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Ligand-free, atom-efficient Suzuki–Miyaura type cross-coupling reactions at room temperature

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ABSTRACT

The atom-efficient cross-coupling reaction of sodium tetraarylborates with aryl iodides and bromides was reported. The reaction can be performed directly using a catalytic system composed of palladium chloride, sodium carbonate and methanol ($PdCl_2/Na_2CO_3$/MeOH) under heat-free conditions at room temperature in an open air conditions. The reactions carried out in an atom-efficient way as 4 equiv of aryl halides coupled effectively with 1 equiv of sodium tetraarylborates to furnish 4 equiv of the corresponding functionalized biaryls in good to excellent yields.

1. Introduction

The palladium-catalyzed Suzuki–Miyaura cross-coupling reaction is one of the most versatile and utilized reactions for the selective construction of carbon–carbon bonds,[1] which has found extensive use in the synthesis of pharmaceutical mediates,[2] polymers,[3] and agrochemicals.[4] Among the approaches described in the literature, numerous efforts have been devoted to the development of ligand-promoted catalytic systems,[5] and great successes have been achieved. However, most of theses ligands are not only sensitive to air oxidation and therefore require careful and air-free handling, but also comparatively difficult to prepare or rather expensive.[6] To circumvent this issue, the development of efficient ligand-free catalytic systems[7] consisting of economical catalysts was still a highly desirable goal.

As a new type of borate source, sodium tetraphenylborate is a stable and commercially available reagent for the organic synthesis.[8] Up to now, only a few reactions involving sodium tetraphenylborate for C–C bond formation have been reported.[9] Furthermore, these known reactivity of sodium tetraphenylborate with electrophonic reagents always suffer from disadvantages, such as atom efficiency, high reaction temperature, long reaction times, and harsh reaction conditions. Hence, to expand the scope and reactivity of sodium tetraphenylborate, development of new, and efficient catalytic protocols is in demand.

Nowadays, considering the simple operate processes, tremendous interest has been focused on the room-temperature reactions. Many reactions were conducted at room temperature, such as Baylis–Hillman reaction,[10] Aldol reaction,[11] Michael addition reaction,[12] asymmetric hydrogenation,[13] and cross-coupling reaction,[14] and so on. Although great success has been achieved, however, the atom-efficient cross-coupling of sodium tetraarylborates at room temperature has not so far been reported. In continuation of our studies on the scope of transitions metals catalyzed organic transformations,[15] in this paper, we report our recent results for the study of the atom-efficient, palladium-catalyzed ligand-free cross-coupling reaction of sodium tetraarylborates with aryl iodides and aryl bromides at room temperature in an open air conditions. We have reinvestigated the procedure with respect to five key variables: (1) atom-efficient (as 4 equiv of aryl halides coupled effectively with 1 equiv of sodium tetraarylborates), (2) ligand-free conditions, (3) short reaction time, (4) low reaction temperature, and (5) simple operate processes.

2. Results and discussion

During our investigation for preparing the biaryl compounds by employing this reaction, surprisingly, we found that the reaction can be run in air without using any ligand. Under this mild condition, we examined the effect of bases using sodium tetraphenylborate and bromobenzene as substrates in the presence of palladium chloride in methanol. The uses of organic base, such as triethylamine, gave the corresponding cross-coupling product in the yield of 64% (Table 1, entry 1). Comparison of inorganic bases utilized showed that sodium bases were more suitable than the potassium ones. For example, the reaction proceeded in high yield within short time in the presence of Na_2CO_3, NaOAc, NaOH or $NaHCO_3$ while it was less satisfactory in the case of K_2CO_3, $KHCO_3$,

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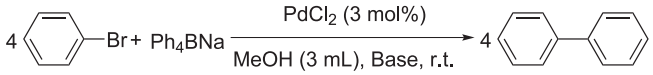
KOH or K_3PO_4, (Table 1, entries 2–9). Further study with varying Na_2CO_3 base equivalents produced mixed conversions revealing that 3.0 equiv of base is necessary to obtain high yield of the cross-coupling product (Table 1, entries 9–13).

Table 1
Effect of bases on the coupling of bromobenzene with Ph_4BNa[a]

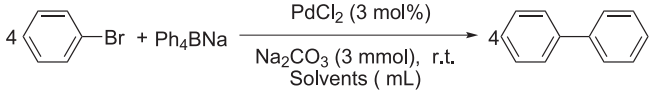


Entry	Base [mmol]	Time [h]	Yield[b] [%]
1	Et_3N (3.0)	12	64
2	KOH (3.0)	12	21
3	KF (3.0)	24	18
4	K_3PO_4 (3.0)	24	<5
5	K_2CO_3 (3.0)	24	<5
6	NaOH (3.0)	12	65
7	$NaHCO_3$ (3.0)	12	75
8	NaOAc (3.0)	12	82
9	Na_2CO_3 (3.0)	3	93
10	Na_2CO_3 (1.5)	3	70
11	Na_2CO_3 (2.0)	3	82
12	Na_2CO_3 (2.5)	3	91
13	Na_2CO_3 (3.5)	3	92

[a] Reaction conditions: bromobenzene (1.0 mmol), Ph_4BNa (0.25 mmol), base, $PdCl_2$ (0.03 mmol), and MeOH (3 mL) stirring at room temperature for the appropriate time.
[b] Isolated yield.

The choice of solvent was also important for the present method. Dimethyl sulfoxide (DMSO), dichloromethane (CH_2Cl_2), and polyethylene glycol (PEG 400) were not effective in the present coupling reaction (Table 2, entries 1–3). Acetonitrile (MeCN), tetrahydrofuran (THF), and ethyl acetate gave quite poor results (Table 2, entries 4–6). Some other aprotic polar solvents, such as *N*, *N*,-dimethylformamide (DMF), dioxane, and acetone, which are commonly used in Pd-catalyzed coupling reactions, gave the corresponding cross-coupling product in moderate yields (Table 2, entries 7–9). Alcoholic solvents, especially MeOH and EtOH gave satisfactory results (Table 2, entries 12 and 13).

