

Enhancing Light-Absorption and Luminescent Properties of Non-Emissive 1,3,4,6,9b-Pentaazaphenalene through Perturbation of Forbidden Electronic Transition by Boron Complexation

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Abstract

We report the improvement of optical properties of the non-emissive molecule through shuffling the molecular orbitals by boron complexation. The 1,3,4,6,9b-pentaazaphenylene (5AP) derivative having the 2-(dimesitylboryl)phenyl group was synthesized through the substitution reaction from the 2-bromophenyl compound. The formation of the B–N dative bond was confirmed by $^{11}\text{B}\{^1\text{H}\}$ NMR spectroscopy and a single-crystal X-ray structure analysis. Most of conventional 5AP derivatives hardly showed emission despite their planar and rigid molecular structures. The previous reports on 5AP derivatives ascribed the non-luminescent behavior to the forbidden transition between frontier orbitals. On the other hand, the 5AP-based boron complex in this work showed enhanced light absorption and luminescence from the HOMO–LUMO transition. Theoretical calculations suggested that the boron complexation should play a critical role in perturbing the forbidden character of the HOMO–LUMO transition. Because the nitrogen atom on the 5AP moiety formed the Lewis acid-base pair with the boron atom, the energy level of the HOMO of 5AP was downshifted. The character of the HOMO–LUMO transition of the boron complex was changed to afford the improved optical properties of the boron complex.

Introduction

The field of π -conjugated molecules has grown rapidly because their optical and electronic properties have large possibility to promote innovations not only in fundamental chemistry but also in applications, such as organic optoelectronic devices^[1–3] and bioprobes^[4–6]. Luminescent organic molecules have attracted particular attention because of their potential applicability in organic light-emitting diodes,^[2] bioimaging,^[5,7] and so on. Various strategies have been proposed to develop new functional π -conjugated materials. Among those strategies, we have recently proposed the conceptual idea for designing π -conjugated material based on element-blocks, which are functional building blocks containing heteroatoms.^[8,9] By combination, assembly and integration with element-blocks, unique functions originating from not only heteroatoms themselves but also electronic interaction between π -conjugation and heteroatoms can be expected. From this standpoint, we have focused on the effect of heteroatoms onto the optoelectronic properties of π -conjugated system.

In this research, as a new potential π -conjugated element-block, azaphenalene (AP) has been focused^[10–13] because of its unique electronic properties originating from the triangular structure.^[11–16] Leupin and Wirz thoroughly investigated electronic properties of the series of AP derivatives, and they revealed that APs have a symmetry-forbidden transition from the first singlet (S_1) excited state to the ground (S_0) state.^[14] As a consequence, the slow radiative process was observed due to the symmetry-forbidden nature of the S_0 – S_1 transition, and

indeed poor luminescent properties are commonly obtained from the AP derivatives. We have also confirmed that pentaazaphenalenenes (5APs) hardly showed emission from their S_1 states, despite that these rings have highly planar structures.

Transformation of non-luminescent π -conjugated scaffolds to luminescent materials has been proposed as a valid strategy for developing new classes of luminescent materials. This approach was successful especially in helicene derivatives.^[17–19] The introduction of appropriate substituents played a critical role in the modification of luminescent behaviors of helicene derivatives. These researches motivated us to investigate the luminescent properties of functionalized 5AP derivatives. In the previous research, it was found that the 5AP derivatives having the amine group at the 2-position were able to exhibit emission attributable to the transition from the S_1 excited state.^[12] Theoretical calculation data suggested the larger oscillation strength of the HOMO–LUMO transition in the presence of the amine group. It is because the contribution of the amine group to the π -conjugated system perturbed the electron-orbital symmetry of the triangular π -conjugated system. Finally, the S_0 – S_1 transition was transformed to be allowed, followed by larger magnitude of light absorption and emission.

Herein, we report that the formation of a boron complex structure is valid for enhancing light-absorption and subsequent luminescent properties through the perturbation of the symmetry-forbidden HOMO–LUMO transition. So far, various boron complexes have been reported,^[20–26] and it is known that their emission behaviors have usually been attributed to the molecular rigidity induced by the boron atom. Our approach focuses on how the Lewis acidity of the boron atom can be utilized to transform a non-luminescent scaffold to a luminescent molecule. Several researches focused on this point mainly about the stimuli-responsive materials.^[27] We synthesized the 5AP-based boron complex with a B–N bond between the dimesitylboryl moiety and the 5AP scaffold. The model compound without the boron complex moiety exhibited poor absorption and almost no emission in the visible region. On the other hand, significant enhancement of light absorption and clear red emission were observed after boron complexation. From the theoretical calculations, it was proposed that the forbidden S_0 – S_1 transition was perturbed by two reasons. One was the downshift of the HOMO of 5AP induced by the B–N dative bond formation. The other was generation of the new electronic orbital induced by boron complexation. As a result, light-absorption ability and emission property were enhanced compared to those of the pristine 5AP derivative. Similar transformation of the transition has been reported in the field of substituted helicene-^[18,19] and pyrene-^[28–30] based materials, the formation of B–N Lewis pair via

complexation was demonstrated in shuffling molecular orbitals to obtain enhanced optical properties.

Result and Discussion

We synthesized the model compound (5AP-Ph, **3**) and the boron complex (5AP-B, **5a**) as described in Scheme 1. To obtain the robust complex with enough stability for various measurements, we designed to construct the dimesitylboryl structure at the 2-position of the 5AP ring. The modified 5AP derivative having the 2'-brominated phenyl group was prepared to form the dative bond with the nitrogen atom in the 5AP ring. We followed the synthetic scheme reported by Shaw *et al.* to introduce the substituent to the 5AP scaffold.^[31] The introduction of the boron atom was performed by the lithiation-substitution strategy. 5AP-B was successfully characterized by ^1H , $^{13}\text{C}\{^1\text{H}\}$ $^{11}\text{B}\{^1\text{H}\}$ NMR, HRMS and single crystal X-ray diffraction (SCXRD, Figure 1).^[32] The B–N bond length determined by SCXRD was 1.697(4) Å, which was longer compared to B–N bond lengths of other boron complexes; 1.550(2) Å (BODIPY without any substituent, CCDC 1408453) or 1.656(2) Å (the boron complex containing 5-membered C-B-N coordination structure, CCDC 1880835^[33]). It may suggest the weak B–N bond in 5AP-B because of the weak basicity of the nitrogen atom of 5AP.^[16] It should be noted that the formation of the B–N dative bond involving the four-coordinated boron atom was also confirmed by the chemical shift of $^{11}\text{B}\{^1\text{H}\}$ NMR spectrum (4.69 ppm).^[34] Another important point in the synthesis of 5AP-B is potential generation of a structural isomer which has a B–N dative bond with the 1-nitrogen atom. During reaction and purification, we did not observe any evidence on the formation of this isomer. DFT calculation supported that the lone pair on the 3-nitrogen atom was more

