Visible light-induced borylation and arylation of small organic

molecules using carbon dots

Tiantong He,^a Heping Wei,^b Yuanbo Zhou,^c Li-ya Jiang,^a Jonathan B. Baell,^a Yang Yu,^{*c} and Fei Huang^{*a}

^aSchool of Pharmaceutical Sciences, Nanjing Tech University, Nanjing 211816, P. R. China

^bSchool of Food Science and Pharmaceutical Engineering, Nanjing Normal University, Nanjing

210023, P. R. China

^cSchool of Environmental Science and Engineering, Nanjing Tech University, Nanjing 211816, P.

R. China

*E-mail: yuyang19880421@yeah.net, huangfei0208@yeah.net

Table of contents

Contents:	page
1. General considerations	S2
2. Preparation and characterization data of carbon dots	S4
3. Optimization of conditions and experimental procedures	S6
4. Mechanistic investigations and proposed mechanism	S14
5. Analytical data for compounds	S19
6. Copies of NMR spectra	S34

1. General considerations

¹H and ¹³C{¹H} NMR spectra were recorded on a Bruker DRX-400 spectrometer and all chemical shift values refer to $\delta_{TMS} = 0.00$ ppm, CDCl₃ (δ (¹H), 7.26 ppm; $\delta(^{13}C)$, 77.16 ppm). UV-vis absorption spectra were recorded with a U-3900 UV-vis spectrophotometer. TEM and HRTEM images were obtained by using JEOL JEM2100F transmission electron microscope at an acceleration voltage of 150 kV. XRD patterns were obtained by using an X-ray diffractometer (Bruker, Germany) with Cu-Ka radiation ($\lambda = 1.5178$ Å). The 2θ scanning range was from 5° to 80° with a scanning speed of 0.1 °/s. The FT-IR spectra (4000 cm⁻¹ to 400 cm⁻¹) in KBr were obtained using Varian Excalibur 3100 FT-IR spectrometer. The Raman spectra performed on laser confocal micro-Raman Spectroscopy (inVia-Reflex). Ultraviolet photoelectron spectroscopy (UPS) was performed on Thermo Scientific ESCALab 250Xi. The gas discharge lamp was used for UPS, with Helium gas admitted and the He I emission line at 21.22 eV employed. The Helium pressure in the analysis chamber during analysis is about 3×10⁻⁸ mbar. The photoreaction instrument (WPP-TEC-1020SL) was purchased from WATTCAS, China. The light source was blue (395 or 495 nm) LEDs which were positioned on the bottom of the reaction vial at a 4 mm distance. The reaction stand was a custom-made aluminum block with build-in water cooling. Analytical TLC plates, Sigma-Aldrich silica gel 60F₂₀₀ were viewed by UV light (254 nm). Column chromatographic purifications were performed on SDZF silica gel 160. All the chemical reagents were purchased from commercial sources and used as received unless otherwise indicated. Compounds 3a-3d¹, 3e², 3f¹, 3g³, 3h-**3i**¹, **3j**⁴, **3k**-**3o**³, **3p**-**3v**¹, **3w**⁵, **6a**-**6c**⁶, **6d**-**6f**⁷, **6g**-**6i**⁶, **6j**⁸, **6k**-**6l**⁶, **6m**⁹, **6n**⁶, **6o**¹⁰, **6p**¹¹, 6q-6r¹², 6s¹³, 6t¹⁴, 7¹⁵, 8¹⁶, 9¹⁷, 10¹⁸, 11¹⁹, 13-15²⁰, and 17-19²¹ were known and their spectroscopic features were in good agreement with that reported in the literatures.

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2. Preparation and characterization data of carbon dots

2.1. Preparation of Carbon Dots.

Synthesis of B-CDots, G-CDots, and R-CDots²²: Blue carbon dots (B-CDots), green carbon dots (G-CDots), and red carbon dots (R-CDots) were synthesized by using different molar ratios of citric acid (CA) to urea in DMF at different temperatures. Typically, B-CDots were prepared via solvothermal synthesis method. A mixture of CA (192 mg, 1 mmol), urea (600 mg, 10 mmol) in 10 mL *N*,*N*-dimethylformamide (DMF) was stirred at 140 °C for 12 h. After cooling to room temperature, the resultant mixture was evaporated all the volatiles under reduced pressure. The residue was purified by silica gel column chromatography (eluent: DCM/MeOH = 20:1, v/v) to afford the corresponding B-CDots as yellow solids. By adjusting the ratios of CA to urea and the temperature of reaction, CDots with different emissive colors can be synthesized. At the ratio of CA to urea = 0.3 and the temperature at 160 °C, the G-CDots were obtained. At the ratio of CA to urea = 0.8 and the temperature at 180 °C, the R-CDots were obtained.

2.2. The characterization of B-CDots



Figure S1 FT-IR spectra of B-CDots, G-CDots, and R-CDots.



Figure S2 (a) UV–vis, PL emission and PL excitation spectra of R-CDots. Conditions: R-CDots (1.0 mg); solvent: H_2O in a volume of 25 mL under an air atmosphere. Excitation wavelength was 510 nm. (b) UV–vis, PL emission and PL excitation spectra of G-CDots. Conditions: G-CDots (1.0 mg); solvent: H_2O in a volume of 25 mL under an air atmosphere. Excitation wavelength was 430 nm.



Figure S3 PL emission spectra of B-CDots at different excitation wavelengths. Conditions: B-CDots (1.0 mg); solvent: H_2O in a volume of 25 mL under an air atmosphere.



Figure S4 UPS spectrum of B-CDots.

Quantum yield (QY) measurement:

Quinine sulfate (QY=54.6% in 0.1 M H_2SO_4) was selected as the reference for the emission range of 400-480 nm (for B-CDots herein). The QY of a sample was then calculated according to the following equation:

$$\phi = \phi' \times \frac{A'}{l'} \times \frac{I}{A} \times \frac{n^2}{n'^2}$$

Where ϕ is the QY of the testing sample, *I* is the testing sample's integrated emission intensity, *n* is the refractive index (1.33 for water), and *A* is the optical density. The superscript "'" refers to the to the quinine sulfate. The solutions of B-CDots and quinine sulfate were prepared with concentrations adjusted such that the optical absorbance values were between 0–0.1 at 350 nm. The PL spectra were measured and the PL intensity was integrated. QY were determined by comparison of the integrated PL intensity *vs* absorbance curves.

3. Optimization of conditions and experimental procedures

3.1. Screening the optimum reaction conditions for the C-H arylation of haloarenes.

Table S1 Screening the optimum reaction conditions^a

	N ₂ BF ₄ +		B-CDots SO, 495 nm LEDs	CI	
	CI 4b	5a		6b	
entry	furan (equiv)	blue LEDs (nm)	B-CDots (mg)	solvent	yield (%)
1	10	440	20	DMSO	45
2	10	460	20	DMSO	46
3	10	495	20	DMSO	56
4	10	530	20	DMSO	36
5	10	495	20	H_2O	NR
6	10	495	20	DCE	9
7	10	495	20	toluene	11
8	10	495	20	MeOH	13
9	10	495	20	DMF	19
10	10	495	20	MeCN	8
11	15	495	20	DMSO	69
12	15	495	15	DMSO	68
13	15	495	10	DMSO	70
14^{b}	15	495	10	DMSO	53
15 ^c	15	495	10	DMSO	24
16	15		10	DMSO	NR
17	15	495		DMSO	17

^{*a*}Reaction conditions: **4b** (0.5 mmol), **5a** (7.5 mmol), B-CDots, solvent (2 mL), rt, N₂, 2 h, 1 W blue LED, isolated yield. NR = No reaction. ^{*b*}air. ^{*c*}O₂.