Table 2
Effect of solvents on the coupling of bromobenzene with Ph_4BNa[a]

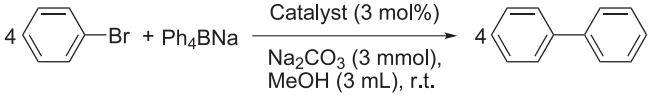


Entry	Solvents [3 mL]	Time [h]	Yield[b] [%]
1	DMSO	16	5
2	CH_2Cl_2	12	5
3	PEG 400	24	<5
4	MeCN	16	18
5	THF	12	28
6	Ethyl acetate	12	32
7	DMF	12	54
8	Acetone	12	58
9	Dioxane	24	60
10	*i*-PrOH	12	48
11	*n*-BuOH	12	48
12	MeOH	3	93
13	EtOH	6	89

[a] Reaction conditions: bromobenzene (1.0 mmol), Ph_4BNa (0.25 mmol), Na_2CO_3 (3.0 mmol), $PdCl_2$ (0.03 mmol). and solvents (3 mL) stirring at room temperature for the appropriate time.
[b] Isolated yield.

We next examined the simple catalyst activity of Ni, Co, and Pd particles. Among them, $PdCl_2$ was the most efficient catalyst for the present atom-efficient room temperature Suzuki–Miyaura cross-coupling reactions (Table 3, entry 7). From Table 3, it can be gathered that Ni and Co pieces were not effective for the reaction even after prolonged the stirring time (Table 3, entries 1–5). Also, Pd/C which is one of the most common heterogeneous catalysts is not an effective catalyst for the present coupling reaction (Table 3, entry 6). When $PdCl_2(PPh_3)_2$ or Pd $(PPh_3)_4$ was used, the coupling proceed smoothly and moderate yields of biphenyl was obtained (Table 3, entries 8 and 9). Strikingly, the cross-coupling reaction carried out in the presence of $NaCO_3$ in MeOH with palladium chloride catalyst at room temperature provided the highest cross-coupling conversion. Furthermore, it is noteworthy that the present protocol is highly efficient as 4 equiv of bromobenzene reacted with 1 equiv of sodium tetraphenylborate cleanly to provide the desire cross-coupling products with high yield in short reaction time.

Table 3
Comparative experiments with simple catalysts[a]



Entry	Catalyst	Time [h]	Yield[b] [%]
1	$NiCl_2 \cdot 5H_2O$	60	<5
2	$NiCl_2(PPh_3)_2$	60	<5
3	$Ni(acac)_2$	60	<5
4	$CoBr_2 \cdot 2H_2O$	60	<5
5	$CoCl(PPh_3)_3$	60	<5
6	Pd/C	12	8
7	$PdCl_2$	3	93
8	$PdCl_2(PPh_3)_2$	12	36
9	Pd $(PPh_3)_4$	12	50

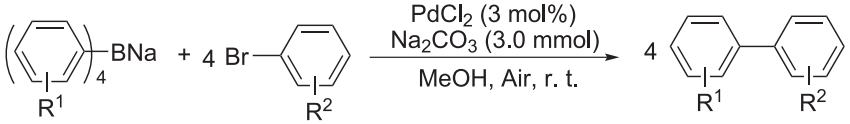
[a] Reaction conditions: bromobenzene (1.0 mmol), Ph_4BNa (0.25 mmol), Na_2CO_3 (3.0 mmol), catalyst (0.03 mmol), and solvents (3 mL) stirring at room temperature for the appropriate time.
[b] Isolated yield.

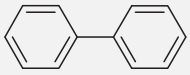
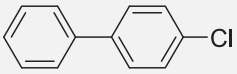
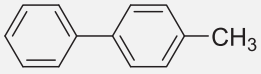
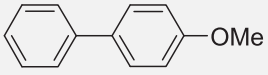
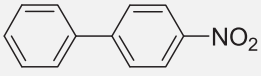
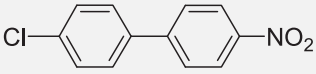
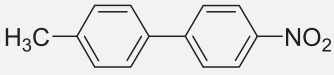
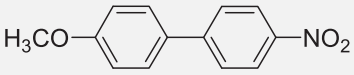
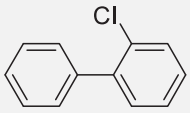
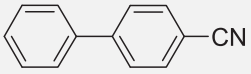
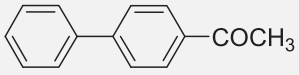
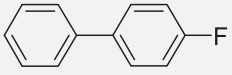
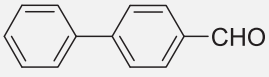
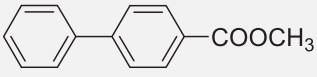
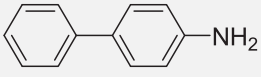
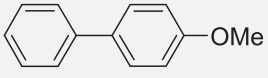
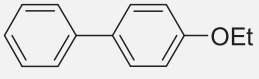
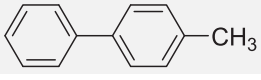
Encouraged by these results, the cross-coupling scope and generality of a variety of aryl bromides with different sodium tetraarylborates was investigated using the optimized conditions and the results are given in Table 4.

As shown in Table 4, aryl bromides with electron-deficient or electron-rich groups showed good to excellent reactivity and furnished the products in short reaction times. It can be seen that bromobenzene and 1-bromo-4-nitrobenzene can be reacted efficiently with different sodium tetraarylborates and furnished the desire functionalized biphenyls in high yields (Table 4, entries 1–8). Furthermore, the reactions of variety of aryl bromides substituted with both electron-deficient (such as acetyl, cyano, fluoro, and nitro) and electron-withdrawing group (such as methyl, methoxyl, ethoxyl, amidine, and acetamido) groups produced good to excellent isolated yields of the functionalized biaryls with sodium tetraphenylborate (Table 4, entries 9–18), and the electron-rich substrates show lower reactivity (Table 4, entries 15–18). The reaction of 1-bromonaphthalene and 2-bromonaphthalene were remarkable furnishing the corresponding coupling products in excellent yields (Table 4, entries 19 and 20). Furthermore, the reaction of heterocyclic bromides with sodium tetraphenylborate also provided the cross-coupling products (Table 4, entries 21–23). It is worth noting that the catalytic system was tolerant to a broad range of functional groups, and aryl bromides with hydroxyl, amidine, carboxylic acid groups underwent the coupling reaction in high yields without any protection.

