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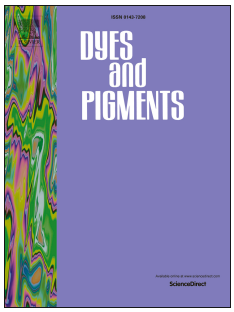

Microwave assisted synthesis and photophysical properties of blue emissive 2-amino-3-carboxamide-1,1′-biaryls and 4-(arylamino)-[1,1′-biphenyl]-3-carboxamides via Suzuki and Chan-Evans-Lam coupling

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PII: S0143-7208(19)30933-7

DOI: https://doi.org/10.1016/j.dyepig.2019.108015

Reference: DYPI 108015

To appear in: *Dyes and Pigments*

Received Date: 25 April 2019

Revised Date: 17 October 2019

Accepted Date: 1 November 2019

Please cite this article as: Novanna M, Kannadasan S, Shanmugam P, Microwave assisted synthesis and photophysical properties of blue emissive 2-amino-3-carboxamide-1,1′-biaryls and 4-(arylamino)-[1,1′-biphenyl]-3-carboxamides via Suzuki and Chan-Evans-Lam coupling, *Dyes and Pigments* (2019), doi: https://doi.org/10.1016/j.dyepig.2019.108015.

Graphical Abstract

Microwave assisted synthesis of 2-amino-3-carboxamide 1, 1'-biaryls derivatives via Suzuki coupling, chemo selective *N*-arylation of biaryl derivatives via Chan-Evans-Lam coupling has been reported. Evaluation of photophysical properties showed luminescence in the blue region with large Stokes shift and high quantum yields.

Microwave assisted synthesis and photophysical properties of blue emissive 2-amino-3-carboxamide 1, 1'-biaryls and 4-(arylamino)-[1, 1'-biphenyl]-3-carboxamides via Suzuki and Chan-Evans-Lam coupling

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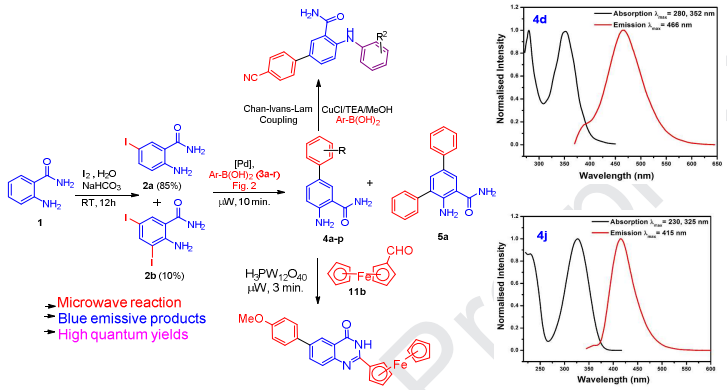
Motakatla Novanna[a], Sathananthan Kannadasan[a*] and Ponnusamy Shanmugam[b*]



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Microwave assisted synthesis and photophysical properties of blue emissive 2-amino-3-carboxamide-1,1'-biaryls and 4-(arylamino)-[1,1'-biphenyl]-3-carboxamides via Suzuki and Chan-Evans-Lam coupling

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ARTICLE INFO

Article history:
Received
Received in revised form
Accepted
Available online

Keywords:
Aminoamides
(Het)aryl boronic acids
Biaryls
Suzuki coupling
Chan-Evans-Lam coupling
Fluorescence quantum yield

ABSTRACT

Abstract: An efficient microwave assisted synthesis of 2-amino-3-carboxamide-1,1'-biaryls derivatives **4a-p** and terphenyl derivative **5a** from 2-amino-5-iodobenzamide **2a**, 2-amino-3,5-diiodobenzamide **2b** and (het)aryl boronic acids via Suzuki coupling has been achieved. Synthetic utility of the product 4-amino-4'-cyano-[1,1'-biphenyl]-3-carboxamide **4j** has been demonstrated for the synthesis of 4-(aryl amino)-[1,1'-biphenyl]-3-carboxamide derivatives **10a-c** via Chan-Evans-Lam coupling reaction. Furthermore, 4-(4'-oxo-3', 4'-dihydro-1'H-spiro[fluorene-9,2'-quinazolin]-6'-yl)benzonitrile **12a** was obtained from biaryl derivative **4j** and fluorenone **11a** and 6(4- methoxyphenyl)2-(ferrocenyl) quinazolin-4(3H)-one **12b** from biaryl derivative **4k** and ferrocenealdehyde **11b** using phosphotungstic acid as green catalyst and solvent free microwave irradiation condition. Remarkably, all the synthesized 2-amino-3-carboxamide-1,1'-biaryls and 4-(aryl amino)-[1,1'-biphenyl]-3-carboxamide derivatives **4a-p** showed luminescence in the blue region with large Stokes shift. Significantly, 2-amino-3-carboxamide-1,1'-biaryls **4d** and **4j** showed high fluorescence quantum yields (Φ_f) 0.54 and 0.84, respectively.

1. Introduction

Biaryl core structures have been found as backbone of the natural products and biomolecules [1-6] (Fig. 1). The electronic structure of biaryls constitutes diverse applications include in asymmetric synthesis as chiral ligands [7,8], as blue emissive layers in organic light-emitting diodes [9-11] (OLEDs), as optical brighteners [12], as synthons for liquid crystals [13] and as spacers in polymerization [14,15]. Utilizing C-C bond formation reactions, methods for the synthesis of biaryls have been developed include Ullmann reaction using copper as catalyst [16,17], other catalysts such as nickel, zinc, manganese, gold, palladium and through homo coupling of aryl Grignard reagent [18], from arynes [19] and metal free synthesis [20]. The Suzuki cross coupling of aryl halides with aryl boronic acids catalyzed by palladium is most utilized reactions in synthetic chemistry for numerous heterocyclic compounds, including biaryl derivatives [21,22]. Chan-Evans-Lam coupling [23] is an effective cross-coupling reaction of amines/alcohols and other nucleophiles with arylboronic acids using copper salts as catalyst to form secondary amines or aryl ethers. Chan-Lam coupling proceeds under mild reaction conditions, thus having an advantage over Buchwald-Hartwig amination [24,25] and Ullmann-Goldberg reaction[26,27]. 2-Aminobenzamide has been utilised as a starting material for the synthesis of various heterocyclic compounds and natural products of biological interest [28-33]. Recently, we have reported the synthesis of 2'-spiro and 2, 3-dihydro quinazolinone and 2-methylamino benzamide derivatives from aryl and heteroaryl 2-amino amides [34].

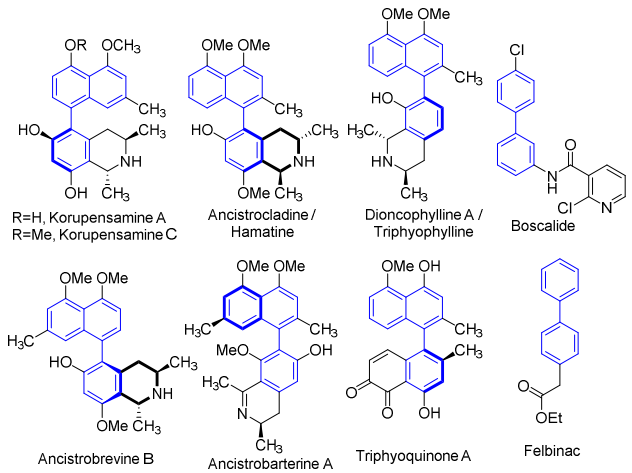
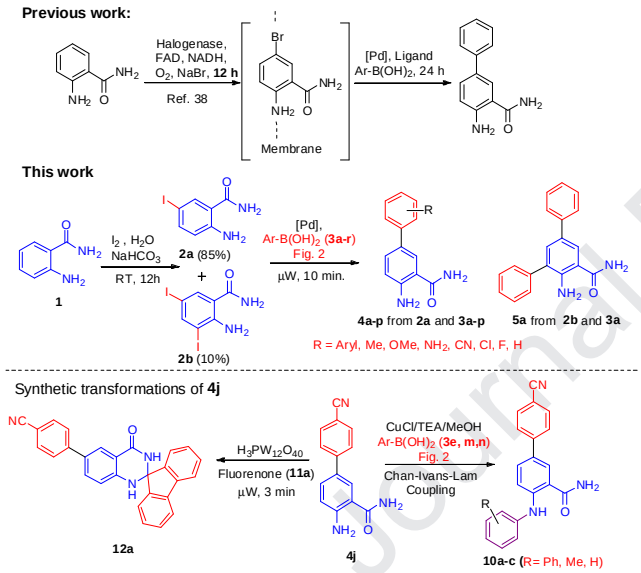


Fig. 1 Natural products and drugs with biaryl backbone

Microwave (MW) irradiation method for the cross coupling reaction is a complementary tool to conventional cross coupling reactions [35-37]. A number of carbocyclic and heterocyclic compounds have been synthesized via MW irradiation pathways with faster reaction times, higher yields and possible minimum by-products. An integrated catalysis arylation pathway via regiodivergent enzymatic C-H activation method is known for biaryl synthesis [38]. Despite biaryls have largely used as synthons in organic chemistry, however, functionalization of biaryls appended with amides is limitedly explored.