We began our studies using 4-chlorobenzene-diazonium salt **4b** and furan **5a** as the model substrates to optimize the reaction conditions (Table S1). We were delighted to find that irradiation of the diazonium salt **4b** and furan **5a** in the presence of 20 mg B-CDots at room temperature for 2 h in DMSO provided the desired product **6b** in 45% yield (Table S1, entry 1). Then, light sources were investigated and results indicated that 495 nm LEDs was the most effective light source up to 56% yield. (Table S1, entries 2–4). Subsequently, various solvents were screened, such as H₂O, DCE, toluene, MeOH, DMF, and MeCN (Table S1, entries 5–10). DMSO was found to be the best choice for this reaction. Increasing the amount of furan from 10 equiv. to 15 equiv. improved the yield to 69% (Table S1, entry 11). Remarkably, screening the amount of B-CDots revealed that using a lower amount of B-CDots (10 mg) could give the corresponding product in higher yield up to 70% (Table S1, entries 12–13). However, when the reaction was performed in an air atmosphere, the yield decreased significantly to only 53% (Table S1, entry 14). The reaction was significantly inhibited when carried out in an oxygen atmosphere, resulting in a yield of only 24% (Table S1, entry 15). These results may be attributed to the weak radical-inhibiting properties of oxygen, as the arylation reaction may be undergoes through a radical pathway. Therefore, nitrogen was found to be the optimal atmosphere for this reaction. Control experiments emphasized the crucial role of the light and the B-CDots (Table S1, entries 16–17).

3.2. Preparation of aryldiazonium salts 4.



A typical procedure for the synthesis of aryldiazonium salts (4a-4p)– Synthesis of 4b: A mixture of the 4-chloroaniline (5 mmol), HBF₄ (48% w/w, 1.2 mL, 10 mmol, 2.1 equiv) and water (2.0 mL) was cooled to 0 °C and a solution of NaNO₂ (345 mg, 5 mmol, 1.0 equiv) in water (1.0 mL) was added dropwise. The reaction mixture was stirred at 0 °C for 40 min. The solid was filtered off and washed with diethyl ether (3×5 mL). The aryldiazonium salts was dried in vacuo for 20 min, affording **4b** (1.06 g, 94%) as a white solid.

3.3. General procedure for the synthesis of arylboronates (3).



The reactions of haloarenes (1) and B_2pin_2 (2)– *Synthesis of 3a:* A mixture of 1-iodo-4-methoxybenzene (0.3 mmol), B_2pin_2 (0.6 mmol, 2.0 equiv), B-CDots (15 mg), Cs_2CO_3 (0.6 mmol, 2.0 equiv) and CH_3CN (3.0 mL) was bubbled with N_2 for 10 min, then sealed and irradiated at room temperature by 10 W blue LED of the

appropriate wavelength (395 nm) for 24 hours. When reaction was finished, water (5 mL) was added, and the reaction mixture was extracted with ethyl acetate (3×10 mL). The combined organic layers were dried over excess anhydrous sodium sulfate, filtered, and concentrated. The resulting crude mixture was purified by silica gel column chromatography (eluent: petroleum ether (60-90 °C)/AcOEt = 25:1, v/v) to afford **3a** (45 mg, 64%) as colorless liquid.



Figure S5 Photograph of the photochemical reaction set-up.

3.4. General procedure for the synthesis of arylated heteroarenes (6).



The reactions of aryldiazonium salts (4) and heteroarenes (5)– Synthesis of 6b: A mixture of 4-chlorobenzene-diazonium salt 4b (0.5 mmol), furan 5a (7.5 mmol, 15 equiv), B-CDots (10 mg), and DMSO (2.0 mL) was bubbled with N₂ for 10 min, then sealed and irradiated at room temperature by 1 W blue LED of the appropriate wavelength (495 nm) for 2 h. When reaction was finished, water (5 mL) was added, and the reaction mixture was extracted with ethyl acetate (3×10 mL). The combined organic layers were dried over excess anhydrous sodium sulfate, filtered, and concentrated. The resulting crude mixture was purified by silica gel column

chromatography (eluent: petroleum ether (60-90 °C)/AcOEt = 100:1, v/v) to afford **6b** (62 mg, 70%) as a white solid.

3.5. General procedure for preparative-scale reaction.



The reactions preparative-scale: A mixture of iodobenzene (1.0 mmol), B₂pin₂ (2.0 mmol, 2.0 equiv), B-CDots (50 mg), Cs₂CO₃ (2.0 mmol, 2.0 equiv) and CH₃CN (6.0 mL) was bubbled with N₂ for 10 min, then sealed and irradiated at room temperature by 10 W blue LED of the appropriate wavelength (395 nm) for 24 h. When reaction was finished, water (30 mL) was added, and the reaction mixture was extracted with ethyl acetate (3 × 20 mL). The combined organic layers were dried over sodium sulfate, filtered, and concentrated. The resulting crude mixture was purified by silica gel column chromatography (eluent: petroleum ether (60-90 °C)/AcOEt = 100:1, v/v) to afford **3a** (120 mg, 59%) as colorless liquid.

3.6. Functionalization of arylboronates and synthesis of adiphenine, benactyzineand the core structure of nomifensine.



Scheme S1 Functionalization of arylboronates.

Synthesis of 7: A mixture of $Pd(Ph_3P)_4$ (0.025 mmol), K_2CO_3 (1 mmol), arylboronate **3i** (0.5 mmol) and 4-iodoanisole (1 mmol) was bubbled with N₂ for 15 min. Under nitrogen condition, DMF (3 mL) was sequentially added. The resulting

reaction mixture was stirred at 90 °C for 12 h. When reaction was finished, water (10 mL) was added, and the reaction mixture was extracted with ethyl acetate (3×10 mL). The combined organic layers were dried over sodium sulfate, filtered, and concentrated. The crude mixture was purified by silica gel column chromatography (eluent: petroleum ether (60-90 °C)/AcOEt = 100:1, v/v) to afford the corresponding product 7 (82.8 mg, 90%) as a white solid.

Synthesis of 8: A mixture of arylboronate 3i (0.3 mmol), Cu₂O (0.03 mmol), imidazole (0.45 mmol) and MeOH (1 mL) was stirred at 40 °C for 12 h. After cooling to room temperature, the organic layers were concentrated. The crude mixture was purified by silica gel column chromatography (eluent: petroleum ether (60-90 °C)/AcOEt = 100:5, v/v) to give the product 8 (31.5 mg, 73%) as a colorless liquid.

Synthesis of 9: A 25 mL Schlenk tube was charged with arylboronate 3i (0.5 mmol) and cooled to 0 °C. Then 30% wt. aq. H₂O₂ (392 μ L, 5 mmol) was added dropwise. The reaction mixture was stirred at room temperature for 6 h. When reaction was finished, water (10 mL) was added, and the reaction mixture was extracted with ethyl acetate (3 × 10 mL). The combined organic layers were dried over sodium sulfate, filtered, and concentrated. The crude mixture was purified by silica gel column chromatography (eluent: petroleum ether (60-90 °C)/AcOEt = 100:1, v/v) to afford the corresponding product 9 (39 mg, 83%) as a colorless liquid.

Synthesis of 10: A mixture of arylboronate 3i (1 equiv, 0.30 mmol), amine (2 equiv, 0.60 mmol), Cu(OAc)₂ (1 equiv, 0.30 mmol, 54 mg), Et₃N (2 equiv, 0.60 mmol, 61 mg, 84 μ L) and MeCN/EtOH (20:1 ratio, 300 μ L) was stirred at 80 °C for 48 h. After cooling to room temperature, the reaction mixture was filtered through Celite, and the filtrate was evaporated to give a residue that was purified by silica gel column chromatography (eluent: petroleum ether (60-90 °C)/AcOEt = 100:4, v/v) afford the desired product 10 (36 mg, 71%) as a white solid.

