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AMVN-initiated expedient synthesis of biaryls by the coupling reaction of unactivated arenes and heteroarenes with aryl iodides†

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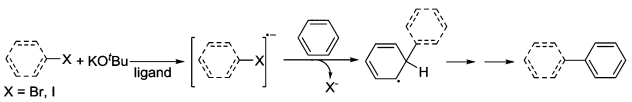
The role of radical initiators AMVN and AIBN has been studied in the potassium *tert*-butoxide mediated biaryl coupling reaction of aryl iodides with unactivated arenes. Radical initiator AMVN promoted carbon–carbon bond formation expeditiously from aryl iodide having various groups such as amino, methoxy, fluoro, methyl, and trifluoromethyl and arenes in the presence of potassium *tert*-butoxide (4 equiv.) at 110 °C in 2–5 h. Substituted arenes such as toluene, xylene, anisole, and fluorobenzene also proceeded to form biaryls under AMVN-initiated reaction conditions. Moreover naphthalene, pyridine, pyrimidine, and pyridazine also coupled with aryl iodides and produced biaryls in 41–82% yields. It seems that AMVN initiates the formation of the aryl radical, which enters the radical chain reaction. The generated aryl radical may combine with the arene leading to a biaryl radical, which upon protonation gives the biphenyl radical anion and *tert*-butanol. The biphenyl radical anion finally reacts with the aryl iodide generating the aryl radical and thus completes the radical chain reaction with concomitant release of biphenyl.

A. Introduction

Biaryls are the privileged cores present in many pharmaceuticals, natural products, agrochemicals and related organic molecules. As a result synthesis of biaryls has attracted considerable interest in academia and industry. Several methodologies have been developed to construct biaryls in the last hundred years. Transition metal catalysts, particularly palladium-based catalysts, are employed for the synthesis of biaryls. However, due to the high cost of palladium, Pd-free methods have attracted considerable interest for the synthesis of biaryls in recent times. Biaryl coupling promoted by *tert*-butoxide together with the ligand is of particular interest as unactivated arenes can be coupled with an aryl anion radical without adding any palladium or transition metal catalyst.

For the first time Itami *et al.* have presented KO^{t}Bu mediated synthesis of hetero-biaryls by coupling heteroarenes with aryl halides under microwave heating conditions. However, the same reaction requires 13 h for completion at 120 °C under conventional heating conditions.[1a] Kwong and Lei *et al.*, Hayashi *et al.*, Shi *et al.*, and others have exploited KO^{t}Bu in various inter- and intramolecular carbon–carbon coupling reactions and the role of KO^{t}Bu in the carbon–carbon bond formation is unambiguously established.[2–5] Very recently light stimulated biaryl synthesis has been established by Rossi *et al.* and Li *et al.*[6c,d,7] It is widely established that the KO^{t}Bu mediated carbon–carbon coupling reaction proceeds by a single electron transfer (Scheme 1).[6a,b] The role of radical initiators has not been explored in the KO^{t}Bu-mediated intermolecular biaryl coupling reaction. Here a KO^{t}Bu-mediated biaryl coupling of unactivated arenes with aryl iodides in the presence of an alkyl diazo radical initiator (*E*)-2,2′-(diazene-1,2-diyl)bis(2,4-dimethylpentanenitrile) (AMVN) is presented.



Scheme 1 Coupling of the aryl radical anion with benzene.

B. Results and discussion

We began the control experiment of the KO^{t}Bu mediated biaryl coupling using 4-iodoanisole as an iodoarene substrate for the optimization of reaction conditions (Table 1). Potassium *tert*-butoxide alone is found to be ineffective for the biaryl coupling

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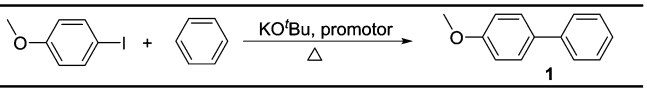
† Electronic supplementary information (ESI) available: NMR (^{1}H, ^{13}C, and ^{13}C-DEPT-135) spectra of biaryls **1–40** and EPR spectra of the reaction mixture. See DOI: 10.1039/c3nj01105d

Table 1 Optimization of reaction conditions[a]



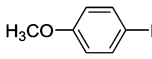
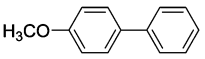
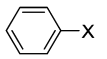
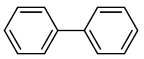
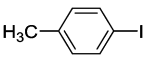
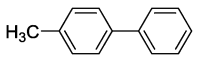
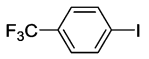
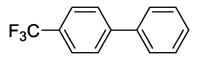
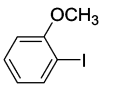
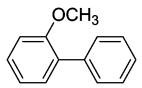
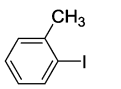
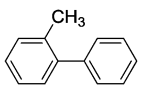
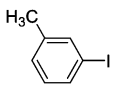
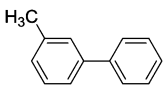
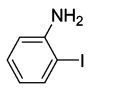
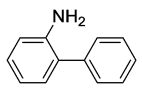
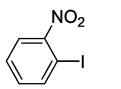
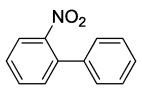
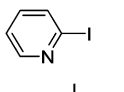
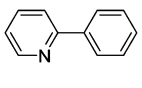
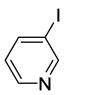
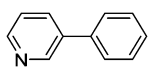
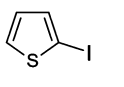
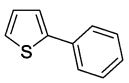
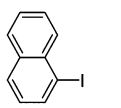
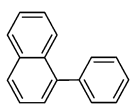
Entry	Initiator/L[b]	Solvent	Time (h)	Yield **1** (%)
1	—	Benzene	24	Trace
2[c]	**AMVN**	**Benzene**	**3**	**87**
3	AIBN	Benzene	20	30
4[d]	AMVN	Benzene	3	66
5[e]	AMVN	Benzene	3	49
6[f]	AMVN	DMF	3	12
7[f]	AMVN	^{t}BuOH	3	32
8	Bathophene	Benzene	20	—
9	Bathocuproine	Benzene	20	13
10	Phenanthroline	Benzene	24	48
11	TMEDA	Benzene	24	—
12	Bipyridyl	Benzene	24	7

[a] Reaction was carried out at the 1 mmol scale using 4-iodoanisole and 4 equiv. of KO^{t}Bu in 3 mL of benzene. [b] 20 mol% of the initiator/ligand was used. [c] 4, 3, and 2 equiv. of KO^{t}Bu was used. [d] 4, 3, and 2 equiv. of KO^{t}Bu was used. [e] 4, 3, and 2 equiv. of KO^{t}Bu was used. [f] Reaction was carried out using 10 mmol of benzene when DMF or ^{t}BuOH (3 mL) was used as solvent in a sealed tube.

reaction as only traces of biaryl **1** were observed in the absence of a radical initiator (entry 1, Table 1). AMVN yielded coupled product **1** in 87% yield in 3 h (entry 2, Table 1). Azoisobutrylonitrile (AIBN) was found to be a poor initiator for the formation of biaryl **1**. Further, we screened DMF and *tert*-butanol as solvents in the biaryl coupling reaction. Both solvents yielded biphenyl **1** in 12 and 32% yields, respectively (entries 6 and 7, Table 1). Other ligands such as phenanthroline, bathophen, bipyridyl, and tetramethylethylenediamine (TMEDA) in the KO^{t}Bu-mediated coupling reaction are compared with the AMVN radical initiator. None of the ligand provided good yield of biaryl **1** under our reaction conditions (entries 8–12, Table 1).

