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Iodine-Catalyzed Suzuki–Miyaura Coupling Performed in Air

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Abstract: Suzuki-type coupling reactions can be performed directly in air using a catalytic system composed of iodine, potassium carbonate, and polyethylene glycol 400 (I_2/K_2CO_3/PEG-400). Iodine was found to be an effective additive for accelerating these couplings. The methodology is also suitable for the coupling of (*E*)-β-bromostyene with phenylboronic acid, with retention of the double bond geometry.

Keywords: accelerating effect; arylboronic acids; cross-coupling reactions; iodine; polyethylene glycol 400 (PEG-400)

Introduction

Since its discovery by Suzuki and Miyaura in 1979, the cross-coupling of aryl halides with arylboronic acids has been considered one of the most powerful, versatile and popular tools for the selective construction of carbon-carbon bonds.[1] The impact of this reaction in organic synthesis is largely attributed to the fact that it provides biaryl compounds which are important structural moieties in numerous polymers, agrochemicals, natural products and pharmaceutical intermediates.[2–5] In the past two decades, advances have been made to develop even more efficient catalytic systems for the Suzuki–Miyaura coupling reaction. Among these improvements, palladium-phosphine complexes are now amongst the most commonly employed catalysts of choice.[6–7] Furthermore, chemists have developed an acceptable catalytic cycle.[1]

However, the drawbacks of Pd catalyst systems, such as their high cost, toxicity and the potential contamination of the products, limit massive applications in large-scale synthesis, particularly in the pharmaceutical industry, where close monitoring of the metal contamination of products is required.[8] The use of a less expensive metal than Pd may be advantageous, as developed and previously reported by our group and others.[9,10] A recent study showed that copper and copper-based nanocolloids are good catalysts for these C–C coupling reactions. However, only the couplings of aryl iodides were investigated with copper alone as catalyst and the additional metals (Pd and Ru) could show better efficiency.[11] Although the study of Goossen and co-workers represents a different way to prepare biaryls by decarboxylative coupling,[12] their catalytic system still includes a Pd complex together with $CuCO_3$ or CuI as the co-catalyst. In addition, the ligand and a molecular sieve are also required. Recently, Fagnou reported the catalytic cross-coupling of unactivated arenes with moderate to good yields. But their catalytic system also needs a Pd complex, copper catalyst and ligand.[13] In view of these findings, we turned back to reconsider the traditional Suzuki–Miyaura coupling reaction, wondering if it could be directly catalyzed by more accessible and less expensive catalysts, even without using synthetic ligands.

Results and Discussion

Poly(ethylene)glycol (PEG) is widely considered as a good recyclable solvent with a low environmental impact. Thus, it has been used for biomedical applications, especially in the field of drug discovery. It is noteworthy that PEG may afford amazingly good results compared with the common solvents.[14] This is perhaps attributable to its special role in catalysis relative to classical phase-transfer catalysts.

We carried out a control catalytic coupling reaction between iodobenzene and 4-methylphenylboronic acid without using a metal catalyst. The catalytic conditions were: 0.3 mmol of aryl halides, 0.4 mmol of arylboronic acids, 0.6 mmol K_2CO_3, 2 mL of PEG-400. As expected, there was no product when the catalytic reaction was conducted in an argon atmosphere. However, to our surprise, we found that the colour of the mixture became gradually yellow when the catalytic reaction was performed in air. After the catalytic reaction had proceeded at 110 °C for 12 h, it was quenched by adding an equivalent of a water-ethyl acetate mixture. The catalytic reactions performed in air or under an argon atmosphere were visibly different (Figure 1). After a series of work-ups, we obtained the desired coupling product with 14% yield from the reaction in air; however, no reaction occurred when the catalytic reaction was performed in argon. Therefore, we conclude tentatively that the oxygen from the air played an important role in catalyzing the Suzuki–Miyaura coupling reactions under these conditions.[15]

Figure 1. The different colours between the catalytic reaction performed in air or argon atmosphere (the reaction was quenched with 2 mL of water and 2 mL of ethyl acetate).

