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ARTICLE

Synthesis of blue-red emissive amido substituted di(het)aryl and tri(het)aryl amine derivatives *via* chemoselective *N*-mono and *N*, *N*-diarylation of (het) aryl amino amides using benzyne/arynes

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Chemoselective *N*-mono and *N*, *N*-diarylation of aryl/hetaryl amino amide reaction using benzyne or arynes afforded amide substituted triaryl amine derivative and diaryl amine derivatives. Scope and limitation of the research work has been studied. The products thus obtained were synthetically transformed to highly functionalized biphenyl bridged heterocycles via Suzuki coupling and condensation with 4,4'-biphenyl dialdehyde. Evaluation of photophysical properties revealed that the triaryl amine derivatives are blue emmisive with high quantum yields while heterocyclic triaryl amine derivatives are blue-red emmisive. The benzofuran derived compound **4i** found as blue emissive with high quantum yiled whereas pyridine derived compound **5j** found as red emissive with low quantum yield.

Introduction

The propeller-shaped triphenylamine (TPA) and its derivatives are a key resource for both theoretical and synthetic chemists due to their promising optical and electrical properties.[1] The notable properties of TPA include easy oxidation of amine and excellent positive charge carrier[2] and the transformation of TPA to free radicals has remarkably utilized as a good electron donor unit in hole transport material applications.[3] TPA and its derivatives are extensively used in electrochromic materials[4], dye-sensitized solar cells (DSSCs)[5], organic field effect transistors, and solid state fluorescent materials for organic light-emitting diode (OLED) device applications.[6] Owing to the semiconducting property of TPA derivatives, these are utilized in many studies related to organic electronics.[7] Utility of TPA molecule as smart fluorescent material is foreseen, as shown in figure 1, compounds (**A-E**) exhibit an array of functional properties such as fluorescence switching, mechanochromism, polymorphism, nano-fabrication, halochromism, compound (**F**) found to show piezo fluorochromism (**G**) illustrate an example for non-doped red emitters for OLED.[8] Significant synthetic approaches for TPA include Ullmann reaction, Suzuki and Heck reaction. [1(c),7,9] Diphenylamine (DPA) derivatives are most commonly used as stabilizers in nitrocellulose-containing explosives and propellants, in the perfumery, as antioxidants, for production of dyes, pharmaceuticals, photography chemicals etc. Figure 1 include few biologically active diphenylamine based compounds (**H-K**).[10] It should be noted that the material functional and biological properties of TPA and DPA are prominently depends on the nature of functional group substitution and position in the aryl groups. Thus, to tune the properties and development of TPA and DPA based organic molecules with different functional groups by minimum synthetic steps is of great potential for practical applications.

Aryl triflate has been employed to generate arynes in situ to undergo a variety of electrophilic, nucleophilic, cycloaddition reactions[11] and extensively used for N-arylation reactions.[12] To the best of our knowledge the reaction of (het)aryne with aryl and heteroaryl amino-amides has not been reported. Thus, herein we report the reactivity profile of (het)arynes towards various positionally placed amino-amides, sulphone amide and photophysical properties of selected fluorescent molecules obtained.

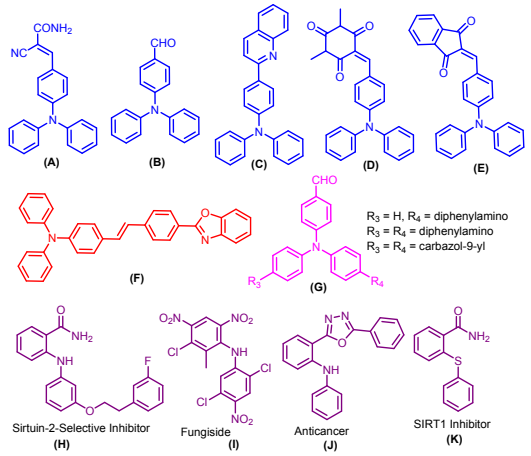

Figure 1 Examples of TPA based smart fluorescent materials and DPA based bio-active compounds

Initial reaction between 1 equiv. of 2-aminobenzamide **1** in dry acetonitrile and 1.2 equiv. of benzyne **2** generated in situ from o-(trimethylsilyl) phenyl triflate and CsF under argon atmosphere at RT for 24 h afforded *N*- mono and *N, N*-di

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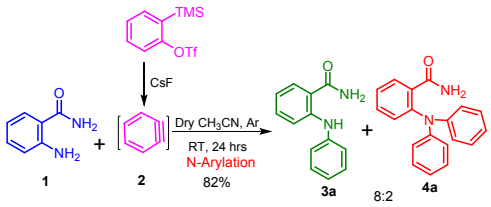
arylated products **3a** and **4a** in 65% and 16% yield, respectively (Scheme 1).



Scheme 1 Synthesis of *N*- mono and *N*, *N*- di arylated products of 2-aminobenzamide

The structure of products **3a** and **4a** was confirmed by spectroscopic data (See SI) and structure of representative product **4a** was confirmed by single-crystal X-ray analysis (Figure 2).[14]

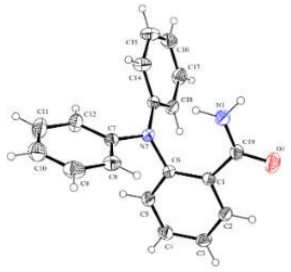


Figure 2 ORTEP diagram of compound **4a** (CCDC 1814895)

In order to optimize the synthesis of compounds **3a** and **4a**, an optimization study was undertaken by varying source of fluoride for the generation of benzyne, mole equivalents of aryne precursor, temperature and time. The reaction performed using 1.2 equiv. of benzyne using CsF as fluoride source in dry ACN under argon atmosphere at 60 °C (Table 1, entry 2) found completed in 3h to afford compounds **3a** and **4a** in 63 and 27% yield, respectively. Increasing the mole equiv. of the aryne precursor lead to improved yield of compound **4a** (Table 1, entry 3). The experiment using 2.4 equiv. of aryne precursor and KF, 18-Crown-6 as fluoride source for the generation of benzyne at RT the reaction completed within 0.5 h with an improved yield of compound **4a** (Table 1, entry 4) which later found as the optimized condition. Further increment in equivalence of aryne precursor did not improve the yield (Table 1, entry 5).

Table 1 Optimization of Synthesis of **3a** and **4a**

entry	F⁻ Source[a]	Equiv. of Aryne Precursor	Time hr	Temp. °C	% Yield of 3a/4a[b]
1	CsF	1.2	24	rt	65/16
2	CsF	1.2	3	60	63/27
3	CsF	2.4	3	60	12/73
4	KF, 18 Crown-6	2.4	0.5	rt	14/79[c]
5	KF, 18 crown-6	4	3	rt	13/76

[a]2.0 equiv. of the fluoride ion source was used for 1 equiv. of aryne precursor; [b]Isolated Yield; [c]Optimized condition.

To demonstrate generality of the method, we investigated the substrate scope by selecting various arynes and hetarynes and a number of positionally placed amido-amides, hetero *o*-amino-amides and *o*-amino sulphonamide as shown in figure 3.

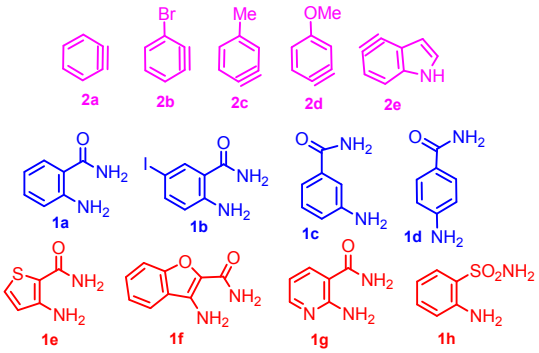


Figure 3. Various arynes, hetarynes, and amino-amides screened

Under optimized condition, all the reactions underwent smoothly to give rise to corresponding arylated products (Figure 4 and Table 2). To understand the positional effect of functional group on arylation *meta* and *para* amine substituted benzamide substrates **1c** and **1d** were chosen to react with benzyne **2a** and gave rise to both mono arylated **3b**, **3c** and diarylated **4b**, **4c** products in excellent combined yield. Comparing the yield of the reaction, amine on *meta* position directed diarylated product in higher yield (Table 2, entries 2 and 3). To examine the diversity of the arynes, Me and OMe substituted arynes **2c** and **2d** were subjected to react with 2-aminobenzamide, however, an inseparable mixture of regioisomer of mono-arylated products 3**d** and **3e**, respectively was obtained (Table 2, entries 4 and 5). The ratio of regioisomer of the products were established from the ^{1}H NMR spectrum of compounds **3d** and **3e** (See foot note table 2 entries 4 and 5). Reaction of compound **1a** with hetaryne indolyne **2e** gave rise to corresponding single regioisomer *N*-mono and *N*, *N*- diarylated products **3f** and **4f**, respectively (Table 2, entry 6). The reaction of benzyne **2a** with 5-iodo anthranilamide **1b** and 3-aminothiophene-2-carboxamide **1e** yielded only mono arylated products **3g** and **3h**, respectively (Table 2, entries 7 and 8). Further exploration on reaction of heterocyclic amino amides **1f** and **1g** with aryne **2a** yielded exclusively diarylated products **4i** and **4j** (Table 2, entries 10 and 11). Reaction of compound **1g** with halogen and methoxy substituted arynes **2b** and **2d** also gave rise to only diarylated products **4k** and **4l** (Table 2, entries 12 and 13). Formation of sole diarylated or mono arylated products may be due to varying electronic nature of heteroatom involved resonance stability of intermediates and electron donating substituent at meta position. When 2-amino benzenesulfonamide **1h** was chosen as a substrate, amine triarylated product **4g** was obtained in 78 % yield and amide diarylated product **4h** was obtained in 13 % yield amide and (Table 2, entry 9).