negatively charged compared to that of the 1-nitrogen atom. (Figure S11), which implied that boron complexation selectively occurred with the 3-nitrogen atom. Two derivatives of 5AP-B with the substituents on the phenyl moiety (**5b** and **5c**) were synthesized according to the similar synthetic route (Scheme 1).

Figure 1 and Scheme 1

First, the UV-vis absorption properties of **3** and **5a** were examined in chloroform (Figure 2, 1.0×10^{-5} M for overall spectra and 1.0×10^{-4} M for inset in visible region). The spectra resembled with those reported for other 5AP derivatives.^[13,14] The strong (molar absorption coefficient (ϵ) $\sim 3 \times 10^4$ M⁻¹cm⁻¹) and weak ($\epsilon \sim 0.3 \times 10^4$ M⁻¹cm⁻¹) absorption bands were observed in the ultraviolet and visible regions, respectively. The strong absorption band was assigned to the allowed π - π^* transition, whereas the weak absorption band was assigned to the forbidden HOMO-LUMO transition.^[11-14] Notably, the ϵ value of 5AP-B was larger than that of 5AP-Ph, suggesting that the HOMO-LUMO transition of 5AP-B should have the more allowed character compared to those of the previous 5AP derivatives as well as 5AP-Ph.^[12-14] From these data, it can be stated that the formation of the boron complex moiety improved the light absorption property of the 5AP.

Figure 2

The photoluminescence (PL) spectra of the 5AP derivatives were measured in chloroform solution (1.0×10^{-4} M). As described in the literature and our previous works, AP derivatives are basically non-emissive due to the symmetry forbidden nature of HOMO–LUMO transition. Indeed, as described in Figure 3, 5AP-Ph hardly exhibited emission in the visible region. On the other hand, 5AP-B showed distinct red-colored emission although the absolute quantum yield was not high ($\Phi_{\text{PL}} < 0.01$). The absolute quantum yield and the fluorescence lifetime could not be determined due to the low emission intensity. From the larger ε value and emission intensity of 5AP-B compared to those of 5AP-Ph, it can be said that poor optical properties of the 5AP were able to be improved by the boron complexation.

Figure 3

The substituent effects of 5AP-B were investigated by evaluating optical properties of 5AP-B-OMe (**5b**) and 5AP-B-CF₃ (**5c**). Figure 4 illustrates UV–vis absorption and photoluminescent spectra. Fluorescence quantum yields and lifetimes were not able to be determined due to low emission intensity. It was observed that these two compounds exhibited similar absorption and photoluminescent properties to those of 5AP-B, meaning that

not the substituent effect but the formation of B-N bond should play an importance role in the enhancement of luminescent properties of 5AP.

Figure 4

To elucidate the effect of the boron complexation on optical properties, we performed theoretical calculations to investigate the electronic structures and characters of the transitions in the 5AP molecules. Density functional theory (DFT) and time-dependent DFT calculations were performed using Gaussian 16 A.03 package at (TD-)CAM-B3LYP/6-311+G(2d,p)/(TD-)B3LYP/6-31+G(d,p) level of theory.^[35] Since theoretical calculations qualitatively reproduced the optical properties of 5AP-B (Tables 1 and 2), the calculation protocol used in this study should be valid.

The electronic structure of 5AP was strongly affected by the complexation of the boron atom with the 3-nitrogen atom. From the results, it was found that the energy level of HOMO of 5AP was drastically lowered (-0.52 eV) by the introduction of boron atom (Figure 5). It is likely that the formation of B–N dative bond should play a critical role in the enhancement of the electronegative nature of the 3-nitrogen atom. Similar effect by the formation of the B–N dative bond is reported in the field of so-called BN isosteres.^[36] It should be noted that the

new energy levels at the intermediate level between the HOMO and LUMO energy levels of 5AP-Ph were generated by the introduction of the dimesitylboryl unit.

Figure 5

The different perturbation by the boron complexation to the frontier molecular orbitals (FMO)s of 5AP-B can be explained by focusing on the unique electronic characteristics of the 5AP ring. 5AP derivatives have spatially separated FMOs derived from the electronic structure consisting of the interaction between the peripheral [12]annulene moiety and the central (9b) nitrogen atom.^[14] As a result, when any structural perturbation or the substituent effect were applied to the 5AP scaffold, either HOMO or LUMO would be selectively affected. It is known that the HOMO of APs is stabilized (called as topological charge stabilization by Gimarc)^[15,37] by the introduction of the nitrogen atoms to 1, 3, 4, 6, 7 and 9 positions. The boron atom increased the electronegative nature of 3-nitrogen atom, where not the LUMO but the HOMO exists. Consequently, the HOMO was strongly downshifted by the formation of the boron complex at the 3-nitrogen atom. TD-DFT single-point calculations suggested the plausible mechanism on the enhanced light absorption properties of 5AP-B compared to 5AP-Ph. The contribution of the transition from the mesityl moiety (HOMO, HOMO-2, HOMO-3 and HOMO-5, Figure 6) to the LUMO of 5AP was observed in the

absorption band of 5AP-B in the visible region according to the TD-DFT calculation (Table 1). It was indicated that the oscillator strength of the S_0-S_1 transition at the optimized geometry of the ground state ($f_{S_0-S_1@S_0opt}$) of 5AP-B was larger than that of 5AP-Ph. The transitions including the mesityl moiety contributed to this enhancement of the oscillator strength. These theoretical data suggested that enhanced light-absorption ability should originate from the perturbation to the S_0-S_1 transition by the newly generated electronic orbitals involving the boron complex moiety.

