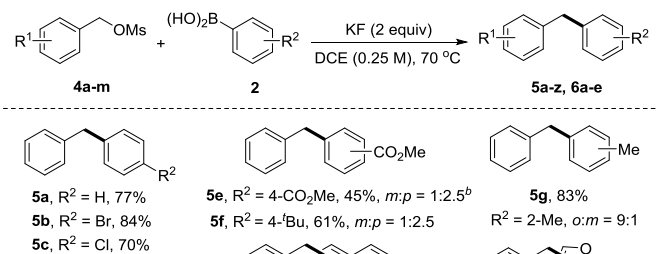
To gain insights into this reaction, mechanistic experiments have been carried out. Considering the previous reports that the coupling of benzyl substrates with arylboronic acids took place with palladium as the catalyst,[2] *a control experiments were first carried out by using 5 mol% Pd(PPh₃)₄ as the additional palladium catalyst introduced into the reaction system. However, the yield of the coupling product was actually droped from 77% to 63% (eq. 1). Thus, the addition of Pd(0) catalyst to the reaction system did not improve the efficiency of the coupling reaction.*



(1)

Moreover, the formation of regioisomers in many cases is not in accordance with the traditional palladium-catalyzed Suzuki-Miyaura coupling. To further clarify whether the coupling reaction is a transition-metal-free process or it is actually catalyzed by trace amount of trasition-metal contaminents,[5] *the coupled plasma mass spectroscopy (ICP-MS) was used to analyze the contents of the transition-metals in the reagents that*

Scheme 4. *Reaction of Benzyl Mesylates with Arylboronic Acids*[a]



[a]*Reaction conditions: the solution of* **4a-m** **(***0.75 mmol),* **2** **(***0.5 mmol***)** *and KF (1.0 mmol) in DCE (2 mL) was stirred at 70* [o]*C for 10-24 h. Isolated yields. All the yields refer to isolated products. Isomeric ratio was determined by* [1]*H NMR spectra.* [b]*In the cases when there was regio-isomers, the boronic acids used and the product ratio were indicated below the products.* [c]*The yield in bracket refers to the reaction with LiO*[t]*Bu as the base instead of KF.* [d]*P*hosphates were used instead of mesylate. [e]*Reaction was conducted with* **4** *(0.5 mmol),* **2** *(1.0 mmol) and LiO*[t]*Bu (1.0 mmol) in DCE (2 mL) at 100* [o]*C.*

are involved in the coupling reaction. The transition-metals analyzed included palladium, copper,[11] *nickel,*[12] *iron*[13] *and cobalt,*[14] *which are commonly used as the catalysts in the reactions of benzyl halides with organic boronic acids or Grignard reagents. The results are summarized in Table 2. Palladium and cobalt are not detected in the substrates, and copper and nickel both are less than 0.5 ppm, and the iron has a highest concentration in KF is 6.252 ppm. The very low concentration level of transition metal in this reaction system seems not likely to catalyzed the coupling reaction.*

Table 2. ICP-MS analysis of trace transition metals[a]

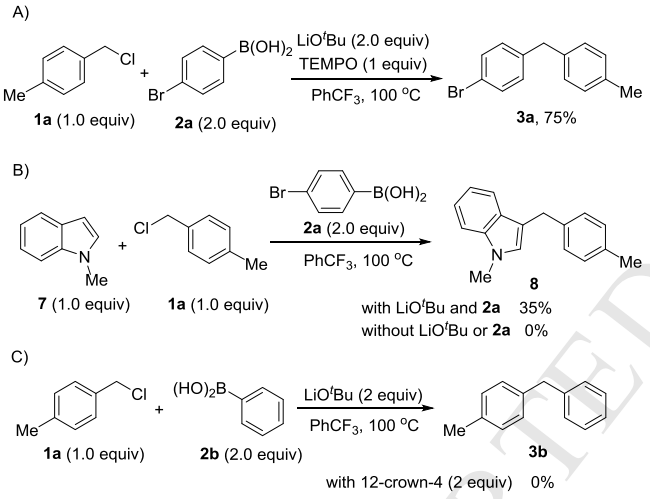
Metal	LiO[t]Bu (99%)[b]	PhB(OH)$_2$[c]	KF (99.99%)[d]
Pd	$< 10^{-3}$	$< 10^{-3}$	$< 10^{-3}$
Cu	3.165×10^{-1}	3.175×10^{-1}	8.878×10^{-3}

Ni	1.845×10^{-1}	1.554×10^{-1}	4.646×10^{-1}
Fe	1.046	1.747	6.252
Co	$< 10^{-3}$	$< 10^{-3}$	$< 10^{-3}$

[a]1 unit = 1 μg/g (ppm); the detection limit is 10^{-9} (ppb). [b]LiO^{t}Bu (99% purity) was purchased from Energy Chemical. [c]$PhB(OH)_2$ was purchased from Alfa. [d]KF (99.99% purity) was purchased from Acros.

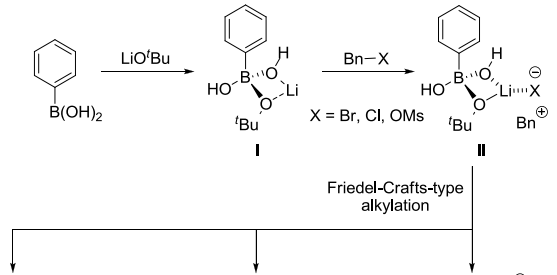
Further experiments were then carried out to confirm if the reaction involves cations as the possible intermediates. Thus, *N*-methylindole was used as the electron-rich aromatic compound to capture the possible cation intermediate under the standard condition. 3-Benzyl-*N*-methylindole was observed as major product in 35% NMR yield. However, in the absence of boronic acid or lithium *t*-butoxide, only trace 3-benzyl-*N*-methylindole was detected (Scheme 5, b). These results suggest that cation is generated with the assistance of boronic acid and lithium *t*-butoxide. Finally, 12-crown-4 was added into the system to chelate the lithium. Under such conditions, no reaction was observed (Scheme 5, c). This result indicates that lithium ion is also essential for the reaction.

Scheme 5. Mechanistic Experiments



Based on these experimental results and the recent reports on the reaction of organoboron reagents with stable carbon cations,[15] the following mechanistic hypothesis is proposed for this transformation (Scheme 6). First, the boronic acid reacts with the metal salt to form complex **I**. The lithium ion activates the C-X bond of benzyl substrate to generate ion pair **II**. Subsequently, Friedel-Craft reaction pathway via the cyclo-members ring via the interaction between the X and benzyl cation leads to the formation of the coupling product and its regioisomer. However, further rigorous mechanistic studies are necessary to substantiate this mechanistic hypothesis.

Scheme 6. Mechanistic Hypothesis



2. Summary

In summary, we have reported a reaction of benzyl halides or mesylates with arylboronic acids without adding any transition-metal catalysts. The reaction is most likely a transition-metal-free process and mechanistic studies suggest that carbon cations may be involved in the reaction pathway. Thus, this coupling reaction may be an unusual Friedel-Crafts-type reaction under basic conditions.

