

# Organic Materials

## Nonalternant Extension of Multiple Resonance Emitter via Palladium-Catalyzed [5+2]-Annulation

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DOI: 10.1055/a-2531-9798

Please cite this article as: Zhuang W, Chong W, Liu J. Nonalternant Extension of Multiple Resonance Emitter via Palladium-Catalyzed [5+2]-Annulation. *Organic Materials* 2024. doi: 10.1055/a-2531-9798

**Conflict of Interest:** The authors declare that they have no conflict of interest.

**This study was supported by** Hong Kong Research Grants Council, 27301720, 17304021, National Natural Science Foundation of China (<http://dx.doi.org/10.13039/501100001809>), 22122114

### Abstract:

Despite the proliferation of multiple resonance (MR) emitters with rigid 1,4-borazine-based skeletons, the straightforward and efficient incorporation of nonhexagonal rings, especially for heptagons, to avoid notorious aggregation-induced quenching effect remains elusive. Here, a green-yellow emitter consisting of two azepines was designed and synthesized via a palladium-catalyzed one-pot twofold [5+2]-annulation reaction with high selectivity and efficiency. The tetrabenzene-fused benzo[1,2-b:5,4-b']bis(azepine) (TBBBA) core induced a highly twisted and dynamically helical rim for the novel MR-skeleton, which reduced  $\pi$ - $\pi$  stacking in the solid state. Moreover, the nonalternant topology facilitated the delocalization of frontier molecular orbitals (FMO) within the twisted geometry, thus achieving red-shifted narrow emission. Our work provides a new synthetic strategy towards nonalternant extension of MR-emitters and gives insights into the electronic effects of multiple azepination on FMO distribution.

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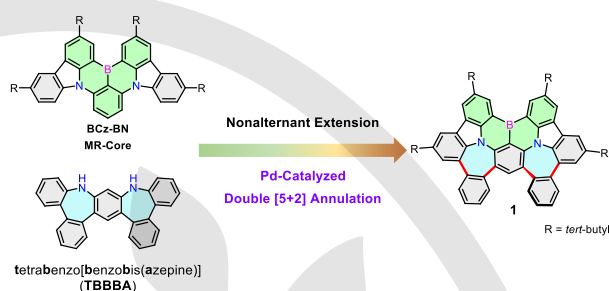
# Nonalternant Extension of Multiple Resonance Emitter via Palladium-Catalyzed [5+2]-Annulation

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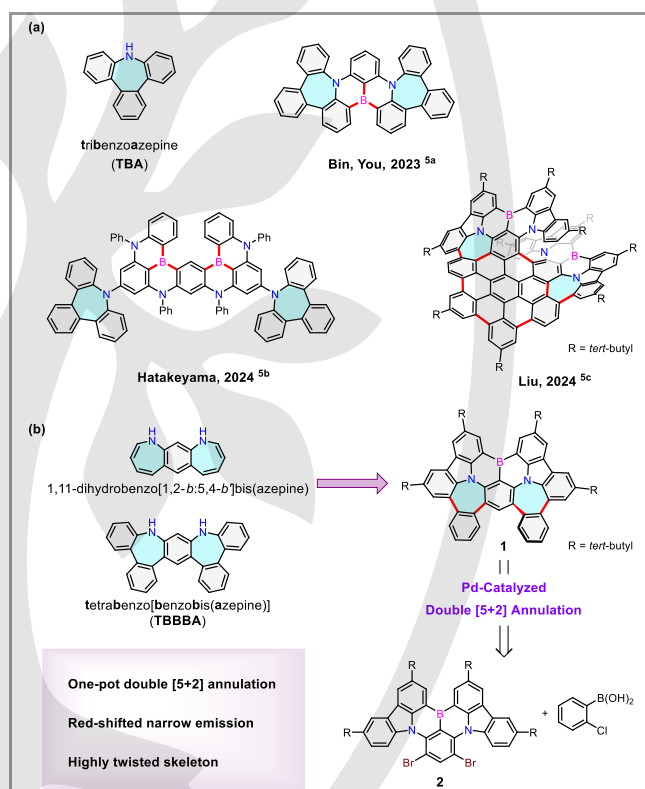
Received:  
Accepted:  
Published online:  
DOI:

**Abstract** Despite the proliferation of multiple resonance (MR) emitters with rigid 1,4-azaborine-based skeletons, the straightforward and efficient incorporation of nonhexagonal rings, especially for heptagons remains elusive. Here, a green-yellow emitter consisting of two azepines was designed and synthesized via a palladium-catalyzed one-pot twofold [5+2]-annulation reaction with high selectivity and efficiency. The tetrabenzene-fused benzo[1,2-*b*:5,4-*b'*]bis(azepine) (TBBBA) core induced a highly twisted and dynamically helical rim for the novel MR-skeleton, which reduced  $\pi$ - $\pi$  stacking in the solid state. Moreover, the nonalternant topology facilitated the delocalization of frontier molecular orbitals (FMO) within the twisted geometry, thus achieving red-shifted narrow emission. Our work provides a new synthetic strategy towards nonalternant extension of MR-emitters and gives insights into the electronic effects of multiple azepination on FMO distribution.

**Key words** Nonalternant extension, Multiple resonance, Annulation, Azepine.

## Introduction

Polycyclic conjugated hydrocarbons (PCHs) are of great interest to the community of chemistry and materials due to their fine-tuned electrochemical and photophysical properties.<sup>1</sup> The ubiquitous synthetic strategies for *de novo* construction or  $\pi$ -extension of PCH skeletons are highly important for the development of diversified boron-nitrogen-containing MR-emitters with thermally activated delayed fluorescence (TADF).<sup>2</sup> Typically, the introduction of nonhexagonal rings (pentagons and heptagons) into graphene molecules induced unique geometric deformations and photophysical properties.<sup>3</sup> In addition, the frontier molecular orbitals (FMO) distributions can be modified by boron and nitrogen atoms in the rigid  $\pi$ -framework, giving rise to efficient narrow emission. In general, the hexagonal arrangement of 1,4-azaborines with a shared tridentate boron atom in the  $\pi$ -conjugated skeleton is essential for MR-effects. The classic MR-core, namely BCz-BN, has a planar  $\pi$ -surface owing to nitrogen-doped pentagons, leading to aggregation-induced quenching (ACQ). Peripheral modification of BCz-BN with bulky groups has improved the efficiency roll-off of organic light-emitting diodes (OLEDs) with marginal red-shifted emission.<sup>4</sup> On the other hand,  $\pi$ -extension with a nonalternant topology



**Figure 1** (a) Reported TBA-based extension of MR-core. (b) This work: Pd-catalyzed double [5+2]-annulation for TBBBA-based extension of MR-emitter. Bonds denoted with red color indicating bond formation in the final step.

might endorse a twisted geometry with significant delocalization of FMO to achieve red-shifted emission with suppressed intermolecular  $\pi$ - $\pi$  stacking.

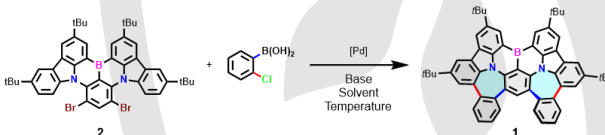
Tribenzoazepine (TBA) is a representative heptagonal donor, which has been utilized as a key building block in the synthesis of sophisticated blue emitters.<sup>5</sup> For instance, Bin and You developed blue MR-emitters with twisted geometry by borylation of TBA-linked intermediates (Figure 1a).<sup>5a</sup> The introduction of heptagons also enhances spin-orbital coupling to suppress efficiency roll-off. Hatakeyama synthesized a TBA-decorated deep-blue MR-emitter based on  $\nu$ -DABNA to achieve

fine-tuned energy levels and color output.<sup>5b</sup> However, less effective  $\pi$ -conjugation restricted those emitters from long-wavelength gamut. Recently, we developed a programmable approach towards nonalternant B,N-embedded helical nanographenes with controllable integration of azepines.<sup>5c</sup> Although the extended TBA units resulted in improved  $\pi$ -conjugation and deep-red circularly polarized luminescence was observed, the photoluminescence quantum yield (PLQY) decreased for such large  $\pi$ -system. Two separate TBA units were introduced in these works. Furthermore, tetrabenzene-fused benzo[1,2-b:5,4-b']bis(azepine) (TBBBA) with a central benzene ring shared by two TBAs, has larger structural constrain than pristine TBA, which is beneficial for geometric deformations. Herein, we report the synthesis of TBBBA-based MR-emitter **1** by Pd-catalyzed double [5+2]-annulation reaction. The geometric and electronic effects on efficient, red-shifted emission have been thoroughly investigated (Figure 1b). Besides, the anion responsive property of **1** is established.

## Results and Discussion

The well-established methods for TBA derivatives mainly rely on a cascade C-N and C-C coupling<sup>6</sup> or twofold C-N formation reaction<sup>7</sup>. Two consecutive or stepwise<sup>8</sup> C-C couplings for the construction of TBA unit are relatively rare. The unprecedented synthesis of TBBBA embedded emitter **1** was initially tried by Pd-catalyzed cross-coupling reaction between compound **2** and 2-chlorobenzeneboronic acid. However, the desired product was not observed under the catalytic system of tetrakis(triphenylphosphine)palladium(0) (Pd(PPh<sub>3</sub>)<sub>4</sub>) or [1,1'-bis(diphenylphosphino)ferrocene]dichloropalladium(II) (Pd(dppf)Cl<sub>2</sub>) (Table 1, entries 1-2). To our delight, the combination of tris(dibenzylideneacetone)dipalladium(0) (Pd<sub>2</sub>(dba)<sub>3</sub>) and tricyclohexylphosphine (PCy<sub>3</sub>) afforded **1** in 10% yield (entry 3). The ligated palladium species of

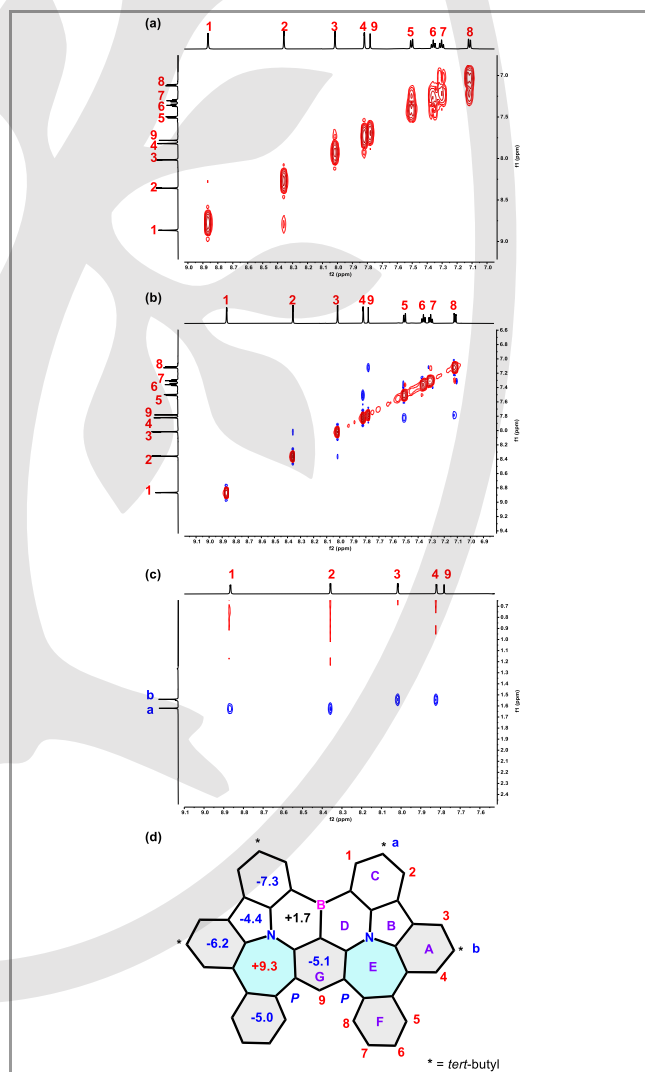
**Table 1.** Optimization of the Reaction Conditions<sup>a</sup>.



Entry	ArB(OH) <sub>2</sub> (eq.)	[Pd]	Base	Solvent	T (°C)	Yield <sup>b</sup>
1	3.0	Pd(PPh <sub>3</sub> ) <sub>4</sub>	K <sub>2</sub> CO <sub>3</sub>	Toluene	110	ND
2	3.0	Pd(dppf)Cl <sub>2</sub>	K <sub>2</sub> CO <sub>3</sub>	Toluene	110	ND
3	3.0	Pd <sub>2</sub> (dba) <sub>3</sub> +PCy <sub>3</sub>	K <sub>2</sub> CO <sub>3</sub>	Toluene	110	10
4	3.0	Pd(PCy <sub>3</sub> ) <sub>2</sub> Cl <sub>2</sub>	K <sub>2</sub> CO <sub>3</sub>	Toluene	110	15
5	3.0	Pd(PCy <sub>3</sub> ) <sub>2</sub> Cl <sub>2</sub>	K <sub>2</sub> CO <sub>3</sub>	dioxane	110	7
6	3.0	Pd(PCy <sub>3</sub> ) <sub>2</sub> Cl <sub>2</sub>	K <sub>2</sub> CO <sub>3</sub>	DMF	110	20
7	3.0	Pd(PCy <sub>3</sub> ) <sub>2</sub> Cl <sub>2</sub>	DBU	DMF	110	ND
8	3.0	Pd(PCy <sub>3</sub> ) <sub>2</sub> Cl <sub>2</sub>	K <sub>3</sub> PO <sub>4</sub>	DMF	110	16
9	3.0	Pd(PCy <sub>3</sub> ) <sub>2</sub> Cl <sub>2</sub>	K <sub>2</sub> CO <sub>3</sub>	DMF	120	23
10	3.0	Pd(PCy <sub>3</sub> ) <sub>2</sub> Cl <sub>2</sub>	K <sub>2</sub> CO <sub>3</sub>	DMF	130	35
11	4.0	Pd(PCy <sub>3</sub> ) <sub>2</sub> Cl <sub>2</sub>	K <sub>2</sub> CO <sub>3</sub>	DMF	130	36*

<sup>a</sup>Unless otherwise noted, all reactions were carried out with **2** (0.1 mmol), boronic acid (0.3 mmol), Pd catalyst (10 mol%), base (8.0 equiv), solvent (3.0 mL), under nitrogen atmosphere for 18 h. ND, not detected. <sup>b</sup>The yield was determined by <sup>1</sup>H NMR with 1,2-dibromoethane as the internal standard. \*Carried out with 0.3 mmol of **2** and 4.0 eq. of boronic acid, isolated yield.

dichlorobis(tricyclohexylphosphine)palladium(II) (Pd(PCy<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub>) gave a slightly increased yield (15%, entry 4). Changing the solvent from toluene to 1,4-dioxane resulted in an inferior result (entry 5). On the other hand, dimethylformamide (DMF) gave a better result, presumably due to the increased solubility of inorganic base (entry 6). Interestingly, organic base 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) was not suitable for this cascade [5+2]-annulation reaction (entry 7). Further adjusting the temperature and the equivalence of boronic acid could improve the yield to 36% (entry 11).<sup>9</sup> The twofold annulation was supposed to proceed via a sequential Suzuki-Miyaura cross-coupling and intramolecular C-H arylation, whereas the different strength of carbon-halogen bonds (C-Br vs. C-Cl) played a pivotal role to achieve high selectivity.<sup>10</sup> The preorganized N-centered bay regions are important for the cascade [5+2]-annulation, which might decrease the energy barrier for the concerted metalation-deprotonation (CMD) process to form eight-membered ring pallada-cycle.<sup>8c</sup> The stepwise construction of  $\pi$ -fused azepine units involving two palladium-catalyst systems has been reported.<sup>8d-e</sup> Generally, the first C-C coupling is completed under biphasic conditions to



**Figure 2** NMR spectra of compound **1** in CD<sub>2</sub>Cl<sub>2</sub> (298 K, 600 MHz). (a) <sup>1</sup>H-<sup>1</sup>H COSY spectrum. (b) <sup>1</sup>H-<sup>1</sup>H NOESY spectrum of aromatic protons. (c) <sup>1</sup>H-<sup>1</sup>H NOESY spectrum of aromatic protons and *tert*-butyl protons. (d) Label of compound **1** and NICS values of each ring in **1**. NICS(0) values were calculated on the C<sub>2</sub>-symmetrical structure at GIAO-B3LYP/6-311+G(d,p) level of theory.

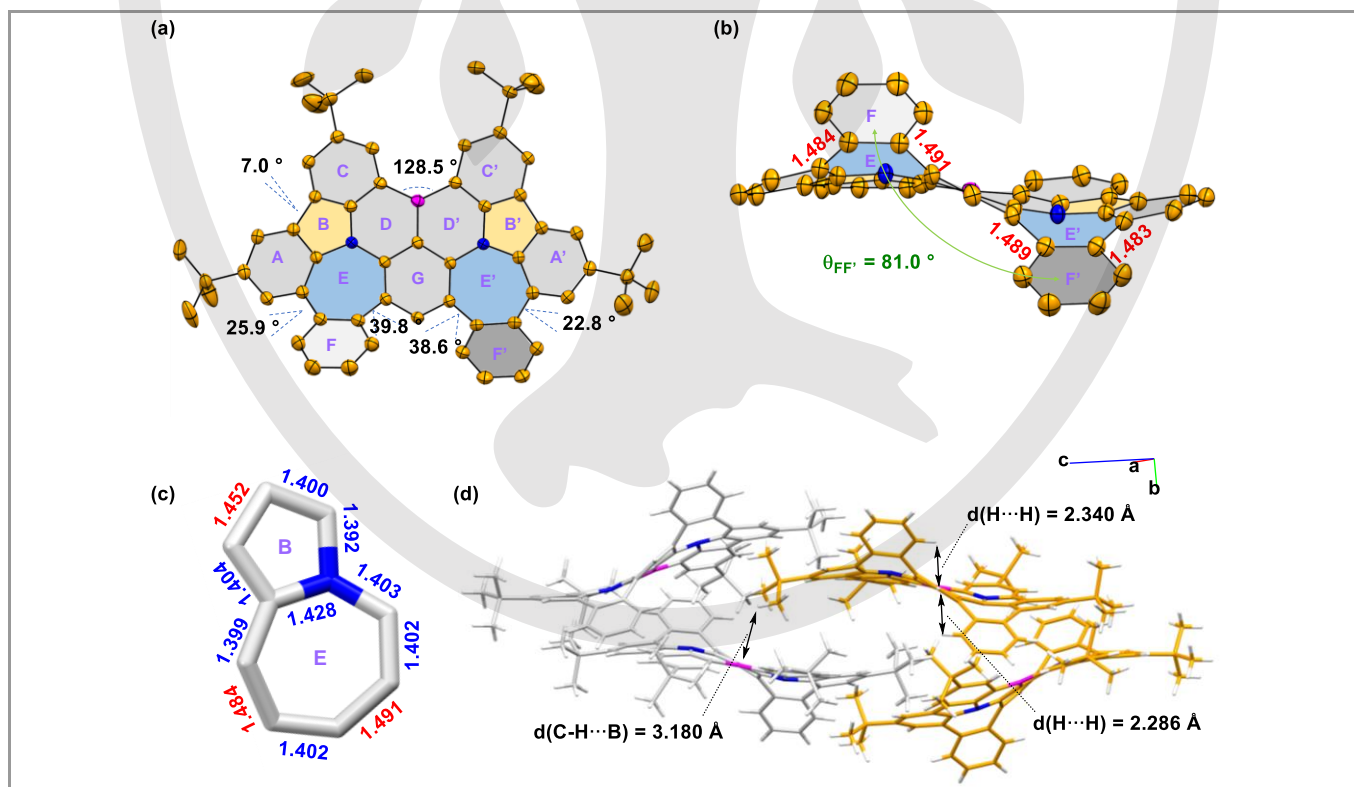
facilitate the transmetalation of boronic acids. Then annulative C-H activation undergoes at anhydrous conditions to prohibit the protonation of aryl-palladium species. The annulation product **1** showed good solubility in common organic solvents. The structure was unambiguously characterized by NMR, mass spectrometry and x-ray crystallographic analysis.

The proton NMR signals indicated that **1** possessed a symmetric structure in CD<sub>2</sub>Cl<sub>2</sub> (Figures 2a-c). The central aromatic proton of TBBBA unit in the twisted circuit showed a sharp singlet peak (labeled as 9).<sup>11</sup> The proton signals were assigned based on the well resolved 2D <sup>1</sup>H-<sup>1</sup>H correlated NMR spectra. The doublet peak of 8 showed strong correlation with peak 9, then peaks 3-7 were assigned correspondingly. The characteristic doublet peak at 8.90 ppm (peak 1) belonged to the *ortho*-position of carbon atom connected to boron atom with a small coupling constant ( $J = 1.9$  Hz). The correlations of peak 2 with peak 1 and peak 3 were observed in COSY and NOESY spectra, respectively. Finally, the aliphatic protons of *tert*-butyl groups were assigned (Figure 2c).

Crystal of compound **1** suitable for X-ray crystal structural analysis was successfully obtained by slow diffusion of methanol into toluene solution at ambient temperature (CCDC number: 2383632). The skeleton of **1** adopted an almost C<sub>2</sub>-symmetric wavy orientation due to the intermolecular C-H... $\pi$  interactions (Figure 3), of which the TBBBA unit was similar to its all carbon analog.<sup>12</sup> The dihedral angles along the newly generated C-C bonds were determined to be 25.9°, 39.8°, 38.6°, and 22.8°, respectively (Figure 3a). The bond lengths of those new C-C bonds were in the range of 1.483-1.491 Å, indicating a single-bonded characteristic (Figure 3b). The deformed phenyl rings F and F' were reaching out from the MR-plane in opposite directions due to the steric repulsion of *meta*-terphenyl moieties,

resulting in a pair of *PP*- and *MM*-twisted configurations in the solid state (Figure 3d). The angle between the mean planes of rings F and F' was 81.0°. Therefore, the  $\pi$ - $\pi$  stacking was negligible. The distances between the proton of ring G and the nearest protons of rings F (2.340 Å) and F' (2.286 Å) were in accordance with the NOESY result. An obvious bond length alternation in the nitrogen-doped heptagonal ring E was found due to the  $\pi$ -localization of benzene rings A, G and F, which was further supported by nuclear-independent chemical shift (NICS) calculations (Figure 2d). The negative NICS(0) values of rings A, G, and F suggested a strong aromatic character. On the contrary, the large positive NICS(0) value of ring E favored an antiaromatic character. Overall, the alternating aromatic/antiaromatic characters of rings in the TBBBA unit could be attributed to the  $\pi$ -localization of benzene rings.<sup>5c</sup>

The fundamental photophysical and electrochemical properties of compound **1** were investigated in solution. The ultraviolet-visible (UV-Vis) absorption and photoluminescence (PL) spectra were obtained in diluted toluene solution (10<sup>-5</sup> M) at room temperature (Figure 4a). The absorption maximum appeared at 513 nm, corresponded to S<sub>0</sub> → S<sub>1</sub> transition (oscillator strength  $f = 0.3799$ ). The optical energy gap (2.28 eV) was estimated from the onset of absorption peak, according to the equation  $E_{\text{gap}}^{\text{opt}}$  (eV) = (1240/ $\lambda_{\text{onset}}$ ). The optical energy gap of compound **1** was sharply decreased by the doubly annulated azepines versus BCz-BN.<sup>13</sup> The red-shifted emission at 540 nm for compound **1** was recorded in toluene, whereas BCz-BN showed a sky-blue emission at 484 nm. The emission of compound **1** possessed a slightly broadened full width at half maximum (FWHM) (36 nm, 0.15 eV). A high photoluminescence quantum yield ( $\Phi_{\text{PL}}$ , 78%) of compound **1** was facilitated in



**Figure 3** Crystallographic analysis of **1**. (a) Top view, hydrogen atoms are omitted for clarity. (b) Side view, hydrogen atoms and *tert*-butyl groups are omitted for clarity. (c) Selected bond lengths of joined pentagon-heptagon (Rings B and E). (d) Packing mode in the solid state, carbon atoms of *PP*- and *MM*-twisted configurations were



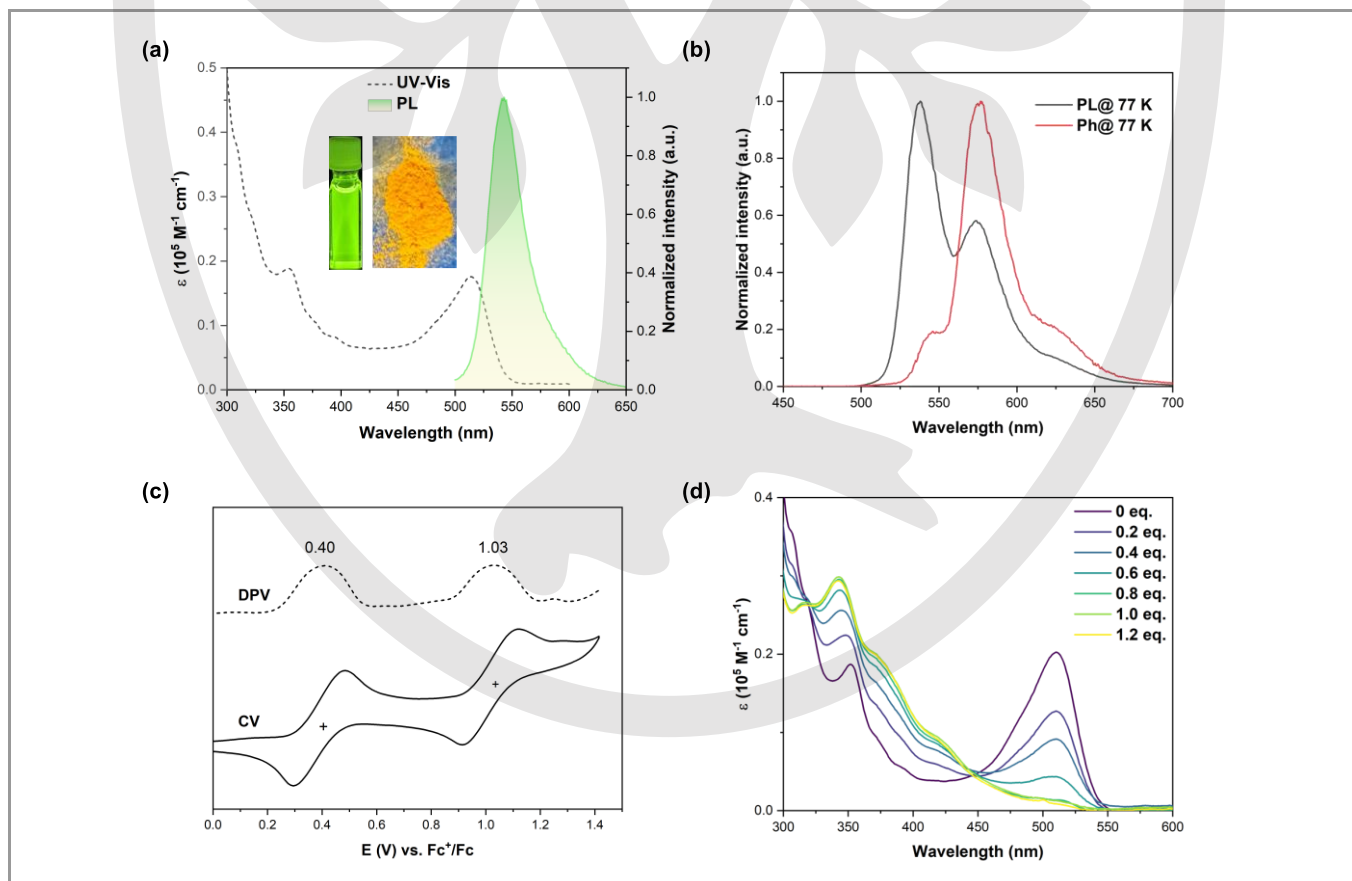
colored in orange and gray, respectively.

nitrogen-purged toluene solution, whereas the  $\Phi_{\text{PL}}$  in non-deaerated solution was lowered to 44%. The lifetimes of prompt and delayed fluorescence were measured to be 12.9 ns and 213.2 ns, respectively. Moreover, the singlet-triplet energy gap ( $\Delta E_{\text{ST}}$ ) was estimated to be 0.15 eV by the onset values of fluorescence and phosphorescence spectra measured at 77 K (Figure 4b). The small  $\Delta E_{\text{ST}}$  was adequate to promote the population of excitons from the lowest triplet ( $T_1$ ) state to the lowest singlet ( $S_1$ ) state resulting in TADF properties. Cyclic voltammetry (CV) and differential pulse voltammetry (DPV) measurements of compound **1** in dichloromethane revealed two reversible oxidation waves at 0.40 and 1.03 V (Figure 4c). The HOMO energy level of **1** was estimated to be -5.20 eV according to  $E_{\text{HOMO}} = -(4.8 + E^{\text{ox}})$  eV, which was much higher than that of BCz-BN (-5.40 eV). The anion-responsive property of compound **1** was further investigated by titration experiments with tetrabutylammonium fluoride (TBAF) in THF (Figure 4d). The negative charge derived from the binding of fluoride anion to the trivalent boron center is stabilized over the TBBBA-annulated MR-skeleton. Upon addition of TABF, the absorption maxima at 508 nm gradually decreased. The absorption intensity spanning from 330 to 450 nm increased after the binding of fluorine anion, indicating the capability of compound **1** as a fluoride sensor.<sup>5c</sup>

To gain detailed information of electronic structure of compound **1**, we conducted density-functional theory (DFT) calculations at B3LYP-D3(BJ)/6-311G(d,p) level of theory. The optimized  $C_2$ -symmetric structure showed atomic separation of the highest occupied (HOMO) and lowest unoccupied (LUMO)

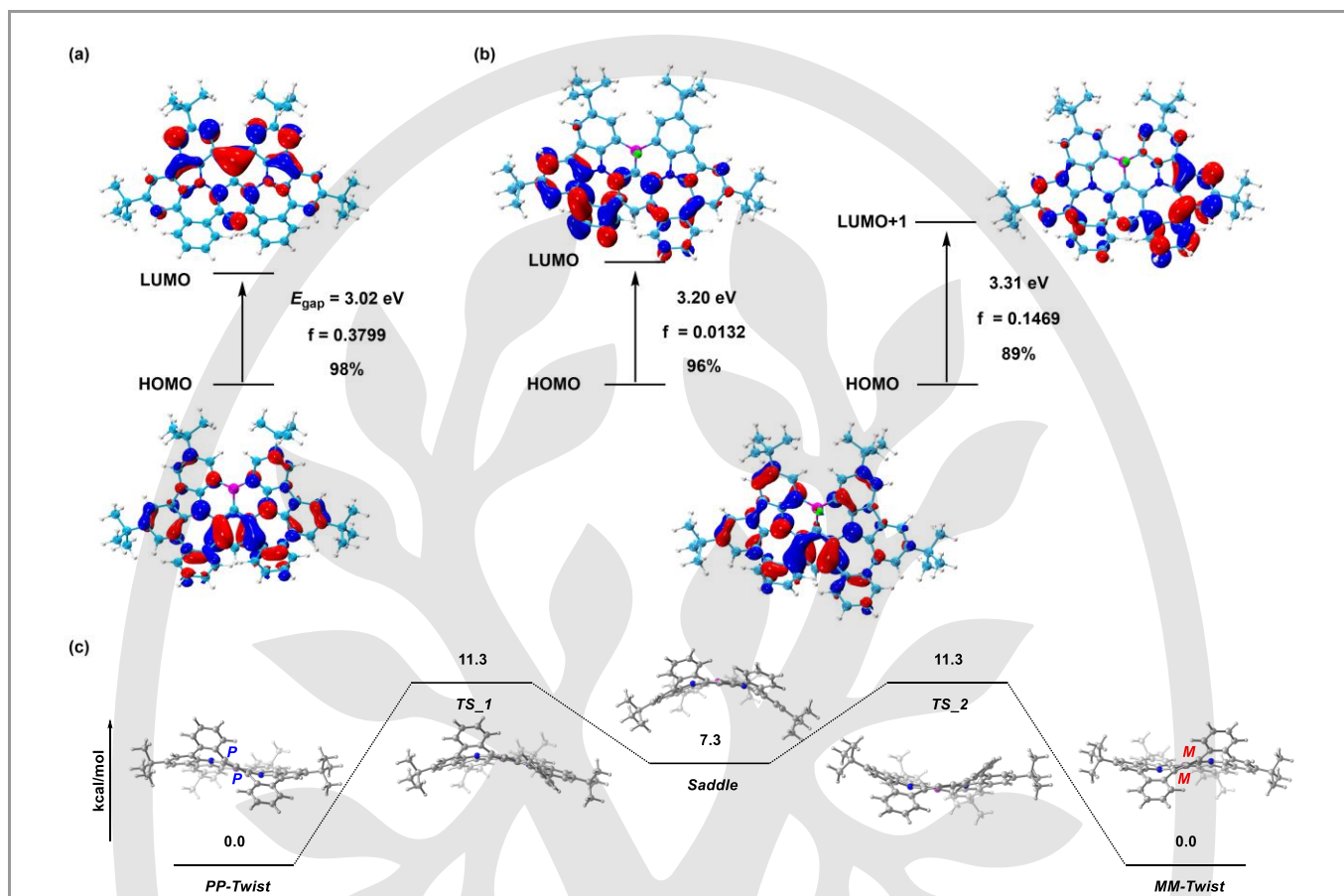
molecular orbitals, which was beneficial for narrowband emission from short-range charge transfer transitions (Figure 5a). Compared to the pristine MR-core (BCz-BN), the calculated HOMO-LUMO gap of compound **1** was narrowed from 3.42 eV to 3.02 eV, indicating the high capability of effective red-shifted emission. The LUMOs of BCz-BN and compound **1** localized similarly on the boron atom and *ortho/para*-positions of carbon atoms linking to the boron atom. However, the HOMO of compound **1** showed significant distribution on peripheral benzene rings (F and F'), indicating improved  $\pi$ -conjugation degree by the incorporation of nonalternant azepines. The calculated absorption spectrum of fluoride adduct of **1** was consistent with the experimental results. Specifically, fluoride adduct of **1** exhibits absorption peaks at 450, 420, and 380 nm, which correspond to the  $S_0 \rightarrow S_1$  (with 96% HOMO  $\rightarrow$  LUMO contribution, oscillator strength  $f = 0.0132$ ),  $S_0 \rightarrow S_2$  (with 89% HOMO  $\rightarrow$  LUMO+1 contribution, oscillator strength  $f = 0.1469$ ) and  $S_0 \rightarrow S_3$  (with 91% HOMO  $\rightarrow$  LUMO+2 contribution, oscillator strength  $f = 0.1797$ ) excitations, respectively (Figure 5b).

The conformational dynamics of compound **1** was theoretically studied at the B3LYP-D3(BJ)/6-31G(d) level of theory (Figure 5c). The *PP*- and *MM*-twisted configurations were energetically more stable than the saddle configuration, consistent with the single crystal X-ray diffraction (SC-XRD) analysis. The energy barrier of 11.3 kcal mol<sup>-1</sup> for the twist-saddle inversion was not sufficient for chiral resolution.



**Figure 4** Photophysical and electrochemical properties of compound **1**. (a) UV-Vis absorption and photoluminescence spectra of compound **1** in toluene ( $10^{-5}$  M). The graph insets showed solution and powder under 365 nm UV-light. (b) Normalized fluorescence and phosphorescence spectra in toluene solution ( $1 \times 10^{-5}$  M, 77 K). (c)

CV and DPV curves in anhydrous  $\text{CH}_2\text{Cl}_2$  with  $\text{Bu}_4\text{NPF}_6$  (1 M) as the electrolyte versus  $\text{Fc}^+/\text{Fc}$ . Scan rate:  $100 \text{ mV s}^{-1}$ . (d) Titration curves of compound **1** with TBAF in THF.



**Figure 5** FMO distributions of compound **1** (a) and the corresponding fluorinated complex (b). Calculated inversion process of compound **1** at the B3LYP-D3(BJ)/6-31G(d) level of theory (c). The Gibbs free energies were given in kcal/mol.

## Conclusions

In summary, we demonstrated the Pd-catalyzed double [5+2]-annulation for the nonalternant extension of multiple resonance core. The incorporation of TBBBA unit into compound **1** induced improved  $\pi$ -conjugation and effective red-shifted narrow-band emission. The high affinity of fluoride to compound **1** was elucidated. The nonalternant extension with azepines induced a highly twisted geometry with dynamic racemization behaviors. Our work reported herein highlights the simplicity of transition-metal catalyzed cascade cross-coupling reaction in the preparation of  $\pi$ -extended MR-emitter with nonalternant topologies, and related works are going on in our group.

## Funding Information

This work was supported by the Hong Kong Research Grants Council (27301720, 17304021), National Natural Science Foundation of China (22122114). J. L. is grateful for the funding from The University of Hong Kong (HKU) and ITC to the SKL. The work described in this paper was partially supported by a grant from the Co-funding Mechanism on Joint Laboratories with the Chinese Academy of Sciences (CAS) sponsored by the Research Grants Council of the Hong Kong Special Administrative Region, China and the CAS (Project No. JLFS/P-701/24 and Project No. JLFS/P-404/24).

## Acknowledgment

We thank Dr. Faan-Fung Hung and Prof. Chi-Ming Che for the assistance in measurements of photophysical properties. We thank the UGC funding administered by HKU for supporting the Time-of-Flight Mass Spectrometry Facilities under the Support for Interdisciplinary Research in Chemical Science. We acknowledge the computer cluster (HPC2021) of HKU for generous allocations of compute resources.

## Supporting Information

YES (this text will be updated with links prior to publication)

## Conflict of Interest

The authors declare that they have no competing interests.

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- (9) General procedure: In a nitrogen-filled glovebox, the starting material compound **2** (240 mg, 0.3 mmol), 2-chlorobenzeneboronic acid (190 mg, 1.2 mmol), Pd(PCy<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> (22 mg, 10 mol%), and K<sub>2</sub>CO<sub>3</sub> (330 mg, 2.4 mmol) were weighed to a 50 mL Schlenk tube. DMF (10.0 mL) was finally injected via a syringe. The tube was sealed with PTFE cap and removed from the glovebox. The reaction was stirred in an oil bath at 130 ° C for 18 hours. After cooling to room temperature, the mixture was extracted with DCM (30 mL × 3). The combined organic phase was dried over Na<sub>2</sub>SO<sub>4</sub>. The solvent was removed under vacuum. The mixture was finally purified by column chromatography with a mixed eluent of *n*-hexane/dichloromethane (v/v = 10:1 - 5:1) to afford compound **1** as a yellow solid (84 mg, 36% yield).  
<sup>1</sup>H NMR (600 MHz, CD<sub>2</sub>Cl<sub>2</sub>) δ 8.90 (d, *J* = 1.9 Hz, 2H), 8.40 (d, *J* = 1.8 Hz, 2H), 8.06 (d, *J* = 1.8 Hz, 2H), 7.86 (d, *J* = 1.9 Hz, 2H), 7.82 (s, 1H), 7.54 (dd, *J* = 8.0, 1.4 Hz, 2H), 7.43 - 7.31 (m, 4H), 7.16 (dd, *J* = 7.8, 1.4 Hz, 2H), 1.66 (s, 18H), 1.58 (s, 18H). <sup>13</sup>C NMR (151 MHz, CD<sub>2</sub>Cl<sub>2</sub>) δ 147.91, 147.83, 146.28, 142.54, 142.47, 140.75, 139.70, 138.26, 133.87, 130.24, 130.11, 129.43, 128.78, 128.76, 128.22, 124.44, 123.60, 123.48, 121.90, 121.12, 117.07, 35.44, 35.21, 32.21, 31.84.
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# Supporting Information

## Nonalternant Extension of Multiple Resonance Emitter via Palladium-Catalyzed [5+2]-Annulation

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## 1. Materials and measurements

All chemicals were purchased from Dieckmann (Hong Kong) or Energy-Chemical (China). Pd<sub>2</sub>(dba)<sub>3</sub>, tris(dibenzylideneacetone)dipalladium(0); Pd(PPh<sub>3</sub>)<sub>4</sub>, tetrakis(triphenylphosphine)palladium(0); Pd(dppf)Cl<sub>2</sub>, bis(diphenylphosphino)ferrocene]dichloropalladium(II); PCy<sub>3</sub>, tricyclohexylphosphine; Pd(PCy<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub>, dichlorobis(tricyclohexylphosphine)palladium(II); TBAF, tetra-*n*-butylammonium fluoride; DBU, 1,8-diazabicyclo(5.4.0)undec-7-ene; DMF, dimethylformamide.

<sup>1</sup>H NMR (400, 600 MHz) and <sup>13</sup>C NMR (151 MHz) spectra were recorded on a Bruker the Avance DRX 400, 600 MHz FT-NMR Spectrometer using CDCl<sub>3</sub>, CD<sub>2</sub>Cl<sub>2</sub> as deuterated solvents. Chemical shifts ( $\delta$ ) are reported in ppm. High resolution mass spectra were obtained on a Bruker Q-ToF Maxis II mass spectrometer.

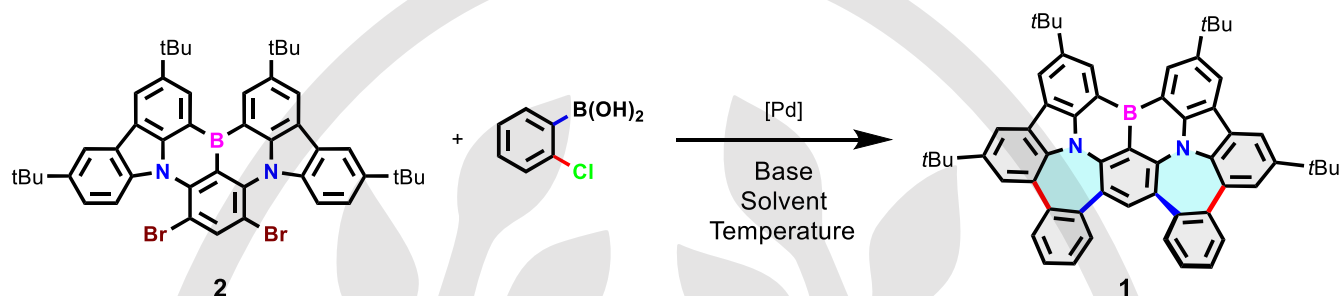
Absorption spectra were measured with Agilent Technologies Cary 60 UV-Vis spectrophotometer in a 1-cm quartz cell. Fluorescence measurements were measured with Agilent Technologies Cary Eclipse fluorescence spectrophotometer at room temperature. Photoluminescence quantum yields ( $\Phi_{PL}$ ) were determined by HAMAMATSU Quantaurus-QY instrument at room temperature. Time-resolved photoluminescence decays were measured with HAMAMATSU Quantaurus-Tau Fluorescence lifetime spectrometer C16361.

Cyclic Voltammetry (CV) measurements were carried out on a CHI660E potentiostat (CH Instruments, USA) in a three-electrode cell in an anhydrous dichloromethane solution of Bu<sub>4</sub>NPF<sub>6</sub> (0.1 M) with a scan rate of 100 mV/s at room temperature. All potential was further calibrated against Fc/Fc<sup>+</sup> by selecting ferrocene (Fc) as a reference.

## 2. Experimental procedures

Compound **2** was synthesized according to the reference<sup>[S1]</sup>.

General procedure for the Pd-catalyzed [5+2]-annulation:



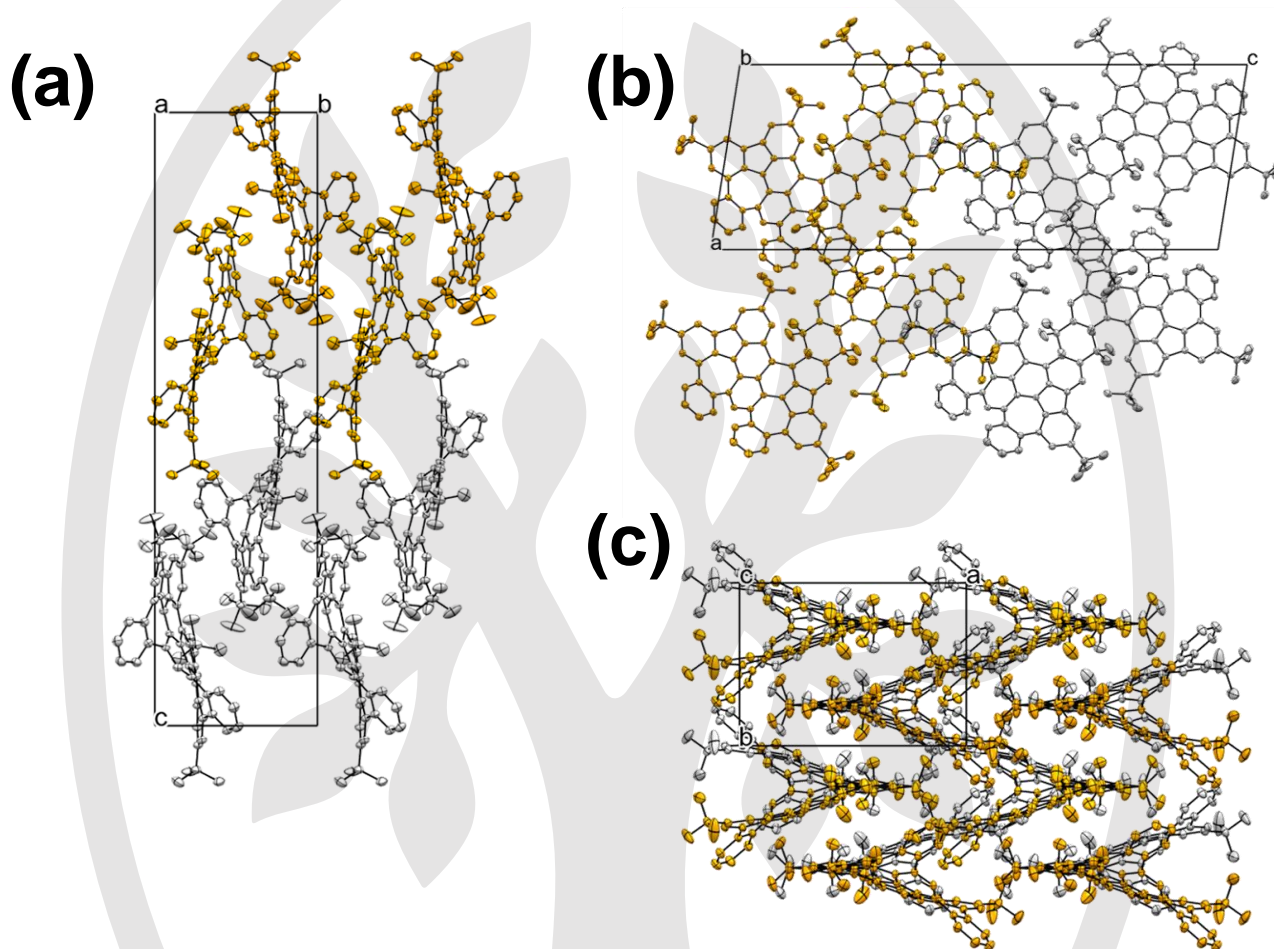
In a nitrogen-filled glovebox, the starting material compound **2** (80 mg, 0.1 mmol), 2-chlorobenzeneboronic acid (47 mg, 0.3 mmol), palladium catalyst and ligand (10 mol% based on [Pd]), and base (0.8 mmol) were weighed to a 10 mL Schlenk tube. The solvent (3.0 mL) was finally injected via a syringe. The tube was sealed with PTFE cap and removed from the glovebox. The reaction was stirred in an oil bath for 18 hours at the indicated temperature. After cooling to room temperature, the mixture was extracted with DCM (30 mL  $\times$  3). The combined organic phase was dried over Na<sub>2</sub>SO<sub>4</sub>. The solvent was removed under vacuum. The crude yield of **1** was determined by <sup>1</sup>H NMR with CH<sub>2</sub>BrCH<sub>2</sub>Br as the internal standard in CDCl<sub>3</sub>.

With the optimal condition in hand (Table 1, entry 10), 0.3 mmol scale reaction was carried out. In a nitrogen-filled glovebox, the starting material compound **2** (240 mg, 0.3 mmol), 2-chlorobenzeneboronic acid (190 mg, 1.2 mmol), Pd(PCy<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> (22 mg, 10 mol%), and K<sub>2</sub>CO<sub>3</sub> (330 mg, 2.4 mmol) were weighed to a 50 mL Schlenk tube. DMF (10.0 mL) was finally injected via a syringe. The tube was sealed with PTFE cap and removed from the glovebox. The reaction was stirred in an oil bath at 130 °C for 18 hours. After cooling to room temperature, the mixture was extracted with DCM (30 mL  $\times$  3). The combined organic phase was dried over Na<sub>2</sub>SO<sub>4</sub>. The solvent was removed under vacuum. The mixture was finally purified by column chromatography with a mixed eluent of *n*-hexane/dichloromethane (v/v = 10:1 – 5:1) to afford compound **1** as a yellow solid (84 mg, 36% yield).

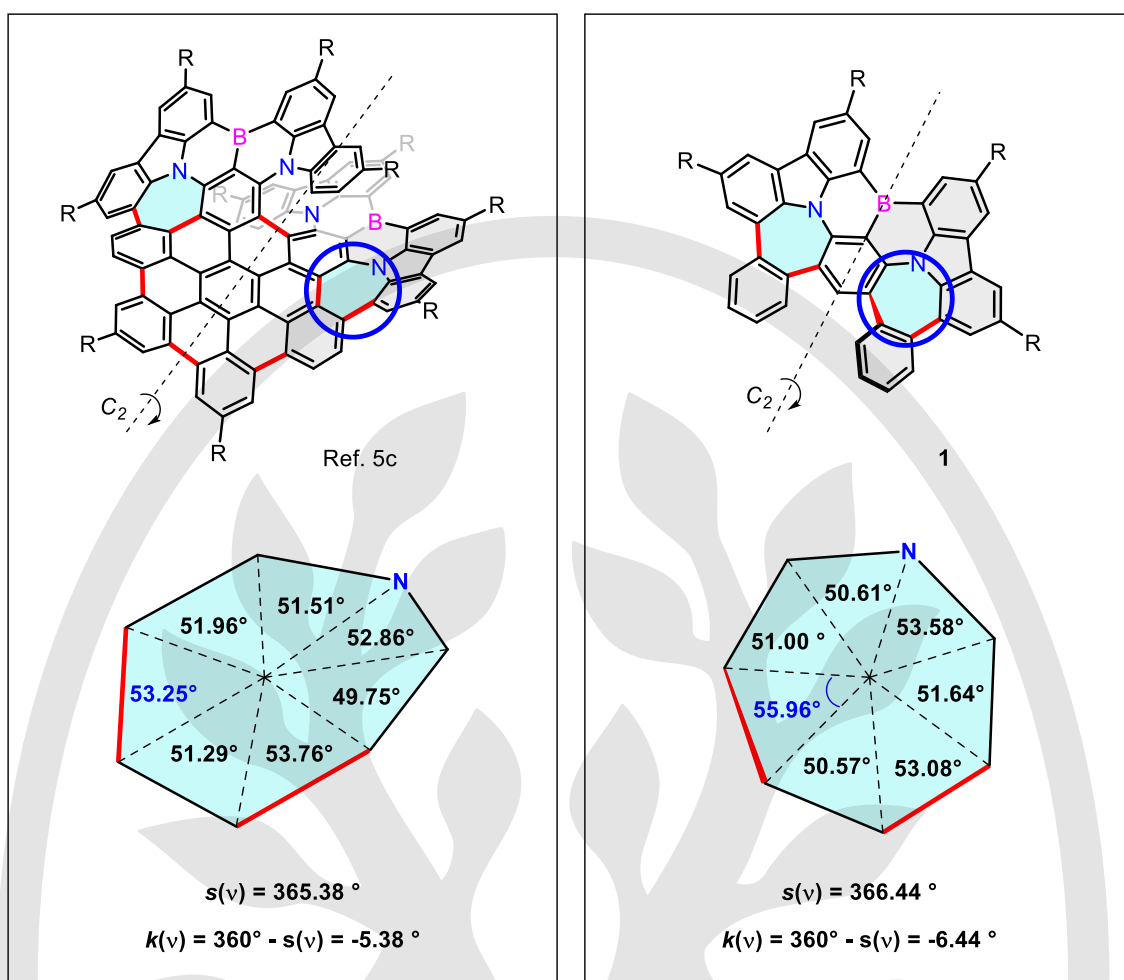
**1**: <sup>1</sup>H NMR (600 MHz, CD<sub>2</sub>Cl<sub>2</sub>)  $\delta$  8.90 (d,  $J$  = 1.9 Hz, 2H), 8.40 (d,  $J$  = 1.8 Hz, 2H), 8.06 (d,  $J$  = 1.8 Hz, 2H), 7.86 (d,  $J$  = 1.9 Hz, 2H), 7.82 (s, 1H), 7.54 (dd,  $J$  = 8.0, 1.4 Hz, 2H), 7.43 – 7.31 (m, 4H), 7.16 (dd,  $J$  = 7.8, 1.4 Hz, 2H), 1.66 (s, 18H), 1.58 (s, 18H). <sup>13</sup>C NMR (151 MHz, CD<sub>2</sub>Cl<sub>2</sub>)  $\delta$  147.91, 147.83, 146.28, 142.54, 142.47, 140.75, 139.70, 138.26, 133.87, 130.24, 130.11, 129.43, 128.78, 128.76, 128.22, 124.44, 123.60, 123.48, 121.90, 121.12, 117.07, 35.44, 35.21, 32.21, 31.84. MS (MALDI-TOF)  $m/z$  [M]<sup>+</sup> Calcd for C<sub>58</sub>H<sub>53</sub>BN<sub>2</sub><sup>+</sup> 788.4306; Found 788.4375.

### 3. X-ray crystallography

Single crystal of **1** was obtained by slow diffusion of methanol into toluene solution. The X-ray crystallographic coordinates for structure reported in this article have been deposited at Cambridge Crystallographic Data Centre (CCDC), under deposition number, CCDC 2383632 for **1**. These data can be obtained free of charge from CCDC via <https://www.ccdc.cam.ac.uk/structures/>.



**Figure S1** Packing of compound **1** in the solid state. Views along the a, b and c axis, respectively. Hydrogen atoms were omitted for clarity. *PP*- and *MM*-enantiomers were colored in orange and gray, respectively.



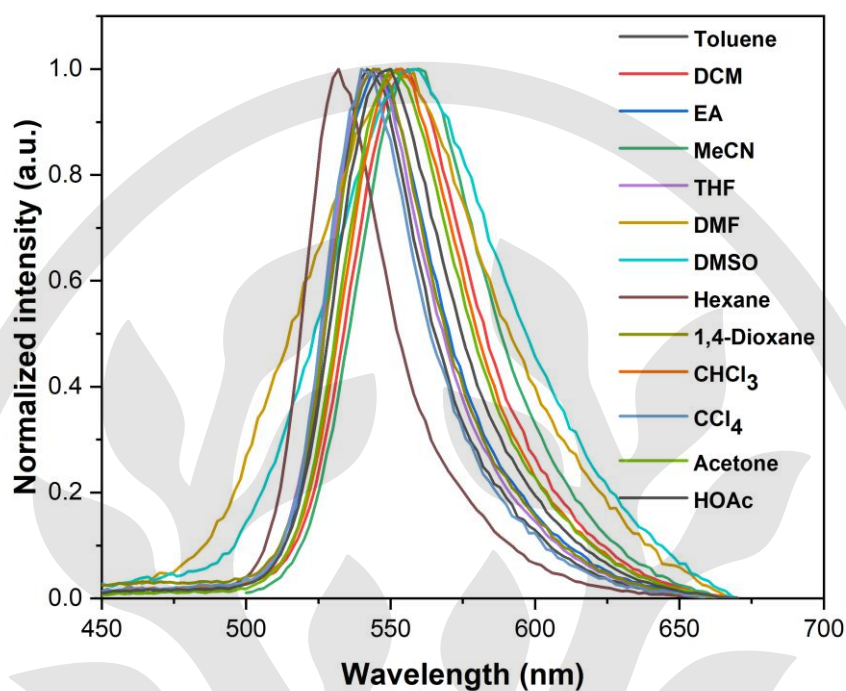
**Figure S2** Structural variants between molecule Ref. 5c (left) and molecule **1** (right).



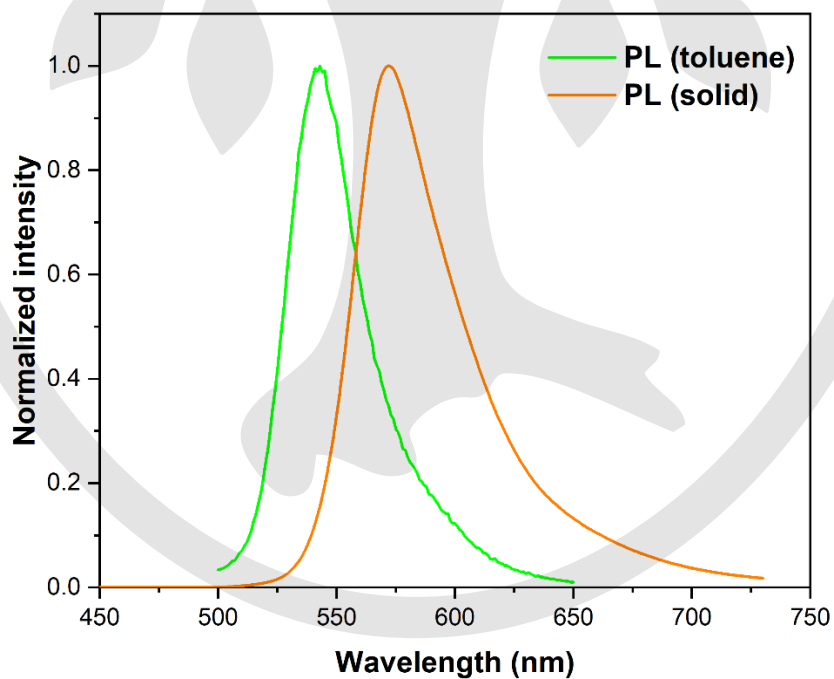
**Table S1.** Crystallographic data and details of the structural refinements of **1**.

Identification code	2383632
Empirical formula	C <sub>58</sub> H <sub>53</sub> BN <sub>2</sub>
Formula weight	788.83
Temperature/K	193.00
Crystal system	monoclinic
Space group	<i>P</i> 2 <sub>1</sub> / <i>c</i>
<i>a</i> /Å	13.5111(3)
<i>b</i> /Å	9.5671(2)
<i>c</i> /Å	36.5844(7)
$\alpha$ /°	90
$\beta$ /°	98.9690(10)
$\gamma$ /°	90
Volume/Å <sup>3</sup>	4671.15(17)
<i>Z</i>	4
$\rho_{\text{calc}}$ /cm <sup>3</sup>	1.122
$\mu$ /mm <sup>-1</sup>	0.483
<i>F</i> (000)	1680.0
Crystal size/mm <sup>3</sup>	0.13 × 0.12 × 0.11
Radiation	CuK $\alpha$ ( $\lambda$ = 1.54178)
2 $\theta$ range for data collection/°	4.89 to 136.39
Index ranges	-16 ≤ <i>h</i> ≤ 10, -11 ≤ <i>k</i> ≤ 9, -44 ≤ <i>l</i> ≤ 43
Reflections collected	33476
Independent reflections	8476 [ <i>R</i> <sub>int</sub> = 0.0366, <i>R</i> <sub>sigma</sub> = 0.0297]
Data/restraints/parameters	8476/0/562
Goodness-of-fit on <i>F</i> <sup>2</sup>	1.048
Final <i>R</i> indexes [ <i>I</i> ≥ 2 $\sigma$ ( <i>I</i> )]	<i>R</i> <sub>1</sub> = 0.0450, <i>wR</i> <sub>2</sub> = 0.1205
Final <i>R</i> indexes [all data]	<i>R</i> <sub>1</sub> = 0.0510, <i>wR</i> <sub>2</sub> = 0.1245

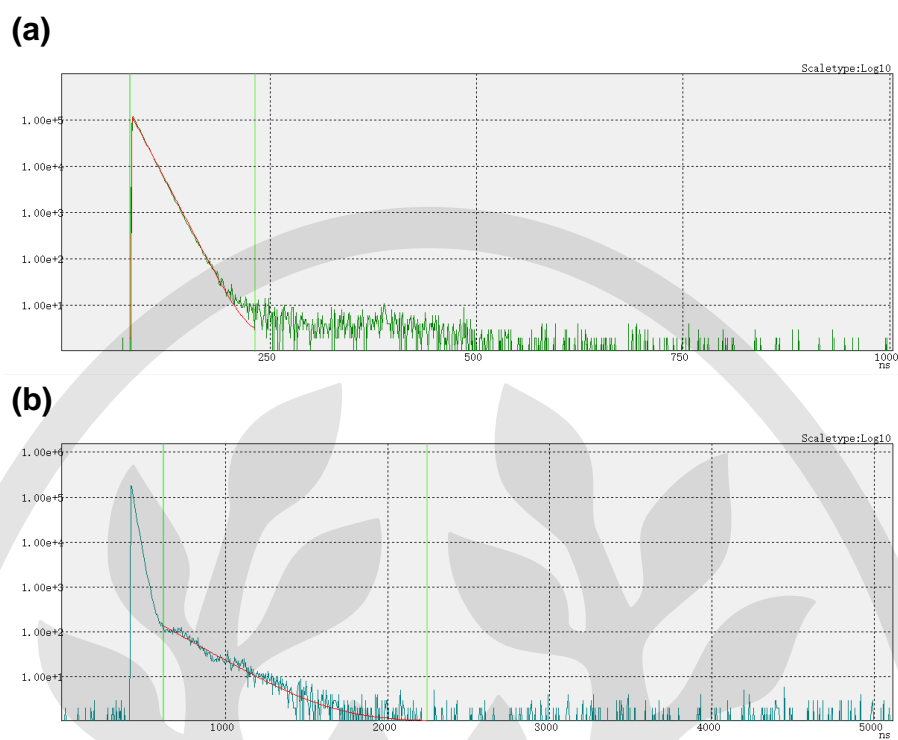
#### 4. Optical properties



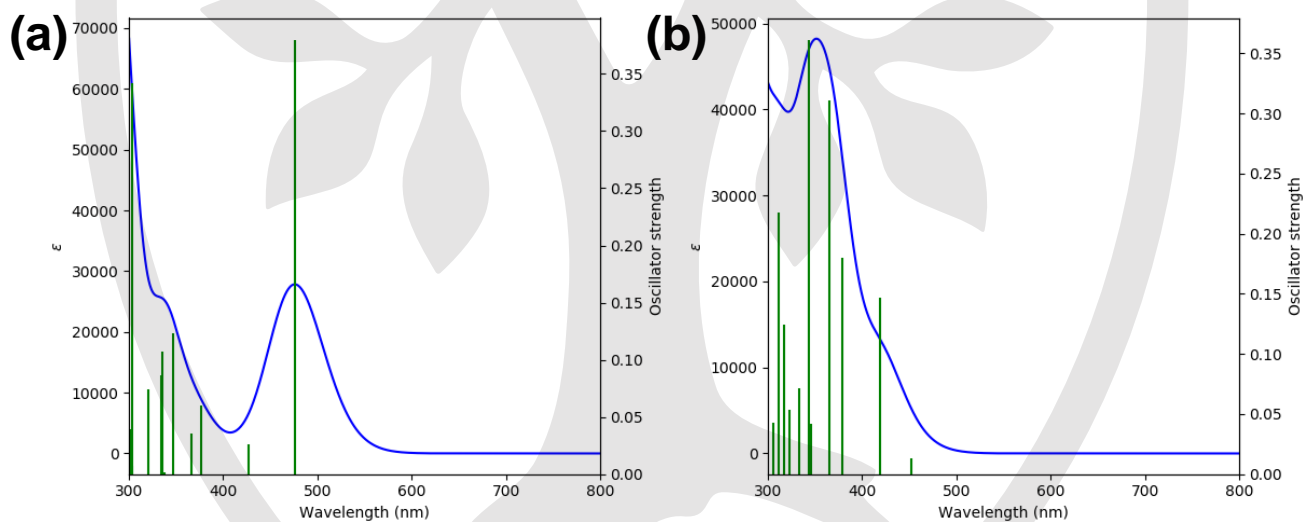
**Figure S3** Normalized fluorescence emission spectra of **1** in different solvents.



**Figure S4** Normalized photoluminescence spectra of **1** in dilute toluene and solid state.



**Figure S5** (a) Lifetime of prompt fluorescence of **1**. (b) Lifetime of delayed fluorescence of **1**.



**Figure S6** Simulated UV-Vis absorption spectra of **1** (a) and the according fluoride adduct **1-F** (b).

## 5. Theoretical calculations

The density functional theory (DFT) calculations were performed with the Gaussian 16 quantum chemistry package<sup>[S2]</sup> employing the PBE0<sup>[S3]</sup> or B3LYP<sup>[S4]</sup> hybrid functional with Grimme's D3BJ dispersion correction<sup>[S5]</sup>. Structures were optimized with the 6-31G(d) basic set. The time-dependent density functional theory (TD-DFT) calculation<sup>[S6]</sup> was conducted after the geometry optimization and considered the solvent used during experiments (toluene) through the self-consistent reaction field (SCRF) method using the SMD variation of the polarizable continuum model (IEFPCM)<sup>[S7]</sup> with the 6-311G(d) basic set. Nucleus independent chemical shifts (NICS) values were calculated using the standard gauge invariant atomic orbital (GIAO)<sup>[S8]</sup> method using B3LYP functional with the 6-311+G(d,p) basic set. The visualizations were completed by using Multiwfn software<sup>[S9]</sup>, VMD<sup>[S10]</sup>, CYLview<sup>[S11]</sup>, or GaussSum<sup>[S12]</sup>.

**Table S2.** Calculated photophysical properties data of **1** and **1-F** at the PBE0/6-311G(d) level.

compd	Excited States	Wavelength [nm]	Oscillator Strength	Transitions
<b>1</b>	S <sub>1</sub>	477	0.3799	HOMO->LUMO (98%)
	S <sub>2</sub>	427	0.0265	HOMO->L+1 (97%)
	S <sub>3</sub>	377	0.0604	HOMO->L+2 (93%)
	S <sub>4</sub>	366	0.0356	H-1->LUMO (22%), HOMO->L+3 (73%)
	S <sub>5</sub>	347	0.1229	H-1->LUMO (72%), HOMO->L+3 (23%)
	S <sub>6</sub>	337	0.0016	H-2->LUMO (85%)
	S <sub>7</sub>	335	0.1074	HOMO->L+4 (82%)
	S <sub>8</sub>	334	0.086	H-3->LUMO (93%)
	S <sub>9</sub>	320	0.0746	H-1->L+1 (80%)
	S <sub>10</sub>	304	0.3419	H-5->LUMO (21%), H-3->L+1 (59%)
<b>1-F</b>	S <sub>1</sub>	452	0.0132	HOMO->LUMO (96%)
	S <sub>2</sub>	419	0.1469	HOMO->L+1 (89%)
	S <sub>3</sub>	378	0.1797	HOMO->L+2 (91%)
	S <sub>4</sub>	366	0.3105	H-1->LUMO (69%), HOMO->L+3 (11%)
	S <sub>5</sub>	346	0.0421	H-1->L+1 (88%)
	S <sub>6</sub>	343	0.3614	H-1->LUMO (16%), HOMO->L+3 (75%)
	S <sub>7</sub>	333	0.0714	H-1->L+2 (11%), HOMO->L+4 (71%)



S <sub>8</sub>	323	0.0537	H-1->L+2 (67%), HOMO->L+4 (16%)
S <sub>9</sub>	317	0.1248	H-2->LUMO (77%)
S <sub>10</sub>	311	0.218	H-3->LUMO (54%), H-3->L+1 (27%)