Figure 6 and Table 1

To obtain insight on emission properties, we considered the data from the TD-DFT optimization calculations. The transition of 5AP-B from the excited state to the ground state was distinctively altered by the formation of the boron complex structure. All optimized structures were confirmed to be the local minima by the TD-DFT frequency calculations. The assignment of the S_0-S_1 transition was different between 5AP-Ph and 5AP-B. Formally, the assignment (“HOMO–LUMO transition”) was the same in both compounds. However, as we discussed above, the HOMO of 5AP-B is no longer classified as the HOMO of 5AP, instead it is the orbital of the mesityl moiety. It can be stated that the HOMO–LUMO transition of 5AP-B has essentially different character compared with that of 5AP-Ph. According to the

calculation, the oscillator strength of the S_0-S_1 transition at the optimized geometry of the excited state ($f_{S_0-S_1@S_{1opt}}$) was hardly altered. These results suggested that the formation of the boron complex structure changed the character of the S_0-S_1 transition, though its radiative decay was not facilitated. Although the origin of the non-radiative decay path in azaphenylene scaffold is still unclear despite the previous extensive studies by Leupin and Wirz,^[14] it may safely be stated that the complexation of the boron atom enhanced the light absorption property and hardly accelerated non-radiative decay path. These two points should cooperatively contribute to the distinct emission from 5AP-B.

Finally, we measured the absorption and PL spectra of 5AP-B in various solvents, such as CH_2Cl_2 , DMF, EtOAc, THF, toluene and $CHCl_3$ (1.0×10^{-4} M) although the quantum yield and the fluorescence lifetime were not able to be collected due to the low emission intensity. The results are summarized in Figure 7 and Table 2. 5AP-B showed slight solvent dependency of its Stokes shift, while the relative intensity of each vibronic structure was altered by changing the type of solvents. The intensity ratio of the peak 1 (0-0 band) toward the peak 2 (1-0 band) varied depending on the solvent polarity. Compared to the spectrum in chloroform, the difference was distinct in the case of DMF, which is the most polar solvent in this solvent set. Similar solvent dependency of the vibronic structures was also observed in pyrene and related derivatives.^[38,39] According to these past works, it is presumably because

the dipole-dipole interaction between the solute 5AP-B and the solvent influences on the vibronic coupling of the excited and the ground states. We also measured the optical spectra of 5AP-B in the mixed solvents with chloroform and MeOH (Figure 8). As we increased the solvent polarity by adding methanol, the behavior was similar to the one which was observed when the solvent was changed to the polar one; the emission intensity decreased and the difference of intensity between the peaks 1 and 2 got smaller. This result significantly supports that the solvent-dependent vibronic structure of 5AP-B mainly derived from the dipole-dipole interaction between the solvents and the solute. From these data, it was proposed that 5AP-B could be potentially applicable in the field of fluorescence sensing for local polarity in various media.^[39] It should be noted that 5AP-B-OMe and 5AP-B-CF₃ also showed similar solvent-dependent emission behaviors.

Figures 7 and 8, Table 2

Conclusion

In this report, we demonstrated the unique strategy for enhancing optical properties of the non-luminescent heterocycle by employing the 5AP-based boron complex. The character of the HOMO–LUMO transition was modulated by the complexation of boron atom to the 3-nitrogen atom, which lowered the HOMO energy level. The results from UV–vis absorption spectroscopy and theoretical calculations suggested that the intrinsically-forbidden HOMO–LUMO transition in the 5AP ring should be drastically perturbed by the contributions of the newly generated electronic orbitals in the mesityl moiety. As a consequence, the complex showed larger molar absorption coefficient. Furthermore, the emission attributable to the HOMO–LUMO transition was also induced. Finally, the complex showed solvent dependency on its vibronic structure, exhibiting the solvent sensing ability. These findings suggested that shuffling the order of molecular orbitals by B–N Lewis pair formation could be another valid strategy to transform the non-emissive dyes to the emissive ones.

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References

- [1] J. R. Sheats, H. Antoniadis, M. Hueschen, W. Leonard, J. Miller, R. Moon, D. Roitman, A. Stocking, *Science* **1996**, 273, 884–888.
- [2] H. Sasabe, J. Kido, *J. Mater. Chem. C* **2013**, 1, 1699.
- [3] H. Sirringhaus, *Adv. Mater.* **2014**, 26, 1319–1335.
- [4] J. Rao, A. Dragulescu-Andrasi, H. Yao, *Curr. Opin. Biotechnol.* **2007**, 18, 17–25.
- [5] T. Kowada, H. Maeda, K. Kikuchi, *Chem. Soc. Rev.* **2015**, 44, 4953–4972.
- [6] Y. Chen, Y. Bai, Z. Han, W. He, Z. Guo, *Chem. Soc. Rev.* **2015**, 44, 4517–4546.
- [7] J.-B. Li, H.-W. Liu, T. Fu, R. Wang, X.-B. Zhang, W. Tan, *Trends Chem.* **2019**, 1, 224–234.
- [8] Y. Chujo, K. Tanaka, *Bull. Chem. Soc. Jpn.* **2015**, 88, 633–643.
- [9] M. Gon, K. Tanaka, Y. Chujo, *Polym. J.* **2018**, 50, 109–126.
- [10] H. Yeo, M. Hirose, K. Tanaka, Y. Chujo, *Polym. J.* **2014**, 46, 688–693.
- [11] H. Watanabe, M. Hirose, K. Tanaka, K. Tanaka, Y. Chujo, *Polym. Chem.* **2016**, 7, 3674–3680.
- [12] H. Watanabe, M. Hirose, K. Tanaka, Y. Chujo, *Chem. Commun.* **2017**, 53, 5036–5039.
- [13] H. Watanabe, K. Tanaka, Y. Chujo, *J. Org. Chem.* **2019**, 84, 2768–2778.
- [14] W. Leupin, J. Wirz, *J. Am. Chem. Soc.* **1980**, 102, 6068–6075.
- [15] M. A. Rossman, N. J. Leonard, S. Urano, P. R. LeBreton, *J. Am. Chem. Soc.* **1985**, 107, 3884–3890.

