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Graphical Abstract

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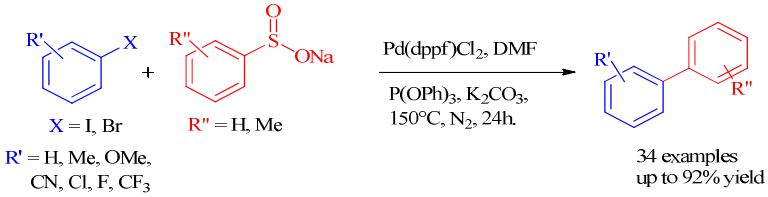

X = I, Br

R' = H, Me, OMe, CN, Cl, F, CF_3

R'' = H, Me

34 examples
up to 92% yield

Tetrahedron

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Palladium catalyzed desulfinylative couplings between aryl sulfinates and aryl bromide/iodide for the synthesis of biaryls

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ABSTRACT

We have synthesized biaryls from the coupling reaction between aryl sulfinates and aryl halides using homogeneous palladium catalytic system. The developed method is simple and efficient. These methodologies are particularly useful to prepare symmetrical as well as unsymmetrical biaryls with excellent product yield. The suggested protocol demonstrated a broad substrate scope.

Introduction

Carbon-carbon (C-C) bond formation is one of the most important reactions in organic synthesis due to its wide applications in pharmaceuticals, biologically active compounds and in advanced material. It is also an important tool in the synthesis of natural products.[1] The most frequently employed methods for the synthesis of unsymmetrical biphenyl derivatives are Suzuki,[2] Stille[3] and Hiyama[4] cross-coupling reactions. Palladium catalyzed cross coupling reactions form an important class of carbon-carbon bond forming reactions. The catalytic activity of Pd-based catalysts can be tuned by phosphine ligands to get the higher stability in the reactions as well as prolonged lifetimes.[5] Palladium and its complexes have been employed as efficient and active catalysts for the cross-coupling reactions.[6] An overview of some of the earlier reported methods for the synthesis of symmetrical and unsymmetrical biaryls by using transition metal-catalyzed homocoupling reactions are presented (Fig. 1).

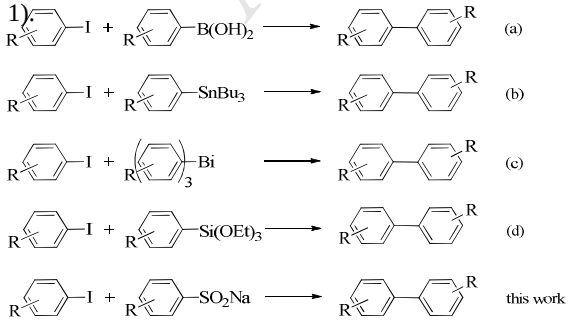


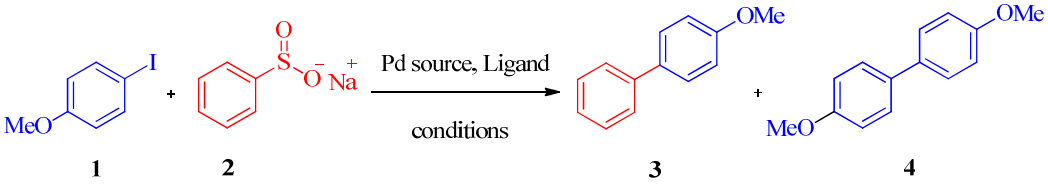
Fig. 1 Synthesis of biaryls by using metal catalyzed coupling methods.

Silver catalyzed C-C coupling of aryl halides with phenylboronic acid[7a] (Fig. 1, route a), Pd-NCs-catalyzed Migitae-Kosugie-Stille cross-coupling reactions[7b] (Fig. 1, route b), palladium catalyzed C-C cross coupling reaction of tri-aryl bismuth with arylhalides[7c] (Fig. 1, route c) and Hiyama cross-coupling reaction of various aryl halides with triethoxy(phenyl)silane[7d] (Fig. 1, route d) are well studied methods for the synthesis of biaryls.

