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Hiyama reaction of aryl bromides with arylsiloxanes catalyzed by a reusable palladium(II)/cationic bipyridyl system in water

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ABSTRACT

A $Pd(NH_3)_2Cl_2$/cationic bipyridyl catalytic system catalyzed the cross-coupling reaction of aryl bromides with arylsiloxanes in water under aerobic conditions in the presence of NaOH to afford biaryls in good to high yields. The reaction was performed at 120 °C and the loading amount of catalyst can be as low as 0.001 mol %. After extraction, the residual aqueous phase can be reused several times with only a slight decrease in activity.

1. Introduction

The palladium-catalyzed cross-coupling of aryl halides and organometallic reagents for the construction of biaryls is one of the most powerful methods in modern organic synthesis.[1] Among organometallic reagents, organostannanes (Stille reaction)[2] and organoborons (Suzuki–Miyaura reaction)[3] are most widely used as coupling partners for transmetallation because of their high functional group tolerances. Related to these organometallic reagents that are used in the cross-coupling reaction, organosilanes (Hiyama reaction) are very attractive due to their low cost, low toxicity, ease of handling, and stability in various chemical media. Because of the low reactivity of organosilanes, the reaction generally requires fluoride anions for the activation of the stable silicon–carbon bond to facilitate the transmetallation step.[4,5] Recently, however, several groups have described the replacement of the fluoride anion by NaOH and achievement of the reaction in water, an environmentally friendly, inflammable, and cheap solvent, which is excellent from a green chemistry point of view.[6] Furthermore, the organic product is easily separated from the aqueous phase, and one of the most important features of catalysis in water is that recycling and reuse of the catalyst is possible, which is highly desirable from an economic viewpoint. To date, studies focusing on the use of both fluoride-free and reusable catalysts in water for the Hiyama reaction are still rare. Recently, Nájera et al. performed oxime-derived palladacycles in a concentrated aqueous NaOH solution-catalyzed Hiyama reaction under heating or microwave irradiation, which showed highly efficient and recyclable properties.[7] Shi and Zhang reported that recycling of the catalyst could be achieved by using $Pd(OAc)_2$ as the catalyst in aqueous NaOH solution with PEG 2000 as an additive.[8]

We have previously developed an air-stable and water-soluble cationic 2,2′-bipyridyl ligand to bring palladium(II) and rhodium(I) complexes into the aqueous phase, leading to the formation of catalyst-recyclable catalytic systems for the Suzuki–Miyaura reaction[9] and phenylacetylenes polymerization.[10] In this paper, we extend the scope of the reusable $Pd(NH_3)_2Cl_2$/cationic 2,2′-bipyridyl catalytic system for the coupling of aryl bromides and arylsiloxanes in water under aerobic conditions without the addition of an additive and examine its reusability.

2. Results and discussion

2.1. Preparation of a cationic bipyridyl ligand and optimization of reaction conditions for the Hiyama reaction

We began with the preparation of a water-soluble cationic bipyridyl ligand. The precursor, 4,4′-bis(bromomethyl)-2,2′-bipyridine, **1**, in dichloromethane was treated with an excess of Me_3N (50% aqueous solution) at room temperature for 24 h. The clear solution was then freeze-dried to give the cationic 2,2′-bipyridyl ligand, **2**, in a quantitative yield (Scheme 1). The catalytic system is

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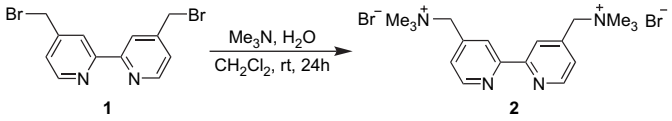
feasible to prepare and can be stored in air by mixing equimolar amounts of **2** with $Pd(NH_3)_2Cl_2$ in water.



Scheme 1. Preparation of the cationic bipyridyl ligand.