Hence, herein we report the synthesis and evaluation of photophysical properties of 2-amino-3-carboxamide substituted 1,1'-biaryls **4** and **5** through MW assisted Suzuki coupling reaction. The biaryls **4** and **5** were synthesised from and 2-amino-5-iodo benzamide **2a** and 2-amino-3,5-diiodo benzamide **2b**. Further, to demonstrate the synthetic utility of the biaryls **4**, compounds 4-(aryl amino)-[1,1'-biphenyl]-3-carboxamides **10** were obtained by Chan-Evans-Lam coupling reaction of **4j** whereas compound **12a** was obtained via HPW catalysed spiro annulation reaction of **4j** (Scheme 1).



Scheme 1 Iodination of **1**, Suzuki coupling of **2a**,**b** and synthetic transformations of **4j**

2. Experimental

2.1. Materials and methods

All the reactions were carried out in oven-dried glassware. CEM Discover-300 microwave synthesiser was used for all the microwave irradiation reactions. 2-Aminobenzamide, (het)aryl boronic acids, and Pd(0) & Pd(II)-catalysts were purchased from Sigma Aldrich and used as received. Progress of reactions was monitored by Thin Layer Chromatography (TLC) using pre-coated Merck TLC plates (Merck 60 F254). The compounds were visualized with a UV light at 254 nm and by staining with iodine, while purification of crude compounds was done by column chromatography using Silica gel (Mesh size 100-200). The structure of new compounds was established by spectroscopic data such as FTIR, ^{1}H NMR, ^{13}C NMR, DEPT-135 and HRMS. The NMR spectra were recorded on Bruker-400 MHz NMR spectrometer (400 MHz for ^{1}H NMR and 100 MHz for ^{13}C NMR) with $CDCl_3$ or $(CD_3)_2SO$ as the solvent and TMS as internal reference. Integrals are in accordance with assignments; Coupling constants (*J*) 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), br s (broad singlet). FTIR spectra were recorded on a Perkin-Elmer RX-IFT-IR and absorbencies are reported in cm^{-1}. ESI HRMS were recorded using Waters(R) Micromass(R) Q-TOF MicroTM Mass Spectrometer. Yields refer to quantities obtained after chromatography Yields refer to quantities obtained after purification by column chromatography. Absorption spectra were recorded using Cary100 Bio UV-Vis spectrophotometer. Steady-state fluorescence spectra were recorded on SHIMADZU RF-6000 spectrofluorophotometer by excitation at the respective absorption maxima. Quantum yields of compounds was estimated by comparison with the known quantum yields of Quinine sulphate in 0.5 M H_2SO_4 solution (Φ=0.54) at an excitation wavelength of 366 nm using the following equation.

$$\Phi = \Phi_R . I/I_R . OD_R/OD . n^2/n^2_R$$

where Φ 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.

2.2. Synthesis

2.2.1. Synthesis of 2-amino-5-iodobenzamide ***2a*** *and 2-amino-3, 5-diiodobenzamide* **2b** [39]*:*

To a stirred solution of anthranilamide **1** (1.0 g, 1.0 equiv.) and iodine (4.6g, 2.5 equiv.) in water (50 mL), sodium bicarbonate ($NaHCO_3$) (0.9g, 1.5 equiv.) was added. The mixture was stirred at RT for 12 h. After completion of the reaction (monitored by TLC), the reaction mixture was extracted with EtOAc and washed with HCl (0.25 M, 50 mL) followed by saturated brine and water. The combined organic solvent was dried over anhydrous Na_2SO_4 and the solvent was removed under vacuum. The crude mixture was purified by a column of silica gel by gradient elution using EtOAc: hexane (20:80) yielded 2-amino-5-iodobenzamide **2a** in 85% yield and 2-amino-3,5-diiodobenzamide **2b** in 10% yield.

2.2.2. General procedure for preparation of 2-amino-3-carboxamide 1,1'-biaryls **4a-p** *and* **5a** *by Suzuki coupling:*

A mixture of compound **2a** or **2b** (0.191 mmol), arylboronic acids **3** (0.229 mmol), Pd(dppf)Cl_2.DCM (8 mg, 0.0095 mmol) and 0.5 N K_2CO_3 (1 mL, 0.5 mmol) in 4 mL of dioxane-MeOH (3:1) was microwave irradiated (power mode) at 200 W for 10 min. After completion of the reaction (TLC), the solvent was removed *in vacuo*, and the residue was extracted with EtOAc and washed with HCl (0.25 M, 20 mL) followed by saturated brine. The organic layer was dried over anhydrous Na_2SO_4 and purified through a silica gel column chromatography by gradient elution using EtOAc:hexane to afford compounds **4a-4p** and **5a** in very good yields.

2.2.3. Synthesis of 4'-cyano-4-(arylamino)-[1,1'-biphenyl]-3-carboxamides **10a-c** *by Chan-Evans-Lam coupling:*

To a mixture of 4-amino-4'-cyano-[1,1'-biphenyl]-3-carboxamide **4j** (0.210 mmol), arylboronic acids **3** (0.252 mmol) in methanol was added cuprous chloride (CuCl) (0.0315 mmol), and Et_3N (0.105 mmol) and stirred at RT for 4h under ambient conditions. After completion of the reaction, the reaction mixture was filtered through celite pad and the filtrate was concentrated and purified by silica gel column chromatography using EtOAc: hexane as eluent to afford 4'-cyano-4-(arylamino)-[1,1'-biphenyl]-3-carboxamides **10a-c** in good yields.

2.2.4. Experimental procedure for synthesis of spiro and cyclic quinazolinones **12a** *and* **12b***:*

A slurry made of biaryls **4j** or **4k** (1.0 equiv.) and carbonyl compounds **11a** or **11b** (1.2 equiv.) and 50% w/w phosphotungstic acid (HPW) was microwave irradiated (standard mode) (50% w/w) at 200 W for 3 min. After the completion of the reaction (monitored by TLC), HPW was filtered off using celite bed. The crude product was purified on a silica gel column chromatography to afford the spiro and cyclic quinazolinones **12a** and **12b** in good yields, respectively.

2.3. Spectroscopic data of synthesized compounds

2.3.1. 2-Amino-5-(dibenzo[b,d]furan-4-yl)benzamide (**4a**): Brown powder: 48 mg, 85% yield; R_f (40% EtOAc-Hexane): 0.49, MP:182-187 ^oC; FTIR (KBr) ν_{max}: 3372, 3193, 1639, 1566, 1444, 1400, 1315, 1263, 1186, 795, 747, 662 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6) δ 8.16 (d, *J* = 7.1 Hz, 1H), 8.07-8.02 (m, 2H), 7.97 (s, 1H), 7.82 (dd, *J* = 8.6, 2.1 Hz, 1H), 7.76-7.70 (m, 2H), 7.55-7.50 (m, 1H), 7.43 (dt, *J* = 14.3, 7.5 Hz, 2H), 7.19 (s, 1H), 6.90 (d, *J* = 8.6 Hz, 1H), 6.78 (s, 2H); ^{13}C NMR (100 MHz, DMSO-d_6): δ 171.8, 155.8, 152.9, 150.3, 132.7, 129.2, 128.0, 126.6, 125.7, 124.6, 124.1, 124.0, 123.5, 122.3, 121.6, 119.3, 117.1, 114.6, 112.3; HRMS-ESI: Calcd. for $C_{19}H_{14}N_2O_2$ $[M+H]^+$ *m/z*: 303.1134; Found 303.1132 and Calcd. for $C_{19}H_{12}NO_2$ $[M-NH_2]^+$ *m/z*: 286.0868; Found 286.0870.