To improve the yield of biaryl products, we tried various additives. We had previously found accidently that a stoichiometric amount of iodine promotes the homocoupling of arylboronic acids with good yields.[16] Thus, we wondered whether iodine, which is inexpensive and readily available, could also accelerate the Suzuki–Miyaura coupling between iodobenzene and 4-methylphenylboronic acid. To our delight, the desired product was obtained with 77% yield when the catalytic reaction was carried out in air with iodine as the additive (20 mol%) at 110 °C for 12 h. In order to control for issuses of potential metal contamination, we carried out experiments in new flasks with new stirring bars and new caps. We also ensured that all of reagents including aryl halides, arylboronic acids, K_2CO_3 and PEG-400 had the low levels of Pd (below 10 ppb) as measured by ICP-MS.[17,18] Furthermore, to make sure of the validity of these results, various research workers in our laboratory independently carried out these experiments, in some cases using different reagents from various known chemical corporations: the results obtained were similar in all cases. Scrutinizing the reaction phenomenon, we observed that the colour of the mixture changed with time as shown in Figure 2. At the beginning of the reaction (picture **A**, Figure 2), idodine was gradually dispersed in the system and then the mixture became transiently dark, transparent and homogeneous upon the catalytic reaction being heated at 110 °C for about 1 min (picture **B**). Then the colour of the system became clearer after another minute (picture **C**) and to our surprise, it turned to colorless after 5 min (picture **D**). From then on, the colour of the system continued to become gradually yellower, eventually turning to brown at 44 h. This raised the question: at what time is the highest conversion of the catalytic reaction obtained?

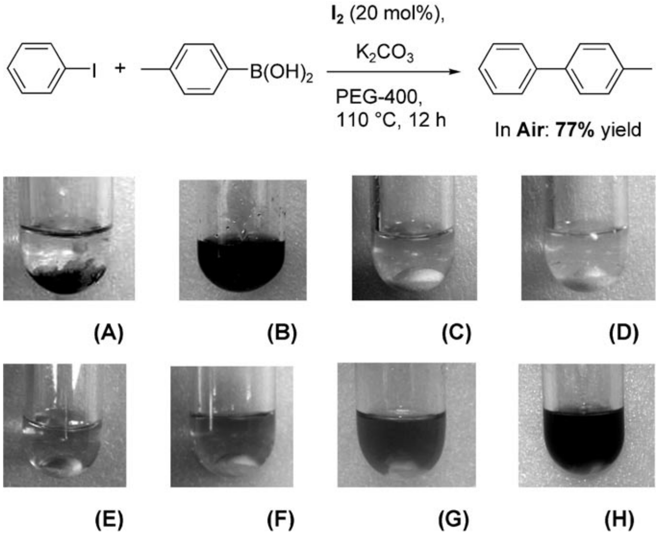


Figure 2. The different colours of the reaction system within 44 h: (**A**) starting state before heating; (**B**) 1 min after heating at 110 °C; (**C**) at 2 min; (**D**) at 5 min; (**E**) at 5 h; (**F**) at 8 h; (**G**) at 22 h; (**H**) at 44 h.

To address this time *vs.* yield issue, we carried out a series of experiments with different reaction times. For example, the reaction after about 44 h was quenched and the product was obtained with only 42% yield after flash column chromatography. In this case, the colour of the mixture did not correlate with the efficiency of the catalytic system. As shown in Figure 3, the I_2/K_2CO_3/PEG-400 system afforded the

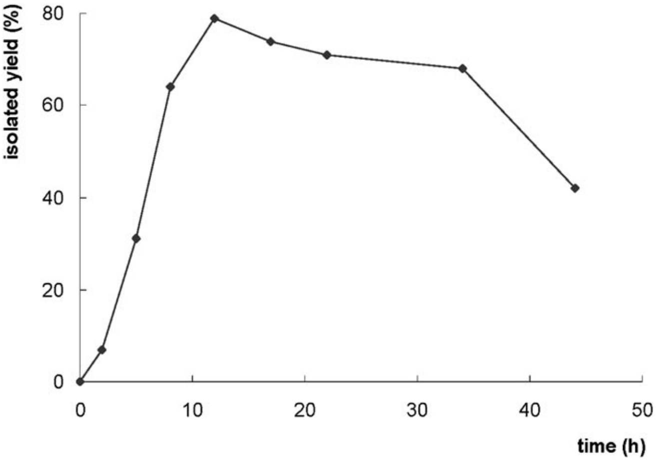
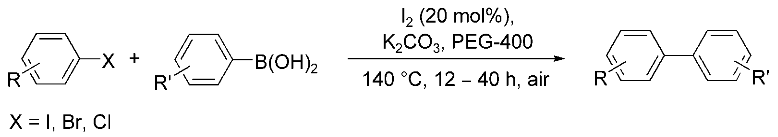


