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Cooperatively assisted N-arylation using organic ionic base–Brønsted acid combination under controlled microwave heating

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ABSTRACT

A new synthetic strategy is developed for the construction of C–N bond through the assistance of Brønsted acid/[DBU][HOAc] without adding any metal catalyst. This is the first efficient S_NAr methodology utilizing fluoro, chloro, bromo, and iodoarenes as coupling partners, which offers excellent yield up to 94% within a very short time.

1. Introduction

The C–N bond formation is an important key reaction having wide applications in the synthesis of organic functional molecules.[1] Usually, C–N bonds are constructed by copper and palladium-catalyzed amination of aryl halides as well as aryl boronic acids.[2] During the recent past, significant advances have been made in the area of amination reactions, which include the development of novel transition metal catalysts and design of new ligands.[3] Although these reaction protocols are endowed with extensive applications, they have limitations, such as usage of toxic transition metals, use of costly ligands, and the successive contamination of the product by these catalysts. Subsequently, there stands enough scope for further exploration and improvement toward amination reactions. In this perspective, transition-metal-free protocol appears particularly attractive.[4] Very recently, the research groups of László Kürti,[5a] James P. Morken,[5b] and Jianbo Wang[5c] have revealed some interesting metal-free amination protocols.

Ionic liquids (ILs) have emerged as novel catalysts and reaction media, because of their attractive applications and properties.[6] Microwave Assisted Organic Synthesis (MAOS) has attained the status of a new discipline in organic synthesis.[7] According to the current synthetic requirements, relevance of microwave (MW) methodology using ionic liquids is particularly welcome.[8]

In C–N bond forming reactions, inorganic bases are usually employed to facilitate the deprotonation/coordination of the nucleophile. However, they suffer from demerits, such as low solubility, high melting points, and sensitivity toward moisture, thereby compelling the use of more polar solvents and inert atmosphere. To overcome these drawbacks, organic ionic bases have been introduced as new and promising promoters for coupling reactions.[9] DBU is widely used as an organic base,[10a–c] and DBU based ionic liquids, such as [DBU][HOAc] are particularly useful as a non-nucleophilic task specific organic ionic base (Fig. 1).[10d]

The construction of C–N bond can be achieved through S_NAr type substitution pattern. However, the existing reports are applicable to highly activated fluorobenzenes and relatively low yields are observed with unactivated fluorobenzenes.[11] Very recently, the research group of Fairlie has described a catalyst free N-arylation strategy with unactivated fluorobenzenes using an excess of K_3PO_4 (5 equiv) at 150–190 °C to achieve the desired transformation.[12]

An up to date literature survey reveals that there is no S_NAr substitution protocol, which is applicable to chloro, bromo, and iodoarenes. With an objective to explore an S_NAr type N-arylation

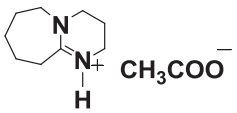

Fig. 1. Structure of the DBU[HOAc].

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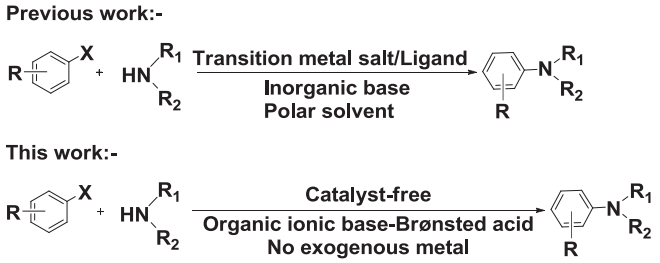
against the well established metal-catalyzed cross coupling protocols, we formulated our strategy to exploit the synthetic potential of various basic ionic liquids for N-arylation of *N*-nucleophiles. In light of the above and as a part of our ongoing research to design new protocols,[13] we describe herein our results on C–N bond formation using a new combination of an organic ionic base with an organic acid under controlled MW (Scheme 1). To the best of our knowledge this is an efficient and conceptually new methodology applied first time for S_NAr type reactions.



Scheme 1. Comparative illustration of previous and present work.

2. Results and discussion

In order to optimize the reaction conditions, a model reaction between bromobenzene and aniline was initially carried out by varying different parameters and the outcome is given in Table 1.