Arenesulfinates have been shown to be more reactive substrates for the synthesis of various aromatic compounds[8]. Recently, arenesulfinates were employed as electrophilic partners for palladium catalyzed Hiyama type cross-coupling reactions.[9] Palladium catalysed desulfitative arylation of 3-haloquinolines with arylsulfinates using additive tetrabutylammonium chloride is reported.[10] Pat Forgione and co-workers reported desulfinylative palladium catalyzed cross-coupling of aryl sulfinates with aryl bromides. High temperature and catalyst loading, higher quantity of arenesulfinate and lower yield are the shortcomings of this protocol.[11] To the best of our knowledge, for the first time, we are reporting the coupling reaction of aryl iodide and sodium arylsulfinate. Sodium aryl sulfinate is currently attracting much attention as it is easy to handle, stable and can be conveniently prepared from the corresponding inexpensive sulfonyl chloride. It is used as an ideal alternative aryl source for the synthesis of biaryl compounds.[12] Arylsulfinate can be used in a palladium catalyzed desulfitative coupling reactions, such as desulfitative C–P coupling of aryl sulfinate metal salts and H-phosphonates,[13] even though arenesulfinates were employed in a desulfinative homocoupling reaction.[14] However, previous reported methods have some drawbacks such as use of high reaction temperature, high catalyst loading and low product yield. Apart from this, by-product formation due to

2 Results and discussion

Table 1. Optimization of reaction parameters.[a]

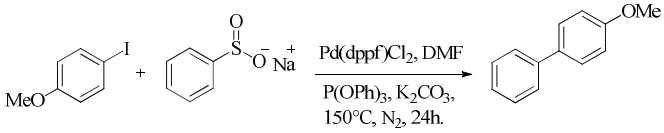


1 **2** **3** **4**

Entry	Catalyst (mol%)	Ligand (mol%)	Base (mmol)	Time (h)	Conversion (%)	Yield(%)[b]	
						3	**4**
1.	$Pd(dppf)Cl_2$ (2.5)	$P(OPh)_3$ (5)	$NaHCO_3$	24	86	79	07
2.	$Pd(dppf)Cl_2$ (2.5)	$P(OPh)_3$ (5)	CS_2CO_3	24	100	64	36
3.	$Pd(dppf)Cl_2$ (2.5)	$P(OPh)_3$ (5)	Na_2CO_3	24	69	67	02
4.	**$Pd(dppf)Cl_2$ (2.5)**	**$P(OPh)_3$ (5)**	**K_2CO_3**	**24**	**100**	**94**	**06**
5.	$Pd(OAc)_2$ (5)	$P(OPh)_3$ (10)	K_2CO_3	48	100	74	26
6.	$PdCl_2$ (5)	$P(OPh)_3$ (10)	K_2CO_3	48	100	75	25
7.	$Pd(PPh_3)_4$ (2.5)	—	K_2CO_3	24	42	42	00
8.	$Pd(PPh_3)_2Cl_2$ (2.5)	$P(OPh)_3$ (5)	K_2CO_3	24	39	39	00
9.	$Pd(dppf)Cl_2$ (2.5)	$P(Ph)_3$ (5)	K_2CO_3	24	66	64	02
10.	$Pd(dppf)Cl_2$ (2.5)	Tri(o-tolyl)phosphine (5)	K_2CO_3	24	95	90	05
11.	$Pd(dppf)Cl_2$ (2.5)	—	K_2CO_3	24	53	51	02
12.	$Pd(OAc)_2$ (5)	Dppf (5)	K_2CO_3	48	90	75	15
13.	$PdCl_2$ (5)	Dppf (5)	K_2CO_3	48	100	71	29
14.	$Pd(dppf)Cl_2$ (2)	$P(OPh)_3$ (4)	K_2CO_3	24	88	82	06
15.	$Pd(dppf)Cl_2$ (2.5)	$P(OPh)_3$ (5)	K_2CO_3	24	100	94	06[c]
16.	$Pd(dppf)Cl_2$ (2.5)	$P(OPh)_3$ (5)	K_2CO_3	24	71	66	05[d]

[a]The reactions were performed by using 4-methoxy iodobenzene **1**(0.5 mmol), sodium aryl sulfinates **2**(0.75 mmol), Palladium source (mol%), ligand source (mol%), Base (1.5 mmol), DMF (2 mL), 150 °C, under N_2, [b]GC yields based on **1**, [c]160 °C, [d]140 °C.

homocoupling is also observed in most of the above reported methods, which is the main drawback. Eventually it also decreases the yield of desired product. Hence a coupling reaction between aryl halide and sodium arylsulfinate was highly desirable which could overcome the above limitations. Herein, we report the synthesis of biaryls using aryl halides and sodium arylsulfinates as starting materials, $Pd(dppf)Cl_2$ as catalyst and $P(OPh)_3$ as ligand in DMF at 150 °C under inert atmosphere (Scheme 1).