2.3.2. 2-Amino-5-(dibenzo[b,d]thiophen-2-yl)benzamide (**4b**): Brown powder: 40 mg, 66% yield; R_f (40% EtOAc-Hexane): 0.47, MP:174-179 ^oC; FTIR (KBr) ν_{max}: 3446, 3330, 3182, 3052, 2920, 1654, 1495, 1463, 1428, 1393, 1313, 1257, 1166, 1116, 1020, 800, 719, 630, 537 cm^{-1}; ^1H NMR (400 MHz, DMSO) δ 8.64 (br s, 1H), 8.48 – 8.46 (m, 1H), 8.02 (dt, *J* = 7.2, 5.5 Hz, 4H), 7.84 (dd, *J* = 8.4, 1.7 Hz, 1H), 7.70 (dd, *J* = 8.6, 2.1 Hz, 1H), 7.52 (dt, *J* = 9.9, 3.5 Hz, 2H), 7.24 (br s, 1H), 6.86 (d, *J* = 8.6 Hz, 1H), 6.76 (br s, 2H); ^{13}C NMR (100 MHz, DMSO-d_6): δ 171.8, 150.2, 139.5, 137.4, 136.6, 136.2, 135.7, 130.9, 127.6, 127.4, 126.5, 125.6, 125.1, 123.6, 122.7, 119.1, 117.6, 114.4; HRMS-ESI: Calcd. for $C_{19}H_{12}NOS$ $[M-NH_2]^+$ *m/z*: 302.0634; Found 302.0556.

*2.3.3. 2-Amino-5-(1H-indol-6-yl)benzamide (***4c**): Brown semi solid: 40 mg, 85% yield; R_f (40% EtOAc-Hexane): 0.48; FTIR (KBr) ν_{max}: 3434, 2352, 2266, 1643, 1018, 821, 766 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6) δ 11.04 (s, 1H), 7.98 (s, 1H), 7.85 (d, *J* = 2.2 Hz, 1H), 7.59 – 7.54 (m, 2H), 7.49 (dd, *J* = 8.5, 2.2 Hz, 1H), 7.32 – 7.29 (m, 2H), 7.11 (s, 1H), 6.78 (d, *J* = 8.5 Hz, 1H), 6.58 (s, 2H), 6.41 (ddd, *J* = 2.9, 1.9, 0.8 Hz, 1H); ^{13}C NMR (100 MHz, DMSO-d_6): δ 171.9, 149.3, 137.1, 134.0, 130.8, 128.7, 127.2, 126.7, 125.9, 120.6, 118.4, 117.5, 114.7, 108.7, 101.3. HRMS-ESI: Calcd. for $C_{15}H_{11}N_2O$ $[M-NH_2]^+$ *m/z*: 235.0866; Found 235.0864.

2.3.4. 2-Amino-5-(pyren-1-yl)benzamide (**4d**): Dark brown powder: 51 mg, 80% yield; R_f (40% EtOAc-Hexane): 0.51, MP:197-201 ^oC; ^1H NMR (400 MHz, DMSO-d_6) δ 8.38 – 8.28 (m, 3H), 8.26 – 8.17 (m, 4H), 8.13 – 8.07 (m, 2H), 7.93 (br s, 1H), 7.90 (s, 1H), 7.49 (dd, *J* = 8.4, 1.9 Hz, 1H), 7.17 (br s, 1H), 6.98 (d, *J* = 8.4 Hz, 1H), 6.86 (br s, 2H); ^{13}C NMR (100 MHz, DMSO-d_6): δ 171.7, 150.1, 137.9, 134.4 131.5, 131.0, 130.0, 128.3, 128.2, 128.0, 127.8, 127.4, 126.8, 125.5, 125.4, 125.2, 125.1, 124.8, 124.7, 117.0, 114.5; HRMS-ESI: Calcd. for $C_{23}H_{14}NO$ $[M-NH_2]^+$ *m/z*: 320.1070; Found 320.1083.

2.3.5. 2-Amino-5-(naphthalen-1-yl)benzamide (**4e**): Brown powder: 41 mg, 82% yield; R_f (40% EtOAc-Hexane): 0.49, MP:148-152 ^oC; FTIR (KBr) ν_{max}: 3343, 3047, 2923, 1653, 1388, 1259, 1160, 781, 580 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.81 (dd, *J* = 8.3, 1.2 Hz, 2H), 7.75 (dd, *J* = 8.3, 0.8 Hz, 1H), 7.43 – 7.33 (m, 4H), 7.30 (dd, *J* = 8.3, 2.0 Hz, 2H), 6.71 (d, *J* = 8.4 Hz, 1H), 5.82 (br s, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 171.1, 148.8, 139.4, 134.8, 133.9, 131.8, 129.4, 128.8, 128.4, 127.5, 126.8, 126.1, 125.8, 125.5, 117.4, 113.7; HRMS-ESI: Calcd. for $C_{17}H_{12}NO$ $[M-NH_2]^+$ *m/z*: 246.0913; Found 246.0915.

2.3.6. 2-Amino-5-(naphthalen-2-yl)benzamide (**4f**): Brown powder: 38 mg, 77% yield; R_f (40% EtOAc-Hexane): 0.49, MP:156-161 ^oC; FTIR (KBr) ν_{max}: 3407, 2922, 1643, 1405, 1265, 1167, 808,746 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6) δ 8.16 (s, 1H), 8.03 (d, *J* = 2.2 Hz, 2H), 7.97 – 7.86 (m, 4H), 7.68 (dd, *J* = 8.6, 2.2 Hz, 1H), 7.48 (dddd, *J* = 16.2, 8.0, 6.9, 1.4 Hz, 2H), 7.19 (s, 1H), 6.84 (d, *J* = 8.6 Hz, 1H), 6.76 (s, 2H); ^{13}C NMR (100 MHz, DMSO-d_6): δ 171.8, 150.3, 137.8, 133.9, 132.0,130.9, 128.6, 128.2, 127.9, 127.6, 126.7, 126.5, 125.8, 125.2, 123.7, 117.6, 114.5; HRMS-ESI: Calcd. for $C_{17}H_{12}NO$ $[M-NH_2]^+$ *m/z*: 246.0913; Found 246.0901.

2.3.7. 4-Amino-[1,1':4',1''-terphenyl]-3-carboxamide (**4g**): White powder: 45 mg, 82% yield; R_f (40% EtOAc-Hexane): 0.49, MP:214-217 ^oC; FTIR (KBr) ν_{max}: 3360, 2923, 1632, 1482, 1388, 1275, 1162, 817, 763, 688, 543 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6) δ 8.01 (br s, 1H), 7.94 (d, *J* = 2.1 Hz, 1H), 7.77 – 7.54 (m, 2H), 7.70 (dd, *J* = 8.2, 1.5 Hz, 4H), 7.56 (dd, *J* = 8.6, 2.1 Hz, 1H), 7.47 (dd, *J* = 10.5, 4.8 Hz, 2H), 7.37 – 7.33(m, 1H), 7.15 (br s, 1H), 6.81 (d, *J* = 8.6 Hz, 1H), 6.73 (br s, 2H); ^{13}C NMR (100 MHz, DMSO-d_6): δ 171.8, 150.3, 140.3, 139.6, 138.1, 130.5, 129.4, 127.7, 127.4, 127.2, 126.9, 126.5, 126.2, 117.5, 116.9, 114.4; HRMS-ESI: Calcd. for $C_{19}H_{16}N_2O$ $[M+H]^+$ *m/z*: 289.1341; Found 289.1340 and Calcd. for $C_{19}H_{14}NO$ $[M-NH_2]^+$ *m/z*: 272.1075; Found 272.1092.