- [16] W. Leupin, D. Magde, G. Persy, J. Wirz, *J. Am. Chem. Soc.* **1986**, *108*, 17–22.
- [17] S. Sahasithiwat, T. Mophuang, L. Menbangpung, S. Kamtonwong, T. Sooksimuang, *Synth. Met.* **2010**, *160*, 1148–1152.
- [18] N. Ito, T. Hirose, K. Matsuda, *Org. Lett.* **2014**, *16*, 2502–2505.
- [19] H. Kubo, T. Hirose, K. Matsuda, *Org. Lett.* **2017**, *19*, 1776–1779.
- [20] R. R. Maar, J. B. Gilroy, *Chem. –Eur. J.* **2018**, *24*, 12449–12457.
- [21] A. Loudet, K. Burgess, *Chem. Rev.* **2007**, *107*, 4891–4932.
- [22] D. Frath, J. Massue, G. Ulrich, R. Ziessel, *Angew. Chem. Int. Ed.* **2014**, *53*, 2290–2310.
- [23] G. Zhang, J. Chen, S. J. Payne, S. E. Kooi, J. N. Demas, C. L. Fraser, *J. Am. Chem. Soc.* **2007**, *129*, 8942–8943.
- [24] K. Umezawa, Y. Nakamura, H. Makino, D. Citterio, K. Suzuki, *J. Am. Chem. Soc.* **2008**, *130*, 1550–1551.
- [25] H. L. Kee, C. Kirmaier, L. Yu, P. Thamyongkit, W. J. Youngblood, M. E. Calder, L. Ramos, B. C. Noll, D. F. Bocian, W. R. Scheidt, et al., *J. Phys. Chem. B* **2005**, *109*, 20433–20443.
- [26] K. Umezawa, A. Matsui, Y. Nakamura, D. Citterio, K. Suzuki, *Chem. –Eur. J.* **2009**, *15*, 1096–1106.
- [27] S. K. Møllerup, S. Wang, *Chem. Soc. Rev.* **2019**, *48*, 3537–3549.
- [28] A. G. Crawford, A. D. Dwyer, Z. Liu, A. Steffen, A. Beeby, L.-O. Pålsson, D. J. Tozer, T. B. Marder, *J. Am. Chem. Soc.* **2011**, *133*, 13349–13362.

- [29] J. Merz, J. Fink, A. Friedrich, I. Krummenacher, H. H. Al Mamari, S. Lorenzen, M. Haehnel, A. Eichhorn, M. Moos, M. Holzapfel, et al., *Chem. –Eur. J.* **2017**, *23*, 13164–13180.
- [30] A. G. Crawford, Z. Liu, I. A. I. Mkhaliid, M.-H. Thibault, N. Schwarz, G. Alcaraz, A. Steffen, J. C. Collings, A. S. Batsanov, J. A. K. Howard, et al., *Chem. –Eur. J.* **2012**, *18*, 5022–5035.
- [31] J. T. Shaw, M. E. O'Connor, R. C. Allen, W. M. Westler, B. D. Stefanko, *J. Heterocycl. Chem.* **1974**, *11*, 627–630.
- [32] CCDC 1908401.
- [33] D. Kunchala, S. Sa, P. Nayak, J. Ponniah S, K. Venkatasubbaiah, *Organometallics* **2019**, *38*, 870–878.
- [34] S. Hermanek, *Chem. Rev.* **1992**, *92*, 325–362.
- [35] Gaussian 16, Revision A.03, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. V. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, D. Williams-Young, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y.

Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. J. Bearpark, J. J. Heyd, E. N. Brothers, K. N. Kudin, V. N. Staroverov, T. A. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. P. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2016.

[36] H. Helten, *Chem. –Eur. J.* **2016**, 22, 12972–12982.

[37] B. M. Gimarc, *J. Am. Chem. Soc.* **1983**, 105, 1979–1984.

[38] A. Nakajima, *Bull. Chem. Soc. Jpn.* **1971**, 44, 3272–3277.

[39] K. Kalyanasundaram, J. K. Thomas, *J. Am. Chem. Soc.* **1977**, 99, 2039–2044.