In order to discover the optimal reaction conditions, the cross-coupling of 4-bromoanisole (1 mmol) with triethoxy(phenyl)silane (1.5 mmol) in the presence of base was first examined (Table 1). We found that conducting the reaction at 120 °C in the presence of 4 equiv NaOH afforded a much higher yield than that at 100 °C (entries 1 and 2); further reducing the amounts of NaOH gave slightly lower yields (entries 3 and 4). However, the reaction using 2 equiv NaOH resulted in the formation of 4-methoxybiphenyl in a near quantitative yield when the reaction mixture was stirred under identical conditions for 3 h (entry 5). In order to reduce the wastage of base, 2 equiv of NaOH was used for the Hiyama coupling reaction in our system. Various bases were tested, and K_3PO_4, K_2CO_3, and Na_2CO_3 were found to result in low product yields (entries 6–8). The best result was obtained when NaOH was used as the base, consistent with the reported fluoride-free Hiyama reaction in the aqueous phase.[6–8] To demonstrate the necessity of this cationic ligand, two additional experiments were performed. Under comparable conditions, 40% of product was produced in the absence of the cationic ligand, **2**, (entry 9) and no 4-methoxybiphenyl was observed when neutral 2,2′-bipyridyl was employed as an ancillary ligand (entry 10). Replacement of triethoxy(phenyl)silane by trimethoxy(phenyl)silane did not show any positive effect in the improvement of the yield (entry 11). In the case of trichlorophenylsilane, white precipitate was formed immediately upon reaction due to the rapid hydrolysis and condensation of the silicon substrate under such reaction conditions (entry 12).

Table 1
Hiyama reaction of 4-bromoanisole **3a** with phenylsiloxane **4** in water under different conditions[a]

Entry	Arylsiloxane	Base (equiv)	Temperature[e] (°C)	Product	Yield[f] (%)
1	$C_6H_5Si(OEt)_3$ (**4a**)	NaOH (4)	100	**5a**	10
2	$C_6H_5Si(OEt)_3$ (**4a**)	NaOH (4)	120	**5a**	92
3	$C_6H_5Si(OEt)_3$ (**4a**)	NaOH (3)	120	**5a**	88
4	$C_6H_5Si(OEt)_3$ (**4a**)	NaOH (2)	120	**5a**	87
5[b]	$C_6H_5Si(OEt)_3$ (**4a**)	NaOH (2)	120	**5a**	99 (87)
6	$C_6H_5Si(OEt)_3$ (**4a**)	K_3PO_4 (2)	120	**5a**	19
7	$C_6H_5Si(OEt)_3$ (**4a**)	K_2CO_3 (2)	120	**5a**	8
8	$C_6H_5Si(OEt)_3$ (**4a**)	Na_2CO_3 (2)	120	**5a**	3
9[c]	$C_6H_5Si(OEt)_3$ (**4a**)	NaOH (2)	120	**5a**	40
10[d]	$C_6H_5Si(OEt)_3$ (**4a**)	NaOH (2)	120	**5a**	0
11	$C_6H_5Si(OMe)_3$ (**4b**)	NaOH (2)	120	**5a**	90 (77)
12	$C_6H_5SiCl_3$ (**4c**)	NaOH (2)	120	**5a**	0

[a] Reaction conditions: 4-bromoanisole **3a** (1 mmol), phenylsiloxane **4** (1.5 mmol), $Pd(NH_3)_2Cl_2$/**2** (0.1 mol %), H_2O (3 mL) for 2 h.
[b] Reaction time: 3 h.
[c] In the absence of ligand **2**.
[d] 2,2′-Bipyridine was used as an auxiliary ligand.
[e] Bath temperature.
[f] GC yields; isolated yields are given in parentheses.

2.2. Reusability study of the residual aqueous phase for the Hiyama reaction

The reusability of the aqueous catalytic system is very important from the practicality and economic viewpoints. The coupling of 4-bromoacetophenone with triethoxy(phenyl)silane was performed using a 0.1 mol % catalyst in order to test the feasibility of this approach (Scheme 2). In the first cycle, the reaction was monitored by GC until the complete consumption of 4-bromoacetophenone. The organic product, 4-phenylacetophenone, was easily separated from the aqueous phase by simple extraction with hexane, and the residual aqueous solution was then subjected to the next reaction run, charged with the same reactants and base. Although an extended reaction time was required for the recycled runs, the reused catalyst still gave the Hiyama reaction product in a 90% yield in the fourth cycle. The requirement of a longer reaction time for the recycled runs is probably due to the gradual decrease in catalytic activity with each extraction.