2.3.8. 3',4-Diamino-[1,1'-biphenyl]-3-carboxamide (**4h**): Brown powder:37 mg, 87% yield; R_f (40% EtOAc-Hexane): 0.46, MP:144-148 ^oC; FTIR (KBr) ν_{max}: 3381, 3289, 3174, 2923, 2856, 1635, 1574, 1484, 1406, 1304, 1246, 1163, 828, 782, 694, 651cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6) δ 7.91 (br s, 1H), 7.75 (d, *J* = 2.1 Hz, 1H), 7.37 (dd, *J* = 8.5, 2.1 Hz, 1H), 7.08 (br s, 1H), 7.03 (t, *J* = 7.9 Hz, 1H), 6.79– 6.75(m, 2H), 6.74 (d, *J* = 8.5 Hz, 1H), 6.58 (br s, 1H), 6.48 – 6.45 (m, 1H), 5.01 (br s, 2H); ^{13}C NMR (100 MHz, DMSO-d_6): δ 171.9, 149.8, 149.3, 141.3, 130.5, 129.6, 127.9, 127.1, 117.2, 114.5, 114.3, 112.5, 111.9; HRMS-ESI: Calcd. for $C_{13}H_{13}N_3O$ $[M+H]^+$ *m/z*: 228.1137; Found 228.1138 and Calcd. for $C_{13}H_{11}N_2O$ $[M-NH_2]^+$ *m/z*: 211.0871; Found 211.0868.

2.3.9. 2',4-Diamino-[1,1'-biphenyl]-3-carboxamide (**4i**): Brown powder: 33 mg, 75% yield; R_f (40% EtOAc-Hexane): 0.47, MP:152-157 ^oC; FTIR (KBr) ν_{max}: 3433, 3395, 3312, 3138, 2923, 1628, 1539, 1492, 1453, 1404, 1285, 1250, 1156, 904, 815, 747, 647, 569, 495, 447 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6) δ 7.79 (br s, 1H), 7.54 (d, *J* = 2.0 Hz, 1H), 7.19 (dd, *J* = 8.4, 2.0 Hz, 1H), 7.03 (br s, 1H), 7.00 – 6.96 (m, 2H), 6.75 (d, *J* = 8.4 Hz, 1H), 6.71 (dd, *J* = 8.5, 1.2 Hz, 1H), 6.60 (td, *J* = 7.4, 1.2 Hz, 1H), 6.53 (br s, 2H), 4.68 (br s, 2H); ^{13}C NMR (100 MHz, DMSO-d_6): δ 171.8, 149.3, 145.5, 132.7, 130.5, 129.2, 127.8, 126.4, 126.3, 117.1, 115.4, 114.8; HRMS-ESI: Calcd. for $C_{13}H_{13}N_3NaO$ $[M+Na]^+$ *m/z*: 250.0956; Found 250.0954 and Calcd. for $C_{13}H_{11}N_2O$ $[M-NH_2]^+$ *m/z*: 211.0871; Found 211.0870.

2.3.10. 4-Amino-4'-cyano-[1,1'-biphenyl]-3-carboxamide (**4j**): Brown powder: 43 mg, 95% yield; R_f (30% EtOAc-Hexane): 0.52, MP:147-151 ^oC; FTIR (KBr) ν_{max}: 3478, 3440, 3404, 3179, 2772, 2224, 1917, 1682, 1656, 1575, 1560, 1485, 1402, 13331276, 1172, 1096, 1014, 950, 901, 883, 819,763 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6) δ 8.02 (br s, 1H), 7.99 (d, *J* = 1.9 Hz, 1H), 7.86 (td, *J* = 8.6, 6.6 Hz, 4H), 7.62 (dd, *J* = 8.7, 2.2 Hz, 1H), 7.20 (br s, 1H), 6.94 (br s, 2H), 6.81 (d, *J* = 8.6 Hz, 1H); ^{13}C NMR (100 MHz, DMSO-d_6): δ 171.5, 151.3, 145.0, 133.1, 130.8,

128.0, 126.4, 124.3, 119.7, 117.6, 114.2, 108.5; HRMS-ESI: Calcd. for $C_{14}H_{11}N_3O$ $[M+H]^+$ *m/z*: 238.0980; Found 238.0975 and Calcd. for $C_{14}H_9N_2O$ $[M-NH_2]^+$ *m/z*: 221.0715; Found 221.0711.

2.3.11. 4-Amino-4'-methoxy-[1,1'-biphenyl]-3-carboxamide (**4k**): Brownish semisolid: 41 mg, 90% yield; R_f (40% EtOAc-Hexane): 0.50; FTIR (KBr) ν_{max}: 3479, 3433, 3376, 3190, 2923, 2854, 1641, 1568, 1490, 1401, 1301, 1260, 1162, 1093, 900, 878, 808, 761, 715 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6) δ 7.95 (br s, 1H), 7.83 (d, *J* = 2.2 Hz, 1H), 7.54 (d, *J* = 8.2 Hz, 2H), 7.47 (dd, *J* = 8.6, 2.2 Hz, 1H), 7.20 (d, *J* = 7.9 Hz, 2H), 7.11 (br s, 1H), 6.76 (d, *J* = 8.5 Hz, 1H), 6.66 (s, 2H), 2.32 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6): δ 171.6, 149.8, 137.7, 135.5, 130.4, 129.7, 126.9, 125.9, 117.4, 114.5, 21.1.

2.3.12. 4-Amino-2'-methyl-[1,1'-biphenyl]-3-carboxamide (**4l**): Brown powder: 36 mg, 84% yield; R_f (40% EtOAc-Hexane): 0.51, MP:142-146 ^oC; FTIR (KBr) ν_{max}: 3426, 3334, 3195, 2922, 2857, 1667, 1622, 1482, 1396, 1312, 1261, 1161, 915, 837, 754, 658, 603 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.23 (d, *J* = 2.0 Hz, 1H), 7.18 – 7.16 (m, 2H), 7.16 – 7.010(m, 3H), 6.65 (d, *J* = 8.4 Hz, 1H), 5.78 (br s, 2H), 5.65 (br s, 2H), 2.20 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 171.7, 148.3, 141.0, 135.5, 133.9, 130.4, 130.2, 129.8, 128.6, 127.1, 125.9, 117.2, 113.7, 20.5; HRMS-ESI: Calcd. for $C_{14}H_{14}N_2O$ $[M+H]^+$ *m/z*: 227.1184; Found 227.1205 and Calcd. for $C_{14}H_{12}NO$ $[M-NH_2]^+$ *m/z*: 210.0919; Found 210.0933.

2.3.13. 4-Amino-4'-methyl-[1,1'-biphenyl]-3-carboxamide (**4m**): Brown powder: 37 mg, 87% yield; R_f (40% EtOAc-Hexane): 0.51, MP:167-171 ^oC; FTIR (KBr) ν_{max}: 3479, 3388, 3287, 3177, 2923, 2854, 1649, 1617, 1487, 1460, 1395, 1302, 1256, 1165, 1110, 904, 814, 725 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.48 (d, *J* = 2.1 Hz, 1H), 7.40 (dd, *J* = 8.5, 2.1 Hz, 1H), 7.34 – 7.31 (m, 2H), 7.14 (d, *J* = 7.9 Hz, 2H), 6.68 (d, *J* = 8.5 Hz, 1H), 5.63 (br s, 4H), 2.30 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 171.6, 148.5, 137.6, 136.4, 131.7, 129.7, 129.5, 126.3, 126.2, 117.9, 114.3, 21.1. HRMS-ESI: Calcd. for $C_{14}H_{14}N_2NaO$ $[M+Na]^+$ *m/z*: 249.1004; Found 249.1005 and Calcd. for $C_{14}H_{12}NO$ $[M-NH_2]^+$ *m/z*: 210.0919; Found 210.0920.

2.3.14. 4-Amino-[1,1'-biphenyl]-3-carboxamide (**4n**): Brown powder: 36 mg, 90% yield; R_f (40% EtOAc-Hexane): 0.52, MP:144-148 ^oC; FTIR (KBr) ν_{max}: 3675, 3383, 3305, 3183, 2922, 2856, 1737, 1641, 1572, 1482, 1402, 1255, 1161, 831, 757, 651 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6) δ 7.97 (br s, 1H), 7.86 (d, *J* = 2.2 Hz, 1H), 7.65 (dd, *J* = 8.3, 1.1 Hz, 2H), 7.50 (dd, *J* = 8.6, 2.2 Hz, 1H), 7.432– 7.38 (m, 2H), 7.26 – 7.23 (m, 1H), 7.13 (br s, 1H), 6.78 (d, *J* = 8.5 Hz, 1H), 6.68 (br s, 2H); ^{13}C NMR (100 MHz, DMSO-d_6): δ 171.7, 150.1, 140.5, 130.6, 129.1, 127.3, 126.8, 126.4, 126.1, 117.4, 114.4.