During our further research, we found that the reactivity of substituted aryl iodides with sodium tetraarylborates were faster and efficient furnishing excellent yields of the cross-coupled biphenyls in a short reaction time (less than 1 h) catalyzed by $PdCl_2$ in MeOH. As shown in Table 5, the reaction of various aryl iodides with both electron-withdrawing and electron-donating substitute

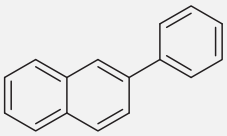
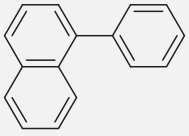
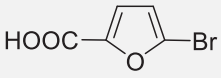
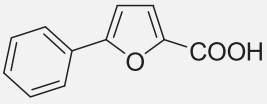
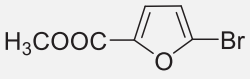
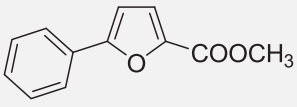
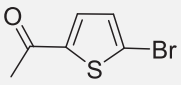
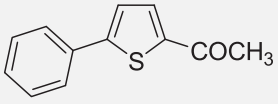
Table 4
Pd-catalyzed cross-coupling of aryl bromides with sodium tetraarylborate[a]



Entry	R^1	R^2	Products	Time [h]	Yield[b] [%]
1	H	H		3	93
2	4-Cl	H		5	90
3	4-CH_3	H		5	86
4	4-OCH_3	H		5	84
5	H	4-NO_2		2	94
6	4-Cl	4-NO_2		3	92
7	4-CH_3	4-NO_2		3	85
8	4-OCH_3	4-NO_2		3	86
9	H	2-Cl		2	91
10	H	4-CN		0.5	93
11	H	4-$COCH_3$		0.5	93
12	H	4-F		0.5	92
13	H	4-CHO		0.5	91
14	H	4-$COOCH_3$		0.5	93
15	H	4-NH_2		6	80
16	H	4-OCH_3		3	87
17	H	4-OC_2H_5		3	89
18	H	4-CH_3		3	88

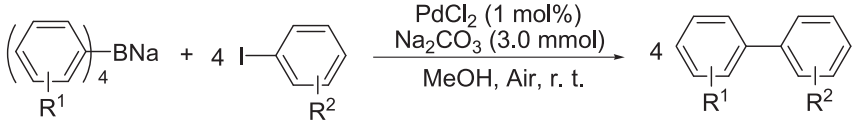
(*continued on next page*)

Table 4 (*continued*)

Entry	R^1	R^2	Products	Time [h]	Yield[b] [%]
19	H	2-Naphthyl		3	90
20	H	1-Naphthyl		3	91
21	H			0.5	81
22	H			0.5	84
23	H			0.5	86

[a] Reaction conditions: aryl bromides (1.0 mmol), Ar_4BNa (0.25 mmol), Na_2CO_3 (3.0 mmol), $PdCl_2$ (0.03 mmol), and MeOlH (3 mL) stirring at room temperature for the appropriate time.
[b] Isolated yield.

Table 5
Pd-catalyzed cross-coupling of aryl iodides with sodium tetraarylborate[a]



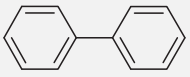
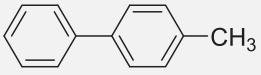
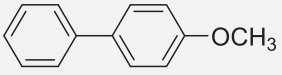
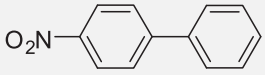
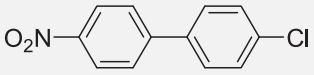
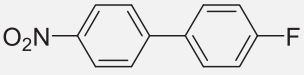
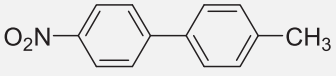
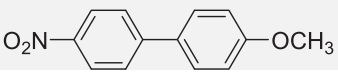
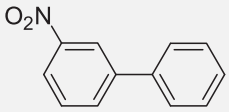
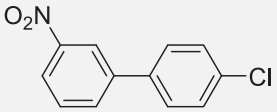
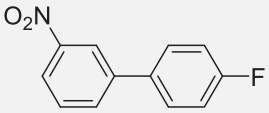
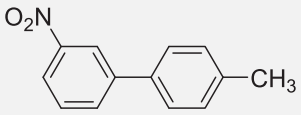
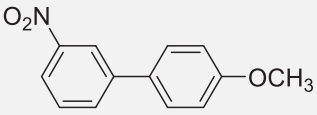
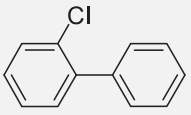
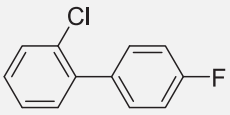
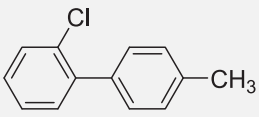
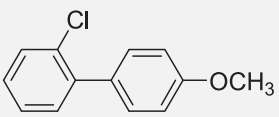
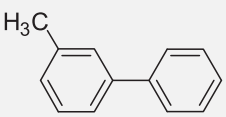
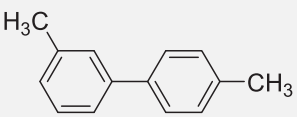
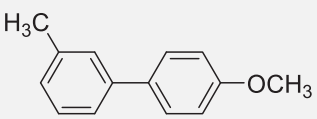
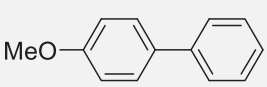
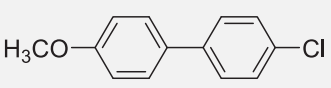
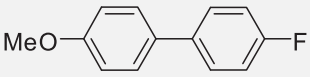
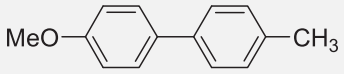
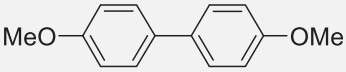
Entry	R^1	R^2	Products	Time [min]	Yield[b] [%]
1	H	H		15	99
2	4-CH_3	H		15	97
3	4-OCH_3	H		15	97
4	H	4-NO_2		10	99
5	4-Cl	4-NO_2		10	98
6	4-F	4-NO_2		10	98
7	4-CH_3	4-NO_2		20	97
8	4-OCH_3	4-NO_2		20	97

Table 5 (*continued*)