Table 2. Synthesized heterocycles **3a-h** and **4a-l**

Sl No.	Aryne	Substrates	Product(s) (% Yield)[a]	
1	**2a**	**1a**	**3a** (14)	**4a** (79)
2	**2a**	**1c**	**3b** (20)	**4b** (67)
3	**2a**	**1d**	**3c** (40)	**4c** (53)
4	**2c**	**1a**	**3d** (20)[b,c]	**4d** (71)
5	**2d**	**1a**	**3e** (19)[b,d]	**4e** (73)
6	**2e**	**1a**	**3f** (44)	**4f** (47)
7	**2a**	**1b**	**3g** (96)	--
8	**2a**	**1e**	**3h** (92)	--
9	**2a**	**1h**	**4g** (78)	**4h** (13)
10	**2a**	**1f**	--	**4i** (96)
11	**2a**	**1g**	--	**4j** (98)
12	**2b**	**1g**	--	**4k** (97)
13	**2d**	**1g**	--	**4l** (93)

[a]Isolated Yield; [b]Isolated as mixture of regioisomers; [c.] Ratio of regioisomers of **3d** was found to 1:0.4 as evidenced from ^{1}H NMR; [d.]Ratio of regioisomers of **3e** was found to 1:0.6 as evidenced from ^{1}H NMR.

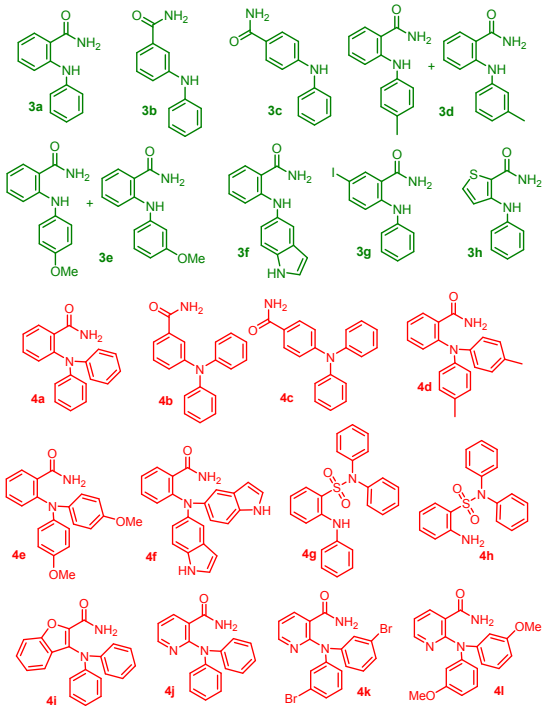
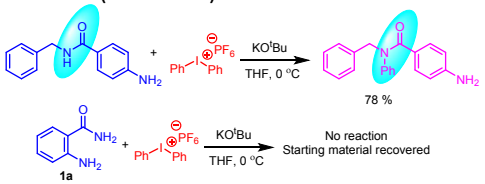


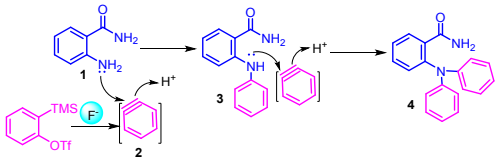
Figure 4 Synthesized di and triaryl amine derivatives from various amino amides and arynes.

Wangs et al. reported[13] selective N-arylation of secondary amide in presence of primary amine. However, there is no report on primary amide arylation in the presence of amine using aryne. Our attempt for primary amide arylation using diphenyliodonium hexafluorophosphate as aryne precursor for substrate **1a** was found to be unreactive and starting material was recovered (Scheme 3). `



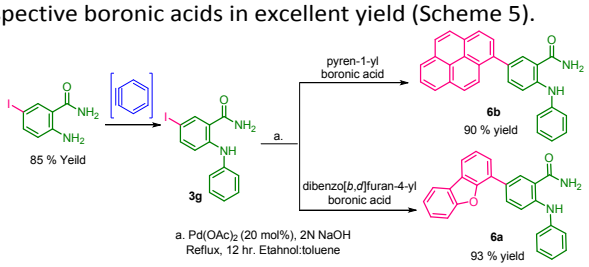
Scheme 3. Attempted amide arylation using diphenyliodoniumhexafluorophosphate as aryne precursor

To explain the formation of products **3** and **4**, a plausible mechanism is proposed in scheme 4. Nucleophilic attack of 2-aminobenzamide **1** on benzyne **2** followed by proton abstraction from HF (generated insitu from the initial abstraction of hydrogen by fluoride ion) led to mono *N*-arylated product **3**. Second arylation is feasible on product **3** in presence of excess of benzyne which led to formation of *N, N*-diarylated compound **4**.



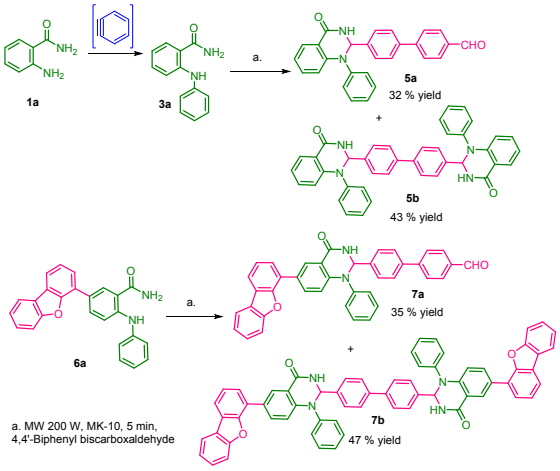
Scheme 4. Plausible Mechanism for the Formation of Compounds **3** and **4.**

In order to demonstrate the synthetic utilities of compounds synthesized, initially dibenzofuran and pyrene substituted *N*-aryl anthranilamide **6a** and **6b** were prepared by Suzuki coupling of 5-iodo *N*-aryl anthranilamide **3g** using respective boronic acids in excellent yield (Scheme 5).



Scheme 5. Synthesis of Dibenzofuran and pyrene substituted *N*-aryl anthranilamide

Further, a microwave assisted Mont.K10 clay catalysed condensation reaction of *N*-aryl anthranilamide **3a** with 4, 4' biphenyl dicarboxaldehyde was envisaged to the formation of structurally unique products. The reaction afforded mono condensed **5a** and bis condensed **5b** hydroquinazolinone derivatives in 32% and 43% yield, respectively. dibenzofuran appended hydroquinazolinone derivatives **7a** and **7b** were prepared in 35% and 47% yields, respectively by microwave assisted Mont. K10 clay catalysed condensation of compound **6a** and 4, 4' biphenyl dicarboxaldehyde (Scheme 6).



Scheme 6. Synthesis of quinazolinones *via* Suzuki coupling and MW assisted condensation

Notably, the compound **4a** in solution appeared yellow under visible light irradiation and blue under UV (365 nm) irradiation driven us to evaluate its photophysical properties. Compound **4a** showed two UV absorption maxima at 377 nm and 397 nm. Upon excitation of the longer wavelength, compound **4a** shows a redshifted emission band ($\Delta\tilde{\nu}$ = 2253 and 2147 cm^{-1}) with two emission maxima at 411 nm and 435 nm, which lies in the blue region (Figure 5, Table 3, Entry 1). The quantum yield of **4a** was measured in MeOH by using quinine sulphate in 0.5 M H_2SO_4 as a reference and showed a significantly high quantum yield Φ = 0.812. This data confirms that compound **4a** is a promising fluorescent triphenylamine based material. Compounds **4j** and **4k** showed UV absorption maxima in the visible region at 519 nm and 504 nm and red shifted emission maxima at 586 and 610 nm, respectively. The compounds showed Stokes shifts $\Delta\tilde{\nu}$=1754 and 3447 cm^{-1} (Figure 5, Table 3, Entries 6 and 7). However, the quantum yield of **4j** and **4k** measured in MeOH (Φ = 0.0006 and 0.0013) by using rhodamine 6G as a reference found to be very low.