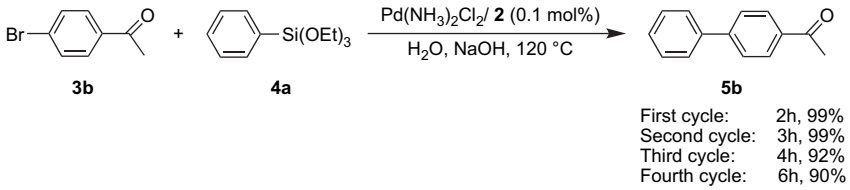
2.3. The Hiyama reaction of aryl bromides with arylsiloxanes

The scope of this aqueous catalytic system for the coupling of various aryl bromides with triethoxy(phenyl)silane was examined and the results are summarized in Table 2. The electron-deficient aryl bromides showed excellent reactivity, giving the cross-coupling products in high yields in the presence of a 0.1–0.01 mol % catalyst with short reaction times (entries 1–5). When methyl 4-bromobenzoate was used as the substrate, the hydrolyzed product was found as the sole cross-coupling product under such reaction conditions (entry 3). 1-Bromo-4-chlorobenzene coupled with triethoxy(phenyl)silane efficiently to afford the corresponding product in excellent yield (entry 6), while a prolonged reaction time of 36 h was needed for the complete reaction when the amount of catalyst loading was reduced to 0.01 mol % (entry 7). Under similar conditions, electron-rich aryl bromides, such as 4-bromoanisole and 4-bromophenol, were arylated using 0.1–0.01 mol % of Pd to give the respective biaryls in high yields (entries 8 and 9). *ortho*-Substituted aryl bromides showed slower reaction times; therefore a higher catalyst loading was used in this reaction system. 2-Bromoacetophenone is more sterically hindered than 2-bromobenzaldehyde, and therefore only a reasonable yield was obtained (entries 10 and 11). The use of 2-bromoanisole afforded the product in good isolated yield in the presence of 1 mol % of catalyst (entry 12). 3-Bromopyridine and 9-bromoanthracene were coupled with triethoxy(phenyl)silane effectively to afford the corresponding products in 67 and 88% isolated yields, respectively (entries 13 and 14).

Table 3 shows the results of the study of the reactivity of various aryl triethoxysilanes in the Hiyama reaction in water. It is apparent that the electronic effect of the aryl ring of the siloxanes had little or no influence on the cross-coupling reaction (entries 1–7). When sterically hindered triethoxy(2-tolyl)silane was used, an excellent reaction rate resulted (entries 8 and 9), and the TON of this reaction was found to be up to 99,000. This result clearly indicated that the rate-determining step for the Hiyama reaction in this system was oxidative addition. The replacement of electron-withdrawing groups such as the acetyl substituent by chloride on aryl bromides led to a decrease in the rate of reaction; therefore, longer reaction times were required to afford good yields (entries 11 and 12). The employment of bromobenzene or deactivated aryl bromides as substrates required higher catalyst loading or longer reaction times in order to obtain satisfactory yields (entries 13–20).

3. Conclusion

In conclusion, we have developed an efficient water-soluble $Pd(NH_3)_2Cl_2$/cationic bipyridyl catalytic system for the coupling of aryl bromides with arylsiloxanes to give biaryls in water under aerobic conditions. The loading of the catalyst in a single batch reaction can be reduced to as low as 0.001 mol %. The residual aqueous phase can be reused several times with only a slight decrease in catalytic activity. The application of this catalyst-reusable and simple-product-separation procedure for other cross-coupling reactions is now under investigation.



Scheme 2. Reuse experiments for the residual catalytic aqueous solution in the Hiyama reaction.

Table 2
Hiyama reaction of aryl bromides **3** with triethoxy(phenyl)silane **4a** in water[a]

Entry	Ar–Br	[Pd] (mol %)	Time (h)	Product	Yield[c] (%)	TON
1	4-BrC_6H_4CHO (**3c**)	0.1	6	**5c**	99 (60)	990
2	4-BrC_6H_4COOH (**3d**)	0.1	6	**5d**	— (86)	860
3[b]	4-BrC_6H_4COOMe (**3e**)	0.1	3	**5d**	— (84)	840
4	4-BrC_6H_4COMe (**3b**)	0.01	6	**5b**	99 (94)	9900
5	4-Br$C_6H_4CF_3$ (**3f**)	0.1	3	**5e**	99 (90)	990
6	4-BrC_6H_4Cl (**3g**)	0.1	4	**5f**	99	990
7	4-BrC_6H_4Cl (**3g**)	0.01	36	**5f**	99 (88)	9900
8	4-BrC_6H_4OMe (**3a**)	0.01	6	**5a**	99 (92)	9900
9	4-BrC_6H_4OH (**3h**)	0.1	24	**5g**	— (78)	780
10	2-BrC_6H_4COMe (**3i**)	1	48	**5h**	— (47)	47
11	2-BrC_6H_4CHO (**3j**)	1	3	**5i**	99 (88)	99
12	2-BrC_6H_4OMe (**3k**)	1	3	**5j**	— (46)	46
13	3-Bromopyridine (**3l**)	0.5	5	**5k**	— (67)	134
14	9-Bromoanthracene (**3m**)	1	24	**5l**	95 (88)	95

[a] Reaction conditions: aryl bromides **3** (1 mmol), triethoxy(phenyl)silane **4a** (1.5 mmol), NaOH (2 mmol), H_2O (3 mL), 120 °C.
[b] 4-Phenylbenzoic acid **5d** was obtained as the product.
[c] GC yields; isolated yields are given in parentheses.

