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Synthesis of Xylyl-Linked Bis-Benzimidazolium Salts and Their Application in the Palladium-Catalyzed Suzuki–Miyaura Cross-Coupling Reaction of Aryl Chlorides

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Abstract: A new series of xylyl-linked bis-benzimidazolium salts were efficiently prepared using a simple preparation method from bis-benzimidazolium precursors featuring highly tunable linkers and wingtips. A highly efficient Suzuki–Miyaura cross-coupling reaction of aryl chlorides within the range of 0.5–2.0 mol% Pd-catalyst loading was observed. Also, di-*ortho*-substituted biaryl synthesis was achieved.

Keywords: bis-benzimidazolium salt; coupling reaction; aryl chloride; di-*ortho*-substituted biaryl; *N*-heterocyclic carbene

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1. Introduction

The palladium-catalyzed Suzuki–Miyaura cross-coupling reaction (SMC), which involves the combination of an aryl halide with an arylboronic acid in the presence of a Pd catalyst, is one of the most practical protocols by which to achieve C–C bond formation [1–5]. Aryl chlorides, which are less expensive and more diverse than aryl bromides and iodides, are challenging compounds to use in SMC reactions due to their low C–Cl bond reactivity [6]. Numerous successful examples using a combination of phosphine ligands with Pd have been reported, however, the disadvantages of using such ligands are their difficult preparation, air-sensitivity, expense, and toxicity [7–9]. The development of Pd catalysts with phosphine-free ligands has thus received a great amount of attention.

Over the past three decades, the replacement of phosphine ligands with *N*-heterocyclic carbenes (NHCs) has been shown to be a good choice. Compared with bulky tertiary phosphines, these new NHC ligands exhibit strong σ-donor but poor π-acceptor properties [10]. Metal–NHC complexes exhibit extraordinary heat, air, and moisture stability due to the high dissociation energies of their metal–carbon bonds [11]. Bis-NHC binds to metals to form more stable complexes compared to monodentate NHC complexes, which has led to the development of such ligands attracting great attention in the literature. In addition, the diversity of bis-NHC compounds is also an advantage, as they have tunable linkers and wingtips. In 1998, a chelating bis-NHC ligand was synthesized by Herrmann and co-workers [12] and applied in the Pd-catalyzed SMC reaction of 4-chloroacetophenone and phenylboronic acid at 120 °C for 48 h, resulting in the desired product being formed with a yield of 60%. Numerous successful examples of SMC reactions between aryl chlorides and arylboronic acids employing Pd–bis-NHC complexes or in-situ-formed $Pd(OAc)_2$/bis-NHC catalyst systems have been previously reported [13–29]. However, high catalyst loading and the variety of the substrates still present challenge.

The catalytic reaction rate is affected by the nature of the NHC ligand. To obtain efficient bis-NHC ligands, a series of new xylyl-linked bis-benzimidazolium salts was prepared by modifying the wingtips and linkers of a bis-NHC precursor. These salts have the following advantages: (1) our linker contains aryl group which can provide electronic effect, (2) our linker has an additional methylene group compared to currently available NHCs in which the aryl group is directly connected to the bis-benzimidazole moiety that offers more conformational flexibility, and (3) the wingtip delivers electronic and steric effects. Those advantages facilitate the oxidative addition and reductive elimination steps of the SMC reaction. We report herein their application in an in-situ-generated $Pd(OAc)_2$/bis-NHC catalyst system for the SMC reaction of aryl chlorides with arylboronic acids (Figure 1).

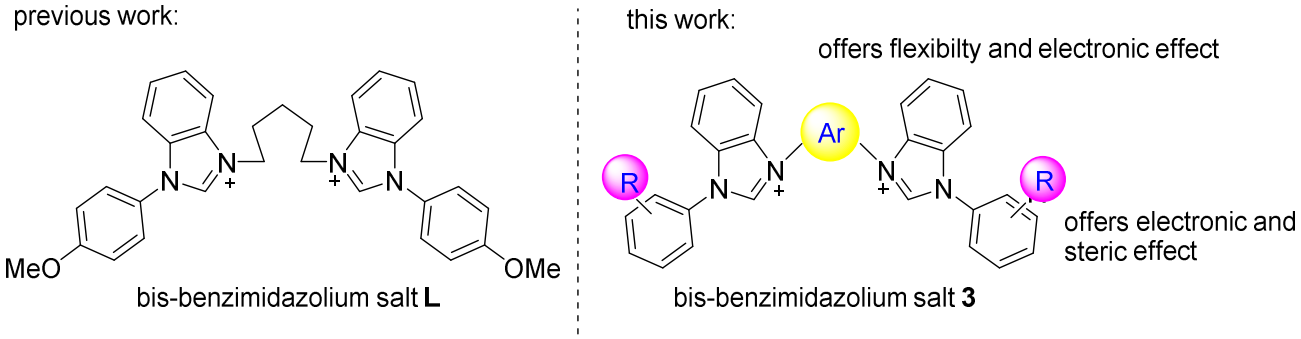


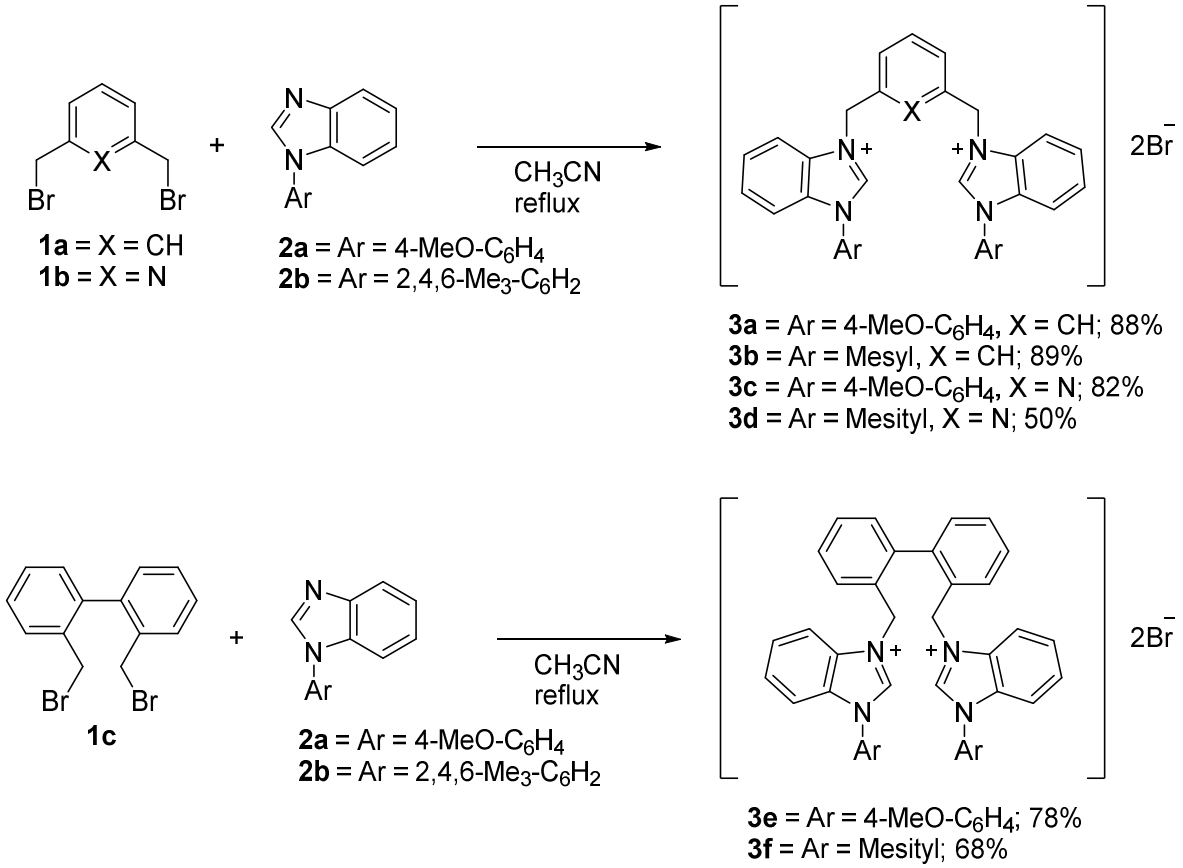
Figure 1. The structures of the new xylyl-linked bis-benzimidazolium salts **3**.

2. Results

2.1. Synthesis and Characterization of the Bis-Benzimidazolium Salts **3**

According to Scheme 1, the bis-benzimidazolium salts **3** were prepared by the combination of two equivalents of the corresponding *N*-arylbenzimidazole **2** and one equivalent of the desired dibromides 1 in acetonitrile under reflux to produce the respective products with yields in the range of 50 to 89%. The newly prepared salts were found to be air- and moisture-stable both in the solid state and in solution, and were characterized by ^{1}H and ^{13}C nuclear magnetic resonance (NMR) spectroscopy.

In the ^{1}H NMR spectra of **3a**–**3d**, the methylene protons could be observed as a singlet, while the ^{1}H NMR spectra of **3e** and **3f** showed an AB spin system for the methylene protons. The benzimidazolium proton signals in the spectra of **3a**–**3f** could be observed in a wide range of between δ 10.15 and 11.57 ppm. The ^{13}C NMR spectra of **3a**–**3f** showed the NCHN resonances between δ 142.4 and 161.0 ppm.