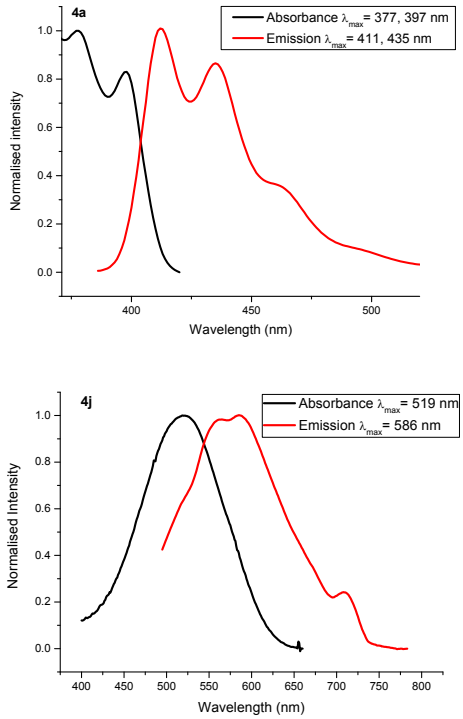


Figure 5 Normalised Absorption and Emission spectrum of compounds **4a** and **4j**

Considerable fluorescence material property showed by compound **4a** and **4j** prompted us to evaluate the photophysical data of the selected compounds **4a**, **4d**, **4e**, **4f**, **4i**, **4k**, and **6b** and the results are reported in Table 3. All of these compounds shows significant absorption and emission behaviour and few compounds shows excellent quantum yield (table 3, entries 1, 2 and 5). Overall, most of the synthesised amido substituted triaryl amine derivatives showed promising fluorescence materials. The solvatochromic effect of compound **4j** in various solvents indicates with increase in the solvent polarity from dichloromethane to MeOH value of compound **4j** showed a blue shift in absorption maxima $\lambda_{max,abs}$ value whereas the emission maxima value $\lambda_{max,\ emi}$ showed a decrease from hexane to acetonitrile and increase in the case of DMSO and MeOH(See SI).

Table 3 Photophysical data for selected compounds (recorded in MeOH at 25 °C)

Entry	Product	Absorption λ_{max}(nm)[a]	Emission λ_{max}(nm)(Φ)	$\Delta\bar{\nu}$(cm^{-1})[d]
1	**4a**	377, 397	412, 434 (**0.812**)[b]	2253, 2147
2	**4d**	376, 393	416, 433 (**0.386**)[b]	2557 2350
3	**4e**	294	371 (0.0137)[b]	7059
4	**4f**	265, 315	385, 450 (0.0342)[b]	11761 9523
5	**4i**	371, 390	401,423 (**0.706**)[b]	2016 2000
6	**4j**	519	586 (0.00060)[c]	1754
7	**4k**	504	610 (0.0013)[c]	3444
8	**6b**	352	463 (0.0043)[b]	6810

[a] Absorption recorded at a concentration of 10^{-5} mol L^{-1}. [b] Quinine sulphate in 0.5 M H_2SO_4 solution was used as the standard to determine the quantum yield. [c] Rhodamine 6G in ethanol was used as the standard to determine the quantum yield. [d] Stokes shift = $\lambda_{max,abs} - \lambda_{max,emi}$ [cm^{-1}].

In conclusion, an efficient procedure for the synthesis of blue and red emissive amido substituted triaryl amine derivatives with high quantum yield via addition of arynes has been established. Scope of the reaction is demonstrated using various aryl amino amides and substituted arynes and hetarynes. *N*-mono arylated product have been synthetically transformed to distinctly functionalized structurally important heterocycles bridged with biphenyl ring. The amido substituted triaryl amine derivatives showed promising fluorescence materials. Further, photo physical properties of the products are valid to extend the research work for practical applications are underway.

Experimental Section

General remarks

All the reactions were carried out in oven-dried glassware. Unless otherwise specified, all reactions were carried out under an atmosphere of argon. Commercially obtained dry CH_3CN was stored under nitrogen over 4 Å molecular sieves. The symmetrical unsymmetrical and hetaryne precursors, amino amides were purchased from Sigma Aldrich and used as received, without any further purification. CsF was dried and stored under nitrogen atmosphere. Progress of reactions was monitored by Thin Layer Chromatography (TLC) using Merck pre-coated TLC plates (Merck 60 F254) and compounds were visualized with a UV light at 254 nm. Further visualization was achieved by staining with iodine. Purification of products was accomplished by column chromatography packed with silica gel 230-400 mesh. The NMR spectra were recorded on Bruker-400 MHz NMR spectrometer (400 MHz for ^{1}H NMR and 125 MHz for ^{13}C NMR) with CDCl3 as the solvent and TMS as internal reference. Integrals are in accordance with

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assignments; Coupling constants were reported in Hertz (Hz). All ^{13}C spectra are proton-decoupled. Multiplicity is indicated as follows: s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), dd (doublet of doublet), dt (doublet triplet), td (triplet of doublet), br s (broad singlet). FTIR spectra were recorded on a Perkin-Elmer RX-IFT-IR spectrometer and absorbencies are reported in cm^{-1}. ESI HRMS were done on a Waters(R) Micromass(R) Q-TOF MicroTM Mass Spectrometer. Yields refer to quantities obtained after chromatography.

Absorption spectra were recorded using Cary100 Bio UV-Vis spectrophotometer. Steady-state fluorescence spectra were recorded on HORIBA JOBIN YVON Fluoromax spectrometer by excitation at the respective absorption maxima. We estimated the quantum yields of our compounds by comparison with the known quantum yields of Quinine sulphate in 0.5 M H_2SO_4 solution (Q=0.54) or Rhodamine 6G in Ethanol (Q=0.94) at an excitation wavelength of 466 nm or 488 nm respectively, using the following equation.

$Q = Q_R . I/I_R . OD_R/OD . n^2/n^2_R$

where Q is the quantum yield, I is the integrated intensity, OD is the optical density, and n is the refractive index. The subscript R refers to the Quinine sulphate or Rhodamine 6G.

Experimental procedures

a. Typical experimental procedure for the preparation of N-Arylated Products:

2-aminobenzamide **1** was subjected to react with benzyne **2** which is generated from 2.2 equivalence of 2-(trimethylsilyl) phenyl trifluoromethanesulfonate using 4 equiv. of KF and 18-crown 6 as fluoride source in dry acetonitrile under nitrogen atmosphere at 70 ˚C. The reaction was monitored with TLC. After the completion of the reaction the crude mixture was purified by silica gel column chromatography to obtain pure compound **3** and **4**. The compounds were characterised by spectroscopic techniques.

b. Typical experimental procedure for Suzuki coupling reaction

A mixture of 5-iodo-2-(phenylamino)benzamide **3g** (1 equiv.), boronic acid (2 equiv.) $Pd(OAc)_2$ (20 mol%,) and 2N Na_2OH (1 mL) in 5 mL of Ethanol:toluene (1:3) mixture was refluxed for 12 hr. After the completion of reaction monitored by TLC, the solvent was removed *in vacuo*, and then residue was extracted with ethyl acetate and washed with dilute HCl followed by brine and distilled water. The crude mixture was dried over Na_2SO_4 and solvent was removed under reduced pressure. The crude mixture was purified by silica gel column chromatography. The product was characterised using different spectroscopic techniques.

c. Typical experimental procedure for the synthesis of 5a, 5b, 7a and 7b

The substrate **3a** or **6a** (1 equiv.) and 4,4' biphenyl dicarboxaldehyde (0.5 equiv.) was microwave irradiated at 200 W in presence of Mont K-10 clay (100 w/w %) for 5 min. The progress of the reaction was monitored by TLC. After the completion of the reaction the crude mixture was filtered through celite pad and Silica gel column purified to obtain pure product. The product was characterised using different spectroscopic techniques.

***2-(phenylamino)benzamide*(3a)**: Colourless powder: 62 mg, 80% yield (when 1.1 equiv. of aryne was used); R_f (30% EtOAc-Hexane):0.42 **FTIR (KBr) λ_{max}:** 3454, 3416, 3339, 3169, 2885, 2735, 1623, 1585, 1513, 1443, 1391, 1316, 1289, 1158, 1078, 889, 743, 693, 625, 560, 500 cm^{-1}; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.43 (s, 1H), 7.39 (dd, *J* = 7.9, 1.4 Hz, 1H), 7.28 – 7.17 (m, 4H), 7.15 – 7.12 (m, 2H), 6.98 – 6.93 (m, 1H), 6.67 (ddd, *J* = 8.1, 6.9, 1.4 Hz, 1H), 5.92 (s, 2H).**^{13}C NMR** ($CDCl_3$/TMS, 100 MHz): δ 115.3, 116.0, 117.5, 121.5, 122.8, 128.3, 129.3, 132.9, 141.2, 146.9, 171.9. **HRMS-ESI**: Calcd. for $C_{13}H_{12}N_2O$ $[M+H]^+$ *m/z*: 213.0910; Found 213.0892.