2.3.15. 4-Amino-4'-fluoro-[1,1'-biphenyl]-3-carboxamide (**4o**): Brown powder: 33 mg, 76% yield; R_f (40% EtOAc-Hexane): 0.50, MP:146-150 ^oC; FTIR (KBr) ν_{max}: 3410, 3205, 1672, 1622, 1562, 1491, 1402, 1229, 1159, 1096, 819, 633 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.45 (d, *J* = 2.1 Hz, 1H), 7.39 – 7.34 (m, 3H), 7.04– 6.99 (m, 2H), 6.69 (d, *J* = 8.5 Hz, 1H), 5.85 (br s, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 171.6, 163.2, 148.6, 131.7, 128.8, 127.9, 127.8, 126.4, 118.0, 115.7, 115.5; HRMS-ESI: Calcd. for $C_{13}H_9FNO$ $[M-NH_2]^+$ *m/z*: 214.0663; Found 214.0674.

2.3.16. 4-Amino-4'-chloro-[1,1'-biphenyl]-3-carboxamide (**4p**): Brown powder: 33 mg, 72% yield; R_f (40% EtOAc-Hexane): 0.51, MP:167-171 ^oC; FTIR (KBr) ν_{max}: 3435, 3383, 3348, 3206, 2923, 2854, 1890, 1581, 1482, 1427, 1409, 1309, 1277, 1166, 1093, 1036, 1011, 901, 879, 815, 762, 720, 703 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.46 (d, *J* = 2.1 Hz, 1H), 7.36 – 7.33 (m, 3H), 7.29 – 7.27 (m, 2H), 6.68 (d, *J* = 8.5 Hz, 1H), 5.83 (br s, 2H), 5.67 (BR s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 171.5, 148.9, 138.9, 132.6, 131.6, 128.9, 128.3, 127.5, 126.4, 118.0, 114.7, 114.3; HRMS-ESI: Calcd. for $C_{13}H_{11}ClN_2O$ $[M+2]^+$ *m/z*: 248.0360; Found 248.0391 and Calcd. for $C_{13}H_9ClNO$ $[M-NH_2]^+$ *m/z*: 230.0373; Found 230.0278.

2.3.17. 4'-Amino-[1,1':3',1''-terphenyl]-5'-carboxamide (**5a**): Brown powder: 31 mg, 83% yield; R_f (40% EtOAc-Hexane): 0.48, MP:201-205 ^oC; FTIR (KBr) ν_{max}: 3421, 3350, 3182, 2922, 2856, 1636, 1582, 1458, 1405, 1312, 1252, 1131, 889, 809, 753, 694, 642, 584, 497 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6) δ 8.11 (br s, 1H), 7.91 (d, *J* = 2.2 Hz, 1H), 7.70– 7.68 (m, 2H), 7.52 – 7.46 (m, 4H), 7.42 – 7.38 (m, 4H), 7.31 (s, 1H), 7.26 (t, *J* = 7.3 Hz, 1H), 6.31(br s, 2H); ^{13}C NMR (100 MHz, DMSO-d_6): δ 172.0, 146.4, 140.3, 139.2, 131.6, 129.5, 129.4, 129.2, 129.0, 127.9, 127.3, 127.0, 126.7, 126.3, 115.8; HRMS-ESI: Calcd. for $C_{19}H_{16}N_2O$ $[M+H]^+$ *m/z*: 289.1341; Found 289.1348 and Calcd. for $C_{19}H_{14}NO$ $[M-NH_2]^+$ *m/z*: 272.1075; Found 272.1066.

2.3.18.4'-Cyano-4-(phenylamino)-[1,1'-biphenyl]-3-carboxamide **(10a):** Colourless crystal : 46 mg, 70% yield; R_f (30% EtOAc-Hexane): 0.51; FTIR (KBr) ν_{max}: 3430, 3206, 2923, 2228, 1667, 1629, 1594, 1495, 1392, 1286, 1238, 998, 824, 743, 700, 546 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6) δ 10.28 (s, 1H), 8.33 (br s, 1H), 8.13 (d, *J* = 2.2 Hz, 1H), 7.94 – 7.87 (m, 4H), 7.75 (dd, *J* = 8.8, 2.2 Hz, 1H), 7.59 (br s, 1H), 7.35 (ddd, *J* = 10.5, 6.3, 2.5 Hz, 3H), 7.23 – 7.21 (m, 2H), 7.05 (dd, *J* = 10.5, 4.2 Hz, 1H); ^{13}C NMR (100 MHz, DMSO-d_6): δ 171.6, 146.3, 144.3, 141.1, 133.2, 131.1, 130.0, 128.5, 127.3, 127.0, 123.2, 121.2, 119.6, 117.5, 115.1, 109.3; HRMS-ESI: Calcd. for $C_{20}H_{15}N_3O$ $[M+H]^+$ *m/z*: 314.1215; Found 314.1280.

2.3.19. 4'-Cyano-4-(p-tolylamino)-[1,1'-biphenyl]-3-carboxamide (**10b**): Brown powder: 44 mg, 65% yield; R_f (40% EtOAc-Hexane): 0.52, MP:208-212 ^oC; FTIR (KBr) ν_{max}: 3445, 3206, 2222, 1656, 1595, 1504, 1392, 1325, 1285, 1237, 808, 651, 498 cm^{-1}; ^1H NMR (400 MHz, DMSO) δ 10.20 (s, 1H), 8.32 (br s, 1H), 8.12 (d, *J* = 2.0 Hz, 1H), 7.89 (dd, *J* = 19.4, 8.2 Hz, 4H), 7.71 (d, *J* = 8.8 Hz, 1H), 7.56 (br s, 1H), 7.23 (d, *J* = 8.8 Hz, 1H), 7.14 (dd, *J* = 23.5, 8.2 Hz, 4H), 2.28 (s, 3H); ^{13}C NMR (100 MHz, DMSO): δ 171.1, 147.0, 144.4, 138.3, 133.2, 132.7, 131.2, 130.5, 128.4, 126.8, 126.7, 122.0, 119.6, 116.8, 114.7, 109.1, 20.9; HRMS-ESI: Calcd. for $C_{21}H_{17}N_3O$ $[M+H]^+$ *m/z*: 328.1372; Found 328.1427.

2.3.20. 4'-Cyano-4-(naphthalen-1-ylamino)-[1,1'-biphenyl]-3-carboxamide (**10c**): Brown powder: 49 mg, 65% yield; R_f (30% EtOAc-Hexane): 0.51, MP:242-245 ^oC; FTIR (KBr) ν_{max}: 3424, 3173, 2225, 1590, 1527, 1403, 1287, 545 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6) δ 10.86 (s, 1H), 8.45 (br s, 1H), 8.21 (d, *J* = 2.0 Hz, 1H), 8.01 – 7.96 (m, 2H), 7.90 (dd, *J* = 19.4, 8.5 Hz, 4H), 7.71 (ddd, *J* = 10.7, 7.4, 2.5 Hz, 3H), 7.58 – 7.52 (m, 4H), 7.11 (d, *J* = 8.8 Hz, 1H); ^{13}C NMR (100 MHz, DMSO-d_6): δ 171.9, 147.8, 143.4, 136.8, 134.9, 133.2, 131.3, 129.0, 128.6, 128.5, 127.1, 126.9, 126.8, 126.6, 124.5, 122.2, 119.6, 118.9, 116.8, 115.1, 109.2; HRMS-ESI: Calcd. for $C_{24}H_{17}N_3O$ $[M+H]^+$ *m/z*: 364.1372; Found 364.1426.