Synthesis of 11: A mixture of CuCl (0.05 mmol), bpy (0.05 mmol), $(PhS)_2$ (0.275 mmol) and arylboronate 3i (0.5 mmol) was bubbled with N₂ for 10 min. Under

nitrogen condition, DMSO (2 mL), H₂O (1 mL) were sequentially added. The resulting reaction mixture was stirred at 80 °C for 12 h. When reaction was finished, water (10 mL) was added, and the reaction mixture was extracted with ethyl acetate (3 \times 10 mL). The combined organic layers were dried over sodium sulfate, filtered, and concentrated. The crude mixture was purified by silica gel column chromatography (eluent: petroleum ether (60-90 °C)/AcOEt = 100:1, v/v) to afford the corresponding product **11** (75 mg, 86%) as a colorless liquid.



Scheme S2 Synthesis of adiphenine, benactyzineand the core structure of nomifensine.

Synthesis of 13: A mixture of arylboronate 3i (0.28 mmol, 1 equiv), K_3PO_4 (0.28 mmol, 1 equiv), Rh catalyst (1.38 mg, 1 mol%) and dry toluene (0.5 mL) was bubbled with N_2 for 10 min. Under nitrogen atmosphere, diazo compound 12 (0.56 mmol, 2 equiv) was dissolved in 1.0 mL dry toluene and slowly added dropwise. The reaction mixture was stirred at 80 °C for 3 h. The reaction mixture was cooled to room temperature and dissolved in 15 mL DCM. The DCM layer was washed with water (2 ×10 mL) and brine (2 ×10 mL). The combined organic layer was dried over anhydrous Na₂SO₄ and concentrated to get the crude product. The crude product was purified by silica gel column chromatography (eluent: petroleum ether (60-90 °C)/AcOEt = 100:6, v/v) to afford the product 13 (63.3 mg, 56%) as a white solid.

Synthesis of 14: A mixture of methyl 2,2-diphenylacetate **13** (91 mg, 0.4 mmol, 1 equiv.), KOH (45 mg, 0.8 mmol, 2 equiv.) and MeOH (4 mL, 0.1M) was stirred at 65 °C overnight. Then, the reaction was cooled to room temperature, acidified to pH = 2

using a 3M HCl aqueous solution, extracted with AcOEt, dried (Na_2SO_4), filtered and concentrated to afford the product 14 (85 mg, 91%) as a white solid.

Synthesis of 15: THF (3 mL, freshly distilled) was stirred at 0 °C for 5 min, adding LiAlH₄ (1.5 mmol) to it and stirring at the same temperature for 5 min. Then, the compound 14 (1 mmol) as dissolved in 3 mL of freshly distilled THF and slowly added to the reaction mixture at 0 °C. The reaction mixture was stirred at room temperature for 12 h. When reaction was finished, water (10 mL) was added, and the reaction mixture was extracted with ethyl acetate (3×10 mL). The combined organic layers were dried over sodium sulfate, filtered, and concentrated. The crude product was purified by silica gel column chromatography (eluent: petroleum ether (60-90 °C)/AcOEt = 12:1, v/v) to afford the corresponding 15 (176 mg, 89%) as a white solid.

Synthesis of 17: A mixture of 2,2-diphenylacetic acid 14 (106 mg, 0.5 mmol, 1 equiv.), Na₂CO₃ (106 mg, 1 mmol, 2 equiv.), diethylamine (207 μ L, 2 mmol, 4 equiv.) and 1,2-DCE (2 mL, 0.125 M) was stirred at 80 °C overnight. Then, the reaction was cooled to room temperature and concentrated. The residue was purified by silica gel column chromatography (eluent: petroleum ether (60-90 °C)/AcOEt = 10:1, v/v) to afford the adiphenine 17 (120 mg, 77%) as a transparent oil.

Synthesis of 18: A mixture of methyl 2,2-diphenylacetate 13 (678 mg, 3 mmol, 1 equiv.), Cs_2CO_3 (195 mg, 0.6 mmol, 0.2 equiv.), $P(OEt)_3$ (1 mL, 6 mmol, 2 equiv.) and DMSO (12 mL, 0.25 M) was bubbled with O_2 for 10 min. The reaction mixture was stirred at room temperature for 24 h. Then, the reaction mixture was extracted with AcOEt (3 × 10 mL), washed with brine (10 mL), dried (Na₂SO₄), filtered and concentrated. The residue was purified by silica gel column chromatography (eluent: petroleum ether (60-90 °C)/AcOEt = 12:1, v/v) to afford the product 18 (232 mg, 64%) as a white solid.

Synthesis of 19: A mixture of methyl 2-hydroxy-2,2-diphenylacetate 18 (150 mg, 0.6 mmol, 1 equiv.), KOH (69 mg, 1.2 mmol, 2 equiv.) and MeOH (6 mL, 0.1 M) was stirred at 65 °C overnight. Then, the reaction was cooled to room temperature, acidified to pH = 2 using a 3M HCl aqueous solution, extracted with AcOEt (3 × 10

mL), dried (Na₂SO₄), filtered and concentrated to afford the product (123 mg, 90 %) as a white solid.

A mixture of the previously prepared 2-hydroxy-2,2diphenylacetic acid (46 mg, 0.2 mmol, 1 equiv.), Na₂CO₃ (42 mg, 0.4 mmol, 2 equiv.), diethylamine (82 μ L, 2 mmol, 10 equiv.) and 1,2-DCE (1 mL) was stirred at 80 °C for 2 days. Then, the reaction mixture was extracted with AcOEt (3 × 10 mL), washed with brine (10 mL), dried (Na₂SO₄), filtered and concentrated. The residue was purified by silica gel column chromatography (eluent: petroleum ether (60-90 °C)/AcOEt = 8:1, v/v) afforded the title compound **19** (27 mg, 60%) as a transparent oil.

4. Mechanistic investigations and proposed mechanism





Scheme S3 Radical trapping experiments of borylation.

Radical trapping study: A mixture of **1a** (0.3 mmol), B_2pin_2 (0.6 mmol, 2.0 equiv), B-CDots (15 mg), Cs_2CO_3 (0.6 mmol, 2.0 equiv), TEMPO or DPE (0.6 mmol, 2.0 equiv), and CH₃CN (3.0 mL) was bubbled with N₂ for 10 min, then sealed and irradiated at room temperature by blue LED of the appropriate wavelength (395 nm) for 24 hours. When reaction was finished, water (5 mL) was added, and the reaction mixture was extracted with ethyl acetate (3 × 10 mL). The combined organic layers were dried over sodium sulfate, filtered, and concentrated. The resulting crude mixture was purified by silica gel column chromatography (eluent: petroleum ether (60-90 °C)/AcOEt = 25:1, v/v) to afford **3a** (16%, 35% yields, respectively) as

colorless liquid. The crude mixture was analyzed by HRMS, showing that aryl radical was trapped by TEMPO and aryl radical-tempo adduct **20** was detected (Figure S6).



Figure S6 HRMS analysis of the formation of aryl radical-tempo adduct 20



Scheme S4 Radical trapping experiments of C-H arylation.