Figure 3. The relationship between the reaction time and the isolated yield of the coupling product.

highest conversion at 12 h (77% yield). To our surprise, the yields of the catalytic reaction decreased after 12 h. It seems that the coupling reaction accelerated by iodine reached an equilibrium at this point, beyond which it was not favourable for the coupling reaction. At this moment, some by-products were also generated which was indicated by TLC. Prolongation of the reaction time did not result in higher conversions.

Subsequently, a further series of optimized experiments were carried out to explore different solvents and bases. First, we found that no product was obtained in the absence of base. Second, various common solvents (such as DMF, DMSO, toluene, dioxane, H_2O, CH_3CN, *i*-PrOH) and various bases (such as Cs_2CO_3, Na_2CO_3 and $K_3PO_4{\cdot}H_2O$) all gave worse results than our original system. Further, other bases such as *t*-BuOK, KF, KOH, NaOH, NaOAc gave almost no product. Thus, we conclude that the combination of PEG-400 with K_2CO_3 was good for catalysis. Other PEGs with different molecular weights were also tested as solvent and similar results were acquired. However, very low yields of desired product were obtained when simple glycols with different structures (such as glycol and propanediol) were employed. This suggested that PEGs acted not only as the solvent but could accelerate the coupling reactions.[14] Looking through the published papers, it can be seen that Tu[19] has reported the rapid and efficient microwave-assisted amination of electron-rich aryl halides without a transition-metal catalyst and Leadbeater[20] also disclosed an example of the transition metal-free Sonogashira-type coupling. Therefore, in this paper we have shown that Suzuki–Miyaura coupling reaction could be carried out without using a transition metal catalyst.

Table 1. Substrate scope of the Suzuki–Miyaura coupling reaction promoted by iodine.[a]



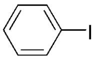
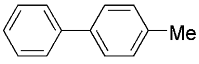
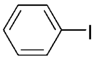
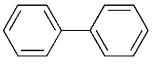
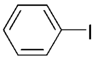
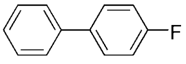
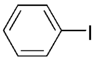
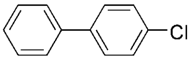
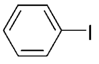
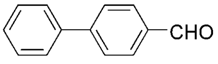
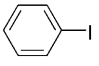
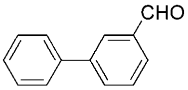
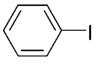
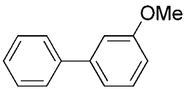
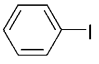
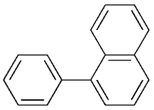
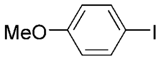
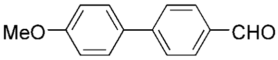
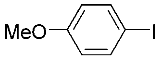
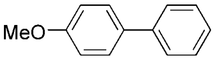
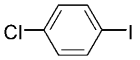
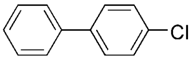
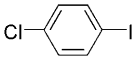
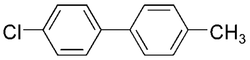
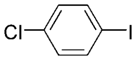
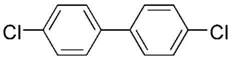
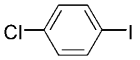
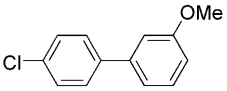
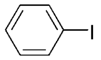
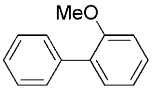
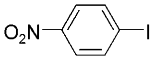
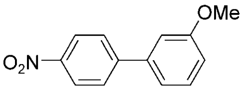
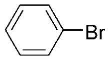
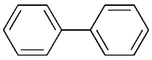
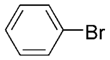
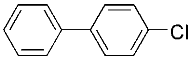
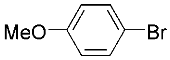
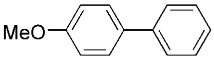
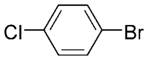
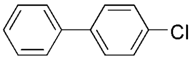
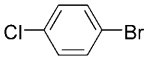
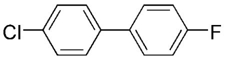
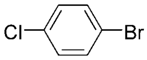
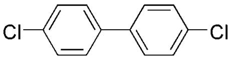
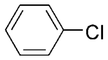
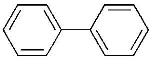
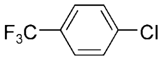
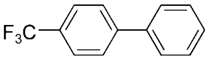
Entry	Aryl halide	Product		Time [h]	Yield [%][b]
1			**1a**	12	80
2			**1b**	18	75
3			**1c**	36	89
4			**1d**	24	>98
5			**1e**	36	37
6			**1f**	36	24
7			**1g**	24	>98
8			**1h**	12	88