A number of basic ionic liquids with diverse counter ions were screened and [DBU][HOAc] was found to be the best. This may be attributed to the fact that [DBU][HOAc] increases the nucleophilicity of the amines and acts as a benign medium to drive the process. Brønsted acids as additives played crucial role as is evident from entries 8–12 (Table 1). The effect of different MW power, temperature and time was then studied in detail resulting in an optimum condition of 100 W, 165 °C and 50 min (Table 1, entry 15). Aniline (2.0 equiv) and *p*-TSA/TFA (1.0 equiv) were established as sufficient to obtain the maximum yield. Some other additives were also screened but none of them could match the efficacy of *p*-TSA or TFA (Table 1, entries 5–8). Further, we refrained from the use of TFA as an additive because of its high toxicity, low boiling point, and problems of functional group tolerance, and therefore resorted on the use of cheaper and safe *p*-TSA. To confirm the cooperative role of [DBU][HOAc]-[*p*-TSA], the reaction was conducted in the sole presence of *p*-TSA (entry 1) or [DBU][HOAc] (entry 4), which was either futile or ended with poor result. These consequences clearly showcase the fundamental cooperative function of [DBU][HOAc]-[*p*-TSA] at play. As there are recent reports regarding the role of metal contaminants in metal free cross coupling reactions,[14] it was thought worthwhile to investigate and exclude the effect of different metal salts on the present investigation. As an effect, addition of 3 mol % of CuI or $Pd(OAc)_2$ or $Ni(OAc)_2$ to either [DBU][HOAc] or *p*-TSA alone did not bring about any noticeable change (entries 25–28), thus not counting the mediation of metal contaminants. The observation (24% yield) using [DBU][HOAc] without an additive under the optimized conditions (entry 31) further approved the role of *p*-TSA as a unique and important additive in this process. A control experiment in the sole presence of DBU[*p*-TSA] was conducted with no observable product (entry 32).

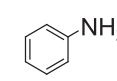
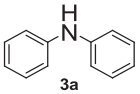
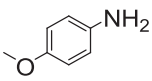
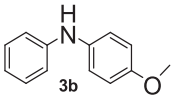
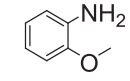
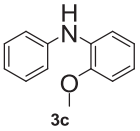
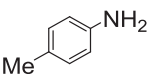
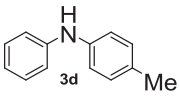
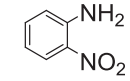
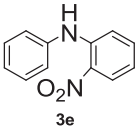
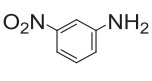
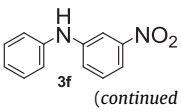
In general, the presence of electron withdrawing groups on aryl halides and electron donating groups on *N*-nucleophiles enhanced