4. Experimental

4.1. General

Chemicals were purchased from commercial suppliers and were used without further purification. With the exception of trimethoxy(phenyl)silane and triethoxy(phenyl)silane, other aryl triethoxyarylsilanes[11] and 4,4′-bis(bromomethyl)-2,2′-bipyridine **1**[12] were prepared according to published procedures. Melting points were recorded using melting point apparatus and were uncorrected. All ^1H and ^{13}C NMR spectra were recorded in deuterium solvents at 25 °C on a Varian 200 NMR spectrometer. GC analysis was performed on an SRI 8610C equipped with a fused silica capillary column.

4.2. Preparation of the cationic bipyridine ligand (2)

4,4′-Bis(bromomethyl)-2,2′-bipyridine **1** (0.5 g, 1.5 mmol) in 10 mL dichloromethane was added Me_3N (50% aqueous solution, 20 mL) and the mixture was stirred at room temperature for 24 h. The clear solution was then evaporated and freeze-dried to give **2** in a quantitative yield. ^1H NMR (D_2O, 200 MHz) δ 3.16 (s, 18H), 5.07 (s, 4H), 7.65 (d, J=5.1 Hz, 2H), 8.24 (s, 2H), 8.75 (d, J=5.1 Hz, 2H); ^{13}C NMR (acetone-*d*, 50 MHz) δ 52.1 (6C), 66.6 (2C), 124.2 (2C), 126.8 (2C), 136.5 (2C), 148.6 (2C), 153.7 (2C); FABMS: *m*/*z*: 379, 381 [M^+−Br] (calcd: 379, 381).

4.3. General procedure for the Hiyama reaction

A 20 mL reactor equipped with a condenser was charged with aryl bromide (1.0 mmol), triethoxy(aryl)silane (1.5 mmol), NaOH (80 mg, 2.0 mmol), and H_2O (2 mL). The aqueous solution of catalyst (1.0 mL, 1.0×10^{-3} mmol Pd/mL) was added to the mixture, which was then stirred under air at 120 °C. After the reaction was completed, the aqueous solution was extracted with hexane or EtOAc. The organic layer was dried over $MgSO_4$ and the solvent was removed under vacuum. Column chromatography on silica gel afforded the desired product.

*4.3.1. 4-Methoxybiphenyl (**5a**)*

White solid. Mp 85–87 °C (lit.[13] 85–87 °C). ^1H NMR ($CDCl_3$, 200 MHz) δ 3.85 (s, 3H), 6.95 (d, J=6.8 Hz, 2H), 7.30–7.32 (m, 1H), 7.40–7.43 (m, 2H), 7.51–7.55 (m, 4H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 55.5, 113.9 (2C), 126.3, 126.4 (2C), 127.7 (2C), 128.3 (2C), 133.3, 140.3, 158.5.

Table 3
Hiyama reaction of aryl bromides **3** with various triethoxy(aryl)silanes **4** in water[a]