3. Experimental section

3.1 General

All solvents were distilled to remove water over Na or CaH_2 prior to use, except the $PhCF_3$. All the coupling reactions were carried out under nitrogen. Column chromatograph was performed on 200-300 mesh silica gal. ^{1}H NMR and ^{13}C NMR spectral were recorded at 400 MHz and 101 MHz with 400MHz WB Solid-State NMR Spectrometer (or Bruker AVANCE III spectrometer) using $CDCl_3$ as solvent. Chemical shifts are reported in ppm. The IR spectra were recorded with a Thermo Electron Corporation Nicolet AVATAR 300 FT-IR spectrometer. Mass spectra were measured on Bruker Apex IV FTMS spectrometer. EI-MS were obtained on MS5975C. The reagents used in this study were purchased from commercial suppliers and were used without further purification.

General Procedure for Reaction of Benzyl Halides with Arylboronic Acids

Arylboronic acid (1.0 mmol), LiO^{t}Bu (1.0 mmol) was added to a Schlenk tube. The tube was charged with nitrogen and then $PhCF_3$ (2 mL) and benzyl chloride (0.5 mmol) were added. The reaction mixture was stirred at 100 °C for 24 h. After the mixture was cooled down to room temperature, solvent was removed under reduced pressure to leave a crude product. The crude product was purified by column chromatography on silica gel, eluting with petroleum ether to afford the coupling product.

1-bromo-4-(4-methylbenzyl)benzene[16] *and 1-bromo-2-(4-methyl benzyl)benzene*[17] *(>20:1) (**3a**).* Following the general procedure, the crude residue was purified by column chromatography on silica gel (eluted with petroleum ether) to afford pure **3a** as a colourless oil (102 mg, 78%, 110 mg, 84%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 (d, J = 8.4 Hz, 2H), 7.46-7.42 (m, 1H), 7.32 (t, J = 7.4 Hz, 2H), 7.26-7.24 (m, 1H), 7.18 (d, J = 7.3 Hz, 2H), 7.10-7.03 (m, 6H), 4.07 (s, 0.05H), 3.88 (s, 2H), 2.31 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 140.4, 137.4, 135.8, 131.5, 130.6, 129.3, 128.8, 119.9, 40.9, 21.0. The carbons of the minor product

did not show on the ^{13}C NMR spectra due to the low concentration and limited scanning times.

*1-Benzyl-4-methylbenzene (**3b**)*[17] Following the general procedure, the crude residue was purified by column chromatography on silica gel (eluted with petroleum ether) to afford pure **3b** as a colorless oil (70 mg, 77%). ^1H NMR (400 MHz, $CDCl_3$) δ 7.26-7.25 (m, 2H), 7.19-7.16 (m, 3H), 7.08 (s, 4H), 3.93 (s, 2H), 2.30 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 141.5, 138.1, 135.6, 129. 2, 128.9, 128.9, 128.5, 126.0, 41.6, 21.1.

*1-methoxy-4-(4-methylbenzyl)benzene (**3c**)*[17] Following the general procedure, the crude residue was purified by column chromatography on silica gel (eluted with petroleum ether) to afford **3c** as a colorless oil (78 mg, 74%). ^1H NMR (400 MHz, $CDCl_3$) δ 7.10-7.04 (m, 6H), 6.81 (d, J = 8.6 Hz, 2H), 3.88 (s, 2H), 3.77 (s, 3H), 2.30 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.9, 138.6, 135.4, 133.6, 129.8, 129.1, 128.7, 113.9, 55.3, 40.6, 21.0.

1-(tert-Butyl)-4-(4-methylbenzyl)benzene[17] *and 1-(tert-butyl)-2-(4-methylbenzyl)benzene (6:1) (**3d**).* Following the general procedure, the crude residue was purified by column chromatography on silica gel (eluted with petroleum ether) to afford **3d** as a colorless oil (83 mg, 70%). ^1H NMR (400 MHz, $CDCl_3$) δ 7.29 (d, J = 8.3 Hz, 2H), 7.12 (s, 1H), 7.10-7.08 (m, 5H), 3.94 (s, 0.3H), 3.91 (s, 1.8H), 1.30 (s, 1.3H), 1.29 (s, 7.8H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 148.7, 138.4, 138.3, 135.5, 129.1, 128.8, 128.4, 125.3, 41.0, 34.4, 31.4, 21.0. The carbons of the minor product did not show on the ^{13}C NMR spectra due to the low concentration and limited scanning times.

1-Methyl-2-(4-methylbenzyl)benzene[18] *and 1-methyl-4-(4-methylbenzyl)benzene*[18] *(9:1) (**3e**).* Following the general procedure, the crude residue was purified by column chromatography on silica gel (eluted with petroleum ether) to afford **3e** as a colourless oil (44 mg, 45%). ^1H NMR (400 MHz, $CDCl_3$) δ 7.15-7.12 (m, 3H), 7.09-7.06 (m, 3H), 7.01 (d, J = 8.0 Hz, 2H), 3.94 (s, 1.8H), 3.90 (s. 0.2H), 2.31 (s, 3.3H), 2.24 (s, 2.7H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 139.2, 138.4 (minor), 137.3, 136.6, 135.5 (minor), 135.4, 130.3, 129.9, 129.1 (minor), 128.8 (minor), 128.7, 126.4, 126.0, 41.1 (minor), 39.0, 21.0, 19.7. The carbons of the minor product did not show on the ^{13}C NMR spectra due to the low concentration and limited scanning times.

1-(4-Methylbenzyl)naphthalene[19] *and 2-(4-methylbenzyl) naphthalene*[20] *(8:1) (**3f**).* Following the general procedure, the crude residue was purified by column chromatography on silica gel (eluted with petroleum ether) to afford **3f** as a colourless oil (70 mg, 60%). ^1H NMR (400 MHz, $CDCl_3$) δ 8.00-7.98 (m, 1H), 7.85-7.83 (m, 1H), 7.74 (d, J = 8.3 Hz, 1H), 7.45-7.38 (m, 3H), 7.28-7.27 (m, 1H), 7.11-7.05 (m, 4H), 4.40 (s, 1.8H), 4.09 (s. 0.2H), 2.31 (s, 0.4H), 2.29 (s, 2.6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 137.6, 136.9, 135.5, 134.0, 132.2, 129.2 (minor), 129.2, 128.9 (minor), 128.7, 128.7, 128.1 (minor), 127.6 (minor), 127.6 (minor), 127.3, 127.1, 127.0 (minor), 126.0, 125.6, 125.6, 125.3 (minor), 124.3, 41.7 (minor), 38.6, 21.0. The other carbons of the minor product did not show on the ^{13}C NMR spectra due to the low concentration and limited scanning times.