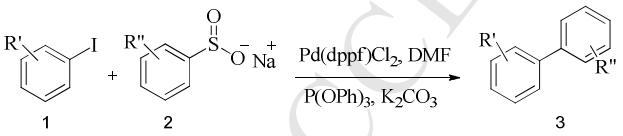


Scheme 1. Reaction between 4-methoxy iodobenzene and sodium aryl sulfinate.

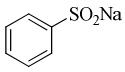
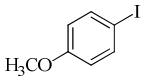
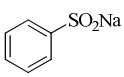
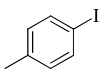
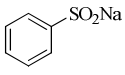
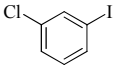
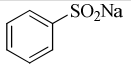
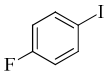
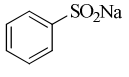
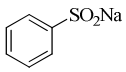
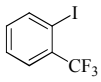
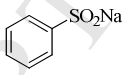
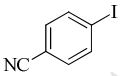
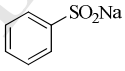
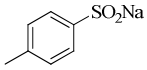
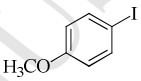
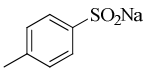
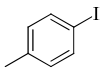
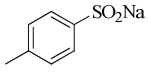
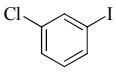
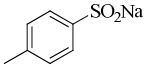
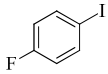
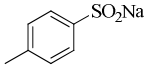
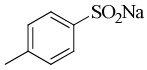
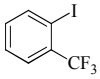
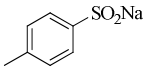
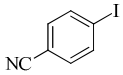
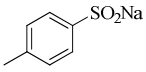
The optimization studies were performed on the coupling reaction of 4-methoxy iodobenzene with sodium arylsulfinates. Initially screening of various bases for desulfinylative coupling was carried out by employing $NaHCO_3$, K_2CO_3, CS_2CO_3 and Na_2CO_3 (Table 1). In the course of this study, it was found that K_2CO_3 is the most effective base as it afforded maximum yield (94 %) of the desired product (Table 1, entries 1-4). It was also found that 1.5 mmol of K_2CO_3 was sufficient for the reaction. We also investigated suitable palladium source as a catalyst for model reaction by employing $Pd(dppf)Cl_2$, $Pd(OAc)_2$, $PdCl_2$, $Pd(PPh_3)_4$ and $Pd(PPh_3)_2Cl_2$ as catalyst (Table 1, entries 4-8). It was observed that $Pd(dppf)Cl_2$ was the best choice as it afforded 94% yield of biaryl with 100% conversion of aryl halide, while $Pd(OAc)_2$, $PdCl_2$, $Pd(PPh_3)_4$ and $Pd(PPh_3)_2Cl_2$ were found to be inferior. When the amount of catalyst $Pd(dppf)Cl_2$ was decreased from 2.5 mol% to 2.0 mol% the yield also decreased from 94% to 82% (Table 1, entry 14). Phosphine ligand plays a very crucial role in homogeneous palladium catalysis with respect to product yield. Therefore, we carried out the model reaction with $Pd(dppf)Cl_2$ as a catalyst in DMF using various ligands. Here we screened three ligands such as triphenyl phosphite [$P(OPh)_3$], triphenyl phosphine [$P(Ph)_3$] and Tri(o-tolyl)phosphine (Table 1, entries 4, 9, 10). The results clearly show that triphenyl phosphite is the most superior ligand than others giving maximum product yield. Triphenyl phosphite is a better ligand than triphenyl phosphine (Table 1, entries 4, 9). The phosphite ligand stabilizes Pd(0) and prevent the formation of inactive palladium black.[15] Triphenyl phosphite is a stronger π-acceptor and a weaker σ-donar than triphenyl phosphine.[16] The selectivity is low in the absence of ligands and only 51 % product yield was obtained (Table 1, entry 11).