Figures and Tables

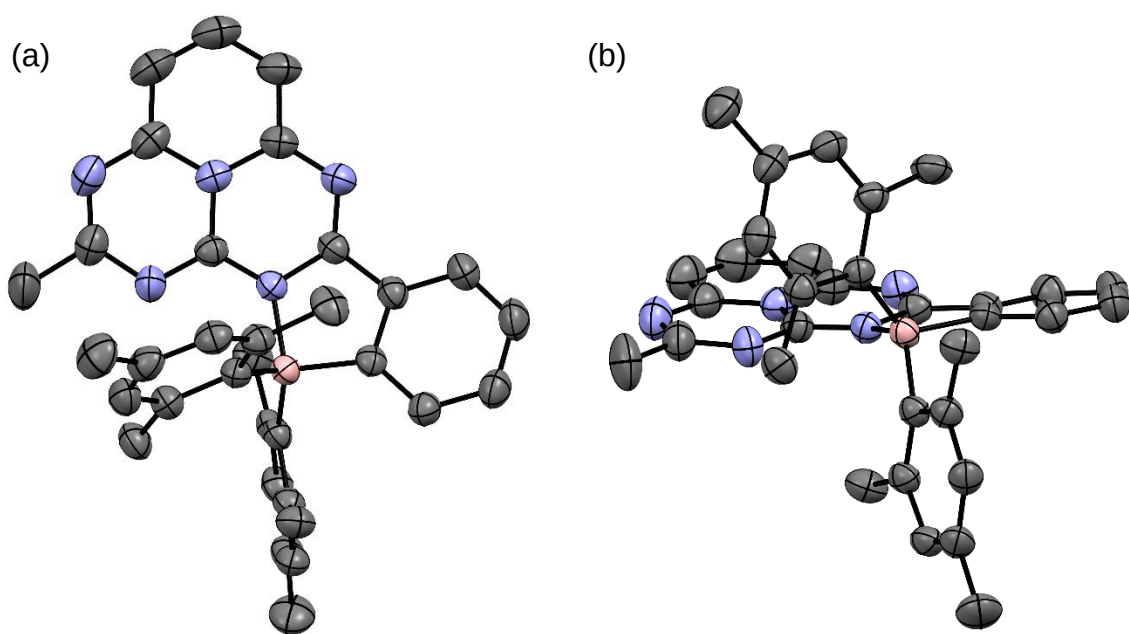
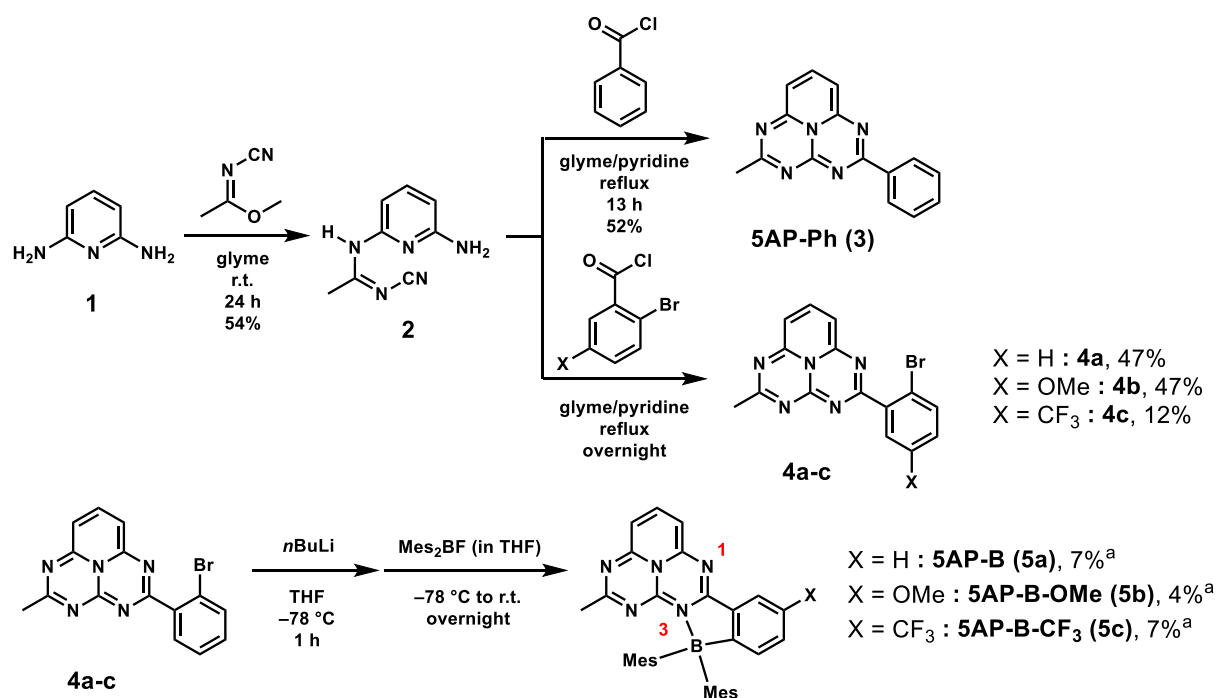


Figure 1. ORTEP (a) top and (b) side views of 5AP-B obtained by a single crystal X-ray structure analysis. Thermal ellipsoid plot is shown at 50% probability level. All hydrogen atoms are omitted for clarity.

Scheme 1. Syntheses of the 5AP ligand, 5AP-Ph (**3**), and the boron complexes **5a-c**



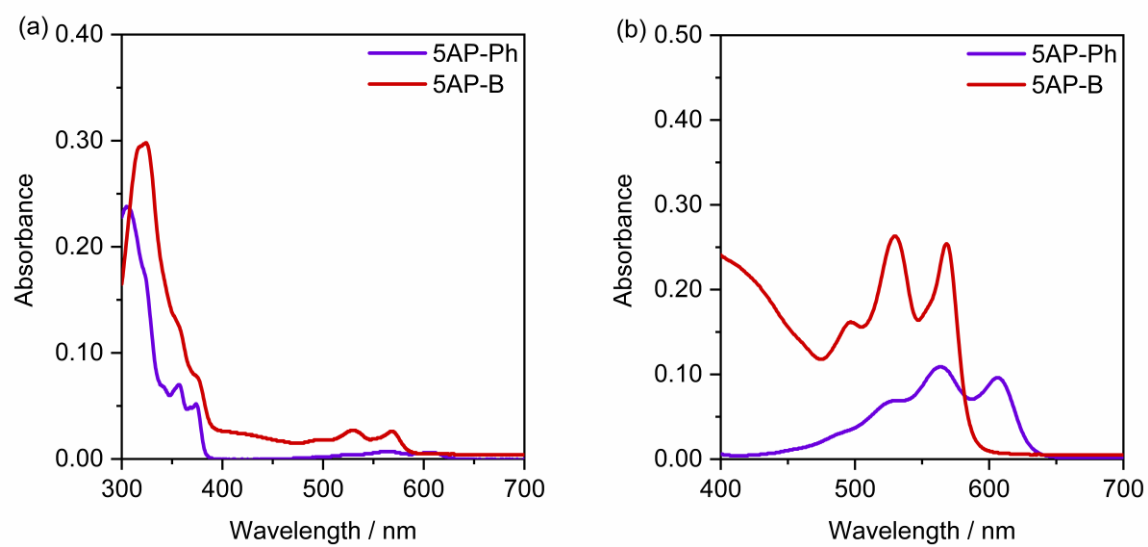


Figure 2. UV-vis absorption spectra of 5AP-Ph and 5AP-B in chloroform ((a) overall spectra, 1.0×10^{-5} M and (b) inset in the visible region, 1.0×10^{-4} M).