Table 1
MW-assisted optimization of the reaction conditions

Entry	Ph–NH_2 (equiv)	Organic ionic base/ metal salt (equiv)	Additive (equiv)	*T* (°C)	*t* min	Yield (%)[a]
1.	1.0	—	*p*-TSA (0.5)	140	50	00
2.	1.0	Bmim[PF_6]	*p*-TSA (0.5)	140	50	Trace
3.	1.0	Bmim[OH]	*p*-TSA (0.5)	140	50	Trace
4.	1.0	[DBU][HOAc]	—	140	30	15
5.	1.0	[DBU][HOAc]	DABCO (1.0)	140	30	20
6.	1.0	[DBU][HOAc]	L-proline (1.0)	140	30	22
7.	1.0	[DBU][HOAc]	$BF_3 \cdot Et_2O$ (1.0)	140	30	20
8.	1.0	[DBU][HOAc]	AcOH (1.0)	140	45	52
9.	1.0	[DBU][HOAc]	*p*-TSA (0.5)	140	45	41
10.	1.0	[DBU][HOAc]	*p*-TSA (1.0)	140	45	61
11.	1.0	[DBU][HOAc]	TFA (0.5)	140	45	43
12.	1.0	[DBU][HOAc]	TFA (1.0)	140	45	64
13.	1.3	[DBU][HOAc]	*p*-TSA (1.0)	140	45	65
14.	1.5	[DBU][HOAc]	*p*-TSA (1.0)	140	45	70
15.	2.0	[DBU][HOAc]	*p*-TSA (1.0)	140	45	73
16.	2.3	[DBU][HOAc]	*p*-TSA (1.0)	140	45	73
17.	2.0	[DBU][HOAc]	*p*-TSA (1.0)	150	45	76
18.	2.0	[DBU][HOAc]	*p*-TSA (1.0)	160	45	79
19.	**2.0**	**[DBU][HOAc]**	***p*-TSA (1.0)**	**165**	**45**	**81**
20.	2.0	[DBU][HOAc]	*p*-TSA (1.0)	170	45	79
21.	**2.0**	**[DBU][HOAc]**	**TFA (1.0)**	**165**	**45**	**81**
22.	2.0	[DBU][Lac]	*p*-TSA (1.0)	165	45	70
23.	2.0	[DBU][*n*-Pr]	*p*-TSA (1.0)	165	45	45
24.	2.0	[DBU][*n*-Bu]	*p*-TSA (1.0)	165	45	39
25.	2.0	[DBU][HOAc]	CuI (0.03)	165	50	22
26.	2.0	[DBU][HOAc]	$Pd(OAc)_2$ (0.03)	165	50	20
27.	2.0	[DBU][HOAc]	$Ni(OAc)_2$ (0.03)	165	50	22
28.	2.0	CuI (0.03)	*p*-TSA (1.0)	165	50	00
29.	2.0	$Pd(OAc)_2$ (0.03)	*p*-TSA (1.0)	165	50	00
30.	2.0	$Ni(OAc)_2$ (0.03)	*p*-TSA (1.0)	165	50	00
31.	2.0	[DBU][HOAc]	—	165	50	24
32.	2.0	[DBU][*p*-TSA]	—	165	50	00

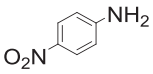
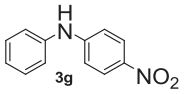
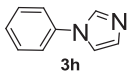
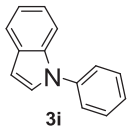
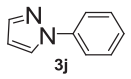
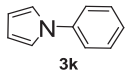
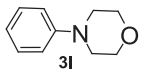
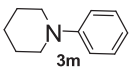
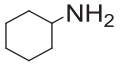
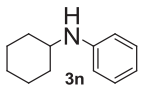
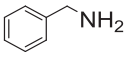
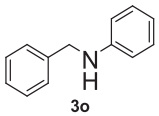
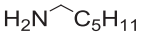
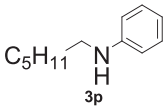
[a] Isolated product yield based on bromobenzene (1 equiv) at 100 W.

Table 2
Coupling of Ar–X with a range of *N*-nucleophiles[a]

Entry	*N*-Nucleophile	*t* (min)	Product	Yield (%)[b]
1.		50	 **3a**	75(X=I) 80(X=Br) 23(X=Cl) 84(X=F)
2.		35	 **3b**	85(X=I) 89(X=Br)
3.		50	 **3c**	77(X=I) 81(X=Br)
4.		35	 **3d**	79(X=I) 82(X=Br)
5.		60	 **3e**	60(X=I) 64(X=Br)
6.		55	 **3f**	69(X=I) 74(X=Br)

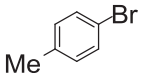
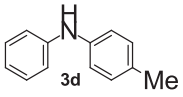
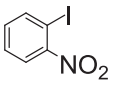
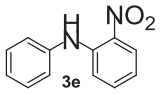
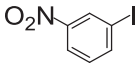
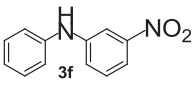
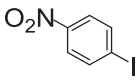
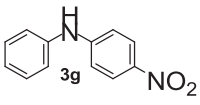
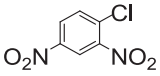
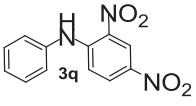
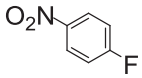
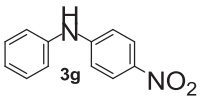
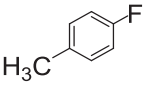
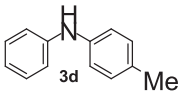
(*continued on next page*)

Table 2 (*continued*)