Entry	Ar^1–Br	Ar^2–Si(OEt)$_3$	[Pd] (mol %)	Time (h)	Product	Yield[c] (%)	TON
1	4-BrC_6H_4COMe (**3b**)	4-MeOC_6H_4Si(OEt)$_3$ (**4d**)	0.1	3	**5m**	99 (70)	990
2	4-BrC_6H_4COMe (**3b**)	4-MeOC_6H_4Si(OEt)$_3$ (**4d**)	0.01	9	**5m**	95 (76)	9500
3	4-BrC_6H_4COMe (**3b**)	4-MeC_6H_4Si(OEt)$_3$ (**4e**)	0.1	3	**5n**	99 (87)	990
4	4-BrC_6H_4COMe (**3b**)	4-MeC_6H_4Si(OEt)$_3$ (**4e**)	0.01	9	**5n**	99 (91)	9900
5	4-BrC_6H_4COMe (**3b**)	4-FC_6H_4Si(OEt)$_3$ (**4f**)	0.1	6	**5o**	99 (68)	990
6	4-BrC_6H_4COMe (**3b**)	4-F_3CC_6H_4Si(OEt)$_3$ (**4g**)	0.1	3	**5p**	99 (76)	990
7	4-BrC_6H_4COMe (**3b**)	4-ClC_6H_4Si(OEt)$_3$ (**4h**)	0.1	6	**5q**	99 (72)	990
8	4-BrC_6H_4COMe (**3b**)	2-MeC_6H_4Si(OEt)$_3$ (**4i**)	0.01	6	**5r**	99	9900
9	4-BrC_6H_4COMe (**3b**)	2-MeC_6H_4Si(OEt)$_3$ (**4i**)	0.001	18	**5r**	99 (89)	99,000
10[b]	4-BrC_6H_4COOMe (**3e**)	4-MeC_6H_4Si(OEt)$_3$ (**4e**)	0.1	3	**5s**	— (68)	680
11	4-BrC_6H_4Cl (**3g**)	4-MeC_6H_4Si(OEt)$_3$ (**4e**)	0.1	24	**5t**	75 (62)	750
12	4-BrC_6H_4Cl (**3g**)	2-MeC_6H_4Si(OEt)$_3$ (**4i**)	0.1	48	**5u**	60 (44)	600
13	C_6H_5Br (**3n**)	4-MeOC_6H_4Si(OEt)$_3$ (**4d**)	1	6	**5a**	83	83
14	C_6H_5Br (**3n**)	4-MeC_6H_4Si(OEt)$_3$ (**4e**)	0.1	48	**5v**	36 (32)	360
15	C_6H_5Br (**3n**)	4-F_3CC_6H_4Si(OEt)$_3$ (**4g**)	1	6	**5e**	— (66)	66
16	4-BrC_6H_4OMe (**3a**)	4-MeOC_6H_4Si(OEt)$_3$ (**4d**)	1	9	**5w**	88 (73)	88
17	4-BrC_6H_4OMe (**3a**)	4-MeC_6H_4Si(OEt)$_3$ (**4e**)	0.1	48	**5x**	45 (37)	450
18	4-BrC_6H_4OMe (**3a**)	4-FC_6H_4Si(OEt)$_3$ (**4f**)	0.1	48	**5y**	35 (28)	350
19	4-BrC_6H_4OMe (**3a**)	2-MeC_6H_4Si(OEt)$_3$ (**4i**)	0.1	48	**5z**	37 (31)	370
20	4-BrC_6H_4OH (**3h**)	2-MeC_6H_4Si(OEt)$_3$ (**4i**)	1	24	**5aa**	— (68)	68

[a] Reaction conditions: aryl bromides **3** (1 mmol), triethoxy(aryl)silane **4** (1.5 mmol), NaOH (2 mmol), H_2O (3 mL), 120 °C.
[b] 4′-Methyl-4-biphenylcarboxylic acid **5s** was obtained as the product.
[c] GC yields; isolated yields are given in parentheses.

*4.3.2. 4-Phenylacetophenone (**5b**)*

White solid. Mp 119–121 °C (lit.[14] 123 °C). ^{1}H NMR ($CDCl_3$, 200 MHz) δ 2.64 (s, 3H), 7.38–7.40 (m, 1H), 7.44–7.48 (m, 2H), 7.61 (d, J=8.4 Hz, 2H), 7.67 (d, J=8.4 Hz, 2H), 8.01 (d, J=8.8 Hz, 2H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 26.8, 127.0 (2C), 127.1, 128.1 (2C), 128.7 (2C), 128.8 (2C), 135.7, 139.7, 145.6, 197.8.

*4.3.3. 4-Phenylbenzaldehyde (**5c**)*

Pale yellow solid. Mp 51–52 °C (lit.[15] 58–59 °C). ^{1}H NMR ($CDCl_3$, 200 MHz) δ 7.36–7.47 (m, 5H), 7.48–7.70 (m, 2H), 8.03 (d, J=7.8 Hz, 2H), 9.99 (s, 1H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 127.2 (2C), 127.5 (2C), 128.3, 128.8 (2C), 130.0 (2C), 135.1, 139.5, 146.9, 191.6.