After studying the role of radical initiators and ligands, substrate scope was explored in the presence of AMVN initiated coupling reaction and results are summarized in Table 2. 4-Iodoanisole coupled with benzene and produced methoxy biphenyl **1** in 87% yield. Next, iodobenzene was coupled with benzene under optimized reaction conditions. Indeed, biaryl **2** was obtained in 96% yield in 3 h (entry 2, Table 2). It is worth mentioning that biaryl **2** was obtained in 60–85% yields in various ligands catalyzed reactions.[1,2] Here biphenyl **2** was not only obtained in excellent yield but also biaryl **2** has been synthesized at the 45 mmol scale under conventional reflux conditions (entry 3, Table 2). Bromobenzene underwent arylation in a similar manner to iodobenzene albeit it gave 68% yield of **2** (entry 4, Table 2). Chlorobenzene was noticed to be sluggish and poor yield (9%) of biaryl **2** was obtained. Next substituted iodobenzenes were explored in the AMVN-initiated biaryl coupling reaction. Iodobenzenes having electron donating CH_3, OCH_3, and NH_2 or electron withdrawing F, CF_3, and NO_2 groups underwent coupling reaction successfully and yielded respective biaryls **2–9** in 3–4 h (entries 5–11, Table 2). Iodoarenes with various functional groups have been exploited under KO^{t}Bu-mediated biaryl coupling reactions.[1,2] However, *ortho*-nitro and *ortho*-amino aryliodides have not been used

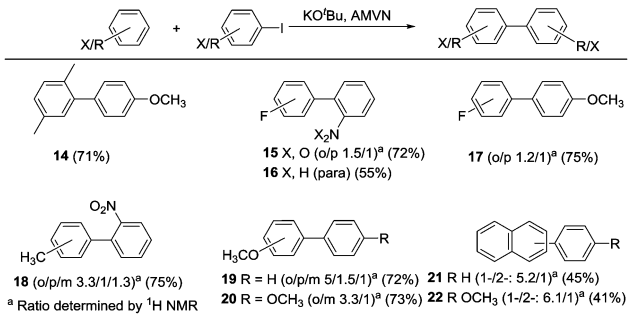
Table 2 AMVN-initiated biaryl synthesis

Entry	Ar–I	Biaryl	t (h)	Yield[a] (%)
1			3	**1** (87)
2			3	**2** (96)
3[b]			24	**2** (85)[b]
4[c]			6	**2** (68)[c]
5			3	**3** (84)
6			3	**4** (71)
7			3	**5** (77)
8			3	**6** (75)
9			3	**7** (80)
10			3	**8** (65)
11			2	**9** (91)
12			3	**10** (85)
13			3	**11** (86)
14			3	**12** (89)
15			3	**13** (83)

[a] Yields were obtained using AMVN, please see the Experimental section for more details. [b] Reaction was carried out at the 49 mmol scale under reflux conditions. [c] Yield obtained from bromobenzene.

in the potassium *tert*-butoxide-mediated biphenyl synthesis despite having further synthetic utilities of amino or nitro groups in functional group transformations and agrochemicals.[8,9] Here 1-iodo-2-nitrobenzene and 1-iodo-2-aminobenzene were successfully utilized for the synthesis of amino and nitro-substituted biphenyls **8** and **9** (entries 10 and 11, Table 2). Furthermore, iodo-heteroarenes such as iodo-pyridine, iodo-thiophene, and iodo-naphthalene were amenable to the reaction conditions and respective biaryls **10–13** were obtained in 70–89% yields (entries 12–15, Table 2).

After successful arylation of benzene, substituted benzenes were explored under optimized reaction conditions (Scheme 2). Electron rich *para*-xylene, toluene, anisole coupled with iodobenzene



^{a} Ratio determined by ^{1}H NMR

Scheme 2 Arylation in substituted arenes.

and *para*-methoxyiodobenzene underwent AMVN initiated carbon–carbon coupling and gave biaryls **14**, **18–20** in 71–75% yields. Electron poor fluorobenzene also showed compatibility with electron rich *para*-methoxyiodobenzene and *ortho*-amino/nitro iodobenzenes leading to fluoro substituted biaryls **15–17** in moderate to good yields. Naphthalene coupled with iodobenzene and *para*-methoxy iodobenzene, however, low yields (41–45%) of 1/2-phenylnaphthyls **21** and **22** were obtained.

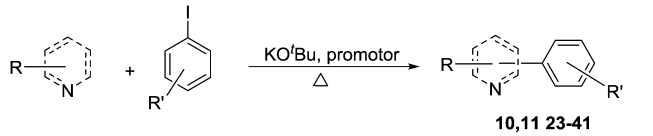
To further extend the scope of carbon–carbon coupling reaction, the coupling reactions of heteroarenes such as pyridine, pyrimidine, and pyridazine were explored with various aryl iodides (Table 3).

Pyridines coupled smoothly with 4-methyl, 4-methoxy, and 2-methoxy iodobenzenes under reaction conditions with the complete conversion of aryl iodides. Pyridine gave a mixture of regioisomers **10**, **11**, and **23** in a 4.5 : 1.3 : 1 ratio when reacted with iodobenzene (entry 1, Table 3). The regioselective outcome and yield remained nearly the same when *para*-methyl iodobenzene was used as a coupling substrate with pyridine and 2-substituted coupled product **24** was observed in a maximum ratio as compared to isomer **25** (entry 2, Table 3). A similar observation was made when 4-methoxy iodobenzene was used as a coupling partner (entry 3, Table 3). On the other hand, 2-methoxy iodobenzene gave a poor ratio (1.5 : 1) of 2- and 3-regioisomers **29** and **30** presumably due to steric hindrance between the methoxy substituent and the nitrogen atom (entry 4, Table 3). Substituted 4-methoxy pyridine also coupled with iodobenzene and 4-methoxy iodobenzene to give biaryls **31** and **32** in 55 and 77% yields, respectively, and 2-position regioisomers were obtained as the major products (entries 5 and 6, Table 3). On the other hand, β-picoline gave a mixture of all four possible regioisomers **33–36** in 60% overall yield (entry 7, Table 3). Other heteroarenes such as pyrimidine and pyridazine were also reacted with 4-iodotoluene to give 4-tolylpyrimidines **37–39** and 4-tolylpyridazines **40–41**, respectively, in 68–76% yields (entries 8 and 9, Table 3).

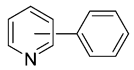
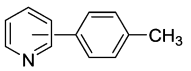
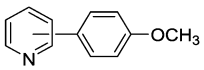
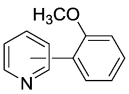
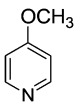
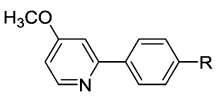
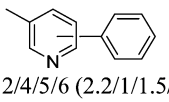
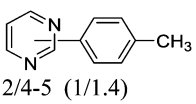
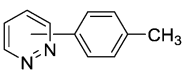
Mechanistic investigation

Several control experiments were carried out to understand the role of AMVN in the biaryl coupling reaction and also the electro-paramagnetic resonance (EPR) spectrum of the reaction mixture was recorded. The EPR spectrum shows a single peak, suggesting the involvement of radicals in the KO^{t}Bu-mediated

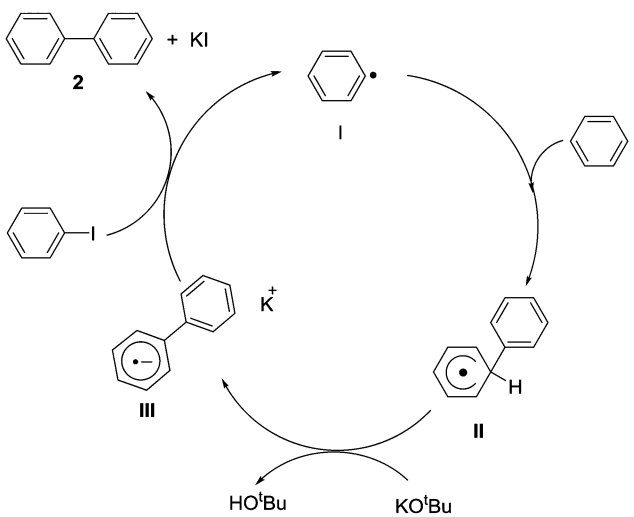
Table 3 Coupling of heteroarenes with aryl iodides



10,11 23-41

Entry	Arene	Biaryl^a (ratio)	Position-(yield%)
1		 2/3/4 (4.3/1.5/1)	**10** 2-(55) **11** 3-(19) **23** 4-(13)
2		 2/3 (3.5/1)	**24** 2-(64) **25** 3-(18)
3		 2/3/4 (4.9/1.5/1)	**26** 2-(50) **27** 3-(16) **28** 4-(11)
4		 2/3 (1.5/1)	**29** 2-(44) **30** 3-(31)
5 6			**31** R′ = H (55) **32** R′ = OCH$_3$ (73)
7		 2/4/5/6 (2.2/1/1.5/2.8)	**33** 2-Ph (18) **34** 4-Ph (8) **35** 5-Ph (12) **36** 6-Ph (22)
8		 2/4-5 (1/1.4)	**37** 2-(32) **38** and **39** 4- and 5-(44)^b
9			**40** 4-(68) **41** 3-(trace)

^{a} Ratio of isomers is based on the isolated yields. ^{b} Combined yield of **38** and **39**.