Entry	*N*-Nucleophile	*t* (min)	Product	Yield (%)[b]
7.		55	 3g	64(X=I) 68(X=Br)
8.		45	 3h	66(X=I) 70(X=Br) 85(X=F)
9.		55	 3i	82(X=I) 91(X=Br) 92(X=F)
10.		50	 3j	71(X=I) 75(X=Br) 88(X=F)
11.		55	 3k	86(X=I) 83(X=Br) 94(X=F)
12.		50	 3l	54(X=I) 57(X=Br)
13.		50	 3m	60(X=I) 67(X=Br)
14.		50	 3n	58(X=I) 63(X=Br) 70(X=F)
15.		55	 3o	79(X=I) 81(X=Br)
16.		45	 3p	63(X=I) 69(X=Br)

[a] Using Aryl halide (1 mmol), *N*-nucleophile (2 mmol), *p*-TSA (1.0 mmol), [DBU][HOAc] (1.5 mL) at 100 W, 165 °C.
[b] Isolated yield based on aryl halide.

Table 3
Coupling of a range of aryl halides with aniline[a]

Entry	Ar–X	*t* (min)	Product	Yield (%)[b]
1.		50	 3d	75
2.		50	 3e	79
3.		50	 3f	83
4.		50	 3g	85
5.		50	 3q	64
6.		40	 3g	87
7.		45	 3d	82

[a] Conditions: aryl halide (1 mmol), aniline (2 mmol), *p*-TSA (1.0 mmol), [DBU][HOAc] (1.5 mL) at 100 W, 165 °C.
[b] Isolated yield based on aryl halide.

the product yield considerably (Table 3, entries 2–6; Table 2, entries 2–4). Further, *ortho*-substituted amines/aryl halides showed lower yields in contrast to *meta*/*para*-substituted analogues, probably due to steric factors (Table 2, entries 3 and 5; Table 3, entry 2). Chlorobenzene, when used as a coupling partner, afforded low yield, although 2,4-dinitrochlorobenzene provided good yield (Table 3, entry 5). Heterocyclic amines, such as indole, pyrrole, imidazole, and pyrazole underwent fast coupling to provide good to excellent yields (Table 2, entries 8–11). Substrates like morpholine, piperidine, cyclohexylamine, and hexylamine afforded reasonably good yields (Table 2, entries 12, 13, 14, and 16), whereas benzylamine performed excellent (Table 2, entry 15). Functional groups appended to aryl halides as well as to *N*-nucleophiles were well tolerated in this coupling process. No biaryls were formed out of the homo-coupling of aryl halides during the investigations.

The recyclability of the ionic liquid was investigated with the same reaction as a model reaction. Upon completion of the reaction, the product was isolated via standard work up procedure, while the aqueous layer containing [DBU][AcOH] was dried to remove water at 60 °C under vacuum and then washed with diethyl ether. The recovered ionic liquid was reused for five times without significant loss of the activity. Results were represented in Fig. 2.

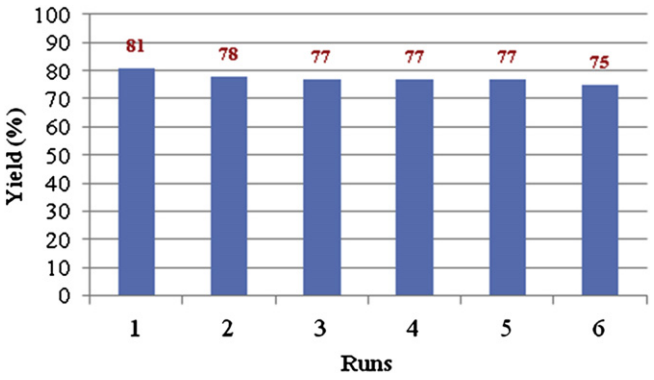


Fig. 2. Reusability of the ionic liquid.

3. Conclusion

In conclusion, we have demonstrated an efficient Brønsted acid accelerated C–N cross coupling reaction in an organic ionic base under controlled MW without the aid of any metal catalyst. Further applications of this approach are underway in our laboratory in order to develop a better understanding of

the overall reaction as well as to make this transformation more useful and practical.