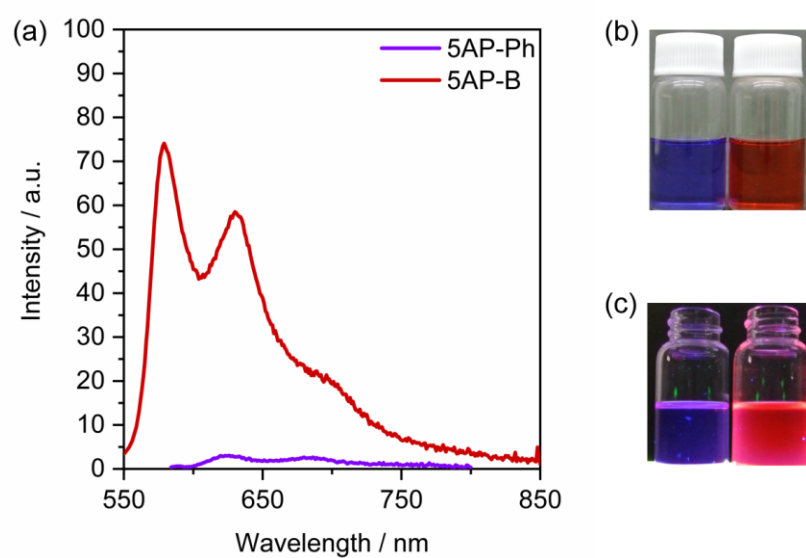


Figure 3. (a) PL spectra of 5AP-Ph and 5AP-B in chloroform (1.0×10^{-4} M). Pictures of the chloroform solutions of 5AP-Ph and 5AP-B (b) without and (c) with UV irradiation (365 nm).

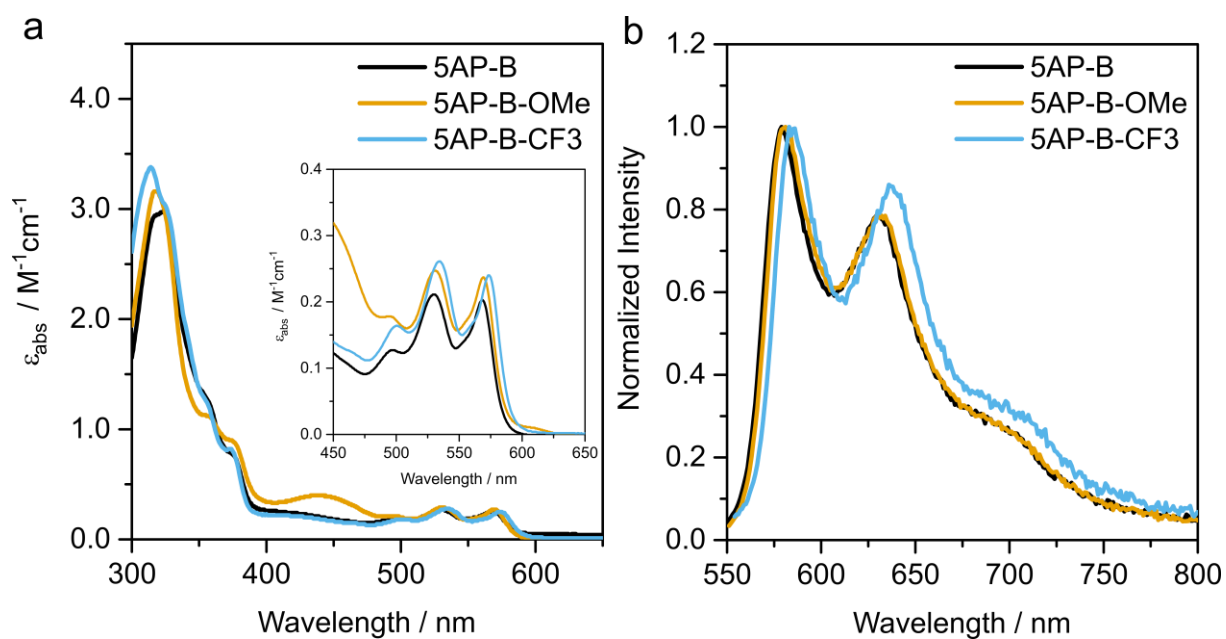


Figure 4. (a) UV-vis absorption spectra of 5AP-B, 5AP-B-OMe and 5AP-B-CF₃ in chloroform (overall spectra were recorded in $1.0 \times 10^{-5} \text{ M}$ and inset in the visible region was recorded in $1.0 \times 10^{-4} \text{ M}$). (b) Photoluminescent spectra of 5AP-B, 5AP-B-OMe and 5AP-B-CF₃ in chloroform ($1.0 \times 10^{-5} \text{ M}$). Excitation wavelength: 530 nm (5AP-B), 531 nm (5AP-B-OMe) and 534 nm (5AP-B-CF₃).