Scheme 3 Mechanism for AMVN-initiated C–H arylation.

biaryl coupling (EPR is described in the ESI,† pp. S37–S38). A reaction between iodobenzene and benzene was studied in the presence of AMVN without adding KO^{t}Bu which failed to provide biaryl **2**. Similarly, potassium *tert*-butoxide alone is not effective for the promotion of carbon–carbon coupling (entry 1, Table 1) which suggests that KO^{t}Bu and AMVN are required for carbon–carbon bond formation from iodobenzene and benzene. The radical initiator presumably initiates the generation of aryl radical **I** (Scheme 3).

Based on the reported hypothesis,[6] it is reasonable to assume that generated phenyl radical **I** reacts with benzene and could produce biphenyl radical **II** which may further react with KO^{t}Bu and generate biphenyl radical anion **III**. The biphenyl radical anion **III** may react with iodobenzene to give desired biphenyl **2** with concomitant release of aryl radical **I** and thus completes the radical chain.

Conclusions

In summary, AMVN initiated synthesis of biaryls from aryl iodides and arenes has been achieved by utilizing potassium *tert*-butoxide base in short reaction time (3–8 h). Synthesis of biphenyl **2** under conventional reflux conditions and at the 49 mmol scale suggests that biaryls could be accessed at a multi-gram scale under conventional reflux conditions. The presented methodology tolerates various functional groups such as methoxy, methyl, fluoro, and trifluoromethyl in aryl-iodides. Moreover, tolerance for *ortho*-nitro and *ortho*-amino functionalities demonstrated further utility of the developed methodology in the synthesis of nitro/amino-substituted biphenyls. In addition, the AMVN initiated biaryl coupling also shows amenability to the heteroarenes: pyridines, pyrimidine, and pyridazine which may have numerous applications in pharmaceuticals and agrochemicals.[8,9]

C. Experimental section

General syntheses

All NMR experiments were carried out using a 400 MHz spectrometer in $CDCl_3$ and NMR chemical shifts are reported in ppm referenced to the solvent peaks of $CDCl_3$ at 7.26 ppm for ^{1}H and 77.16 (±0.06) ppm for ^{13}C, respectively. High resolution mass analysis is performed on a quadruple-time of flight (Q-TOF) mass spectrometer equipped with an ESI source (+ve). Benzene, xylene, toluene, anisole and mesitylene were dried over calcium hydride. Arenes, aryl iodides, and azoisobutrylonitrile (AIBN) were purchased from Sigma-Aldrich. Potassium *tert*-butoxide (KO^{t}Bu), 97% purity, was purchased from SpectroChem, India and stored in desiccators. Anhydrous DMF and DMSO were obtained from Sigma-Aldrich with sure seal septa. Azomethylvaleronitrile (AMVN) was purchased from Hubei Datong Bio-Chemical Technology Co. Ltd., China. Silica gel (100–200 mesh size) was used for column chromatography. TLC analysis of reaction mixtures was performed using silica gel plates. Sealed-tubes were purchased from Aldrich. All the reactions were performed in hood otherwise stated.

4-Methoxybiphenyl (1).[2a] 4-Iodo anisole (232 mg, 0.99 mmol), potassium *tert*-butoxide (440 mg, 3.9 mmol), and AMVN (52 mg, 0.21 mmol) were added into benzene (3 mL) in a sealed tube. The white coloured reaction mixture was heated at 110 °C for 3 h. After this, the reaction mixture was poured over water (50 mL), extracted with ethyl acetate (25 mL × 3), dried over Na_2SO_4, and concentrated on a rotary evaporator. The resultant white solid was purified by column chromatography using hexane over silica gel. Yield 0.16 g (87%), ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 (t, J = 8.0 Hz, 4H), 7.40 (t, J = 8.0 Hz, 2H), 7.29 (t, J = 8.0 Hz, 1H), 6.97 (d, J = 8.0 Hz, 2H), 3.84 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.2, 140.8, 133.8, 128.7, 128.2, 126.8, 126.7, 114.2, 55.4. GCMS (ESI) m/z 184.0, calcd for $C_{13}H_{12}O$: 184.0.

Synthesis of biaryls: biphenyl (2).[2a] Iodobenzene (206 mg, 1.01 mmol), potassium *tert*-butoxide (450 mg, 4.01 mmol), and azomethylvaleronitrile (AMVN) (49 mg, 0.2 mmol) were added into benzene (3 mL) in a sealed tube. The white coloured reaction mixture was heated at 110 °C for 3 h. The progress of the reaction was monitored by TLC. After this, the reaction mixture was poured into water, extracted with ethyl acetate, (25 mL × 3), dried over Na_2SO_4, and concentrated on a rotary evaporator. The resultant white solid was purified by column chromatography using hexane over silica gel. Yield 0.15 g (96%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 (d, J = 8.0 Hz, 4H), 7.43 (t, J = 8.0 Hz, 4H), 7.34 (t, J = 8.0 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.3, 128.0, 127.2, 127.3. GCMS (ESI) m/z 154.1, calcd for $C_{12}H_{10}$: 154.1.

Synthesis of biphenyl (2) from bromobenzene. Reaction was carried out at the 1 mmol scale using bromobenzene by following the similar procedure as described for iodobenzene. The reaction mixture was heated for 8 h. Yield 105 mg (68%).

Synthesis of biphenyl (2) at the 49 mmol scale under refluxing conditions. Iodobenzene (9.99 g, 49 mmol) and KO^{t}Bu (21.99 g, 196 mmol) were added to a single neck (500 mL) flask containing 130 mL of benzene. After this, AMVN (2.43 g, 9.8 mmol) was added to the reaction mixture. In a reaction flask fitted with a reflux condenser under N_2 the reaction mixture was refluxed for 24 h at 110 °C. Standard workup and purification yielded 6.414 g (85%) of biphenyl **1**.

4-Methyl-1,1′-biphenyl (3).[2a] 4-Iodo toluene (218 mg, 1.0 mmol), potassium *tert*-butoxide (450 mg, 4.01 mmol), and AMVN (52 mg, 0.21 mmol) were added into benzene (3 mL) in a sealed tube. The white coloured reaction mixture was heated at 110 °C for 3 h. After this, the reaction mixture was poured over water (50 mL), extracted with ethyl acetate (25 mL × 3), dried over Na_2SO_4, and concentrated over a rotary evaporator. This resulted in a colourless semi-solid, which was purified by column chromatography using hexane over silica gel. Yield 0.142 g (84%), ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 (d, J = 4.0 Hz, 2H), 7.49 (d, J = 4.0 Hz, 2H), 7.42 (t, J = 6.0 Hz, 2H), 7.32 (d, J = 8.0 Hz, 1H), 7.22 (d, J = 4.0 Hz, 2H), 2.39 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.2, 138.4, 137.0, 129.5, 128.7, 127.0, 126.98, 126.97, 21.1. GCMS (ESI) m/z 168.1, calcd for $C_{13}H_{12}$: 168.1.