**Table S3.** The cartesian coordinates (Å) of some optimized structures are listed as follows:

Ground state of **1**



N	-0.23660069	1.26267502	0.00000000	C	-2.05429769	-0.52694398	0.21600400
B	2.15134331	2.82022202	-0.43670400	C	-5.73546069	-0.12563498	-0.89606500
C	0.04140131	7.60750902	-1.42594300	C	-6.55185569	1.08670702	-1.37811000
H	0.73964931	7.27515002	-2.19873900	H	-6.12998769	1.52122002	-2.28842100
H	-0.25276869	8.63259802	-1.66631500	H	-7.57507469	0.77490202	-1.60333700
H	0.57130331	7.62994702	-0.46973800	H	-6.60525869	1.86793702	-0.61488300
N	4.53926331	1.26263402	-0.87342000	C	-6.42019069	-0.69307798	0.36826100
C	-2.16028569	7.29632902	-0.29180100	H	-6.40943069	0.04226602	1.17722000
H	-1.69000469	7.27497502	0.69495200	H	-7.46160269	-0.95153198	0.15326300
H	-2.41132269	8.33460002	-0.52996600	H	-5.92221669	-1.59591698	0.72886600
H	-3.09472969	6.73396702	-0.22876600	C	-5.75303369	-1.19325298	-2.01343500
C	-1.21032469	6.71316302	-1.36273900	H	-5.22379269	-2.10080698	-1.71444700
C	-1.90313269	6.75821502	-2.74363900	H	-6.78293469	-1.47125598	-2.25787900
H	-2.83204669	6.18326902	-2.75008000	H	-5.27625769	-0.81169098	-2.92021600
H	-2.14811569	7.79001802	-3.01409100	C	-1.29251869	-1.53777198	0.98616100
H	-1.24942469	6.34676202	-3.51728100	C	-2.00815169	-2.36887498	1.86563800
C	-0.87284869	5.25534202	-1.00312200	H	-3.08026169	-2.24617398	1.94713900
C	0.44119031	4.81498302	-0.80831600	C	-1.38329169	-3.31617398	2.66449600
H	1.25518731	5.50679802	-0.96471000	H	-1.97237469	-3.93697498	3.32971800
C	-1.91552769	4.31494402	-0.89546700	C	0.00197331	-3.42891998	2.62703200
H	-2.94023469	4.61022702	-1.08976000	H	0.51805131	-4.13968198	3.26221400
C	0.77051431	3.48656202	-0.46836600	C	0.72850531	-2.59411098	1.78920300
C	-1.63907869	2.99600402	-0.56391200	H	1.80971631	-2.65160598	1.80218500
C	-0.30822769	2.62144502	-0.31149900	C	0.11227431	-1.65288998	0.94345700
C	-2.43127469	1.78831002	-0.46070300	C	1.02913131	-0.84398898	0.09485000
C	-1.55751369	0.74920802	-0.07388100	C	0.96608331	0.54951402	-0.11268100
C	-3.78237169	1.54245302	-0.70038100	C	2.15133231	1.27545602	-0.43671300
H	-4.41593769	2.36417402	-1.00506100	C	3.53218331	3.48653902	-0.40505600
C	-4.27891769	0.24721002	-0.57386900	C	3.86153131	4.81496202	-0.06514100
C	-3.40116869	-0.74581098	-0.10767400	H	3.04754531	5.50678602	0.09127200
H	-3.78647169	-1.74677998	0.03325400	C	5.17558031	5.25531002	0.12962200



C	-0.61683558	4.75713696	-1.01030900	C	-6.31031258	4.05985196	-0.23887900
C	1.73462642	4.38340996	-1.42971300	C	-5.90123958	2.75885096	-0.53002000
C	-0.79705658	3.48487696	-0.46267900	C	-4.52932558	2.45616196	-0.57094300
C	1.59049442	3.09325996	-0.91717500	C	-3.10541658	0.43588896	-0.72849400
C	0.34073342	2.69088696	-0.42719800	C	-2.94734558	-0.94371404	-1.02270500
C	2.46180042	1.94428696	-0.81424000	C	-1.80757758	-1.55037704	-0.48471800
C	1.70149242	0.89501896	-0.23794400	C	-3.75133358	-1.75669104	-1.97224600
C	3.78783742	1.74617196	-1.19635900	C	-3.02578058	-2.63516504	-2.80419100
C	4.37981342	0.49526696	-1.03025400	C	-3.63609958	-3.47648404	-3.72376600
C	3.61937242	-0.51084704	-0.41124900	C	-5.01780258	-3.43125104	-3.87328400
C	2.30208442	-0.34093504	0.03922600	C	-5.74918658	-2.54087104	-3.09977200
C	5.81593342	0.18186596	-1.48359200	C	-5.15394458	-1.70963104	-2.13258300
C	6.50362542	1.40068296	-2.12443200	C	-6.03226758	-0.76229404	-1.40719500
C	6.66406842	-0.25957104	-0.26889400	C	-5.62432358	0.52778996	-1.02605700
C	5.79004642	-0.95665904	-2.52861400	C	-6.60309358	1.51914496	-0.75379600
C	1.65854842	-1.38475404	0.86934400	C	-7.95910958	1.20135996	-0.68682100
C	2.46945942	-2.15523004	1.72019400	C	-8.37245658	-0.11465004	-0.87805500
C	1.95208642	-3.16297004	2.52342900	C	-7.39515858	-1.05391704	-1.24741300
C	0.58158942	-3.40332204	2.51107200	C	-9.83496058	-0.56584904	-0.72945700
C	-0.23986058	-2.62556604	1.70572400	C	-10.76480058	0.59591896	-0.33603800
C	0.26646642	-1.61693804	0.86437000	C	-10.34382658	-1.15129204	-2.06670900
C	-0.72806458	-0.85835004	0.06421400	C	-9.92978558	-1.64804904	0.36991700
C	-0.78001258	0.54838496	-0.05789900	F	-1.95936458	2.83304496	1.61771000
C	-2.01479758	1.19690696	-0.26578600	H	-0.89813158	7.58009096	-1.00937300
C	-3.54551558	3.35912696	-0.19389800	H	-1.29680358	6.98636096	-2.62722400
C	-3.99793758	4.65158396	0.09478100	H	-0.34326458	8.46319196	-2.43780300
C	-5.35225458	5.03853296	0.04808300	H	1.52519142	7.50075796	-0.17767400
C	-5.80969158	6.47891096	0.34495900	H	2.81517642	6.93347896	-1.24026600
C	-6.72661558	6.48897696	1.58918100	H	1.97331142	8.44532696	-1.61304900
C	-6.59136558	7.03222796	-0.86846600	H	0.54178942	6.02695096	-4.12840200
C	-4.62852758	7.42881796	0.61706200	H	2.22697942	6.05097896	-3.60348500



H	1.39349542	7.57428496	-3.94660800	H	-3.03130158	-4.13462504	-4.33850600
H	-1.48959858	5.39285396	-1.07779200	H	-5.51996158	-4.05282904	-4.60689400
H	2.70098642	4.70529096	-1.80337700	H	-6.81462758	-2.45978704	-3.27169500
H	4.32676242	2.57358396	-1.63891400	H	-8.66264058	1.98996896	-0.45432700
H	4.07046142	-1.48362704	-0.26159000	H	-7.70855358	-2.07022904	-1.44821400
H	5.96458142	1.74605896	-3.01060700	H	-10.76737458	1.38363296	-1.09438900
H	7.51834942	1.13263496	-2.43381200	H	-11.79074358	0.23003396	-0.23181600
H	6.57845242	2.23551696	-1.42234300	H	-10.46947158	1.04054796	0.61797600
H	7.69211942	-0.48009504	-0.57689700	H	-10.27826458	-0.40407104	-2.86228300
H	6.69244442	0.53019196	0.48672600	H	-11.38866858	-1.46829004	-1.97574300
H	6.25609942	-1.15668004	0.20198000	H	-9.75711458	-2.01934504	-2.37549400
H	6.80550942	-1.19370104	-2.86506800	H	-10.96556058	-1.98429104	0.49150300
H	5.19753842	-0.66426104	-3.39966500	H	-9.58038658	-1.25324004	1.32764200
H	5.34978242	-1.86822304	-2.11858700	H	-9.31843058	-2.52025304	0.12788800
H	3.52953042	-1.93803904	1.76739400				
H	2.61005642	-3.73429604	3.16941800	<i>TS</i>			
H	0.14794842	-4.16879804	3.14573700	N	0.51183005	1.03090293	0.00000000
H	-1.31174158	-2.77663604	1.74005400	B	-1.81666195	-0.60914207	-0.41257600
H	-3.25461058	5.36753496	0.42008600	C	0.43163505	-5.32501007	-1.48973600
H	-7.61428858	5.87024296	1.43775300	H	-0.08561195	-4.94911707	-2.37969500
H	-7.06006658	7.50821696	1.81620300	H	0.75671105	-6.34937907	-1.70364900
H	-6.19294258	6.09803396	2.45947800	H	-0.29106495	-5.37246107	-0.66677300
H	-7.47370458	6.42667096	-1.08805600	N	-4.32801895	0.78311093	-0.40794400
H	-6.92480758	8.05885596	-0.67789700	C	2.33609005	-5.08635207	0.10787400
H	-5.95971658	7.03527896	-1.76104500	H	1.65985105	-5.07871907	0.97026000
H	-3.94361958	7.47115696	-0.23396200	H	2.61800205	-6.12636507	-0.09763800
H	-4.05768958	7.12124896	1.49655800	H	3.24531505	-4.54575407	0.39125000
H	-5.00372158	8.44114796	0.79848800	C	1.65329405	-4.45826507	-1.12962600
H	-7.36939758	4.29483596	-0.22409800	C	2.63290405	-4.48582907	-2.32578000
H	-1.73968858	-2.63062704	-0.52830100	H	3.54693705	-3.92047707	-2.11501200
H	-1.94560558	-2.63169804	-2.73688400	H	2.92458705	-5.51729107	-2.55914900

H	2.16895705	-4.05077507	-3.21820500	C	2.05073605	5.06582393	1.57258100
C	1.26915005	-3.00142907	-0.81717000	H	2.87367205	4.87670893	2.25170700
C	-0.05349795	-2.54314807	-0.86145600	C	1.61972405	6.37555193	1.40883600
H	-0.84192995	-3.22945707	-1.14047400	H	2.09360305	7.18241593	1.96022400
C	2.27439705	-2.08333207	-0.45040000	C	0.61556605	6.62307693	0.47840000
H	3.31036805	-2.40337307	-0.38044700	H	0.31746605	7.63710893	0.22749200
C	-0.42513895	-1.21349007	-0.56812700	C	-0.04496595	5.54770493	-0.10404800
C	1.95270605	-0.75932307	-0.17918500	H	-0.83162895	5.78267193	-0.80864100
C	0.61594005	-0.33646307	-0.27712800	C	0.26025905	4.19504493	0.18005800
C	2.71510105	0.39404193	0.22810400	C	-0.78120595	3.15629793	-0.14135200
C	1.81486705	1.48226493	0.34578000	C	-0.69911895	1.73613493	-0.15443200
C	4.07644505	0.51629593	0.50273600	C	-1.88699195	0.93457193	-0.31762600
H	4.71069505	-0.35636407	0.39742700	C	-3.13005795	-1.37738407	-0.21067100
C	4.58337105	1.75311893	0.88626700	C	-3.31321095	-2.73572507	0.12825200
C	3.67192805	2.81703093	0.99309900	H	-2.44096295	-3.37406607	0.12699800
H	4.08229105	3.79027693	1.22229200	C	-4.54666795	-3.27283407	0.52374800
C	2.28162205	2.73305393	0.77899100	C	-4.72286895	-4.76162207	0.87326100
C	6.07367305	2.00275593	1.17030600	C	-5.16911295	-4.89922307	2.34746100
C	6.91080805	0.71759793	1.03312600	H	-4.42016995	-4.46870707	3.02172400
H	6.86247805	0.30880393	0.01740100	H	-6.11990795	-4.38895707	2.53439800
H	7.96213105	0.93499593	1.25238000	H	-5.30104395	-5.95589707	2.61102000
H	6.57905405	-0.05810107	1.73282600	C	-5.80061995	-5.37757107	-0.04914300
C	6.24448205	2.53582193	2.61187700	H	-6.76749295	-4.87573707	0.06344800
H	5.86251805	1.81326193	3.34191700	H	-5.50349495	-5.29847307	-1.10104500
H	7.30436405	2.71586593	2.82970600	H	-5.94617495	-6.43889007	0.18720100
H	5.70907105	3.47897693	2.76364900	C	-3.42221195	-5.56755207	0.69035100
C	6.62240005	3.04510993	0.16832200	H	-3.05645895	-5.51991507	-0.34187500
H	6.09573905	4.00199893	0.24589400	H	-2.62552295	-5.21152107	1.35350500
H	7.68641005	3.23340393	0.35761800	H	-3.60460495	-6.62116807	0.92991300
H	6.51555705	2.68744693	-0.86196500	C	-5.64945395	-2.40137107	0.63699000
C	1.47999705	3.97757993	0.88074400	H	-6.60667195	-2.77201407	0.99319500