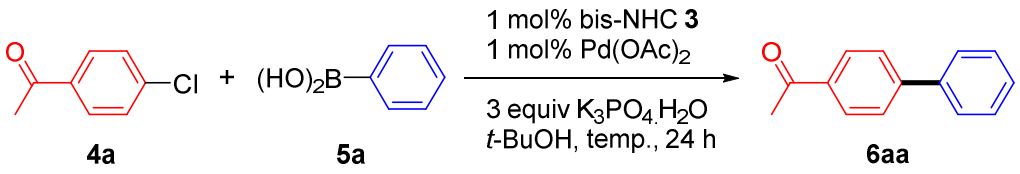


Scheme 1. Overview of the synthesis of bis-benzimidazolium salts **3**.

2.2. The Suzuki–Miyaura Cross-Coupling Reaction

Continuing our previous studies on the application of in-situ-formed catalyst systems for the SMC reaction [28,29], 4-chloroacetophenone **4a** and phenylboronic acid **5a** were used as model starting materials (Table 1). Under classical conditions ($K_3PO_4 \cdot H_2O$, $Pd(OAc)_2$, *t*-BuOH, 30 °C, 24 h), the activity of the **L**/$Pd(OAc)_2$ catalyst system was first compared with that of **3b**/$Pd(OAc)_2$ (Table 1, entries 1 and 2). It was found that the xylyl-bridged bis-benzimidazolium precursor **3b** showed better activity in comparison to alkyl-linked bis-benzimidazolium salt **L** (Table 1, entries 1 and 2). Next, the activity of the **3**/$Pd(OAc)_2$ catalyst systems was compared. Upon increasing the reaction temperature to 80 °C, the gas chromatography (GC) yield of **6aa** increased from 21% to 88% (Table 1, entries 2 and 3). The focus was shifted to investigate the influence that the xylyl-linked spacers and wingtips have on the benzimidazole ring. With the same wingtip on the benzimidazole ring (**3b**, **3d**, and **3f**), the bis-benzimidazolium precursor with a benzene ring as a xylyl-linked spacer showed better activity in comparison to when pyridine or biphenyl were incorporated in the xylyl-linked bridge bis-benzimidazolium salts (Table 1, entries 3, 6, and 8). The same results were also observed using bis-benzimidazolium salts **3a**, **3c**, and **3e** (Table 1, entries 4, 5, and 7). The activity of the bis-benzimidazolium salts with a mesityl group on the benzimidazole ring as the wingtip (**3d** and **3f**) was better than that when a methoxyphenyl group was incorporated as a wingtip (**3c** and **3e**), regardless of whether pyridine or biphenyl was present as the xylyl-linked bridge in the bis-benzimidazolium salts (Table 1, entries 5–8). However, both **3a** and **3b** exhibited similar catalytic activity (Table 1, entries 3 and 4), an observation that shows that having a mesityl group on the benzimidazole ring leads to a sterically hindered effect, which is beneficial in the reductive elimination step of the catalytic cycle.

Table 1. Screening the activity of the in-situ-formed bis-NHC/Pd catalyst [1].



Entry	Ligand	Temperature (°C)	4a GC Yield (%) [2]	6aa GC Yield (%) [2]
1	**L**	30	88	7
2	**3b**	30	78	21
3	**3b**	80	5	88
4	**3a**	80	5	87
5	**3c**	80	62	31
6	**3d**	80	25	70
7	**3e**	80	71	25
8	**3f**	80	37	58

[1] Reaction conditions: **4a** (1.0 mmol), **5a** (1.5 mmol), bis-NHC **3** (1 mol%), $Pd(OAc)_2$ (1 mol%), $K_3PO_4 \cdot H_2O$ (3.0 mmol) in *t*-BuOH (3.0 mL) for 24 h under a N_2 atmosphere. [2] Determined by gas-chromatography-flame ionization detection (GC-FID) using undecane as an internal standard.

The effects of different solvents, bases, and Pd loading amounts on the catalytic activity of this reaction are summarized in Table 2. Most of the solvents tested gave the products in good to excellent yields (87–94%, Table 2, entries 1–4) in this work, except for a mixed solvent of *t*-butanol (BuOH)/H_2O, the use of which led to a poor product yield (55%, Table 2, entry 5). It was observed that 1,4-dioxane was the best choice of solvent for producing products with higher conversion rates (Table 2, entry 2). The replacement of $K_3PO_4 \cdot H_2O$ with KO^{t}Bu or KOAc led to lower GC yields of the respective products (Table 2, entries 6 and 9) and when K_2CO_3 or Cs_2CO_3 was used instead, excellent yields were observed (Table 2, entries 7 and 8). After screening Pd loading amount, the coupling reaction could be carried out in the presence of 0.5 mol% Pd $(OAc)_2$/3b catalyst for 6 h in 98% yield (Table 2, entry 13).

Table 2. Optimization of reaction conditions [1].

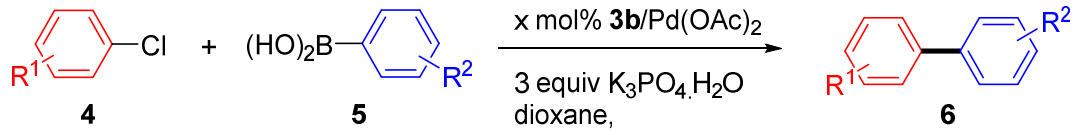
Entry	3b/$Pd(OAc)_2$ (mol%)	Solvent	Base	Time (h)	4a GC Yield (%) [2]	6aa GC Yield (%) [2]
1	1.0	Toluene	$K_3PO_4 \cdot H_2O$	24	0	91 (91) [3]
2	1.0	1,4-Dioxane	$K_3PO_4 \cdot H_2O$	24	0	94 (94) [3]
3	1.0 [4]	1,4-Dioxane	$K_3PO_4 \cdot H_2O$	24	–	(20) [3]
4	1.0	CH_3CN	$K_3PO_4 \cdot H_2O$	24	7	87
5	1.0	*t*-BuOH	$K_3PO_4 \cdot H_2O$	24	5	88
6	1.0	*t*-BuOH/H_2O [5]	$K_3PO_4 \cdot H_2O$	24	31	55
7	1.0	1,4-Dioxane	KO^{t}Bu	24	1	4
8	1.0	1,4-Dioxane	K_2CO_3	24	13	82
9	1.0	1,4-Dioxane	Cs_2CO_3	24	–	(93) [3]
10	1.0	1,4-Dioxane	KOAc	24	86	8
11	1.0	1,4-Dioxane	$K_3PO_4 \cdot H_2O$	12	0	96
12	1.0	1,4-Dioxane	$K_3PO_4 \cdot H_2O$	6	0	99 (98) [3]
13	1.0	1,4-Dioxane	$K_3PO_4 \cdot H_2O$	3	60	35
14	0.5	1,4-Dioxane	$K_3PO_4 \cdot H_2O$	6	0	99 (98) [3]
15	0.1	1,4-Dioxane	$K_3PO_4 \cdot H_2O$	6	65	30
16	0.05	1,4-Dioxane	$K_3PO_4 \cdot H_2O$	6	90	0.4

[1] Reaction conditions: **4a** (1.0 mmol), **5a** (1.5 mmol), **3b**/$Pd(OAc)_2$ (x mol%, **3b**:Pd = 1:1), base (3.0 mmol) in solvent (3.0 mL) under a N_2 atmosphere. [2] Determined by GC-FID using undecane as an internal standard. [3] Isolated yield in parentheses. [4] **L**/$Pd(OAc)_2$ was used. The reaction was carried out at 110 °C. [5] *t*-BuOH/H_2O = 6/4 (vol/vol).

The scope of the SMC reaction was studied after screening the optimized reaction conditions (Table 3). The coupling reactions of aryl chlorides **4a**, **4b**, and **4c** with electron-withdrawing groups proceeded in quantitative yields in line with an increase in the catalyst

loading and temperature (**6aa**–**6ca**). Similarly, the SMC reaction was carried out at 80 °C in the presence of the catalyst with 1.0 mol% loading using *m*-chloropropiophenone and *p*-chloropropiophenone as starting materials and quantitative yields of the desired products **6da** and **6ea** were obtained. With other electron-withdrawing groups at the para position, such as in **4f** and **4i**, 96% and 90% isolated yields were obtained, respectively (**6fa** and **6ia**), whereas, the coupling reactions of 1-chloro-2-nitrobenzene, **4g**, and 1-chloro-2,4-dinitrobenzene, **4h**, with phenylboronic acid showed good yields (81–89%) at 100 °C. Aryl chlorides (**4a**, **4d**, **4e**, **4f**, and **4i**) bearing electron-withdrawing groups at their *m*- or *p*-positions were coupled with 1-naphthylboronic acid at 100 °C in the presence of a catalyst with 1.5 mol% loading to give the respective products in yield of 90–99% (**6ab**–**6ib**). It was observed that the coupling reactions of benzyl chloride with phenylboronic acid or 1-naphthylboronic acid led to 95% and 99% yields of **6ja** and **6jb**, respectively, under the same reaction conditions. The aryl chlorides **4k** and **4l** with electron-donating groups gave the corresponding products (**6ka** and **6la**) in poor yields. Interestingly, *o*-chlorotoluene was coupled with phenylboronic acid in the presence of a 1 mol% **3b**/$Pd(OAc)_2$ catalyst at 80 °C (**6ma**) to give the desired product in 95% yield. Finally, the di-*ortho*-substituted biaryl syntheses of *o*-nitroarenes (**4n** and **4g**) with 1-naphthylboronic acid (**5b**) led to excellent yields of the respective products, with a 93% yield of **6hb** and a 92% yield of **6gb** observed.