2-(4-Methylbenzyl)furan[21] *and 3-(4-methylbenzyl)furan (16:1) (**3g**).* Following the general procedure, the crude residue was purified by column chromatography on silica gel (eluted with petroleum ether) to afford **3g** as a colourless oil (37 mg, 43%). ^1H NMR (400 MHz, $CDCl_3$) δ 7.31 (d, J = 1.0 Hz, 1H), 7.12-7.10 (m, 4H), 6.38 (dd, J = 3.1, 1.9 Hz, 1H), 5.99 (dd, J = 3.1, 0.7 Hz, 1H), 3.93 (s, 2H), 3.73 (s, 0.1H), 2.32 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.9, 141.4, 136.0, 135.1, 129.2, 128.6, 110.2, 106.0, 34.1, 21.1. The other carbons of the minor product did not show on the ^{13}C NMR spectra due to the low concentration and limited scanning times.

2-(4-Methylbenzyl)furan[21] *and 3-(4-methylbenzyl)furan (5:2) (**3g**).* Following the general procedure, the crude residue was purified by column chromatography on silica gel (eluted with petroleum ether) to afford **3g** as a colourless oil (34 mg, 39%). ^1H NMR (400 MHz, $CDCl_3$) δ 7.34 (s, 0.3H), 7.31 (s, 0.7H), 7.20 (s, 0.3H), 7.11 (s, 3H), 7.10 (s, 1H), 6.28-6.27 (m, 0.7H), 6.23 (s, 0.3H), 5.98 (d, J = 3.1 Hz, 0.7H), 3.92 (s, 1.5H), 3.72 (s, 0.5H), 2.32 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.9, 143.0 (minor), 141.4, 139.5 (minor), 137.3 (minor), 136.0, 135.6 (minor), 135.1, 129.2, 129.1 (minor), 128.6, 128.4 (minor), 124.5 (minor), 111.2 (minor), 110.2, 106.0, 34.1, 30.8 (minor), 21.0.

2-(4-Methylbenzyl)thiophene[22] *and 3-(4-methylbenzyl) thiophene*[22] *(3:2) (**3h**).* Following the general procedure, the crude residue was purified by column chromatography on silica gel (eluted with petroleum ether) to afford pure **3h** as a pale yellow oil (42 mg, 45%). ^1H NMR (400 MHz, $CDCl_3$) δ 7.23-7.21 (m, 0.5H), 7.14-7.09 (m, 4.5H), 6.91-6.89 (m, 1.4H), 6.78-6.77 (m, 0.6H), 4.10 (s, 1.2H), 3.93 (s, 0.8H), 2.31 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.5 (minor), 141.9, 137.6, 137.4 (minor), 136.1 (minor), 135.7, 129.3, 129.2 (minor), 128.7, 128.5, 128.5 (minor), 126.8 (minor), 125.6, 125.0 (minor), 123.9 (minor), 121.1, 36.2, 35.7 (minor), 21.1, 21.1 (minor).

2-(4-Methylbenzyl)thiophene[22] *with 3-(4-methylbenzyl) thiophene*[22] *(5:4) (**3h**).* Following the general procedure, the crude residue was purified by column chromatography on silica gel (eluted with petroleum ether) to afford **3h** as a pale yellow oil (41 mg, 44%). ^1H NMR (400 MHz, $CDCl_3$) δ 7.24-7.22 (m, 0.6H), 7.15-7.09 (m, 4.4H), 6.92-6.89 (m, 1.5H), 6.79-6.78 (m, 0.5H), 4.11 (s, 1.1H), 3.93 (s, 0.9H), 2.32 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.5 (minor), 141.8, 137.6, 137.4 (minor), 136.0 (minor), 135.6, 129.2, 129.2 (minor), 128.6, 128.5, 128.5 (minor), 126.8 (minor), 125.6, 125.0 (minor), 123.8 (minor), 121.1, 36.1, 35.7 (minor), 21.1, 21.0 (minor).

1-Benzyl-4-bromobenzene[17] *with 1-benzyl-2-bromobenzene*[23] *(17:1) (**3i**).* Following the general procedure, the crude residue was purified by column chromatography on silica gel (eluted with petroleum ether) to afford **3i** as a colourless oil (82 mg, 63%). ^1H NMR (400 MHz, $CDCl_3$) δ 7.38 (d, J = 8.3 Hz, 2H), 7.29-7.26 (m, 2H), 7.21-7.13 (m, 3H), 7.04 (d, J = 8.3 Hz, 2H), 4.11 (s, 0.1H), 3.91 (s, 1.9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 140.5, 140.2, 131.6, 130.7, 128.9, 128.6, 126.4, 120.0, 41.3. The carbons of the minor product did not show on the ^{13}C NMR spectra due to the low concentration and limited scanning times.

*1-(4-Bromobenzyl)-2-methylbenzene (**3j**).*[17] Following the general procedure, the crude residue was purified by column chromatography on silica gel (eluted with petroleum ether) to afford **3j** as a colourless oil (106 mg, 81%). ^1H NMR (400 MHz, $CDCl_3$) δ 7.26 (d, J = 8.4 Hz, 2H), 7.06-7.03 (m, 3H), 6.97-6.95 (m, 1H), 6.87 (d, J = 8.3 Hz, 2H), 3.81 (s, 2H), 2.10 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 139.5, 138.3, 136.6, 131.5, 130.5, 130.5, 130.0, 126.8, 126.2, 119.8, 39.0, 19.7.

4-(4-Bromobenzyl)-1,1'-biphenyl[24] *with 4-(2-bromobenzyl)-1,1'-biphenyl (19:1) (**3k**).* Following the general procedure, the crude residue was purified by column chromatography on silica gel

(eluted with petroleum ether) to afford **3k** as a white solid (87 mg, 54%). IR (film) 3026, 1486, 1011, 760, 737 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.56-7.54 (m, 2H), 7.49 (d, J = 8.2 Hz, 2H), 7.41-7.38 (m, 4H), 7.32-7.30 (m, 1H), 7.19 (d, J = 8.1 Hz, 2H), 7.06 (d, J = 8.3 Hz, 2H), 4.13 (s, 0.1H), 3.92 (s, 1.9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 140.9, 140.1, 139.6, 139.4, 131.7, 130.8, 129.4, 128.8, 127.4, 127.3, 127.1, 120.1, 41.0. The carbons of the minor product did not show on the ^{13}C NMR spectra due to the low concentration and limited scanning times.

*1-Bromo-4-cinnamylbenzene (**3l**).*[25] Following the general procedure, the crude residue was purified by column chromatography on silica gel (eluted with petroleum ether) to afford **3l** as a colourless oil (26 mg, 19%). ^1H NMR (400 MHz, $CDCl_3$) δ 7.42 (d, J = 8.3 Hz, 2H), 7.35-7.33 (m, 2H), 7.31-7.27 (m, 2H), 7.22-7.19 (m, 1H), 7.11 (d, J = 8.2 Hz, 2H), 6.43 (d, J = 15.8 Hz, 1H), 6.30 (dt, J = 15.7, 6.7 Hz, 1H) , 3.49 (d, J = 6.7 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 139.1, 137.3, 131.6, 130.4, 128.6, 128.4, 127.3, 126.2, 120.0, 38.7.