Radical trapping study: A mixture of 4-chlorobenzene-diazonium salt **4b** (0.5 mmol), furan (7.5 mmol, 15 equiv), B-CDots (10 mg), TEMPO or DPE (0.3 mmol, 1.0 equiv), and DMSO (2.0 mL) was bubbled with N₂ for 10 min, then sealed and irradiated at room temperature by blue LED of the appropriate wavelength (495 nm) for 2 hours. When reaction was finished, water (5 mL) was added, and the reaction mixture was extracted with ethyl acetate (3×10 mL). The combined organic layers were dried over sodium sulfate, filtered, and concentrated. The resulting crude mixture can be purified by silica gel column chromatography (eluent: petroleum ether (60-90 °C)/AcOEt = 100:1, v/v) to afford **6b** (21%, 30% yields, respectively) as a white solid. The crude mixture was analyzed by HRMS, indicating that aryl radical

and furan radical were trapped by TEMPO and aryl radical-tempo adduct **21** (Figure S7) and furan radical-tempo adduct **22** (Figure S8) were detected.



Figure S7 HRMS analysis of the formation of aryl radical-tempo adduct 21.



Figure S8 HRMS analysis of the formation of furan radical-tempo adduct 22.

Intermediate detection study: A mixture of 1a (0.3 mmol), B_2pin_2 (0.6 mmol, 2.0 equiv), B-CDots (15 mg), Cs_2CO_3 (0.6 mmol, 2.0 equiv), and CH_3CN (3.0 mL) was bubbled with N_2 for 10 min, then sealed and irradiated at room temperature by blue LED of the appropriate wavelength (395 nm) for 24 hours. The crude mixture was analyzed by HRMS, which revealed the presence of intermediate VI. (Figure S9).



Figure S9 HRMS analysis of the formation of intermediate VI with ammonium cation.

4.2. ESR (Electron Spin Resonance) test

A mixture of 1-iodo-4-methylbenzene **1b** (0.3 mmol), B_2pin_2 (0.6 mmol, 2.0 equiv), B-CDots (15 mg), Cs_2CO_3 (0.6 mmol, 2.0 equiv), 5,5-dimethyl-1-pyrroline N-oxide (DMPO, 0.6 mmol, 2.0 equiv) and CH₃CN (3.0 mL) was bubbled with N₂ for 10 min, then sealed and irradiated at room temperature by blue LED of the appropriate wavelength (395 nm) for 10 min. Electron Spin Resonance (ESR) spectrum was recorded on a Bruker EMXplus-6/1 at room temperature and a carbon radical was found (Figure S10).



Figure S10 ESR spectrum of a mixture under irradiation of visible light for 10 min.

4.3. Fluorescence quenching experiments

Fluorescence quenching experiments for borylation: Rigorously degassed solutions of each component were prepared under nitrogen atmosphere prior to each set of experiments. In a typical experiment, a 4×10^{-2} mg/mL solution of B-CDots in MeCN was added the appropriate amount of quencher in a quartz cuvette. The

solutions were irradiated at 395 nm and luminescence was measured at 370 nm. The relative intensity I_0/I was calculated as a function of quencher concentration (Figure S11).



Figure S11 Fluorescence quenching experiments for borylation. (a) Fluorescence quenching of B-CDots by **1a**, **2a** and Cs_2CO_3 . (b) Fluorescence emission spectra of B-CDots in different concentrations of 4-iodoanisole **1a** in MeCN. (c) Stern–Volmer plots. Excitation wavelength for fluorescence was set at 370 nm.

Fluorescence quenching experiments for C–H arylation: Rigorously degassed solutions of each component were prepared under nitrogen atmosphere prior to each set of experiments. In a typical experiment, a 4×10^{-2} mg/mL solution of B-CDots in DMSO was added the appropriate amount of quencher in a quartz cuvette. The solutions were irradiated at 495 nm and luminescence was measured at 370 nm. The relative intensity I_0/I was calculated as a function of quencher concentration (Figure S12).



Figure S12 Fluorescence quenching experiments for C–H arylation. (a) Fluorescence quenching of B-CDots by **4b**, and **5a**. (b) Fluorescence emission spectra of B-CDots in different concentrations of aryldiazonium salt **4b** in DMSO. (c) Stern–Volmer plots. Excitation wavelength for fluorescence was set at 370 nm.

4.4. Proposed mechanism of C-H arylation



Scheme S5 Proposed mechanism of C-H arylation.

A plausible mechanism was proposed, as depicted in Scheme S5. Under visiblelight irradiation, the electron of B-CDots is excited to the conduction band. The B-CDots having high reductive potential could reduce an aryldiazonium salt **4** via a single-electron transfer to furnish the corresponding aryl radical **VII** and release a dinitrogen molecule. The generated aryl radical **VII** reacts with heteroarene **5a** to afford radical intermediate **VIII**, which would be subsequently oxidized by the B-CDots radical cation to form carbocation intermediate. Finally, deprotonation of **IX** would lead to arylation product **6**.

5. Analytical data for compounds



2-(4-Methoxyphenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3a): Colorless liquid. X = Cl, 67%; X = I, 64%. ¹H NMR (400 MHz, CDCl₃) δ 7.76 (d, *J* = 8.6 Hz, 2H), 6.90 (d, *J* = 8.7 Hz, 2H), 3.83 (s, 3H), 1.34 (s, 12H). ¹³C{¹H} NMR (100 MHz, CDCl₃) δ 162.3, 136.6, 113.4, 83.7, 55.2, 24.9.



4,4,5,5-Tetramethyl-2-(*p*-tolyl)-1,3,2-dioxaborolane (3b): Colorless liquid. X = Cl, 65%; X = I, 75%. ¹H NMR (400 MHz, CDCl₃) δ 7.71 (d, *J* = 7.5 Hz, 2H), 7.19 (d, *J* = 7.5 Hz, 2H), 2.37 (s, 3H), 1.35 (s, 12H). ¹³C{¹H} NMR (100 MHz, CDCl₃) δ 141.5, 134.9, 128.7, 83.8, 24.9, 21.8.



4,4,5,5-Tetramethyl-2-(*m***-tolyl)-1,3,2-dioxaborolane (3c):** Colorless liquid. X = I, 67%. ¹H NMR (400 MHz, CDCl₃) δ 7.66 (s, 1H), 7.65 – 7.60 (m, 1H), 7.32 – 7.26 (m, 2H), 2.37 (s, 3H), 1.36 (s, 12H). ¹³C{¹H} NMR (100 MHz, CDCl₃) δ 137.3, 135.5, 132.2, 131.9, 127.8, 83.8, 24.9, 21.4.



4,4,5,5-Tetramethyl-2-(*o***-tolyl)-1,3,2-dioxaborolane (3d):** Colorless liquid. X = I, 61%. ¹H NMR (400 MHz, CDCl₃) δ (d, *J* = 7.8 Hz, 1H), 7.32 (t, *J* = 7.5 Hz, 1H), 7.16 (t, *J* = 6.3 Hz, 2H), 2.54 (s, 3H), 1.35 (s, 12H). ¹³C{¹H} NMR (100 MHz, CDCl₃) δ 145.0, 136.0, 130.9, 129.9, 124.8, 83.5, 25.0, 22.4.



2-(4-Ethylphenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**3e**): Colorless liquid. X = Br, 60%; X = I, 67%. ¹H NMR (400 MHz, CDCl₃) δ 7.75 (d, *J* = 8.0 Hz, 2H), 7.23 (d, *J* = 8.0 Hz, 2H), 2.67 (q, *J* = 7.6 Hz, 2H), 1.35 (s, 12H), 1.25 (t, *J* = 7.6 Hz, 3H). ¹³C{¹H} NMR (100 MHz, CDCl₃) δ 147.9, 135.0, 127.5, 83.7, 29.2, 24.9, 15.6.



4,4,5,5-Tetramethyl-2-(4-(methylthio)phenyl)-1,3,2-dioxaborolane (3f): White solid. X = Br, 73%. ¹H NMR (400 MHz, CDCl₃) δ 7.71 (d, *J* = 8.3 Hz, 2H), 7.22 (d, *J* = 8.3 Hz, 2H), 2.49 (s, 3H), 1.34 (s, 12H). ¹³C{¹H} NMR (100 MHz, CDCl₃) δ 142.7, 135.2, 125.1, 83.9, 24.9, 15.2.