3-(phenylamino)benzamide (**3b**): Colourless powder: 16 mg, 22% yield; R_f (30% EtOAc-Hexane):0.43; **FTIR (KBr) λ_{max}:** 3453, 3420, 3343, 3201, 2885, 2363, 1657, 1598, 1521, 1416, 1378, 1303, 1289, 1258, 1063, 788, 653, 615, 560 cm^{-1}; **^{1}H NMR (400 MHz, CDCl3)** δ 7.44 – 7.43 (m, 1H), 7.25 – 7.18 (m, 4H), 7.17 – 7.12 (m, 2H), 7.04 – 7.01 (m, 2H), 6.91 (t, J = 7.4 Hz, 1H), 5.91 (s, 2H); **^{13}C NMR** ($CDCl_3$/TMS, 100 MHz): δ 114.0, 115.9, 116.1, 118.8, 118.9, 120.2, 122.0, 123.5, 124.0, 124.6, 129.5, 134.5, 139.2, 142.1, 144.0, 169.6; **HRMS-ESI**: Calcd. for $C_{13}H_{12}N_2O$ $[M+H]^+$ *m/z*: 213.0910; Found 213.0862.

4-(phenylamino)benzamide (**3c**): Colourless powder: 31 mg, 40% yield; R_f (30% EtOAc-Hexane):0.40; **FTIR (KBr) λ_{max}:** 3553, 3473, 3343,2976, 2635, 2360, 1652, 1554, 1501, 1444, 1388, 1329, 1279, 1248, 1043, 712, 623, 625, 573 cm^{-1}; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.66 – 7.62 (m, 2H), 7.28 – 7.23 (m, 2H), 7.09 (ddd, *J* = 3.0, 2.5, 1.4 Hz, 2H), 7.00 – 6.92 (m, 3H), 5.98 (s, 1H), 5.74 (s, 2H); **^{13}C NMR** ($CDCl_3$/TMS, 100 MHz): δ 115.0, 120.1, 122.9, 124.1, 129.2, 129.5, 141.0, 147.3, 168.9; **HRMS-ESI**: Calcd. For $C_{13}H_{12}N_2O$ $[M+H]^+$ *m/z*: 213.0910; Found 213.0892.

2-(p-tolylamino)benzamide (**3d**) **:** Colourless powder: 17 mg, 20% yield; R_f (30% EtOAc-Hexane): 0.46; **FTIR (KBr) λ_{max}:** 3363, 3327, 3149, 1650, 1601, 1556, 1508, 1467, 1273, 766, 686, 675, 653, 637, 503 cm^{-1}; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.50 (d, *J* = 7.3 Hz, 1H), 8.02 (dtd, *J* = 5.8, 4.4, 1.7 Hz, 1H), 7.36 – 7.29 (m, 2H), 7.21 – 7.05 (m, 4H), 7.04 – 6.96 (m, 5H), 6.93 – 6.90 (m, 3H), 6.80 – 6.71 (m, 4H), 6.69 – 6.52 (m, 4H), 6.37 (s, 3H), 2.33 (s, 3H), 2.28 (d, *J* = 3.1 Hz, 3H), 2.24 (d, *J* = 2.8 Hz, 3H); **^{13}C NMR** ($CDCl_3$/TMS, 100 MHz): δ 20.7, 20.9, 21.5, 114.8, 115.3, 115.5, 116.2, 117.0, 117.4, 118.4, 119.2, 119.8, 122.2, 122.3, 122.5, 123.0, 123.6, 125.6, 125.8, 125.9, 128.5, 129.1, 129.2, 129.8, 129.9, 130.0, 131.6, 132.7, 132.8, 138.6, 139.1, 139.3, 141.3, 145.0, 145.3, 145.4, 145.6, 145.7, 146.5, 147.2, 147.5, 147.8, 168.5, 172.3; **HRMS-ESI**: Calcd. for $C_{14}H_{14}N_2O$ $[M]^+$ *m/z*: 226.0586; Found 226.0605.

2-((3-methoxyphenyl)amino)benzamide (**3e**): Brown colured liquid: 19 mg, 19% yield; R_f (40% EtOAc-Hexane): 0.46; **FTIR (KBr) λ_{max}:** 3465, 3328, 3137, 2829, 1566, 1503, 1489, 1368, 1313, 1254, 1148, 1125, 878, 810, 764, 754, 675, 653,

637, 503 cm^{-1}; **^{1}H NMR (400 MHz, CDCl$_3$)** δ 9.41 (s, 1H), 9.31 (s, 1H), 7.40 – 7.34 (m, 3H), 7.31 – 7.29 (m, 2H), 7.23 – 7.06 (m, 8H), 6.97 – 6.94 (m, 1H), 6.82 – 6.80 (m, 2H), 6.74 – 6.72 (m, 2H), 6.70 – 6.66 (m, 3H), 6.60 – 6.56 (m 1H), 6.52 – 6.50 (m, 2H), 5.92 (s, 2H), 3.73 (s, 3H), 3.71 (s, 4H); **^{13}C NMR (100 MHz, CDCl$_3$)** δ 172.1, 71.9, 160.6, 156.3, 148.4, 146.1, 142.6, 133.9, 133.0, 130.0, 128.3, 125.2, 117.8, 116.3, 115.8, 114.6, 114.2, 113.6, 108.3, 106.8, 55.5, 55.2; **HRMS-ESI**: Calcd. for $C_{14}H_{14}N_2O_2Na$ [M+Na]$^+$ *m/z*:265.0653; Found 265.0699.

2-((1H-indol-5-yl)amino)benzamide (**3f**): Brown powder: 41 mg, 44% yield; R_f (30% EtOAc-Hexane): 0.42; **FTIR (KBr) λ$_{max}$:** 3765, 3542, 3333, 3214, 2635, 1568, 1412, 1358, 1334, 1273, 1138, 1125, 978, 868, 763, 673, 641, 630, 513 cm^{-1}; **^{1}H NMR (400 MHz, CDCl$_3$)** δ 9.35 (s, 1H), 8.27 (s, 1H), 7.39 (s, 1H), 7.31 (d, *J* = 7.9 Hz, 1H), 7.22 (d, *J* = 8.4 Hz, 1H), 7.09 – 7.06 (m, 2H), 6.97 – 6.94 (m, 2H), 6.52 (t, *J* = 7.5 Hz, 1H), 6.38 (d, *J* = 0.6 Hz, 1H), 6.04 (s, 2H); **^{13}C NMR (100 MHz, CDCl$_3$)** δ 172.6, 149.2, 133.8, 133.4, 133.2, 133.1, 132.9, 128.6, 128.3, 125.1, 122.5, 120.2, 116.1, 114.4, 113.9, 111.8, 106.6, 102.4; **HRMS-ESI**: Calcd. for $C_{15}H_{13}N_3ONa$ [M+Na]$^+$ *m/z*: 274.0656; Found 274.0675.

5-iodo-2-(phenylamino)benzamide (**3g**)*:* Colourless powder: 61 mg, 96% yield; R_f (30% EtOAc-Hexane): 0.43; **FTIR (KBr) λ$_{max}$:** 3428, 3380, 3177, 2813, 1688, 1627, 1593, 1503, 1398, 1313, 1276, 1158, 1128, 1082, 889, 808, 785, 744, 695, 658, 627, 501 cm^{-1}; **^{1}H NMR** (400 MHz, CDCl$_3$) δ 9.46 (s, 1H), 7.73 (d, *J* = 2.1 Hz, 1H), 7.49 (dd, *J* = 8.9, 2.1 Hz, 1H), 7.35 – 7.30 (m, 2H), 7.18 (d, *J* = 7.5 Hz, 2H), 7.09 – 7.05 (m, 2H), 5.91 (s, 2H); **^{13}C NMR** (CDCl$_3$/TMS, 100 MHz): δ117.2, 117.9, 122.0, 123.5, 129.4, 136.6, 140.4, 141.2, 146.2, 170.4; **HRMS-ESI**: Calcd. for $C_{13}H_{11}IN_2O$ [M+H]$^+$ *m/z*: 338.9616; Found 338.9642.

3-(phenylamino)thiophene-2-carboxamide (**3h**): Colourless powder: 70 mg, 92% yield; R_f (30% EtOAc-Hexane): 0.45; **FTIR (KBr) λ$_{max}$:** 3364, 3327, 3190, 1687, 1633, 1585, 1551, 1489, 1459, 1403, 1335, 1279, 1164, 1103, 1029, 903, 848, 782, 741, 703, 636, 570, 538 cm^{-1}; **^{1}H NMR** (400 MHz, CDCl$_3$) δ ^{1}H NMR (400 MHz, CDCl$_3$) δ 9.37 (s, 1H), 7.27 – 7.23 (m, 2H), 7.21 – 7.18 (m, 1H), 7.11 – 7.07 (m, 3H), 6.99 – 6.95 (m, 2H), 5.84 (s, 2H); **^{13}C NMR** (CDCl$_3$/TMS, 100 MHz): δ104.5, 119.2, 120.0, 121.9, 122.6, 128.2, 129.3, 129.6, 141.8, 150.5, 167.2; **HRMS-ESI**: Calcd. for $C_{11}H_{10}N_2OS$ [M+H]$^+$ *m/z*: 218.0314; Found 218.0317.