Table 3. In-situ-generated **3b**/$Pd(OAc)_2$ catalyst catalyzed Suzuki–Miyaura cross-coupling reactions [1].



4 **5** **6**

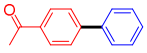
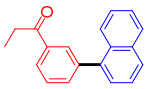
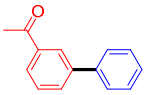
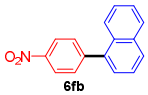
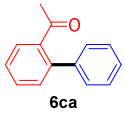
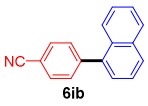
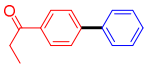
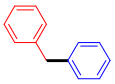
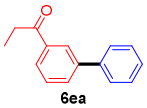
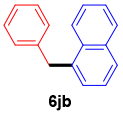
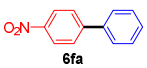
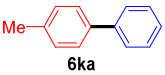
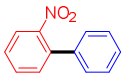
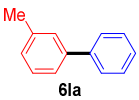
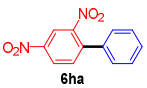
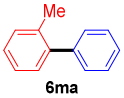
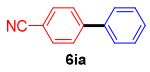
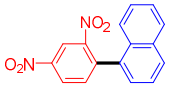
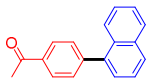
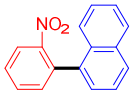
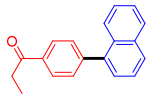
Entry	3b/$Pd(OAc)_2$ (mol%)	Temp. (°C)	6	Yield (%)	Entry	3b/$Pd(OAc)_2$ (mol%)	Temp. (°C)	6	Yield (%)
1	0.5	80	 **6aa**	99	12	1.5	100	 **6eb**	92
2	1.0	80	 **6ba**	99	13	1.5	100	 **6fb**	92
3	1.0	100	 **6ca**	98	14	1.5	100	 **6ib**	90
4	1.0	80	 **6da**	99	15	1.0	80	 **6ja**	95
5	1.0	80	 **6ea**	99	16	1.5	100	 **6jb**	99
6	1.0	80	 **6fa**	96	17	1.0	80	 **6ka**	17 [2]
7	1.0	100	 **6ga**	81	18	1.0	80	 **6la**	27 [2]
8	1.0	100	 **6ha**	89	19	1.0	80	 **6ma**	95

Table 3. *Cont.*

Entry	3b/Pd(OAc)$_2$ (mol%)	Temp. (°C)	6	Yield (%)	Entry	3b/Pd(OAc)$_2$ (mol%)	Temp. (°C)	6	Yield (%)
9	1.0	80	 6ia	90	20	2.0	100	 6hb	93
10	1.5	100	 6ab	99	21	2.0	100	 6gb	92
11	1.5	100	 6db	97					

[1] Reaction conditions: **4** (1.0 mmol), **5** (1.5 mmol), **3b**/Pd(OAc)$_2$ (x mol%, **3b**:Pd = 1:1), $K_3PO_4 \cdot H_2O$ (3.0 mmol) in 1,4-dioxane (3.0 mL) under a N_2 atmosphere. Isolated yield was reported. [2] GC-FID yield was reported by using undecane as an internal standard.

3. Materials and Methods

3.1. General Methods

Unless otherwise stated, commercially available materials were received from Aldrich and Acros and used without further purification. Acetonitrile was distilled over calcium hydride prior to its use. Toluene, 1,4-dioxane, and *t*-BuOH were distillated over sodium prior to its use. Reactions were monitored using pre-coated silica gel 60 (F-254) plates. The products were purified by column chromatography (silica gel, 0.040–0.063 μm), eluting with *n*-hexane/ethyl acetate. ^{1}H and ^{13}C NMR spectra were recorded using an Agilent Mercury 400 spectrometer(Agilent Technologies Inc., Santa Clara, CA, USA), with the *J*-values given in Hz. Chemical shifts (δ) were referenced to $CDCl_3$ (δ = 7.26 ppm) in the ^{1}H NMR spectra and $CDCl_3$ (δ = 77.0 ppm) in the ^{13}C NMR spectra. Copies of ^{1}H and ^{13}C NMR spectra of all compounds are provided as Supplementary Materials. Melting points were determined using Thermo 1001D digital melting point apparatus and are uncorrected. GC-FID was recorded using a Shimadzu GC-2014 spectrometer (Shimadzu Co., Kyoto, Japan) equipped with a capillary column (SPB®®-5, 60 m × 0.25 mm × 0.25 μm). The conversion yields, GC yields, and ratios were determined using undecane as an internal standard. High-resolution mass spectra were recorded using a Finnigan/Thermo Quest MAT 95XL mass spectrometer (Finnigan MAT LCQ, San Jose, CA, USA) via either electron impact (EI) or electrospray ionization (ESI) methods. 1,3-Bis-(bromomethyl)benzene **1a** [30], 2,6-bis-(bromomethyl)pyridine **1b** [31], 2,2′-bis-(bromomethyl)benzene **1c** [32], and 1-(4-methoxyphenyl)-1*H*-benzo[d]imidazole **2a** [29] were synthesized according to modified literature procedures.

3.2. Experimental Procedures and Spectral Data

3.2.1. Synthesis of 1-(2,4,6-Trimethylphenyl)-1H-benzimidazole **2b**

Procedure for 2-(2′,4′,6′-trimethylanilido)nitrobenzene (**S1**) [33]. A sealed tube was charged with 2-fluoronitrobenzene (0.15 mL, 1.43 mmol), 2,4,6-trimethylaniline (0.30 mL, 2.14 mmol), and anhydrous potassium fluoride (0.08 g, 1.43 mmol). The reaction mixture was heated at 180 °C for 48 h. After completion of the reaction (monitored by TLC), the mixture was cooled to room temperature and then quenched with water (15 mL). The aqueous phase was extracted with EtOAc (30 mL × 3). The combined organic layers were dried over $MgSO_4$ and then filtered. The solvent was evaporated under reduced pressure to afford crude product which was purified by chromatography to afford **S1** as an orange solid (0.35 g, 97%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 9.12 (s, 1H, NH), 8.22 (d, *J* = 7.6 Hz, 1H), 7.27 (t, *J* = 7.6 Hz, 1H), 7.00 (s, 2H), 6.68 (t, *J* = 7.6 Hz, 1H, 6.38 (d, *J* = 8.8 Hz, 1H), 2.33 (s, 3H),

2.15 (s, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 144.7, 137.3, 136.3, 136.1, 132.6, 131.9, 129.4, 126.7, 116.2, 115.0, 21.0, 18.1.

Procedure for *N*-(2′,4′,6′-trimethylphenyl)-1,2-phenylenediamine (**S2**) [33][5]. A 250 mL round-bottom flask was charged with 2-(2′,4′,6′-trimethylanilido)nitrobenzene **S1** (2.18 g, 8.49 mmol) and ethanol (60 mL). The reaction mixture was heated at 60 °C. After the 2-(2′,4′,6′-trimethylanilido)nitrobenzene was dissolved completely, the solution was added ammonium chloride solution (0.125 g/1 mL H_2O, 30 mL, 85.0 mmol), and iron (4.74 g, 85.0 mmol). The reaction mixture was refluxed for 1.5 h. After completion of the reaction (monitored by TLC), solvent was removed under reduced pressure, the residue was added with H_2O (3 mL). The aqueous layer was extracted with EtOAc (3 mL × 3). The combined organic layers were dried over $MgSO_4$ and then filtered. The solvent was evaporated under reduced pressure to afford **S2** as a deep purple solid (1.59 g, 99%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 6.93 (s, 2H), 6.79 (d, *J* = 7.2 Hz, 1H), 6.74 (t, *J* = 7.2 Hz, 1H), 6.64 (t, *J* = 7.2 Hz, 1H), 6.23 (d, *J* = 7.2 Hz, 1H), 4.76 (s, 1H, NH), 3.63 (s, 2H, NH), 2.30 (s, 3H), 2.12 (s, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 136.9, 135.6, 134.7, 133.9, 133.3, 129.3, 120.2, 120.0, 116.2, 114.9, 20.8, 18.0.