Table 1. (Continued)

Entry	Aryl halide	Product		Time [h]	Yield [%][b]
9			**1i**	36	65
10			**1j**	12	84
11			**1d**	36	55
12			**1k**	36	74
13			**1l**	24	47
14			**1m**	12	90
15			**1n**	12	90
16			**1o**	24	>98
17			**1b**	28	73
18			**1d**	28	66
19			**1j**	36	66
20			**1d**	36	74
21			**1p**	36	86
22			**1l**	40	90
23			**1b**	40	28
24			**1q**	40	29

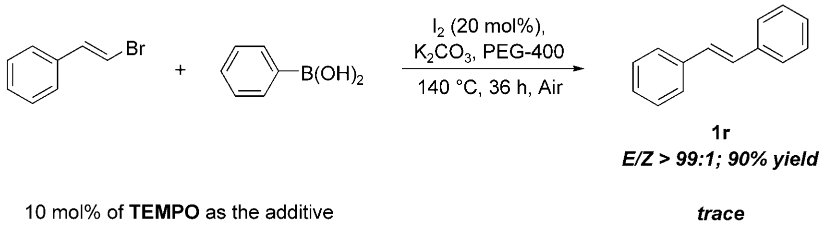
[a] *Reaction conditions:* 0.06 mmol of I_2, 0.3 mmol of aryl halides, 0.4 mmol of arylboronic acids, 0.6 mmol K_2CO_3, 2 mL of PEG-400, 140 °C, 12–40 h, in air.

[b] Isolated yield.

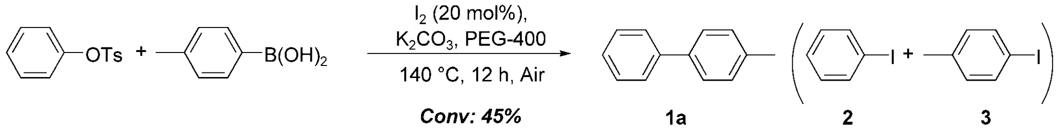
Elevated temperature (140 °C) gave a higher conversion of the catalytic reaction when comparing the same time-points (12 h) (Table 1, entry 1). High yields were obtained for the couplings of various aryl halides and arylboronic acids with different reaction times at 140 °C (summarized in Table 1). As to the aryl halides, the highest yields of the corresponding coupling products were also obtained (entries 4, 7, 14–16). Notably, I_2/K_2CO_3/PEG-400 could not catalyze the couplings of aryl iodides and heteroarylboronic acids. Subsequently, various aryl bromides and chlorides were investigated as the substrates. The coupling of these difficult substrates could also be carried out sucessfully using iodine as the additive (entries 17–24).

Furthermore, we also applied our protocol to the coupling of (*E*)-*β*-bromostyrene with phenylboronic acid (Scheme 1) with the desired product being obtained with high yield (90%). In this case, it is remarkable that the double bond geometry of the vinyl bromide was retained under these reaction conditions. However, the same catalytic reaction in the presence of 10 mol% of TEMPO (2,2,6,6-tetramethyl-1-piperidin-1-yloxy) gave no corresponding coupling product, as corroborated by GC-MS. Thus, we began to consider this type of coupling as being a possible radical reaction.[21]

The coupling between the phenyl tosylate and 4-methylphenylboronic acid was conducted with our protocol as shown in Scheme 2. Although the conver-



Scheme 1. Coupling reaction of vinyl bromide with phenylboronic acid using the I_2/K_2CO_3/PEG-400 system.



