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Hypervalent iodine promoted aromatization of exocyclic β-enaminones for the synthesis of *meta*-*N*,*N*-diarylaminophenols†

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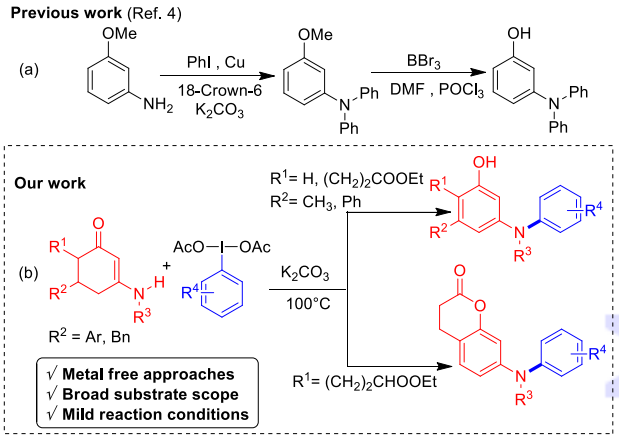
Abstract. A metal and additive free milder cascade approach for the synthesis of *meta*-*N*,*N*-diarylamino phenols (DAAP) starting from exocyclic β-enaminones has been developed. The feasibility of the process is accounted by the suitable molecular geometry of β-enaminones for tandem *N*-arylative *α*-iodination and aromatization under milder basic conditions. Furthermore, the developed strategy has been extended for *meta*-*N*-benzyl-*N*-arylaminophenols (BAAP) synthesis. 4-Ethylpropionyl-2-cyclohexenone has been explored to give 7-diarylamino chroman-2-one (DAAC) employing similar *one-pot* approach. The plausible mechanistic steps were drawn based upon isolation of a stable intermediate and structural identification through X-ray crystallographic analysis.

Keywords: aromatization; β-enaminones; hypervalent iodine reagents; triarylamines; metal free reactions



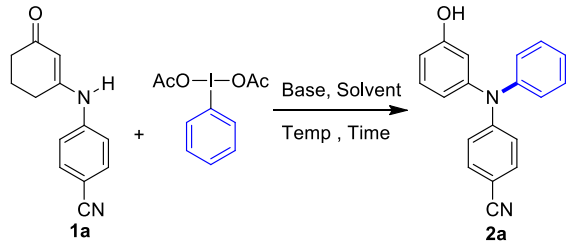
Scheme 1. Synthesis of *N*,*N*-disubstituted aminophenol.

Implementation of highly selective, efficient and environmentally benign chemical processes for replicating the contemporary synthetic strategies is the long standing goal of organic chemistry. Triarylamines are important structural motif with diverse range of applications in the synthesis of natural products, dyes and polymers.[1] Particularly diarylamino phenols and diarylamino coumarins are potential analogues of triarylamine class of compounds which have shown prominent photophysical, electrochemical and pharmacological properties.[2] Recently, due to their efficient electron donating and hole transporting abilities, these compounds have been broadly applied in organic electroluminescence (EL),[3] organic light emitting diodes (OLEDs),[4] organic field-effect transistors,[5] photovoltaic functional materials[6] non-linear materials[7] and xerography.[8]

During last few decades, a plethora of methodologies have been developed for the synthesis of triarylamine derivatives mostly using either Ullmann[9] or Buchwald[10] coupling approaches of *N*-arylation of anilines. Traditionally, triaryl amines have been prepared by ligand-accelerated catalysis in Ullmann condensation by copper salt,[11] palladium catalyzed coupling of amine precursors with different aryl halides[12] or coupling of *N*,*N*-bis(4-methoxyphenyl)amine with methyl 4-iodobenzoate,[13] Iron catalyzed aromatic amination of aryl bromides with Grignard amide as coupling partner[14] and amination of chloroarenes with diarylamines catalyzed by $NiCl_2(PCy_3)_2$ using Grignard reagent as base.[15] In all the above mentioned methods phenolic substrate has been avoided due to its higher sensitivity with cross coupling reagents and as a consequence methoxy derivatives were used as alternatives. Therefore, an additional demethylation step is required for the synthesis of anticipated diarylaminophenol (Scheme 1).[4] On the contrary, 7-diarylamino-substituted coumarin derivatives are generally prepared from the condensation of corresponding diarylamino phenols and acetoacetic ester using 70% H_2SO_4 as catalyst, but environmental hazards have made the process limited.[3c] Therefore, development of new efficient