2-(diphenylamino)benzamide (**4a**): Colourless crystals: 79 mg, 79% yield; R_f (30% EtOAc-Hexane): 0.40; **FTIR (KBr) λ$_{max}$:** 3421, 3328, 3242, 3134, 3030, 2923, 2854, 1945, 1671, 1588, 1486, 1448, 1373, 1278, 1247, 1153, 1082, 1035, 970, 919, 880, 820, 783, 752, 694, 621, 509 cm^{-1}; **^{1}H NMR** (400 MHz, CDCl$_3$) δ 7.94 (dd, *J* = 7.8, 1.3 Hz, 1H), 7.40 (td, *J* = 7.8, 1.5 Hz, 1H), 7.25 (t, *J* = 7.6 Hz, 2H), 7.17 (dd, *J* = 12.7, 4.3 Hz, 4H), 7.07 (d, *J* = 7.9 Hz, 1H), 6.93 (t, *J* = 8.9 Hz, 6H), 5.58 (s, 1H); **^{13}C NMR** (CDCl$_3$/TMS, 100 MHz): δ121.5, 122.4, 123.0, 126.1, 129.3, 129.4, 130.3, 131.7, 132.8, 145.1, 147.4, 168.0; **HRMS-ESI**: Calcd. for $C_{19}H_{16}N_2O$ [M]$^+$ *m/z*: 288.1063; Found 288.0989.

3-(diphenylamino)benzamide (**4b**): Yellow powder: 70 mg, 67% yield; R_f (30% EtOAc-Hexane): 0.48; **FTIR (KBr) λ$_{max}$:** 3521, 3429, 3343, 3235, 3132, 2943, 2854, 1845, 1691, 1488, 1448, 1353, 1298, 1237, 1143, 1052, 1035, 919, 862, 820, 762, 752, 684, 621, 506 cm^{-1}; **^{1}H NMR (400 MHz, CDCl$_3$)** δ 7.43 (t, *J* = 1.9 Hz, 1H), 7.31 – 7.28 (m, 1H), 7.21 – 7.10 (m, 6H), 7.01 – 6.93 (m, 6H), 6.06 (s, 2H); **^{13}C NMR** (CDCl$_3$/TMS, 100 MHz): δ 120.9, 122.0, 123.4, 124.5, 126.7, 129.4, 134.7, 147.3, 148.4, 169.5; **HRMS-ESI**: Calcd. for $C_{19}H_{16}N_2O$ [M+H]$^+$ *m/z*: 289.1063; Found 289.1141.

4-(diphenylamino)benzamide (**4c**): Yellow powder: 56 mg, 53% yield; R_f (30% EtOAc-Hexane): 0.46; **FTIR (KBr) λ$_{max}$:** 3411, 3458, 3422, 3314, 3200, 2973, 2844, 1845, 1761, 1658, 1448, 1353, 1228, 1156, 1072, 1055, 960, 919, 860, 822, 773, 752, 674, 623, 509 cm^{-1}; **^{1}H NMR** (400 MHz, CDCl$_3$) δ 7.59 – 7.56 (m, 2H), 7.24 – 7.20 (m, 4H), 7.07 – 7.01 (m, 6H), 6.95 – 6.93 (m, 2H), 5.83 (s, 2H); **^{13}C NMR** (CDCl$_3$/TMS, 100 MHz): δ 120.6, 124.2, 125.3, 125.6, 128.6, 129.5, 146.8, 151.3, 168.9; **HRMS-ESI**: Calcd. for $C_{19}H_{16}N_2O$ [M+H]$^+$ *m/z*: 289.1063; Found 289.1106.

2-(di-p-tolylamino)benzamide (**4d**): Yellow powder: 82 mg, 71% yield; R_f (30% EtOAc-Hexane): 0.45; **FTIR (KBr) λ$_{max}$:** 3323, 3253, 2935, 2845, 1733, 1673, 1513, 1462, 1441, 1356, 1314, 1268, 1164, 979, 754, 643, 625, 542 cm^{-1}; **^{1}H NMR (400 MHz, CDCl$_3$)** δ 8.07 – 8.02 (m, 1H), 7.48 – 7.42 (m, 1H), 7.34 – 7.26 (m, 1H), 7.13 – 7.08 (m, 2H), 7.05 – 7.02 (m, 2H), 6.90 – 6.73 (m, 5H), 5.73 (s, 1H), 2.28 (d, *J* = 3.2 Hz, 3H), 2.23 (d, *J* = 2.8 Hz, 3H); **^{13}C NMR (100 MHz, CDCl$_3$)** δ 168.0, 147.7, 147.5, 145.5, 145.4, 145.2, 145.0, 139.3, 132.8, 132.7, 132.7, 132.5, 131.7, 130.1, 130.0, 129.9, 129.8, 129.1, 126.0, 125.8, 123.8, 123.5, 123.1, 122.9, 122.6, 122.4, 119.7, 119.1, 21.4, 20.7; **HRMS-ESI**: Calcd. for $C_{21}H_{20}N_2ONa$ [M+Na]$^+$ *m/z*: 339.1173; Found 339.1149.

2-(bis(4-methoxyphenyl)amino)benzamide (**4e**): Brown coloured liquid: 93 mg, 73% yield; R_f (40% EtOAc-Hexane): 0.41; **FTIR (KBr) λ$_{max}$:** 3443, 3312, 3261, 2845, 2742, 1919, 1728, 1612, 1573, 1448, 1326, 1315, 1247, 1144, 868, 742, 673, 632, 503 cm^{-1}; **^{1}H NMR (400 MHz, CDCl$_3$)** δ 7.89 (ddd, *J* = 7.7, 4.1, 1.5 Hz, 1H), 7.37 – 7.30 (m, 1H), 7.21 – 7.12 (m, 1H), 7.05 (dd, *J* = 8.0, 0.9 Hz, 1H), 6.98 (dd, *J* = 7.9, 1.1 Hz, 1H), 6.92 – 6.90 (m, 1H), 6.81 – 6.77 (m, 2H), 6.72 – 6.67 (m, 3H), 6.47 (dd, *J* = 9.0, 5.0 Hz, 1H), 6.41 – 6.33 (m, 1H), 5.99 (s, 1H), 3.66 (d, *J* = 3.8 Hz, 4H), 3.60 (d, *J* = 4.9 Hz, 2H); **^{13}C NMR (100 MHz, CDCl$_3$)** δ 168.5, 168.4, 160.5, 156.2, 155.5, 149.6, 148.4, 146.2, 145.3, 144.9, 141.5, 140.1, 139.2, 132.7, 132.6, 132.5, 131.5, 130.6, 130.0, 129.6, 128.7, 126.3, 125.7, 125.1, 124.0, 115.1, 114.7, 114.7, 114.1, 113.3, 108.9, 108.1, 107.0, 106.9, 55.4, 55.2; **HRMS-ESI**: Calcd. for $C_{21}H_{20}N_2O_3$ [M]$^+$ *m/z*: 348.1274; Found 348.1203.

2-(di(1H-indol-5-yl)amino)benzamide (**4f**): Brown powder: 63 mg, 47% yield; R_f (30% EtOAc-Hexane): 0.38; **FTIR (KBr) λ$_{max}$:** 3825, 3652, 3453, 3326, 2743, 1656, 1583, 1448, 13674, 1256, 1221, 1123, 933, 854, 724, 630, 508 cm^{-1}; **^{1}H NMR (400**

MHz, DMSO-d6) δ 11.00 (d, *J* = 20.1 Hz, 2H), 7.64 (d, *J* = 7.7 Hz, 1H), 7.59 (s, 1H), 7.38 (t, *J* = 7.4 Hz, 2H), 7.29 – 7.26 (m, 4H), 7.20 (s, 1H), 7.14 (t, *J* = 7.5 Hz, 1H), 7.03 (s, 2H), 6.98 (d, *J* = 8.0 Hz, 1H), 6.78 (d, *J* = 8.7 Hz, 2H), 6.26 (s, 2H); **^{13}C NMR (100 MHz, DMSO-d6)** δ 168.4, 162.8, 150.0, 147.7, 142.2, 132.8, 132.4, 131.6, 130.7, 128.5, 126.2, 124.4, 123.7, 119.3, 114.8, 112.2, 101.4; **HRMS-ESI**: Calcd. for $C_{23}H_{18}N_4O$ $[M+Na]^+$ *m/z*: 389.1078; Found 389.1072.