4-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)phenol (3g): White solid. X = Cl, 68%; X = Br, 69%; X = I, 74%. ¹H NMR (400 MHz, CDCl₃) δ 7.70 (d, *J* = 8.5 Hz, 2H), 6.82 (d, *J* = 8.5 Hz, 2H), 5.45 (s, 1H), 1.33 (s, 12H). ¹³C{¹H} NMR (100 MHz, CDCl₃) δ 158.5, 136.9, 114.9, 83.8, 24.9.



4-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)aniline (3h): White solid. X = Cl, 69%; X = Br, 79%; X = I, 75%. ¹H NMR (400 MHz, CDCl₃) δ 7.62 (d, *J* = 8.4 Hz, 2H), 6.65 (d, *J* = 8.5 Hz, 2H), 3.84 (s, 2H), 1.32 (s, 12H). ¹³C{¹H} NMR (100 MHz, CDCl₃) δ 149.4, 136.5, 114.2, 83.4, 24.9.

Bpin

4,4,5,5-Tetramethyl-2-phenyl-1,3,2-dioxaborolane (3i): Colorless liquid. X = I, 66%. ¹H NMR (400 MHz, CDCl₃) δ 7.83 (d, *J* = 7.5 Hz, 2H), 7.47 (t, *J* = 7.4 Hz, 1H), 7.38 (t, *J* = 7.3 Hz, 2H), 1.36 (s, 12H). ¹³C{¹H} NMR (100 MHz, CDCl₃) δ 134.9, 131.4, 127.8, 83.9, 25.0.

Bpin Me

4-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)aniline (3j): Colorless liquid. X

= Br, 54%. ¹H NMR (400 MHz, CDCl₃) δ 7.65 (d, *J* = 8.4 Hz, 1H), 7.63 – 7.56 (m, 1H), 6.99 (dd, *J* = 10.0, 8.2 Hz, 1H), 2.27 (d, *J* = 1.6 Hz, 3H), 1.34 (s, 12H). ¹³C{¹H} NMR (100 MHz, CDCl₃) δ 163.8 (d, *J* = 247.0 Hz), 138.5 (d, *J* = 5.6 Hz), 134.4 (d, *J* = 8.3 Hz), 124.4 (d, *J* = 16.3 Hz), 114.7 (d, *J* = 21.3 Hz), 84.0, 24.9, 14.4 (d, *J* = 3.8 Hz).



4-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)benzonitrile (3k): White solid. X = Cl, 83%; X = Br, 81%; X = I, 80%. ¹H NMR (400 MHz, CDCl₃) δ 7.87 (d, J = 8.3 Hz, 1H), 7.63 (d, J = 8.3 Hz, 1H), 1.34 (s, 6H). ¹³C{¹H} NMR (100 MHz, CDCl₃) δ 135.2, 131.3, 119.0, 114.6, 84.6, 24.9.

Bpin CF₃

4,4,5,5-Tetramethyl-2-(4-(trifluoromethyl)phenyl)-1,3,2-dioxaborolane (3l): White solid. X = I, 51%. ¹H NMR (400 MHz, CDCl₃) δ 7.92 (d, J = 7.8 Hz, 2H), 7.62 (d, J = 7.9 Hz, 2H), 1.36 (s, 12H). ¹³C{¹H} NMR (100 MHz, CDCl₃) δ 135.2, 132.9 (q, J = 32.1 Hz), 124.5 (q, J = 3.8 Hz), 124.3 (q, J = 272.4 Hz), 84.4, 24.9.



4,4,5,5-Tetramethyl-2-(4-nitrophenyl)-1,3,2-dioxaborolane (3m): White solid. X = I, 71%, X = Br, 69%. ¹H NMR (400 MHz, CDCl₃) δ 8.17 (d, J = 8.7 Hz, 2H), 7.95 (d, J = 8.7 Hz, 2H), 1.35 (s, 12H). ¹³C{¹H} NMR (100 MHz, CDCl₃) δ 149.9, 135.8, 122.5, 84.7, 24.9.



1-(4-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)ethan-1-one (3n): White solid. X = Cl, 81%; X = Br, 79%. ¹H NMR (400 MHz, CDCl₃) δ 7.92 (d, J = 8.3 Hz, 2H), 7.88 (d, J = 8.3 Hz, 2H), 2.60 (s, 3H), 1.34 (s, 12H). ¹³C{¹H} NMR (100 MHz, CDCl₃) δ 198.6, 139.1, 135.0, 127.4, 84.3, 26.8, 24.9.



4-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)benzaldehyde (30): White solid. X = Br, 66%. ¹H NMR (400 MHz, CDCl₃) δ 10.05 (s, 1H), 7.96 (d, *J* = 8.0 Hz, 2H), 7.86 (d, *J* = 8.1 Hz, 2H), 1.36 (s, 12H). ¹³C{¹H} NMR (100 MHz, CDCl₃) δ 192.8, 138.2, 135.4, 128.8, 84.5, 24.9.



Methyl 4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzoate (3p): White solid. X = Br, 76%. ¹H NMR (400 MHz, CDCl₃) δ 8.01 (d, J = 8.3 Hz, 2H), 7.86 (d, J = 8.3 Hz, 2H), 3.91 (s, 3H), 1.34 (s, 12H). ¹³C{¹H} NMR (100 MHz, CDCl₃) δ 167.2, 134.8, 132.4, 128.7, 84.3, 52.3, 24.9.



Methyl 3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzoate (3q): White solid. X = Br, 70%. ¹H NMR (400 MHz, CDCl₃) δ 8.46 (s, 1H), 8.11 (d, *J* = 7.8 Hz, 1H), 7.97 (d, *J* = 7.4 Hz, 1H), 7.43 (t, *J* = 7.6 Hz, 1H), 3.90 (s, 3H), 1.34 (s, 12H). ¹³C{¹H} NMR (100 MHz, CDCl₃) δ 167.2, 139.3, 135.9, 132.4, 129.7, 127.9, 84.2, 52.1, 24.9.



2-([1,1'-Biphenyl]-4-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3r): White solid. X = I, 68%; X = Br, 64%. ¹H NMR (400 MHz, CDCl₃) δ 7.96 (d, J = 8.2 Hz, 2H), 7.67 (d, J = 8.0 Hz, 4H), 7.48 (t, J = 7.5 Hz, 2H), 7.39 (t, J = 7.3 Hz, 1H), 1.41 (s, 12H). ¹³C{¹H} NMR (100 MHz, CDCl₃) δ 144.0, 141.1, 135.4, 128.9, 127.7, 127.3, 126.6, 83.9, 25.0.



4,4,5,5-Tetramethyl-2-(naphthalen-1-yl)-1,3,2-dioxaborolane (3s): White solid. X = Br, 70%. ¹H NMR (400 MHz, CDCl₃) δ 8.82 (d, J = 8.4 Hz, 1H), 8.13 (d, J = 6.8 Hz, 1H), 7.97 (d, J = 8.2 Hz, 1H), 7.87 (d, J = 7.5 Hz, 1H), 7.58 (t, J = 6.9 Hz, 1H), 7.51 (t, J = 6.9 Hz, 2H), 1.46 (s, 12H). ¹³C{¹H} NMR (100 MHz, CDCl₃) δ 137.1, 135.8, 133.3, 131.7, 128.6, 128.5, 126.5, 125.6, 125.1, 83.8, 25.1.