method that replaces the tedious approaches to synthesize diarylaminophenols would be highly desired from synthetic and mechanistic perspective. After the seminal work by Varvoglis on iodophenylation of 2-amino-1,4-benzoquinones, Du and Zhao reported the α-iodination and concurrent *N*-phenylation of β-enaminones in high yields.[16d, 22c] Recently, the same author has also demonstrated dehalogenative aromatization of *N,N*-diaryl α-iodo enaminone in a single step for -NO_2 substituted compounds.[16b] Also, the reported procedures[16] revealed that aromatization of exocyclic β-enaminones still remained a big challenge for synthetic organic chemists especially under *one-pot* metal free conditions. In recent years, hypervalent iodine reagents[17,18,19] have been widely used as oxidants for the construction of C-N and C-C bonds, but there is no single precedent found in literature where $PhI(OAc)_2$ was used for *one-pot* aromatization of exocyclic enaminones.

Table 1 Optimization of *N*-phenylation and aromatization of exo-cyclic β-enaminones[a]



Entry	Base	Solvent	Temperature [°C]	Time [h]	Yield [%][b]
1	Et_3N	DMF	60	6	nd
2	Et_3N	PEG-400	90	6	40
3	Et_3N	Toluene	90	6	12
4	DABCO	Toluene	90	6	Trace
5	DBU	CH_3CN	100	6	21
6	KF	CH_3CN	100	6	44
7	Cs_2CO_3	CH_3CN	100	6	59
8	Na_2CO_3	CH_3CN	100	6	70
9[c]	**K_2CO_3**	**CH_3CN**	**100**	**6**	**89**
10[d]	K_2CO_3	CH_3CN	100	6	75
11[e]	K_2CO_3	CH_3CN	100	6	70
12	K_2CO_3	CH_3CN	100	7	89
13	K_2CO_3	CH_3CN	100	5	78
14	K_2CO_3	CH_3CN	60	6	10
15	K_2CO_3	CH_3CN	80	6	74
16	K_2CO_3	DMF	100	6	10
17	K_2CO_3	PEG-400	100	6	77
18	Cs_2CO_3	Toluene	100	6	30
19	K_2CO_3	Toluene	100	6	40

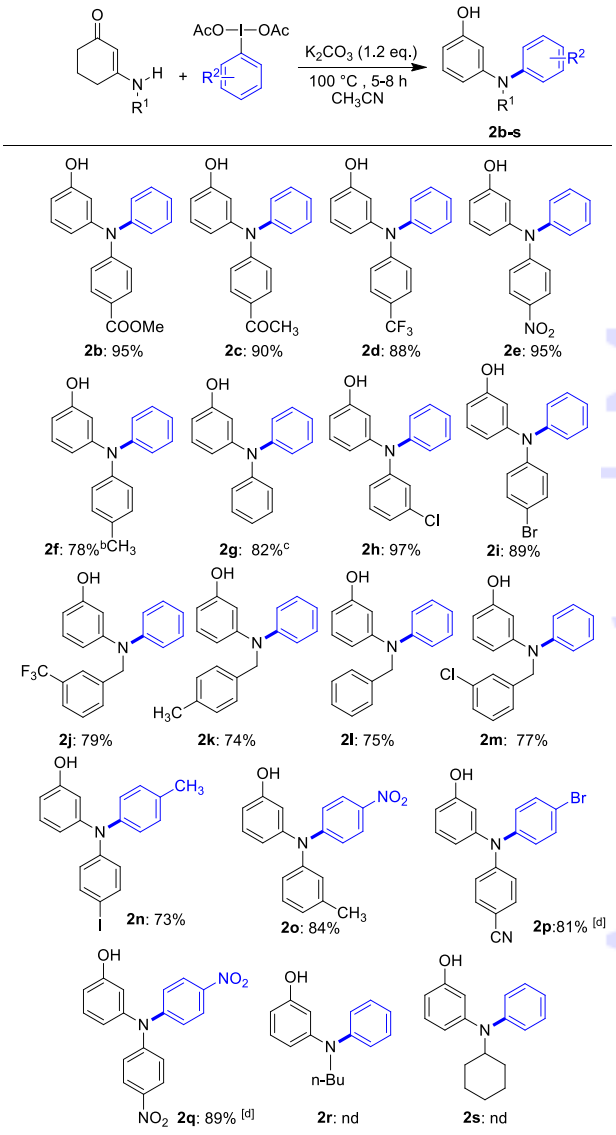
[a]Reaction conditions: **1a** (0.38 mmol), $PhI(OAc)_2$ (0.45 mmol) and K_2CO_3 (0.45 mmol) in solvent (2 mL) at given temperature for selected time;
[b]Isolated yields of the product; nd = not detected;
[c]1.2 equiv of $PhI(OAc)_2$ was used.
[d]1 equiv of $PhI(OAc)_2$ was used;
[e] 2 equiv of $PhI(OAc)_2$ was used.