1,1′-4-(Trifluoromethyl)-biphenyl (4).[6c] 1-Iodo-4-(trifluoromethyl)benzene (274 mg, 1.01 mmol), potassium *tert*-butoxide (450 mg, 4.01 mmol) and AMVN (52 mg, 0.21 mmol) were added into benzene (3 mL) in a sealed tube. The white coloured reaction mixture was heated at 110 °C. The progress of the reaction was monitored by TLC. The reaction mixture was heated for 4 h. Standard workup and purification gave 157 mg (71%) of biphenyl **4** as a semisolid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 (bs, 4H), 7.59 (d, J = 6.0 Hz, 2H), 7.46 (t, J = 8.0 Hz, 2H), 7.40 (t, J = 8.0 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.0, 139.8, 129.0, 128.2, 127.4, 127.3, 125.73, 125.7, 122.8.

2-Methoxy-1,1′-biphenyl (5).[2a] 2-Iodo anisole (234 mg, 1.0 mmol), potassium *tert*-butoxide (460 mg, 4.1 mmol) and AMVN (48 mg, 0.19 mmol) were added into benzene (3 mL) in a sealed tube. The white coloured reaction mixture was heated at 110 °C. The progress of the reaction was monitored by TLC. The reaction mixture was heated for 3 h. Standard workup and purification gave biphenyl **5** as a solid. Yield 0.141 g (77%), ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 (d, J = 4.0 Hz, 2H), 7.47 (t, J = 8.0 Hz, 2H), 7.38 (t, J = 8.0 Hz, 3H), 7.10 (d, J = 6.0 Hz, 1H), 7.04 (d, J = 4.0 Hz, 1H). 3.85 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.6, 138.7, 131.0, 130.8, 129.6, 128.7, 128.1, 127.0, 120.9, 111.3, 55.6. GCMS (ESI) m/z 184.0, calcd for $C_{13}H_{12}O$: 184.1.

2-Methyl-1,1′-biphenyl (6).[2a] 2-Iodo toluene (221 mg, 1.01 mmol), potassium *tert*-butoxide (456 mg, 4.02 mmol), and AMVN (54 mg, 0.22 mmol) were added into benzene (3 mL) in a sealed tube. The white coloured reaction mixture was heated at 110 °C for 3 h. Standard workup and purification gave colourless liquid of **6**. Yield 0.126 g (75%), ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 (t, J = 8.0 Hz, 2H), 7.32 (q, J = 7.0 Hz, 3H), 7.26–7.22 (m, 4H), 2.26 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.97, 141.94, 135.4, 130.3, 129.8, 129.2, 128.1, 127.2, 126.8, 125.8, 20.5. GCMS (ESI) m/z 168.1, calcd for $C_{13}H_{12}$: 168.1.

3-Methyl-1,1′-biphenyl (7).[2a] 3-Iodo toluene (220 mg, 1.1 mmol), potassium *tert*-butoxide (448 mg, 5.0 mmol) and AMVN (49 mg, 0.2 mmol) were added into benzene (3 mL) in a sealed tube. The white coloured reaction mixture was heated at 110 °C for 3 h. Standard workup gave colourless liquid, which was purified by column chromatography using hexane over silica gel. Yield 0.134 g (80%), ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 (d, J = 4.0 Hz, 2H), 7.43 (q, J = 8.0 Hz, 4H), 7.34 (t, J = 6.0 Hz, 2H), 7.18 (d, J = 4.0 Hz, 1H), 2.44 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.4, 141.3, 138.4, 128.7, 128.69, 128.03, 128.01, 127.2, 127.19, 124.3, 21.6. GCMS (ESI) m/z 168.0, calcd for $C_{13}H_{12}$: 168.1.

[1,1′-Biphenyl]-2-amine (8).[10] 2-Iodo aniline (219 mg, 1.0 mmol), potassium *tert*-butoxide (447 mg, 3.99 mmol) and AMVN (57 mg, 0.23 mmol) were added into benzene (3 mL) in a sealed tube. The white coloured reaction mixture was heated at 110 °C. The progress of the reaction was monitored by TLC. The reaction mixture was heated for 3 h. After this, the reaction mixture was poured into a saturated solution of sodium bicarbonate, extracted with ethyl acetate, (25 mL × 3), dried over Na_2SO_4, and concentrated on a rotary evaporator. The resultant colourless semi-solid was purified by column chromatography using a 9 : 1 mixture of hexane : EtOAc over silica gel. Yield 0.109 g (65%), ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 (t, J = 2.0 Hz, 3H), 7.36–7.31 (m, 2H), 7.16–7.11 (m, 2H), 6.81 (t, J = 8.0 Hz, 1H), 6.76 (d, J = 4.0 Hz, 1H), 3.72 (bs, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.5, 139.5, 130.5, 129.1, 128.8, 128.5, 127.7, 127.2, 118.6, 115.6. HRMS (ESI) m/z 170.0980, calcd for $C_{12}H_{11}N + H^+$: 170.0964.

2-Nitro-1,1′-biphenyl (9).[11] 2-Iodo nitrobenzene (251 mg, 1.01 mmol), potassium *tert*-butoxide (556 mg, 4.02 mmol), and AMVN (51 mg, 0.21 mmol) were added into benzene (3 mL) in a sealed tube. The white coloured reaction mixture was heated at 110 °C for 2 h. Standard workup resulted in yellow oil which was purified by column chromatography using hexane over silica gel. Yield 0.181 g (91%), ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (d, J = 4.0 Hz, 1H), 7.60 (tt, J = 8.0, 1.0 Hz, 1H), 7.48 (d, J = 4.0 Hz, 1H), 7.42 (t, J = 4.0 Hz, 4H), 7.32 (d, J = 2.0 Hz, 1H), 7.30 (d, J = 2.0 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.4, 136.4, 132.3, 132.0, 128.7, 128.3, 128.2, 127.9, 127.1, 124.1. GCMS (ESI) m/z 199.0, calcd for $C_{12}H_9NO_2$: 199.0.

2-Phenylpyridine (10).[1a,5b] 2-Iodopyridine (206 mg, 1.01 mmol), potassium *tert*-butoxide (550 mg, 4.9 mmol), and AMVN (72.0 mg, 0.25 mmol) were added into benzene (3 mL) in a sealed tube. The white coloured reaction mixture was heated at 110 °C for 3 h. After this, the reaction mixture was poured over water (50 mL), extracted with ethyl acetate, (25 mL × 3), dried over Na_2SO_4, and concentrated over a rotary evaporator. This resulted in colourless oil which was purified by column chromatography using hexane–EtOAc (9 : 1) over silica gel. Yield 0.132 g (85%) ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.69 (d, J = 2.0 Hz, 1H), 7.98 (d, J = 4.0 Hz, 2H), 7.76–7.70 (m, 2H), 7.47 (t, J = 8.0 Hz, 2H), 7.40 (t, J = 6.0 Hz, 1H), 7.21 (t, J = 8.0, 0.5 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.4, 149.6, 139.3, 136.8, 129.0, 128.8, 127.0, 122.1, 120.6. HRMS (ESI) m/z 156.0819 (calcd for $C_{11}H_9N$ + H: 156.0808).

3-Phenylpyridine (11).[1a,5b] Reaction was carried out at the 1 mmol scale using 3-iodopyridine (205 mg, 1.0 mmol), potassium *tert*-butoxide (440 mg, 3.99 mmol), and AMVN (52 mg, 0.21 mmol), which were added into benzene (3 mL) in a sealed tube. Yield 0.133 g (86%), ^{1}H NMR (400 MHz), ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.84 (d, J = 1.0 Hz, 1H), 8.58 (d, J = 4.0 Hz, 1H), 7.86 (td, J = 4.0, 1.0 Hz, 1H), 7.57 (d, J = 4.0 Hz, 2H), 7.47 (t, J = 4.0 Hz, 2H), 7.40 (d, J = 4.0 Hz, 1H), 7.35 (q, J = 4.0 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.5, 148.3, 137.9, 136.7, 134.5, 129.1, 128.1, 127.2, 123.6. HRMS (ESI) m/z 156.0819, calcd for $C_{11}H_9N$ + H: 156.0808.