Procedure for 1-(2,4,6-trimethylphenyl)-1*H*-benzimidazole (**2b**) [34][6]. To a solution of *N*-(2′,4′,6′-trimethylphenyl)-1,2-phenylenediamine **S2** (0.40 g, 1.8 mmol) and sulfamic acid (19.0 mg, 0.20 mmol) in methanol (10 mL) was added triethyl orthoformate (1.2 mL, 6.9 mmol) at rt. After stirring overnight at rt (monitored by TLC), methanol was removed by rotary evaporator. H_2O (3 mL) was added to the residue. The aqueous layer was extracted with EtOAc (3 mL × 3). The combined organic layers were dried over $MgSO_4$ and then filtered. The solvent was evaporated under reduced pressure to afford crude product which was purified by chromatography to afford **2b** as a deep purple solid (0.37 g, 90%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.89 (d, *J* = 8.0 Hz, 1H), 7.87 (s, 1H), 7.32 (t, *J* = 7.2 Hz, 1H), 7.26 (t, *J* = 7.2 Hz, 1H), 7.05–7.02 (m, 3H), 2.39 (s, 3H), 1.92 (s, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 143.1, 142.8, 139.0, 136.0, 133.9, 130.8, 129.1, 123.2, 122.1, 120.1, 109.9, 20.9, 17.2.

3.2.2. General Procedures for the Synthesis of Bis-Benzimidazolium Salts **3**

Procedure for bis-benzimidazolium salts **3a–d**. A 10 mL round-bottom flask was charged with dibromide **1a** or **1b** (1.0 equiv), benzimidazole **2a** or **2b** (2.0 equiv to bromide), and MeCN (5.0 mL). After refluxing for 18 h, the precipitate was formed. The precipitate was filtered off, washed with EtOAc, and dried to afford pure product.

Procedure for 3,3′-(1,3-Phenylenebis(methylene))bis(1-(4-methoxyphenyl)-1*H*-benzo[d] imidazol-3-ium) dibromide (**3a**). 1,3-bis-(bromomethyl)benzene **1a** (46.5 mg, 0.18 mmol) and 1-(4-methoxyphenyl)-1*H*-benzo[d]imidazole **2a** (79.5 mg, 0.36 mmol) were used to afford **3a** as white solid in 88% yield (0.10 g). Mp = 282–283 °C; ^{1}H NMR (DMSO, 400 MHz): δ 10.36 (s, 2H), 7.97 (s, 1H), 7.94 (d, *J* = 8.0 Hz, 2H), 7.78–7.76 (m, 6H), 7.68–7.58 (m, 6H), 7.48 (t, *J* = 8.0 Hz, 1H), 7.26 (d, *J* = 8.8 Hz, 4H), 5.86 (s, 4H), 3.89 (s, 6H); ^{13}C NMR (DMSO, 100 MHz): δ 158.6, 140.8, 132.4, 129.7, 128.7, 127.6, 127.0, 126.7, 125.4, 124.9, 124.8, 123.7, 113.4, 112.1, 111.7, 57.7, 53.8. HRMS-MALDI-TOF(*m*/*z*) $[M\text{-}Br]^+$ Calculated for $C_{36}H_{32}BrN_4O_2^+$: 631.1703, found: 631.1706.

Procedure for 3,3′-(1,3-Phenylenebis(methylene))bis(1-mesityl-1*H*-benzo[d]imidazol-3-ium) dibromide (**3b**). 1,3-bis-(bromomethyl)benzene **1a** (0.10 g, 0.38 mmol) and 1-(2,4,6-trimethylphenyl)-1*H*-benzimidazole **2b** (0.18 g, 0.77 mmol) were used to afford **3b** as white solid in 89% yield (0.25 g). Mp = 210–213 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 11.47 (s, 2H), 8.51 (s, 1H), 8.23 (d, *J* = 8.4 Hz, 2H), 7.69 (d, *J* = 8.0 Hz, 2H), 7.67 (t, *J* = 8.4 Hz, 2H), 7.54 (t, *J* = 8.0 Hz, 2H), 7.33 (t, *J* = 8.0 Hz, 1H), 7.18 (d, *J* = 8.4 Hz, 2H), 7.06 (s, 4H), 6.26 (s, 4H), 2.37 (s, 6H), 1.99 (s, 12H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 142.4, 141.6, 135.0, 134.2, 131.5, 130.7, 130.3, 130.2, 130.1, 129.4, 128.2, 128.0, 127.8, 115.2, 112.9, 50.7, 21.1, 17.6. HRMS-MALDI-TOF(*m*/*z*) $[M\text{-}Br]^+$ Calculated for $C_{40}H_{40}BrN_4^+$: 655.2431, found: 655.2435.

Procedure for 3,3′-(Pyridine-2,6-diylbis(methylene))bis(1-(4-methoxyphenyl)-1*H*-benzo[d] imidazol-3-ium) dibromide (**3c**). 2,6-bis-(bromomethyl)pyridine **1b** (41.5 mg, 0.16 mmol)

and 1-(4-methoxyphenyl)-1*H*-benzo[d]imidazole **2a** (72.1 mg, 0.33 mmol) were used to afford **3c** as white solid in 82% yield (0.095 g). Mp = 283–284 °C; ^{1}H NMR (DMSO, 400 MHz): δ 10.15 (s, 2H), 8.06 (t, *J* = 7.6 Hz, 1H), 7.79 (t, *J* = 7.6 Hz, 4H), 7.68–7.55 (m, 8H), 7.47 (t, *J* = 7.6 Hz, 2H), 7.20 (d, *J* = 8.4 Hz, 4H), 5.92 (s, 4H), 3.89 (s, 6H); ^{13}C NMR (DMSO, 100 MHz): δ 160.5, 152.9, 144.8, 142.8, 131.0, 130.97, 127.2, 126.8, 126.5, 125.4, 123.0, 115.3, 113.8, 113.4, 55.7, 50.8. HRMS-MALDI-TOF(*m*/*z*) [M-Br]$^+$ Calculated for $C_{35}H_{31}BrN_5O_2^+$: 632.1656, found: 632.1657.

Procedure for 3,3′-(Pyridine-2,6-diylbis(methylene))bis(1-mesityl-1*H*-benzo[d]imidazol-3-ium) dibromide (**3d**)**.** 2,6-bis-(bromomethyl)pyridine **1b** (24.7 mg, 0.09 mmol) and 1-(2,4,6-trimethylphenyl)-1*H*-benzimidazole **2b** (44.4 mg, 0.18 mmol) were used to afford **3d** as white solid in 50% yield (0.034 g). Mp = 204–205 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 11.57 (s, 2H), 7.97 (d, *J* = 8.0 Hz, 2H), 7.78–7.75 (m, 5H), 7.58 (t, *J* = 8.0 Hz, 2H), 7.23 (d, *J* = 8.0 Hz, 2H), 7.10 (s, 4H), 6.42 (s, 4H), 2.40 (s, 6H), 2.04 (s, 12H); ^{13}C NMR ($CDCl_3$, 400 MHz): δ 152.9, 143.1, 141.8, 139.5, 135.1, 131.5, 130.9, 130.2, 128.6, 128.1, 127.9, 123.5, 114.6, 113.0, 52.2, 21.2, 17.7; HRMS-MALDI-TOF(*m*/*z*) [M-Br]$^+$ Calculated for $C_{39}H_{39}BrN_5^+$: 656.2383, found: 656.2377.

General Procedures for Preparation of bis-benzimidazolium salts **3e** and **3f**. A 10 mL round-bottom flask was charged with dibromide **1c** (1.0 equiv), benzimidazole **2a** or **2b** (2.0 equiv to bromide), and MeCN (5.0 mL). After refluxing for 18 h, the precipitate was formed. The precipitate was filtered off, washed with EtOAc, and dried to afford pure product.

Procedure for 3,3′-([1,1′-Biphenyl]-2,2′-diylbis(methylene))bis(1-(4-methoxyphenyl)-1*H*-benzo[d]imidazol-3-ium) dibromide (**3e**)**.** 2,2′-bis((bromomethyl)benzene **1c** (46.0 mg, 0.14 mmol) and 1-(4-methoxyphenyl)-1*H*-benzo[d]imidazole **2a** (62.2 mg, 0.29 mmol) were used to afford **3e** as white solid in 78% yield (0.083 g). Mp = 200–201 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 10.52 (s, 2H), 7.68–7.53 (m, 12H), 7.49 (d, *J* = 7.6 Hz, 2H), 7.35 (t, *J* = 7.6 Hz, 2H), 7.26 (t, *J* = 7.6 Hz, 2H), 7.11 (d, *J* = 8.8 Hz, 4H), 6.88 (d, *J* = 7.6 Hz, 2H), 6.26 (d, *J* = 16.0 Hz, 2H), 5.91 (d, *J* = 16.0 Hz, 2H), 3.87 (s, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 161.0, 142.0, 138.5, 131.2, 131.1, 131.0, 129.8, 129.7, 129.4, 129.3, 127.72, 127.65, 126.1, 125.1, 115.7, 114.2, 113.5, 55.8, 50.3. HRMS-MALDI-TOF(*m*/*z*) [M-Br]$^+$ Calculated for $C_{42}H_{36}BrN_4O_2^+$: 707.2016, found: 707.2017.