Entry	R^1	R^2	Products	Time [min]	Yield[b] [%]
9	H	3-NO_2		10	98
10	4-Cl	3-NO_2		15	96
11	4-F	3-NO_2		15	96
12	4-CH_3	3-NO_2		20	96
13	4-OCH_3	3-NO_2		20	95
14	H	2-Cl		10	96
15	4-F	2-Cl		20	94
16	4-CH_3	2-Cl		20	92
17	4-OCH_3	2-Cl		30	92
18	H	3-Me		10	98
19	4-CH_3	3-Me		20	96
20	4-OCH_3	3-Me		20	96
21	H	4-OMe		10	99
22	4-Cl	4-OMe		20	97
23	4-F	4-OMe		20	96

(*continued on next page*)

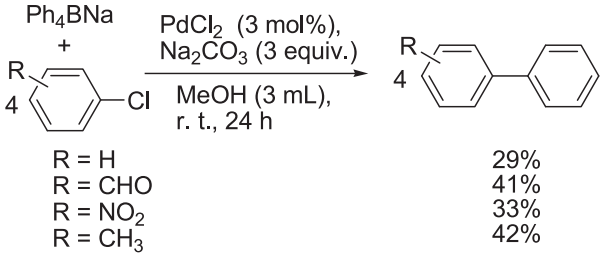
Table 5 (*continued*)

Entry	R^1	R^2	Products	Time [min]	Yield[b] [%]
24	4-Me	4-OMe		20	97
25	4-OMe	4-OMe		20	96

[a] Reaction conditions: aryl iodides (1.0 mmol), Ar_4BNa (0.25 mmol), Na_2CO_3 (3.0 mmol), $PdCl_2$ (0.01 mmol), and MeOH (3 mL) stirring at room temperature for the appropriate time.
[b] Isolated yield.

groups furnished excellent yields of the functionalized biphenyls. Notably, the cross-coupling reactivity with aryl iodides was found to be efficient even with a lower palladium catalyst loading (1 mmol %) when compared to the corresponding reactivity with aryl bromides.

Further study indicated that aryl chlorides can also react with sodium tetraphenylborate under $PdCl_2/Na_2CO_3$/MeOH conditions. However, the yields of biaryls were very poor even prolonged the reaction time (Scheme 1).



Scheme 1. Palladium-catalyzed cross-coupling of aryl chlorides with sodium tetraphenylborate.

3. Conclusion

In conclusion, we have developed an atom-efficient, ligand-free palladium-catalyzed atom-efficient Suzuki–Miyaura cross-coupling reaction under mild conditions in short reaction times. Sodium tetraarylborate underwent the coupling reaction with various aryl bromides or aryl iodides in good to excellent isolated yields at room temperature in an open air atmosphere condition. It is noteworthy that the present protocol can be performed in a highly atom-efficient way as 4 equiv of aryl halides reacted with 1 equiv of sodium tetraphenylborate at room temperature.

4. Experimental

4.1. General

^{1}H NMR spectra were recorded on a Brucker AM 400 MHz and Brucker AC-E 200 MHz spectrometers in $CDCl_3$ with TMS as an internal standard. ^{13}C NMR spectra were obtained on a Brucker AM-400 operating at 100 MHz or a Brucker AC-E 200 operating at 50 MHz. IR spectra were recorded on an Alpha Centauri FI-IR spectrometer. Mass spectra were recorded on a HP 5988A and GC/MS/DS instruments. Elemental analyses were carried out on Carlo Erba-1106 instruments. Purification of products was performed via flash chromatography with 200–400 mesh silica gel (15:1 petroleum/diethyl ether). All substrates and reagents were obtained commercially which were prepared by standard procedures.

4.2. Typical experimental procedure for the atom-efficient Suzuki–Miyaura cross-coupling reaction

A mixture of aryl halides (1 mmol), sodium tetraphenylborate (0.25 mmol), Na_2CO_3 (3 mmol), $PdCl_2$ (0.03 mmol for aryl bromides, 0.01 mmol for aryl iodides), and MeOH (3 mL) was stirred at room temperature in an open air for the indicated time until complete consumption of starting material as monitored by TLC. Then the mixture was diluted with H_2O (10 mL) and extracted with Et_2O (4×10 mL). The combined organic layers were washed with brine (10 mL), dried over $MgSO_4$, and concentrated in vacuo. The residue was purified by flash column chromatography on silica gel (petroleum ether/EtOAc, 60:1) to give the corresponding biaryl compound.

4.3. Typical experimental procedure for the synthesis of $NaBAr_4$[16]

Slow addition of a solution of (0.09 mol) of aryl bromides in Et_2O (150 mL) to Mg turnings (0.11 mol) in Et_2O (150 mL), followed by refluxing for 30 min, gave a dark gray solution of the aryl Grignard reagent. Upon addition of $NaBF_4$ (0.15 mol), the heterogeneous reaction mixture was stirred for 48 h, during which time the solution became brown and a fine precipitate formed. The reaction mixture was then added to Na_2CO_3 (38 g) in water (1 L), stirred for 20 min, and then filtered. The mixture was extracted with Et_2O (4×100 mL) and the combined organic layer was dried over Na_2SO_4 and concentrated in vacuo. The residue was recrystallized from petroleum ether.

4.4. Spectral data

4.4.1. Biphenyl. Mp (°C): 69–70,[17] 71.[18] IR (ν/cm^{-1}): 3032, 1943, 1596, 1568, 1479, 1008, 984, 729; ^{1}H NMR (400 MHz, $CDCl_3$): δ=7.59 (d, J=7.2 Hz, 4H), 7.44 (t, J=8.0 Hz, 4H), 7.36–7.32 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ=141.2, 128.7, 127.2, 127.1. MS m/z (%): 154 (M^+, 100), 76 (50).

4.4.2. 4-Methylbiphenyl. MP (°C): 46–47,[17] 46–48.[19] IR (ν/cm^{-1}): 3038, 2932, 1607, 1568, 1444, 1130, 1006, 822; ^{1}H NMR (400 MHz, $CDCl_3$): δ=7.57 (d, J=8.0 Hz, 2H), 7.49 (d, J=7.6 Hz, 2H), 7.42 (t, J=7.6 Hz, 2H), 7.33–7.30 (m, 1H), 7.24 (d, J=8.0 Hz, 2H), 2.39 (s, 3H); ^{13}C NMR (100 MHz, CD_3COCD_3): δ=141.5, 138.6, 137.4, 130.0, 129.3, 127.5, 127.2, 127.1, 20.7. MS m/z (%): 168 (M^+, 100), 152 (24).