*4.3.4. 4-Phenylbenzoic acid (**5d**)*

White solid. Mp 222–223 °C (lit.[16] 227–229 °C). ^{1}H NMR (DMSO-*d*, 200 MHz) δ 2.49 (s, 1H), 7.45–7.49 (m, 3H), 7.70–7.80 (m, 4H), 7.99–8.02 (m, 2H); ^{13}C NMR (DMSO-*d*, 50 MHz) δ 126.7, 128.1 (2C), 129.1 (2C), 130.0, 131.2 (2C), 131.6 (2C), 139.0, 144.2, 167.1.

*4.3.5. 4-(Trifluoromethyl)biphenyl (**5e**)*

White solid. Mp 68–70 °C (lit.[17] 70–70.5 °C). ^{1}H NMR ($CDCl_3$, 200 MHz) δ 7.40 (t, J=7.2 Hz, 1H), 7.47 (d, J=7.2 Hz, 2H), 7.60 (d, J=7.2 Hz, 2H), 7.69 (s, 4H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 122.8 (q, J_{C-F}=272.4 Hz), 125.5 (2C), 125.6, 127.1 (2C), 127.3 (2C), 128.0 (2C), 128.8 (2C), 139.6, 144.7.

*4.3.6. 4-Chlorobiphenyl (**5f**)*

White solid. Mp 74–76 °C (lit.[13] 74–76 °C). ^{1}H NMR ($CDCl_3$, 200 MHz) δ 7.34–7.45 (m, 5H), 7.50–7.56 (m, 4H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 126.6 (2C), 127.2, 128.3 (2C), 128.5 (2C), 128.6 (2C), 132.9, 139.2, 139.5.

*4.3.7. 4-Phenylphenol (**5g**)*

White solid. Mp 148–150 °C (lit.[18] 146–147 °C). ^{1}H NMR (acetone-*d*, 200 MHz) δ 3.02 (s, 1H), 6.90–8.59 (m, 9H); ^{13}C NMR (acetone-*d*, 50 MHz) δ 116.4 (2C), 126.9, 127.0 (2C), 128.6 (2C), 129.4 (2C), 132.9, 141.6, 157.8.

*4.3.8. 2-Acetylbiphenyl (**5h**)*

Yellow oil.[6f] ^{1}H NMR ($CDCl_3$, 200 MHz) δ 2.00 (s, 3H), 7.32–7.35 (m, 2H), 7.36–7.45 (m, 5H), 7.49–7.54 (m, 2H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 30.0, 127.3, 128.5 (2C), 128.7, 130.1 (2C), 130.5 (2C), 140.3, 140.6, 140.7, 204.5.

*4.3.9. 2-Phenylbenzaldehyde (**5i**)*

Yellow oil.[15] ^{1}H NMR ($CDCl_3$, 200 MHz) δ 7.36–7.47 (m, 6H), 7.47–7.65 (m, 2H), 8.03 (d, J=7.8 Hz, 1H), 9.99 (s, 1H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 127.4, 127.6, 128.0, 128.3 (2C), 129.9 (2C), 130.6, 133.4, 133.6, 137.6, 145.8, 192.1.

*4.3.10. 2-Methoxybiphenyl (**5j**)*

Colorless oil.[13] ^{1}H NMR ($CDCl_3$, 200 MHz) δ 3.84 (s, 3H), 7.00–7.10 (m, 2H), 7.34–7.38 (m, 3H), 7.43–7.47 (m, 2H), 7.57–7.59 (m, 2H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 55.6, 110.9, 120.4, 126.5, 127.6 (2C), 128.2, 129.1 (2C), 130.2, 130.4, 138.0, 155.8.

*4.3.11. 3-Phenylpyridine (**5k**)*

Colorless oil.[15] ^{1}H NMR ($CDCl_3$, 200 MHz) δ 7.31–7.51 (m, 4H), 7.53–7.60 (m, 2H), 7.83–7.98 (m, 1H), 8.57 (dd, J=1.8, 4.6 Hz, 1H), 8.83 (d, J=1.8 Hz, 1H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 123.4, 127.0 (2C), 128.0, 129.0 (2C), 134.2, 136.6, 137.7, 148.2, 158.3.

*4.3.12. 9-Phenylanthracene (**5l**)*

Yellow solid. Mp 155–157 °C (lit.[19] 153–155 °C). ^{1}H NMR ($CDCl_3$, 200 MHz) δ 7.28–7.37 (m, 2H), 7.39–7.50 (m, 4H), 7.51–7.60 (m, 3H), 7.62–7.67 (m, 2H), 8.03 (d, J=8.2 Hz, 2H), 8.48 (s, 1H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 125.0 (2C), 125.2 (2C), 126.5 (2C), 126.7 (2C), 127.3 (2C), 128.2 (2C), 130.2, 131.1 (2C), 131.3, 136.9 (2C), 138.7 (2C).