General Procedure for the Preparation of Benzyl Mesylates

To a flask that was charged with the benzyl alcohol (10 mmol), triethylamine (20 mmol) in THF (25 mL) cooled at 0 ^oC, was added mesyl chloride (20 mmol) in THF (50 mL) over half an hour. Then the mixture was allowed to stir at room temperature for about 20-30 min. Cold water was added to the mixture, then the mixture was extracted with diethyl ether (125 mL x 1). Triethylamine (5 mol) was added into the crude product solution to remove the unreacted mesyl chloride. Then the solution was washed with saturated aqueous $NaHCO_3$ (10 mL), cold water (25 mL) and brine (25 mL). The solution was dried over anhydrous Na_2SO_4. Removal of the solvent under reduced pressure gave the benzyl mesylate products, which are used in the coupling reaction without further purification.

*Benzyl methanesulfonate (**4a**).* Following the general procedure, **4a** was obtained as a colourless oil (1.39 g, 75%). ^1H NMR (400 MHz, $CDCl_3$) δ 7.43-7.39 (m, 5H), 5.24 (s, 2H), 2.90 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 133.4, 129.4, 128.9, 128.9, 71.6, 38.4.

*2-Methylbenzyl methanesulfonate **(4b).*** Following the general procedure, **4b** was obtained as a pale yellow oil (1.54 g, 77%). ^1H NMR (400 MHz, $CDCl_3$) δ 7.36-7.28 (m, 2H), 7 .23-7.17(m, 2H), 5.25 (s, 2H), 2.86 (s, 3H), 2.40 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 137.8, 131.4, 130.8, 130.3, 129.9, 126.3, 70.2, 38.2, 18.8.

*2-Bromobenzyl methanesulfonate (**4c**).* Following the general procedure, **4c** was obtained as a pale yellow oil (2.09 g, 79%). ^1H NMR (400 MHz, $CDCl_3$) δ 7.61 (dd, J = 8.0, 0.8 Hz, 1H), 7.50 (dd, J = 7.6, 1.4 Hz, 1H), 7.37 (td, J = 7.5, 0.9 Hz, 1H), 7.26 (td, J = 7.8, 1.6 Hz, 1H), 5.32 (s, 2H), 3.02 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 133.1, 132.9, 130.9, 130.8, 127.9, 123.8, 70.9, 38.0.

*2-Chlorobenzyl methanesulfonate (**4d**).* Following the general procedure, **4d** was obtained as a pale yellow oil (1.85 g, 84%). ^1H NMR (400 MHz, $CDCl_3$) δ 7.51-7.49 (m, 1H), 7.44-7.42 (m, 1H), 7.37-7.30 (m, 2H), 5.34 (s, 2H), 3.02 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 134.1, 131.3, 130.8, 130.8, 129.8, 127.3, 68.7, 38.0.

*4-Bromobenzyl methanesulfonate (**4e**).* Following the general procedure, **4e** was obtained as a pale yellow oil (1.96 g, 74%). ^1H NMR (400 MHz, $CDCl_3$) δ 7.55 (d, J = 8.4 Hz, 2H), 7.30 (d, J = 8.3 Hz, 2H), 5.19 (s, 2H), 2.95 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 132.5, 132.1, 130.4, 123.7, 70.4, 38.4.

*3-Iodobenzyl methanesulfonate (**4f**).* Following the general procedure, **4f** was obtained as a white solid (2.63 g, 84%). ^1H NMR (400 MHz, $CDCl_3$) δ 7.76-7.72 (m, 2H), 7 .38 (d, J = 7.6 Hz, 1H), 7.15 (t, J = 7.8 Hz, 1H), 5.16 (s, 2H), 2.97 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 138.4, 137.5, 135.7, 130.6, 127.8, 94.4, 70.0, 38.3.

*[1,1'-Biphenyl]-4-ylmethyl methanesulfonate (**4g**).* Following the general procedure, **4g** was obtained as a white solid (2.03 g, 77%). ^1H NMR (400 MHz, $CDCl_3$) δ 7.64-7.57 (m, 4H), 7.50-7.43 (m, 4H), 7.38-7.35 (m, 1H), 5.28 (s, 2H), 2.94 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 142.4, 140.2, 132.3, 129.4, 128.9, 127.8, 127.6, 127.2, 71.3, 38.4.

*3-Nitrobenzyl methanesulfonate (**4i**).* Following the general procedure, **4i** was obtained as a white solid (1.87 g, 81%). ^1H NMR (400 MHz, $CDCl_3$) δ 8.28-8.24 (m, 2H), 7 .78 (d, J = 7.7 Hz, 1H), 7.62 (t, J = 7.9 Hz, 1H), 5.34 (s, 2H), 3.09 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 148.4, 135.8, 134.3, 130.1, 124.1, 123.2, 69.2, 38.2.

*Methyl 4-(((methylsulfonyl)oxy)methyl)benzoate (**4j**).* Following the general procedure, **4j** was obtained as a white solid (1.93 g, 79%). ^1H NMR (400 MHz, $CDCl_3$) δ 8.08 (d, J = 8.3 Hz, 2H), 7 .49 (d, J = 8.3 Hz, 2H), 5.29 (s, 2H), 3.93 (s, 3H), 2.98 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.4, 138.3, 131.0, 130.1, 70.2, 52.3, 38.3.

*3-Phenylprop-2-yn-1-yl methanesulfonate (**4l**).* Following the general procedure, **4l** was obtained as a pale yellow oil (1.69 g, 80%). ^1H NMR (400 MHz, $CDCl_3$) δ 7.47-7.45 (m, 2H), 7.39-7.32 (m, 3H), 5.09 (s, 2H), 3.16 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 131.9, 129.5, 128.5, 121.2, 89.4, 80.8, 58.4, 39.1.

*Phenethyl methanesulfonate (**4m**).* Following the general procedure, **4m** was obtained as a pale yellow oil (1.52 g, 76%). ^1H NMR (400 MHz, $CDCl_3$) δ 7.35-7.31 (m, 2H), 7.28-7.23 (m, 3H), 4.42 (t, J = 6.9 Hz, 2H), 3.05 (t, J = 6.9 Hz, 2H), 2.83 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 136.4, 129.0, 128.7, 127.1, 70.3, 37.3, 35.7.

General Procedure for the Preparation of Benzyl phosphates

Benzyl alcohol (10 mmol), DMAP (1 mmol) and triethylamine (11 mmol) were dissolved in THF (100 mL). The diethyl chlorophosphate (11 mmol) was added *via* syringe over 30 min. The mixture was allowed to react at room temperature overnight. Then the mixture was quenched with saturated aqueousNH_4Cl, extracted with diethyl ether (75 mL x 3). The combined organic phase was dried over anhydrous Na_2SO_4 and then concentrated to give the crude product, which was purified by column chromatography (eluted with petroleum ether:ethyl acetate = 5:1 to 2:1).