2-Phenylthiophene (12).[12] 2-Iodothiophene (212 mg, 1.01 mmol), potassium *tert*-butoxide (461 mg, 4.1 mmol), and AMVN (33 mg, 0.20 mmol) were added into benzene (6 mL) in a sealed tube. The white coloured reaction mixture was heated at 110 °C. The progress of the reaction was monitored by TLC. The reaction mixture was heated for 3 h. After this, the reaction mixture was poured over water (70 mL), extracted with ethyl acetate, (25 mL × 3), dried over Na_2SO_4, and concentrated over a rotary evaporator, to result in colourless oil which was purified by column chromatography using hexane over silica gel. Yield 0.142 g (89%), ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 (d, J = 4.0 Hz, 2H), 7.37 (d, J = 6.0 Hz, 2H), 7.31–7.26 (m, 3H),

7.07 (q, J = 7.0 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.5, 134.4, 128.9, 127.5, 126.0, 124.8, 123.1. GCMS (ESI) m/z 160.0, calcd for $C_{10}H_8S$: 160.0.

1-Phenylnaphthalene (13).[2a] 1-Iodonaphthalene (256 mg, 1.01 mmol), potassium *tert*-butoxide (451 mg, 5.01 mmol), and AMVN (47 mg, 0.19 mmol) were added into benzene (3 mL) in a sealed tube. The white coloured reaction mixture was heated at 110 °C for 3 h. After this, the reaction mixture was poured over water (70 mL), extracted with ethyl acetate, (25 mL × 3), dried over Na_2SO_4, and concentrated over a rotary evaporator. The resultant residue was purified by column chromatography using hexane over silica gel. Yield 0.169 g (83%), mp 240–242 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (d, J = 4.0 Hz, 2H), 7.86 (d, J = 4.0 Hz, 1H), 7.54–7.47 (m, 6H), 7.45–7.40 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.8, 140.3, 133.8, 131.6, 130.1, 128.3, 127.2, 126.9, 126.04, 126.03, 125.8, 125.4. GCMS (ESI) m/z 204.0, calcd for $C_{16}H_{12}$: 204.0.

4′-Methoxy-2,5-dimethyl-1,1′-biphenyl (14).[5b] 1-Iodo-4-methoxybenzene (234 mg, 1.0 mmol), potassium *tert*-butoxide (480 mg, 4.2 mmol), and AMVN (58 mg, 0.22 mmol) were added into *para*-xylene (3 mL) in a sealed tube. The white coloured reaction mixture was heated at 110 °C. The progress of the reaction was monitored by TLC. The reaction mixture was heated for 24 h. After this, the reaction mixture was poured over water (50 mL), extracted with ethyl acetate, (25 mL × 3), dried over Na_2SO_4, and concentrated over a rotary evaporator. The resultant semisolid was purified by column chromatography using hexane over silica gel. Yield 0.15 g (71%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.23 (d, J = 4.0 Hz, 2H), 7.13 (d, J = 4.0 Hz, 1H), 7.03 (d, J = 4.0 Hz, 2H), 6.93 (d, J = 4.0 Hz, 2H), 3.84 (s, 3H), 2.32 (s, 3H), 2.21 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.8, 141.4, 135.2, 134.5, 132.3, 130.6, 130.3, 130.2, 127.7, 113.5, 55.3, 20.9, 20.0. GCMS (ESI) m/z 212.0, calcd for $C_{15}H_{16}O$: 212.0.

2-Fluoro-2′-nitro-1,1′-biphenyl and 4′-fluoro-2-nitro-1,1′-biphenyl (15).[13,14] 2-Iodo-nitrobenzene (252 mg, 1.01 mmol), potassium *tert*-butoxide (452 mg, 4.01 mmol), and AMVN (52 mg, 0.21 mmol) were added into fluorobenzene (3 mL) in a sealed tube. The white coloured reaction mixture was heated at 110 °C. The progress of the reaction was monitored by TLC. The reaction mixture was heated for 5 h. Yield 0.157 g (72%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (d), 7.86 (t), 7.65 (t), 7.60 (t), 7.55–7.45 (m), 7.44–7.21 (m), 7.12–7.02 (m). ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.0, 163.9, 163.5, 161.54, 161.47, 158.1, 149.1, 139.5, 135.3, 135.1, 132.4, 130.3, 129.8, 128.4, 124.8, 124.6, 124.2, 121.7, 115.6, 115.3, 115.1, 115.07. GCMS (ESI) m/z 217.0, calcd for $C_{12}H_8O_2NF$: 217.0.

4′-Fluoro-[1,1′-biphenyl]-2-amine (16).[15] 2-Iodoaniline (221 mg, 1.01 mmol), potassium *tert*-butoxide (460 mg, 4.1 mmol), and AMVN (54 mg, 0.22 mmol) were added into benzene (3 mL) in a sealed tube. The white coloured reaction mixture was heated at 110 °C for 3 h. After this, the reaction mixture was poured into a saturated solution of sodium bicarbonate, extracted with ethyl acetate (25 mL × 3), dried over Na_2SO_4, and concentrated on a rotary evaporator. The resultant colourless semisolid was purified by column chromatography using a 8 : 2 mixture of hexane : EtOAc over silica gel. In this case, *para* isomer **8** was observed as a major product and other isomers could not be isolated/detected. Yield 0.103 g (55%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44–7.34 (m, 3H), 7.18–7.09 (m, 3H), 6.81 (t, J = 8.0 Hz, 1H), 6.75 (d, J = 4.0 Hz, 1H), 3.74 (bs, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 130.5, 130.4, 130.3, 129.2, 129.1, 129.0, 128.8, 128.5, 124.8, 118.7, 116.2, 115.8, 115.6, 114.0, 113.5. GCMS (ESI) m/z 187.1, calcd for $C_{12}H_{10}FN$: 187.1.

2-Fluoro-4′-methoxy-1,1′-biphenyl and 4-fluoro-4′-methoxy-1,1′-biphenyl (17).[16] 4-Iodo anisole (236 mg, 1.01 mmol), potassium *tert*-butoxide (448 mg, 4.0 mmol), and AMVN (5.0 mg, 0.20 mmol) were added into fluorobenzene (3 mL) in a sealed tube. The white coloured reaction mixture was heated at 110 °C. The progress of the reaction was monitored by TLC. The reaction mixture was heated for 5 h. After this, the reaction mixture was poured over water (70 mL), extracted with ethyl acetate (25 mL × 3), dried over Na_2SO_4, and concentrated over a rotary evaporator. The resultant white colourless liquid was purified by column chromatography using hexane over silica gel. Yield 0.157 g (72%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 (t), 7.40 (t), 7.36–7.23 (m), 7.19–7.09 (m), 6.96 (m), 3.85 (s), 3.84 (s). ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.6, 159.2, 130.5, 130.49, 130.2, 130.1, 128.4, 128.3, 128.2, 124.3, 124.28, 122.3, 116.2, 115.6, 114.3, 114.26, 113.9, 113.5, 113.4, 113.3, 55.4, 55.3. GCMS (ESI) m/z 202.1, calcd for $C_{13}H_{11}FO$ + H: 202.1.