2.3.21.4-(4'-Oxo-3',4'-dihydro-1'H-spiro[fluorene-9,2'-quinazolin]-6'-yl)benzonitrile (**12a**): Yellow semisolid: 67 mg, 80% yield; R_f (30% EtOAc-Hexane): 0.51; FTIR (KBr) ν_{max}: 3435, 3284, 3044, 2921, 2230, 1648, 1607, 1495, 1328, 1286, 1168, 1019, 818, 729, 656, 539 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6) δ 8.64 (d, *J* = 1.4 Hz, 1H), 8.14 (d, *J* = 2.3 Hz, 1H), 7.88 (s, 4H), 7.81 (d, *J* = 7.5 Hz, 2H), 7.75 (dd, *J* = 8.5, 2.4 Hz, 1H), 7.65 (d, *J* = 1.2 Hz, 1H), 7.54 (d, *J* = 7.4 Hz, 2H), 7.45 (td, *J* = 7.5, 1.1 Hz, 2H), 7.30 (td, *J* = 7.5, 1.0 Hz, 2H), 6.82 (d, *J* = 8.5 Hz, 1H); ^{13}C NMR (100 MHz, DMSO-d_6): δ 163.9, 148.7, 148.2, 144.7, 138.5, 133.3, 132.5, 130.5, 129.0, 127.2, 126.7, 126.0,

124.2, 128.8, 119.6, 115.7, 114.6, 109.1, 77.4; HRMS-ESI: Calcd. for $C_{27}H_{17}N_3O$ $[M+H]^+$ *m/z*: 400.1372; Found 400.1429.

2.3.22. 6-(4-Methoxyphenyl)-2-(ferrocenyl)quinazolin-4(3H)-one (**12b**): Brown powder: 54 mg, 65% yield; R_f (40% EtOAc-Hexane): 0.51, MP:197-201 ^oC; FTIR (KBr) ν_{max}: 3409, 3066, 2924, 1615, 1533, 1479, 1124, 754, 617 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 10.56 (br s, 1H), 8.45 (d, *J* = 2.1 Hz, 1H), 7.94 (dd, *J* = 8.5, 2.2 Hz, 1H), 7.71 (d, *J* = 8.5 Hz, 1H), 7.56 (d, *J* = 8.1 Hz, 2H), 7.24 (d, *J* = 7.9 Hz, 2H), 5.09 – 5.08 (m, 2H), 4.51 – 4.50 (m, 2H), 4.18 (s, 5H), 2.36 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 163.3, 154.6, 148.9, 138.9, 137.7, 136.9, 133.7, 129.8, 127.8, 127.0, 124.0, 120.7, 71.5, 70.1, 68.0, 21.2; HRMS-ESI: Calcd. for $C_{25}H_{20}FeN_2O_2$ $[M+H]^+$ *m/z*: 437.1952; Found 437.1936.

3. Results and discussion

Initially, a mixture of 1.0 equiv. of 2-amino-5-iodobenzamide **2a** [39] and 1.2 equiv. of dibenzo[b,d]furan-4-ylboronic acid **3a** and 5 mol% $Pd(OAc)_2$, Na_2CO_3 as base in toluene was MW irradiated (100 Watts) for 5 minutes. The reaction afforded 2-amino-5-(dibenzo[b,d]furan-4-yl) benzamide **4a** in 20% yield (Table 1, entry 1, see ESI).

In order to optimize the reaction conditions, parameters such as MW power and irradiation time, base, solvent system, and catalyst and catalyst loading were considered. The reaction under conventional heating yielded desired product **4a** in lower yield and longer reaction time implying that under MW condition afforded optimum yield with shorter reaction time. Hence, the condition shown in table 1, entry 19 was found to be optimum (see Table 1, ESI).

Encouraged by the preliminary results, and to demonstrate the scope and diversity of the reaction, iodoamino amides **2a-b** and a variety of aryl and hetero aryl boronic acids **3a-r** were screened for the reaction (Fig. 2). Thus, under optimised condition, reaction of amino amides **2a-b** with aryl and hetero aryl boronic acids afforded 2-amino-3-carboxamide 1,1'-biaryl derivatives **4a-p** and 4'-amino-[1,1':3',1''-terphenyl]-5'-carboxamide **5a** in very good to excellent yields, except boronic acids **3q** and **3r** did not react with **2a** due to steric hindrance.

From the results shown in Table 1, it has been observed that boronic acids with heteroaryl moiety afforded biaryls with higher yields up to 85% (Table 1, entries 1-3). It should be noted that versatile functional groups such as $-NH_2$, -CN, -F, -Cl remain unreactive and observed only selective Suzuki coupled products (Table 1, entries 15 and 16) [40]. In line with literature [41], we have observed the coupling reaction of **2a** with aryl boronic acids undergone only C-C bond forming Suzuki coupling reaction to provide biaryl derivatives **4** and did not observe any self Buchwald N-C cross coupling products, namely, diphenyl amino amide derivative of **2a**. A plausible mechanism for the formation of biaryl derivative **4a** is depicted in Scheme 1 of ESI.

In addition to spectroscopic characterizations such FTIR and NMR analysis of the products, a notable α-cleavage of amides (N-CO bond) resulting M-16 (i.e M-NH_2) peak with the loss of neutral amine is observed for all biaryl compounds and is evident from HR-ESI-MS analysis [42].

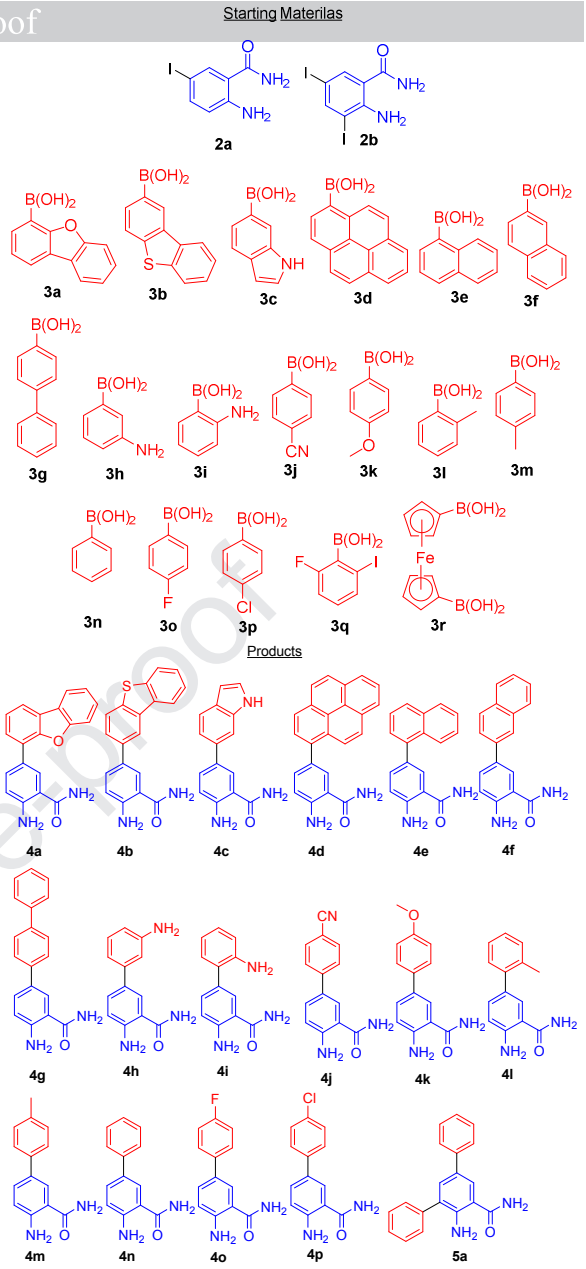


Fig. 2 Screened iodoamino amides and aryl/hetero aryl boronic acids and biaryl products

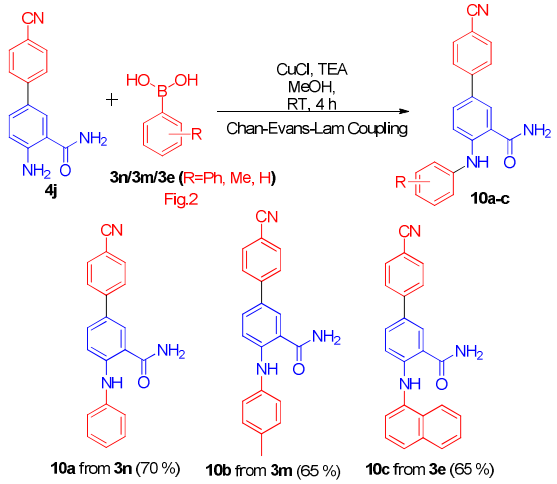
Table 1 Scope of the reaction[a]