*4-Methoxybenzyl phosphate (**4h**).* Following the general procedure, **4h** was obtained as a colourless oil (1.88 g, 69%). ^1H NMR (400 MHz, $CDCl_3$) δ 7.33 (d, J = 8.7 Hz, 2H), 6.89 (d, J = 8.7 Hz, 2H), 5.00 (d, J = 8.4 Hz, 2H), 4.09-4.04 (m, 4H), 3.81 (s, 3H), 1.18 (t, J = 7.0 Hz, 6H, overlapped); ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.8, 129.8, 128.2 (J_{CP} = 6.5 Hz), 113.9, 68.9 (J_{CP} = 5.5 Hz), 63.7 (J_{CP} = 5.8 Hz), 55.3, 16.1 (J_{CP} = 6.9 Hz).

*Cinnamyl diethyl phosphate (**4k**).* Following the general procedure, **4k** was obtained as a colourless oil (1.70 g, 65%). ^1H

NMR (400 MHz, $CDCl_3$) δ 7.41-7.38 (m, 2H), 7.35-7.31 (m, 2H), 7.28-7.25 (m, 1H), 6.68 (d, *J* = 15.9 Hz, 1H), 6.31 (dt, *J* = 15.8, 6.2 Hz, 1H), 4.72-4.68 (m, 2H), 4.17-4.10 (m, 4H), 1.34 (t, *J* = 7.1 Hz, 6H, overlapped); ^{13}C NMR (101 MHz, $CDCl_3$) δ 136.1, 133.9, 128.6, 128.2, 126.7, 123.6 (J_{CP} = 6.8 Hz), 67.9 (J_{CP} = 5.6 Hz), 63.8 (J_{CP} = 5.8 Hz), 16.1 (J_{CP} = 6.7 Hz).

Reaction of Benzyl Mesylates with Arylboronic Acids

Arylboronic acid (0.5 mmol), KF (1.0 mmol) were added to a Schlenk tube. The tube was charged with nitrogen and then DCE (2 mL) and benzyl esters (0.75 mmol) were added. The mixture was stirred at 70 ^{o}C for 10-24 h. After the mixture was cooled down to room temperature, solvent was removed to give a crude product, which was purified by column chromatography on silica gel, eluted with petroleum ether or petroleum ether:ethyl acetate = 30:1 to afford the product. In some cases, the reaction was carried out at 100 ^{o}C with LiO^tBu as the base, as indicated in Scheme 4.

*Diphenylmethane (**5a**).*[2h] Following the general procedure, the crude residue was purified by column chromatography on silica gel (eluted with petroleum ether) to afford pure **5a** as a colourless oil (66 mg, 77%). ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 7.31-7.27 (m, 4H), 7.21-7.19 (m, 6H), 3.99 (s, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) *δ* 141.2, 129.0, 128.5, 126.1, 42.0.

*1-Benzyl-4-bromobenzene (**5b**).*[17] Following the general procedure, the crude residue was purified by column chromatography on silica gel (eluted with petroleum ether) to afford **5b** as a colourless oil (104 mg, 84%). ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 7.39-7.36 (m, 2H), 7.29-7.25 (m, 2H), 7.21-7.17 (m, 1H), 7.15-7.13 (m, 2H), 7.04-7.02 (m, 2H), 3.90 (s, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) *δ* 140.5, 140.2, 131.6, 130.7, 128.9, 128.6, 126.4, 120.0, 41.4.

1-Benzyl-4-chlorobenzene (**5c**).[26] Following the general procedure, the crude residue was purified by column chromatography on silica gel (eluted with petroleum ether) to afford **5c** as a colourless oil (71 mg, 70%). ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 7.29-7.19 (m, 5H), 7.17-7.13 (m, 2H), 7.10-7.08 (m, 2H), 3.92 (s, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) *δ* 140.6, 139.6, 132.0, 130.3, 128.9, 128.6, 126.3, 41.3.

*1-Benzyl-4-methoxybenzene (**5d**).*[27] Following the general procedure, the crude residue was purified by column chromatography on silica gel (eluted with petroleum ether) to afford **5d** as a colourless oil (96 mg, 97%). ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 7.29-7.24 (m, 2H), 7.20-7.16 (m, 3H), 7.10 (d, *J* = 8.6 Hz, 2H), 6.82 (d, *J* = 8.6 Hz, 2H), 3.92 (s, 2H), 3.77 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) *δ* 158.0, 141.6, 133.3, 129.9, 128.8, 128.4, 126.0, 113.9, 55.3, 41.1.

Methyl 4-benzylbenzoate[17] *and methyl 3-benzylbenzoate (2.5:1) (**5e**).* Following the general procedure, the crude residue was purified by column chromatography on silica gel (eluted with petroleum ether:ethyl acetate = 30:1) to afford **5e** as a colourless oil (57 mg, 45%). ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 7.95 (d, *J* = 8.2 Hz, 1.4H), 7.90-7.87 (m, 0.6H), 7.35-7.15 (m, 7H), 4.01 (s, 2H), 3.88 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) *δ* 167.2 (minor), 167.1, 146.5, 141.5 (minor), 140.5 (minor), 140.1, 133.6 (minor), 130.4 (minor), 130.1 (minor) 129.8, 129.0, 128.9 (minor), 128.6, 128.6 (minor), 128.6 (minor), 128.1, 127.5 (minor), 126.4, 126.3 (minor), 52.1 (minor), 52.0, 41.9, 41.7 (minor).

1-Benzyl-4-(tert-butyl)benzene[28] *and 1-benzyl-3-(tert-butyl) benzene (2.5:1) (**5f**).* Following the general procedure, the crude residue was purified by column chromatography on silica gel (eluted with petroleum ether) to afford pure **5f** as a colourless oil (68 mg, 61%). ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 7.30-7.16 (m, 7.3H), 7.12-7.10 (m, 1.4H), 6.97-6.96 (m, 0.3H), 3.97 (s, 0.5H), 3.94 (s, 1.4H), 1.29 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) *δ* 151.3 (minor), 148.9, 141.3, 140.7 (minor), 138.1, 129.0, 129.0 (minor), 128.6, 128.5, 128.2 (minor), 126.1 (minor), 126.0, 126.0 (minor), 125.4, 123.1 (minor), 42.3 (minor), 41.5, 34.7 (minor), 34.4, 31.5, The other carbons of the minor product did not show on the ^{13}C NMR spectra due to the low concentration and limited scanning times.