We also performed model reactions with $Pd(OAc)_2$ and $PdCl_2$ (5mol%) in presence of Dppf (1,1′-bis(diphenylphosphino)ferrocene) ligand (5mol%) at 150 °C for 48h which afforded 75% and 71% yield of the product respectively (Table 1, entries 12,13). The optimum temperature was found to be 150 °C for the model reaction. Increase in temperature to 160 °C, did not improve the product yield, whereas significant decrease in the product yield was observed when the temperature was decreased to 140 °C (Table 1, entries 4, 15, 16). The reaction time was 24h for aryl iodides and 26h for aryl bromide derivatives to achieve maximum conversions.

Table 2. Reaction between aryl iodides and aryl sulfinates.[a]



1 2 3

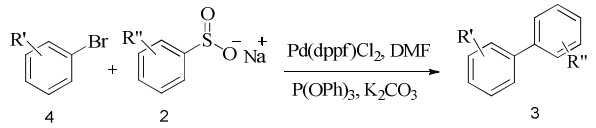
Entry	Ar-X	Ar-SO_2Na	Yield (%)[b]
1			(3a) 91
2			(3b) 92
3			(3c) 90
4			(3d) 88
5			(3e) 88
6			(3f) 87
7			(3g) 86
8			(3h) 87
9			(3c) 90
10			(3i) 91
11			(3j) 88
12			(3k) 87
13			(3l) 86
14			(3m) 86
15			(3n) 84
16			(3o) 85

[a]The reactions were performed by using aryl iodides (0.5 mmol), aryl sulfinates (0.75 mmol), $Pd(dppf)Cl_2$ (2.5 mol%), $P(OPh)_3$ (5 mol%), K_2CO_3 (1.5 mmol), DMF (2 mL), 150 °C, 24h under N_2. [b]Isolated yield.

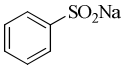
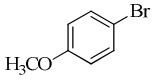
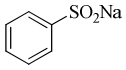
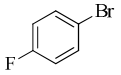
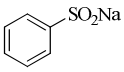
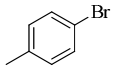
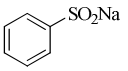
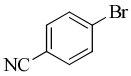
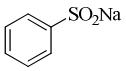
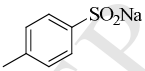
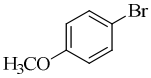
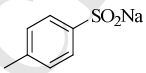
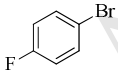
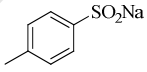
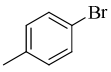
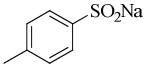
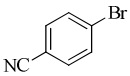
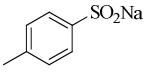
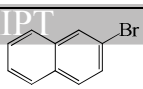
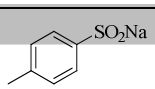
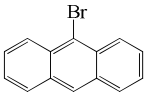
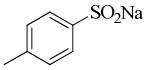
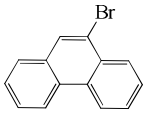
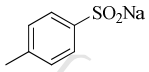
All above experiments reveal that the optimized reaction conditions are 4-methoxy iodobenzene (0.5 mmol), sodium arylsulfinates (0.75 mmol), $Pd(dppf)Cl_2$ (2.5 mol%), $P(OPh)_3$ (5 mol%), K_2CO_3 (1.5 mmol), DMF (2 mL), 150 °C temperature and 24h reaction time under inert atmosphere. To examine the scope of this desulfinylative cross-coupling reaction, we have investigated the reactions using a variety of aryl iodides and aryl sulfinates as substrates under the optimized reaction conditions. The results are shown in Table 2. Aryl iodides with many valuable functional groups present on aromatic ring such as -OCH_3, -Cl, -F, -CH_3, -CF_3 and -CN were well tolerated to give

the desired unsymmetrical biaryl in good to high yields (Table 2, entries 1–16). Regardless of their electronic characters, aryl sulfinates coupled smoothly with aryl iodides bearing both electron-deficient and electron-rich substituents, to afford the corresponding products in good to excellent yields. It was also observed that the yield was lower in the case of ortho substituted aryl halides than those obtained with the para substituted ones, which might be due to steric factors.