Scheme 2. Coupling reaction of phenyl tosylate with 4-methylphenylboronic acid using I_2/K_2CO_3/PEG-400 system.

sion of the catalytic reaction was not high (45%), it is noteworthy that, besides the desired coupling product, small amounts of iodobenzene and 4-iodotoluene were obtained as by-products which were proved by GC-MS. Thus, we believe that these aryl halides are probably generated from the reactants will also suggests the possible radical mechanism.

In addition, it is well known that iodine acts as electron acceptor, due to the presence of vacant antibonding orbitals. It is possible, therefore, that iodine can act as a catalyst because of its Lewis acidity. We speculated that the transition from the deep colour to a transparent solution that is obtained during the reaction after several times (pictures **A–D** in Figure 2), may be due to the coordination of iodine with the aromatic compound/boronic acid. Moreover, iodine also acts as an oxidant. In the presence of some oxidants, aryl radicals will be generated from arylboronic acids[22] and obviously, in this case the oxygen in the air is an important factor for the success of the reaction. Our further work will focus on exploring the putative radical mechanism in this new type of coupling reactions.

Conclusions

In summary, it is of great interest to find that the traditional Suzuki–Miyaura coupling could be performed in air with an I_2/K_2CO_3/PEG-400 catalytic system without using a transition metal catalyst. The iodine was an effective and indispensable additive for accelerating the couplings. This methodology is also suitable for the coupling of (*E*)-β-bromostyene with phenylboronic acid, which could maintain the double bond geometry. All in all, it provides a fascinating alternative to the traditional transition metal-catalyzed reaction conditions because the novel coupling reaction is more economic, easily operable and more accessible, which will open up new opportunities for the industrial synthesis of high-value pharmaceutical intermediates.[23] Further work is in progress with the aim of understanding the reaction mechanisms. Furthermore, we are seeking to expand potential applications of similar catalytic protocols to other coupling processes of similar industrial interest.

Experimental Section

General Experimental Details

All reactions were directly carried out in air. All arylboronic acids or esters and other chemical reagents were purchased from Aldrich or Alfa. Flash column chromatography was performed using silica gel (300–400 mesh). Analytical thin-layer chromatography was carried out using glass plates pre-coated with 200–400 mesh silica gel impregnated with a fluorescent indicator (254 nm). NMR spectra were measured in $CDCl_3$ on a Varian Inova-400 NMR spectrometer (400 MHz or 300 MHz) with TMS as an internal reference. Products were characterized by comparison of ^1H and ^{13}C NMR data with values in the literatures.

General Procedure for Iodine-Mediated Suzuki–Miyaura Coupling Reactions of Arylboronic Acid and Aryl Halides

A Schlenk tube (10 mL) was charged with potassium carbonate (2.0 equiv.), iodine (0.2 equiv.), arylboronic acid (1.0 equiv.) and any remaining solids (aryl halides) in the solvent of PEG-400 (2 mL), aryl halide (1.3 equiv.) was added directly. The tube was sealed under air, and the mixture was heated to 140 °C and stirred for 12–40 h. After cooling to room temperature, the mixture was diluted with water, and the combined aqueous phases were extracted three times with ethyl acetate. The organic layers were combined, dried over Na_2SO_4, and concentrated to yield the crude product, which was further purified by silica gel chromatography.

4-Methylbiphenyl (1a): ^{1}H NMR (CDCl$_3$, 300 MHz): $\delta=2.37$ (s, 3H, CH$_3$), 7.22 (d, $J=7.5$ Hz, 2H, ArH), 7.30 (t, $J=7.2$ Hz, 1H, ArH), 7.40 (t, $J=7.5$ Hz, 2H, ArH), 7.48 (d, $J=7.8$ Hz, 2H, ArH), 7.56 (d, $J=7.5$ Hz, 2H, ArH); ^{13}C NMR (75 MHz, CDCl$_3$): $\delta=141.6$, 138.8, 137.4, 129.9, 129.2, 127.4, 127.4, 21.6.

Biphenyl (1b): ^{1}H NMR (CDCl$_3$, 400 MHz): $\delta=7.36$ (t, $J=7.2$ Hz, 2H, ArH), 7.45 (d, $J=7.2$ Hz, 4H, ArH), 7.60 (d, $J=7.2$ Hz, 4H, ArH); ^{13}C NMR (100 MHz, CDCl$_3$): $\delta=141.7$, 129.2, 127.7, 127.6.