*4.3.13. 4-Acetyl-4′-methoxybiphenyl (**5m**)*

Pale yellow solid. Mp 153–155 °C (lit.[20] 152–153 °C). ^{1}H NMR ($CDCl_3$, 200 MHz) δ 2.62 (s, 3H), 3.85 (s, 3H), 6.98 (d, J=8.8 Hz, 2H), 7.56 (d, J=8.8 Hz, 2H), 7.62 (d, J=8.4 Hz, 2H), 7.98 (d, J=8.8 Hz, 2H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 26.8, 55.4, 114.3 (2C), 126.5 (2C), 128.2 (2C), 128.8, 132.1 (2C), 135.1, 145.2, 159.7, 198.2.

*4.3.14. 4-Acetyl-4′-methylbiphenyl (**5n**)*

White solid. Mp 120–121 °C (lit.[21] 121–122 °C). ^{1}H NMR ($CDCl_3$, 200 MHz) δ 2.40 (s, 3H), 2.62 (s, 3H), 7.26 (d, J=8.3 Hz, 2H), 7.52 (d, J=8.3 Hz, 2H), 7.66 (d, J=8.6 Hz, 2H), 8.00 (d, J=8.6 Hz, 2H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 21.1, 26.5, 126.8 (2C), 126.9 (2C), 128.7 (2C), 129.5 (2C), 135.5, 136.8, 138.1, 145.5, 197.4.

*4.3.15. 4-Acetyl-4′-fluorobiphenyl (**5o**)*

White solid. Mp 103–104 °C (lit.[22] 104.3 °C). ^{1}H NMR ($CDCl_3$, 200 MHz) δ 2.62 (s, 3H), 7.14 (t, J=8.8 Hz, 2H), 7.55–7.59 (m, 2H), 7.61 (d, J=8.4 Hz, 2H), 8.00 (d, J=8.4 Hz, 2H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 26.8, 115.8 (2C), 126.9 (2C), 128.7 (2C), 128.8 (2C), 135.6, 135.8, 144.5, 163.9 (q, J_{C-F}=246.0 Hz), 197.4.

*4.3.16. 4-Acetyl-4′-trifluoromethylbiphenyl (**5p**)*

Yellow solid. Mp 122–123 °C (lit.[23] 120–121 °C). ^{1}H NMR ($CDCl_3$, 200 MHz) δ 2.64 (s, 3H), 7.65–7.71 (m, 6H), 8.04 (d, J=8.6 Hz, 2H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 20.8, 124.0 (q, J_{C-F}=270.0 Hz), 125.8 (q, J_{C-F}=3.8 Hz, 2C), 127.3, 127.5, 128.9, 130.1 (q, J_{C-F}=31.9 Hz), 136.4, 143.2, 144.0, 197.3.

*4.3.17. 4-Acetyl-4′-chlorobiphenyl (**5q**)*

White solid. Mp 102–103 °C (lit.[24] 100–101 °C). ^{1}H NMR ($CDCl_3$, 200 MHz) δ 2.62 (s, 3H), 7.40–7.65 (m, 6H), 8.02 (d, J=6.7 Hz, 2H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 26.5, 126.9 (2C), 128.3 (2C), 128.8 (2C), 129.0 (2C), 134.3, 136.0, 138.1, 144.2, 197.3.

*4.3.18. 4-Acetyl-2′-methylbiphenyl (**5r**)*

Colorless oil.[25] ^{1}H NMR ($CDCl_3$, 200 MHz) δ 2.27 (s, 3H), 2.64 (s, 3H), 7.25–7.30 (m, 4H), 7.43 (d, J=8.6 Hz, 2H), 8.01 (d, J=8.6 Hz, 2H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 20.4, 26.6, 125.9, 127.8, 128.1 (2C), 129.4 (3C), 130.5, 135.1, 135.6, 140.7, 146.9, 197.7.

*4.3.19. 4′-Methyl-4-biphenylcarboxylic acid (**5s**)*

White solid. Mp 246–247 °C (lit.[21] 248 °C). ^{1}H NMR (DMSO-*d*, 200 MHz) δ 2.47 (s, 3H), 7.30 (d, J=8.3 Hz, 2H), 7.69 (d, J=8.3 Hz, 2H), 7.85 (d, J=8.5 Hz, 2H); ^{13}C NMR (DMSO-*d*, 50 MHz) δ 20.6, 126.3 (2C), 126.7 (2C), 129.6 (2C), 129.8 (2C), 131.3, 136.1, 137.6, 144.0, 166.9.