Table 3. Reaction between aryl bromides and aryl sulfinates.[a]



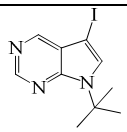
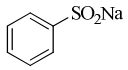
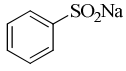
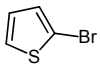
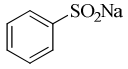
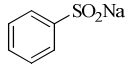
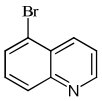
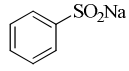
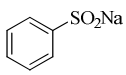
4 2 3

Entry	Ar-X	Ar-SO_2Na	Yield (%)[b]
1			(3a)90
2			(3b)91
3			(3e)87
4			(3c)89
5			(3h)87
6			(3c)89
7			(3i)90
8			(3l)87
9			(3j)89
10			(3o)85
11			(3q)82
12			(3r)78
13			(3s)81

[a]The reactions were performed by using aryl bromides (0.5 mmol), aryl sulfinates (0.75 mmol), $Pd(dppf)Cl_2$ (2.5 mol%), $P(OPh)_3$ (5 mol%), K_2CO_3 (1.5 mmol), DMF (2 mL), 150 °C, 26h under N_2. [b]Isolated yield.

In order to investigate the scope of aryl halides in the coupling with aryl sulfinates, different aryl bromides were employed in the reaction (Table 3, entries1-13). Electron donating and electron-withdrawing aryl bromides readily coupled to give good yields of respective unsymmetrical biaryl products. A trace amount of biphenyl was detected as a by-product in the reactions of aryl iodides and aryl bromides.

Table 4. Reaction between various aryl halides and aryl sulfinates.[a]

Entry	Ar-X	Ar-SO_2Na	Yield (%)[b]
1			(3P) 79
2			(3t)80
3			(3t)78
4			(3u)81
5			(3v)84
6			(3a)00

[a]The reactions were performed by using aryl bromides (0.5 mmol), aryl sulfinates (0.75 mmol), $Pd(dppf)Cl_2$ (2.5 mol%), $P(OPh)_3$ (5 mol%), K_2CO_3 (1.5 mmol), DMF (2 mL), 150 °C, 26h under N_2. [b]Isolated yield.

Additionally, the reaction was carried out quite efficiently when the scope of this catalytic system was further extended to the coupling of heteroaryl halides with aryl sulfinates to yield biaryls

(Table 4, entries1-5). However, no product was formed when chlorobenzene was used in the coupling with sodium benzenesulfinate under optimized reaction conditions (Table 4, entry 6). The mechanism (Scheme 1) is consistent with the one proposed by Pat Forgione and co-workers.[11]

Conclusions

In conclusion, we have developed a simple and efficient method for the desulfinylative cross-coupling reaction between aryl sulfinates and aryl halides. Controlling the extent of homocoupling of aryl halide and increasing the yield of desired product efficiently by the catalyst $Pd(dppf)Cl_2$ is the highlight of this protocol. The developed methodology tolerates wide range of electron donating, electron withdrawing and sterically hindered functional groups and afforded the respective biphenyls with low palladium loadings. Coupling product afforded by less reactive aryl bromide is the advantage of this method.

Experimental Section

General

The Palladium catalysts were purchased from Sigma-Aldrich. All chemicals were purchased from Sigma Aldrich, Alfa Asear and commercial suppliers. The resulting products were purified by column chromatography on silica gel (100-200 mesh; petroleum ether). The reaction was monitored by TLC and GC analysis performed on PerkinElmer Clarus 480. GC equipped with flame ionized detector with capillary column (Elite- 1701, 30m X 0.32 X 0.25) using N_2 as carrier gas. GC-MS (Shimadzu QP 2010) instrument with EI detector and capillary column (Elite – 1, 30m, 0.32mm ID, 0.25 μm film thickness) using helium carrier gas. ^{1}H and ^{13}C NMR spectra were recorded with 400 MHz and 101 MHz spectrometer.