N,N-diphenyl-2-(phenylamino)benzenesulfonamide (**4g**): Green powder: 91 mg, 78% yield; R_f (15% EtOAc-Hexane): 0.47; **FTIR (KBr) λ_{max}:** 3643, 3489, 3312, 3071, 2983, 1673, 1583, 1343 1157, 976, 742, 687, 512 cm^{-1}; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.55 (d, *J* = 8.2 Hz, 1H), 7.40 (s, 1H), 7.21 (td, *J* = 7.6, 1.5 Hz, 6H), 7.15 (t, *J* = 7.8 Hz, 2H), 7.12 – 7.08 (m, 4H), 7.06 – 7.02 (m, 2H), 6.93 (d, *J* = 7.3 Hz, 1H), 6.88 (d, *J* = 8.4 Hz, 2H), 6.67 – 6.63 (m, 1H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 143.0, 141.3, 140.4, 134.3, 131.3, 129.3, 128.7, 127.7, 123.9, 123.2, 120.8, 118.5, 116.2; **HRMS-ESI**: Calcd. for $C_{24}H_{20}N_2O_2SNa$ $[M+Na]^+$ *m/z*:423.1043; Found 423.1087.

2-amino-N,N-diphenylbenzenesulfonamide (**4h**): Green powder: 12 mg, 13% yield; R_f (15% EtOAc-Hexane): 0.37; **FTIR (KBr) λ_{max}:** 3475, 3338, 2654, 1765, 1442, 1334, 1222, 934, 726, 641, 523 cm^{-1}; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.34 (dd, *J* = 8.1, 1.4 Hz, 1H), 7.30 – 7.26 (m, 4H), 7.23 (t, *J* = 1.7 Hz, 1H), 7.22 (d, *J* = 1.7 Hz, 2H), 7.20 (dd, *J* = 2.3, 1.6 Hz, 2H), 7.18 – 7.17 (m, 1H), 7.16 – 7.14 (m, 1H), 6.61 (dd, *J* = 8.3, 0.9 Hz, 1H), 6.54 (td, *J* = 7.1, 3.6 Hz, 1H), 4.79 (s, 2H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 145.8, 141.4, 134.4, 130.8, 129.2, 128.8, 127.6, 120.9, 117.3, 116.8; **HRMS-ESI**: Calcd. for $C_{18}H_{16}N_2O_2S$ $[M+Na]^+$ *m/z*:347.0830; Found 347.0790.

3-(diphenylamino)benzofuran-2-carboxamide (**4i**): Yellow powder: 88 mg, 96% yield; R_f (30% EtOAc-Hexane): 0.42; **FTIR (KBr) λ_{max}:** 3177, 3100, 2992, 2947, 1635, 1596, 1556, 1477, 1397, 1345, 1262, 1158, 1026, 932, 820, 754, 701, 676, 594 cm^{-1}; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.86 – 7.82 (m, 2H), 7.76 (s, 1H), 7.36 – 7.30 (m, 7H), 7.16 – 7.11 (m, 3H), 6.90 – 6.87 (m, 2H), 6.62 (dd, *J* = 7.3, 0.8 Hz, 1H), 6.43 (dd, *J* = 7.9, 0.8 Hz, 1H), 5.83 (s, 1H); **^{13}C NMR** ($CDCl_3$/TMS, 100 MHz): δ 112.9, 117.8, 118.6, 121.7, 123.0, 123.4, 124.6, 125.7, 126.7, 128.5, 128.6, 128.8, 129.0, 129.4, 129.6, 135.3, 137.2, 149.9, 166.3, 166.9, 168.9; **HRMS-ESI**: Calcd. for $C_{21}H_{16}N_2O_2$ $[M+H]^+$ *m/z*: 329.1012; Found 329.1054.

2-(diphenylamino)nicotinamide (**4j**): Red powder: 95 mg, 98% yield; R_f (30% EtOAc-Hexane): 0.46; **FTIR (KBr) λ_{max}:** 3379, 3112, 3050, 2906, 1952, 1643, 1605, 1590, 1509, 1439, 1363, 1265, 1186, 1139, 1109, 1025, 952, 827, 755, 690, 643, 556, 512 cm^{-1}; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.97 (dd, *J* = 7.3, 1.9 Hz, 1H), 8.31 (dd, *J* = 8.1, 1.5 Hz, 1H), 8.00 (dd, *J* = 6.4, 1.9 Hz, 1H), 7.52 (ddd, *J* = 5.7, 3.4, 1.8 Hz, 5H), 7.46 (dd, *J* = 3.7, 1.8 Hz, 2H), 7.42 – 7.37 (m, 1H), 7.20 – 7.16 (m, 2H), 6.81 – 6.76 (m, 1H); **^{13}C NMR** ($CDCl_3$/TMS, 100 MHz): δ 108.1, 122.5, 122.6, 124.1, 126.2, 127.0, 127.7, 129.4, 133.8, 141.4, 143.7, 144.6, 150.6, 178.5; **HRMS-ESI**: Calcd. for $C_{18}H_{15}N_3O$ $[M]^+$ *m/z*: 289.0941; Found 289.0940.

2-(bis(4-bromophenyl)amino)nicotinamide (**4k**):Purple powder: 125 mg, 97% yield; R_f (30% EtOAc-Hexane): 0.41; **FTIR (KBr) λ_{max}:** 3268, 3150, 3012, 2813, 1942, 1867, 1718, 1678, 1509, 1342, 1156, 1111, 1034, 867, 756, 648, 567, 504 cm^{-1}; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.90 (dd, *J* = 7.4, 1.9 Hz, 1H), 8.04 (dd, *J* = 6.4, 1.9 Hz, 1H), 7.67 – 7.64 (m, 2H), 7.45 – 7.43 (m, 2H), 7.40 – 7.34 (m, 2H), 7.32 (d, *J* = 0.8 Hz, 4H), 7.29 – 7.25 (m, 1H), 6.89 – 6.85 (m, 1H); **HRMS-ESI**: Calcd. for $C_{18}H_{13}Br_2N_3O$ $[M+H]^+$ *m/z*: 445.9025; Found 445.9041.

2-(di-p-tolylamino)nicotinamide (**4l**): Red powder: 118 mg, 93% yield; R_f (25% EtOAc-Hexane): 0.44; **FTIR (KBr) λ_{max}:** 3463, 3214, 3128, 2868, 1865, 17033, 1657, 1548, 1432, 1256, 1192, 1142, 935, 783, 689, 613, 510 cm^{-1}; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 9.03 (dd, *J* = 7.4, 2.0 Hz, 1H), 8.03 (dd, *J* = 6.3, 2.0 Hz, 1H), 7.71 (d, *J* = 3.0 Hz, 1H), 7.41 – 7.37 (m, 3H), 7.23 – 7.20 (m, 1H), 7.02 (d, *J* = 9.0 Hz, 3H), 6.79 (dd, *J* = 5.5, 2.0 Hz, 2H), 3.85 (s, 6H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 177.8, 160.1, 155.5, 145.7, 144.9, 144.1, 134.2, 129.3, 128.1, 125.0, 121.7, 114.5, 107.9, 104.6, 55.6; **HRMS-ESI**: Calcd. for $C_{20}H_{19}N_3O_3$ $[M]^+$ *m/z*:349.1126; Found 349.1144.

4'-(4-oxo-1-phenyl-1,2,3,4-tetrahydroquinazolin-2-yl)-[1,1'-biphenyl]-4-carbaldehyde (**5a**): Colourless powder: 30 mg, 32% yield; R_f (30% EtOAc-Hexane): 0.45; **FTIR (KBr) λ_{max}:** 3170, 3056, 2914, 2846, 2740, 2360, 1937, 1729, 1663, 1600, 1482, 1381, 1299, 1245, 1220, 1164, 1118, 1039, 1009, 904, 812, 757, 699, 645, 559, 493 cm^{-1}; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 10.00 (s, 1H), 8.87 (s, 1H), 7.95 (d, *J* = 7.7 Hz, 1H), 7.86 (d, *J* = 8.2 Hz, 2H), 7.61 (d, *J* = 8.1 Hz, 2H), 7.55 (d, *J* = 8.2 Hz, 2H), 7.49 (d, *J* = 8.2 Hz, 2H), 7.32 (t, *J* = 7.8 Hz, 3H), 7.26 – 7.21 (m, 1H), 7.18 – 7.12 (m, 2H), 7.06 (d, *J* = 8.3 Hz, 1H), 6.95 (t, *J* = 7.5 Hz, 1H), 6.26 (d, *J* = 4.1 Hz, 1H); **^{13}C NMR** ($CDCl_3$/TMS, 100 MHz): δ 72.3, 118.6, 119.6, 121.0, 122.8, 124.7, 125.3, 127.5,127.6, 128.2, 128.5, 129.0, 129.6, 130.2, 133.6, 135.3, 137.8, 139.6, 141.0, 144.8, 145.5,146.2, 164.5, 191.8; **HRMS-ESI**: Calcd. for $C_{27}H_{20}N_2O_2$ $[M+H]^+$ *m/z*:405.1295; Found 405.1291.