4-Fluorobiphenyl (1c): ^{1}H NMR (CDCl$_3$, 300 MHz): $\delta=7.12$ (t, $J=8.7$ Hz, 2H, ArH), 7.34 (t, $J=7.1$ Hz, 1H, ArH), 7.43 (t, $J=7.2$ Hz, 2H, ArH), 7.51–7.56 (m, 4H, ArH); ^{13}C NMR (100 MHz, CDCl$_3$): $\delta=164.1$, 161.7, 140.7, 137.8, 137.8, 129.3, 129.2, 129.1, 127.7, 127.5, 116.2, 116.0.

4-Chlorobiphenyl (1d): ^{1}H NMR (CDCl$_3$, 400 MHz): $\delta=7.33$–7.45 (m, 5H, ArH), 7.49–7.55 (m, 4H, ArH); ^{13}C NMR (75 MHz, CDCl$_3$): $\delta=140.4$, 140.1, 133.8, 129.5, 129.4, 129.4, 129.3, 128.8, 128.1, 127.4, 110.2.

Biphenyl-4-carbaldehyde (1e): ^{1}H NMR (400 MHz, CDCl$_3$): $\delta=7.42$–7.51 (m, 2H, ArH), 7.64 (d, $J=7.6$ Hz, 2H, ArH), 7.76 (d, $J=8.0$ Hz, 2H, ArH), 7.96 (d, $J=8.0$ Hz, 2H, ArH), 10.06 (s, 1H, CHO); ^{13}C NMR (100 MHz, CDCl$_3$): $\delta=192.4$, 147.6, 140.2, 135.6, 130.7, 129.5, 128.9, 128.1, 127.8.

Biphenyl-3-carbaldehyde (1f): ^{1}H NMR (400 MHz, CDCl$_3$): $\delta=7.40$ (s, 1H, ArH), 7.41–7.49 (m, 3H, ArH), 7.62 (t, $J=6.8$ Hz, 3H, ArH), 7.86 (d, $J=7.2$ Hz, 2H, ArH), 8.10 (s, 1H, ArH), 10.09 (s, 1H, CHO); ^{13}C NMR (100 MHz, CDCl$_3$): $\delta=192.9$, 142.7, 140.2, 137.4, 133.6, 130.0, 129.5, 129.1, 128.7, 128.5, 127.6.

3-Methoxylbiphenyl (1g): ^{1}H NMR (300 MHz, CDCl$_3$): $\delta=3.76$ (s, 3H, CH$_3$O), 6.80 (d, $J=7.8$ Hz, 1H, ArH), 7.08 (t, $J=9.3$ Hz, 6H, ArH), 7.23–7.36 (m, 2H, ArH), 7.50 (d, $J=7.5$ Hz, 2H, ArH); ^{13}C NMR (100 MHz, CDCl$_3$): $\delta=160.4$, 143.2, 141.5, 130.2, 129.2, 127.9, 127.6, 120.1, 113.3, 113.1, 55.7.

1-Phenylnaphthalene (1h): ^{1}H NMR (300 MHz, CDCl$_3$): $\delta=7.45$–7.49 (m, 6H, ArH), 7.82–7.84 (m, 6H, ArH); ^{13}C NMR (75 MHz, CDCl$_3$): $\delta=133.82$, 130.46, 129.86, 128.64, 128.26, 126.20.

4-Methoxylbiphenyl-4′-carbaldehyde (1i): ^{1}H NMR (300 MHz, CDCl$_3$): $\delta=3.87$ (s, 3H, CH$_3$O), 7.01 (d, $J=6.3$ Hz, 2H, ArH), 7.60 (d, $J=6.6$ Hz, 2H, ArH) ,7.71 (d, $J=6.0$ Hz, 2H, ArH), 7.93 (d, $J=6.0$ Hz, 2H, ArH), 10.04 (s, 1H, CHO); ^{13}C NMR (75 MHz, CDCl$_3$): $\delta=192.4$, 130.8, 129.0, 127.6, 119.4, 114.9, 55.9.

4-Methoxylbiphenyl (1j): ^{1}H NMR (300 MHz, CDCl$_3$): $\delta=3.86$ (s, 3H, CH$_3$O), 6.96–7.00 (m, 2H, ArH), 7.26 (s, 1H, ArH), 7.40–7.44 (m, 2H, ArH), 7.52–7.57 (m, 4H, ArH); ^{13}C NMR (100 MHz, CDCl$_3$): $\delta=129.2$, 128.6, 127.2, 127.1, 114.7, 55.8.