1-Benzyl-2-methylbenzene[28] *and 1-benzyl-3-methylbenzene*[28] *(9:1) (**5g**).* Following the general procedure, the crude residue was purified by column chromatography on silica gel (eluted with petroleum ether) to afford **5g** as a colourless oil (76 mg, 83%). ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 7.27-7.23 (m, 2H), 7.19-7.09 (m, 6.7H), 7.00-6.97 (m, 0.3H), 3.97 (s, 1.8H), 3.93 (s, 0.2H), 2.30 (s, 0.3H), 2.23 (s, 2.7H); ^{13}C NMR (101 MHz, $CDCl_3$) *δ* 141.3 (minor), 141.1 (minor), 140.5, 139.0, 138.1 (minor), 136.7, 130.3, 130.0, 129.8 (minor), 129.0, 128.8, 128.5 (minor), 128.5, 128.4 (minor), 126.9 (minor), 126.5, 126.0, 126.0, 42.0 (minor), 39.5, 21.5 (minor), 19.7. The other carbons of the minor product did not show on the ^{13}C NMR spectra due to the low concentration and limited scanning times.

1-Benzylnaphthalene[25] *and 2-benzylnaphthalene (C^1:C^2 = 2:1) (**5h**).* Following the general procedure, the crude residue was purified by column chromatography on silica gel (eluted with petroleum ether) to afford **5h** as a white solid (67 mg, 60%). ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 7.98-7.96 (m, 0.7H), 7.84-7.81 (m, 0.7H), 7.77-7.72 (m, 1.6H), 7.60 (s, 0.3H), 7.43-7.37 (m, 2.7H), 7.25-7.17 (m, 6H), 4.42 (s, 1.4H), 4.11 (s, 0.6H); ^{13}C NMR (101 MHz, $CDCl_3$) *δ* 141.1 (minor), 140.7, 138.7 (minor), 136.7, 134.1, 133.7 (minor), 132.3, 132.2 (minor), 129.1 (minor), 128.8, 128.8 (minor), 128.6, 128.5, 128.2 (minor), 127.7 (minor), 127.7 (minor), 127.4, 127.2, 127.2 (minor), 126.3 (minor), 126.2 , 126.1, 125.6, 125.4 (minor), 124.4, 42.2 (minor), 39.1.

2-Benzylfuran[2e] *and 3-benzylfuran*[2e] *(5:1) (**5i**).* Following the general procedure, the crude residue was purified by column chromatography on silica gel (eluted with petroleum ether) to afford **5i** as a colourless oil (32 mg, 41%). ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 7.35 (s, 0.2H), 7.32-7.20 (m, 6H), 6.28 (dd, *J* = 3.0, 1.9 Hz, 0.8H), 6.24 (s, 0.2H), 6.00 (d, *J* = 3.1 Hz, 0.8H), 3.97 (s, 1.7H), 3.77 (s, 0.3H); ^{13}C NMR (101 MHz, $CDCl_3$) *δ* 154.6, 143.1 (minor), 141.5, 139.6 (minor), 138.2, 128.7, 128.6 (minor), 128.5, 128.4 (minor), 126.5, 126.2 (minor), 111.3 (minor), 110.2, 106.2, 34.5, 31.2 (minor). The other carbons of the minor product did not show on the ^{13}C NMR spectra due to the low concentration and limited scanning times.

2-Benzylthiophene[2e] *and 3-benzylthiophene*[2e] *(2:1) (**5j**).* Following the general procedure, the crude residue was purified by column chromatography on silica gel (eluted with petroleum ether) to afford **5j** as a pale yellow oil (45 mg, 52%); ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 7.31-7.18 (m, 5.3H), 7.13-7.12 (m, 0.7H), 6.92-6.89 (m, 1.3H), 6.79-6.78 (m, 0.7H), 4.15 (s, 1.3H), 3.97 (s, 0.7H); ^{13}C NMR (101 MHz, $CDCl_3$) *δ* 144.1, 141.5 (minor), 140.6 (minor), 140.4, 128.8 (minor), 128.6 (minor), 128.6, 128.5, 126.8, 126.5, 126.2 (minor), 125.6 (minor), 125.2, 124.0, 121.3 (minor), 36.6 (minor), 36.1.

*1-Benzyl-2-methylbenzene (**5k**).*[17] Following the general procedure, the crude residue was purified by column chromatography on silica gel (eluted with petroleum ether) to

afford **5k** as a colourless oil (73 mg, 80%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28-7.24 (m, 2H), 7.20-7.09 (m, 7H), 3.98 (s, 2H), 2.24 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ ^{13}C NMR (101 MHz, $CDCl_3$) δ 140.4, 138.9, 136.6, 130.3, 130.0, 128.8, 128.4, 126.5, 126.0, 125.9, 39.5, 19.7.

*1-(4-Methoxybenzyl)-2-methylbenzene (**5l**).*[29] Following the general procedure, the crude residue was purified by column chromatography on silica gel (eluted with petroleum ether) to afford **5l** as a colourless oil (103 mg, 97%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.13-7.06 (m, 4H), 7.02 (d, J = 8.5 Hz, 2H), 6.80 (d, J = 8.5 Hz, 2H), 3.90 (s, 2H), 3.75 (s, 3H), 2.22 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.9, 139.4, 136.6, 132.5, 130.3, 129.9, 129.7, 126.4, 126.1, 113.9, 55.3, 38.6, 19.7.

*1-Bromo-2-(4-methoxybenzyl)benzene (**5m**).* Following the general procedure, the crude residue was purified by column chromatography on silica gel (eluted with petroleum ether) to afford **5m** as a colourless oil (115 mg, 83%). IR (film) 2828, 1609, 1511, 1246, 1026, 743 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 (d, J = 8.0 Hz 1H), 7.23-7.19 (m, 1H), 7.11-7.06 (m, 4H), 6.83 (d, J = 8.6 Hz, 2H), 4.04 (s, 2H), 3.77 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.1, 140.8, 132.9, 131.6, 131.0, 130.0, 127.8, 127.5, 124.8, 113.9, 55.3, 40.9.

*2-(2-Bromobenzyl)furan and 3-(2-bromobenzyl)furan (9:1) (**5n**).* Following the general procedure, the crude residue was purified by column chromatography on silica gel (eluted with petroleum ether) to afford **5n** as a colourless oil (45 mg, 38%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 (d, J = 7.5 Hz, 1H), 7.26-7.21 (m, 3H), 7.12-7.09 (m, 4H), 4.08 (s, 0.2H), 4.07 (s, 1.8H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 139.8, 138.0, 133.0, 132.1, 131.1 (minor), 131.0, 130.3, 129.7 (minor), 129.0 (minor), 128.6, 128.2 (minor), 128.2, 127.6 (minor), 127.6, 127.2 (minor), 126.5 (minor), 124.9, 41.4 (minor), 41.1. The other carbons of the minor product did not show on the ^{13}C NMR spectra due to the low concentration and limited scanning times. EI-MS (*m/z*, relative intensity) 282 (M^+, 37), 280 (28), 247 (23), 245 (22), 201 (39), 166 (80), 165 (100), 82 (40).