4.4.3. 3-Methylbiphenyl. Oil,[20] IR (ν/cm^{-1}): 3030, 2920, 1696, 1601, 1480, 1072, 1033, 752, 697; ^{1}H NMR (400 MHz, $CDCl_3$): δ=7.59–7.56 (m, 2H), 7.45–7.38 (m, 4H), 7.35–7.31 (m, 2H), 7.16 (t, J=7.6 Hz, 1H), 2.42 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ=141.3,

141.2, 138.3, 128.7, 128.6, 128.0, 127.2, 124.3, 21.5. MS *m*/*z* (%): 168 (M^+, 100), 153 (35), 76 (44).

4.4.4. 4-Methoxybiphenyl. Mp (°C) 87–88,[17] 85–87.[19] IR (ν/cm^{-1}): 3034, 2908, 1604, 1592, 1486, 918, 823, 756; ^{1}H NMR (400 MHz, $CDCl_3$): δ=7.56–7.51 (m, 4H), 7.41 (t, *J*=7.6 Hz, 2H), 7.30 (t, *J*=7.6 Hz, 1H), 6.98 (d, *J*=7.2 Hz, 2H), 3.85 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ=159.1, 140.8, 133.7, 128.7, 128.1, 126.7, 126.6, 114.2, 55.3. MS *m*/*z* (%): 184 (M^+, 100), 169 (M^+-CH_3, 48).

4.4.5. 4-Nitrobiphenyl. Mp (°C): 112–114,[17] 114.[18] IR (ν/cm^{-1}): 3063, 1601, 1570, 1525, 1357, 1074, 853, 740; ^{1}H NMR (400 MHz, $CDCl_3$): δ=8.30 (d, *J*=8.0 Hz, 2H), 7.74 (d, *J*=8.0 Hz, 2H), 7.63 (d, *J*=7.6 Hz, 2H), 7.52–7.45 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ=147.6, 47.0, 138.7, 129.1, 128.9, 127.8, 127.4, 124.1. MS *m*/*z* (%): 199 (M^+, 100), 152 (85), 151 (30).

4.4.6. 3-Nitrobiphenyl. Mp (°C): 60–61, 62.[18] IR (ν/cm^{-1}): 3082, 2924, 1625, 1569, 1351, 1064, 853, 748; ^{1}H NMR (400 MHz, $CDCl_3$): δ=8.45 (s, 1H), 8.20 (d, *J*=8.0 Hz, 1H), 7.91 (d, *J*=8.0 Hz, 1H), 7.65–7.59 (m, 3H), 7.52–7.26 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ=148.7, 142.8, 138.6, 133.0, 129.7, 129.1, 128.5, 127.1, 122.0, 121.9. MS *m*/*z* (%): 199 (M^+, 80), 152 (100), 153 (52).

4.4.7. 1-Phenylnaphthalene. Oil.[17,18] IR (ν/cm^{-1}): 3056, 1592, 1494, 1395, 802, 779, 761, 617; ^{1}H NMR (400 MHz, $CDCl_3$): δ=7.90 (d, *J*=8.0 Hz, 2H), 7.85 (d, *J*=8.0 Hz, 1H), 7.54–7.40 (m, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ=140.7, 140.2, 133.8, 131.6, 130.1, 128.4, 128.2, 127.6, 127.2, 126.9, 126.0, 125.7, 125.4. MS *m*/*z* (%): 204 (M^+, 100).

4.4.8. 2-Phenylnaphthalene. Mp (°C) 96–97,[17] 95–96.[43] IR (ν/cm^{-1}): 3053, 1947, 1597, 1494, 1453, 1130, 893, 860; ^{1}H NMR (400 MHz, $CDCl_3$): δ=8.03 (s, 1H), 7.92–7.85 (m, 3H), 7.73 (t, *J*=8.0 Hz, 3H), 7.51–7.46 (m, 4H), 7.39–7.23 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ=141.0, 138.5, 133.6, 132.6, 128.8, 128.4, 128.2, 127.6, 127.4, 127.3, 126.3, 125.9, 125.8, 125.6. MS *m*/*z* (%): 204 (M^+, 100).

4.4.9. 2-Chloridebiphenyl. Oil,[21] IR (ν/cm^{-1}): 3059, 2924, 1642, 1462, 1420, 750, 697; ^{1}H NMR (400 MHz, $CDCl_3$): δ=7.48–7.38 (m, 6H), 7.36–7.26 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ=140.5, 139.4, 132.5, 131.4, 129.9, 129.4, 128.5, 128.0, 127.6, 126.8. MS *m*/*z* (%): 188 (M^+, 100), 152 (60).

4.4.10. 4-Acetylbiphenyl. Mp (°C) 120–121,[17] 121.[18] IR (ν/cm^{-1}): 3032, 2998, 1678, 1599, 1400, 1359, 837, 687; ^{1}H NMR (400 MHz, $CDCl_3$): δ=8.03 (d, *J*=8.0 Hz, 2H), 7.68 (d, *J*=8.0 Hz, 2H), 7.62 (d, *J*=7.6 Hz, 2H), 7.47 (t, *J*=7.6 Hz, 2H), 7.41 (d, *J*=7.6 Hz, 1H), 2.65 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ=197.7, 145.7, 139.8, 135.8, 128.9, 128.8, 128.2, 127.2, 127.1, 26.7. MS *m*/*z* (%): 196 (M^+, 42), 181 (100), 152 (59).

4.4.11. 4-Ethoxybiphenyl. Mp (°C)69–71.[25] IR (ν/cm^{-1}): 3034, 2927, 1601, 1483, 1450, 1249, 1047, 760; ^{1}H NMR (400 MHz, $CDCl_3$): δ=7.56–7.50 (m, 4H), 7.41 (t, *J*=8.0 Hz, 2H), 7.31–7.28 (m, 1H), 6.96 (d, *J*=8.8 Hz, 2H), 4.07 (q, *J*=7.2 Hz, 2H), 1.44 (t, *J*=7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ=158.5, 140.8, 133.6, 128.7, 128.1, 126.7, 126.6, 114.7, 63.5, 14.9. MS *m*/*z* (%): 198 (M^+, 68), 170 (100).