4. Experimental section

4.1. General remarks

Microwave reactions were performed in a CEM Discover benchMate single-mode microwave reactor with a new sealed pressure regulation 10-mL pressurized vial with 'snap-on' cap and Teflon-coated magnetic stir bar. The standard temperature control system for the Discover System consists of a non-contact calibrated infrared sensor, which monitors and controls the temperature conditions of the reaction vessel located in the instrument cavity. The glassware used in the experiments was carefully cleaned with aqua regia before use. Column chromatography was performed using Merck silica gel (100–200 mesh). Thin layer chromatography (TLC) was performed using silica gel 60/Kieselguhr F_{254} precoated on Aluminum sheets (thickness 0.2 mm), commercially available from Merck. Visualization of spots on TLC plate was accomplished with UV light and by staining in I_2 chamber.

All the melting points were determined in open capillary tubes and are uncorrected. ^{1}H and ^{13}C NMR spectra were recorded on 300 MHz and 75 MHz JEOL AL300 FTNMR spectrometer, respectively, at a temperature of 300 K. NMR chemical shifts are expressed in δ values with reference to tetramethylsilane (TMS) as internal standard. Product yields refer to isolated yields after column chromatography.

4.2. Reagents

All the chemicals (including aryl halides and amines) were purchased from Sigma–Aldrich, USA and E. Merck, Germany. New reagent bottles (Aldrich) of $BF_3{\cdot}OEt_2$ [≥46.5% BF_3 basis], 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) [≥99.0%], L-proline [≥98.0%], 1,4-diazabicyclo[2.2.2]octane (DABCO) [≥99.0%], 1-butyl-3-methylimidazolium hexafluorophosphate (bmIm[PF_6]) [≥98.5%], 1-butyl-3-methylimidazolium bromide (bmIm[Br]) [≥97.0%], acetic acid (≥99.99%, based on metal analysis), trifluoroacetic acid [≥99%] and *p*-toluenesulfonic acid monohydrate [≥98.5%] were used. 1-Butyl-3-methylimidazolium hydroxide (bmIm[OH]), [DBU][HOAc], DBU[*n*-propionic acid], DBU[lactic acid], DBU[*n*-butyric acid], and DBU[*p*-TSA] were prepared according to the reported literature procedures.[15,16]

4.3. General procedure for the MW-assisted C–N cross coupling

In a new sealed pressure regulation 10-mL pressurized vial were placed aryl halide (1 mmol), *p*-toluenesulfonic acid (1 mmol, 0.172 g), [DBU][HOAc] (1.5 mL), *N*-nucleophile (2 mmol), and a Teflon-coated magnetic stir bar. The vessel was closed with a snap-on cap, stirred at room temperature for 5 min and then placed into the MW cavity. Microwave irradiation of 100 W at a set temperature of 165 °C was used and the reaction mixture was held under these conditions for the specified time. After completion of the reaction (monitored through TLC), the mixture was cooled to room temperature and was poured to a vessel containing distilled water. This was extracted with ethyl acetate (3×10 mL) and the combined organic phase was washed with brine (2×10 mL), dried over Na_2SO_4, and was concentrated under rotary vacuum evaporator. The crude product was purified by column chromatography using a mixture of ethyl acetate/*n*-hexane as eluent.

4.4. Physical and spectral data of products

*4.4.1. Diphenylamine (**3a**).*[17] Colorless solid; mp 52–54 °C. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): δ=7.27 (t, *J*=6.9 Hz, 4H, ArH), 7.07 (d, *J*=6.9 Hz, 4H, ArH), 6.94 (t, *J*=6.6 Hz, 2H, ArH), 5.67 ppm (br s, 1H, NH). ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C, TMS): δ=143.0, 129.2, 120.9, 117.7 ppm.

*4.4.2. 4-Methoxy-N-phenylaniline (**3b**).*[17] Colorless solid; mp 106–107 °C. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): δ=7.24–7.17 (m, 2H, ArH), 7.08 (d, *J*=8.7 Hz, 2H, ArH), 6.91–6.79 (m, 5H, ArH), 5.48 (br s, 1H, NH), 3.79 ppm (s, 3H, OCH_3). ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C, TMS): δ=155.3, 145.1, 135.7, 129.3, 122.2, 119.5, 115.6, 114.6, 55.6 ppm.

*4.4.3. 2-Methoxy-N-phenylaniline (**3c**).*[17] Yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): δ=7.29–7.25 (m, 3H, ArH), 7.15–7.12 (m, 2H, ArH), 6.95–6.85 (m, 4H, ArH), 6.14 (br s, 1H, NH), 3.88 ppm (s, 3H, OCH_3). ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C, TMS): δ=148.2, 142.7, 133.0, 129.2, 121.6, 121.1, 120.8, 118.6, 114.6, 110.5, 55.6 ppm.

*4.4.4. 4-Methyl-N-phenylaniline (**3d**).*[17] Colorless solid; mp 86–87 °C. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): δ=7.25–7.21 (m, 3H, ArH), 7.10–7.01 (m, 5H, ArH), 6.87 (br s, 1H, ArH), 5.61 (br s, 1H, NH), 2.30 ppm (s, 3H, CH_3). ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C, TMS): δ=143.9, 140.2, 130.9, 129.8, 129.3, 120.2, 118.9, 116.8, 20.7 ppm.

*4.4.5. 2-Nitro-N-phenylaniline (**3e**).*[18] Yellow powder; mp 73–75 °C. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): δ=9.49 (br s, 1H, NH), 8.20 (d, *J*=8.4 Hz, 1H, ArH), 7.43–7.33 (m, 3H, ArH), 7.28–7.20 (m, 4H, ArH), 6.78 ppm (t, *J*=7.2 Hz, 1H, ArH). ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C, TMS): δ=143.1, 138.7, 135.7, 133.1, 129.7, 126.6, 125.6, 124.4, 117.5, 116.0 ppm.

*4.4.6. 3-Nitro-N-phenylaniline (**3f**).*[18] Red solid; mp 85–87 °C. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): δ=7.84 (s, 1H, ArH), 7.70 (d, *J*=7.8 Hz, 1H, ArH), 7.36–7.25 (m, 4H, ArH), 7.15–7.05 (m, 3H, ArH), 5.94 ppm (br s, 1H, NH). ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C, TMS): δ=149.3, 145.1, 140.9, 130.0, 129.7, 123.2, 121.8, 119.9, 114.7, 110.2 ppm.

*4.4.7. 4-Nitro-N-phenylaniline (**3g**).*[17] Yellow solid; mp 132–133 °C. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): δ=8.13 (d, *J*=9.0 Hz, 2H, ArH), 7.41 (t, *J*=7.8 Hz, 2H, ArH), 7.25–7.14 (m, 3H, ArH), 6.93 (d, *J*=9.3 Hz, 2H, ArH), 6.25 ppm (br s, 1H, NH). ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C, TMS): δ=153.4, 145.6, 140.1, 129.9, 126.5, 125.7, 125.4, 118.1 ppm.

*4.4.8. N-Phenyl-imidazole (**3h**).*[17] Light yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): δ=7.85 (s, 1H, ArH), 7.49–7.44 (m, 2H, ArH), 7.39–7.36 (m, 3H, ArH), 7.28 (s, 1H, ArH), 7.20 ppm (s, 1H, ArH). ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C, TMS): δ=137.3, 135.6, 130.4, 129.8, 127.4, 121.4, 118.2 ppm.

*4.4.9. N-Phenyl-indole (**3i**).*[17] Colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): δ=7.68 (d, *J*=7.2 Hz, 1H, ArH), 7.56 (d, *J*=8.1 Hz, 1H, ArH), 7.50–7.45 (m, 4H, ArH), 7.32–7.29 (m, 2H, ArH), 7.20–7.15 (m, 2H, ArH), 6.69 ppm (d, *J*=8.4 Hz, 1H, ArH). ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C, TMS): δ=139.8, 135.8, 129.6, 129.3, 127.9, 126.4, 124.3, 122.3, 121.1, 120.3, 110.5, 103.5 ppm.

*4.4.10. N-Phenyl pyrazole (**3j**).*[19] Light yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): δ=7.87 (d, *J*=2.1 Hz, 1H, ArH), 7.70–7.65 (m, 3H, ArH), 7.42 (t, *J*=7.5 Hz, 2H, ArH), 7.26 (t, *J*=7.5 Hz, 1H, ArH), 6.41 ppm (s, 1H, ArH). ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C, TMS): δ=140.9, 140.0, 129.2, 126.6, 126.2, 119.0, 107.4 ppm.