Procedure for 3,3′-([1,1′-Biphenyl]-2,2′-diylbis(methylene))bis(1-mesityl-1*H*-benzo[d]imidazol-3-ium) dibromide (**3f**)**.** 2,2′-bis((bromomethyl)benzene **1c** (36.5 mg, 0.11 mmol) and 1-(2,4,6-trimethylphenyl)-1*H*-benzimidazole **2b** (54.3 mg, 0.24 mmol) were used to afford **3f** as white solid in 68% yield (0.059 g). Mp = 297–298 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 11.00 (s, 2H), 7.89 (d, *J* = 7.6 Hz, 2H), 7.70 (t, *J* = 7.6 Hz, 2H), 7.61 (t, *J* = 7.6 Hz, 2H), 7.52 (d, *J* = 7.6 Hz, 2H), 7.46 (t, *J* = 7.6 Hz, 2H), 7.37 (t, *J* = 7.6 Hz, 2H), 7.25 (d, *J* = 7.6 Hz, 2H), 7.07 (s, 4H), 7.04 (d, *J* = 7.6 Hz, 2H), 6.55 (d, *J* = 16.8 Hz, 2H), 5.97 (d, *J* = 16.8 Hz, 2H), 2.38 (s, 6H), 2.05 (s, 6H), 2.01 (s, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 143.4, 141.7, 138.0, 135.1, 135.0, 131.5, 131.4, 131.3, 130.6, 130.2, 129.44, 129.39, 128.3, 128.1, 126.7, 114.7, 113.0, 49.7, 21.2, 17.8, 17.7. HRMS-MALDI-TOF(*m*/*z*) [M-Br]$^+$ Calculated for $C_{46}H_{44}BrN_4^+$: 731.2744, found: 731.2742.

3.2.3. General Procedures for Suzuki–Miyaura Cross-Coupling Reactions under N_2

All manipulations were carried out under nitrogen using dried solvent. $Pd(OAc)_2$ (1 mol%), salt **3b** (1 mol%) and 1,4-dioxane (3 mL) were charged to the Schlenk tube at 80 °C for 1 h, followed by the addition of arylboronic acid **5** (1.50 mmol), aryl chloride **4** (1.00 mmol), and $K_3PO_4 \cdot H_2O$ (3.00 mmol) at the prescribed temperature for the prescribed time. After completion of the reaction, monitored by TLC, the reaction was quenched by water (3.0 mL). The aqueous layer was extracted with EtOAc (3.0 mL × 3). The organic layer was dried over anhydrous $MgSO_4$ and then filtered. The solvent was evaporated under reduced pressure and the corresponding crude product of the Suzuki−Miyaura coupling reaction was purified by chromatography.

4-Acetylbiphenyl (**6aa**) [29]. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.04 (d, *J* = 7.6 Hz, 2H), 7.69 (d, *J* = 7.6 Hz, 2H), 7.63 (d, *J* = 7.6 Hz, 2H), 7.47 (t, *J* = 7.6 Hz, 2H), 7.43–7.38 (m, 1H), 2.64 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 197.7, 145.7, 139.8, 135.8, 128.92, 128.88, 128.2, 127.2, 127.2, 26.6.

3-Acetylbiphenyl (**6ba**) [35]. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.19 (s, 1H), 7.94 (d, *J* = 7.6 Hz, 1H), 7.80 (d, *J* = 7.6 Hz, 1H), 7.63 (d, *J* = 7.2 Hz, 2H), 7.54 (t, *J* = 7.6 Hz, 1H), 7.47 (t, *J* = 7.2 Hz, 2H), 7.41–7.37 (m, 1H), 2.66 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 197.8, 141.4, 139.9, 137.4, 131.5, 128.8, 128.7, 127.6, 127.0, 126.95, 126.7, 26.5.

2-Acetylbiphenyl (**6ca**) [36]. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.57–7.50 (m, 2H), 7.44–7.39 (m, 5H), 7.36–7.34 (m, 2H), 2.01 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 205.0, 140.8, 140.6, 140.5, 130.7, 130.2, 128.8, 128.6, 127.85, 127.82, 127.4, 30.4.

4′-Phenylpropiophenone (**6da**) [29]. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.05 (d, *J* = 8.4 Hz, 2H), 7.68 (d, *J* = 8.4 Hz, 2H), 7.63 (d, *J* = 7.8 Hz, 2H), 7.47 (t, *J* = 7.8 Hz, 2H), 7.43–7.38 (m, 1H), 3.05 (q, *J* = 7.2 Hz, 2H), 1.26 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR ($CDCl_3$,100 MHz): δ 200.5, 145.5, 139.9, 135.6, 128.9, 128.6, 128.2, 127.23, 127.19, 31.8, 8.3.

3′-Phenylpropiophenone (**6ea**) [29]. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.20 (s, 1H), 7.95 (d, *J* = 7.6 Hz, 1H), 7.78 (d, *J* = 7.6 Hz, 1H), 7.63 (d, *J* = 7.6 Hz, 2H), 7.53 (t, *J* = 7.6 Hz, 1H), 7.48 (t, *J* = 7.6 Hz, 2H), 7.43–7.36 (m, 1H), 3.07 (q, *J* = 7.2 Hz, 2H), 1.27 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 200.7, 141.6, 140.2, 137.3, 131.5, 129.0, 128.9, 127.7, 127.1, 126.8, 126.6, 31.9, 8.2.

4-Nitrobiphenyl (**6fa**) [37]. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.30 (d, *J* = 8.4 Hz, 2H), 7.74 (d, *J* = 8.4 Hz, 2H), 7.63 (d, *J* = 7.2 Hz, 2H), 7.55–7.41 (m, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 147.6, 147.0, 138.7, 129.1, 128.9, 127.8, 127.3, 124.1.

2-Nitrobiphenyl (**6ga**) [37]. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.86 (d, *J* = 7.6 Hz, 1H), 7.62 (t, *J* = 7.6 Hz, 1H), 7.51–7.39 (m, 5H), 7.34–7.32 (m, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 149.2, 137.3, 136.3, 132.2, 131.9, 128.7, 128.2, 128.1, 127.9, 124.0.

2,4-Dinitrobiphenyl (**6ha**) [29]. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.71 (d, *J* = 2.4 Hz, 1H), 8.47 (dd, *J* = 8.8, 2.4 Hz, 1H), 7.67 (d, *J* = 8.8 Hz, 1H), 7.50–7.47 (m, 3H), 7.36–7.33 (m, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 148.8, 146.6, 142.1, 135.1, 133.2, 129.4, 128.9, 127.5, 126.4, 119.6.

4-Cyanobiphenyl (**6ia**) [38]. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.73 (d, *J* = 8.4 Hz, 2H), 7.69 (d, *J* = 8.4 Hz, 2H), 7.59 (d, *J* = 7.6 Hz, 2H), 7.49 (t, *J* = 7.6 Hz, 2H), 7.46–7.40 (m, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 145.2, 138.7, 132.2, 128.8, 128.4, 127.3, 126.9, 118.6, 110.5.

1-(4-(Naphthalen-1-yl)phenyl)ethan-1-one (**6ab**) [29]. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.10 (d, *J* = 7.6 Hz, 2H), 7.94–7.84 (m, 3H), 7.61 (d, *J* = 7.6 Hz, 2H), 7.57–7.43 (m, 4H), 2.69 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 197.9, 145.8, 139.0, 135.9, 133.7, 131.1, 130.3, 128.4, 128.35, 128.33, 126.9, 126.4, 126.0, 125.5, 125.3, 26.7.

1-(4-(Naphthalen-1-yl)phenyl)propan-1-one (**6db**) [29]. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.10 (d, *J* = 8.0 Hz, 2H), 7.94–7.84 (m, 3H), 7.60 (d, *J* = 8.0 Hz, 2H), 7.57–7.42 (m, 4H), 3.09 (q, *J* = 7.2 Hz, 2H), 1.29 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 200.1, 145.2, 138.8, 135.5, 133.6, 130.9, 130.0, 128.2, 128.1, 127.8, 126.7, 126.2, 125.8, 125.3, 125.1, 31.6, 8.1.

1-(3-(Naphthalen-1-yl)phenyl)propan-1-one (**6eb**) [29]. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.09 (s, 1H), 8.04 (d, *J* = 8.4 Hz, 1H), 7.94–7.89 (m, 2H), 7.81 (d, *J* = 8.0 Hz, 1H), 7.69 (d, *J* = 8.0 Hz, 1H), 7.61–7.50 (m, 3H), 7.44 (t, *J* = 8.4 Hz, 2H), 3.05 (q, *J* = 7.2 Hz, 2H), 1.25 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 200.1, 140.7, 138.8, 136.7, 134.0, 133.5, 131.1, 129.2, 128.2, 128.1, 127.8, 126.7, 126.5, 126.0, 125.6, 125.2, 125.0, 31.5, 7.9.

1-(4-Nitrophenyl)naphthalene (**6fb**) [37]. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.37 (d, *J* = 8.4 Hz, 2H), 7.94 (dd, *J* = 8.4, 2.4 Hz, 2H), 7.78 (d, *J* = 8.4 Hz, 1H), 7.68 (d, *J* = 8.4 Hz, 2H), 7.59–7.41 (m, 4H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 147.6, 147.1, 137.7, 133.7, 130.9, 128.9, 128.5, 127.1, 126.7, 126.2, 125.3, 125.1, 123.6.

