ORGANOMETALLICS

Palladium-Catalyzed Reductive Cross-Coupling Reaction of Aryl Chromium(0) Fischer Carbene Complexes with Aryl lodides

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S Supporting Information

ABSTRACT: The first palladium-catalyzed reductive cross-couplings of aryl chromium(0) carbene complexes with aryl iodides have been realized. This coupling reaction shows excellent functional group tolerance and high efficiency. Mechanistically, aryl chromium(0) carbene complexes undergo transmetalation with arylpalladium species to generate palladium(II) carbene intermediates, which is followed by migratory insertion. The catalytic cycle is then completed by hydrogen transfer and reductive elimination. Consistent with the mechanistic hypothesis, density functional theory (DFT) calculations support the involvement of a palladium carbene intermediate, and



carbene migratory insertion is a facile step with an energy barrier of 5.1 kcal/mol. The carbene transfer step and the hydrogen transfer step are confirmed as the rate-limiting steps in the catalytic cycle.

INTRODUCTION

Group 6 Fischer carbene complexes, as represented by chromium(0) Fischer carbenes, have been extensively studied over the decades, and they have been proven to be valuable in organic chemistry.¹ In general, the metal carbonyl fragments of these complexes can be viewed as functional groups to activate the carbenic carbon to an electrophilic center, similar to the case for a carbon in a carbonyl group.² The chromium(0) Fischer carbene complexes react with both nucleophiles and electrophiles or undergo cycloaddition reactions with alkenes or alkynes to form cyclic compounds.^{3,4} These transformations have found wide applications in synthetic organic chemistry due to the versatile chemical properties of the group 6 Fischer carbene complexes.

More importantly, the transfer of carbene ligands from the group 6 Fischer carbene complexes to other transition-metal centers, in particular the late transition metals, can generate new carbene complexes and thus significantly alter the chemical behavior of Fischer carbene complexes. Traditionally, the carbene ligand transfer from group 6 metals to other stoichiometric transition metal species has been known for a long time.⁵ The seminal work by Sierra and co-workers on palladiumcatalyzed self-dimerization of chromium(0) carbene complexes demonstrated potential applications of catalytic carbene transfer reactions with catalytic amounts of palladium catalyst.^{6,7} Previous experimental and mechanistic investigations have revealed that Pd(0) catalysts are highly efficient in catalyzing carbene transfer processes. As shown in Scheme 1a, the carbene ligand of Cr(0) carbene complexes undergoes two sequential transmetalations to the palladium(0) catalyst via dimetallacyclopropane

Scheme 1. Pd-Catalyzed Reaction of Chromium(0) Fischer Carbene Complexes through Carbene Transfer

a) Pd(0)-catalyzed carbene transfer reaction (refs. 6,7)

b) Cross-coupling reaction of diazo compounds (refs. 13,14)

$$\begin{array}{c} N_{2} & ArPd^{\parallel}X \\ R & R' \\ R & R' \\ \end{array} \xrightarrow{} Pd^{\parallel}X \\ R & R' \\ \end{array} \xrightarrow{} Pd^{\parallel}X \\ R & R' \\ \end{array} \xrightarrow{} Cross-coupling \\ Product \\ \end{array}$$

$$\begin{array}{c} cross-coupling \\ R & R' \\ R & R' \\ \end{array} \xrightarrow{} Cr(CO)_{5} \\ R & R' \\ R & R' \\ \end{array} \xrightarrow{} Cross-coupling \\ R & R' \\ R & R' \\ \end{array} \xrightarrow{} Cross-coupling \\ Product \\ \end{array}$$

intermediate A. The final dimerization product is formed through reductive elimination of a Pd(0) bis-carbene species.

Carbene transfer processes of chromium(0) Fischer carbene complexes are also known for other transition-metal catalysts, such as copper,⁸ nickel,⁹ rhodium,¹⁰ and gold,¹¹ allowing for the efficient construction of various structures. However, in contrast to the rich chemical properties of chromium(0) Fischer carbene complexes, the scope of transformations based on metal-catalyzed carbene transfer processes is still rather limited.

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To the best of our knowledge, the catalytic cross-coupling reaction of chromium(0) Fischer carbene complexes with other cross-coupling partners based on a transition-metal-catalyzed carbene transfer process has not yet been extensively explored. 12,14j,k

We and others have recently developed the transition-metalcatalyzed cross-coupling reaction of metal carbene species through migratory insertion, which has been demonstrated to be a powerful strategy for C–C bond formation (Scheme 1b).^{13,14} Both stable diazo compounds and nonstabilized diazo compounds generated in situ from *N*-tosyl hydrazones have been utilized as carbene precursors in these transformations. In the reaction mechanism, the palladium carbene species **B** undergoes migratory insertion to generate a C–C bond, followed by various reactions. These types of coupling reactions are quite general, and a series of cross-couplings under transition-metal catalysis, especially under palladium catalysis, has been established.

In connection to our interest in catalytic carbene-coupling transformations, we envisioned the possibility of using chromium(0) carbene complexes as metal carbene precursors in transition-metal-catalyzed carbene cross-coupling involving migratory insertion (Scheme 1c). Thus, a chromium(0) Fischer carbene complex is expected to undergo carbene transfer with the aryl palladium(II) intermediate C to form Pd(II) carbene intermediate D, which then undergoes migratory insertion to afford cross-coupling products. The realization of such a transformation should significantly expand the realm of catalytic carbene transfer reactions of Fischer carbene complexes as well as carbene-based coupling reactions. We have recently reported the palladium-catalyzed coupling of vinyl chromium(0) carbenes with 2-iodophenols and 2-iodoanilines proceeding via a carbene transfer process.^{14j} Herein we further report our experimental and mechanistic study on palladium-catalyzed reductive coupling of aryl iodides with aryl chromium(0)carbenes along the migratory insertion coupling reaction. A detailed mechanistic study by density functional theory (DFT) calculations supports the involvement of palladium-(II) carbene as the reactive intermediate, which undergoes a facile migratory insertion step with a very low energy barrier (5.1 kcal/mol).