4,4,5,5-Tetramethyl-2-(naphthalen-1-yl)-1,3,2-dioxaborolane (3t): White solid. X = I, 77%; X = Br, 73%. ¹H NMR (400 MHz, CDCl₃) δ 8.41 (s, 1H), 7.91 (d, *J* = 7.7 Hz, 1H), 7.89 – 7.80 (m, 3H), 7.57 – 7.45 (m, 2H), 1.41 (s, 13H). ¹³C{¹H} NMR (100 MHz, CDCl₃) δ 136.4, 135.2, 133.0, 130.5, 128.8, 127.8, 127.1, 127.0, 126.0, 84.0, 25.1.



2-(Benzo[b]thiophen-6-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3u): White solid. X = Br, 50%. ¹H NMR (400 MHz, CDCl₃) δ 8.39 (d, J = 0.6 Hz, 1H), 7.83 (d, J = 8.0 Hz, 1H), 7.78 (d, J = 8.0 Hz, 1H), 7.52 (d, J = 5.4 Hz, 1H), 7.35 (d, J = 5.4 Hz, 1H), 1.38 (s, 12H). ¹³C{¹H} NMR (100 MHz, CDCl₃) δ 141.9, 139.5, 129.9, 129.7, 128.3, 124.0, 123.1, 84.0, 25.0.



2-(Dibenzo[*b,d*]**furan-3-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane** (3v): White solid. X = Br, 64%. ¹H NMR (400 MHz, CDCl₃) δ 8.48 (s, 1H), 7.99 (d, *J* = 7.6 Hz, 1H), 7.96 (d, *J* = 8.3 Hz, 1H), 7.59 (d, *J* = 8.3 Hz, 2H), 7.46 (t, *J* = 8.4 Hz, 1H), 7.36 (t, *J* = 7.5 Hz, 1H), 1.41 (s, 12H). ¹³C{¹H} NMR (100 MHz, CDCl₃) δ 158.5, 156.3, 133.9, 127.9, 127.3, 124.2, 124.1, 123.0, 120.9, 111.8, 111.3, 84.0, 25.0.



4-(4,4,6-Trimethyl-1,3,2-dioxaborinan-2-yl)aniline (3w): Colorless liquid. X = I, 65%. ¹H NMR (400 MHz, CDCl₃) δ 7.63 (d, *J* = 8.4 Hz, 2H), 6.65 (d, *J* = 8.4 Hz, 2H), 4.36 – 4.26 (m, 1H), 3.75 (s, 2H), 1.83 (dd, *J* = 13.8, 3.0 Hz, 1H), 1.56 (dd, *J* = 13.8, 11.6 Hz, 1H), 1.36 (s, 3H), 1.35 (s, 3H), 1.33 (d, *J* = 6.2 Hz, 3H).¹³C{¹H} NMR (100 MHz, CDCl₃) δ 148.6, 135.4, 114.2, 70.7, 64.8, 46.2, 31.5, 28.3, 23.4.



4-(4,4,6,6-Tetramethyl-1,3,2-dioxaborinan-2-yl)aniline (3x): Colorless liquid. X = I, 54%. ¹H NMR (400 MHz, CDCl₃) δ 7.66 (d, *J* = 8.3 Hz, 2H), 6.66 (d, *J* = 8.4 Hz, 2H), 3.75 (s, 2H), 1.89 (s, 2H), 1.41 (s, 12H). ¹³C {¹H} NMR (100 MHz, CDCl₃) δ 148.6, 135.5, 114.2, 70.6, 49.1, 31.9. HRMS (ESI) m/z calcd for C₁₃H₂₁BNO₂ [M + H]⁺: 234.1660, found: 234.1664.



2-(4-Fluorophenyl)furan (6a): White solid, 64%. ¹H NMR (400 MHz, CDCl₃) δ 7.69 – 7.61 (m, 2H), 7.46 (d, J = 1.2 Hz, 1H), 7.14 – 7.03 (m, 2H), 6.59 (d, J = 3.3 Hz, 1H), 6.47 (dd, J = 3.3, 1.8 Hz, 1H). ¹³C{¹H} NMR (100 MHz, CDCl₃) δ 162.3 (d, J =246.8 Hz), 153.3, 142.2, 127.4, 125.7 (d, J = 8.0 Hz), 115.8 (d, J = 21.9 Hz), 111.8, 104.8 (d, J = 1.3 Hz).



2-(4-Chlorophenyl)furan (6b): White solid, 70%. ¹H NMR (400 MHz, CDCl₃) δ 7.60 (d, J = 8.6 Hz, 2H), 7.48 (d, J = 1.7 Hz, 1H), 7.36 (d, J = 8.6 Hz, 2H), 6.65 (d, J = 3.4 Hz, 1H), 6.48 (dd, J = 3.4, 1.8 Hz, 1H). ¹³C{¹H} NMR (100 MHz, CDCl₃) δ 153.1, 142.4, 133.2, 129.5, 129.0, 125.1, 111.9, 105.6.



2-(4-Bromophenyl)furan (6c): White solid, 72%. ¹H NMR (400 MHz, CDCl₃) δ 7.54 (d, J = 8.8 Hz, 2H), 7.50 (d, J = 8.8 Hz, 2H), 7.48 (d, J = 1.7 Hz, 1H), 6.66 (d, J = 3.4 Hz, 1H), 6.48 (dd, J = 3.4, 1.8 Hz, 1H). ¹³C{¹H} NMR (100 MHz, CDCl₃) δ 153.1, 142.5, 131.9, 129.9, 125.4, 121.2, 111.9, 105.7.



2-(3- Bromophenyl)furan (6d): Yellow liquid, 54%. ¹H NMR (400 MHz, CDCl₃) δ 7.83 (t, J = 1.7 Hz, 1H), 7.59 (dd, J = 7.8, 1.1 Hz, 1H), 7.48 (d, J = 1.6 Hz, 1H), 7.38 (ddd, J = 8.0, 1.8, 0.9 Hz, 1H), 7.24 (t, J = 7.9 Hz, 1H), 6.67 (d, J = 3.4 Hz, 1H), 6.48 (dd, J = 3.4, 1.8 Hz, 1H). ¹³C{¹H} NMR (100 MHz, CDCl₃) δ 152.5, 142.7, 132.9, 130.3, 130.2, 126.8, 123.0, 122.4, 111.9, 106.2.



2-(2- Bromophenyl)furan (6e): Yellow liquid, 58%. ¹H NMR (400 MHz, CDCl₃) δ 7.83 (dd, J = 7.9, 1.6 Hz, 1H), 7.68 (dd, J = 8.0, 1.0 Hz, 1H), 7.55 (d, J = 1.4 Hz, 1H), 7.38 (t, J = 8.2 Hz, 1H), 7.22 (d, J = 3.4 Hz, 1H), 7.14 (td, J = 7.9, 1.7 Hz, 1H), 6.56 (dd, J = 3.4, 1.8 Hz, 1H). ¹³C{¹H} NMR (100 MHz, CDCl₃) δ 151.4, 142.3, 134.2, 131.3, 128.9, 128.5, 127.4, 119.7, 111.5, 110.7.



2-(4-Iodophenyl)furan (6f): White solid, 67%. ¹H NMR (400 MHz, CDCl₃) δ 7.70 (d, J = 8.5 Hz, 2H), 7.47 (d, J = 1.7 Hz, 1H), 7.41 (d, J = 8.5 Hz, 2H), 6.66 (d, J = 3.4 Hz, 1H), 6.48 (dd, J = 3.4, 1.8 Hz, 1H). ¹³C{¹H} NMR (100 MHz, CDCl₃) δ 153.1, 142.6, 137.9, 130.4, 125.6, 111.9, 105.8, 92.6.