4-(1-Naphthyl)benzonitrile (**6ib**) [38]. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.93 (d, *J* = 7.2 Hz, 2H), 7.80–7.76 (m, 3H), 7.62 (d, *J* = 8.4 Hz, 2H), 7.57–7.45 (m, 3H), 7.40 (d, *J* = 7.2 Hz, 1H);

^{13}C NMR ($CDCl_3$, 100 MHz): δ 145.2, 137.8, 133.5, 131.8, 130.6, 130.4, 128.5, 128.3, 126.8, 126.4, 125.9, 125.1, 124.9, 118.6, 110.8.

Diphenylmethane (**6ja**) [39]. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.31–7.27 (m, 4H), 7.22–7.20 (m, 6H), 3.99 (s, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 141.1, 128.9, 128.4, 126.0, 41.9.

1-Benzylnapthalene (**6jb**) [40]. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.99 (d, *J* = 8.0 Hz, 1H), 7.86–7.84 (m, 1H), 7.76 (d, *J* = 8.0 Hz, 1H), 7.46–7.40 (m, 3H), 7.29–7.24 (m, 3H), 7.20–7.16 (m, 3H), 4.45 (s, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 140.5, 136.5, 133.9, 132.1, 128.6, 128.58, 128.4, 127.2, 127.1, 125.9, 125.9, 125.5, 124.2, 38.9.

4-Methylbiphenyl (**6ka**) [37]. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.58 (d, *J* = 7.2 Hz, 2H), 7.49 (d, *J* = 8.0 Hz, 2H), 7.42 (t, *J* = 7.2 Hz, 2H), 7.34–7.30 (m, 1H), 7.25 (d, *J* = 8.0 Hz, 2H), 2.40 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 141.1, 138.3, 137.0, 129.5, 128.7, 127.0, 21.1.

3-Methylbiphenyl (**6la**) [41]. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.60 (d, *J* = 7.2 Hz, 2H), 7.46–7.40 (m, 4H), 7.37–7.33 (m, 2H), 7.18 (d, *J* = 7.2 Hz, 1H), 2.44 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 141.3, 141.2, 138.2, 128.6, 127.9, 127.87, 127.1, 124.2, 21.4.

2-Methylbiphenyl (**6ma**) [29]. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.41 (t, *J* = 7.2 Hz, 2H), 7.35–7.31 (m, 3H), 7.26–7.24 (m, 4H,), 2.27 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 141.9, 141.89, 135.3, 130.3, 129.8, 129.1, 128.0, 127.2, 126.7, 125.7, 20.4.

1-(2,4-Dinitrophenyl)naphthalene (**6hb**) [42]. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.93 (s, 1H), 8.55 (d, *J* = 8.4 Hz, 1H), 7.96 (t, *J* = 9.2 Hz, 2H), 7.74 (d, *J* = 8.4 Hz, 1H), 7.57–7.52 (m, 2H), 7.46 (t, *J* = 7.6 Hz, 1H), 7.38–7.34 (m, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 149.8, 147.4, 141.6, 134.5, 133.4, 133.2, 130.7, 129.7, 128.8, 127.2, 126.6, 126.5, 126.1, 125.2, 124.1, 119.9.

1-(2-Nitrophenyl)naphthalene (**6gb**) [43]. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.08 (d, *J* = 8.4 Hz, 1H), 7.91 (d, *J* = 8.4 Hz, 2H), 7.71 (t, *J* = 7.2 Hz, 1H), 7.61 (t, *J* = 8.4 Hz, 1H), 7.52–7.39 (m, 5H), 7.35 (d, *J* = 7.2 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 149.8, 135.5, 135.3, 133.4, 133.1, 132.5, 131.4, 128.6, 128.6, 128.5, 126.6, 126.0, 125.6, 125.2, 124.8, 124.23.

4. Conclusions

In summary, a series of new xylyl-linked bis-benzimidazolium salts **3a**–**3f** were effectively synthesized via a simple synthetic route using cheap reactants. The changing of both the linkers and wingtips of the xylyl-linked bis-benzimidazolium salts **3a**–**3f** led to different steric and electronic effects being observed. It was found in the Suzuki–Miyaura cross-coupling reactions of aryl chlorides that bis-benzimidazolium salts featuring benzene as a xylyl-linked spacer (**3a** and **3b**) led to higher yields of the respective products being formed, whereas when pyridine (**3c** and **3d**) and biphenyl (**3e** and **3f**) were used as linkers lower yields were observed. Comparing the bis-NHC precursors **3a** and **3b**, the precursor with a sterically demanding wingtip (**3b**) led to the product being formed in a higher yield than when a precursor was used with an electronically demanding wingtip (**3a**). Various aryl chlorides, including carbonyl-, nitro-, and nitrile-functionalized compounds, were coupled with arylboronic acids to give the respective products in good to excellent yields at 80–100 °C using the in-situ-generated bis-NHC **3b**/Pd catalyst system, with a loading in the range of 0.5–2.0 mol%. In addition, in di-*ortho*-substituted biaryl syntheses excellent yields were observed when 1-chloro-2,4-dinitrobenzene and 1-chloro-2-nitrobenzene were coupled with 1-naphthylboronic acid.

Supplementary Materials: The following are available online at https://www.mdpi.com/article/10.3390/catal11070817/s1, Figure S1: ^{1}H NMR spectrum of 2-(2′,4′,6′-trimethylanilido)nitrobenzene **S1** in $CDCl_3$, Figure S2: ^{13}C NMR spectrum of 2-(2′,4′,6′-trimethylanilido)nitrobenzene **S1** in $CDCl_3$, Figure S3: ^{1}H NMR spectrum of *N*-(2′,4′,6′-trimethylphenyl)-1,2-phenylenediamine **S1** in $CDCl_3$, Figure S4: ^{13}C NMR spectrum of *N*-(2′,4′,6′-trimethylphenyl)-1,2-phenylenediamine **S2** in $CDCl_3$, Figure S5: ^{1}H NMR spectrum of 1-(2,4,6-trimethylphenyl)-1*H*-benzimidazole **2b** in $CDCl_3$, Figure S6: ^{13}C NMR spectrum of 1-(2,4,6-trimethylphenyl)-1*H*-benzimidazole **2b** in $CDCl_3$, Figure S7: ^{1}H NMR spectrum of (3,3′-(1,3-phenylenebis(methylene))bis(1-(4-methoxyphenyl)-1*H*-benzo[d]imidazol-3-ium)) dibromide (**3a**) in DMSO-d_6, Figure S8: ^{13}C NMR spectrum of (3,3′-