Herein, $PhI(OAc)_2$ was explored for the synthesis of triarylaminophenols (DAAP, BAAP and DAAC) from exocyclic β-enaminones following *one-pot* α-iodination, *N*-arylation and aromatization in a cascade approach under metal and additive free milder basic conditions. Furthermore, such a transformation would complement the recent methods of transition metal catalysed triarylamine synthesis and strengthening the potential efficacy of the reaction platform.

In this study, the role of $PhI(OAc)_2$ for *N*-arylation and aromatization of exocyclic β-enaminones to *N,N*-diarylaminophenol synthesis under metal free milder basic conditions were critically investigated in *one-pot* fashion. To get highest yield of the product, optimization studies were performed to fix the reaction co-ordinates such as base, solvent, temperature and time (Table 1, entries 1-19).

Exhaustive examinations revealed that 4-(3-oxocyclohex-1-enylamino)benzonitrile (**1a**) (1 equiv), $PhI(OAc)_2$ (1.2 equiv), K_2CO_3 (1.2 equiv) in

Table 2. Metal free dehydrohalogenative aromatization of exocyclic β-enaminones.



[a] Isolated yields of the products; Reaction conditions: β-enaminone (100 mg), $PhI(OAc)_2$ (1.2 equiv) and K_2CO_3 (1.2 equiv) in CH_3CN at 100 °C;
[b] reaction time 8 h. [c] reaction time 7 h.
[d] reaction time 4 h.

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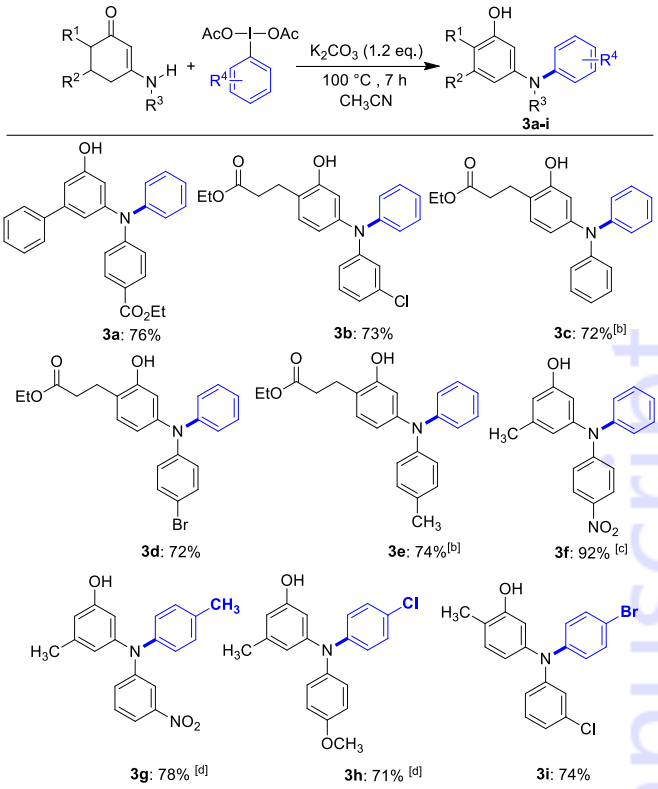
acetonitrile (2 ml) at 100 °C for 6 h were found to be suitable condition to give the *meta*-(*N*-(4-cyanophenyl)-*N*-phenyl)aminophenol (**2a**) in 89% yield (Table 1, entry 9).