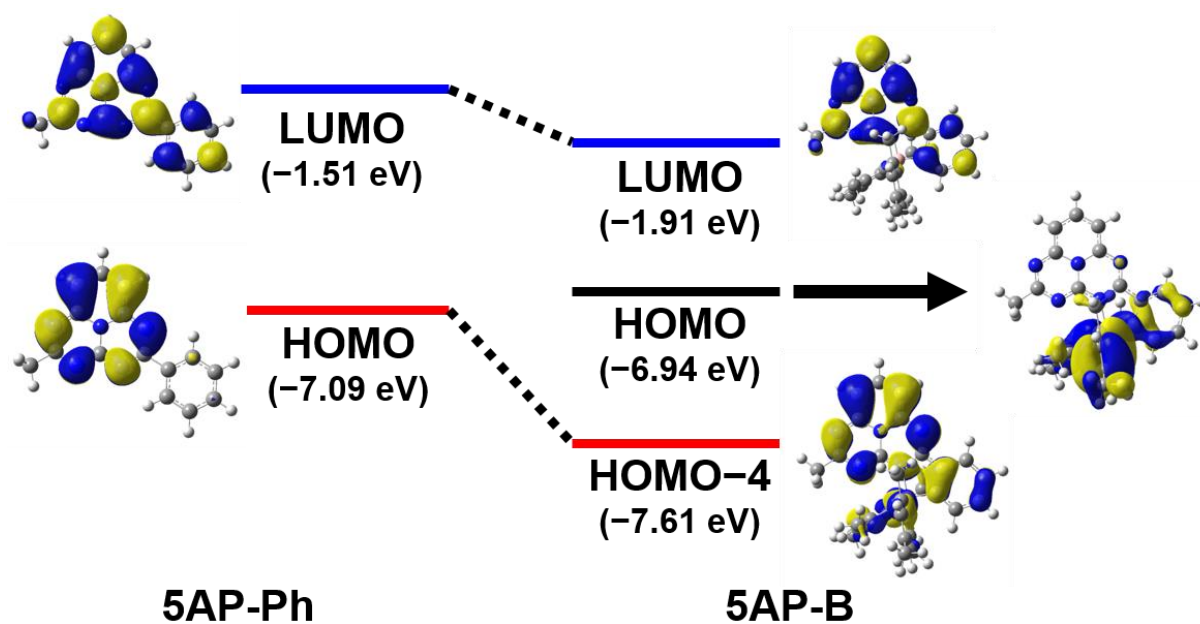


Figure 5. Schematic diagram representing the effect by the complexation of boron atom to 3-nitrogen atom. The Kohn-Sham orbitals and the energy levels were calculated at CAM-B3LYP/6-311+G(2d,p)//B3LYP/6-31+G(d,p) level of theory.

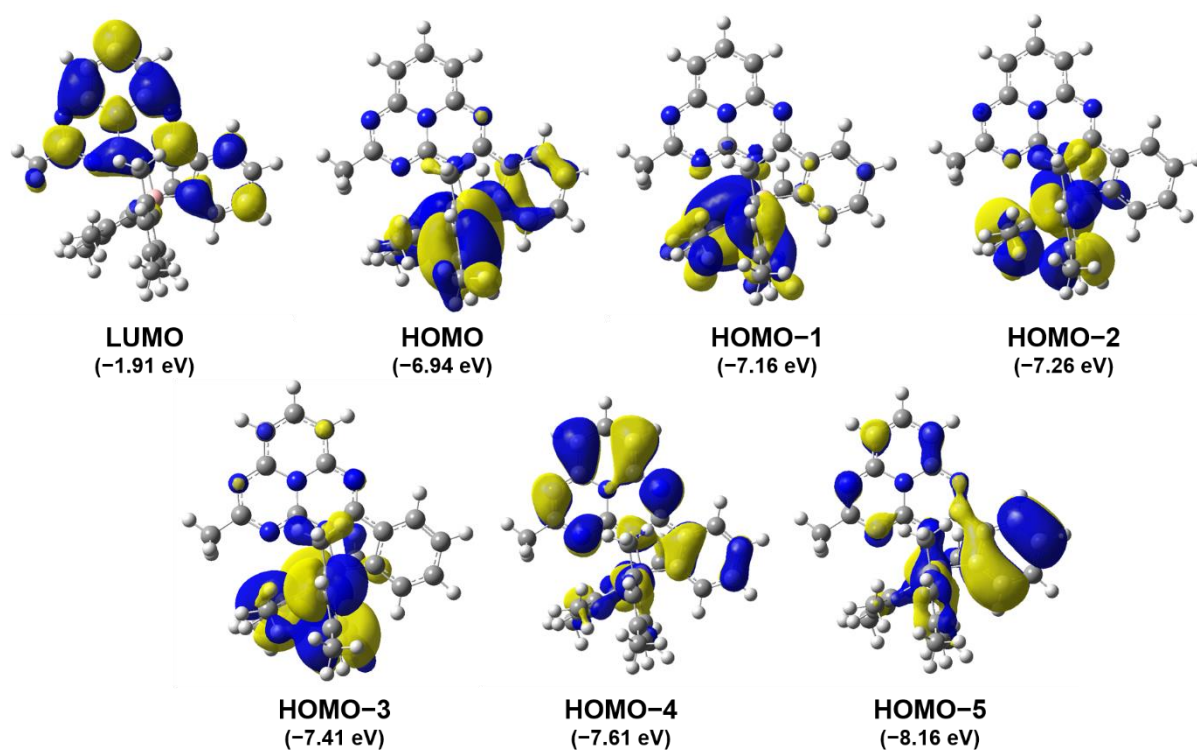


Figure 6. Selected Kohn-Sham orbitals of 5AP-B calculated at CAM-B3LYP/6-311+G(2d,p)//B3LYP/6-31+G(d,p) level of theory.