Desulfinylative palladium-catalyzed cross-coupling of aryl sulfinates with aryl halides; General procedure

A mixture of aryl halides (0.5 mmol), aryl sulfinates (0.75 mmol), $Pd(dppf)Cl_2$ (2.5 mol%), $P(OPh)_3$ (5 mol%), K_2CO_3 (1.5 mmol) and 2 mL of DMF in a schlenk tube was heated to 150 °C under inert atmosphere (24h for aryl iodides and 26h for aryl bromides). The reaction mixture was cooled to room temperature, diluted with ethyl acetate and filtered through a plug of Celite. The filtrate was washed sequentially with H_2O and brine. The organic layer was separated, dried (Na_2SO_4), and concentrated under vacuum. The crude product was purified by column chromatography (silica gel; petroleum ether). All the products were analyzed by GC-MS. ^{1}H NMR, ^{13}C NMR and IR of only representative products are given, as all the products are highly reported.

Biphenyl (3a).[17a] (71.0 mg, 91%) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 – 7.57 (m, 4H), 7.45 (dd, J = 10.3, 4.8 Hz, 4H), 7.40 – 7.31 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 141.21, 128.74, 127.24, 127.16. GCMS (m/z/rel.int.): 154(M^+): 51(7.7), 76(22.2), 152(28.8), 153(42.3), 154(100).

4-methoxy-1, 1'-biphenyl (3b).[17a] (85.0 mg, 92%) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 – 7.50 (m, 4H), 7.44 – 7.37 (m, 2H), 7.33 – 7.26 (m, 1H), 7.01 – 6.94 (m, 2H), 3.84 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.10, 140.79, 133.76, 128.68, 128.12, 126.70, 126.62, 114.17, 55.32. GCMS (m/z/rel.int.): 184(M^+): 63(5.8), 115(35.4), 141(56.8), 169(51.2), 184(100).

4-methyl-1, 1'-biphenyl (3c).[17a] (76.0 mg, 90%) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 – 7.58 (m, 2H), 7.52 (d, J = 8.1 Hz, 2H), 7.45 (dd, J = 10.4, 4.8 Hz, 2H), 7.34 (dd, J = 10.4, 4.2 Hz, 1H), 7.28 (d, J = 7.8 Hz, 2H), 2.42 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 141.17, 138.36, 137.00, 129.47, 128.70, 126.99, 126.97, 21.10. GCMS (m/z/rel.int.): 168(M^+): 82(12.5), 152(26.0), 165(26.7), 167(69.0), 168(100).

3-chloro-1, 1'-biphenyl (3d).[17a] (83.0 mg, 88%) as a yellow liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 (dd, J = 8.4, 1.0 Hz, 3H), 7.49 – 7.41 (m, 3H), 7.40 – 7.28 (m, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.03, 139.77, 134.60, 129.96, 128.87, 127.84, 127.26, 127.19, 127.09, 125.28. GCMS (m/z/rel.int.): 188(M^+): 63(9.0), 76(23.5), 152(48.7), 153(28.4), 188(100).

4-fluoro-1, 1'-biphenyl (3e).[17a] (76.0 mg, 88%) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 (qd, *J* = 5.1, 3.0 Hz, 4H), 7.43 (dd, *J* = 10.3, 4.8 Hz, 2H), 7.38 – 7.30 (m, 1H), 7.17 – 7.07 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.66, 161.21, 140.23, 137.30, 128.88 – 128.51, 127.22, 126.98, 115.68, 115.46. GCMS (m/z/rel.int.): 172(M^+): 63(3.1), 73(5.3), 85(12.2), 171(38.2), 172(100).

2-methyl-1, 1'-biphenyl (3f).[17b] (74.0 mg, 87%) as a colourless liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 (ddd, *J* = 7.6, 2.8, 0.9 Hz, 2H), 7.37 (ddd, *J* = 6.2, 2.3, 0.9 Hz, 3H), 7.32 – 7.25 (m, 4H), 2.31 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 141.96, 135.33, 130.30, 129.79, 129.19, 128.06, 127.24, 126.75, 125.75, 20.46. GCMS (m/z/rel.int.): 168(M^+): 63(7.9), 82(21.8), 153(49.3), 165(40.9), 168(100).