2-(4-(Trifluoromethyl)phenyl)furan (6g): White solid, 54%. ¹H NMR (400 MHz, CDCl₃) δ 7.76 (d, J = 8.2 Hz, 2H), 7.63 (d, J = 8.3 Hz, 2H), 7.52 (d, J = 1.4 Hz, 1H), 6.77 (d, J = 3.4 Hz, 1H), 6.52 (dd, J = 3.4, 1.8 Hz, 1H). ¹³C{¹H} NMR (100 MHz, CDCl₃) δ 152.7, 143.2, 134.1, 129.1 (q, J = 32.4 Hz), 125.8 (q, J = 3.9 Hz), 124.3 (q, J = 271.8 Hz), 123.9, 112.1, 107.1.



4-(Furan-2-yl)benzonitrile (6h): White solid, 65%. ¹H NMR (400 MHz, CDCl₃) δ 7.72 (d, J = 8.5 Hz, 2H), 7.63 (d, J = 8.6 Hz, 2H), 7.53 (d, J = 1.3 Hz, 1H), 6.80 (d, J = 3.4 Hz, 1H), 6.52 (dd, J = 3.4, 1.8 Hz, 1H). ¹³C{¹H} NMR (100 MHz, CDCl₃) δ 151.9, 143.6, 134.6, 132.5, 123.9, 118.9, 112.2, 110.2, 108.1.



2-(4-Nitrophenyl)furan (6i): White solid, 71%. ¹H NMR (400 MHz, CDCl₃) δ 8.26 – 8.20 (m, 2H), 7.82 – 7.75 (m, 2H), 7.57 (d, *J* = 1.3 Hz, 1H), 6.87 (d, *J* = 3.5 Hz, 1H), 6.55 (dd, *J* = 3.5, 1.8 Hz, 1H). ¹³C{¹H} NMR (100 MHz, CDCl₃) δ 151.8, 146.5, 144.3, 136.6, 124.4, 124.1, 112.5, 109.1.



1-(4-(Furan-2-yl)phenyl)ethan-1-one (6j): White solid, 61%. ¹H NMR (400 MHz, CDCl₃) δ 7.95 (d, J = 8.7 Hz, 2H), 7.72 (d, J = 8.6 Hz, 2H), 7.51 (d, J = 1.7 Hz, 1H), 6.78 (d, J = 3.4 Hz, 1H), 6.50 (dd, J = 3.4, 1.8 Hz, 1H), 2.59 (s, 3H). ¹³C{¹H} NMR (100 MHz, CDCl₃) δ 197.5, 152.9, 143.4, 135.6, 134.9, 129.0, 123.6, 112.2, 107.6, 26.6.



2-Phenylfuran (6k): Colorless liquid, 55%. ¹H NMR (400 MHz, CDCl₃) δ 7.70 (d, *J* = 7.2 Hz, 2H), 7.49 (d, *J* = 1.8 Hz, 1H), 7.40 (t, *J* = 7.7 Hz, 2H), 7.28 (t, *J* = 7.4 Hz, 1H), 6.67 (d, *J* = 3.3 Hz, 1H), 6.49 (dd, *J* = 3.3, 1.8 Hz, 1H). ¹³C{¹H} NMR (100 MHz, CDCl₃) δ 154.1, 142.2, 131.0, 128.8, 127.5, 123.9, 111.8, 105.1.



2-(*p***-Tolyl)furan (6l):** Colorless liquid, 41%. ¹H NMR (400 MHz, CDCl₃) δ 7.60 (d, J = 8.2 Hz, 2H), 7.47 (d, J = 1.7 Hz, 1H), 7.22 (d, J = 8.1 Hz, 2H), 6.62 (d, J = 3.3 Hz, 1H), 6.48 (dd, J = 3.3, 1.8 Hz, 1H), 2.39 (s, 3H). ¹³C{¹H} NMR (100 MHz, CDCl₃) δ 154.3, 141.8, 137.3, 129.5, 128.4, 123.9, 111.7, 104.3, 21.4.



2-(4-Isopropylphenyl)furan (6m): White solid, 45%. ¹H NMR (400 MHz, CDCl₃) δ 7.61 (d, J = 8.3 Hz, 1H), 7.45 (d, J = 1.8 Hz, 1H), 7.25 (d, J = 8.2 Hz, 1H),

6.60 (d, *J* = 3.3 Hz, 1H), 6.46 (dd, *J* = 3.3, 1.8 Hz, 1H), 3.01 – 2.86 (m, 1H), 1.27 (d, *J* = 6.9 Hz, 4H). ¹³C{¹H} NMR (100 MHz, CDCl₃) δ 154.2, 148.2, 141.7, 128.6, 126.7, 123.8, 111.5, 104.3, 33.9, 23.9.



2-(4-Methoxyphenyl)furan (6n): White solid, 35%. ¹H NMR (400 MHz, CDCl₃) δ 7.62 (d, J = 8.9 Hz, 2H), 7.44 (d, J = 1.8 Hz, 1H), 6.94 (d, J = 8.9 Hz, 2H), 6.53 (d, J = 3.3 Hz, 1H), 6.46 (dd, J = 3.3, 1.8 Hz, 1H), 3.84 (s, 3H). ¹³C{¹H} NMR (100 MHz, CDCl₃) δ 159.2, 154.1, 141.5, 125.4, 124.2, 114.2, 111.7, 103.5, 55.4.



2-(Naphthalen-1-yl)furan (60): White solid, 54%. ¹H NMR (400 MHz, CDCl₃) δ 8.43 (d, J = 9.2 Hz, 1H), 7.91 (d, J = 7.3 Hz, 1H), 7.86 (d, J = 8.2 Hz, 1H), 7.75 (d, J = 7.2 Hz, 1H), 7.65 (d, J = 1.7 Hz, 1H), 7.58 – 7.50 (m, 3H), 6.75 (d, J = 3.3 Hz, 1H), 6.61 (dd, J = 3.3, 1.8 Hz, 1H). ¹³C{¹H} NMR (100 MHz, CDCl₃) δ 153.6, 142.5, 134.1, 130.5, 128.8, 128.7, 128.6, 126.7, 126.3, 126.0, 125.7, 125.5, 111.5, 109.4.



2-(Naphthalen-2-yl)furan (6p): White solid, 56%. ¹H NMR (400 MHz, CDCl₃) δ 8.16 (s, 1H), 7.90 – 7.76 (m, 4H), 7.54 (d, J = 1.7 Hz, 1H), 7.52 – 7.43 (m, 2H), 6.78 (d, J = 3.4 Hz, 1H), 6.53 (dd, J = 3.3, 1.8 Hz, 1H). ¹³C{¹H} NMR (100 MHz, CDCl₃) δ 154.2, 142.5, 133.7, 132.8, 128.5, 128.3, 128.2, 127.9, 126.6, 126.0, 122.5, 122.3, 112.0, 105.7.



2-(4-Chlorophenyl)thiophene (6q): White solid, 60%. ¹H NMR (400 MHz, CDCl₃) δ 7.54 (d, *J* = 8.5 Hz, 2H), 7.35 (d, *J* = 8.5 Hz, 3H), 7.32 – 7.28 (m, 2H), 7.09 (t, *J* = 4.3 Hz, 1H). ¹³C{¹H} NMR (100 MHz, CDCl₃) δ 143.2, 133.3, 133.0, 129.1, 128.3, 127.2, 125.3, 123.6.



2-(4-Methoxyphenyl)thiophene (6r): White solid, 50%. ¹H NMR (400 MHz, CDCl₃) δ 7.55 (d, J = 8.9 Hz, 2H), 7.24 – 7.19 (m, 2H), 7.06 (dd, J = 5.1, 3.6 Hz, 1H), 6.93 (d, J = 8.9 Hz, 2H), 3.84 (s, 3H). ¹³C{¹H} NMR (100 MHz, CDCl₃) δ 159.3, 144.5, 128.1, 127.4, 127.3, 123.9, 122.2, 114.4, 55.5.