Entry	Amino amide **2**	Boronic acid **3**	Biaryl Product	% yield[c]
1	**2a**	**3a**	**4a**	85
2	**2a**	**3b**	**4b**	78
3	**2a**	**3c**	**4c**	85
4	**2a**	**3d**	**4d**	80
5	**2a**	**3e**	**4e**	82
6	**2a**	**3f**	**4f**	77
7	**2a**	**3g**	**4g**	82
8	**2a**	**3h**	**4h**	87
9	**2a**	**3i**	**4i**	75
10	**2a**	**3j**	**4j**	95
11	**2a**	**3k**	**4k**	90
12	**2a**	**3l**	**4l**	84
13	**2a**	**3m**	**4m**	87
14	**2a**	**3n**	**4n**	90
15	**2a**	**3o**	**4o**	76
16	**2a**	**3p**	**4p**	72
17	**2a**	**3q**	-	-
18	**2a**	**3r**	-	-
19	**2b**	**3n**	**5a**[b]	83

[a] All the reactions were carried out by reacting 1 equiv. of **2a** and 1.2 equiv. of **3a** ; [b] 2.2 equiv. of **3n** was used; [c]Isolated yield.

Similarly, for the most of the 2-amino-3-carboxamide-1,1'-biaryl compounds synthesized, we have observed M-16 (i.e M-NH_2) as a base peak. Further, the peculiar mass spectral behavior, protonation during mass spectral analysis and elimination of neutral molecules i.e amines from amides is studied extensively [43-47] to substantiate our observations.

The availability of functional group diversity in the 1,1'-biaryls products prompted us to examine their synthetic utility. Thus, firstly *N*-arylation of amine through Chan-Evans-Lam reaction was considered.



Scheme 2 Synthesis of **10a-c** from **4j a**nd **3n/3m/3e** through Chan-Evans-Lam coupling

Thus, the reaction between **4j** and aryl boronic acid **3n** in CH_3OH using Et_3N as base and CuCl as catalyst afforded 4'-cyano-4-(phenylamino)-[1,1'-biphenyl]-3-carboxamide **10a** in 70% yield. Compound **10a** was thoroughly characterized by spectroscopic data including single-crystal XRD method (Fig. 3) [48]. Similarly, compounds **10b-c** were synthesised from biaryl **4j** and aryl boronic acids **3m** and **3e**, respectively (Scheme 2). A plausible mechanism for the formation of compound **10a** is depicted in Scheme 2 of ESI.

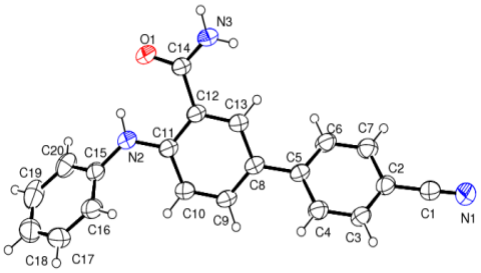
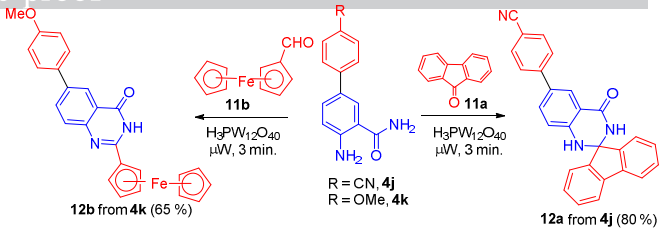


Fig. 3 ORTEP diagram of compound **10a** (CCDC-1889388)

To further demonstrate the synthetic utility of 1,1' biaryls, spiro and cyclic quinazolinones heterocyclic derivatives were synthesised as shown in Scheme 3. Therefore, 4-(4'-oxo-3',4'-dihydro-1'H-spiro [fluorene-9,2'-quinazolin]-6'-yl)benzonitrile **12a** was synthesised from the reaction between biaryl **4j** and 9H-fluoren-9-one **11a** in 80% yield using phosphotungstic acid(HPW) as catalyst and MW irradiation condition. Similarly, 6-(4-methoxyphenyl)-2-(ferrocen-2-yl) quinazolin-4(3H)one **12b** was synthesised in 65% yield by the reaction of biaryl **4k** with ferrocene-2-carboxaldehyde **11b**.

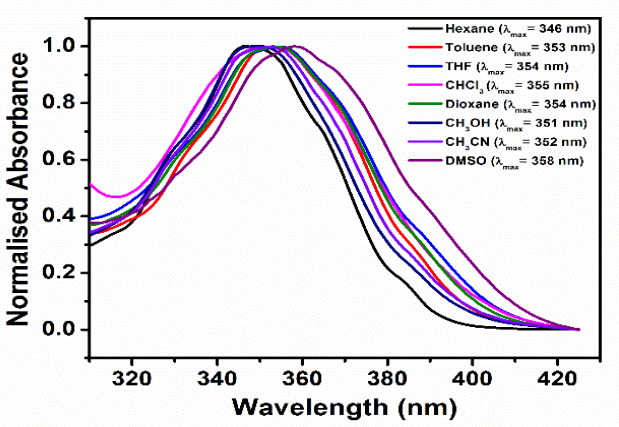


Scheme 3 Synthesis of spiro and cyclic quinazolinones heterocyclic derivatives **12a-b** from **4j, 11a /4k, 11b**

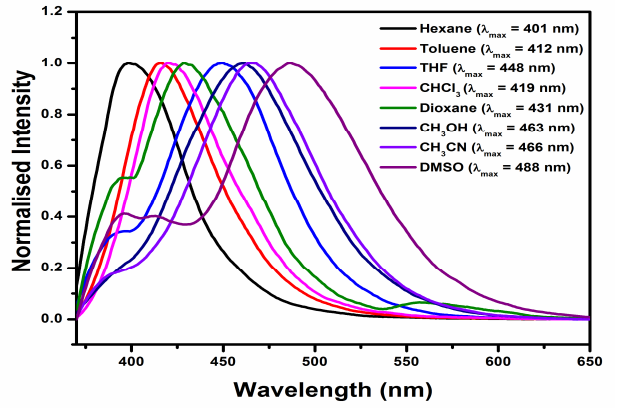
3.1. Photophysical studies

The structural uniqueness of the biaryl compounds obtained herein encouraged us to explore their photophysical properties.

Based on structural perspective, compound **4d** was selected for the evaluation of photophysical properties. Thus, UV absorption and emission of compound **4d** were recorded in MeOH and showed an absorption maxima at 351 nm and emission maxima at 463 nm, respectively. To find out the influence of polarity solvent effect for the compound **4d**, a solvatochromism study was undertaken. Solvents such as hexane, toluene, THF, chloroform, acetonitrile, DMSO in the increasing order of polarity were used for the study.



(a)



(b)

Fig. 4 Solvatochromism for the compound **4d** recorded at C = 10^{-4} M at 298 K; (a) Normalised absorption spectra; (b) Normalised emission spectra.

Table 2 Absorption and Emission Maxima of compound **4d** in various polarity of solvents

Entry	Solvent	Absorption[a] $\lambda_{max,\ abs}$ (nm)	Emission[b] $\lambda_{max,\ emi}$ (nm)
1	Hexane	346	401
2	Toluene	353	412
3	THF	354	448
4	$CHCl_3$	355	419
5	Dioxane	354	431
6	MeOH	351	463
7	CH_3CN	352	466
8	DMSO	358	488

[a]Recorded at C = 10^{-4} M at 298 K; [b]Excited at the longest wavelength of the absorption maxima

The results revealed that a red shift in the emission maxima from 401 nm to 488 nm was observed as the polarity of the solvent was increased and found highest emission wavelength at 488 nm in DMSO (Table 2, Fig. 4). This may be due to the electron rich pyrene system makes compound **4d** more polar in the excited state as polarity of solvent increased resulting in the red shift [49].