With the optimised reaction conditions in hand, we further proceeded to explore the substrates scope with different arylamine substituted β-enaminones (both

electron rich and deficient). Under the standard conditions, electron deficient functional groups such as *p*-CO_2CH_3, *p*-$COCH_3$ and *p*-CF_3 on the arylamine substituted β-enaminones **1b-d** afforded the corresponding DAAPs **2b-d** in 88-95% yield (Table 2). Notably, electron withdrawing *p*-NO_2-aryl substituted β-enaminone **1e** excellently gave in 95% yield of DAAP **2e**, contrary to the previously reported reaction.[16] Gratifyingly, electron rich arylamine substituted β-enaminones **1f** and **1g** also gave the respective DAAPs **2f** and **2g** in 78 and 82% yields respectively, but the reaction took modest longer time for its completion (Table 2). Moreover, haloarylamine substituted β-enaminones **1h** and **1i** were found to be highly reactive and gave **2h** and **2i** in considerably good yields (89-97%) (Table 2). Interestingly, *m*-CF_3, *p*-CH_3, H- and *m*-Cl-benzyl amine substituted β-enaminones **1j-m** underwent aromatization delivering the corresponding BAAPs **2j-m** in good yields (Table 2). Eencouraged by these results, we next tested different electron rich and electron deficient diacetoxyiodobenzene derivatives and checked the versatility and regiospecificity of the present method. Electron rich *p*-methyldiacetoxyiodobenzene smoothly reacted with β-enaminone **1n** to afford **2n** in good yield. Gratifyingly, electron deficient diacetoxyiodobenzene also gave excellent result when it reacted with **1o** to give **2o** in 84% yield. Electron withdrawing β-enaminone **1a** satisfactorily gave **2p** in 81% yield when it reacted with *p*-bromo substituted $PhI(OAc)_2$ derivative. Interestingly, both electron withdrawing substrate **1b** and iodine(III) reagent reacted well under optimized condition gave corresponding **2q** in 89% yields in 3 h. In all the reactions with substituted diacetoxyiodobenzene regiospecific *N*-arylation was observed. Moreover, the *N*-alkyl amine substituted β-enaminones were attempted under the same conditions unfortunately no products **2r-s** were observed (Table 2). To see the substrate versatility and effect of functional groups methyl, 5-Ph and 4-$C_2H_4CO_2C_2H_5$ substituted β-enaminones **1r-w** (supporting information) were selected for this study. 5-Ph substituted β-enaminone **1r** was treated under same conditions no significant effect of phenyl group was observed for its aromatization and corresponding phenyl-substituted DAAP **3a** was obtained in 76% yield (Table 3). Further, 4-alkylester substituted β-enaminones (**1s-w**, supporting information) as novel molecule was synthesized following our earlier reports[20] and subjected to similar reaction. No major role of alkyl group was observed on their reactivity and subsequently alkyl ester-substituted DAAPs **3b-e** were produced in considerably good yields (Table 3). In continuation of our study, methyl substituted

Table 3. Dehydrohalogenative aromatization of aryl and alkyl substituted exocyclic-β-enaminones[a]



[a] Yield refers to isolated products; Reaction conditions: β-enaminone (100 mg), $PhI(OAc)_2$ (1.2 equiv) and K_2CO_3 (1.2 equiv) in CH_3CN at 100 °C.
[b] reaction time 11 h.
[c] reaction time 6h.
[d] reaction time 12 h.

electron rich and deficient β-enaminones (**1x-za**, supporting information) were also tested with various substituted and unsubstituted $PhI(OAc)_2$ derivatives. 5-methyl substituted electron deficient substrates (**1x-y**) were subjected to aromatization under optimized conditions gave excellent yields of the desired products **3f-g**. However, electron rich $PhI(OAc)_2$ took longer time to furnish desired product in satisfactory yield. Halogen substituted $PhI(OAc)_2$ derivatives smoothly reacted with substrate **1z-za** afforded **3h-i** in 71-74% yields respectively.

Previous reports indicated that 7-*N*,*N*-diarylsubstituted coumarins are well known for their huge applications in organic light emitting diodes (OLEDs).[4] Interestingly, when the same reactions in Table 3 (**1s-w**) were subjected to prolonged heating (36 h) under same condition, the DAACs **4a-d** were identified as major products in reasonably good yields (Table 4) and could be useful intermediate for 7-*N*,*N*-diarylsubstituted coumarin synthesis.

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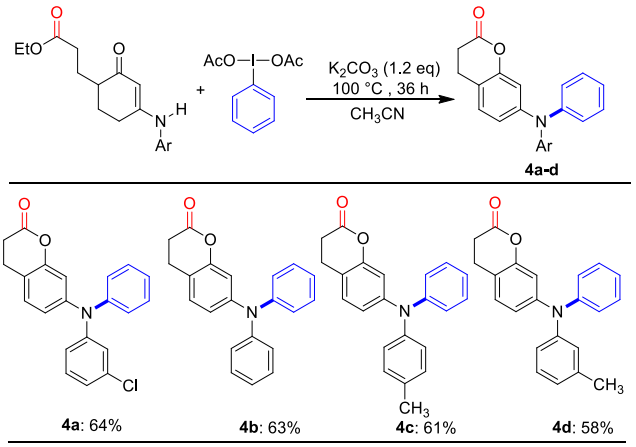
Table 4. One-pot approach for dehydrohalogenative aromatization and cyclization[a]



[a] Isolated yields; Reaction conditions: ethyl 3-(4-N-arylamino-2-oxocyclohex-3-enyl)propanoate (100 mg), $PhI(OAc)_2$ (1.2 equiv) and K_2CO_3 (1.2 equiv) in CH_3CN at 100 °C for 36 h.

To understand the possible mechanistic pathway, series of reactions have been performed to identify intermediates. In our screening, when we treated **1a** under the same conditions at room temperature we observed a new spot on TLC in major quantity. This compound was further isolated and identified by NMR and ESI-MS spectroscopic studies and detected as 2-iodo-diarylamino-substituted enaminones (**5a**) in 65% yield. Finally, the structure of **5a** was confirmed by the single crystal X-ray crystallographic analysis (Figure 1, **5a**).

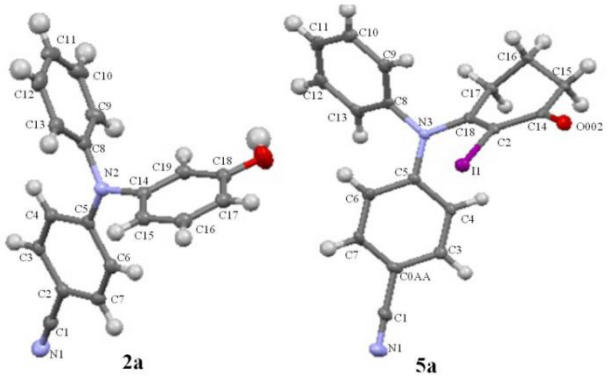
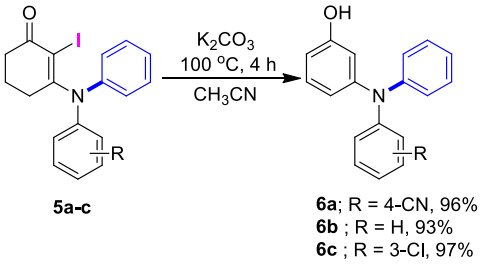


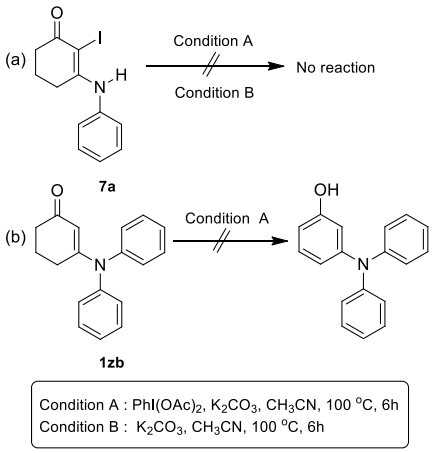
Figure 1. Molecular structures of **2a** and **5a** determined by X-ray crystallography.

Next to prove the involvement of **5a** in the reaction mechanism, when we treated it with K_2CO_3 in CH_3CN solvent at 100 °C the corresponding DAAP product **6a** was formed in 96% yield (Scheme 2). Similar method was applied for the synthesis of **6b-c** from intermediates **5b-c** (supporting information) in 93-97% yields respectively (Scheme 2). The presence of long conjugation of "N-C=C-C=O" in *β*-enaminone might stabilize the molecule and hinders the aromatization to arylamine synthesis. However, in the present study, when the *β*-enaminone gets *N*-arylated under the optimized conditions, the planarity as well as long conjugation of the molecule gets distorted resulting into a facile structural orientation for rapid C=C bond generation and simultaneous removal of C2 iodine atom to give DAAP products.



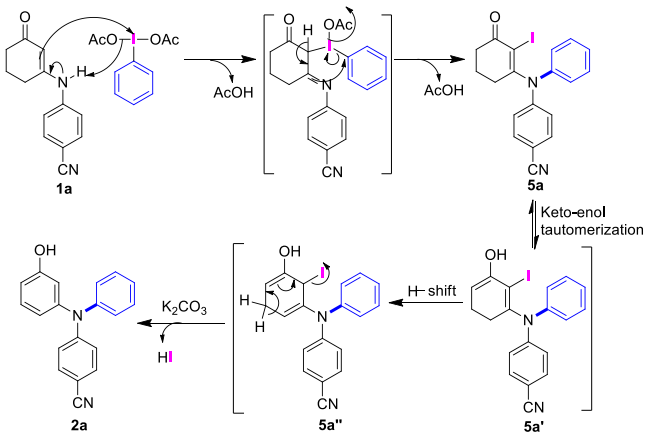
Scheme 2. Aromatization of 2-iododiaryl substituted *β*-enaminone to DAAP synthesis.

Further, the addition of TEMPO in the reaction mixture did not affect the formation of desired product indicated the non-radical pathway of the reaction (supporting information). Moreover, two additional experiments were also conducted to understand selectivity and mechanistic pathway of the reaction. When 2-iodo-arylamino-substituted enaminone[21b] (**7a**) subjected to aromatization under conditions A and B, no product was formed (Scheme. 3, (a)). Similarly, treatment of *N*-phenylated *β*-enaminone **1zb** under the reaction condition A, did not led to the formation of desired product (Scheme. 3 (b)). Therefore, these experiments indicated that the exact structural pattern or active sites present in *β*-enaminones (**1a-zb**) are essential for its reactivity with $PhI(OAc)_2$ to produce DAAP, BAAP and DAAC products.



Scheme 3. (a) aromatization of 2-iodo-3-(phenylamino)cyclohex-2-enone; (b) aromatization of 3-(diphenylamino)cyclohex-2-enone.

On the basis of the precedent literature[21a, 22] and intermediate detection, a plausible mechanism for the aromatization process has been drawn in Scheme 4. The first step involves the ligand exchange reaction between **1a** and $PhI(OAc)_2$ which leads to the formation of stable intermediate **5a** through iodine-to-nitrogen 1,3 phenyl migration mechanism. Recently, Shafir and co-workers described the *N*-arylation, α-iodination sequence of imidazoles that proceeds *via* iodine-to-nitrogen 1,3 phenyl migration pathway.[21a] Moreover, the ligand exchange reaction further supported by the regiospecific formation of only one aromatised product (**2n-q** and **3f-i**) with substituted diacetoxyiodobenzenes (Table 2 and 3). Intermediate **5a** might exist in equilibrium with its enol form **5a′** under basic condition. Due to the *α*-iodinated *N*-phenylation of β-enaminone, the conjugation of N-C=C-C=O moiety gets destroyed hence facilitating the keto-enol tautomerization



Scheme 4. Possible mechanism for $PhI(OAc)_2$ mediated *N*-phenylation and aromatization of exocyclic-β-enaminones.

rendering the hydride shift[23] to form **5a″**. Subsequently base promoted rapid dehydroiodination of **5a″** finally affords the product **2a** and the structure was finally confirmed by X-ray crystallography (Figure 1, **2a**).

In conclusion, the present study demonstrates a novel and versatile strategy for *one-pot N*-arylation and dehydrohalogenative aromatizaton of exocyclic β-enaminones to corresponding *N,N*-disubstituted aminophenols. This convenient method offers high compatibility with various functional groups to afford potentially useful compounds in quantitative yields. Furthermore similar approach also gave 7-(*N,N*-diaryl)amino dihydrocoumarin strating from 4-(ethoxypropanoyl)enaminones. These studies might inspire the further development of metal free aromatization of functional β-enaminones to synthesis the precursors for organic light emitting materials.

Experimental Section

β-enaminone **1a** (100 mg, 0.4717 mmol), diacetoxyiodobenzene (0.5660 mmol) and K_2CO_3 (0.5660 mmol) were taken in an oven dried reaction vial (40 mL) and acetonitrile (2 ml) was added to it. The reaction mixture was heated to 100 ºC for 6 h under magnetic stirring. The progress of reaction was monitored by TLC (EtOAc and n-hexane = 5: 95 as the mobile phase). After the completion, the reaction mixture was extracted with ethyl acetate (3x2 ml) by adding 1 mL water and dried on anhydrous Na_2SO_4. Evaporation of the combined organic layer under reduced pressure followed by column chromatography (hexane: ethyl acetate = 95:5) over silica gel (mesh 60-120) afforded 89% yield of the 3-*N,N*-disubstituted aminophenol (**1**) as white solid. mp: 158-160 ° C.

"CCDC for compound **2a**: 1049274 and for compound **5a**: 1049341 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via. www.ccdc.cam.ac.uk/data_request/cif."

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References

[1] a) B. Schlummer, U. Scholz, *Adv. Synth. Catal.* **2004,** *346*, 1599-1626; b) P.A. Lewis, Pigment Handbook, ed. John Wiley & Sons, New York, **1988**. c) Y. Nishikitani, M. Kobayashi, S. Uchida, T. Kubo, *Electrochim. Acta.* **2001**, *46*, 2035-2040; d) W.Shi, L. Wang, M. Umar, T. Awut, H. Mi, C. Tana, I. Nurullaa, *Polym. Int.* **2009,** *58*, 800-806.

[2] a) M. Negwer, *Organic chemical drugs and their synonyms: An international survey*, Akad.Verlag, Berlin, 7th edn, **1994**; b) J. Safaei-Ghomi, Z. Akbarzadeh, A. ziarati, *RSC Adv.* 2014 **4,** 16385-16390.

[3] a) R.H. Friend, R.W. Gymer, A.B. Holmes, J.H. Burroughes, R.N. Marks, C. Taliani, D. C. Bradley, D.A.D Santos, J.L. Bredas, M. Logdlund, W.R. Salaneck, **1999,** *Nature*, *397*, 121-128; b) R. D. Fagan, E. Hauptman, R. Shaprio , A. Casalnuovo, *J. Am. Chem. Soc.* **2000**, *122*, 5043-5051; c) C-T. Chen, C-L. Chiang. Y-C. Lin, L-H. Chan, C-H. Huang, Z-W. Tsai, C-T. Chen, *Org. Lett.* **2003,** *5*, 1261-1264; d) U. Mitschke, P. Bauerle, *J. Mater. Chem.* **2000,** *10*, 1471-1507.

[4] M-k. Leung. C-C. Chang, M-H. Wu, K-H, Chuang, J-H. Lee, S-J. Shieh, S-C, Lin, C-F. Chiu, *Org. Lett.* **2006,** *8*, 2623-2626.

[5] a) Y. Song, C. Di, X. Yang, S. Li, W. Xu, Y. Liu, L. Yang, Z. Shuai, D. Zhang, D.A. Zhu, *J. Am. Chem. Soc.* **2006,** *128*, 15940-15941; b) A. Cravino, S. Roquet, O. Aleveque, P. Leriche, P. Frere, J. Roncali, *Chem. Mater.* **2006**, *18*, 2584-2590; c) T. P. I. Saragi, T. F. Lieker, J. Salbeck, *Adv. Funct. Mater.* **2006,** *16*, 966-974.

[6] a) Q. P. Wu, Y. J. Xu, X. B. Cheng, M. Liang, Z. Sun, S. Xue, *Sol. Energy*, **2012,** *86*, 764-770; b) P. Hagberg, T. Marinado, K. M. Karlsson, K. Nonomura, P. Qin, G. Boschloo, T. Brinck, A. Hagfeldt, L. Sun, *J. Org. Chem.* **2007**, *72*, 9550-9556.

[7] a) G. Bordeau, R. Lartia, G. Metge, C. Fiorini-Debuisscher, F. Charra, M.-P. Teulade-Fichou, *J. Am. Chem. Soc.*, **2008**, *130*, 16836-16837; b) A. Bhaskar, G. Ramakrishna, Z. Lu, R. Twieg, J. M. Hales, D. J. Hagan, E. Van Stryland and T. Goodson III, *J. Am. Chem. Soc.* **2006,** *128*, 11840-11849.

[8] a) M. Stolka, J. F. Yanus, D. M. Pai, *J. Phys. Chem.* **1984**, *88*, 4707-4714; b) P. M. Borsenberger , D. S. Weiss, Organic Photoreceptors for Imaging Systems, Marcel Dekker, New York, **1993**.

[9] a) S. V. Ley, A. W. Thomas, *Angew. Chem., Int. Ed.* **2003**, *42*, 5400-5444; b) J. Hassan, M. Sevignon, C, Gozzi. E. Schulz, Lemaire, *Chem. Rev.* **2002**, *102*, 1359-1469.

[10] J. P. Wolfe, H. Tomori, J. P. Sadighi, J. J. Yin, S. L. Buchwald, *J. Org. Chem.* **2000**, *65*, 1158-1174.

[11] H. B. Goodbrand, N. X. Hu, *J. Org. Chem.* **1999**, *64*, 670-674.

[12] a) D. S. Surry, S. L. Buchwald, *J. Am. Chem. Soc.* **2007**, *129*, 10354-10355; b) S. Thayumanavan, S. Barlow, S. R. Marder, *Chem. Mater.* **1997,** *9*, 3231-3235.

[13] H. Murata, P. M. Lahti, *J. Org. Chem.* **2007**, *72*, 4974-4977.

[14] T. Hatakeyama, R. Imayoshi, Y. Yoshimoto, S. K., Ghorai, M. Jin, H. Takaya, K. Norisuye, Y. Sohrin, M. Nakamura, *J. Am. Chem. Soc.* **2012**, *134*, 20262-20265.

[15] X. Li, W. Wu, X. Fan, L. Yang, *Org. Biomol. Chem.* **2014**, *12*, 1232-1236.

[16] a) T. Ishikawa, E. Uedo, R. Tani, S. Saito, *J. Org. Chem.* **2001**, *66*, 186-191. b) X-L. Yun, W-Y. Bi, J-H. Huang, Y. Liu, D. Z-Negrerie, Y-F. Du, K. Zhao; *Tetrahedron Letters;* **2012**, *53*, 5076‑5080. d) I. Papoutsis, S. Spyroudis, A. Varvoglis, C. P. Raptopoulou, *Tetrahedron*, **1997**, *53*, 6097-6112.

[17] a) Z. Jia, E. Galvez, R. M. Sebastian, R. Pleixats, A. A-Larena, E. Martin, A. Vallribera, A. Shafir, *Angew. Chem. Int. Ed.* **2014**, *53*, 11298-11301; b) R. Narayan, A. P. Antonchick, *Chem. Eur. J.* **2014**, *20*, 4568-4572; c) S. H. Cho, J. Yoon, S. Chang, *J. Am. Chem. Soc.* **2011**, *133*, 5996-6005.

[18] For recent reviews see a) A. Yoshimura, V. V. Zhdankin, *Chem. Rev.* **2016**, *116*, 3328-3435; b) A. M. Arnold, A. Ulmer, T. Gulder, *Chem. Eur. J.* **2016**, *22*, 8728-8739. c) D-Q. Dong, S-H. Hao, Z-L. Wang, C. Chen, *Org. Biomol. Chem.*, **2014**, *12*, 4278-4289.

[19] Y. Wu, I. Arenas, L. M. Broomfield, E. Martin, A. Shafir, *Chem. Eur. J.* **2015**, *21*, 18779-18784.

[20] a) D. Sharma, Bandna, C. B. Reddy, A. K. Shil, N. R. Guha, P. Das, *Rsc Adv.* **2013**, *3*, 10335-10340; b) D. Sharma, Bandna, A. K. Shil, B. Singh, P. Das, *Synlett.* **2012**, *23*, 1199-1204.

[21] a) Y. Wu, S. Izquierdo, P. Vidossich, A. Lledos, A. Shafir, *Angew. Chem. Int. Ed.* **2016**, *55*, 7152-7156. b) J. M. Kim, J. E. Na, J. N. Kim, *Tetrahedron Letters.* **2003,** *44*, 6317-6318.

[22] a) S. Manna, K. Matcha, A. P. Antonchick, *Angew. Chem. Int. Ed.* **2014**, *53*, 8163-8166; b) A. P. Antonchick, R. Samanta, K. Kulikov, J. Lategahn, *Angew. Chem. Int. Ed.* **2011**, *50*, 8605-8608; c) Y. Chen, T. Ju, J. Wang, W. Yu, Y. Du, K. Zhao, *Synlett*, **2010**, *2*, 231-234.

[23] M. T. Barros, S. S. Dey, C. D. Maycock, *Eur. J. Org. Chem.* **2013**, *4*,742-747.

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