2-Methyl-2′-nitro-1,1′-biphenyl, 3′-methyl-2-nitro-1,1′-biphenyl, and 4′-methyl-2-nitro-1,1′-biphenyl (18).[13] 1-Iodo-2-nitrobenzene (251 mg, 1.01 mmol), potassium *tert*-butoxide (448 mg, 4.0 mmol) and, AMVN (56 mg, 0.22 mmol) were added into toluene (3 mL) in a sealed tube. The white coloured reaction mixture was heated at 110 °C. The progress of the reaction was monitored by TLC. The reaction mixture was heated for 5 h. After this, the reaction mixture was poured over water (70 mL), extracted with ethyl acetate, (25 mL × 3), dried over Na_2SO_4, and concentrated over a rotary evaporator. The resultant yellow oil was purified by column chromatography using hexane over silica gel. Yield 0.16 g (75%), ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (d), 7.81 (t), 7.63–7.53 (m), 7.50 (t), 7.43 (t), 7.31–7.20 (m), 7.10 (t), 2.39 (s), 2.38 (s), 2.1 (s). ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.4, 149.3, 149.2, 139.0, 138.4, 138.2, 138.1, 137.5, 137.3, 136.6, 136.5, 136.4, 136.3, 135.6, 134.4, 132.0, 131.95, 130.0, 129.5, 129.0, 128.98, 128.7, 128.6, 128.5, 128.3, 128.27, 128.2, 128.0, 127.9, 127.8, 125.8, 125.0, 124.1, 124.0, 21.4, 21.3, 19.9. GCMS (ESI) m/z 213.0, calcd for $C_{13}H_{11}NO_2$: 213.0.

2-Methoxy-1,1′-biphenyl, 3-methoxy-1,1′-biphenyl and 4-methoxy-1,1′-biphenyl (19).[6d] Iodobenzene (204 mg, 1.0 mmol), potassium *tert*-butoxide (451 mg, 4.0 mmol), and AMVN (48 mg, 0.20 mmol) were added into anisole (3 mL) in a sealed tube. The white coloured reaction mixture was heated at 110 °C for 10 h. After this, the reaction mixture was poured over water (70 mL), extracted with ethyl acetate, (25 mL × 3), dried over Na_2SO_4, and concentrated over a rotary evaporator. The resultant colourless semi-solid was purified by column chromatography using hexane over silica gel. Yield 0.133 g (72%), ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 (m), 7.53 (m), 7.40 (m), 7.32 (m), 7.19 (m), 7.13 (m), 7.03 (m), 6.98 (m), 3.86 (s), 3.85 (s), 3.80 (s).

^{13}C NMR (100 MHz, $CDCl_3$) δ 160.0, 159.2, 159.5, 142.8, 141.1, 140.9, 138.6, 133.8, 130.9, 130.8, 129.8, 129.6, 128.8, 128.6, 128.2, 128.0, 127.4, 127.2, 126.9, 126.8, 126.7, 120.9, 119.7, 114.2, 113.9, 112.9, 112.7, 111.3, 55.6, 55.4, 55.3. GCMS (ESI) m/z 184.0 calcd for $C_{13}H_{12}O$: 184.0.

2,4′-Dimethoxy-1,1′-biphenyl and 3,4′-dimethoxy-1,1′-biphenyl (20).[5c] 4-Iodo anisole (235 mg, 1.0 mmol) potassium *tert*-butoxide (458 mg, 4.0 mmol), and AMVN (52 mg, 0.21 mmol) were added into anisole (3 mL) in a sealed tube. The white coloured reaction mixture was heated at 110 °C for 15 h. After this, the reaction mixture was poured over water (150 mL), extracted with ethyl acetate, (25 mL × 3), dried over Na_2SO_4, and concentrated over a rotary evaporator. The resultant semi-solid was purified by column chromatography using hexane over silica gel. In this case, the *meta*-isomer was not observed by ^{1}H and ^{13}C NMR spectroscopy. Yield 0.156 g (73%), ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 (m), 7.46 (m), 7.29 (m), 7.12 (m), 7.07 (m), 7.00 (m), 6.95 (m), 6.84 (m), 3.84 (s), 3.838 (s), 3.831 (s), 3.80 (s). ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.9, 158.7, 158.65, 156.5, 133.5, 130.9, 130.7, 130.6, 130.4, 129.7, 128.2, 128.16, 127.7, 120.8, 119.3, 114.2, 113.5, 112.5, 112.0, 111.2, 55.5, 55.4, 55.3, 55.27. GCMS (ESI) m/z 214.1 calcd for $C_{14}H_{14}O_2$: 214.1.

1-Phenylnaphthalene and 2-phenylnaphthalene (21).[2a,6d] Iodobenzene (204 mg, 1.0 mmol), potassium *tert*-butoxide (460 mg, 4.02 mmol), and AMVN (48 mg, 0.19 mmol) were added into naphthalene (128 mg, 1.0 mmol) in a sealed tube. The white coloured reaction mixture was heated at 110 °C. The reaction mixture was heated for 8 h. After this, the reaction mixture was poured over water (70 mL), extracted with ethyl acetate (25 mL × 3), dried over Na_2SO_4, and concentrated over a rotary evaporator. The resultant white colourless liquid was purified by column chromatography using hexane over silica gel. Yield 92 mg (45%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (s), 7.90 (m), 7.86 (m), 7.76 (m), 7.72 (m), 7.57–7.40 (m), 7.37 (m). ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.2, 140.8, 140.3, 138.6, 133.8, 133.7, 133.6, 132.6, 131.6, 130.1, 128.9, 128.4, 128.3, 128.2, 127.65, 127.63, 127.4, 127.3, 127.2, 126.9, 126.3, 126.03, 126.01, 125.9, 125.8, 125.6, 125.4, 124.4. HRMS (ESI) m/z 205.0826, calcd for $C_{16}H_{12}$ + H: 205.1012.

1-(4-Methoxyphenyl)naphthalene and 2-(4-methoxyphenyl)-naphthalene (22).[6d] 4-Iodo anisole (234 mg, 1.0 mmol), potassium *tert*-butoxide (448 mg, 4.0 mmol), and AMVN (52 mg, 0.21 mmol) were added into naphthalene (128 mg, 1.0 mmol) in a sealed tube. The white coloured reaction mixture was heated at 110 °C. The reaction mixture was heated for 8 h. After this, the reaction mixture was poured over water (100 mL), extracted with ethyl acetate (25 mL × 3), dried over Na_2SO_4, and concentrated over a rotary evaporator. The resultant white colourless solid was purified by column chromatography using hexane over silica gel. Yield 95 mg (41%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.0 (s), 7.96–7.84 (m), 7.73 (m), 7.67 (m), 7.54–7.42 (m), 7.05 (m), 7.30 (s), 3.88 (s). ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.3, 159.0, 139.9, 138.2, 133.9, 133.8, 133.7, 133.1, 132.3, 131.8, 131.1, 128.4, 128.34, 128.26, 128.1, 127.6, 127.3, 126.9, 126.2, 126.1, 125.9, 125.7, 125.4, 125.0, 114.3, 113.7, 29.7, 29.4. Two signals could not be detected in ^{13}C NMR presumable due to overlap of signals. GCMS (ESI) m/z 234.1 calcd for $C_{17}H_{14}O$: 234.1.

2-Phenylpyridine (10).[1a,5b] Iodobenzene (206 mg, 1.01 mmol), potassium *tert*-butoxide (448 mg, 4.0 mmol), and AMVN (48 mg, 0.19 mmol) were added into pyridine (3 mL) in a sealed tube. The white coloured reaction mixture was heated at 110 °C for 5 h. After this, the reaction mixture was poured over water (70 mL), extracted with ethyl acetate (25 mL × 3), dried over Na_2SO_4, and concentrated over a rotary evaporator. The resultant white colourless liquid which was purified by column chromatography using a 8 : 2 mixture of hexane : EtOAc over silica gel yielded three fractions; (i) first fraction, yield 85 mg (55%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.69 (d, J = 2.0 Hz, 1H), 8.00 (d, J = 8.0 Hz, 2H), 7.76–7.70 (m, 2H), 7.47 (t, J = 8.0 Hz, 2H), 7.40 (t, J = 8.0 Hz, 2H), 7.23–7.19 (t, J = 8.0 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.5, 149.7, 139.4, 136.7, 129.0, 128.8, 126.9, 122.1, 120.6. HRMS (ESI) m/z 156.0829, calcd for $C_{11}H_9N$ + H: 156.0808.

3-Phenylpyridine (11).[1a,5b] Second fraction, yield 30 mg (19%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.84 (d, J = 2.0 Hz, 1H), 8.57 (dd, J = 8.0, 2.0 Hz, 1H), 7.86 (d, J = 8.0 Hz, 1H), 7.56 (d, J = 8.0 Hz, 2H), 7.46 (t, J = 8.0 Hz, 2H), 7.40 (t, J = 8.0 Hz, 1H), 7.34 (q, J = 8.0 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.4, 148.3, 137.8, 136.7, 134.4, 129.1, 128.1, 127.2, 123.6. GCMS (ESI) m/z 155.0, calcd for $C_{11}H_9N$: 155.0.

4-Phenylpyridine (23).[1a,5b] Third fraction, yield 20 mg (13%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.64 (d, J = 8.0 Hz, 2H), 7.62 (d, J = 8.0 Hz, 2H), 7.50–7.42 (m, 5H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.1, 150.09, 148.5, 138.1, 129.1, 127.0, 121.7. GCMS (ESI) m/z 155.0, calcd for $C_{11}H_9N$: 155.0.

2-(4-Methylphenyl)pyridine (24).[5b] 4-Iodotoluene (220 mg, 1.01 mmol), potassium *tert*-butoxide (458 mg, 4.02 mmol), and AMVN (50 mg, 0.21 mmol) were added into pyridine (3 mL) in a sealed tube. The white coloured reaction mixture was heated at 110 °C for 8 h. After this, the reaction mixture was poured over water (70 mL), extracted with ethyl acetate (25 mL × 3), dried over Na_2SO_4, and concentrated over a rotary evaporator. The resultant white colourless liquid which was purified by column chromatography using hexane over silica gel gave two fractions: (i) first fraction, yield 0.108 g (64%) ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.66 (d, J = 4.0 Hz, 1H), 7.88 (d, J = 8.0 Hz, 1H), 7.73–7.67 (m, 2H), 7.27 (d, J = 8.0 Hz, 2H), 7.18 (dt, J = 6.0, 0.5 Hz, 2H), 2.39 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.5, 149.6, 138.9, 136.7, 136.6, 129.5, 126.8, 121.8, 120.3, 21.3. HRMS (ESI) m/z 170.0919, calcd for $C_{12}H_{11}N$ + H: 170.0964.

3-(4-Methylphenyl)pyridine (25).[5b] Second fraction, yield 31 mg (18%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.82 (d, J = 0.5 Hz, 1H), 8.55 (dd, J = 4.0, 0.5 Hz, 1H), 7.85 (dd, J = 8.0, 0.5 Hz, 1H), 7.47 (d, J = 8.0 Hz, 2H), 7.34 (dd, J = 6.0, 0.5 Hz, 1H), 7.26 (d, J = 8.0 Hz, 2H), 2.40 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.1, 148.0, 138.0, 136.7, 134.9, 134.3, 129.8, 127.0, 123.6, 21.2. GCMS (ESI) m/z 169.1, calcd for $C_{12}H_{11}N$: 169.1.

2-(4-Methoxyphenyl)pyridine (26).[5b] 4-Iodo anisole (237 mg, 1.01 mmol), potassium *tert*-butoxide (450 mg, 4.01 mmol), and AMVN (50 mg, 0.21 mmol) were added into pyridine (3 mL) in a

sealed tube. The white coloured reaction mixture was heated at 110 °C for 8 h. After this, the reaction mixture was poured over water (70 mL), extracted with ethyl acetate (25 mL × 3), dried over Na_2SO_4, and concentrated over a rotary evaporator, which resulted in white colourless liquid. Purification by column chromatography using hexane over silica gel gave three fractions: (i) first fraction, yield 93 mg (50%) ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.63 (d, J = 4.0 Hz, 1H), 7.93 (d, J = 8.0 Hz, 2H), 7.66 (dt, J = 7.0, 1.0 Hz, 1H), 7.64 (d, J = 4.0 Hz, 1H), 7.16–7.13 (m, 2H), 7.23–7.19 (t, J = 8.0 Hz, 1H), 3.84 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.5, 157.1, 149.5, 136.7, 132.0, 128.2, 121.4, 119.8, 114.1, 55.4. HRMS (ESI) m/z 186.0937, calcd for $C_{12}H_{11}NO$ + H: 186.0913.

3-(4-Methoxyphenyl)pyridine (27).[5b] Second fraction, yield 30 mg (16%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.80 (d, J = 2.0 Hz, 1H), 8.52 (dd, J = 4.0, 0.5 Hz, 1H), 7.85 (dt, J = 8.0, 0.5 Hz, 1H), 7.50 (d, J = 8.0 Hz, 2H), 7.32 (q, J = 6.0 Hz, 1H), 6.99 (d, J = 8.0 Hz, 2H), 2.40 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.8, 147.7, 147.6, 134.1, 130.1, 128.2, 123.6, 114.6, 55.4. HRMS (ESI) m/z 186.0932, calcd for $C_{12}H_{11}N$ O + H: 186.0913.

4-(4-Methoxyphenyl)pyridine (28).[5b] Third fraction, yield 20 mg (11%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.60 (d, J = 4.0 Hz, 2H), 7.59 (dd, J = 8.0, 2.0 Hz, 2H), 7.47 (d, J = 8.0 Hz, 2H), 7.00 (d, J = 8.0 Hz, 2H), 3.85 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.7, 149.7, 148.3, 130.2, 128.2, 121.2, 114.6, 55.4. HRMS (ESI) m/z 186.0899, calcd for $C_{12}H_{11}NO$ + H: 186.0913.

2-(2-Methoxyphenyl)pyridine (29).[5b] 2-Iodo anisole (235 mg, 1.0 mmol), potassium *tert*-butoxide (456 mg, 4.02 mmol), and AMVN (51 mg, 0.21 mmol) were added into pyridine (3 mL) in a sealed tube. The white coloured reaction mixture was heated at 110 °C. The progress of the reaction was monitored by TLC. The reaction mixture was heated for 8 h. After this, the reaction mixture was poured over water (70 mL), extracted with ethyl acetate (25 mL × 3), dried over Na_2SO_4, and concentrated overa rotary evaporator, resulting in white colourless liquid. Purification by column chromatography using hexane over silica gel gave two fractions: (i) first fraction, yield 82 mg (44%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.69 (d, J = 4.0 Hz, 1H), 7.79 (d, J = 8.0 Hz, 1H), 7.74 (dd, J = 6.0, 1.0 Hz, 1H), 7.69 (dt, J = 8.0, 1.0 Hz, 1H), 7.36 (dt, J = 8.0, 1.0 Hz, 1H), 7.19 (dt, J = 8.0, 0.5 Hz, 1H), 7.06 (t, J = 8.0 Hz, 1H), 6.99 (d, J = 8.0 Hz, 1H), 3.83 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.9, 156.1, 149.3, 131.2, 129.0, 125.6, 125.2, 121.7, 121.1, 121.0, 111.4, 55.6. HRMS (ESI) m/z 186.0977, calcd for $C_{12}H_{11}NO$ + H: 186.0913.

3-(2-Methoxyphenyl)pyridine (30).[5b] Second fraction, yield 0.057 g (31%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.70 (d, J = 1.0 Hz, 1H), 8.48 (dd, J = 8.0, 0.5 Hz, 1H), 7.80 (t, J = 8.0 Hz, 1H), 7.32–7.23 (m, 3H), 6.98 (t, J = 8.0 Hz, 1H), 6.93 (d, J = 8.0 Hz, 1H), 3.75 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.6, 150.0, 147.7, 134.3, 130.6, 129.9, 129.6, 126.9, 122.6, 121.1, 111.3, 55.5. HRMS (ESI) m/z 186.0927, calcd for $C_{12}H_{11}NO$ + H: 186.0913.