3-(4-Methoxyphenyl)-1-methyl-1*H***-pyrrole (6s):** White solid, 53%. ¹H NMR (400 MHz, CDCl₃) δ 7.82 (d, *J* = 9.0 Hz, 2H), 6.98 (d, *J* = 9.0 Hz, 2H), 6.89 (s, 1H), 6.67 (d, *J* = 4.1 Hz, 1H), 6.29 (d, *J* = 4.1 Hz, 1H), 3.95 (s, 3H), 3.87 (s, 3H). ¹³C{¹H} NMR (100 MHz, CDCl₃) δ 160.9, 147.9, 146.5, 126.0, 123.7, 114.2, 109.9, 98.9, 55.6, 33.4.



2-(4-Chlorophenyl)pyridine (6t): White solid, 25%. ¹H NMR (400 MHz, CDCl₃) δ 8.61 (d, *J* = 4.8 Hz, 1H), 7.86 (d, *J* = 8.7 Hz, 2H), 7.72 – 7.65 (m, 1H), 7.62 (d, *J* = 8.0 Hz, 1H), 7.36 (d, *J* = 8.7 Hz, 2H), 7.18 – 7.14 (m, 1H). ¹³C{¹H} NMR (100 MHz, CDCl₃) δ 156.4, 149.9, 134.0, 137.0, 135.3, 129.1, 128.3, 122.5, 120.5.



2-(4-Chlorophenyl)pyridine (7): White solid, 90%. ¹H NMR (400 MHz, CDCl₃) δ 7.59 (t, *J* = 8.9 Hz, 4H), 7.46 (t, *J* = 7.6 Hz, 2H), 7.35 (t, *J* = 7.3 Hz, 1H), 7.02 (d, *J* = 8.6 Hz, 2H), 3.88 (s, 3H). ¹³C{¹H} NMR (100 MHz, CDCl₃) δ 159.2, 140.9, 133.8, 128.8, 128.3, 126.9, 126.8, 114.3, 55.4.



1-Phenyl-1*H***-imidazole (8):** Colorless liquid, 73%. ¹H NMR (400 MHz, CDCl₃) δ 7.83 (s, 1H), 7.45 (t, *J* = 7.7 Hz, 2H), 7.41 – 7.30 (m, 3H), 7.26 (s, 1H), 7.18 (s, 1H). ¹³C{¹H} NMR (100 MHz, CDCl₃) δ 137.4, 135.6, 130.4, 129.9, 127.5, 121.5, 118.3.



Phenol (9): Colorless liquid, 83%. ¹H NMR (400 MHz, CDCl₃) δ 7.26 (t, J = 7.8 Hz, 2H), 6.96 (t, J = 7.4 Hz, 1H), 6.87 (d, J = 7.9 Hz, 2H), 6.17 (s, 1H). ¹³C{¹H} NMR (100 MHz, CDCl₃) δ 155.5, 129.8, 120.9, 115.5.



Diphenylamine (10): White solid, 71%. ¹H NMR (400 MHz, CDCl₃) δ 7.39 (t, J = 7.9 Hz, 4H), 7.18 (d, J = 7.8 Hz, 4H), 7.07 (t, J = 7.3 Hz, 2H), 5.75 (s, 1H). ¹³C{¹H} NMR (100 MHz, CDCl₃) δ 143.1, 129.4, 121.0, 117.8.



Diphenylsulfane (11): Colorless liquid, 86%. ¹H NMR (400 MHz, CDCl₃) δ 7.41 (d, J = 7.4 Hz, 4H), 7.35 (t, J = 7.5 Hz, 4H), 7.29 (t, J = 6.8 Hz, 1H). ¹³C{¹H} NMR (100 MHz, CDCl₃) δ 135.8, 131.1, 129.3, 127.1.



Methyl 2,2-diphenylacetate (13): White solid, 56%. ¹H NMR (400 MHz, CDCl₃) 7.39 – 7.33 (m, 8H), 7.33 – 7.26 (m, 2H), 5.08 (s, 1H), 3.77 (s, 3H). ¹³C{¹H} NMR (100 MHz, CDCl₃) δ 173.1, 138.7, 128.7, 128.6, 127.4, 57.1, 52.4.



2,2-Diphenylacetic acid (14): White solid, 91%. ¹H NMR (400 MHz, CDCl₃) δ 11.15 (s, 1H), 7.40 – 7.33 (m, 8H), 7.32 – 7.27 (m, 2H), 5.08 (s, 1H). ¹³C{¹H} NMR (100 MHz, CDCl₃) δ 179.0, 138.0, 128.8, 127.6, 57.1.



2,2-Diphenylethan-1-ol (15): White solid, 89%. ¹H NMR (400 MHz, CDCl₃) δ 7.39 – 7.31 (m, 4H), 7.31 – 7.22 (m, 6H), 4.27 – 4.21 (m, 1H), 4.21 – 4.16 (m, 2H), 1.63 (s, 1H). ¹³C{¹H} NMR (100 MHz, CDCl₃) δ 141.5, 128.8, 128.4, 126.9, 66.2, 53.7.



2-(Diethylamino)ethyl 2,2-diphenylacetate (17): Transparent oil, 77%. ¹H NMR (400 MHz, CDCl₃) δ 7.37 – 7.30 (m, 8H), 7.30 – 7.24 (m, 2H), 5.06 (s, 1H), 4.25 (t, *J* = 6.2 Hz, 2H), 2.70 (t, *J* = 6.2 Hz, 2H), 2.53 (q, *J* = 7.1 Hz, 4H), 0.99 (t, *J* = 7.1 Hz, 6H). ¹³C{¹H} NMR (100 MHz, CDCl₃) δ 172.6, 138.8, 128.7, 128.6, 127.3, 63.6, 57.2, 51.1, 47.6, 11.9.



Methyl 2-hydroxy-2,2-diphenylacetate (18): White solid, 64%. ¹H NMR (400 MHz, CDCl₃) δ 7.49 – 7.40 (m, 4H), 7.40 – 7.30 (m, 6H), 4.25 (s, 1H), 3.87 (s, 3H) ¹³C{¹H} NMR (100 MHz, CDCl₃) δ 175.1, 141.9, 128.3, 128.2, 127.5, 81.2, 53.7.



2-(Diethylamino)ethyl 2-hydroxy-2,2-diphenylacetate (19): Transparent oil, 60%. ¹H NMR (400 MHz, CDCl₃) δ 7.53 – 7.39 (m, 4H), 7.38 – 7.27 (m, 6H), 4.42 (s, 1H), 4.33 (t, *J* = 5.9 Hz, 2H), 2.68 (t, *J* = 5.9 Hz, 2H), 2.47 (q, *J* = 7.1 Hz, 4H), 0.95 (t, *J* = 7.1 Hz, 6H). ¹³C{¹H} NMR (100 MHz, CDCl₃) δ 174.5, 142.2, 128.1, 128.0, 127.5, 81.2, 65.1, 51.0, 47.3, 11.9.

6. Copies of NMR spectra












S39



S40



S41













S47











































210	200	100	100	170	160	150	140	120	120	110	100	00	00	70	60	50	40	20	20	10	0	10
210	200	190	100	170	100	150	140	130	120	110	100	90	00	10	00	50	40	30	20	10	0	- 10
										f	1 (ppm)										







10.0	9.5	9.0	8.5	8.0	7.5	7.0	6.5	6.0	5.5	5.0	4.5	4.0	3.5	3.0	2.5	2.0	1.5	1.0	0.5	0.0
										f1 (ppi	m)									





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210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 f1 (ppm)



















210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 f1 (ppm)





210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 f1 (ppm)