2,2'-([1,1'-biphenyl]-4,4'-diyl)bis(1-phenyl-2,3-dihydro quinazolin-4(1H)-one) (**5b**): Colourless powder: 60 mg, 43% yield; R_f (30% EtOAc-Hexane): 0.45; **FTIR (KBr) λ_{max}:** 3643, 3201, 3059, 3035, 2922, 2853, 2361, 2340, 1929, 1667, 1606, 1495, 1452, 1375, 1304, 1252, 1233, 1183, 1156, 1111, 1003, 956, 907, 862, 823, 798, 752, 696, 646, 618, 592, 555, 521, 456, 418 cm^{-1}; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 9.82 (d, *J* = 4.4 Hz, 1H), 9.12 (d, *J* = 4.0 Hz, 1H), 7.91 (d, *J* = 7.8 Hz, 2H), 7.43 (d, *J* = 8.1 Hz, 4H), 7.37 (d, *J* = 7.8 Hz, 1H), 7.29 (m, 9H), 7.18 (d, *J* = 8.1 Hz, 4H), 7.13 – 7.09 (m, 4H), 6.91 (t, *J* = 7.5 Hz, 2H), 6.23 (dd, *J* = 16.2, 4.2 Hz, 2H); **^{13}C NMR** ($CDCl_3$/TMS, 100 MHz): δ 72.0, 72.2, 118.9, 119.8, 120.9, 121.0,122.3,122.8, 124.3, 124.6, 127.0, 127.2, 128.4, 128.5, 129.6,133.6, 133.7, 139.9, 140.2, 144.5, 145.5, 145.8, 165.0, 165.2; **HRMS-ESI**: Calcd. for $C_{40}H_{30}N_4O_2$ $[M]^+$ *m/z*:598.1909; Found 598.1906.

5-(dibenzo[b,d]furan-4-yl)-2-(phenylamino)benzamide (6a): Colourless powder: 52 mg, 93% yield; R_f (30% EtOAc-Hexane): 0.45; **FTIR (KBr) λ_{max}:** 3639, 3392, 3354, 3184, 3051, 2923, 2856, 1833, 1708, 1636, 1590, 1526, 1457, 1392, 1320, 1250, 1186, 1113, 909, 879, 828, 795, 740, 700, 657, 601, 560, 497 cm^{-1}; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 9.66 (s, 1H), 8.07 (d, *J* = 2.0 Hz, 1H), 7.99 (d, *J* = 7.4 Hz, 1H), 7.90 (dd, *J* = 7.6, 1.0 Hz, 1H), 7.85 (dd, *J* = 8.8, 1.9 Hz, 1H), 7.60 (d, *J* = 8.2 Hz, 1H), 7.55 (dd, *J* = 7.6, 1.0 Hz, 1H), 7.48 (d, *J* = 8.7 Hz, 2H), 7.42 (d, *J* = 7.6 Hz, 1H), 7.39 – 7.34 (m, 3H), 7.30 (d, *J* = 7.4 Hz, 2H), 7.08 (t, *J* = 7.2 Hz, 1H), 6.01 (s, 2H); **^{13}C NMR** ($CDCl_3$/TMS, 100 MHz): δ 111.8, 114.0, 115.3, 115.8, 119.1, 120.7, 121.8, 122.9, 123.2, 123.3, 124.2, 125.8, 127.2, 128.6, 129.3, 133.2, 140.9, 146.1, 153.1, 156.1, 171.9; **HRMS-ESI**: Calcd. for $C_{25}H_{18}N_2O_2Na$ $[M+Na]^+$ *m/z*:401.1266; Found 401.1212.

2-(phenylamino)-5-(pyren-1-yl)benzamide (**6b**): Brown powder: 70 mg, 90 % yield; R_f (20% EtOAc-Hexane): 0.45; **FTIR (KBr) λ_{max}:** 3532, 3493, 3355, 3285, 3152, 2924, 2857, 1789, 1659, 1576, 1566, 1448, 1383, 1314, 1267, 1168, 919, 879, 834, 783, 742, 645, 607, 510, cm^{-1}; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 9.68 (s, 1H), 8.20 – 8.13 (m, 4H), 8.07 (s, 2H), 8.04 – 7.97 (m, 2H), 7.93 (d, *J* = 7.8 Hz, 1H), 7.69 (s, 1H), 7.53 (dd, *J* = 22.1, 9.2 Hz, 2H), 7.39 – 7.30 (m, 4H), 7.08 (t, *J* = 7.0 Hz, 1H), 5.97 (s, 2H); **^{13}C NMR (100 MHz, $CDCl_3$/TMS)** δ 171.9, 145.8, 141.1, 136.6, 135.1, 131.5, 130.9, 130.5, 130.2, 129.4, 128.6, 127.6, 127.4, 126.1, 125.2, 125.0, 124.9, 124.8, 124.7, 123.2, 121.8, 115.7, 115.22; **HRMS-ESI**: Calcd. for $C_{29}H_{20}N_2O$ $[M+H]^+$ *m/z*: 413.1276; Found 413.1260.

4'-(6-(dibenzo[b,d]furan-4-yl)-4-oxo-1-phenyl-1,2,3,4-tetrahydroquinazolin-2-yl)-[1,1'-biphenyl]-4-carbaldehyde (**7a**): Colourless powder: 26 mg, 35% yield; R_f (40% EtOAc-Hexane): 0.42; **FTIR (KBr) λ_{max}:** 3988, 3193, 3055, 2923, 2856, 2733, 2367, 1930, 1666, 1603, 1496, 1456, 1370, 1254, 1184, 1009, 910, 825, 752, 703, 643, 557, 500 cm^{-1}; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 9.99 (s, 1H), 8.51 (s, 1H), 8.33 (bs, 1H), 8.06 – 8.02 (m, 1H), 7.96 (d, *J* = 7.6 Hz, 1H), 7.86 (t, *J* = 7.7 Hz, 3H), 7.64 – 7.58 (m, 5H), 7.54 (t, *J* = 6.4 Hz, 3H), 7.43 (s, 1H), 7.39 – 7.33 (m, 4H), 7.25 (t, *J* = 4.7 Hz, 2H), 7.16 (t, *J* = 8 Hz, 2H), 6.28 (d, *J* = 3.5 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 191.8, 156.0, 146.1, 144.9, 144.7, 140.7, 139.9, 139.2, 135.3, 134.2, 130.2, 129.8, 129.0, 128.4, 127.6, 127.2, 126.3, 125.2, 124.9, 124.4, 124.1, 123.6, 123.4, 123.2, 122.8, 120.6, 119.5, 118.3, 115.9, 114.0, 111.8, 72.7; **HRMS-ESI**: Calcd. for $C_{39}H_{26}N_2O_3$ $[M-H]^+$ *m/z*:569.1343; Found 569.1370.

2,2'-([1,1'-biphenyl]-4,4'-diyl)bis(6-(dibenzo[b,d]furan-4-yl)-1-phenyl-2,3-dihydroquinazolin-4(1H)-one) (**7b**): Colourless powder: 57 mg, 47% yield; R_f (55% EtOAc-Hexane): 0.40; **FTIR (KBr) λ_{max}:** 3427, 2923, 2855, 2360, 2254, 1663, 1607, 1498, 1455, 1370, 1290, 1257, 1186, 999, 906, 827, 756, 700, 639, 562, 509 cm^{-1}; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 9.63 (s, 1H), 9.15 (s, 1H), 8.47 (d, *J* = 9.9 Hz, 2H), 7.98 (t, *J* = 9.3 Hz, 2H), 7.93 (d, *J* = 7.5 Hz, 2H), 7.84 (d, *J* = 7.6 Hz, 2H), 7.57 – 7.46 (m, 10H), 7.38 – 7.30 (m, 12H), 7.25 (s, 6H), 7.16 – 7.12 (m, 2H), 6.29 (d, *J* = 3.8 Hz, 2H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 165.0, 156.0, 153.1, 145.4, 145.2, 144.1, 140.3, 140.1, 139.3, 134.0, 129.7, 129.6, 129.0, 128.3, 127.3, 127.1, 126.3, 124.8, 124.6, 124.1, 123.2, 122.7, 120.6, 119.5, 119.3, 118.7, 114.0, 111.8, 72.2; **HRMS-ESI**: Calcd. for $C_{64}H_{42}N_2O_4$ $[M-H]^+$ *m/z*:929.2346; Found 929.2357.

Conflicts of interest

There are no conflicts to declare

Supporting Information: Copies of ^{1}H NMR, ^{13}C NMR, DEPT-135, and HRMS of all the compound and absorption and emission spectra for selected compounds are provided.