4-Methoxy-2-phenylpyridine (31).[17] Iodo benzene (206 mg, 1.01 mmol), potassium *tert*-butoxide (456 mg, 4.02 mmol) and AMVN (51 mg, 0.21 mmol) were added into 4-methoxy pyridine (2 mL) in a sealed tube. The white coloured reaction mixture was heated at 110 °C. The progress of the reaction was monitored by TLC. The reaction mixture was heated for 8 h. After this, the reaction mixture was poured over water (70 mL), extracted with ethyl acetate (25 mL × 3), dried over Na_2SO_4, and concentrated on a rotary evaporator. The white colourless liquid was purified by column chromatography using hexane–EtOAc (8 : 2) over silica gel. Yield 0.102 g (55%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.51 (d, J = 7.0 Hz, 1H), 7.94 (d, J = 8.0 Hz, 2H), 7.45 (t, J = 8.0 Hz, 2H), 7.39 (t, J = 8.0 Hz, 1H), 7.22 (dd, J = 4.0 Hz, 1H), 6.76 (dd, J = 8.0, 2.0 Hz, 1H), 3.89 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.4, 159.3, 150.9, 139.5, 129.0, 128.7, 127.0, 108.1, 106.9, 55.2. HRMS (ESI) m/z 186.0905, calcd for $C_{12}H_{11}NO$ + H: 186.0913.

4-Methoxy-2-(4-methoxyphenyl)pyridine (32). 4-Iodo anisole (232 mg, 0.99 mmol), potassium *tert*-butoxide (450 mg, 4.0 mmol) and AMVN (52 mg, 0.21 mmol) were added into 4-methoxy pyridine (2.5 mL) in a sealed tube. The white coloured reaction mixture was heated at 110 °C. The progress of the reaction was monitored by TLC. The reaction mixture was heated for 8 h. After this, the reaction mixture was poured over water (70 mL). Standard workup resulted in white colourless liquid. Purification by column chromatography using hexane over silica gel gave a white coloured semi-solid. Yield 0.157 g (73%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.48 (d, J = 8.0 Hz, 1H), 7.91 (d, J = 8.0 Hz, 2H), 7.16 (d, J = 2.0 Hz, 1H), 6.98 (d, J = 8.0 Hz, 2H), 6.74 (dd, J = 8.0, 2.0 Hz, 1H), 3.90 (s, 3H), 3.85 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.7, 160.7, 158.59, 158.56, 150.3, 128.4, 114.1, 107.7, 106.2, 55.4, 55.3. HRMS (ESI) m/z 216.0998, calcd for $C_{13}H_{13}NO_2$ + H: 216.1019.

3-Methyl-2-phenylpyridine (33).[18] Iodobenzene (204 mg, 1.0 mmol), potassium *tert*-butoxide (452 mg, 4.01 mmol), and AMVN (48 mg, 0.19 mmol) were added into 3-methyl pyridine (3 mL) in a sealed tube. The white coloured reaction mixture was heated at 110 °C. The progress of the reaction was monitored by TLC. The reaction mixture was heated for 8 h. Standard workup and purification by column chromatography using hexane over silica gel gave four fractions: (i) second fraction, yield 30 mg (18%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.53 (d, J = 2.0 Hz 1H), 7.60 (d, J = 8.0 Hz, 1H), 7.51 (d, J = 8.0 Hz, 2H), 7.44 (t, J = 6.0 Hz, 2H), 7.39 (d, J = 6.0 Hz, 1H), 7.19 (q, J = 3.0 Hz, 1H), 2.35 (s, 3H). HRMS (ESI) m/z 170.1126, calcd for $C_{12}H_{11}N$ + H: 170.0969.

3-Methyl-4-phenylpyridine (34).[15] Fourth fraction, yield 14 mg (8%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.54 (s, 1H), 8.50 (t, J = 4.0 Hz, 1H), 7.49–7.43 (m, 3H), 7.33–7.31 (m, 3H), 2.33 (s, 3H). HRMS (ESI) m/z 170.1084, calcd for $C_{12}H_{11}N$ + H: 170.0969.

3-Methyl-5-phenylpyridine (35).[19] Third fraction, yield 20 mg (12%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.68 (s, 1H), 8.44 (s, 1H), 7.88 (s, 1H), 7.55 (t, J = 8.0 Hz, 2H), 7.48 (t, J = 8.0 Hz, 2H), 7.44 (d, J = 8.0 Hz, 1H), 2.47 (s, 3H). HRMS (ESI) m/z 170.1159, calcd for $C_{12}H_{11}N$ + H: 170.0969.

5-Methyl-2-phenylpyridine (36).[20] First fraction, yield 37 mg (22%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.54 (s, 1H), 7.96 (d, J = 8.0 Hz, 2H), 7.63 (q, J = 8.0 Hz, 2H), 7.46 (t, J = 8.0 Hz, 2H), 7.39 (t, J = 8.0 Hz, 1H), 2.38 (s, 3H). HRMS (ESI) m/z 170.1009, calcd for $C_{12}H_{11}N$ + H: 170.0969.

2-(*para*-Tolyl)pyrimidine (37).[21] *para*-Iodotoluene (218 mg, 1.0 mmol), potassium *tert*-butoxide (450 mg, 4.0 mmol), and AMVN (50 mg, 0.2 mmol) were added into pyrimidine (0.5 mL)

in a sealed tube. The white coloured reaction mixture was heated at 110 °C for 12 h. The progress of the reaction was monitored by TLC. After this, the reaction mixture was poured over aqueous saturated $NaHCO_3$ (50 mL), extracted with ethyl acetate (25 mL × 4), dried over Na_2SO_4, and concentrated over a rotary evaporator. This resulted in orange coloured liquid. Purification by column chromatography using hexane : EtOAc (9 : 1) over silica gel gave three fractions: (i) first fraction, yield 18 mg (32%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.77 (d, J = 4.8 Hz, 2H), 8.31 (d, J = 8.2 Hz, 2H), 7.28 (d, J = 8.5 Hz, 2H), 7.14 (t, J = 4.8 Hz, 1H), 2.41 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.8, 157.2, 141.1, 134.8, 129.4, 128.1, 118.8, 21.5. GCMS (ESI) m/z 169.9, calcd for $C_{11}H_{10}N_2$: 170.0.

4-(*para*-Tolyl)pyrimidine (38) and 5-(*para*-tolyl)pyrimidine (39).[21,22] Second and third fractions. Yield 50 mg (44%). 4-(*para*-Tolyl)pyrimidine (**38**): ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.22 (s, 1H), 8.70 (d, J = 5.4 Hz, 1H), 7.97 (d, J = 8.2 Hz, 2H), 7.66 (d, J = 5.4 Hz, 1H), 7.29 (d, J = 8.2 Hz, 2H), 2.40 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.9, 159.0, 157.24, 141.6, 133.7, 129.8, 127.1, 116.7, 21.4. 5-(*para*-tolyl)pyrimidine (**39**): ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.16 (s, 1H), 8.91 (s, 2H), 7.45 (d, J = 7.9 Hz, 2H), 7.24 (d, J = 4.7 Hz, 2H), 2.40 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.2, 154.7, 139.1, 134.3, 131.3, 130.2, 126.8, 21.2. GCMS (ESI) m/z 170.0 (6.3 and 6.5 min), calcd for $C_{11}H_{10}N_2$: 170.0.

4-(*para*-Tolyl)pyridazine (40).[21] Yield (116 mg, 68%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.43 (s, 1H), 9.17 (d, J = 5.2 Hz, 1H), 7.62 (dd, J = 5.4 Hz, 2.5 Hz, 1H), 7.56 (d, J = 8.2 Hz, 2H), 7.32 (d, J = 7.9 Hz, 2H), 2.41 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.3, 149.8, 140.6, 138.6, 131.5, 130.3, 126.9, 123.0, 21.3. GCMS (ESI) m/z 170.0, 7.2 min, calcd for $C_{11}H_{10}N_2$: 170.

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