4.4.12. 4-Carboxaldehydebiphenyl. Mp (°C)57–58,[17] 57–59.[18] IR (ν/cm^{-1}): 3356, 3027, 2835, 1695, 1600, 1170, 1001, 832; ^{1}H NMR (400 MHz, $CDCl_3$): δ=10.06 (s, 1H), 7.95 (d, *J*=8.0 Hz, 2H), 7.75 (d, *J*=8.4 Hz, 2H), 7.64 (d, *J*=6.8 Hz, 2H), 7.50–7.42 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ=191.9, 147.2, 139.7, 135.2, 130.2, 129.0, 128.4, 127.7, 127.3. MS *m*/*z* (%): 181 (M^+, 100), 152 (68), 76 (46).

4.4.13. 4-Cyanobiphenyl. Mp (°C): 85–86,[17] 86–87.[26] IR (ν/cm^{-1}): 2227, 1606, 1485, 1526, 1354, 1068, 768; ^{1}H NMR (400 MHz, $CDCl_3$): δ=7.69 (q, *J*=8.8 Hz, 4H), 7.59–7.55 (m, 1H), 7.49–7.40 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): δ=145.5, 139.0, 132.5, 129.0, 128.6, 127.6, 127.1, 118.9, 110.8. MS *m*/*z* (%): 179 (M^+, 100), 151 (14), 76 (23).

4.4.14. Biphenyl-4-amine. Mp (°C) 45–47.[27] IR (ν/cm^{-1}): 3422, 3203, 3026, 2926, 1624, 1482, 1259, 834; ^{1}H NMR (400 MHz, $CDCl_3$): δ=7.55–7.52 (m, 2H), 7.43–7.36 (m, 4H), 7.26 (t, *J*=8.4 Hz, 1H), 6.75 (d, *J*=8.0 Hz, 2H), 3.71 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ=145.8, 141.1, 131.6, 128.7, 126.4, 126.3, 115.4. MS *m*/*z* (%): 169 (M^+, 100), 141 (7).

4.4.15. Methyl biphenyl-4-carboxylate. Mp (°C) 115–116,[17] 115.5–116.5.[29] IR (ν/cm^{-1}): 3030, 2945, 1938, 1716, 1603, 1111, 1002, 697; ^{1}H NMR (400 MHz, $CDCl_3$): δ=8.10 (d, *J*=8.4 Hz, 2H), 7.66–7.59 (m, 4H), 7.47–7.36 (m, 3H), 3.92 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ=167.0, 145.6, 139.9, 130.1, 128.9, 128.3, 128.1, 127.2, 127.0, 52.1. MS *m*/*z* (%): 212 (M^+, 57), 181 (100), 152 (75), 76 (24).

4.4.16. 5-Phenyl-2-furoic acid. Mp (°C) 153–154,[17] 152–155.[30] IR (ν/cm^{-1}): 3033, 2897, 1678, 1525, 1475, 1452, 1025, 917; ^{1}H NMR (400 MHz, $CDCl_3$): δ=11.52 (s, 1H), 7.81 (d, *J*=7.2 Hz, 2H), 7.45–7.35 (m, 4H), 6.79 (d, *J*=3.6 Hz, 1H); ^{13}C NMR (100 MHz, CD_3COCD_3): δ=159.2, 157.6, 144.7, 130.2, 129.5, 129.4, 125.1, 120.4, 107.8. MS *m*/*z* (%): 188 (M^+, 100), 115 (42).

4.4.17. 5-Acetyl-2-phenylthiophene. Mp (°C) 114–115,[17] 115.[31] IR (ν/cm^{-1}): 3026, 1649, 1447, 1361, 1278, 924, 809; ^{1}H NMR (400 MHz, $CDCl_3$): δ=7.66–7.58 (m, 2H), 7.43–7.26 (m, 5H), 2.56 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ=190.6, 152.7, 143.0, 133.4, 133.2, 129.1, 129.0, 126.2, 123.8, 26.5. MS *m*/*z* (%): 202 (M^+, 58), 187 (100), 115 (50).

4.4.18. Methyl 5-phenylfuran-2-carboxylate. Mp (°C): 58–60.[17] IR (ν/cm^{-1}): 3025, 2952, 1717, 1145, 988, 695; ^{1}H NMR (400 MHz, $CDCl_3$): δ=7.78 (d, *J*=7.6 Hz, 2H), 7.43–7.32 (m, 3H), 7.24 (d, *J*=7.2 Hz, 1H), 6.73 (d, *J*=7.6 Hz, 1H), 3.91 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ=159.2, 157.5, 143.5, 129.4, 128.9, 128.8, 124.8, 106.8, 51.8. MS *m*/*z*(%): 202 (M^+, 100), 171 (80), 115 (99).

4.4.19. 4-Fluoro-biphenyl. Mp (°C): 73–73.5,[36] 73–74, IR (ν/cm^{-1}): 3051, 2936, 1892, 1622, 1523, 1228, 1159, 835, 756; ^{1}H NMR (400 MHz, $CDCl_3$): δ=7.59 (d, *J*=8.0 Hz, 1H), 7.55–7.52 (m, 2H), 7.46–7.41 (m, 3H), 7.34 (t, *J*=7.6 Hz, 3H), 7.12 (t, *J*=8.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ=162.4 (d, *J*=244.6 Hz, 1C), 141.2, 140.2, 137.3, 128.8, 128.6, 128.5, 127.2, 127.1, 115.6 (d, *J*=21.4 Hz, 1C). MS *m*/*z* (%): 172 (M^+, 100).

4.4.20. 4-Methyl-4′-nitrobiphenyl. Mp (°C) 140-141.[34] IR (ν/cm^{-1}): 3052, 2932, 2847, 1637, 1599, 1513, 1340, 1104, 822, 749; ^{1}H NMR (400 MHz, $CDCl_3$): δ=8.29 (d, *J*=9.2 Hz, 2H), 7.72 (d, *J*=8.8 Hz, 2H), 7.53 (d, *J*=8.4 Hz, 2H), 7.31 (d, *J*=8.8 Hz, 2H), 2.43 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ=147.6, 146.8, 139.1, 135.8, 129.9, 127.5, 127.2, 124.1, 21.2. MS *m*/*z* (%): 213 (M^+, 100), 165 (38), 152 (48).