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Key Words

Triarylamine / Diarylamine / N-arylation / Benzyne / hetaryne / amino amide / Fluorescence

References and notes

1 For reviews: (*a*) H.-J. Yen and G.-S. Liou, *Polym. Chem.,* 2018, **9**, 3001-3018; (*b*) P. Agarwala and D. *J.* Kabra, *Mater. Chem. A,* 2017, **5**, 1348-1373; (*c*) X. Lian, Z. Zhao and D. Cheng, *Mol. Cryst. Liq. Cryst.,* 2017, **648**, 223-235; (*d*) A. Wakamiya, H. Nishimura and Y. J. Murata, *Syn. Org. Chem. Jpn.,* 2016, **74**, 1128-1135; (*e*) Y. N. Luponosov, A. N. Solodukhin and S. A. Ponomarenko, *Polym. Sci. Ser. C,* 2014, **56**, 104–134; (*f*) A. Iwan and D. Sek, *Prog. Polym. Sci.,* 2011, **36**, 1277-1325.

2 M. Wan, G. Sang, Y. Zou, S. Tan and Y. Li, *J. Appl. Polym. Sci.,* 2009**, 113**, 1415-1421.

3 (*a*) K. Zhang, L. Wang, Y. Liang, S. Yang, J. Liang, F. Cheng and J. Chen, *Synth. Met.,* 2012, **162**, 490–496; (*b*) Y. K. Kim, D. C. Shin, S. H. Kim, C. H. Ko, H. S. Yu, Y. S. Chae and S. K. Kwon, *Adv. Mater.,* 2001, **13**, 1690-1693; (*c*) E. Bellmann, S. E. Shaheen, S. Thayumanavan, S. Barlow, R. H. Grubbs, S. R. Marder, B. Kippelen and N. Peyghambarian, *Chem. Mater.,* 1998, **10**, 1668-1676; (*d*) M. M. Wienk and R. A. J. Janssen, *J. Am. Chem. Soc.,* 1997, **119**, 4492-4501.

4 (*a*) M. Ouyang, G. Wang and C. Zhang, *Electrochim. Acta*., 2011, **56**, 4645–4649; (*b*) Q. Gang, H. Abu and Y. W. Zhi, *J. Mater. Chem.,* 2011, **21**, 7678–7685; (*c*) S. -H. Hsiao, G.-S. Liou, Y. -C. Kung and Y.-J. Lee, *Eur. Polym. J.* 2010, **46**, 1355–1366; (*d*) S. Beaupré, J. Dumas and M. Leclerc, *Chem. Mater.,* 2006, **18**, 4011.

5 (*a*) K. Seintis, Ç. Şahin, I. Sigmundová, E. Stathatos, P. Hrobárik and M. Fakis, J. *Phys. Chem. C*, 2018, **122**, 20122; (*b*) M. Liang, W. Xu, F. Cai, P. Chen, B. Peng, J. Chen and Z. *J.* Li, *Phys. Chem. C,* 2007, **111**, 4465-4472; (*c*) D. P. Hagberg, T. Edvinsson, T.

Marinado, G. Boschloo, A. Hagfeldtand and L. Sun, *Chem. Commun*., 2006, 2245-2247; (*c*) M. Velusamy, K. R. J. Thomas, J. T. Lin, Y. Hsu and K. Ho, *Org. Lett.,* 2005, **7**, 1899-1902; (*d*) T. Kitamura, M. Ikeda, K. Shigaki, T. Inoue, N. A. Anderson, X. Ai, T. Q. Lian and S. Yanagida, *Chem. Mater.,* 2004, **16**, 1806-1812.

6 (*a*) A. Mahmood, *Sol. Energy,* 2016, **123**, 127−144; (*b*) A. Mishra, M. K. R. Fischer and P. Bäuerle, *Angew. Chem. Int. Ed.,* 2009, **48**, 2474−2499; (*c*) H.-N. Tian, X.-C. Yang, J.-X. Pan, R.-K. Chen, M. Liu, Q.-Y. Zhang, A. Hagfeldt and L.-C. Sun, *Adv. Funct. Mater.,* 2008, **18**, 3461−3468; (*d*) D. P. Hagberg, T. Edvinsson, T. Marinado, G. Boschloo, A. Hagfeldt and L. Sun, *Chem. Commun.,* 2006, 2245-2247; (*e*) Z. Q. Jiang, Y. Chen, C. Yang, Y. Cao, Y. T. Tao, J. Qin and D. Ma, *Org. Lett.,* 2009, **11**, 1503−1506.

7 R. Rybakiewicz, M. Zagorska and A. Pron, *Chem. Pap.,* 2017, **71**, 243**–**268.

8 (*a*) P. S. Hariharan, N. S. Venkataramanan, D. Moon and S. P. Anthony, *J. Phys. Chem. C,* 2015, **119**, 9460−9469; (*b*) P. S. Hariharan, G. Parthasarathy, A. Kundu, S. Karthikeyan, Y. Sagara, D. Moon and S. P. Anthony, *Cryst. Growth Des.,* 2018, **18**, 3971−3979; (*c*) P. S. Hariharan, E. M. Mothi, D. Moon and S. P. Anthony, *ACS Appl. Mater. Interfaces,* 2016, **8**, 33034−33042; (*d*) P. Xue, P. Chen, J. Jia, Q. Xu, J. Sun, B. Yao, Z. Zhang and R. Lu, *Chem. Commun.,* 2014, **50**, 2569-2571; (*e*) P. S. Hariharan, P. Gayathri, A. Kundu, S. Karthikeyan, D. Moon and S. P. Anthony, *CrystEngComm.,* 2018, **20**, 643−651.

9 T. Manifar and S. Rohani, *Can. J. Chem. Eng.,* 2004, **82**, 323-334.

10 (*a*) O. Drzyzga, *Chemosphere,* 2003, **53**, 809-818; (*b*) I. Tanaka, H. Shizuka, Y. Takayama, T. Morita, *J. Am. Chem. Soc.,* 1970, **92**, 7270-7277; (*c*) D. E. A. Rahman, *Chem. Pharm. Bull.,* 2013, **61**, 151-159; (*d*) T. Suzuki, M. N. A. Khan, H. Sawada, E. Imai, Y. Itoh, K. Yamatsuta, N. Tokuda, J. Takeuchi, T. Seko and H. Nakagawa, *J. Med. Chem.,* 2012**, 55**, 5760-5773; (*e*) H. Li, A. Guan, G. Huang, C.-L. Liu, Z. Li, Y. Xie and J. Lan, *Bioorg. Med. Chem.* 2016, **24**, 453-461; (*f*) T. Suzuki, K. Imai, E. Imai, S. Iida, R. Ueda, H. Tsumoto, H. Nakagawa and N. Miyata, *Bioorg. Med. Chem,* 2009, **17**, 5900-5905.

11 For reviews see: (*a*) J. Shi and Y. Li, *Chem. Soc. Rev.,* 2017, **46**, 1707-1719; (*b*) F. I. M. Idiris and C. R. Jones, *Org. Biomol. Chem.,* 2017, **15**, 9044; (*c*) J.-A. Garcı´a-Lo´pez and M. F. Greaney, *Chem. Soc. Rev.,* 2016, **45**, 6766-6798; (*d*) C. Holden, and M. F. Greaney, *Angew. Chem., Int. Ed.,* 2014, **53**, 5746-5749; (*e*) A. V. Dubrovskiy, N. A. Markina and R. C. Larock, *Org. Biomol. Chem.,* 2013, **11**, 191-218; (*f*) P. M. Tadross, B. M. Stoltz, *Chem. Rev.,* 2012, **112**, 3550-3577; (*g*) C. M. Gampe, and E. M. Carreira, *Angew. Chem., Int. Ed.,* 2012, **51**, 3766-3778; (*h*) A. Bhunia, S. R. Yetra and A. T. Biju, *Chem. Soc. Rev.,* 2012, **41**, 3140-3152; (*i*) H. Yoshida, J. Ohshita and A. Kunai, *Bull. Chem. Soc. Jpn.,* 2010, **83**, 199-219; For a review on hetarynes see: A. E. Goetz, T. K. Shah and N. K. Garg, *Chem. Commun.,* 2015, **51**, 34-45.

12 For a review see: S. S. Bhojgude, A. Bhunia and A. T. Biju, *Acc. Chem. Res.,* 2016, **49**, 1658-1670.

13 M. Wang and Z. Huang, *Org. Biomol. Chem.*, 2016, **14**, 10185-10188

14 CCDC 1814895 (**4a**) contains the supplementary crystallographic data for this paper. This data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data request/cif.

Graphical abstract

Chemoselective synthesis of amide substituted triaryl amine and diaryl amine derivatives by N-mono and *N*, *N*-diarylation of aryl/hetaryl amino amides using benzyne/arynes has been acheived. Selected triarylamine derivative showed blue-red emission with high quantum yield. Synthesized products were synthetically transformed to highly functionalized biphenyl bridged heterocycles.