*1-Bromo-2-(4-chlorobenzyl)benzene and 1-bromo-2-(3-chlorobenzyl)benzene (9:1) (**5o**).* Following the general procedure, the crude residue was purified by column chromatography on silica gel (eluted with petroleum ether) to afford **5o** as a pale yellow oil (108 mg, 77%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 (d, J = 8.0 Hz, 1H), 7.36-7.34 (m, 1H), 7.24-7.17 (m, 2H), 7.09 (dt, J = 7.8, 1.8 Hz, 1H), 6.30 (dd, J = 2.9, 2.0 Hz, 0.9H), 6.28 (s, 0.1H), 6.03 (d, J = 2.7 Hz, 1H), 4.10 (s, 1.8H), 3.89 (s, 0.2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.2, 141.6, 137.7, 132.8, 130.7, 128.2, 127.5, 124.5, 110.4, 107.0, 34.7. The other carbons of the minor product did not show on the ^{13}C NMR spectra due to the low concentration and limited scanning times.

*1-Benzyl-2-chlorobenzene (**5p**).*[17] Following the general procedure, the crude residue was purified by column chromatography on silica gel (eluted with petroleum ether) to afford **5p** as a colourless oil (84 mg, 84%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37-7.35 (m, 1H), 7.30-7.27 (m, 2H), 7.22-7.12 (m, 6H), 4.10 (s, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 139.5, 138.7, 134.3, 131.0, 129.6, 129.0, 128.5, 127.7, 126.8, 126.3, 39.2.

*1-Chloro-2-(4-methoxybenzyl)benzene (**5q**)*[30] Following the general procedure, the crude residue was purified by column chromatography on silica gel (eluted with petroleum ether) to afford **5q** as a colourless oil (106 mg, 91%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25-7.23 (m, 1H), 7.03-6.99 (m, 5H), 6.72 (d, J = 8.6 Hz, 2H), 3.93 (s, 2H), 3.65 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.2, 139.2, 134.2, 131.6, 130.9, 130.0, 129.6, 127.6, 126.9, 114.0, 55.3, 38.4

1-Chloro-2-(2-methylbenzyl)benzene and 1-chloro-2-(3-methylbenzyl)benzene[31] *(9:1) (**5r**).* Following the general procedure, the crude residue was purified by column chromatography on silica gel (eluted with petroleum ether) to afford **5r** as a colourless oil (84 mg, 77%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40-7.38 (m, 1H), 7.25-7.13 (m, 5H), 7.00-6.98 (m, 1.2H), 6.90-6.88 (m, 0.9H), 4.06 (s, 2H), 2.31 (s, 0.3H), 2.24 (s, 2.7H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 138.0, 137.5, 136.8, 134.3, 131.0 (minor), 130.3, 129.7 (minor), 129.7, 129.5 (minor), 129.3, 128.4 (minor), 127.5, 127.0 (minor), 126.8, 126.6, 126.1, 126.0 (minor), 36.7, 19.5. The other carbons of the minor product did not show on the ^{13}C NMR spectra due to the low concentration and limited scanning times.

*1-Bromo-4-(4-methoxybenzyl)benzene (**5s**).*[30] Following the general procedure, the crude residue was purified by column chromatography on silica gel (eluted with petroleum ether) to afford **5s** as a white solid (127 mg, 92%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 (d, J = 8.4 Hz, 2H), 7.07-7.02 (m, 4H), 6.82 (d, J = 8.6 Hz, 2H), 3.86 (s, 2H), 3.77 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.2, 140.6, 132.6, 131.5, 130.6, 129.8, 119.8, 114.0, 55.3, 40.4.

*1-Benzyl-3-iodobenzene (**5t**).* Following the general procedure, the crude residue was purified by column chromatography on silica gel (eluted with petroleum ether) to afford **5t** as a colourless liquid (109 mg, 74%); IR (film) 1562, 1494, 1063, 768, 700, 657 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55-7.52 (m, 2H), 7.31-7.27 (m, 2H), 7.24-7.21 (m, 1H), 7.19-7.13 (m, 3H), 7.02-6.98 (m, 1H), 3.91 (s, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.6, 140.2, 137.9, 135.2, 130.2, 128.9, 128.6, 128.2, 126.4, 94.6, 41.5; EI-MS (m/z, relative intensity) 294 (M^+, 98), 167 (100), 165 (96), 152 (43), 83 (31), 63 (14), 28 (21).

*1-Iodo-3-(4-methoxybenzyl)benzene (**5u**).* Following the general procedure, the crude residue was purified by column chromatography on silica gel (eluted with petroleum ether) to afford **5u** as a white solid (134 mg, 83%). m.p. 38-40 ºC; IR (film) 2831, 1509, 1246, 1177, 1035, 807, 783, 688 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53-7.51 (m, 2H), 7.12 (d, J = 7.7 Hz, 1H), 7.07 (d, J = 8.6 Hz, 2H), 7.00 (t, J = 7.7 Hz, 1H), 6.83 (d, J = 8.6 Hz, 2H), 3.85 (s, 2H), 3.78 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.2, 144.1, 137.8, 135.1, 132.3, 130.2, 129.9, 128.1, 114.0, 94.6, 55.3, 40.6; EI-MS (*m/z*, relative intensity) 324 (M^+, 100), 197 (45), 166 (39), 153 (43), 121 (58), 91 (23), 76 (17).

*1-(4-Bromobenzyl)-3-iodobenzene and 1-bromo-3-(3-iodobenzyl)benzene (6:1) (**5v**).* Following the general procedure, the crude residue was purified by column chromatography on silica gel (eluted with petroleum ether) to afford **5v** as a colorless liquid (155 mg, 83%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55-7.51 (m, 2H), 7.40 (d, J = 8.3 Hz, 1.7H), 7.35-7.31 (m, 0.3H), 7.15-7.07 (m, 1.3H), 7.04-6.99 (m, 2.7H), 3.87 (s, 0.3H), 3.85 (s, 1.7H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 142.9, 142.6 (minor), 142.5 (minor), 139.2, 137.8 (minor), 137.8, 135.6 (minor), 135.5, 131.9 (minor), 131.7, 130.6, 130.3 (minor), 130.3, 130.2 (minor), 129.6 (minor), 128,2 (minor), 128.2, 127.6 (minor), 122.7 (minor), 120.3, 94.7, 41.0 (minor), 40.8.

*4-(4-Methoxybenzyl)-1,1'-biphenyl (**5w**).* Following the general procedure, the crude residue was purified by column chromatography on silica gel (eluted with petroleum ether : ethyl acetate = 30:1) to afford **5i** as a white solid (127 mg, 93%). m.p. 83-86 ºC; IR (film) 1510, 1247, 1036, 750, 696, 652 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.56 (d, J = 7.6 Hz, 2H), 7.52-7.50 (m, 2H), 7.41 (t, J = 7.6 Hz, 2H), 7.33-7.30 (m, 1H), 7.25-7.23 (m, 2H), 7.14 (d, J = 8.6 Hz, 2H), 6.85 (d, J = 8.6 Hz, 2H), 3.96 (s, 2H), 3.79 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.1, 141.1, 140.7, 139.0, 133.1, 129.9, 129.2, 128.7, 127.2, 127.1, 127.0, 114.0, 55.3, 40.7; EI-MS (*m/z*, relative intensity) 274 (M^+, 100), 272 (31), 243 (23), 197 (13), 165 (35), 121 (23), 77(11).

*Bis(4-methoxyphenyl)methane (**5x**).*[30] Following the general procedure, the crude residue was purified by column chromatography on silica gel (eluted with petroleum ether:ethyl acetate = 30 : 1) to afford **5x** as a white solid (104 mg, 91%): ^1H NMR (400 MHz, $CDCl_3$) δ 7.08 (d, J = 8.6 Hz, 4H), 6.82 (d, J = 8.6 Hz, 4H), 3,86 (s, 2H), 3.76 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.9, 133.7, 129.7, 113.9, 55.3, 40.1.

*1-(tert-Butyl)-4-(4-methoxybenzyl)benzene and 1-(tert-butyl)-3-(4-methoxybenzyl) benzene (9:1) (**5y**).* Following the general procedure, the crude residue was purified by column chromatography on silica gel (eluted with petroleum ether) to afford pure **5y** as a colorless oil (58 mg, 46%); ^1H NMR (400 MHz, $CDCl_3$) δ 7.29 (d, J = 8.2 Hz, 2H), 7.12-7.09 (m, 4H), 6.84-6.81 (m, 2H), 3,92 (s, 0.2H), 3.89 (s, 1.8H), 3.77 (s, 3H), 1.29 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.9, 148.8, 138.6, 133.4, 129.9, 129.8 (minor), 128.4, 128.1 (minor), 125.9 (minor), 125.3, 113.9, 55.3, 41.3 (minor), 40.5, 34.4, 31.4, the other carbons of the minor product shown no signal due to the low concentration and limited scanning times; EI-MS (*m/z*, relative intensity) 254 (M^+, 42), 239 (100), 197 (21), 121 (46).

*1-(4-Methoxybenzyl)-3-nitrobenzene (**5z**).*[2e] Following the general procedure, the crude residue was purified by column chromatography on silica gel (eluted with petroleum ether:ethyl acetate = 10:1) to afford **5z** as a white solid (97 mg, 80%): ^1H NMR (400 MHz, $CDCl_3$) δ 8.06-8.04 (m, 2H), 7.51-7.44 (m, 2H), 7.10 (d, J = 8.5 Hz, 2H), 6.86 (d, J = 8.6 Hz, 2H), 4.02 (s, 2H), 3.79 (s, 3H), 2.23 (s, 2.70H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.4, 143.7, 135.0, 131.4, 129.9, 129.3, 123.6, 121.3, 114.2, 55.3, 40.6

*1-Benzyl-3-nitrobenzene (**6a**).*[2e] Following the general procedure, the crude residue was purified by column chromatography on silica gel (eluted with petroleum ether: ethyl acetate = 10:1) to afford **6a** as a white solid (51 mg, 48%). ^1H NMR (400 MHz, $CDCl_3$) δ 8.07-7.05 (m, 2H), 7.51 (d, J = 7.6 Hz, 1H), 7.46-7.42 (m, 1H), 7.32 (t, J = 7.4 Hz, 2H), 7.26-7.24 (m, 1H), 7.18 (d, J = 7.3 Hz, 2H), 4.08 (s, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 148.5, 143.2, 139.4, 135.1, 129.4, 128.9, 128.8, 126.8, 123.7, 121.4, 41.5.

*Methyl 4-benzylbenzoate (**6b**).*[2e] Following the general procedure, the crude residue was purified by column chromatography on silica gel (eluted with petroleum ether) to afford pure **6b** as a colourless liquid (64 mg, 57%); ^1H NMR (400 MHz, $CDCl_3$) δ 7.96-7.94 (m, 2H), 7.31-7.21 (m, 5H), 7.18-7.16 (m, 2H), 4.02 (s, 2H), 3.89 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.1, 146.5, 140.1, 129.8, 129.0, 128.6, 128.1, 126.4, 52.0, 41.9.

*1-Cinnamyl-4-methoxybenzene (**6c**).*[30] Following the general procedure, the crude residue was purified by column chromatography on silica gel (eluted with petroleum ether) to afford **6c** as a colourless oil (106 mg, 95%). ^1H NMR (400 MHz, $CDCl_3$) δ 7.36-7.34 (m, 2H), 7.30-7.26 (m, 2H), 7.21-7.14 (m, 3H), 6.86-6.84 (m, 2H), 6.43 (d, J = 15.8 Hz, 1H), 6.33(dt, J = 15.7, 6.5 Hz, 1H), 3.79 (s, 3H), 3.49 (d, J = 6.5 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.1, 137.6, 132.2, 130.8, 129.7, 129.6, 128.5, 127.1, 126.2, 114.0, 55.3, 38.5.

*1-Methyl-4-(3-phenylprop-2-yn-1-yl)benzene and 1-methyl-3-(3-phenylprop-2-yn-1-yl)benzene (3:1) (**6d**).* Following the general procedure, the crude residue was purified by column chromatography on silica gel (eluted with petroleum ether) to afford **6d** as a colourless oil (96 mg, 93%). ^1H NMR (400 MHz, $CDCl_3$) δ 7.45-7.42 (m, 2H), 7.31-7.27 (m, 4.5H), 7.32-7.31 (m, 0.8H), 7.14 (d, J = 7.9 Hz, 1.5H), 7.06-7.05 (m, 0.2H), 3.79 (s, 0.5H), 3.78 (s, 1.5H), 2.35 (s, 0.7H), 2.33 (s, 2.3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 138.2 (minor), 136.7 (minor), 136.2, 133.7, 131.7, 129.2, 128.8 (minor), 128.5 (minor), 128.2, 127.9, 127.8, 127.4 (minor), 125.0 (minor), 123.8, 87.9, 87.7 (minor), 82.5 (minor), 82.5, 25.7 (minor), 25.4, 21.4 (minor), 21.1. The other carbons of the minor product did not show on the ^{13}C NMR spectra due to the low concentration and limited scanning times.

*1,2-Diphenylethane (**6e**).*[32] Following the general procedure, the crude residue was purified by column chromatography on silica gel (eluted with petroleum ether) to afford **6e** as a white solid (30 mg, 33%). ^1H NMR (400 MHz, $CDCl_3$) δ 7.22-7.18 (m, 4H), 7.15-7.09 (m, 6H), 2.86 (s, 4H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 141.8, 128.5, 128.3, 125.9, 37.9.

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Supplementary data

Copies of ^{1}H and/or ^{13}C spectra for isolated products. This material is available free of charge *via* the Internet at xxxxxxx.