*4.3.20. 4-Chloro-4′-methylbiphenyl (**5t**)*

White solid. Mp 125–126 °C (lit.[26] 122 °C). ^{1}H NMR ($CDCl_3$, 200 MHz) δ 2.39 (s, 3H), 7.23–7.26 (m, 2H), 7.36–7.53 (m, 6H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 21.1, 126.8 (2C), 128.1 (2C), 128.8 (2C), 129.6 (2C), 133.0, 137.1, 139.6.

*4.3.21. 4′-Chloro-2-methylbiphenyl (**5u**)*

Colorless oil.[27] ^{1}H NMR ($CDCl_3$, 200 MHz) δ 2.25 (s, 3H), 7.20–7.26 (m, 6H), 7.38 (d, J=8.6 Hz, 2H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 21.1, 126.8 (2C), 128.1 (2C), 128.8 (2C), 129.6 (2C), 133.0, 137.4, 139.6.

*4.3.22. 4-Methylbiphenyl (**5v**)*

White solid. Mp 43–45 °C (lit.[15] 46 °C). ^{1}H NMR ($CDCl_3$, 200 MHz) δ 2.42 (s, 3H), 7.24–7.28 (m, 2H), 7.32–7.36 (m, 1H), 7.42–7.51 (m, 2H), 7.51–7.53 (m, 2H), 7.58–7.61 (m, 2H); ^{13}C NMR ($CDCl_3$,

50 MHz) δ 21.5, 126.6, 128.3 (2C), 128.4 (2C), 129.0 (2C), 129.1 (2C), 136.5, 137.9, 140.6.

4.3.23. 4,4′-Dimethoxybiphenyl (**5w**)

Pale yellow solid. Mp 178–180 °C (lit.[13] 178–180 °C). ^{1}H NMR ($CDCl_3$, 200 MHz) δ 3.84 (s, 6H), 6.96 (d, J=8.8 Hz, 4H), 7.48 (d, J=8.8 Hz, 4H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 55.5 (2C), 114.4 (4C), 127.3 (4C), 133.0 (2C), 158.0 (2C).

4.3.24. 4-Methoxy-4′-methylbiphenyl (**5x**)

White solid. Mp 113–114 °C (lit.[13] 113–114 °C). ^{1}H NMR ($CDCl_3$, 200 MHz) δ 2.38 (s, 3H), 3.84 (s, 3H), 6.95 (d, J=8.8 Hz, 2H), 7.21 (d, J=8.0 Hz, 2H), 7.44 (d, J=8.0 Hz, 2H), 7.50 (d, J=8.8 Hz, 2H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 21.5, 55.5, 113.8 (2C), 126.2 (2C), 127.6 (2C), 129.0 (2C), 133.3, 135.9, 137.5, 158.3.

4.3.25. 4-Fluoro-4′-methoxybiphenyl (**5y**)

White solid. Mp 88–90 °C (lit.[28] 87.3–87.8 °C). ^{1}H NMR ($CDCl_3$, 200 MHz) δ 3.85 (s, 3H), 6.95–6.99 (m, 2H), 7.08–7.12 (m, 2H), 7.45–7.51 (m, 4H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 55.5, 113.9 (2C), 115.2 (2C), 127.6 (2C), 127.8, 132.3 (2C), 134.5, 158.7, 162.4 (q, J_{C-F}=243.2 Hz).

4.3.26. 4-Methoxy-2′-methylbiphenyl (**5z**)

Colorless oil.[27] ^{1}H NMR ($CDCl_3$, 200 MHz) δ 2.27 (s, 3H), 3.84 (s, 3H), 6.94 (d, J=8.6 Hz, 2H), 7.21–7.27 (m, 6H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 20.5, 55.3, 113.5 (2C), 125.7, 126.9, 129.8, 130.1, 130.2 (2C), 134.4, 135.4, 141.5, 158.5.

4.3.27. 4-Hydroxy-2′-methylbiphenyl (**5aa**)

Pale yellow oil.[29] ^{1}H NMR ($CDCl_3$, 200 MHz) δ 2.28 (s, 3H), 4.86 (s, 1H), 6.88 (dd, J=8.8 Hz, 2H), 7.18–7.25 (m, 6H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 20.5, 114.9, 126.9, 129.8, 130.2, 130.4, 134.5, 135.4, 141.5, 154.4.

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