(1,3-phenylenebis(methylene))bis(1-(4-methoxyphenyl)-1*H*-benzo[d]imidazol-3-ium)) dibromide (**3a**) in DMSO-d_6, Figure S9: ^{1}H NMR spectrum of (3,3′-(1,3-phenylenebis(methylene))bis(1-mesityl-1*H*-benzo[d]imidazol-3-ium)) dibromide (**3b**) in $CDCl_3$, Figure S10: ^{13}C NMR spectrum of (3,3′-(1,3-phenylenebis(methylene))bis(1-mesityl-1*H*-benzo[d]imidazol-3-ium)) dibromide (**3b**) in $CDCl_3$, Figure S11: ^{1}H NMR spectrum of (3,3′-(pyridine-2,6-diylbis(methylene))bis(1-(4-methoxyphenyl)-1*H*-benzo[d]imidazol-3-ium)) dibromide (**3c**) in DMSO-d_6, Figure S12: ^{13}C NMR spectrum of (3,3′-(pyridine-2,6-diylbis(methylene))bis(1-(4-methoxyphenyl)-1*H*-benzo[d]imidazol-3-ium)) dibromide (**3c**) in DMSO-d_6, Figure S13: ^{1}H NMR spectrum of (3,3′-(pyridine-2,6-diylbis(methylene))bis(1-mesityl-1*H*-benzo[d]imidazol-3-ium)) dibromide (**3d**) in $CDCl_3$, Figure S14: ^{13}C NMR spectrum of (3,3′-(pyridine-2,6-diylbis(methylene))bis(1-mesityl-1*H*-benzo[d]imidazol-3-ium)) dibromide (**3d**) in $CDCl_3$, Figure S15: ^{1}H NMR spectrum of 3,3′-([1,1′-biphenyl]-2,2′-diylbis(methylene))bis(1-(4-methoxyphenyl)-1*H*-benzo[d]imidazol-3-ium) dibromide (**3e**) in $CDCl_3$, Figure S16: ^{13}C NMR spectrum of 3,3′-([1,1′-biphenyl]-2,2′-diylbis(methylene))bis(1-(4-methoxyphenyl)-1*H*-benzo[d]imidazol-3-ium) dibromide (**3e**) in $CDCl_3$, Figure S17: ^{1}H NMR spectrum of 3,3′-([1,1′-biphenyl]-2,2′-diylbis (methylene))bis(1-mesityl-1*H*-benzo[d]imidazol-3-ium) dibromide (**3f**) in $CDCl_3$, Figure S18: ^{13}C NMR spectrum of 3,3′-([1,1′-biphenyl]-2,2′-diylbis(methylene))bis(1-mesityl-1*H*-benzo[d]imidazol-3-ium) dibromide (**3f**) in $CDCl_3$, Figure S19: ^{1}H NMR spectrum of 4-acetylbiphenyl (**6aa**) in $CDCl_3$, Figure S20: ^{13}C NMR spectrum of 4-acetylbiphenyl (**6aa**) in $CDCl_3$, Figure S21: ^{1}H NMR spectrum of 3-acetylbiphenyl (**6ba**) in $CDCl_3$, Figure S22: ^{13}C NMR spectrum of 3-acetylbiphenyl (**6ba**) in $CDCl_3$, Figure S23: ^{1}H NMR spectrum of 2-acetylbiphenyl (**6ca**) in $CDCl_3$, Figure S24: ^{13}C NMR spectrum of 2-acetylbiphenyl (**6ca**) in $CDCl_3$, Figure S25: ^{1}H NMR spectrum of 4′-phenylpropiophenone (**6da**) in $CDCl_3$, Figure S26: ^{13}C NMR spectrum of 4′-phenylpropiophenone (**6da**) in $CDCl_3$, Figure S27: ^{1}H NMR spectrum of 3′-phenylpropiophenone (**6ea**) in $CDCl_3$, Figure S28: ^{13}C NMR spectrum of 3′-phenylpropiophenone (**6ea**) in $CDCl_3$, Figure S29: ^{1}H NMR spectrum of 4-nitrobiphenyl (**6fa**) in $CDCl_3$, Figure S30: ^{13}C NMR spectrum of 4-nitrobiphenyl (**6fa**) in $CDCl_3$, Figure S31: ^{1}H NMR spectrum of 2-nitrobiphenyl (**6ga**) in $CDCl_3$, Figure S32: ^{13}C NMR spectrum of 2-nitrobiphenyl (**6ga**) in $CDCl_3$, Figure S33: ^{1}H NMR spectrum of 2,4-dinitrobiphenyl (**6ha**) in $CDCl_3$, Figure S34: ^{13}C NMR spectrum of 2,4-dinitrobiphenyl (**6ha**) in $CDCl_3$, Figure S35: ^{1}H NMR spectrum of 4-cyanobiphenyl (**6ia**) in $CDCl_3$, Figure S36: ^{13}C NMR spectrum of 4-cyanobiphenyl (**6ia**) in $CDCl_3$, Figure S37: ^{1}H NMR spectrum of diphenylmethane (**6ja**) in $CDCl_3$, Figure S38: ^{13}C NMR spectrum of diphenylmethane (**6ja**) in $CDCl_3$, Figure S39: ^{1}H NMR spectrum of 4-methylbiphenyl (**6ka**) in $CDCl_3$, Figure S40: ^{13}C NMR spectrum of 4-methylbiphenyl (**6ka**) in $CDCl_3$, Figure S41: ^{1}H NMR spectrum of 3-methylbiphenyl (**6la**) in $CDCl_3$, Figure S42: ^{13}C NMR spectrum of 3-methylbiphenyl (**6la**) in $CDCl_3$, Figure S43: ^{1}H NMR spectrum of 2-methylbiphenyl (**6ma**) in $CDCl_3$, Figure S44: ^{13}C NMR spectrum of 2-methylbiphenyl (**6ma**) in $CDCl_3$, Figure S45: ^{1}H NMR spectrum of 1-(4-(naphthalen-1-yl)phenyl)propan-1-one (**6db**) in $CDCl_3$, Figure S46: ^{13}C NMR spectrum of 1-(4-(naphthalen-1-yl)phenyl)propan-1-one (**6db**) in $CDCl_3$, Figure S47: ^{1}H NMR spectrum of 1-(4-nitrophenyl)naphthalene (**6fb**) in $CDCl_3$, Figure S48: ^{13}C NMR spectrum of 1-(4-nitrophenyl)naphthalene (**6fb**) in $CDCl_3$, Figure S49: ^{1}H NMR spectrum of 4-(1-naphthyl)benzonitrile (**6ib**) in $CDCl_3$, Figure S50: ^{13}C NMR spectrum of 4-(1-naphthyl)benzonitrile (**6ib**) in $CDCl_3$, Figure S51: ^{1}H NMR spectrum of 1-(3-(naphthalen-1-yl)phenyl)propan-1-one (**6eb**) in $CDCl_3$, Figure S52: ^{13}C NMR spectrum of 1-(3-(naphthalen-1-yl)phenyl)propan-1-one (**6eb**) in $CDCl_3$, Figure S53: ^{1}H NMR spectrum of 1-benzylnapthalene (**6jb**) in $CDCl_3$, Figure S54: ^{13}C NMR spectrum of 1-benzylnapthalene (**6jb**) in $CDCl_3$, Figure S55: ^{1}H NMR spectrum of 1-(2-nitrophenyl)naphthalene (**6gb**) in $CDCl_3$, Figure S56: ^{13}C NMR spectrum of 1-(2-nitrophenyl)naphthalene (**6gb**) in $CDCl_3$, Figure S57: ^{1}H NMR spectrum of 1-(2,4-dinitrophenyl)naphthalene (**6hb**) in $CDCl_3$, Figure S58: ^{13}C NMR spectrum of 1-(2,4-dinitrophenyl)naphthalene (**6hb**) in $CDCl_3$.

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References

1. Miyaura, N.; Suzuki, A. Palladium-Catalyzed Cross-Coupling Reactions of Organoboron Compounds. *Chem. Rev.* **1995**, *95*, 2457–2483. [CrossRef]
2. Stanforth, S.P. Catalytic Cross-Coupling Reactions in Biaryl Synthesis. *Tetrahedron* **1998**, *54*, 263–303. [CrossRef]
3. Suzuki, A. Recent advances in the cross-coupling reactions of organoboron derivatives with organic electrophiles, 1995–1998. *J. Organomet. Chem.* **1999**, *576*, 147–168. [CrossRef]
4. Mingji, D.; Liang, B.; Wang, C.; You, Z.; Xiang, J.; Dong, G.; Chen, J.; Yang, Z. A Novel Thiourea Ligand Applied in the Pd-Catalyzed Heck, Suzuki and Suzuki Carbonylative Reactions. *Adv. Synth. Catal.* **2004**, *346*, 1669–1673. [CrossRef]
5. Suzuki, A.; Yamamoto, Y. Cross-coupling Reactions of Organoboranes: An Easy Method for C–C Bonding. *Chem. Lett.* **2011**, *40*, 894–901. [CrossRef]
6. Grushin, V.V.; Alper, H. Transformations of Chloroarenes, Catalyzed by Transition-Metal Complexes. *Chem. Rev.* **1994**, *94*, 1047–1062. [CrossRef]
7. Littke, A.F.; Fu, G.C. Palladium-Catalyzed Coupling Reactions of Aryl Chlorides. *Angew. Chem. Int. Ed.* **2002**, *41*, 4176–4211. [CrossRef]
8. Corbet, J.-P.; Mignani, G. Selected Patented Cross-Coupling Reaction Technologies. *Chem. Rev.* **2006**, *106*, 2651–2710. [CrossRef]
9. Wong, S.M.; Yuen, O.Y.; Choy, P.Y.; Kwong, F.Y. When Cross-Coupling Partners Meet Indolylphosphines. *Coord. Chem. Rev.* **2015**, *293–294*, 158–186. [CrossRef]
10. Schwarz, J.B.; Böhm, V.P.W.; Gardiner, M.G.; Grosche, M.; Hermann, W.A.; Hieringer, W.; Raudaschl-Sieber, G. Polymer-Supported Carbene Complexes of Palladium: Well-Defined, Air-Stable, Recyclable Catalysts for the Heck Reaction. *Chem. Eur. J.* **2000**, *6*, 1773–1780. [CrossRef]
11. Hermann, W.A.; Öfele, K.; Preysing, D.; Herdtweck, E. Metal complexes of acyclic diaminocarbenes: Links between *N*-heterocyclic carbene (NHC)- and Fischer-carbene complexes. *J. Organomet. Chem.* **2003**, *684*, 235–248. [CrossRef]
12. Herrmann, W.A.; Reisinger, C.-P.; Spiegler, M. Chelating *N*-heterocyclic carbene ligands in palladium-catalyzed heck-type reactions. *J. Organomet. Chem.* **1998**, *557*, 93–96. [CrossRef]
13. Zhang, C.; Trudell, M.L. Palladium-bisimidazol-2-ylidene complexes as catalysts for general and efficient Suzuki cross-coupling reactions of aryl chlorides with arylboronic acids. *Tetrahedron Lett.* **2000**, *41*, 595–598. [CrossRef]
14. Özdemir, İ.; Çetinkaya, B.; Demir, S.; Gürbüz, N. Palladium-catalyzed Suzuki-Miyaura reaction using saturated *N*-heterocyclic ligands. *Catal. Lett.* **2004**, *97*, 37–40. [CrossRef]
15. Özdemir, İ.; Gök, Y.; Gürbüz, N.; Çetinkaya, E.; Çetinkaya, B. Suzuki-Miyaura Reaction of Unactivated Aryl Chlorides Using Beznimidazol-2-Ylidene Ligands. *Synth. Commun.* **2004**, *34*, 4135–4144. [CrossRef]
16. Özdemir, İ.; Gök, Y.; Gürbüz, N.; Çetinkaya, E.; Çetinkaya, B. Palladium-Catalyzed Suzuki Reaction Using 1,3-Dialkylbenzimidazol-2-ylidene Ligands in Aqueous Media. *Heteroat. Chem.* **2004**, *15*, 419–423. [CrossRef]
17. Shi, M.; Qian, H.-X. A new dimeric bidentated NHC–Pd(II) complex from trans-cyclohexane-1,2-diamine for Suzuki reaction and Heck reaction. *Tetrahedron* **2005**, *61*, 4949–4955. [CrossRef]
18. Xu, Q.; Duan, W.-L.; Lei, Z.-Y.; Zhu, Z.-B.; Shi, M. A novel cis-chelated Pd(II)–NHC complex for catalyzing Suzuki and Heck-type cross-coupling reactions. *Tetrahedron* **2005**, *61*, 11225–11229. [CrossRef]
19. Demir, S.; Özdemir, İ.; Çetinkaya, B. Use of bis(benzimidazolium)–palladium system as a convenient catalyst for Heck and Suzuki coupling reactions of aryl bromides and chlorides. *Appl. Organometal. Chem.* **2006**, *20*, 254–259. [CrossRef]
20. Özdemir, İ.; Demir, S.; Çetinkaya, B. Novel tetrahydropyrimidinium/palladium system as a convenient catalysts: Suzuki coupling reactions of aryl chlorides. *Arkivoc* **2007**, *13*, 71–78. [CrossRef]
21. Liu, Z.; Zhang, T.; Shi, M. Cyclometalated cis-Chelated Bidentate N-Heterocyclic Carbene Palladium Complexes: Synthetic, Structural, and Catalytic Studies. *Organometallics* **2008**, *27*, 2668–2671. [CrossRef]
22. Avery, K.B.; Devine, W.G.; Kormos, C.M.; Leadbeater, N.E. Use of a silicon carbide multi-well plate in conjunction with microwave heating for rapid ligand synthesis, formation of palladium complexes, and catalyst screening in a Suzuki coupling. *Tetrahedron Lett.* **2009**, *50*, 2851–2853. [CrossRef]
23. Yilmaz, U.; Şireci, N.; Deniz, S.; Küçükbay, H. Synthesis and microwave-assisted catalytic activity of novel bis-benzimidazoles salts bearing furfuryl and thenyl moieties in Heck and Suzuki cross-coupling reactions. *Appl. Organometal. Chem.* **2010**, *24*, 414–420.
24. Micksch, M.; Strassner, T. Palladium(II) Complexes with Chelating Biscarbene Ligands in the Catalytic Suzuki–Miyaura Cross-Coupling Reaction. *Eur. J. Org. Chem.* **2012**, 5872–5880. [CrossRef]
25. Li, Y.; Tang, J.; Gu, J.; Wang, Q.; Sun, P.; Zhang, D. Chiral 1,2-Cyclohexane-Bridged Bis-NHC Palladium Catalysts for Asymmetric Suzuki–Miyaura Coupling: Synthesis, Characterization, and Steric Effects on Enantiocontrol. *Organometallics* **2014**, *33*, 876–884. [CrossRef]