*4.4.11. N-Phenyl pyrrole (**3k**).*[17] Clear crystalline solid; mp 58–60 °C. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): δ=7.44–7.39 (m, 4H, ArH), 7.29–7.21 (m, 1H, ArH), 7.10 (t, *J*=5.1 Hz, 2H, ArH),

6.36 ppm (t, J=1.8 Hz, 2H, ArH). ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C, TMS): δ=140.7, 129.5, 125.6, 120.5, 119.3, 110.4 ppm.

*4.4.12. N-Phenyl-morpholine (**3l**).*[17] Pale crystalline solid; mp 51–53 °C. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): δ=7.30 (t, J=7.5 Hz, 2H, ArH), 6.92–6.87 (m, 3H, ArH), 3.87–3.84 (m, 4H, CH_2), 3.16–3.13 ppm (m, 4H, CH_2). ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C, TMS): δ=151.3, 129.1, 120.0, 115.7, 66.9, 49.3 ppm.

*4.4.13. N-Phenyl-piperidine (**3m**).*[17] Colorless liquid. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): δ=7.26 (t, J=7.5 Hz, 2H, ArH), 6.95 (d, J=8.1 Hz, 2H, ArH), 6.83 (t, J=7.2 Hz, 1H, ArH), 3.16 (t, J=5.7 Hz, 4H, CH_2), 1.74–1.69 (m, 4H, CH_2), 1.60–1.57 ppm (m, 2H, CH_2). ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C, TMS): δ=152.2, 129.0, 119.1, 116.5, 50.7, 25.9, 24.3 ppm.

*4.4.14. N-Cyclohexylaniline (**3n**).*[17] Colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): δ=7.16 (t, J=7.2 Hz, 2H, ArH), 6.66 (t, J=6.6 Hz, 1H, ArH), 6.58 (d, J=7.5 Hz, 2H, ArH), 3.48 (br s, 1H, NH), 3.28–3.19 (m, 1H), 2.06–2.02 (m, 2H), 1.77–1.72 (m, 2H), 1.66–1.62 (m, 1H), 1.38–1.07 ppm (m, 5H). ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C, TMS): δ=147.3, 129.2, 116.7, 113.1, 51.6, 33.4, 25.9, 25.0 ppm.

*4.4.15. N-Benzylaniline (**3o**).*[20] Colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): δ=7.35–7.13 (m, 7H, ArH), 6.73–6.61 (m, 3H, ArH), 4.31 (s, 2H, $PhCH_2$), 4.01 ppm (br s, 1H, NH). ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C, TMS): δ=148.2, 139.5, 129.3, 128.7, 127.5, 127.3, 117.6, 112.9, 48.3 ppm.

*4.4.16. N-Hexylaniline (**3p**).*[22] Colorless liquid. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): δ=7.24–7.13 (m, 2H, ArH), 6.98–6.89 (m, 1H, ArH), 6.69–6.57 (m, 2H, ArH), 3.57 (br s, 1H, NH), 3.11 (t, J=6.9 Hz, 2H, CH_2), 1.65–153 (m, 2H, CH_2), 1.32–1.31 (m, 6H, CH_2), 0.89 ppm (br s, 3H, CH_3). ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C, TMS): δ=148.5, 129.2, 121.0, 120.9, 117.0, 112.7, 44.0, 31.6, 29.5, 26.8, 22.6, 14.0 ppm.

*4.4.17. 2,4-Dinitro-N-phenylaniline (**3q**).*[21] Orange-red solid; mp 156–157 °C. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): δ=9.97 (br s, 1H, NH), 9.18 (s, 1H, ArH), 8.18 (d, J=9.3 Hz, 1H, ArH), 7.50 (d, J=7.2 Hz, 1H, ArH), 7.40–7.14 ppm (m, 5H, ArH). ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C, TMS): δ=147.0, 137.4, 136.7, 131.1, 130.2, 129.9, 127.7, 125.5, 124.0, 116.0 ppm.

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Supplementary data

Copies of ^{1}H and ^{13}C NMR spectra for all the products are provided in Supplementary Data. Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.tet.2012.11.078.

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