2-(trifluoromethyl)-1, 1'-biphenyl (3g).[17c] (96.0 mg, 86%) as a yellow liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (d, *J* = 7.5 Hz, 1H), 7.55 (t, *J* = 7.5 Hz, 1H), 7.45 (t, *J* = 7.6 Hz, 1H), 7.41 – 7.36 (m, 3H), 7.32 (dd, *J* = 5.9, 3.5 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 141.38, 139.80, 131.99, 131.24, 128.91, 127.63, 127.28, 126.00, 125.47, 122.75. GCMS (m/z/rel.int.): 222(M^+): 76(5.1), 100(6.0), 152(13.9), 201(35.1), 222(100).

1, 1'-biphenyl]-4-carbonitrile (3h).[17a] (78.0 mg, 87%) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 – 7.64 (m, 4H), 7.58 (dd, *J* = 5.2, 3.3 Hz, 2H), 7.50 – 7.44 (m, 2H), 7.44 – 7.38 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.64, 139.14, 132.55, 129.07, 128.62, 127.70, 127.19, 118.89, 110.89. GCMS (m/z/rel.int.): 179(M^+): 63(5.0), 76(11.8), 151(15.9), 178(26.8), 179(100).

4-methoxy-4'-methyl-1, 1'-biphenyl (3i).[17d] (91.0 mg, 91%) as a white solid.^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 – 7.48 (m, 2H), 7.45 (d, *J* = 8.1 Hz, 2H), 7.27 – 7.22 (m, 2H), 7.00 – 6.94 (m, 2H), 3.84 (s, 3H), 2.38 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.88, 137.92, 136.34, 133.70, 133.02, 129.42, 127.93, 126.56, 114.12, 55.32, 21.06. GCMS (m/z/rel.int.): 198(M^+): 99(6.8), 128(9.0), 155(34.6), 183(54.4), 198(100).

4, 4'-dimethyl-1, 1'-biphenyl (3j).[17d] (81.0 mg, 88%) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 (d, *J* = 8.1 Hz, 4H), 7.24 (d, *J* = 7.9 Hz, 4H), 2.39 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 138.25, 136.68, 129.42, 126.79, 21.09. GCMS (m/z/rel.int.): 182(M^+): 51(2.5), 89(13.5), 152(11.4), 167(48.8), 182(100).

3-chloro-4'-methyl-1, 1'-biphenyl (3k).[17e] (88.0 mg, 87%) as a colourless liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 – 7.53 (m, 1H), 7.48 – 7.41 (m, 3H), 7.37 – 7.33 (m, 1H), 7.32 – 7.28 (m, 1H), 7.28 – 7.24 (m, 2H), 2.39 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 142.95, 137.72, 136.87, 134.55, 129.9, 129.59, 127.13, 126.80, 125.06, 21.12. GCMS (m/z/rel.int.): 202(M^+): 81(25.8), 152(25.1), 166(21.5), 167(55.6), 202(100).

4-fluoro-4'-methyl-1, 1'-biphenyl (3l).[17e] (80.0 mg, 86%) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 – 7.50 (m, 2H), 7.47 – 7.42 (m, 2H), 7.25 (d, J = 7.8 Hz, 2H), 7.17 – 7.08 (m,

2H), 2.40 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.49, 161.05, 137.46, 137.13, 137.02, 129.53, 126.84, 115.64, 115.43, 21.08. GCMS (m/z/rel.int.): 186(M^+): 82(9.7), 91(11.0), 165(30.0), 168(30.9), 186(100).

2, 4'-dimethyl-1, 1'-biphenyl (3m).[17f] (79.0 mg, 86%) as a yellow liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 – 7.21 (m, 8H), 2.41 (s, 3H), 2.29 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 141.83, 138.99, 136.36, 135.38, 130.27, 129.84, 129.06, 128.76, 127.05, 125.73, 21.18, 20.53. GCMS (m/z/rel.int.): 182(M^+): 82(12.6), 115(11.8), 152(24.4), 167(100), 182(82.8).

4'-methyl-2-(trifluoromethyl)-1, 1'-biphenyl (3n).[17g] (100 mg, 84%) as a colourless liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (d, J = 7.9 Hz, 1H), 7.53 (t, J = 7.7 Hz, 1H), 7.43 (t, J = 7.9 Hz, 1H), 7.31 (d, J = 7.6 Hz, 1H), 7.21 (m, 4H), 2.40 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 137.28, 136.98, 136.78, 132.12, 131.21, 128.78, 128.42, 127.09, 125.98, 21.21. GCMS (m/z/rel.int.): 236(M^+): 117(13.0), 167(27.9), 196(14.0), 201(17.5), 236(100).