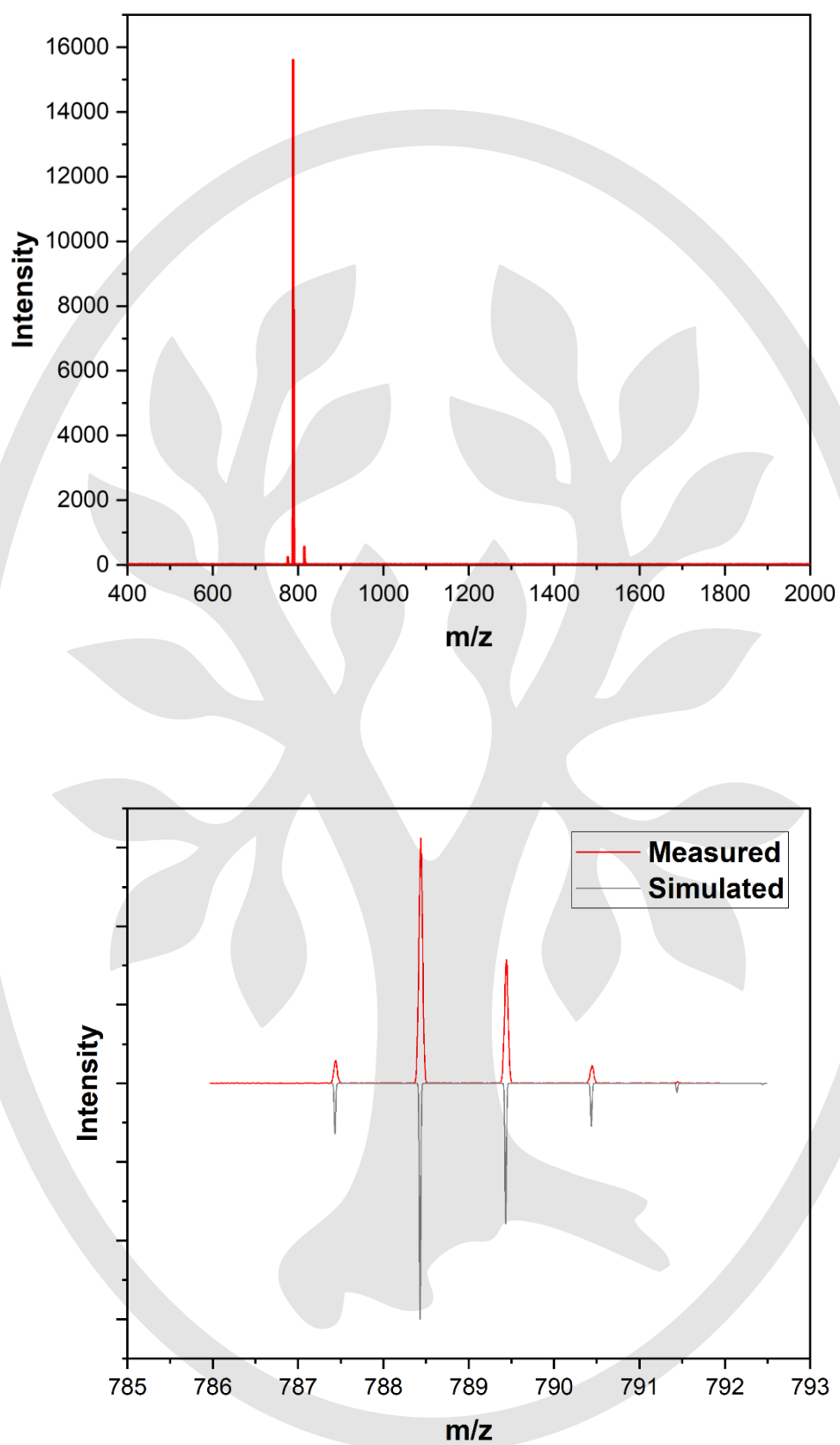
C	-5.51320595	-1.05422107	0.32161900	H	-10.21098995	3.29924493	0.04361300
C	-4.27186495	-0.58589707	-0.14394400	H	-10.68694595	1.64747693	-0.38027900
C	-3.16081095	1.56665193	-0.47474200	C	-9.52024295	2.81064293	2.69400200
C	-3.23020195	2.95585093	-0.67675100	H	-10.50428495	3.01665093	3.13281700
C	-2.06405395	3.66679093	-0.39772400	H	-8.86582495	2.42711293	3.48487700
H	-2.19928595	4.73505093	-0.36169200	H	-9.10331495	3.76207793	2.34771900
C	-4.34209695	3.72475593	-1.30567200				
C	-3.95597995	4.70876593	-2.23951200	Saddle			
H	-2.90357695	4.80891593	-2.48502900	N	-0.01931434	1.60550456	0.00000000
C	-4.87535695	5.53178593	-2.88117300	B	-2.35743734	-0.02881944	-0.42425400
H	-4.53144395	6.27733293	-3.59272200	C	-0.05244734	-4.77055444	-1.34045000
C	-6.23402595	5.36101293	-2.62670300	H	-0.36173634	-4.37028744	-2.31262300
H	-6.97619395	5.97213993	-3.13278800	H	0.28012766	-5.80284444	-1.49714300
C	-6.63952195	4.36341593	-1.74708800	H	-0.93172534	-4.80403144	-0.68702400
H	-7.70126995	4.19034993	-1.61014900	N	-4.86981034	1.35577056	-0.07245500
C	-5.72129095	3.54285093	-1.06438900	C	1.46700766	-4.59005344	0.63329000
C	-6.26013495	2.46419493	-0.20499200	H	0.62017566	-4.55183744	1.32799800
C	-5.64294895	1.21151093	-0.07323500	H	1.74822866	-5.64100344	0.49270900
C	-6.37486095	0.10496893	0.41736600	H	2.31227666	-4.08070444	1.10803300
C	-7.67191895	0.25383293	0.91125800	C	1.09232166	-3.94596544	-0.72203100
H	-8.19078595	-0.62048307	1.28701400	C	2.30575866	-4.01700244	-1.67794000
C	-8.25670895	1.52013393	0.94322200	H	3.17294066	-3.48345244	-1.27463300
C	-7.53493495	2.58445293	0.37262900	H	2.60285366	-5.05995044	-1.84342500
H	-7.99436895	3.56630793	0.35719500	H	2.06181666	-3.57219844	-2.64933200
C	-9.64773995	1.78641693	1.54258100	C	0.70442366	-2.47370444	-0.49847500
C	-10.29144395	0.50665793	2.10740000	C	-0.57459734	-1.97909044	-0.78065800
H	-10.44082595	-0.25018607	1.32880900	H	-1.32312434	-2.65572944	-1.16908700
H	-9.68258695	0.06538593	2.90467700	C	1.64944766	-1.58688644	0.06002300
H	-11.27371595	0.74251793	2.53180700	H	2.62803666	-1.94719144	0.36484600
C	-10.58505995	2.35413593	0.45112700	C	-0.95600734	-0.63359244	-0.57291700
H	-11.58318595	2.54289293	0.86500800	C	1.33726866	-0.24404844	0.22240300

C	0.07008966	0.22430056	-0.18121800	C	-0.18315534	4.69366956	-0.18828300
C	2.02599766	0.89100256	0.79453700	C	-1.30985234	3.71640956	-0.00124100
C	1.20453166	2.02188756	0.58489900	C	-1.24327434	2.30093056	-0.07127300
C	3.23346066	0.98688456	1.48835400	C	-2.43434734	1.50348956	-0.18947100
H	3.82270466	0.08977756	1.63935400	C	-3.66780234	-0.81339144	-0.22858700
C	3.62901066	2.21950456	2.00746800	C	-3.83956634	-2.20131144	-0.02363400
C	2.84271166	3.34117856	1.68616000	H	-2.98286034	-2.84011444	-0.17388700
H	3.16886866	4.31115756	2.04262900	C	-5.03329434	-2.78013744	0.42759400
C	1.67530366	3.30173056	0.90359800	C	-5.18760534	-4.29784244	0.63263200
C	4.88845766	2.40189256	2.87071300	C	-5.50380334	-4.59168044	2.11765200
C	5.62714466	1.07160356	3.10691700	H	-4.69653334	-4.23123144	2.76519200
H	5.97284966	0.62681656	2.16669300	H	-6.43223134	-4.10886844	2.44035400
H	6.50861766	1.24363556	3.73464300	H	-5.61708134	-5.67083544	2.27883300
H	4.99101266	0.34145156	3.62002400	C	-6.34613834	-4.81545844	-0.25129900
C	4.48436266	2.98021656	4.24660900	H	-7.29511234	-4.32869544	-0.00238000
H	3.79870466	2.30217056	4.76716000	H	-6.14124434	-4.62598444	-1.31107300
H	5.37089166	3.12216856	4.87694200	H	-6.47923034	-5.89588444	-0.11546200
H	3.98507366	3.94988856	4.14927800	C	-3.91307034	-5.07654744	0.25394000
C	5.86511866	3.37582156	2.17080600	H	-3.63935334	-4.92267644	-0.79608600
H	5.41893166	4.36502156	2.02348600	H	-3.05899034	-4.78699044	0.87711700
H	6.77175966	3.50737056	2.77407700	H	-4.07911334	-6.14978844	0.39990300
H	6.16036566	2.99130656	1.18797100	C	-6.10924934	-1.92696344	0.74443700
C	1.14419066	4.53820156	0.28414300	H	-7.03011934	-2.33185644	1.15502300
C	2.07247766	5.57733356	0.06647900	C	-5.98695934	-0.55495344	0.56509800
H	3.10708366	5.41980956	0.34718100	C	-4.79426534	-0.03463244	0.02820300
C	1.72706366	6.78436856	-0.52519700	C	-3.71209034	2.14906856	-0.17432000
H	2.47633666	7.55838256	-0.66532100	C	-3.80026034	3.55386956	-0.23842900
C	0.41971666	6.95903456	-0.96612600	C	-2.60394534	4.25227756	-0.07787000
H	0.11356366	7.87662356	-1.46085300	H	-2.70149934	5.32500556	0.00676000
C	-0.49673234	5.92766956	-0.80320200	C	-4.97960334	4.35985956	-0.67321500
H	-1.47938534	6.07391056	-1.23148600	C	-4.71234834	5.40735656	-1.57917300

H	-3.70391634	5.52115156	-1.96273400	H	-8.39917634	4.02202456	1.41644100
C	-5.69906334	6.27781156	-2.02927300	C	-9.91994034	2.11233856	2.57944500
H	-5.44465634	7.07186656	-2.72581400	C	-10.50658634	0.77396956	3.06501400
C	-7.01268634	6.09472956	-1.60407100	H	-10.75590034	0.11236056	2.22748400
H	-7.80781334	6.74606756	-1.95608600	H	-9.81250134	0.24454856	3.72762300
C	-7.30915234	5.03127456	-0.75923900	H	-11.42885734	0.95645756	3.62780400
H	-8.34545434	4.84716556	-0.49825000	C	-10.97330534	2.80029056	1.67985200
C	-6.31780934	4.15713156	-0.27319900	H	-11.91358334	2.93646856	2.22804500
C	-6.75393834	2.99607956	0.53436300	H	-10.63990834	3.78762256	1.34332600
C	-6.13704534	1.73891456	0.45056200	H	-11.18008034	2.19486556	0.79008400
C	-6.82092634	0.58220856	0.88837900	C	-9.64590634	2.99639456	3.81814300
C	-8.05051634	0.66869656	1.54357600	H	-10.56894734	3.14792156	4.39119100
H	-8.53213934	-0.24495844	1.87240500	H	-8.90732034	2.52520556	4.47641000
C	-8.61239334	1.92116656	1.79290900	H	-9.26169534	3.98248256	3.53707800
C	-7.95069534	3.04616056	1.26786800				







**Figure S9** MALDI-TOF mass spectra of compound **1**.

## 7. References

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