Similarly, all the synthesized biaryl compounds were evaluated for photophysical characteristics such as absorption ($\lambda_{max,\ abs}$), emission ($\lambda_{max,\ emi}$), Stokes shift ($\Delta\bar{\upsilon}$) and quantum yield (Φ). Figure 1 of ESI shows normalized absorption and emission spectra of all the synthesized biaryls. The biaryl compounds exhibited absorption maxima in the range of 230 to 370 nm, while emission maxima ranges from 405-466 nm. Stokes shifts were calculated for all the compounds and the amine substituted biaryl derivative **4i** found to have highest Stokes shift value 8784 cm^{-1} while the lowest Stokes shift value 4248 cm^{-1} for compound **4c**. The complete photophysical data along with fluorescence quantum yield (Φ_f) for the synthesized biaryls is summarized in Table 3. Interestingly,4-amino-4'-cyano-[1,1'-biphenyl]-3-carboxamide **4j** and 2-amino-5-(pyren-1-yl)benzamide **4d** showed quantum yields 0.844 and 0.514, respectively [50]. Terphenyl derivatives **4g** (0.336), **5a** (0.291) and methyl substituted biaryl derivatives **4l** (0.327), **4m** (0.237) showed relatively good quantum yields.

Table 3 Photophysical properties of biaryl derivatives **4a-p** and **5a**

Entry	Product	Absorption[a] $\lambda_{max,\ abs}$ (nm)	Emission $\lambda_{max,\ emi}$ (nm)	Stokes shift (cm^{-1})[b]	Quantum yield (Φ_f)[c]
1	**4a**	290, 321	412	6881	0.0874
2	**4b**	278, 370	417	8278	0.0380
3	**4c**	304, 360	425	4248	0.0541
4	**4d**	280, 352	466	6950	0.5143
5	**4e**	262, 307	408	8064	0.1971
6	**4f**	278, 310	417	8278	0.0662
7	**4g**	250, 311	417	8174	0.3362
8	**4h**	285, 350	416	4533	0.1834
9	**4i**	273, 310	426	8784	0.1590
10	**4j**	230, 325	415	6673	0.8449
11	**4k**	287, 350	418	4648	0.1579
12	**4l**	273, 341	406	4695	0.3276
13	**4m**	228, 348	405	4639	0.2378
14	**4n**	290, 345	414	4831	0.1641
15	**4o**	286, 348	415	4639	0.2333
16	**4p**	296, 353	416	4290	0.1104
17	**5a**	295, 355	425	4640	0.2916

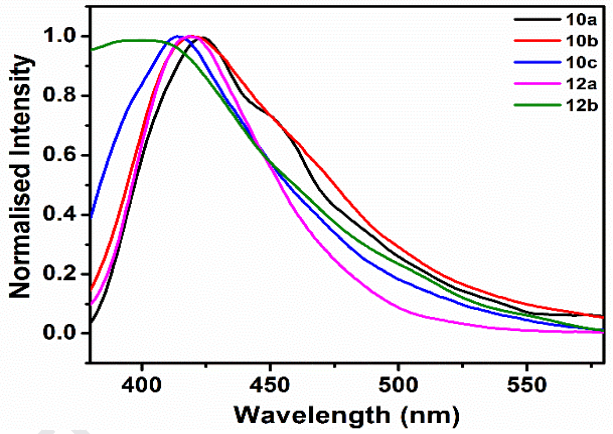
[a]Recorded in CH_3CN at 298 K; [b]Stokes shift = $\lambda_{max,\ abs}$ - $\lambda_{max,\ emi}$ [cm^{-1}]; [c]Determined with quinine sulfate as a standard (0.5 M H_2SO_4) Φ_f = 0.54 at excitation wavelength 366 nm.

In contrast, synthetically transformed biaryl derivatives **10a-c** and **12a-b** showed low quantum yields compared to biaryls derivatives **4j** and **4k** (Table 4, Fig. 5).

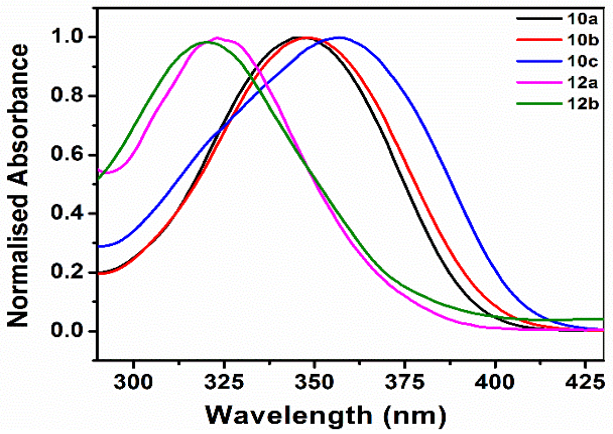
Table 4 Absorption and emission maxima of compounds **10a-c**, **12a,b**

Entry	Compound	Absorption[a] $\lambda_{max,\ abs}$ (nm)	Emission $\lambda_{max,\ emi}$ (nm)	Stokes shift, (cm^{-1})[b]	Quantum yield (Φ_f)[c]
1	**10a**	346	423	(5261)	0.0208
2	**10b**	348	420	(4926)	0.0035
3	**10c**	357	415	(3915)	0.0028
4	**12a**	324	418	(6941)	0.0904
5	**12b**	320	400	(6250)	0.0372

[a]Recorded in CH_3CN at 298 K; [b]Stokes shift = $\lambda_{max,\ abs}$ - $\lambda_{max,\ emi}$ (cm^{-1}); [c]Determined with quinine sulfate as a standard (0.5 M H_2SO_4) Φ_f = 0.54 at excitation wavelength 366 nm.



(a)



(b)

Fig. 5 (a) Normalised absorption spectra of biaryl derivatives **10a-c** and **12a-b** recorded in CH_3CN at C = 10^{-4} M at 298 K; (b) Normalised emission spectra of biaryl derivatives **10a-c** and **12a-b** recorded in CH_3CN at C = 10^{-4} M at 298 K.

Noteworthy, among all the synthesised blue emissive biaryls **4a-p,** and **5a,** compounds **4d** and **4j** showed high fluorescence quantum yield (Table 4) and thus could have a significant application in materials for organic light-emitting diode [51].

In conclusion, we have demonstrated a microwave assisted synthesis of 2-amino-3-carboxamide 1,1'-biaryls derivatives via Suzuki coupling reaction and the synthetic utility has been demonstrated by the preparation of 4-(phenylamino)-[1,1'-biphenyl]-3-carboxamides via Chan-Evans-Lam reaction and 4-(4'-oxo-3',4'-dihydro-1'H-spiro[fluorene-9,2'-quinazolin]-6'-yl)benzonitrile and 6-(4-methoxyphenyl)-2-(ferrocenyl)quinazolin-4(3H)-one via HPW catalysed condensation reaction. All the compounds were evaluated for photophysical properties and found luminescence in the blue region.

Supporting Information

Copies of FTIR, ^{1}H NMR, ^{13}C NMR, DEPT-135, HRMS spectra for all the new compounds and single crystal XRD data for compound **10a** are provided.

Conflicts of interest

There are no conflicts to declare.

Funding Information

M. N. thanks UGC (New Delhi) for the award of RGNF. PS thanks financial support from the DST (New Delhi) vide Grant No. SB/EMEQ-044/2014.

Acknowledgements

P. S. thanks the Director, CSIR-CLRI and S. K. thanks the Chancellor, VIT-Vellore for providing infrastructure facilities.

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Highlights

- Microwave assisted synthesis of blue emissive 2-amino-3-carboxamide 1, 1'-biaryls and amino-terphenyl-carboxamide derivatives via Suzuki coupling.
- Chemo selective synthesis of 4-(aryl amino)-[1, 1'-biphenyl]-3-carboxamide derivatives via Chan-Evans-Lam coupling reaction.
- HPW catalyzed synthesis of 4-(4'-oxo-3', 4'-dihydro-1'H-spiro[fluorene-9,2'-quinazolin]-6'-yl)benzonitrile and 6-(4-methoxyphenyl)-2-(ferrocenyl) quinazolin-4(3H)-one under solvent free microwave irradiation condition.
- All the synthesized compounds have been evaluated for photophysical properties, showed luminescence in the blue region with large Stokes shift and high quantum yields.

Declaration of interests

☒ The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

☐The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: