# **Supporting Information**

## **Table of Contents**

1.	General information	2
2.	General procedures	3
2.	.1 General procedure for preparation of alkynes	3
2.	.2 General procedure for preparation of various 2-substituted quinolines	3
2.	.3 General procedure for electrophilic aromatic borylation of 2-substituted quinolines	4
2.	.4 General procedure for bromine-alkyl group exchange with trialkyl-aluminiums	4
3.	Photographs of <b>1a-6e</b> in solid state under day and UV light	5
4.	UV-vis absorption and fluorescence spectra	7
4. st	.1 UV-vis absorption and fluorescence spectra of <b>1a-6e</b> in $CH_2Cl_2$ (DCM) and in the solid rate (Spincoated film prepared from a $CH_2Cl_2$ solution)	7
4.	.2 Solvatochromism studies with organoboron <b>2a</b>	12
4.	.3 UV and PL Spectra for <b>2a</b> in various solvents	12
5.	Measurement of fluorescence lifetime	13
6.	Thermo-gravimetric analysis (TGA) curve	16
7.	X-ray Crystallography	18
7.	.1 Crystal data	19
7.	2 ORTEP diagrams	20
7.	.3 Molecular packing patterns in the crystals in 2a, 5a and 6b	22
8.	DFT studies:	24
9.	HOMO- LUMO for optimized crystal geometries	28
10.	Bio-imaging studies	29
11.	Characterization data	32

#### 1. General information

Unless otherwise specified, all reactions were carried out in oven dried vials or reaction vessels with magnetic stirring under argon atmosphere. Dried solvents and liquid reagents were transferred by oven-dried syringes or hypodermic syringe cooled to ambient temperature in a desiccators. All experiments were monitored by analytical thin layer chromatography (TLC). TLC was performed on pre-coated silica gel plates. After elution, plate was visualized under UV illumination at 254 nm for UV active materials. Further visualization was achieved by staining KMnO<sub>4</sub> and charring on a hot plate. Solvents were removed in vacuo and heated with a water bath at 35 °C. Silica gel finer than 200 mesh was used for flash column chromatography. Columns were packed as slurry of silica gel in hexane and equilibrated with the appropriate solvent mixture prior to use. The compounds were loaded neat or as a concentrated solution using the appropriate solvent system. The elution was assisted by applying pressure with an air pump.

Melting points are uncorrected and recorded using digital Buchi Melting Point Apparatus B-540. <sup>1</sup>H NMR spectra and <sup>13</sup>C NMR spectra were recorded on Bruker AV, 400/500, MHz spectrometers in appropriate solvents using TMS as internal standard or the solvent signals as secondary standards and the chemical shifts are shown in  $\delta$  scales. Multiplicities of <sup>1</sup>H NMR signals are designated as s (singlet), br.s. (broad singlet), d (doublet), dd (doublet of doublet), t (triplet), m (multiplet)...etc. HRMS (ESI) data were recorded on a Thermo Scientific Q-Exactive, Accela 1250 pump. UV–visible absorption spectra were measured with a Perkin Elmer LAMBDA 950 UV/Vis Spectrophotometers. Fluorescence spectra were recorded by Photon Technology International, QuantaMaster<sup>TM</sup> 400 Spectrofluorometer and absolute quantum yields were determined using a calibrated integrating sphere system. Absolute quantum yields of the powder samples were recorded on Horiba Fluoromax Quanta- $\phi$  with a calibrated integrating sphere system. Time-resolved fluorescence spectra were measured using a Horiba - Lifetime Fluorescence Spectrofluorometers system equipped with a PLP-10 picosecond light pulser (LED wavelengths: 470 or 570 nm). Single-crystal data was collected on a Bruker SMART APEX II CCD diffractometer with graphite-monochromatized (MoK<sub> $\alpha$ </sub>= 0.71073Å) radiation.

## 2. General procedures

#### 2.1 General procedure for preparation of alkynes

The terminal alkynes  $\mathbf{a}^1$ ,  $\mathbf{b}^2$ ,  $\mathbf{c}^3$ ,  $\mathbf{d}^4$ ,  $\mathbf{e}^5$  and  $\mathbf{f}^6$  are prepared according to literature known procedures.



## 2.2 General procedure for preparation of various 2-substituted quinolines

The quinolines **1-6** were prepared by the method previously reported by us with slight modifications.<sup>7</sup> To a screw-cap vial containing stir bar, were added 2-amino benzaldehydes (0.3 mmol), terminal alkynes (0.36 mmol, 1.2 equiv.), PPh<sub>3</sub>AuCl (5 mol %), AgOTf (5 mol %), dry DCE (2 ml) and *p*-anisidine (25 mol %). The reaction vial was fitted with cap, evacuated and filled with nitrogen and heated at 100 °C for 12 h. The reaction mixture was allowed to bring to ambient temperature. The reaction mixture was diluted with ethyl acetate and filtered through a plug of silica gel. The filtrate was concentrated under reduced pressure and the resulting residue was purified by column chromatography (hexane/EtOAc) to give the desired 2-substituted quinolines.

<sup>&</sup>lt;sup>1</sup> B. Blanco, A. Sedes, A. Peón, H. Lamb, A. R. Hawkins, L. Castedoc, C. González-Bello, Org. Biomol. Chem., 2012, **10**, 3662.

<sup>&</sup>lt;sup>2</sup> M. Planells, A. Abate, D. J. Hollman, S. D. Stranks, V. Bharti, J. Gaur, D. Mohanty, S. Chand, H. J. Snaith, N. Robertson, *J. Mater. Chem. A*, 2013, **1**, 6949.

<sup>&</sup>lt;sup>3</sup> V. V. Filichev, I. V. Astakhova, A. D. Malakhov, V. A. Korshun, E. B. Pedersen, Chem. Eur. J., 2008, 14, 9968.

<sup>&</sup>lt;sup>4</sup> M. Hayashi, R. Sakamoto, H. Nishihara, Chem. Eur. J., 2012, 18, 8610.

<sup>&</sup>lt;sup>5</sup> S. Grunder, D. M. Torres, C. Marquardt, A. Błaszczyk, R. Krupke, M. Mayor, Eur. J. Org. Chem., 2011, 478-496.

<sup>&</sup>lt;sup>6</sup> R. C. Lirag, Ha T. M. Le, O. Š. Miljanić, Chem. Commun., 2013, 49, 4304.

<sup>&</sup>lt;sup>7</sup> a) N. T. Patil, V. S. Raut, *J. Org. Chem.*, 2010, **75**, 6961; b) N. T. Patil, V. S. Raut, R. B. Tella, *Chem. Comm.*, 2013, **49**, 570-572; c) H. Li, C. Wang, H. Huang, X. Xu, Y. Li *Tetrahedron Lett.*, 2011, **52**, 1108-1111.



#### 2.3 General procedure for electrophilic aromatic borylation of 2-substituted quinolines

To a stirred solution of 2-substituted quinolines (0.65 mmol) and *i*-Pr<sub>2</sub>NEt (0.65 mmol) in  $CH_2Cl_2$  (5 ml) at 0 °C was added BBr<sub>3</sub> (1.0 M in  $CH_2Cl_2$ , 1.9 mmol). After being stirred at rt for 24 h, saturated aqueous K<sub>2</sub>CO<sub>3</sub> solution was added to the reaction mixture. The reaction mixture was poured into water, the organic layer was separated and extracted with  $CH_2Cl_2$ , washed with water and brine. The organic layer was dried over  $Na_2SO_4$  and concentrated under reduced pressure to afford crude products which was washed with hexane to give quinoline-borane complexes. The products this obtained were used directly for next reaction.

## 2.4 General procedure for bromine-alkyl group exchange with trialkyl-aluminiums

To a stirred solution of quinoline-borane complex (0.35 mmol) in 1:1 toluene/CH<sub>2</sub>Cl<sub>2</sub> (10 ml) at room temperature was added R<sub>3</sub>Al (1.1 M in hexane, 0.77 mmol), After being stirred at this temperature for 30 min, the reaction was quenched by adding water. The organic layer was extracted with  $CH_2Cl_2$  and washed with water followed by brine. The organic layer was dried over MgSO<sub>4</sub> and then concentrated and the resultant residue was purified by silica-gel column chromatography by using pet ether/EtOAc mixture as eluent to products.

Compound	Day light	UV light
1a		
2a		
2b		
2c		
3a		
3b	- 200	
4a		
4b	e en	a la
4c		

# 3. Photographs of 1a-6e in solid state under day and UV light

5a	
6a	
6b	
60	
6d	
6e	

## 4. UV-vis absorption and fluorescence spectra

4.1 UV-vis absorption and fluorescence spectra of 1a-6e in CH<sub>2</sub>Cl<sub>2</sub> (DCM) and in the solid state (Spincoated film prepared from a CH<sub>2</sub>Cl<sub>2</sub> solution)











## 4.2 Solvatochromism studies with organoboron 2a

Solvent	$\lambda_{abs}$	λ <sub>em</sub>	Stokes shift	$\Phi_{\rm f}$
			(cm <sup>-1</sup> )	
Hexane	455 nm	472 nm	0790	0.78
Toluene	445 nm	505 nm	2268	0.59
CHCl <sub>3</sub>	437 nm	528 nm	3940	0.53
Ethyl Acetate	430 nm	533 nm	4488	0.45
THF	433 nm	537 nm	4468	0.44
$CH_2Cl_2$	433 nm	546 nm	4774	0.56
MeOH	426 nm	545 nm	5121	0.35
Acetone	425 nm	558 nm	5598	0.49
CH <sub>3</sub> CN	422 nm	574 nm	6268	0.35
DMF	430 nm	569 nm	5676	0.31
DMSO	431 nm	578 nm	5898	0.22

## 4.3 UV and PL Spectra for 2a in various solvents



## 5. Measurement of fluorescence lifetime

The fluorescence lifetime for all organoborons **1a-6e** were measured in  $CH_2Cl_2$  upon excitation at 431 nm and 591 nm. All compounds have more or less similar lifetime values ranging in between 2.5 -6.9 ns.









## 6. Thermo-gravimetric analysis (TGA) curves for selected organoborons



## 7. X-ray Crystallography

X-ray intensity data measurements of compounds 2a, 3a, 4a, 5a and 6b were carried out on a Bruker SMART APEX II CCD diffractometer with graphite-monochromatized (MoK<sub> $\alpha$ </sub>= 0.71073Å) radiation. The X-ray generator was operated at 50 kV and 30 mA. A preliminary set of cell constants and an orientation matrix were calculated from three sets of 36 frames. Data were collected with  $\omega$  scan width of 0.5° at different settings of  $\varphi$  and  $2\theta$ with a frame time of 10 sec for 2a, 3a, 6b and 15 ,20 sec for 4a, 5a respectively, keeping the sample-to-detector distance fixed at 5.00 cm. The X-ray data collection was monitored by APEX2 program (Bruker, 2006).<sup>8</sup> All the data were corrected for Lorentzian, polarization and absorption effects using SAINT and SADABS programs (Bruker, 2006). SHELX-97 was used for structure solution and full matrix least-squares refinement on  $F^{2,9}$  All the hydrogen atoms were placed in geometrically idealized position and constrained to ride on their parent atoms. An ORTEP view of all five compounds were drawn with 50% probability displacement ellipsoids and H atoms are shown as small spheres of arbitrary radii.

<sup>&</sup>lt;sup>8</sup> Bruker (2006). APEX2, SAINT and SADABS. Bruker AXS Inc., Madison, Wisconsin, USA.

<sup>&</sup>lt;sup>9</sup> G. M. Sheldrick, Acta Crystallogr., 2008, A64, 112.

## 7.1 Crystal data

	2a	<b>3</b> a	<b>4</b> a	<b>5</b> a	6b
Mol. formula	$C_{29}H_{25}BN_2$	C <sub>27</sub> H <sub>20</sub> BN	$C_{29}H_{23}BN_2$	C <sub>25</sub> H <sub>20</sub> B N	$C_{21}H_{25}B N_2$
Mr	412.32	369.25	410.30	345.23	316.24
Temp. (K)	200(2)	293(2)	293(2)	150(2)	150(2)
Crystal system	monoclinic	monoclinic	triclinic	monoclinic	triclinic
Space group	$P2_1/n$	$P2_{1}/c$	<i>P</i> -1	$P2_1/n$	<i>P</i> -1
a/Å	17.3899(3)	8.8980(4)	9.3145(5)	13.9351(7)	7.9636(2)
b/Å	10.3122(2)	7.0675(3)	9.7778(6)	9.0239(5)	8.8054(2)
c/Å	26.5129(5)	30.3620(14)	12.5665(7)	14.1194(8)	14.8492(5)
α/°	90	90	83.550(3)	90	106.476(2)
β/°	108.4870(10)	98.000(3)	84.896(3)	92.128(3)	90.570(2)
γ/°	90	90	76.744(3)	90	116.512(2)
V/Å <sup>3</sup>	4509.15(14)	1890.78(15)	1104.59(11)	1774.28(17)	882.12(4)
Z, $D_{calc}/g \text{ cm}^{-3}$	8, 1.215	4, 1.297	2, 1.234	4, 1.292	2, 1.191
μ/mm <sup>-1</sup>	0.070	0.074	0.071	0.074	0.069
F (000)	1744	776	432	728	340
θ max/°	25.00	25.00	25.00	25.00	25.00
Absor.	multi-scan	multi-scan	multi-scan	multi-scan	multi-scan
correction					
Refln. collected	63086	13377	15850	22665	12311
Unique refln.	7928	3338	3879	3108	3115
Observed refln.	6507	2420	3046	2911	2747
R <sub>int</sub>	0.0588	0.0472	0.0305	0.0478	0.0213
No. of parameter	581	265	291	247	221
$R_1_{obs}, R_1_{all}$	0.0776,	0.0576,	0.0586,	0.1623,	0.0417,
	0.0965	0.0804	0.0755	0.1655	0.0481
$wR_2$ _obs,	0.1548,	0.1232,	0.1330,	0.4284,	0.1004,
$wR_2\_all$	0.1640	0.1344	0.1416	0.4295	0.1044
GoF	1.150	1.068	1.114	1.212	1.027

$\Delta \rho_{\text{max}}, \Delta \rho_{\text{min}}/e \text{\AA}^{-3}$	0.246, -0.255	0.187, -0.198	0.317, -0.200	0.588,-0.596	0.238, -0.188
CCDC	1408898	1408899	1408900	1408901	1408902

## 7.2 ORTEP diagrams





## 7.3 Molecular packing patterns in the crystals in 2a, 5a and 6b



Organoboron 2a:

Organoboron 5a:



Organoboron 6b:



Note: The single crystal packing of organoborons 2a, 3a and 4a is provided in the main text.

## 8. DFT studies:

We also investigated the electrochemical properties of N,C-chelate four-coordinate organoborons to evaluate their potential applicability in electronic devices by DFT studies. The absorption bands of all N,C-chelate four-coordinate organoborons be essentially assigned due to the intramolecular charge-transfer transition from the highest occupied molecular orbital (HOMO) delocalized over the orbitals from the aromatic substituent at 2 position of quinoline moiety to the lowest unoccupied molecular orbital (LUMO) mainly localized on quinoline rings and the boron centers. The calculated HOMO energy level of all N,C-chelate four-coordinate organoborons between -0.0743 to -0.1084. The LUMO energy level is between -0.2128 to -0.1884. The energy gap ( $\Delta$ ) varied between 0.0880 Hartee and 0.1235 Hartee.

Sr.No	Organoboron	НОМО	LUMO	$\Delta$ (Hartee)	Wavelength
		(Hartee)	(Hartee)		(nm)
1	1a	-0.2123	-0.0898	0.1224	371.9
2	2a	-0.1891	-0.0821	0.1070	425.8
3	2b	-0.1899	-0.0826	0.1073	424.6
4	2c	-0.1884	-0.1003	0.0880	517.2
5	<b>3</b> a	-0.1957	-0.0895	0.1061	429.1
6	3b	-0.2063	-0.1084	0.0979	465.4
7	4a	-0.2045	-0.0872	0.1173	388.4
8	4b	-0.2013	-0.0927	0.1085	419.6
9	4c	-0.2128	-0.1065	0.1063	428.6
10	5a	-0.2113	-0.0878	0.1235	368.9
11	6a	-0.1901	-0.0743	0.1157	393.5
12	6b	-0.1910	-0.0753	0.1156	393.8
13	6c	-0.1913	-0.0752	0.1160	392.5
14	6d	-0.1937	-0.0795	0.1142	398.9
15	6e	-0.2035	-0.0944	0.1091	417.6







4b















4c





0.1235









6a







-0.1901

¢ -0.0878



0.1157

НОМО



6b









0.1156



LUMO

-0.0753



Br Br

6e

6c



-0.1937

0.1142



-0.0795

, Me Ń Me

-0.2035

۲

0.1091

-0.0944

Organo-	НОМО	LUMO
boron		
<b>3</b> a		
4a		
5a		

# 9. HOMO- LUMO for optimized crystal geometries

#### 10. Bio-imaging studies

**Materials:** MCF-7 cells were obtained from National Centre for Cell Science, Pune, India. Dulbecco's Modified Eagle Medium (DMEM), Dulbecco's Phosphate Buffered Saline (DPBS), Fetal Bovine Serum (FBS), MTT (3-(4,5-dimethylthiazol-2-yl)-2,5-diphenyl tetrazolium bromide), DAPI and coverslips for confocal microscopy were purchased from Sigma-Aldrich, USA.

**Sample preparation for** *in vitro* **studies**: The stock solutions (10 mM) of the organic molecules were prepared in DMSO solvent. Each time, the freshly prepared stock solutions were used for all the cell culture experiments.

**Cell viability assay**: Cell viability assay was performed in MCF-7 cells using MTT (3-(4,5dimethylthiazol-2-yl)-2,5-diphenyl tetrazolium bromide) reagent according to published reports.<sup>10</sup> Briefly, compounds at concentration of 1,10 and 20 $\mu$ M dissolved in DMSO were added to the cells in media without FBS in 96 well plate. DMSO was used as a control. MTT assay was carried out after 24 h incubation. A MTT solution (20 $\mu$ l, 5mg/mL) was prepared in PBS pH 7.4 then added to each well and incubated for 3 h. The purple formazan crystals formed were dissolved by addition of 150 $\mu$ l of DMSO for 5 min absorbance was measured using Biotek Synergy HT, microplate reader. IC<sub>50</sub> was determined by using ED50V10 excel add-on software. Finally, the absorbance of solution was measured using a multimode reader (Biotek Synergy) at 570 nm.

**Cell culture**: MCF-7 cells were seeded on the cover slips in a 6 well plate at a density of 10<sup>5</sup> cells/mL in Dulbecco's Modified Eagle's Medium+Ham's F12 containing 10% Fetal Bovine Serum and a 0.1% antibiotic solution for 24 h at 37 °C and 5% CO<sub>2</sub> for adherence.

**Confocal imaging**: The cells were then treated with 1 $\mu$ M concentration of different organic molecules for 30 min. After through washing with 1X PBS (pH 7.4), the cells were permeated using the cells 0.2% triton X. After permeation, cells were incubated with 1  $\mu$ g/mL of DAPI solution for 10 min. The cells were again washed twice with 1X PBS (pH 7.4). Finally, images were captured using a confocal scanning laser microscope (Leica, TCS, SP8, Germany). While bio-imaging, cells were treated with compounds and then co-stained with nuclear stain DAPI. However except compound **2c**, all other compounds show

<sup>&</sup>lt;sup>10</sup> S. N. Ramteke, G. R. Walke, B. N. Joshi, S. Rapole, P. Kulkarni, Free Radic Res, 2014, 12, 1417.

interference due to DAPI stain ( $\lambda_{Em}$ : 470-490 nm). Thus images were captured without DAPI using 100X oil emersion objective.



**Confocal images of MCF 7 cells**. 1A, 2A, 3A showing optical image and 1B, 2B, 3B showing fluorescence image after MCF 7 cells treated with 1  $\mu$ M of **3a**, **5a**, **6a** for 30 min respectively. 4A showing fluorescence image after MCF 7 cells treated with 1  $\mu$ M of **2c** for 30 min, 4C showing nucleus stained by DAPI and 4B merged images of 4A and 4C.



Cell viability assay in MCF-7 cells using MTT reagent

Results obtained from MTT assay revealed that all the selected organoborons exhibit almost no toxicity at 1  $\mu$ M concentration and do not cause any morphological abnormality to MCF-7 cells. This result indicates the bio-compatibility of these novel fluorescent organoborons with cancerous cells and therefore could have potential application in bio-imaging.

#### 11. Characterization data

**2-substituted quinolines:** 



(1): light yellow solid, 88% yield; mp = 198-199 °C;  $R_f = 0.90$  (Pet. ether/EtOAc = 90/10); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta = 8.17$  (t, J = 8.2 Hz, 2 H), 7.98 (s, 1 H), 7.96 - 7.88 (m, 2 H), 7.87 - 7.83 (m, 1 H), 7.82 - 7.78 (m, 1 H), 7.74 (ddd, J = 1.6, 6.8, 8.5 Hz, 1 H), 7.57 - 7.50 (m, 1 H), 7.42 - 7.34 (m, 2 H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta = 152.2$ , 148.0, 145.4, 141.1, 140.4, 136.6, 129.9, 129.4, 127.5, 126.5, 125.3, 124.5, 124.3, 122.6, 122.4, 117.8, 113.2; HRMS (ESI) calcd for C<sub>17</sub>H<sub>12</sub>NS (M<sup>+</sup>+ H) 262.0685, found 262.0683.



(2): light yellow solid, 92% yield; mp = 162-163 °C;  $R_f = 0.75$  (Pet. ether/EtOAc = 90/10); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  = 8.23 - 8.13 (m, 2 H), 8.11 - 8.01 (m, 2 H), 7.87 - 7.78 (m, 2 H), 7.77 - 7.67 (m, 1 H), 7.55 - 7.46 (m, 1 H), 7.36 - 7.28 (m, 4 H), 7.26 - 7.15 (m, 6 H), 7.14 - 7.04 (m, 2 H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  = 156.9, 149.0, 148.3, 147.4, 136.6, 133.2, 129.5, 129.3, 128.4, 127.4, 126.9, 125.9, 124.8, 123.3, 123.1, 118.6; HRMS (ESI) calcd for C<sub>27</sub>H<sub>21</sub>N<sub>2</sub> (M<sup>+</sup>+ H) 373.1699, found 373.1698.



(3): light yellow solid, 88% yield; mp = 148-149 °C;  $R_f = 0.82$  (Pet. ether/EtOAc = 90/10); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta = 8.46$  (d, J = 9.3 Hz, 1 H), 8.37 (d, J = 8.3 Hz, 1 H), 8.34 - 8.27

(m, 3 H), 8.26 - 8.19 (m, 2 H), 8.18 - 8.13 (m, 2 H), 8.10 (d, J = 9.3 Hz, 1 H), 8.07 - 8.02 (m, 1 H), 8.00 - 7.95 (m, 1 H), 7.88 (d, J = 8.3 Hz, 1 H), 7.83 (ddd, J = 1.6, 6.8, 8.4 Hz, 1 H), 7.65 (ddd, J = 1.2, 6.9, 8.3 Hz, 1 H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta = 159.7$ , 148.3, 136.2, 135.9, 131.6, 131.4, 130.9, 129.8, 129.8, 128.8, 128.2, 128.0, 127.7, 127.6, 127.4, 126.9, 126.6, 126.0, 125.4, 125.1, 124.9, 124.8, 123.8; HRMS (ESI) calcd for C<sub>25</sub>H<sub>16</sub>N (M<sup>++</sup> H) 330.1277, found 330.1277.



(4): light yellow solid, 82% yield; mp = 155-156 °C;  $R_f = 0.85$  (Pet. ether/EtOAc = 90/10); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  = 8.46 - 8.38 (m, 2 H), 8.32 (d, J = 8.6 Hz, 1 H), 8.23 (d, J = 8.6 Hz, 1 H), 8.18 (d, J = 7.8 Hz, 2 H), 7.99 (d, J = 8.6 Hz, 1 H), 7.92 - 7.86 (m, 1 H), 7.82 - 7.72 (m, 3 H), 7.59 (ddd, J = 1.3, 6.8, 8.2 Hz, 1 H), 7.55 - 7.49 (m, 2 H), 7.45 (dt, J = 1.3, 7.6 Hz, 2 H), 7.37 - 7.30 (m, 2 H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)  $\delta$  = 156.3, 148.3, 140.6, 138.6, 138.5, 136.9, 129.8, 129.7, 129.3, 129.0, 127.5, 127.2, 126.4, 126.0, 123.5, 120.3, 120.1, 118.7, 113.1, 109.8; HRMS (ESI) calcd for C<sub>27</sub>H<sub>19</sub>N<sub>2</sub> (M<sup>+</sup>+ H) 371.1543, found 371.1541.



(5): off white solid, 90% yield; mp = 118-119 °C  $R_f$  = 0.88 (Pet. ether/EtOAc = 90/10); <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  = 8.82 (d, J = 8.1 Hz, 1 H), 8.76 (d, J = 8.1 Hz, 1 H), 8.33 (d, J = 8.3 Hz, 1 H), 8.26 (d, J = 8.6 Hz, 1 H), 8.16 - 8.07 (m, 1 H), 8.03 - 7.91 (m, 3 H), 7.86 - 7.68 (m, 4 H), 7.68 - 7.60 (m, 2 H), 7.60 - 7.52 (m, 1 H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)  $\delta$  = 159.5, 148.1, 137.4, 136.3, 131.4, 130.9, 130.5, 130.3, 129.8, 129.7, 129.1, 128.8, 127.6, 127.1, 127.1, 126.9, 126.8, 126.7, 126.6, 123.3, 123.0, 122.6; **HRMS (ESI)** calcd for  $C_{23}H_{16}N$  (M<sup>++</sup> H) 306.1277, found 306.1278.



(6): off white solid, 86% yield; mp = 180-181 °C  $R_f$  = 0.82 (Pet. ether/EtOAc = 90/10); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  = 8.17 - 8.06 (m, 4 H), 7.84 (d, J = 8.6 Hz, 1 H), 7.80 - 7.74 (m, 1 H), 7.72 - 7.65 (m, 1 H), 7.50 - 7.42 (m, 1 H), 6.89 - 6.79 (m, 2 H), 3.06 (s, 6 H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  = 157.3, 151.3, 148.4, 136.2, 129.3, 128.4, 127.3, 126.7, 125.3, 118.3, 112.2, 40.3; HRMS (ESI) calcd for C<sub>17</sub>H<sub>17</sub>N<sub>2</sub> (M<sup>+</sup>+ H) 249.1386, found 249.1386.

**Organoborons:** 



(1a): bluish solid, 91% yield; mp = 207-208 °C;  $R_f$  = 0.55 (Pet. ether/EtOAc = 80/20); <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  = 8.56 (d, J = 8.5 Hz, 1 H), 8.33 (d, J = 8.5 Hz, 1 H), 8.18 - 8.11 (m, 1 H), 7.99 - 7.94 (m, 1 H), 7.92 (d, J = 8.2 Hz, 1 H), 7.88 - 7.82 (m, 1 H), 7.71 (d, J = 8.5 Hz, 1 H), 7.57 (t, J = 7.5 Hz, 1 H), 7.48 - 7.37 (m, 2 H), 0.43 (s, 6 H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)  $\delta$  = 154.5, 146.5, 142.5, 140.6, 140.5, 133.4, 131.6, 129.0, 126.5, 126.4, 126.0, 125.8, 124.5, 123.4, 122.3, 116.6, 8.9; HRMS (ESI) calcd for C<sub>19</sub>H<sub>17</sub>NBS (M<sup>+</sup>+ H) 302.1169, found 302.1169.



(2a): greenish yellow solid, 90% yield; mp = 168-169 °C;  $R_f$  = 0.60 (Pet. ether/EtOAc = 80/20); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  = 8.55 (d, J = 8.8 Hz, 1 H), 8.29 (d, J = 8.6 Hz, 1 H), 7.96 - 7.86 (m, 2 H), 7.83 - 7.72 (m, 2 H), 7.61 - 7.49 (m, 1 H), 7.42 - 7.36 (m, 1 H), 7.36 - 7.28 (m, 4 H), 7.26 - 7.19 (m, 4 H), 7.15 - 7.07 (m, 2 H), 7.00 - 6.89 (m, 1 H), 0.23 (s, 6 H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  = 157.2, 150.5, 147.6, 142.1, 139.8, 131.1, 129.4, 129.3, 128.7, 127.0, 125.7, 125.4, 125.3, 123.4, 123.3, 123.0, 121.4, 119.7, 115.5, 9.2; HRMS (ESI) calcd for C<sub>29</sub>H<sub>26</sub>N<sub>2</sub>B (M<sup>+</sup>+ H) 413.2184, found 413.2179.



(2b): yellow solid, 73% yield; mp = 155-156 °C  $R_f$  = 0.70 (Pet. ether/EtOAc = 90/10); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  = 8.52 (d, J = 8.8 Hz, 1 H), 8.30 (d, J = 8.6 Hz, 1 H), 7.90 (d, J = 8.1 Hz, 1 H), 7.93 (d, J = 8.6 Hz, 1 H), 7.81 - 7.76 (m, 2 H), 7.56 (d, J = 7.3 Hz, 1 H), 7.39 (s, 1 H), 7.29 (d, J = 7.6 Hz, 5 H), 7.22 (s, 4 H), 7.09 (d, J = 7.1 Hz, 2 H), 6.96 (d, J = 8.3 Hz, 1 H), 1.43 (br. s., 2 H), 1.35 (s, 2 H), 1.30 (br. s., 13 H), 1.04 - 0.79 (m, 10 H), 0.29 (t, J = 7.6 Hz, 6 H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  = 158.3, 150.0, 147.7, 142.3, 139.7, 131.2, 129.4, 129.2, 128.7, 125.8, 125.1, 123.2, 123.0, 122.6, 122.4, 120.1, 115.3, 113.2, 31.9, 31.4, 30.2, 29.7, 29.4, 22.7, 17.1, 14.1, 14.1, 10.0; HRMS (ESI) calcd for C<sub>43</sub>H<sub>54</sub>N<sub>2</sub>B (M<sup>++</sup> H) 609.4153, found 609.4155.



(2c): red solid, 94% yield; mp = 289-290 °C;  $R_f$  = 0.30 (CH<sub>2</sub>Cl<sub>2</sub>/MeOH = 95/05); <sup>1</sup>H NMR (400 MHz, CD<sub>2</sub>Cl<sub>2</sub>)  $\delta$  = 9.10 - 9.01 (m, 1 H), 8.50 (d, J = 8.8 Hz, 1 H), 7.98 (d, J = 7.3 Hz, 2 H), 7.86 (d, J = 8.6 Hz, 1 H), 7.71 (d, J = 8.6 Hz, 1 H), 7.68 - 7.60 (m, 1 H), 7.43 - 7.32 (m, 5 H), 7.26 - 7.17 (m, 6 H), 6.98 (dd, J = 2.4, 8.6 Hz, 1 H); <sup>13</sup>C NMR (100 MHz, CD<sub>2</sub>Cl<sub>2</sub>)  $\delta$  = 147.1, 145.2,

132.9, 130.3, 129.7, 128.3, 127.7, 127.0, 126.3, 125.5, 124.9, 123.9, 121.2, 120.6, 115.8; **HRMS** (ESI) calcd for C<sub>27</sub>H<sub>20</sub>N<sub>2</sub>BBr<sub>2</sub> (M<sup>+</sup>+ H) 543.0060, found 543.0061.



(3a): dark yellow solid, 88% yield; mp = 192-193 °C;  $R_f$  = 0.62 (Pet. ether/EtOAc = 80/20); <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  = 9.05 (d, J = 9.2 Hz, 1 H), 8.96 (d, J = 9.2 Hz, 1 H), 8.83 (d, J = 8.9 Hz, 1 H), 8.53 (d, J = 9.2 Hz, 1 H), 8.49 (s, 1 H), 8.30 (d, J = 9.2 Hz, 1 H), 8.27 - 8.20 (m, 2 H), 8.15 (q, J = 8.9 Hz, 2 H), 8.06 - 7.95 (m, 2 H), 7.95 - 7.87 (m, 1 H), 7.66 (t, J = 7.5 Hz, 1 H), 0.46 (s, 6 H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)  $\delta$  = 159.7, 148.3, 140.2, 136.2, 135.9, 131.6, 130.9, 129.9, 128.8, 128.7, 128.5, 128.0, 127.7, 127.4, 126.9, 126.7, 126.5, 126.0, 125.5, 125.3, , 125.1, 124.8, 123.8, 122.1, 119.7, 1.0; HRMS (ESI) calcd for C<sub>27</sub>H<sub>21</sub>N<sub>2</sub>B (M<sup>+</sup>+ H) 370.1785, found 370.1785.



(3b): reddish solid, 92% yield; mp = 155-156 °C;  $R_f$  = 0.30 (DCM/MeOH = 95/05); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  = 8.43 (d, J = 9.3 Hz, 1 H), 8.34 - 8.21 (m, 5 H), 8.18 - 8.09 (m, 5 H), 8.08 - 8.03 (m, 1 H), 7.92 - 7.86 (m, 2 H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  = 160.1, 146.9, 135.4, 135.2, 133.3, 131.8, 131.5, 131.4, 130.9, 129.6, 128.8, 128.3, 128.2, 128.0, 127.7, 127.4, 126.1, 125.6, 125.3, 125.1, 124.9, 124.8, 124.6, 120.5; HRMS (ESI) calcd for C<sub>25</sub>H<sub>16</sub>N<sub>2</sub>BBr<sup>81</sup>Br (M<sup>++</sup> H) 497.9586, found 497.9588.



(4a): yellow solid, 90% yield; mp = 201-202 °C;  $R_f$  = 0.56 (Pet. ether/EtOAc = 80/20); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  = 8.70 (d, J = 8.8 Hz, 1 H), 8.44 (d, J = 8.6 Hz, 1 H), 8.17 (d, J = 8.1 Hz, 1 H), 8.20 (d, J = 7.6 Hz, 2 H), 8.12 (d, J = 8.8 Hz, 1 H), 8.01 - 7.95 (m, 2 H), 7.90 (ddd, J = 1.6, 7.0, 8.7 Hz, 1 H), 7.69 - 7.62 (m, 3 H), 7.56 (dd, J = 2.0, 8.1 Hz, 1 H), 7.51 - 7.43 (m, 2 H), 7.37 - 7.30 (m, 2 H), 0.39 (s, 6 H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  = 156.9, 142.1, 140.7, 140.6, 139.9, 134.1, 131.5, 128.9, 127.6, 126.6, 125.9, 123.6, 123.6, 123.5, 123.4, 120.2, 120.0, 115.7, 110.3, 9.1; HRMS (ESI) calcd for C<sub>29</sub>H<sub>24</sub>N<sub>2</sub>B (M<sup>+</sup>+ H) 411.2027, found 411.2028.



(4b): yellow solid, 70% yield; mp = 188-189 °C  $R_f$  = 0.72 (Pet. ether/EtOAc = 90/10); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  = 8.68 (d, J = 8.8 Hz, 1 H), 8.45 (d, J = 8.8 Hz, 1 H), 8.21 (d, J = 7.8 Hz, 3 H), 8.14 (d, J = 8.8 Hz, 1 H), 7.99 (d, J = 8.1 Hz, 1 H), 7.96 - 7.93 (m, 1 H), 7.90 (d, J = 8.3 Hz, 1 H), 7.68 - 7.64 (m, 1 H), 7.62 (d, J = 8.1 Hz, 2 H), 7.58 - 7.55 (m, 1 H), 7.49 (d, J = 7.1 Hz, 2 H), 7.34 (t, J = 7.3 Hz, 2 H), 1.37 (br. s., 2 H), 1.29 (s, 11 H), 1.24 (br. s., 1 H), 1.16 (dd, J = 7.7, 13.8 Hz, 4 H), 1.03 (dd, J = 7.5, 13.8 Hz, 4 H), 0.96 - 0.79 (m, 6 H), 0.40 (t, J = 7.6 Hz, 6 H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  = 157.9, 142.3, 140.8, 140.5, 139.4, 137.1, 135.5, 131.6, 129.9, 129.7, 129.1, 128.9, 127.5, 127.4, 127.3, 127.0, 126.6, 126.0, 125.9, 123.6, 123.4, 122.8, 120.4, 120.3, 120.1, 119.9, 118.8, 115.5, 110.2, 109.9, 31.9, 29.7, 29.4, 22.7, 17.1, 17.0, 14.1, 10.1; HRMS (ESI) calcd for C<sub>43</sub>H<sub>52</sub>N<sub>2</sub>B (M<sup>++</sup> H) 607.4153, found 607.4155.



(4c): orange solid, 92% yield; mp = 231-232 °C;  $R_f$  = 0.40 (DCM/MeOH = 95/05); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  = 8.44 - 8.36 (m, 2 H), 8.22 - 8.16 (m, 3 H), 8.09 (d, J = 8.9 Hz, 1 H), 8.04 (d, J = 2.1 Hz, 1 H), 8.00 (d, J = 8.5 Hz, 1 H), 7.84 (dd, J = 2.3, 9.0 Hz, 1 H), 7.79 - 7.74 (m, 2 H), 7.54 - 7.49 (m, 2 H), 7.46 (dt, J = 1.2, 7.6 Hz, 2 H), 7.36 - 7.31 (m, 2 H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  = 156.7, 146.9, 140.6, 139.0, 138.1, 136.0, 133.3, 131.4, 129.6, 129.4, 129.0, 128.3, 127.3, 126.0, 123.5, 120.4, 120.3, 120.2, 119.6, 118.2, 113.2, 109.8; HRMS (ESI) calcd for C<sub>27</sub>H<sub>18</sub>N<sub>2</sub>BBr<sup>81</sup>Br (M<sup>++</sup> H) 540.9904, found 540.9903.



(5a): bluish green solid, 88% yield; mp = 242-243 °C;  $R_f$  = 0.80 (Pet. ether/EtOAc = 90/10); <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  = 8.91 - 8.85 (m, 1 H), 8.83 - 8.73 (m, 4 H), 8.67 - 8.61 (m, 1 H), 8.51 - 8.42 (m, 1 H), 8.01 - 7.97 (m, 1 H), 7.91 (ddd, J = 1.6, 7.0, 8.8 Hz, 1 H), 7.79 - 7.72 (m, 3 H), 7.69 (ddd, J = 1.4, 6.9, 8.2 Hz, 1 H), 7.66 - 7.61 (m, 1 H), 0.58 (s, 6 H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)  $\delta$  = 158.4, 142.0, 140.0, 131.2, 131.1, 128.8, 128.2, 126.9, 126.7, 126.6, 126.5, 125.0, 124.0, 123.3, 123.2, 123.0, 122.6, 119.1, 10.9; HRMS (ESI) calcd for C<sub>25</sub>H<sub>21</sub>NB (M<sup>+</sup>+ H) 346.1762, found 346.1762.



(6a): yellow solid, 91% yield; mp = 154-156 °C;  $R_f$  = 0.62 (Pet. ether/EtOAc = 80/20); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  = 8.54 (d, J = 8.6 Hz, 1 H), 8.17 (d, J = 8.8 Hz, 1 H), 7.89 - 7.80 (m, 3 H), 7.80 - 7.72 (m, 1 H), 7.48 (t, J = 7.6 Hz, 1 H), 7.05 - 6.94 (m, 1 H), 6.73 - 6.65 (m, 1 H), 3.14 (s, 6 H), 0.41 - 0.21 (m, 6 H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta = 157.8$ , 152.4, 142.2, 139.3, 130.8, 128.7, 126.6, 124.9, 124.5, 123.9, 122.5, 115.4, 110.4, 109.9, 40.4, 9.54; HRMS (ESI) calcd for C<sub>19</sub>H<sub>22</sub>N<sub>2</sub>B (M<sup>+</sup>+ H) 289.1871, found 289.1871.



(6b): yellow solid, 82% yield; mp = 154-156 °C;  $R_f$  = 0.70 (Pet. ether/EtOAc = 90/10); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  = 8.47 (d, J = 8.8 Hz, 1 H), 8.20 (d, J = 8.8 Hz, 1 H), 7.93 - 7.79 (m, 3 H), 7.74 (ddd, J = 1.6, 7.0, 8.7 Hz, 1 H), 7.55 - 7.43 (m, 1 H), 6.95 (d, J = 2.7 Hz, 1 H), 6.69 (dd, J = 2.4, 8.6 Hz, 1 H), 3.13 (s, 6 H), 1.02 - 0.86 (m, 4 H), 0.40 - 0.26 (m, 6 H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  = 159.0, 152.1, 142.5, 139.2, 130.9, 128.6, 126.3, 126.2, 125.0, 123.5, 122.0, 115.2, 111.0, 109.7, 40.4, 9.9; HRMS (ESI) calcd for C<sub>21</sub>H<sub>26</sub>N<sub>2</sub>B (M<sup>+</sup>+ H) 317.2184, found 317.2182.



(6c): yellow solid, 77% yield; mp = 176-177 °C  $R_f$  = 0.75 (Pet. ether/EtOAc = 90/10); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  = 8.48 (d, J = 8.8 Hz, 1 H), 8.20 (d, J = 8.8 Hz, 1 H), 7.88 - 7.79 (m, 3 H), 7.78 - 7.70 (m, 1 H), 7.48 (t, J = 7.5 Hz, 1 H), 6.96 (dd, J = 0.5, 2.2 Hz, 1 H), 6.69 (dd, J = 2.4, 8.6 Hz, 1 H), 3.14 (s, 6 H), 1.34 - 1.21 (m, 14 H), 1.07 - 0.77 (m, 14 H), 0.33 (t, J = 7.7 Hz, 6 H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  = 158.9, 152.0, 142.4, 139.2, 130.9, 128.6, 126.3, 126.2, 125.0, 123.5, 122.0, 115.2, 111.0, 109.7, 40.4, 31.9, 29.7, 29.6, 29.4, 22.7, 14.1, 9.9; HRMS (ESI) calcd for C<sub>33</sub>H<sub>50</sub>N<sub>2</sub>B (M<sup>++</sup> H) 485.4095, found 485.4097.



(6d): orange solid, 64% yield; mp = 289-290 °C;  $R_f$  = 0.62 (Pet. ether/EtOAc = 80/20); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  = 8.44 (d, J = 8.9 Hz, 1 H), 8.28 (d, J = 8.9 Hz, 1 H), 7.90 (d, J = 8.9 Hz, 1 H), 7.83 (d, J = 8.5 Hz, 1 H), 7.74 - 7.71 (m, 1 H), 7.56 - 7.50 (m, 1 H), 7.41 (dd, J = 1.5, 8.2 Hz, 2 H), 7.36 - 7.31 (m, 2 H), 7.17 - 7.13 (m, 2 H), 7.11 - 7.08 (m, 1 H), 6.92 - 6.88 (m, 2 H), 6.82 (d, J = 2.4 Hz, 1 H), 6.62 (dd, J = 2.6, 8.7 Hz, 1 H), 6.60 - 6.56 (m, 2 H), 2.99 (s, 6 H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  = 160.2, 153.1, 140.7, 139.3, 133.5, 131.1, 128.4, 127.1, 125.3, 125.0, 124.5, 124.0, 123.7, 115.4, 114.1, 111.7, 110.2, 40.3; HRMS (ESI) calcd for C<sub>29</sub>H<sub>26</sub>N<sub>2</sub>B (M<sup>++</sup> H) 413.2117, found 413.2114.



(6e): red solid, 95% yield; mp = 168-169 °C;  $R_f$  = 0.32 (CH<sub>2</sub>Cl<sub>2</sub>/MeOH = 95/05); <sup>1</sup>H NMR (500 MHz, CD<sub>2</sub>Cl<sub>2</sub>)  $\delta$  = 9.10 (d, J = 9.0 Hz, 1 H), 8.38 - 8.24 (m, 1 H), 7.95 - 7.84 (m, 2 H), 7.77 - 7.67 (m, 2 H), 7.60 - 7.51 (m, 1 H), 7.24 - 7.16 (m, 1 H), 6.78 - 6.61 (m, 1 H), 3.19 (s, 6 H); <sup>13</sup>C NMR (125 MHz, CD<sub>2</sub>Cl<sub>2</sub>)  $\delta$  = 157.3, 152.2, 148.2, 144.4, 137.2, 132.5, 130.2, 129.1, 129.0, 128.0, 127.2, 126.0, 118.6, 112.5, 112.2, 40.6; HRMS (ESI) calcd for C<sub>17</sub>H<sub>16</sub>N<sub>2</sub>BBr<sup>81</sup>Br (M<sup>++</sup> H) 418.9747, found 418.9745. Note: The compounds is either insoluble or partially soluble in almost all of the organic solvents examined.











-0.01

-1.61











CHLOROFORM-d

8.51 8.51 8.51 8.31 7.7.7 7.7.80 7.23 7.23 7.23 6.97 6.97

#### -0.23 -0.23 -0.23 -0.23 -0.23 -0.23 -0.23 -0.23



<sup>1</sup>H NMR (400 MHz), CDCl<sub>3</sub>

