RESULTS AND DISCUSSION

Reaction Optimization and Scope. At the outset, the complex pentacarbonyl (methoxy)(phenyl)carbene chromium(0) (1a) was selected as a model compound to react with biphenyl iodide (2a) with Et₃SiH as the reductant. We were delighted to find that, in the presence of 5 mol % Pd(PPh₃)₄ and 2 equiv of Et₃N, the expected product 4-(methoxy-(phenyl)methyl)-1,1'-biphenyl (3a) could be isolated in 31% yield (Table 1, entry 1). To optimize the reaction conditions, a series of solvents were then tested with $Pd(PPh_3)_4$ as the catalyst (entries 2-4); however, the best result was observed from the reaction run in 1,2-dichloroethane (DCE) solvent (entry 1). Slightly improved results could be obtained by carrying out the reaction at lower temperature and with increased loading of the reductant Et₃SiH (entries 5-7). Furthermore, diphenylmethylsilane was found to be a better reductant than Et₃SiH, which could give the product in 64% yield (entry 8). Finally, by screening the amine bases and adjusting the substrate ratio, the reaction could be further improved to afford the product in 76% yield (entry 9). We also carried out control experiments to test the roles of both amines and silanes. These showed that the reductive product could be obtained in

Table 1. Optimization of the Reaction Conditions^a

	Cr(C	O) ₅ Me + Ph 2a	Pd(PPh ₃)₄ Base, solvent	(5 mol%) R ₃ SiH , temp	OMe 3a	Ph
entry	1a:2a	base (equiv)	solvent	R ₃ SiH (equiv)	T (°C)	yield (%) ^b
1	1:1	$Et_3N(2)$	DCE	$Et_3SiH(1.2)$	80	31
2	1:1	Et ₃ N (2)	THF	Et ₃ SiH (1.2)	80	15
3	1:1	$Et_3N(2)$	PhMe	Et ₃ SiH (1.2)	80	28
4	1:1	$Et_3N(2)$	dioxane	Et ₃ SiH (1.2)	80	5
5	1:1	$Et_3N(2)$	DCE	Et ₃ SiH (1.2)	70	38
6	1:1	Et ₃ N (2)	DCE	Et ₃ SiH (1.2)	90	33
7	1:1	Et ₃ N (2)	DCE	Et ₃ SiH (2.0)	70	45
8	1:1	Et_3N (2)	DCE	Ph ₂ MeSiH (2.0)	70	64
9	1.5:1	BnMe ₂ N (2)	DCE	Ph ₂ MeSiH (2.0)	70	76
10	1.5:1	$Et_2NH(2)$	DCE	Ph ₂ MeSiH (2.0)	70	12
11	1.5:1		DCE	Ph ₂ MeSiH (2.0)	70	15
12	1.5:1	BnMe ₂ N (2)	DCE		70	0
13	1.5:1	$Et_2NH(2)$	DCE	Ph_2MeSiD	70	72 ^c

^{*a*}If not otherwise noted, reaction conditions are as follows: **1a** (0.10 mmol), **2a** (0.10 mmol), Pd(PPh₃)₄ (5 mol %), Et₃N (2 equiv), and Et₃SiH (1.2 equiv) in a solvent stirred at 80 °C for 5 h. ^{*b*}The yields refer to the products isolated by silica gel column chromatography. ^{*c*}>99 atom % D was observed in the ¹H NMR spectrum.

decreased yields without amine (entry 11) and that no reductive product was obtained in the absence of phenylmethylsilane (entry 12). The deuterated product **3a** (>99% D) was isolated in 72% yield (entry 13), suggesting that diphenylmethylsilane served as the hydride source in the catalytic cycle. According to these control experiments, we could presume that the reductive coupling reaction could be promoted in the presence of amine, probably due to its coordination to dissociated $Cr(CO)_{s}$ to accelerate the carbene transfer process.^{12d}

Under the same reaction conditions, the scope of this transformation was first explored by using various aryl chromium(0)carbene complexes 1a-p (Scheme 2). We found that the reaction shows an obvious dependence on the electronic properties of the substituents on the para position. The reactions with substrates bearing electron-donating groups, such as a methoxy group (3b), methyl group (3c) could give higher yields in comparison to those with electron-withdrawing substituents, chloro group (3e), fluoro group (3f), and trifluoromethyl group (3g). The reactions with the substrates bearing meta and ortho substituents gave the products in moderate yields (3h-k). The reactions with carbene substrates bearing a naphthyl group (31), furyl group (3m), and thienyl group (3n) also proceeded smoothly to afford the coupling products. Finally, the reactions with chromium(0) carbenes bearing ethoxyl and benzyloxy groups afforded the corresponding products 30,p in 77% and 64% yields, respectively.

Next, the scope of aryl iodides was investigated (Scheme 3). A series of aryl iodides 2b–1 bearing both electron-withdrawing and electron-donating groups were found to be compatible with this protocol. Functional groups, such as a methyloxycarbonyl group (4c), cyano group (4d), and carbonyl groups (4e,f), are

Scheme 2. Scope of Aryl Chromium(0) Carbene Complexes in Pd-Catalyzed Reductive Coupling with Aryl Iodide^{*a*}



"Reaction conditions: 1a-p (0.30 mmol), 2a (0.20 mmol), Pd(PPh₃)₄ (5 mol %), Me₂BnN (2 equiv) and Ph₂MeSiH (2 equiv) stirred at 70 °C for 5 h. All of the yields refer to the products isolated with silica gel column chromatography.

Scheme 3. Scope of Aryl Iodides in Pd-Catalyzed Reductive Coupling Reactions with a Phenyl Chromium(0) Carbene Complex^a



^{*a*}Reaction conditions: **1a** (0.30 mmol), **2b–l** (0.20 mmol), Pd(PPh₃)₄ (5 mol %), Me₂BnN (2 equiv) and Ph₂MeSiH (2 equiv) stirred at 70 °C for 5 h. All of the yields refer to the products isolated by silica gel column chromatography.

tolerated, and the reactions afford the desired products in excellent yields. Moreover, a naphthyl group (4i), thienyl group (4j), and dibenzofuranyl group (4k) also tolerate the reaction conditions to give the corresponding coupling products in good yields.

Mechanistic Considerations. We speculated that this reductive coupling reaction may proceed by two different mechanisms. The first possible mechanism involves the palladium carbene intermediate as we originally proposed (Scheme 4, path a). Thus, upon oxidative addition of catalytic palladium(0) species A to aryl iodide, the generated aryl palladium species B reacts with phenyl chromium(0) carbene to give the Pd carbene intermediate C through carbene transfer. The carbene

Scheme 4. Proposed Possible Pathways



intermediate C undergoes a migratory insertion step to afford the alkyl palladium species D.¹⁵ Ligand exchange with hydrosilane¹⁶ and subsequent reductive elimination afford the final product F and regenerate the Pd(0) catalytic species A. An alternative mechanism is also possible (Scheme 4, path b). The nucleophilic attack of Ph₂MeSiH to the chromium carbene complex generates the alkyl chromium species G.¹⁷ This then undergoes transmetalation with the aryl palladium species B to afford palladium species H. Finally, reductive elimination of H produces the product F and releases the Pd(0) species for the next catalytic cycle.

To identify which mechanism in Scheme 4 is more reasonable, mechanistic experiments were carried out (Scheme 5). Benzyl bromide (5a) and phenyl chromium(0) carbene 1a were employed as the substrates (Scheme 5a). We reasoned

Scheme 5. Mechanistic Experiments



that if **1a** reacts with the benzyl palladium species to generate a Pd carbene (path a), subsequent β -hydride elimination would produce the vinyl ether products; however, if the reaction proceeds through path b, there should be no intermediate leading to the formation of β -H elimination vinyl ether products. Indeed, we could observe a 7% yield of the vinyl ether products with a 2.7:1 *Z*:*E* isomer ratio, together with large amounts of self-dimerization products (Scheme 5a, condition A). Changing the base from Me₂BnN to K₂CO₃, we could obtain the vinyl ethers in slightly improved yield (Scheme 5a, condition B). In both cases, the product **6c** which should be formed through path b was not observed.

Moreover, the benzyl bromide palladium species **5b** was able to react with phenyl chromium(0) carbene **1a** (Scheme 5b). The reaction gives the vinyl ethers in excellent yields with the same 2.7:1 Z:E ratio, which further confirms the formation of Pd carbene intermediate **C** and the migratory insertion/ β -H elimination mechanism (i.e., path a). Thus, all of the experimental observations seem to support the assumption that this coupling reaction undergoes the Pd(II) carbene pathway.

During the reaction scope study, significant electronic effects of the substituents of the chromium(0) carbene species were observed. Since such information should provide valuable insights into the reaction mechanism, we then proceeded to study the electronic effects of the reaction in detail with a Hammett linear free energy correlation (Scheme 6). Thus, the relative rate constants were measured over a range of aryl chromium(0) carbene species bearing para substituents on the aromatic ring. The Hammett correlation analysis of the data showed a negative reaction constant with a substantially large value ($\rho = -2.93$). This substantial negative ρ value indicates that there should be a significantly positive charge buildup at the carbenic carbon of the chromium carbene during the reaction process.

Scheme 6. Electronic Effects of the Reaction: Hammett Linear Free Energy Correlation Study



This Hammett correlation result is consistent with the mechanism involving path a as shown in Scheme 4, in which the Cr(0) carbene reacts with the aryl palladium(II) intermediate via a carbene transfer reaction to form Pd(II) carbene intermediate C. In this process, the carbenic ligand transfer from the zerovalent chromium(0) center to a positively charged Pd(II) species would make the carbenic carbon more electron deficient. Thus, the electron-donating group on the aryl ring of Cr(0) carbene should favor such a carbene transfer process. Moreover, because of the electron-accepting nature of the carbene ligand of the Pd carbene intermediate according to earlier studies by Sierra and co-workers,¹⁸ the increased electron density on the aryl ring would stabilize the Pd carbene intermediate C. In the case of path b, the nucleophilic attack of Ph2MeSiH to the chromium carbene complex should be favored by electron-withdrawing substituents on the aromatic ring, while the following transmetalation step might be less significantly affected by the electronic substituents because the aromatic ring is attached to an sp³ carbon. Overall, if the reaction follows the mechanism of path b, the electronic effects would be expected to be either opposite (a positive ρ value) or trivial (a very small ρ value), which is in contradiction with the experimental observation. Consequently, the Hammett correlation experiment supports that the reaction more likely follows the mechanism of path a.

Computational Study. To gain further insights into the reaction mechanism, we performed a DFT mechanistic study using Gaussian $09^{19,20}$ to locate the pathway of the representative reaction shown in Table 1. It has been reported that the active catalyst in palladium-catalyzed C–C couplings was often a monophosphine palladium species, when a bulky phosphine ligand was applied.^{21–23} Accordingly, we used PdPPh₃ as the active catalyst in mechanistic computations. On the other hand, we further considered the possibility of using a bis-phosphine palladium complex as an active catalyst to mediate the reaction, but it is unlikely, as detailed in Figure S5 in the Supporting Information. In an analysis of our computed energetic results, Scheme 7 sketches the catalytic cycle of the transformation,





which comprises five steps: namely, oxidative addition (step 1), carbene transfer (step 2), migratory insertion (step 3), hydrogen transfer (step 4), and reductive elimination (step 5).

Figure 1 shows the free energy profile for steps 1-3 of the catalytic cycle, with the optimized geometries displayed in

Figure S6 in the Supporting Information. The reaction begins with the oxidative addition of biphenyl iodide (2a) to PdPPh₃, which could proceed via two possible pathways. Along the black pathway, the iodide atom of 2a first binds to the Pd center of PdPPh₃, giving the intermediate IM1, followed by migration of the biphenyl group to the Pd center via the transition state TS1, leading to the addition intermediate IM2 with a broken C-I bond. Alternatively, 2a first coordinates to the active catalyst, resulting in the π complex IM1', which then passes TS1' to break the C-I bond, giving IM2'. The trans effect between the biphenylyl group and PPh3 ligand makes IM2' 10.8 kcal/mol less stable than IM2, but it can isomerize to IM2 easily with a barrier of 5.5 kcal/mol (isoTS). On comparison of the two pathways, the blue pathway is kinetically more favorable. Overall, the oxidative addition is thermodynamically favorable by 26.0 kcal/mol.

Subsequent to the oxidative addition, step 2 transfers the carbene moiety (Ph-C-OMe) of the Cr(0) Fischer carbene 1a to the palladium center of IM2. To begin with, the formal Cr=Cbond of the Cr(0) carbene 1a coordinates to the Pd(II) center of IM2 by crossing TS2, resulting in the dimetallacyclopropane intermediate IM3.¹⁸ After the Cr(CO)₅ moiety leaves from IM3 via crossing a barrier of 6.4 kcal/mol (TS3), the intermediate IM4 is formed. IM4 features palladium carbene character with a Pd=C bond length of 1.991 Å, even shorter than that (2.005 Å) in the X-ray structure of a well-recognized palladium carbene complex.²⁴ Previously, we have also characterized the metal carbene character of similar palladium complexes.²¹ Overall, relative to IM2, the carbene transfer overcomes a barrier of 26.7 kcal/mol (TS3) and is slightly endergonic by 2.3 kcal/mol. Note that the process from IM2 to IM4 releases $Cr(CO)_5$, which can be stabilized by forming the complex 1p with the base Me₂BnN. The formation of 1p drives IM4 down by 10.6 kcal/mol; thus, the amine benefits the reaction by stabilizing the unstable $Cr(CO)_5$ moiety. The palladium carbene IM4 is also not stable, easily undergoing migratory insertion by striding a low barrier of 5.1 kcal/mol (TS4), giving the 21.5 kcal/mol more stable intermediate **IM5**. The facile migratory insertion of **IM4** is consistent with our previous DFT calculations for the palladium carbenes generated from different precusors.²¹

The pathway for steps 4 and 5 of the catalytic cycle is shown in Figure 2, with optimized structures included in Figure S7 in the Supporting Information. Subsequent to the formation of stable IM5, hydrosilane [Si]H ($[Si] = SiPh_2Me$) reacts with IM5. To deliver the product 3a, the hydrogen of [Si]H should transfer to the carbene carbon of IM5 for depalladation. We first considered a stepwise mechanism, proceeding via σ -bond metathesis between Si-H and Pd-I bonds, followed by reductive elimination to form a C-H bond to produce 3a. A transition state (TS5') describing the D to \bar{E} process in path b (Scheme 4) could be located, but the barrier (42.1 kcal/mol, TS5' relative to IM5) for the metathesis is obviously too high, considering that the reaction could be performed at 70 °C. Another pathway starting from IM4 was also found to be unlikely (see Figure S8 in the Supporting Information). Instead, a mechanism described by TS5 is much more favorable, TS5 being 14.3 kcal/mol lower than TS5'. As depicted by the optimized structure of TS5, hydrogen transfer, depalladation, and Pd-Si bond formation take place concertedly. The short Pd-H distance (1.639 Å) indicates that the hydrogen transfer is facilitated by the Pd center. A similar mechanism has been reported previously, but the favorability of the mechanism depends on catalytic systems.²⁵ Relative to IM5, the hydrogen transfer spans a barrier of 27.9 kcal/mol and is exergonic by 16.2 kcal/mol.

After hydrogen transfer to deliver the product 3a, the resulting IM6 undergoes reductive elimination via TS6, followed by dissociation to release [Si]I byproduct and regenerate PdPPh₃.When Figures 1 and 2 are combined, carbene transfer with a barrier of 26.7 kcal/mol and hydrogen transfer with a barrier of 27.9 kcal/mol are the rate-determining steps of the transformation. The barriers are somewhat high but are in the reasonable range, considering the fact that the transformations were required to be run at elevated temperature.



Figure 1. Free energy profile for steps 1-3 of the catalytic cycle.



Figure 2. Free energy profile for steps 4 and 5 of the catalytic cycle. The key bond length in the optimized structure of TS5 is given in angstroms, and the trivial hydrogen atoms in TS5 are omitted for clarity.

With regard to path b in Scheme 4, we considered the subprocess along the path: $1a + [Si]H \rightarrow G + [Si]^+$ (Scheme 4, path b). The step is endergonic by 32.2 kcal/mol, indicating that it has a kinetic barrier at least higher than 32.2 kcal/mol, which is higher than the rate-determining barrier of 27.9 kcal/mol for path a. Therefore, the mechanism via path b can be ruled out.

CONCLUSION

We have developed the first reductive cross-coupling of aryl chromium(0) Fischer carbene complexes with aryl iodide using hydrosilane as the hydrogen source. The implication of this study is that aryl chromium(0) carbene complexes could be considered as versatile Pd carbene precursors for catalytic crosscoupling reactions through a migratory insertion step. The computational studies support our original hypothesis that the Pd carbene formation and its migratory insertion are involved in this catalytic cycle. Furthermore, the DFT calculations further confirm that carbene transfer and hydrogen transfer are the rate-limiting steps of the catalytic cycle. This work should open up new opportunities for palladium-catalyzed transformations of chromium(0) Fischer carbenes based on Pd carbene migratory insertion. Further exploration of the transition-metal-catalyzed cross-coupling reactions of chromium(0) carbene complexes are currently underway in our laboratories.

EXPERIMENTAL SECTION

General Information. All reactions were performed under a nitrogen atmosphere in oven-dried reaction flasks. All solvents were freshly distilled and degassed according to ref 31. The boiling point of petroleum ether was between 60 and 70 °C. Commercially available reagents were used as received. For chromatography, 200-300 mesh silica gel (Qingdao, China) was used. ¹H NMR spectra were recorded on a Bruker ARX 400 spectrometer (400 MHz); ¹³C NMR spectra were recorded on a Bruker ARX 400 spectrometer (100 MHz). The data for NMR spectra are reported as follows: chemical shifts (δ) are reported in ppm, and coupling constants (J) are in hertz (Hz). IR spectra were recorded on a Nicolet 5MX-S infrared spectrometer and are reported in terms of frequency of absorption (cm⁻¹). Mass spectra

were obtained on an Agilent 7890A/5975C instrument, and HRMS were obtained on a Bruker APEX IV FTMS apparatus. All of the starting materials were purchased and used without further purification (PE, petroleum ether; EA, ethyl acetate). The chromium(0) Fischer carbene complexes were prepared according to the literature procedure: 2a,c,i,j,k;^{26a} 2b,d-h;^{26b} 2l,m;^{26c} 2n;^{26d} 2p,q.⁷

Typical Experimental Procedure for the Pd-Catalyzed Reductive Cross-Coupling Reactions of Aryl lodides with Aryl Chromium(0) Fischer Carbene Complexes. Aryl chromium(0) carbene complex 1a (93.6 mg, 0.30 mmol), 4-biphenyl iodide (2a) (56.0 mg, 0.20 mmol), and Pd(PPh₃)₄ (11.6 mg, 5 mol %) were successively placed in a 10 mL Schlenk reaction flask. The reaction flask was then degassed and charged with N2 three times, and 1,2-dichloroethane (2 mL) was introduced using a syringe. After that, Me₂BnN (30.1 μ L, 2 equiv) and Ph₂MeSiH (42.1 μ L, 2 equiv) were then added to the solution. The resulting solution was then stirred at 60 °C for 3 h. After completion of the reaction, the mixture was cooled to room temperature, filtered through a short plug of silica gel, and washed with the eluent (petroleum ether/EtOAc 30/1). Solvent was then removed in vacuo to provide a crude mixture, which was purified by silica gel column chromatography to afford the pure product.

4-(Methoxy(phenyl)methyl)-1,1'-biphenyl (3a):27 yield 76% (41.6 mg, purified by silica gel column chromatography using PE/EA 40/1 as eluent, $R_f = 0.40$; white oil; ¹H NMR (400 MHz, CDCl₃) δ 3.41 (s, 3H), 5.28 (s, 1H), 7.26–7.28 (m, 1H), 7.32–7.36 (m, 3H), 7.38–7.43 (m, 6H), 7.53–7.57 (m, 4H); $^{13}\mathrm{C}$ NMR (100 MHz, CDCl₃) δ 57.1, 85.2, 127.0, 127.1, 127.2, 127.3, 127.6, 128.0 128.5, 128.8, 140.4, 140.9, 141.2, 142.0.

4-(Methoxy(phenyl)methyl)-1,1'-biphenyl (deuterated) (3a'): yield 72% (41.6 mg, purified by silica gel column chromatography using PE/EA 40/1 as eluent, $R_f = 0.40$); white oil; ¹H NMR (400 MHz, CDCl₃) δ 3.41 (s, 3H), 7.25-7.26 (m, 1H), 7.32-7.36 (m, 3H), 7.38-7.43 (m, 6H), 7.54-7.57 (m, 4H); ¹³C NMR (100 MHz, CDCl₃) δ 57.1, 126.9, 127.1, 127.2, 127.3, 127.3, 127.6, 128.5, 128.8, 140.4, 140.9, 141.1, 142.0.

4-(Methoxy(4-methoxyphenyl)methyl)-1,1'-biphenyl (3b): yield 85% (51.7 mg, purified by silica gel column chromatography using PE/EA 20/1 as eluent, $R_f = 0.35$); white oil; IR (film): 2926, 1937, 1510, 1454, 1244, 851, 734, 700 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 3.40 (s, 3H), 3.78 (s, 3H), 5.25 (s, 1H), 6.88 (d, J = 8.7 Hz, 2H), 7.29 (d, J = 8.8 Hz, 2H), 7.32–7.34 (m, 1H), 7.40–7.43 (m, 4H),

7.54–7.58 (m, 4H); ¹³C NMR (100 MHz, CDCl₃) δ 55.3, 57.0, 84.8, 113.9, 127.1, 127.2, 127.2, 128.3, 128.7, 134.0, 134.2, 140.3, 140.9, 141.5, 159.1; HRMS (ESI) m/z calcd for C₂₁H₂₀O₂Na (M + Na)⁺ 327.1361, found 327.1356.

4-(*Methoxy*(*p*-tolyl)*methy*l)-1,1'-*biphenyl* (**3***c*): yield 90% (51.9 mg, purified by silica gel column chromatography using PE/EA 40/1 as eluent, $R_f = 0.40$); white oil; IR (film): 2939, 2982, 1941, 1599, 1512, 1091, 800, 697 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 2.31 (s, 3H), 3.38 (s, 3H), 5.24 (s, 1H), 7.14–7.22 (m, 2H), 7.25–7.27 (m, 2H), 7.28–7.31 (m, 1H), 7.37–7.41 (m, 4H), 7.52–7.56 (m, 4H); ¹³C NMR (100 MHz, CDCl₃) δ 21.2, 57.1, 85.1, 127.0, 127.1, 127.2, 127.3, 127.3, 128.8, 129.2, 137.3, 139.1, 140.3, 141.0, 141.5; HRMS (ESI) *m*/*z* calcd for C₂₁H₂₀ONa (M + Na)⁺ 311.1406, found 311.1414.

4,4"-(Bethoxymethylene)di-1,1'-biphenyl (**3d**): yield 72% (50.5 mg, purified by silica gel column chromatography using PE/EA 40/1 as eluent, $R_{\rm f}$ = 0.40); white solid; IR (film): 2952, 2926, 1939, 1593, 1487, 1090, 759, 695 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 3.44 (s, 3H), 5.33 (s, 1H), 7.30–7.34 (m, 2H), 7.39–7.41 (m, 3H), 7.43–7.46 (m, 5H), 7.56–7.58 (m, 8H); ¹³C NMR (100 MHz, CDCl₃) δ 57.2, 85.0, 127.1, 127.3, 127.4, 128.8, 130.1, 140.5, 140.9, 141.1; HRMS (ESI) *m/z* calcd for C₂₆H₂₂ONa (M + Na)⁺ 373.1563, found 373.1568.

4-((4-Chlorophenyl)(methoxy)methyl)-1,1'-biphenyl (**3e**): yield 62% (38.2 mg, purified by silica gel column chromatography using PE/EA 40/1 as eluent, $R_f = 0.40$); yellow oil; IR (film): 2957, 2918, 1940, 1593, 1487, 1089, 763, 697 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 3.39 (s, 3H), 5.25 (s, 1H), 7.30–7.31 (m, 4H), 7.36–7.43 (m, SH), 7.54–7.57 (m, 4H); ¹³C NMR (100 MHz, CDCl₃) δ 57.1, 84.5, 127.1, 127.3, 127.3, 128.3, 128.6, 128.7, 128.8, 133.3, 134.3, 140.7, 140.7, 140.8; HRMS (ESI) m/z calcd for C₂₀H₁₇ClONa (M + Na)⁺ 331.0860, found 331.0869.

4-((4-Fluorophenyl)(methoxy)methyl)-1,1'-biphenyl (**3f**): yield 42% (24.6 mg, purified by silica gel column chromatography using PE/EA 40/1 as eluent, $R_f = 0.40$); yellow oil; IR (film): 2959, 2925, 1601, 1507, 1229, 1086, 835, 754 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 3.39 (s, 3H), 5.26 (s, 1H), 7.00–7.04 (m, 2H), 7.32–7.36 (m, 3H), 7.37–7.44 (m, 4H), 7.54–7.57 (m, 4H); ¹³C NMR (100 MHz, CDCl₃) δ 57.0, 84.5, 115.4 (d, $J_F = 21.5$ Hz), 127.1, 127.3 (d, $J_F =$ 3.0 Hz), 127.3, 128.6 (d, $J_F = 8.1$ Hz), 128.8, 134.3, 137.9 (d, $J_F =$ 3.0 Hz), 140.6, 140.8, 140.9, 162.4 (d, $J_F = 245.8$ Hz); HRMS (ESI) m/z calcd for C₂₀H₁₇FONa (M + Na)⁺ 315.1156, found 315.1160.

4-(Methoxy(4-(trifluoromethyl)phenyl)methyl)-1,1'-biphenyl (**3g**): yield 42% (28.8 mg, purified by silica gel column chromatography using PE/EA 40/1 as eluent, $R_{\rm f}$ = 0.40); white oil; IR (film): 3022, 2929, 1939, 1556, 1485, 1325, 1078, 758, 698 cm⁻¹;¹H NMR (400 MHz, CDCl₃) δ 3.46 (s, 3H), 5.45 (s, 1H), 7.41–7.48 (m, 5H), 7.54–7.57 (m, 4H), 7.50–7.58 (m, 4H); ¹³C NMR (100 MHz, CDCl₃) δ 57.1, 85.3, 125.0, 125.8, 126.0, 126.2, 127.1, 127.2, 127.4, 128.0, 128.8, 139.4, 140.5, 140.9, 141.1; HRMS (ESI) *m/z* calcd for C₂₁H₁₇F₃ONa (M + Na)⁺ 365.1123, found 365.1131.

4-(*Methoxy*(3-methoxyphenyl)methyl)-1, 1'-biphenyl (**3h**): yield 79% (48.1 mg, purified by silica gel column chromatography using PE/EA 20/1 as eluent, $R_f = 0.30$); white oil; IR (film): 2953, 2918, 2826, 1596, 1487, 1289, 1257, 1094, 1042 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 3.42 (s, 3H), 3.80 (s, 3H), 5.26 (s, 1H), 6.79–6.82 (m, 1H), 6.96–6.98 (m, 2H), 7.25–7.26 (m, 1H), 7.32–7.34 (m, 1H), 7.40– 7.43 (m, 4H), 7.53–7.57 (m, 4H); ¹³C NMR (100 MHz, CDCl₃) δ 55.2, 57.1, 85.1, 112.4, 112.9, 119.4, 127.1, 127.2, 127.2, 127.3, 128.7, 129.5, 140.4, 140.9, 141.1, 143.6, 159.8; HRMS (ESI) *m*/*z* calcd for C₂₁H₂₀O₂Na (M + Na)⁺ 327.1356, found 327.1360.

4-((3-Chlorophenyl)(methoxy)methyl)-1,1'-biphenyl (3i): Yie ld 56% (34.6 mg, purified by silica gel column chromatography using PE/EA 40/1 as eluent, $R_{\rm f}$ = 0.35); yellow oil; IR (film): 2951, 2908, 1590, 1494, 1191, 1105, 764 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 3.41 (s, 3H), 5.25 (s, 1H), 7.24–7.27(m, 3H), 7.33–7.35 (m, 1H), 7.38–7.44 (m, 5H), 7.55–7.57 (m, 4H); ¹³C NMR (100 MHz, CDCl₃) δ 57.1, 84.6, 125.0, 126.9, 127.1, 127.3, 127.4, 127.7, 128.8, 129.7, 134.4, 140.4, 140.7, 144.2; HRMS (ESI) *m/z* calcd for C₂₀H₁₇ClONa (M + Na)⁺ 331.0860, found 331.0874.

4-(Methoxy(2-methoxyphenyl)methyl)-1,1'-biphenyl (**3***j*): yield 51% (31.0 mg, purified by silica gel column chromatography using PE/EA 20/1 as eluent, $R_f = 0.35$); white oil; IR (film): 2925, 2895, 1935, 1587, 1488, 1091, 757, 698 cm⁻¹;¹H NMR (400 MHz, CDCl₃) δ 3.41 (s, 3H), 3.82 (s, 3H), 5.73 (s, 1H), 6.86–6.88(m, 1H), 6.97–7.01 (m, 1H), 7.31–7.33 (m, 1H), 7.39–7.46 (m, 5H), 7.50–7.51 (m, 2H), 7.53–7.57 (m, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 55.5, 57.1, 78.5, 110.6, 120.8, 126.8, 126.9, 127.1, 127.4, 128.4, 128.7, 130.5, 140.0, 141.1, 141.2, 156.7; HRMS (ESI) m/z calcd for C₂₁H₂₀O₂Na (M + Na)⁺ 327.1356, found 327.1360.

4-(Methoxy(o-tolyl)methyl)-1,1'-biphenyl (**3k**): yield 55% (31.7 mg, purified by silica gel column chromatography using PE/EA 40/1 as eluent, $R_{\rm f}$ = 0.45); white oi; IR (film): 2957, 2911, 1946, 1600, 1479, 1179, 1080, 761, 693 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 2.30, (s, 3H), 3.41 (s, 3H), 5.45 (s, 1H), 7.18–7.20 (m, 1H), 7.32–7.48 (m, 8H), 7.53–7.57 (m, 4H); ¹³C NMR (100 MHz, CDCl₃) δ 19.5, 57.2, 82.4, 126.1, 126.8, 127.1, 127.3, 127.5, 128.0, 128.8, 130.6, 134.0, 135.9, 139.5, 140.0, 140.4, 140.9; HRMS (ESI) *m/z* calcd for C₂₁H₂₀ONa (M + Na)⁺ 311.1406, found 311.1404.

2-([1,1'-Biphenyl]-4-yl(methoxy)methyl)naphthalene (31): yield 56% (36.3 mg, purified by silica gel column chromatography using PE/EA 40/1 as eluent, $R_{\rm f}$ = 0.45); white solid; IR (film): 2951, 2911, 2357, 1603, 1485, 1445, 1111, 817, 746 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 3.47 (s, 3H), 5.46 (s, 1H), 7.32–7.34, (m, 1H), 7.40–7.42 (m, 2H), 7.45–7.48 (m, 5H), 7.55–7.57 (m, 4H), 7.80–7.88 (m, 4H); ¹³C NMR (100 MHz, CDCl₃) δ 57.1, 85.3, 125.0, 125.8, 125.9, 126.2, 127.1, 127.2, 127.3, 127.5, 127.7, 128.0, 128.4, 128.8, 133.0, 133.3, 139.4, 140.5, 140.9, 141.1; HRMS (ESI) m/z calcd for C₂₄H₂₀ONa (M + Na)⁺ 347.1406, found 347.1400.

3-([1,1'-Biphenyl]-4-yl(methoxy)methyl)furan (**3m**): yield 65% (34.4 mg, purified by silica gel column chromatography using PE/EA 30/1 as eluent, R_f = 0.45); yellow oil; IR (film): 2955, 2911, 2359, 1588, 1481, 1452, 1096, 871, 753 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 3.38 (s, 3H), 5.24 (s, 1H), 6.36 (d, *J* = 1.1, 1H), 7.32 (m, 1H), 7.35 (m, 1H), 7.38–7.39 (m, 1H), 7.42–7.45 (m, 4H), 7.58–7.60 (m, 4H); ¹³C NMR (100 MHz, CDCl₃) δ 56.7, 78.1, 109.4, 117.8, 127.0, 127.1, 127.2, 127.3, 127.3 128.8, 140.1, 140.2, 140.7, 140.8, 143.4; HRMS (ESI) *m*/*z* calcd for C₁₈H₁₆O₂Na (M + Na)⁺ 287.1043, found 287.1048.

2-([1,1'-Biphenyl]-4-yl(methoxy)methyl)thiophene (3n): yield 60% (33.6 mg, purified by silica gel column chromatography using PE/EA 40/1 as eluent, $R_f = 0.40$); yellow oil; IR (film): 2955, 2920, 2365, 1588, 1481, 1081, 756, 701 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 3.43 (s, 3H), 5.52 (s, 1H), 6.88–6.89 (m, 1H), 6.93–6.95 (m, 1H), 7.29–7.42 (m, 2H), 7.44–7.49 (m, 4H), 7.58–7.60 (m, 4H); ¹³C NMR (100 MHz, CDCl₃) δ 57.0, 81.2, 125.4, 125.6, 126.5, 127.1, 127.3, 127.3, 127.3, 128.8, 129.4, 140.3, 140.8, 140.8, 146.1; HRMS (ESI) *m*/*z* calcd for C₁₈H₁₆OSNa (M + Na)⁺ 303.0814, found 303.0822.

4-(Ethoxy(phenyl)methyl)-1,1'-biphenyl (**30**): yield 77% (44.4 mg, purified by silica gel column chromatography using PE/EA 40/1 as eluent, $R_f = 0.45$); white oil; IR (film): 3062, 3019, 2360, 1600, 1488, 1188, 1102, 768, 734 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 1.28 (t, J = 7.0 Hz, 3H), 3.55 (q, J = 7.0 Hz, 2H), 5.39 (s, 1H), 7.24–7.26 (m, 1H), 7.30–7.34 (m, 3H), 7.38–7.42 (m, 6H), 7.52–7.56 (m, 4H); ¹³C NMR (100 MHz, CDCl₃) δ 15.4, 64.7, 83.3, 127.0, 127.1, 127.2, 127.2, 127.4, 127.5, 128.5, 128.8, 140.3, 141.0, 141.7, 142.5; HRMS (ESI) m/z calcd for C₂₁H₂₀ONa (M + Na)⁺ 311.1407, found 311.1412.

4-((Benzyloxy)(phenyl)methyl)-1,1'-biphenyl (**3p**): yield 64% (44.9 mg, purified by silica gel column chromatography using PE/EA 40/1 as eluent, $R_{\rm f}$ = 0.40); white oil; IR (film): 2954, 2920, 1609, 1501, 1448, 1089, 1058, 761, 695 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 4.58 (s, 2H), 5.49 (s, 1H), 7.28–7.31 (m, 2H), 7.32–7.38 (m, 7H), 7.40–7.46 (m, 6H), 7.54–7.58 (m, 4H); ¹³C NMR (100 MHz, CDCl₃) δ 70.6, 82.3, 127.1, 127.2, 127.2, 127.3, 127.6, 127.6, 127.8, 128.2, 128.4, 128.5, 128.8, 138.4, 140.4, 140.9, 141.2, 142.1; HRMS (ESI) *m/z* calcd for C₂₆H₂₂ONa (M + Na)⁺ 373.1563, found 373.1566.

1-(tert-Butyl)-4-(methoxy(phenyl)methyl)benzene (**4a**):²⁷ yield 65% (31.0 mg, purified by silica gel column chromatography using

PE/EA 40/1 as eluent, $R_{\rm f}$ = 0.45); white oil; ¹H NMR (400 MHz, CDCl₃) δ 1.29 (s, 9H), 3.38 (s, 3H), 5.22 (s, 1H), 7.24–7.27 (m, 3H), 7.32–7.35 (m, 6H); ¹³C NMR (100 MHz, CDCl₃) δ 32.6, 35.7, 58.3, 86.5, 126.5, 127.8, 128.1, 128.6, 129.6, 140.3, 143.4, 151.5.

1-Methoxy-4-(methoxy(phenyl))methyl)benzene (**4b**):²⁷ yield 74% (31.4 mg, purified by silica gel column chromatography using PE/EA 20/1 as eluent, $R_{\rm f} = 0.35$); white oil; ¹H NMR (400 MHz, CDCl₃) δ 3.36 (s, 3H), 3.78 (s, 3H), 5.20 (s, 1H), 6.84–6.86 (m, 2H), 7.24–7.26 (m, 3H), 7.32–7.33 (m, 4H); ¹³C NMR (100 MHz, CDCl₃) δ 55.3, 56.9, 85.0, 113.8, 126.8, 127.3, 128.3, 128.4, 134.3, 142.3, 159.0.

Methyl 4-(*methoxy*(*phenyl*))*methyl*)*benzoate* (4c):²⁸ yield 65% (31.2 mg, purified by silica gel column chromatography using PE/EA 40/1 as eluent, $R_f = 0.40$); white oil; ¹H NMR (400 MHz, CDCl₃) δ 3.39 (s, 3H), 3.89 (s, 3H), 5.28 (s, 1H), 7.32–7.33 (m, 4H), 7.43 (d, J = 8.3 Hz, 2H), 7.99 (d, J = 8.3 Hz, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 52.1, 57.1, 85.0, 126.7, 127.0, 127.8, 128.6, 129.3, 129.8, 141.3, 147.3, 166.9.

4-(Methoxy(phenyl))methyl)benzonitrile (4d):²⁷ yield 50% (20.7 mg, purified by silica gel column chromatography using PE/EA 30/1 as eluent, $R_f = 0.40$); yellow oil; ¹H NMR (400 MHz, CDCl₃) δ 3.38 (s, 3H), 5.26 (s, 1H), 7.26–7.37 (m, 5H), 7.47 (d, J = 8.3 Hz, 2H), 7.61 (d, J = 8.1 Hz, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 57.1, 84.7, 111.2, 118.8, 127.1, 127.3, 128.2, 128.7, 132.3, 140.7, 147.6.

1-(4-(Methoxy(phenyl))methyl)phenyl)ethanone (4e):²⁷ yield 65% (29.2 mg, purified by silica gel column chromatography using PE/EA 30/1 as eluent, $R_{\rm f}$ = 0.40); white oil; ¹H NMR (400 MHz, CDCl₃) δ 2.57 (s, 3H), 3.39 (s, 3H), 5.28 (s, 1H), 7.32–7.34 (m, 5H), 7.46 (d, *J* = 8.2 Hz, 2H), 7.91 (d, *J* = 8.2 Hz, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 26.6, 57.0, 85.2, 126.9, 127.5, 128.0, 128.4, 128.6, 136.5, 142.0, 147.6, 198.5.

4-(*Methoxy(phenyl)methyl)benzaldehyde* (**4f**): yield 74% (31.1 mg, purified by silica gel column chromatography using PE/EA 30/1 as eluent, $R_f = 0.40$); yellow oil; IR (film): 2923, 2846, 2815, 1698, 1609, 1457, 1210, 1098, 802, 693 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 3.40 (s, 3H), 5.30 (s, 1H), 7.26–7.29 (m, 1H), 7.29–7.34 (m, 4H), 7.53 (d, *J* = 8.1 Hz, 2H), 7.84 (d, *J* = 8.3 Hz, 2H), 9.98 (s, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 57.1, 85.0, 127.0, 127.3, 128.0, 128.7, 129.9, 135.6, 141.0, 149.1, 191.9; HRMS (ESI) *m*/*z* calcd for C₁₅H₁₄O₂Na (M + Na)⁺ 249.0886, found 249.0889.

1-(Methoxy(phenyl))methyl)-3-methylbenzene (**4g**):²⁷ yield 90% (38.2 mg, purified by silica gel column chromatography using PE/EA 40/1 as eluent, $R_{\rm f}$ = 0.40); white oil; ¹H NMR (400 MHz, CDCl₃) δ 2.32 (s, 3H), 3.37 (s, 3H), 5.20 (s, 1H), 7.04–7.06 (m, 1H), 7.14–7.16 (m, 2H), 7.18–7.22 (m, 1H), 7.31–7.36 (m, 5H); ¹³C NMR (100 MHz, CDCl₃) δ 21.5, 57.0, 85.5, 124.0, 126.9, 127.4, 127.5, 128.3, 128.4, 128.6, 138.1, 142.0, 142.2.

1-Methoxy-3-(methoxy(phenyl))methyl)benzene (4h):²⁷ yield 80% (31.4 mg, purified by silica gel column chromatography using PE/EA 30/1 as eluent, $R_{\rm f}$ = 0.35); white oil; ¹H NMR (400 MHz, CDCl₃) δ 3.38 (s, 3H), 3.80 (s, 3H), 5.68 (s, 1H), 6.84–6.86 (m, 1H), 6.95–6.99 (m, 1H), 7.20–7.22 (m, 2H), 7.27–7.30 (m, 2H), 7.37–7.39 (m, 2H), 7.45–7.47 (m, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 55.4, 57.1, 78.8, 110.6, 120.8, 126.8, 127.0, 127.1, 128.1, 128.3, 130.6, 142.1, 156.6.

2-(Methoxy(phenyl)methyl)naphthalene (41):²⁹ yield 61% (30.3 mg, purified by silica gel column chromatography using PE/EA 40/1 as eluent, $R_{\rm f}$ = 0.45); white solid; ¹H NMR (400 MHz, CDCl₃) δ 3.46 (s, 3H), 5.92 (s, 1H), 7.26–7.32 (m, 3H), 7.42–7.45 (m, 3H), 7.57–7.62 (m, 2H), 7.79–7.86 (m, 3H), 8.05–8.08 (m, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 57.3, 83.3, 124.1, 125.3, 125.4, 125.5, 126.0, 127.4, 127.5, 128.4, 128.7, 131.2, 135.1, 135.5, 136.8, 141.4.

2-(Methoxy(phenyl)methyl)thiophene (4j):³⁰ yield 42% (17.2 mg, purified by silica gel column chromatography using PE/EA 30/1 as eluent, $R_{\rm f}$ = 0.40); yellow oil; ¹H NMR (400 MHz, CDCl₃) δ 3.39 (s, 3H), 5.46 (s, 1H), 6.83–6.84 (m, 1H), 6.91–6.93 (m, 1H), 7.25–7.27 (m, 1H), 7.30–7.31 (m, 1H), 7.34–7.43 (m, 4H); ¹³C NMR (100 MHz, CDCl₃) δ 57.0, 81.4, 125.3, 125.5, 126.4, 126.9, 127.9, 128.1, 128.2, 128.5, 141.3, 146.3.

3-(Methoxy(phenyl)methyl)dibenzo[b,d]furan (4k): yield 60% (33.1 mg, purified by silica gel column chromatography using PE/EA 30/1 as eluent, $R_f = 35$); white solid; IR (film): 2952, 2930,

1939, 1596, 1487, 1095, 736, 699 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 3.48 (s, 3H), 5.98 (s, 1H), 7.21–7.26 (m, 2H), 7.30–7.34 (m, 3H), 7.52–7.55 (m, 3H), 7.58–7.60 (m, 2H), 7.83 (d, *J* = 7.6 Hz, 1H), 7.91 (d, *J* = 7.6 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 57.3, 79.7, 111.8, 119.7, 120.7, 122.8, 123.1, 124.3, 124.6, 126.3, 126.9, 127.1, 127.6, 128.4, 134.0, 141.3, 153.7, 156.2; HRMS (ESI) *m*/*z* calcd for C₂₀H₁₆O₂Na (M + Na)⁺: 311.1043, found 311.1040.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.organomet.7b00657.

Experimental procedures, characterization data, ¹H and ¹³C NMR spectra, and DFT calculation details (PDF) Cartesian coordinates for calculated structures (XYZ)

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Notes

The authors declare no competing financial interest.

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