4'-methyl-[1, 1'-biphenyl]-4-carbonitrile (3o).[17h] (100 mg, 84%) as a colourless liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 – 7.62 (m, 4H), 7.48 (d, *J* = 8.2 Hz, 2H), 7.27 (d, *J* = 8.0 Hz, 2H), 2.40 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.56, 138.72, 136.22, 132.54, 129.81, 127.43, 127.03, 119.04, 110.47, 21.18. GCMS (m/z/rel.int.): 193(M^+): 83(3.5), 95(10.1), 165(19.7), 192(45.4), 193(100).

7-(tert-butyl)-5-phenyl-7H-pyrrolo [2, 3-d]pyrimidine (3p). (100 mg, 79%) as a white solid**.** ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.23 (s, 1H), 8.87 (d, *J* = 15.2 Hz, 1H), 7.62 – 7.56 (m, 2H), 7.53 (s, 1H), 7.44 (t, *J* = 7.6 Hz, 2H), 7.30 (t, *J* = 7.4 Hz, 1H), 1.83 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 151.07, 149.64, 148.05, 148.03, 133.51, 129.10, 126.97, 126.81, 123.99, 114.58, 57.60, 29.22. GCMS (m/z/rel.int.): 251(M^+): 115(4.6), 140(11.0), 168(5.4), 195(100), 251(16.9). IR(ATR)ν(cm^{-1})3045,2973,2870,1587,1538,1460,1426,1370,1328,1204,944,752,692,616,548,501.

2-(p-tolyl) naphthalene (3q).[17i] m. p. 93-95 °C, (90.0 mg, 82%) as a white solid. GCMS (m/z/rel.int.): 218(M^+): 94(12.2), 107(13.5), 108(12.4), 217(34.2), 218(100).

9-(p-tolyl) anthracene (3r). [17j] m. p. 107-110 °C, (105 mg, 78%) as a yellow solid. GCMS (m/z/rel.int.): 268(M^+): 113(11.5), 126(26.7), 252(46.3), 253(38.0), 268(100).

9-(p-tolyl)phenanthrene (3s).[17k] m. p. 78-80 °C, (109 mg, 81%) as a white solid. GCMS (m/z/rel.int.): 268(M^+): 126(24.7), 132(14.3), 252(41.5), 253(36.63), 268(100).

2-phenylthiophene (3t).[17l] (63.0 mg, 78%) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 (dd, *J* = 7.8, 7.2 Hz, 2H), 7.50 – 7.16 (m, 5H), 7.13 – 6.99 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.42, 134.39, 128.88, 128.01, 127.46, 127.17, 125.95, 124.80, 123.07. GCMS (m/z/rel.int.): 160(M^+): 45(6.0), 77(7.0), 89(8.0), 115(38.0), 160(100). IR(ATR) ν(cm^{-1})3066,2921,2849,1600,1489,1447,1255,1204,1029,825,756,692.

3-phenylpyridine (3u).[17m] (63.0 mg, 81%) as a colourless liquid. GCMS (m/z/rel.int.): 155(M^+): 51(10.0), 77(7.0), 102(11.0), 127(16.0), 155(100).

5-phenylquinoline (3v).[17n] (87.0 mg, 84%) as a yellow solid. ^{1}H NMR (400 MHz, $cdcl_3$) δ 8.90 (d, *J* = 2.5 Hz, 1H), 8.22 (dt, *J* = 18.1, 8.8 Hz, 2H), 7.73 (t, *J* = 7.8 Hz, 1H), 7.55 – 7.31 (m, 6H), 6.88 (ddd, *J* = 27.1, 7.9, 4.5 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.51, 149.69, 147.82, 140.57, 139.10, 136.76, 135.09, 129.99, 129.40, 128.30, 127.60, 126.79, 121.13, 119.47, 115.78. GCMS (m/z/rel.int.): 205(M^+): 77(11.0), 102(17.0), 151(9.0), 176(19.0), 205(100). IR(ATR) ν(cm^{-1})3058,2926,1592,1502,1468,1387,1238,957,807,756,697,569.

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