4.4.21. 4-Methoxy-4′-nitrobiphenyl. Mp (°C) 106-108.[35] IR (ν/cm^{-1}): 3066, 2926, 1598, 1509, 1342, 1248, 1181, 1103, 1012, 826, 752; ^{1}H NMR (400 MHz, $CDCl_3$): δ=8.27 (d, *J*=9.2 Hz, 2H), 7.69 (d, *J*=8.8 Hz, 2H), 7.58 (d, *J*=7.6 Hz, 2H), 7.02 (d, *J*=6.4 Hz, 2H), 3.88 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ=160.4, 147.2, 146.5, 131.0, 128.5, 127.0, 124.1, 114.6, 55.4. MS *m*/*z* (%): 229 (M^+, 100), 199 (27), 139 (68).

4.4.22. 4-Chloro-4′-nitrobiphenyl. Mp (°C): 112–113.[37] IR (ν/cm^{-1}): 3072, 2931, 1595, 1510, 1476, 1342, 1092, 1004, 854, 817, 749; ^{1}H NMR (400 MHz, $CDCl_3$): δ=8.30 (d, *J*=7.6 Hz, 2H), 7.71 (d, *J*=7.2 Hz, 2H), 7.56 (d, *J*=7.6 Hz, 2H), 7.47 (d, *J*=8.4 Hz, 2H); ^{13}C NMR

(100 MHz, $CDCl_3$): δ=147.2, 146.3, 137.2, 135.3, 129.4, 128.6, 127.7, 124.2. MS *m*/*z* (%): 233 (M^+, 68), 202 (41), 152 (100).

4.4.23. 4-Fluoro-4′-nitrobiphenyl. Mp (°C): 125–126,[38] 127–128. IR (ν/cm^{-1}): 3076, 2844, 1597, 1515, 1481, 1346, 1232, 1107, 833, 752; ^1H NMR (400 MHz, $CDCl_3$): δ=8.30 (d, *J*=8.0 Hz, 2H), 7.70 (d, *J*=8.8 Hz, 2H), 7.62–7.58 (m, 2H), 7.19 (t, *J*=8.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ=164.6, 162.1, 147.0, 146.5, 134.9, 129.1 (d, *J*=8.4 Hz, 1C), 127.6, 124.2, 116.2 (d, *J*=22.1 Hz, 1C). MS *m*/*z* (%): 217 (M^+, 95), 187 (56), 170 (100).

4.4.24. 4-Methyl-3′-nitrobiphenyl. Mp (°C): 75.5–76.5,[31] 79–80. IR (ν/cm^{-1}): 3085, 2922, 1512, 1346, 1087, 804, 738; ^1H NMR (400 MHz, $CDCl_3$): δ=8.43 (t, *J*=2.0 Hz, 1H), 8.17 (d, *J*=8.0 Hz, 1H), 7.90 (d, *J*=8.0 Hz, 1H), 7.59 (t, *J*=8.0 Hz, 1H), 7.53 (d, *J*=8.4 Hz, 2H), 7.30 (d, *J*=8.4 Hz, 2H), 2.41 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ=142.8, 138.5, 135.7, 132.8, 129.8, 129.6, 126.9, 121.7, 121.6, 109.7, 21.1. MS *m*/*z* (%): 213 (M^+, 100), 165 (52).

4.4.25. 4-Methoxy-3′-nitrobiphenyl. Mp (°C) 70–71.[39] IR (ν/cm^{-1}): 3081, 2962, 1607, 1512, 1457, 1348, 1246, 1021, 830, 805, 741; ^1H NMR (400 MHz, $CDCl_3$): δ=8.40 (s, 1H), 8.14 (d, *J*=8.4 Hz, 1H), 7.86 (d, *J*=8.4 Hz, 1H), 7.59–7.55 (m, 3H), 7.01 (d, *J*=8.4 Hz, 2H), 3.87 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ=160.0, 148.7, 142.4, 132.5, 131.0, 129.6, 128.2, 121.2, 114.5, 55.4. MS *m*/*z* (%): 229 (M^+, 100), 214 (10), 149 (23).

4.4.26. 4-Chloro-3′-nitrobiphenyl. Mp (°C) 90–92.[40] IR (ν/cm^{-1}): 3081, 2861, 1521, 1495, 1351, 1084, 1005, 822, 735; ^1H NMR (400 MHz, $CDCl_3$): δ=8.42 (t, *J*=2.0 Hz, 1H), 8.22 (d, *J*=8.0 Hz, 1H), 7.88 (d, *J*=8.0 Hz, 1H), 7.63 (t, *J*=4.0 Hz, 1H), 7.56 (d, *J*=8.4 Hz, 2H), 7.47 (d, *J*=8.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ=148.8, 141.6, 137.1, 134.8, 132.8, 129.9, 129.4, 128.4, 122.3, 121.8. MS *m*/*z* (%): 233 (M^+, 64), 152 (100).

4.4.27. 4-Fluoro-3′-nitrobiphenyl. Mp (°C) 89–90.[41] IR (ν/cm^{-1}): 3042, 1622, 1552, 1466, 1423, 1152, 880, 693; ^1H NMR (400 MHz, $CDCl_3$): δ=8.41 (t, *J*=2.0 Hz, 1H), 8.20 (d, *J*=8.0 Hz, 1H), 8.87 (d, *J*=8.0 Hz, 1H), 7.63–7.21 (m, 3H), 7.19 (t, *J*=4.8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ=164.3, 161.9, 148.7, 141.8, 134.8, 132.9, 129.8, 128.9 (d, *J*=9.4 Hz, 1C), 122.0, 121.8, 116.1 (d, *J*=21.3 Hz, 1C). MS *m*/*z* (%): 217 (M^+, 96), 170 (100).

4.4.28. 2-Chloro-4′-methylbiphenyl. Oil,[22] IR (ν/cm^{-1}): 3025, 1922, 1514, 1467, 1071, 1034, 817, 754; ^1H NMR (400 MHz, $CDCl_3$): δ=7.45 (d, *J*=8.0 Hz, 1H), 7.35–7.23 (m, 7H), 2.41 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ=140.5, 137.4, 136.5, 132.5, 131.4, 129.9, 129.3, 128.8, 128.3, 126.8, 21.2. MS *m*/*z* (%): 202 (M^+, 100), 165 (82).

4.4.29. 2-Chloro-4′-methoxybiphenyl. Oil,[21] IR (ν/cm^{-1}): 3060, 2954, 2836, 1611, 1515, 1466, 1248, 1178, 1036, 832, 758; ^1H NMR (400 MHz, $CDCl_3$): δ=7.47–7.44 (m, 1H), 7.40–7.38 (m, 2H), 7.34–7.26 (m, 3H), 6.97 (d, *J*=7.2 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ=159.1, 140.1, 132.6, 131.8, 131.4, 130.6, 129.9, 128.2, 126.8, 113.4 55.3. MS *m*/*z* (%): 218 (M^+, 100), 203 (24), 175 (29).

4.4.30. 2-Choloro-4′-fluorobiphenyl. Oil,[21] IR (ν/cm^{-1}): 3061, 2926, 1892, 1602, 1513, 1468, 1228, 1159, 835, 756; ^1H NMR (400 MHz, $CDCl_3$): δ=7.48–7.43 (m, 1H), 7.43–7.38 (m, 2H), 7.35–7.25 (m, 3H), 7.12 (t, *J*=8.8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ=163.6, 161.1, 139.5, 135.4, 132.5, 131.3, 131.2 (d, *J*=8.4 Hz, 1C), 130.0, 128.7, 126.9, 115.0 (d, *J*=21.3 Hz, 1C). MS *m*/*z* (%): 206 (M^+, 100), 170 (60).

4.4.31. 4-Chloro-4′-methoxybiphenyl. Mp (°C) 113–114,[42] 114–115. IR (ν/cm^{-1}): 2960, 1605, 1483, 1286, 1255, 1036, 812, 733; ^1H NMR (400 MHz, $CDCl_3$): δ=7.49–7.45 (m, 4H), 7.36 (d, *J*=8.4 Hz, 2H), 6.97 (d, *J*=8.8 Hz, 2H), 3.84 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ=159.4, 139.3, 132.7, 132.5, 128.8, 128.0, 127.9, 114.3, 55.3. MS *m*/*z* (%): 246 (M^+, 84), 231 (100), 202 (89).

4.4.32. 3,4′-Dimethylbiphenyl. Oil,[23] IR (ν/cm^{-1}): 3024, 2920, 1902, 1606, 1483, 1451, 1039, 821, 779; ^1H NMR (400 MHz, $CDCl_3$): δ =7.48 (d, *J*=8.4 Hz, 1H), 7.38 (d, *J*=8.4 Hz, 2H), 7.31 (t, *J*=7.6 Hz, 1H), 7.23 (d, *J*=7.6 Hz, 2H), 7.14 (d, *J*=7.6 Hz, 2H), 2.41 (s, 3H), 2.39 (s, 3H); ^{13}C NMR (100 MHz, CD_3COCD_3): δ=141.1, 138.4, 138.2, 136.9, 129.4, 128.6, 127.8, 127.7, 127.0, 124.1, 21.5, 21.1. MS *m*/*z* (%): 182 (M^+, 100), 165 (43).

4.4.33. 4-Methoxy-3′-methylbiphenyl. Mp (°C): 51–52.[24] IR (ν/cm^{-1}): 3032, 2951, 1605, 1514, 1498, 1249, 1184, 1028, 833, 785; ^1H NMR (400 MHz, $CDCl_3$): δ=7.54–7.46 (m, 2H), 7.35 (d, *J*=9.2 Hz, 2H), 7.30 (t, *J*=7.6 Hz, 1H), 7.12 (d, *J*=7.6 Hz, 1H), 6.98–6.94 (m, 2H), 3.84 (s, 3H), 2.41 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ=159.0, 140.8, 138.3, 138.7, 128.6, 128.1, 127.5, 127.4, 123.8, 114.1, 55.3, 21.5. MS *m*/*z* (%): 198 (M^+, 100), 183 (M^+-CH_3, 49), 155 (40).

4.4.34. 4-Methoxy-4′-methylbiphenyl. Mp (°C) 110–111,[28] 110–112. IR (ν/cm^{-1}): 3019, 2953, 1607, 1493, 1248, 1180, 1037, 807; ^1H NMR (400 MHz, $CDCl_3$): δ=7.51 (d, *J*=8.8 Hz, 2H), 7.44 (d, *J*=8.4 Hz, 2H), 7.22 (d, *J*=8.0 Hz, 2H), 6.96 (d, *J*=8.4 Hz, 2H), 3.84 (s, 3H), 2.38 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ=158.9, 137.9, 136.3, 133.7, 129.4, 127.9, 126.6, 114.1, 55.3, 21.0. MS *m*/*z* (%): 198 (M^+, 100), 183 (58).

4.4.35. 4,4′-Dimethoxybiphenyl. Mp (°C) 178–180.[32] IR (ν/cm^{-1}): 2954, 2912, 1605, 1499, 1257, 1246, 1179, 1038, 1010, 821; ^1H NMR (400 MHz, $CDCl_3$): δ=6.95 (d, *J*=8.0 Hz, 4H), 7.47 (d, *J*=8.4 Hz, 4H), 3.84 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ=158.7, 133.4, 127.7, 114.1, 55.3. MS *m*/*z* (%): 214 (M^+, 100), 199 (M^+-CH_3, 87), 171 (24).

4.4.36. 4-Fluoro-4′-methoxybiphenyl. Mp (°C) 90–91,[33] 92–93. IR (ν/cm^{-1}): 3013, 2966, 1893, 1602, 1495, 1289, 1234, 1035, 825; ^1H NMR (400 MHz, $CDCl_3$): δ=7.50–7.44 (m, 4H), 7.09 (t, *J*=8.8 Hz, 2H), 6.96 (d, *J*=8.8 Hz, 2H), 3.82 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ =163.3, 160.9, 159.1, 136.9, 132.8, 128.1 (d, *J*=7.6 Hz, 1C), 128.0, 115.5 (d, *J*=21.4 Hz, 1C), 114.2, 55.3. MS *m*/*z* (%): 202 (M^+, 100), 187 (M^+-CH_3, 57), 159 (66), 133 (47).

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