4-Chloro-4′-methylbiphenyl (1k): ^{1}H NMR (400 MHz, CDCl$_3$): $\delta=2.38$ (s, 3H), 7.24 (t, $J=8.0$ Hz, 2H), 7.36–7.63 (m, 6H); ^{13}C NMR (100 MHz, CDCl$_3$): $\delta=140.0$, 137.9, 137.5, 133.5, 130.1, 129.3, 128.6, 127.3, 21.6.

4, 4′-Dichlorobiphenyl (1l): ^{1}H NMR (300 MHz, CDCl$_3$): $\delta=7.33$ (d, $J=8.4$ Hz, 4H, ArH), 7.40 (d, $J=8.1$ Hz, 4H, ArH); ^{13}C NMR (75 MHz, CDCl$_3$): $\delta=138.9$, 134.0, 129.5, 128.7.

4-Chloro-3′-methoxylbiphenyl (1m): ^{1}H NMR (400 MHz, CDCl$_3$): $\delta=3.86$ (s, 3H), 6.90–6.93 (m, 1H), 7.09 (t, $J=2.0$ Hz, 1H), 7.14 (d, $J=7.6$ Hz, 1H), 7.34–7.41 (m, 3H), 7.50–7.52 (m, 2H); ^{13}C NMR (100 MHz, CDCl$_3$): $\delta=160.5$, 141.9, 140.0, 133.9, 130.4, 129.3, 128.9, 119.9, 113.3, 113.3, 55.8.

2-Methoxylbiphenyl (1n): ^{1}H NMR (300 MHz, CDCl$_3$): $\delta=3.70$ (s, 3H, CH$_3$O), 6.87–6.96 (m, 2H, ArH), 7.21 (t, $J=6.3$ Hz, 3H, ArH), 7.31 (t, $J=7.2$ Hz, 2H, ArH), 7.44 (d, $J=7.5$ Hz, 2H, ArH); ^{13}C NMR (100 MHz, CDCl$_3$): $\delta=156.8$, 138.9, 131.3, 129.9, 129.0, 128.4, 127.3, 121.2, 111.6, 55.9.

4-Nitro-3′-methoxylbiphenyl (1o): ^{1}H NMR (400 MHz, CDCl$_3$): $\delta=6.97$–7.00 (m, 1H), 7.13 (t, $J=2.0$ Hz, 1H), 7.41 (t, $J=8.0$ Hz, 1H), 7.71 (d, $J=8.4$ Hz, 2H), 8.27 (d, $J=8.8$ Hz, 2H); ^{13}C NMR (100 MHz, CDCl$_3$): $\delta=160.6$, 147.9, 140.6, 130.7, 128.3, 124.5, 120.3, 114.6, 113.7, 55.9.

4-Chloro-4′-fluorobiphenyl (1p): ^{1}H NMR (400 MHz, CDCl$_3$): $\delta=7.12$ (t, $J=8.8$ Hz, 2H, ArH), 7.38–7.51 (m, 6H, ArH); ^{13}C NMR (100 MHz, CDCl$_3$): $\delta=164.3$, 161.8, 139.1, 136.6, 136.5, 133.8, 129.4, 128.7, 116.3, 116.1.

4-Trifluoromethylbiphenyl (1q): mp 69–70 °C; ^{1}H NMR (400 MHz, CDCl$_3$): $\delta=7.35$ (t, $J=7.6$ Hz, 1H, ArH), 7.40–7.49 (m, 3H, ArH), 7.60 (d, $J=7.2$ Hz, 3H, ArH), 7.69 (s, 2H, ArH); ^{13}C NMR (100 MHz, CDCl$_3$): $\delta=129.5$, 129.2, 128.7, 127.9, 127.7, 127.7, 126.2.

(*E*)-1,2-diphenylethene (1r): ^{1}H NMR (400 MHz, CDCl$_3$): $\delta=7.13$ (s, 2H), 7.24–7.30 (m, 2H), 7.38 (t, $J=7.6$ Hz, 4H), 7.54 (d, $J=7.2$ Hz, 4H); ^{13}C NMR (100 MHz, CDCl$_3$): $\delta=137.8$, 129.2, 128.1, 127.0.

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