26. Charbonneau, M.; Addoumieh, G.; Oguadinma, P.; Schmitzer, A.R. Support-Free Palladium–NHC Catalyst for High Recyclable Heterogeneous Suzuki–Miyaura Coupling in Neat Water. *Organometallics* **2014**, *33*, 6544–6549. [CrossRef]
27. Thapa, R.; Kilyanek, S.M. Synthesis and structural characterization of 20-membered macrocyclic rings bearing *trans*-chelating bis(N-heterocyclic carbene) ligands and the catalytic activity of their palladium(II) complexes. *Dalton Trans.* **2019**, *48*, 12577–12590. [CrossRef]
28. Lin, Y.-R.; Chiu, C.-C.; Chiu, H.-T.; Lee, D.-S.; Lu, T.-J. Bis-benzimidazolium-palladium system catalyzed Suzuki–Miyaura coupling reaction of aryl bromides under mild conditions. *Appl. Organometal. Chem.* **2017**, *32*, e3896. [CrossRef]
29. Chiu, C.-C.; Chiu, H.-T.; Lee, D.-S.; Lu, T.-J. An efficient class of bis-NHC salts: Applications in Pd-catalyzed reactions under mild reaction conditions. *RSC Adv.* **2018**, *8*, 26407–26415. [CrossRef]
30. Tran, V.M.; Nguyen, T.K.N.; Sorna, V.; Loganathan, D.; Kuberan, B. Synthesis and Assessment of Glycosaminoglycan Priming Activity of Cluster-xylosides for Potential Use as Proteoglycan Mimetics. *ACS Chem. Biol.* **2013**, *8*, 949–957. [CrossRef]
31. Yu, K.-K.; Li, K.; Hou, J.-T.; Yu, X.-Q. Coumarin-TPA Derivative: A reaction-based ratiometric fluorescent probe for Cu(I). *Tetrahedron Lett.* **2013**, *54*, 5771–5774. [CrossRef]
32. Cervantes-Reyes, A.; Rominger, F.; Rudolph, M.; Hashmi, A.S.K. Gold(I) Complexes Stabilized by Nine- and Ten-Membered N-Heterocyclic Carbene Ligands. *Chem. Eur. J.* **2019**, *25*, 11745–11757. [CrossRef] [PubMed]
33. Liu, H.; Fridman, N.; Tamm, M.; Eisten, M.S. Addition of E–H (E = N, P, C, O, S) Bonds to Heterocumulenes Catalyzed by Benzimidazolin-2-iminato Actinide Complexes. *Organometallics* **2017**, *36*, 3896–3903. [CrossRef]
34. Chan, A.; Scheidt, K.A. Highly Stereoselective Formal [3+3] Cycloaddition of Enals and Azomethine Imines Catalyzed by N-Heterocyclic Carbenes. *J. Am. Che. Soc.* **2007**, *129*, 5334–5335. [CrossRef] [PubMed]
35. Glannerini, M.; Vila, C.; Hornillos, V.; Feringa, B.L. One-Pot, Fast and Modular Approach to Alkyl- and Aryl Ketones via Sequential 1,2-Addition,Pd-Catalyzed Cross-Coupling of Organolithium Reagents with Weinreb Amides. *Chem. Commun.* **2016**, *52*, 1206–1209. [CrossRef]
36. Liu, Z.; Tan, H.; Wang, L.; Fu, T.; Xia, Y.; Zhang, Y.; Wang, J. Transition-Metal-Free Intramolecular Carbene Aromatic Substitution/Büchner Reaction: Synthesis of Fluorenes and [6,5,7]Benzo-fused Rings. *Angew. Chem. Int. Ed.* **2015**, *54*, 3056–3060. [CrossRef]
37. Mao, P.; Yang, L.; Xiao, Y.; Yuan, J.; Liu, X.; Song, M. Suzuki cross-coupling catalyzed by palladium(II) complexes bearing 1-aryl-3,4,5,6-tetrahydropyrimidine ligands. *J. Organomet. Chem.* **2012**, *705*, 39–43. [CrossRef]
38. Chen, L.; Lang, H.; Fang, L.; Yu, J.; Wang, L. Nickel-Catalyzed Desulfitative Suzuki–Miyaura Cross-Coupling of *N*,*N*-Disulfinylmethylamines and Arylboromic Acids. *Eur. J. Org. Chem.* **2014**, *2014*, 6385–6389. [CrossRef]
39. Han, C.; Zhang, Z.; Xu, S.; Wang, K.; Chen, K.; Zhao, J. Palladium-Catalyzed Hiyama Coupling of Benzylic Ammonium Salts via C–N Bond Cleavage. *J. Org. Chem.* **2019**, *84*, 16308–16313. [CrossRef]
40. Piontek, A.; Ochędzan-Siodłak, W.; Bisz, E.; Szostak, M. Nickel-Catalyzed C(sp^2)-C(sp^3) Kumada Cross-Coupling of Aryl Tosylates with Alkyl Grignard Reagents. *Adv. Synth. Catal.* **2019**, *361*, 2329–2335. [CrossRef]
41. Liu, H.; Yin, B.; Gao, Z.; Li, Y.; Jiang, H. Transition-metal-free highly chemo- and regioselective arylation of unactivated arenes with aryl halides over recyclable heterogeneous catalysts. *Chem. Commun.* **2012**, *48*, 2033–2035. [CrossRef] [PubMed]
42. Lücke, A.-L.; Wlechmann, S.; Freese, T.; Schmidt, A. Suzuki–Miyaura Cross-Coupling Reactions in Acetic Acid Employing Sydnone-Derived Catalyst Systems. *Synlett* **2017**, *28*, 1990–1993.
43. Song, B.; Knauber, T.; Gooßen, L.J. Decarboxylative Cross-Coupling of Mesylates Catalyzed by Copper/Palladium Systems with Customized Imidazolyl Phosphine Ligands. *Angew. Chem. Int. Ed.* **2013**, *52*, 2954–2958. [CrossRef] [PubMed]