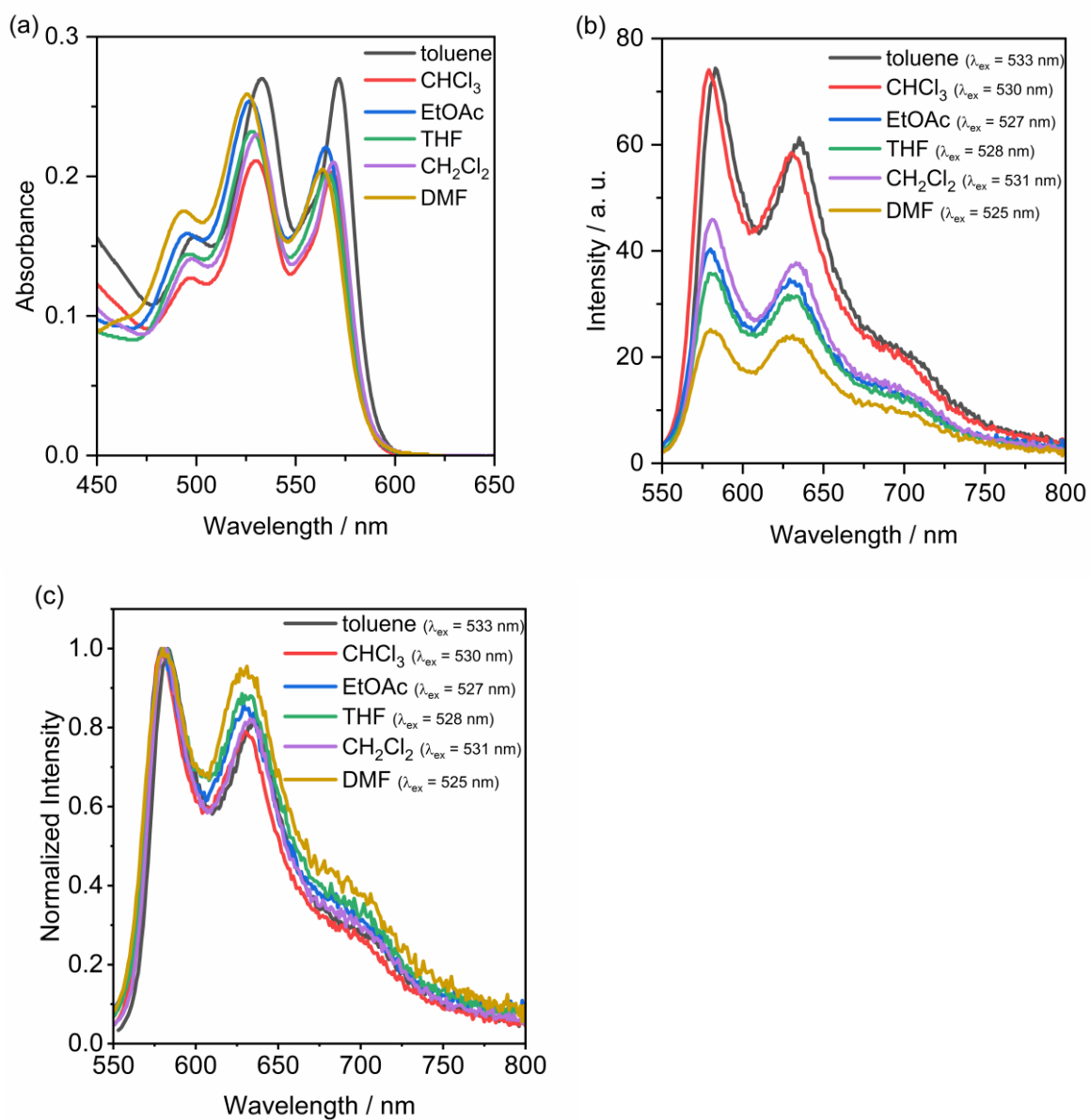


Figure 7. Solvent dependencies of (a) UV-vis absorption and (b), (c) PL spectra of 5AP-B. All spectra were recorded in 1.0×10^{-4} M.

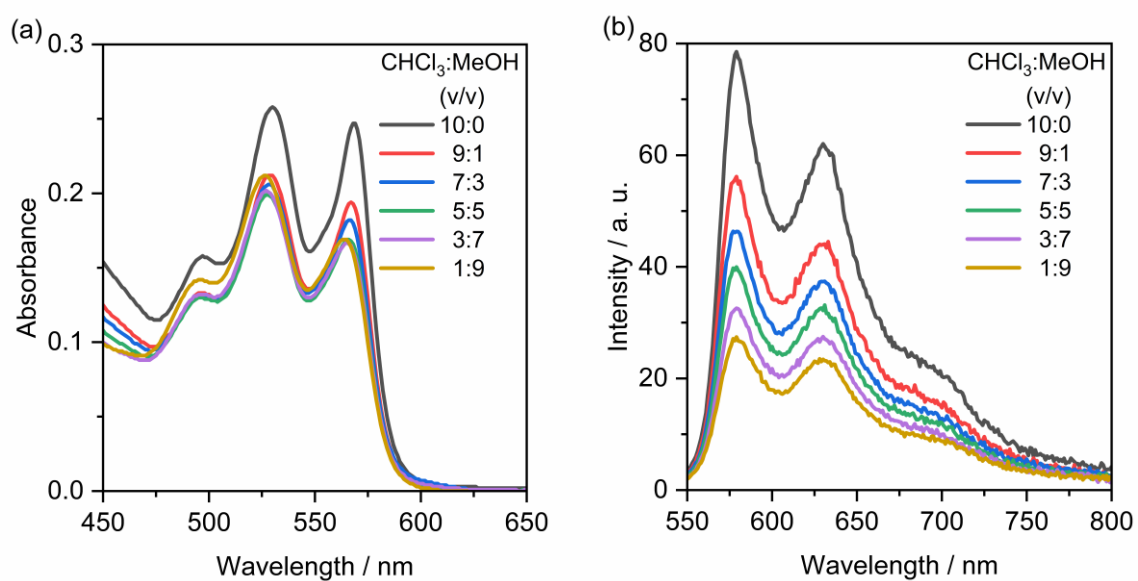


Figure 8. Solvent dependencies of (a) UV-vis absorption and (b) PL spectra of 5AP-B (excited at the peak top at the longest wavelength ($\lambda_{\text{ex}} \sim 530$ nm)). All spectra were collected at the concentration of 1.0×10^{-4} M.

Table 1. Result of TD-DFT calculation of 5AP-Ph and 5AP-B calculated at CAM-B3LYP/6-311+G(2d,p)//B3LYP/6-31+G(d,p) level of theory

Absorption (at the optimized ground state)				Emission (at the optimized excited state 1)		
Compound	λ_{S0-S1} / nm	f_{S0-S1}	Assignment ^a (Weight)	λ_{S1-S0} / nm	f_{S1-S0}	Assignment ^a (Weight)
5AP-Ph (3)	493.41	0.0136	H $\rightarrow$ L (0.68248)	573.20	0.0125	H $\rightarrow$ L(0.67304)
						H $\rightarrow$ L+1(0.15878)
			H-5 $\rightarrow$ L (-0.13605)			
			H-4 $\rightarrow$ L (0.62783)			
5AP-B (5a)	455.47	0.0417	H-3 $\rightarrow$ L (0.15309)	480.90	0.0094	H $\rightarrow$ L(0.67267)
			H-2 $\rightarrow$ L (-0.11326)			H $\rightarrow$ L+1(0.15380)
			H $\rightarrow$ L (-0.10913)			

^a H and L represent HOMO and LUMO, respectively.

Table 2. Solvent dependency of optical properties of 5AP-B

Solvent	ϵ^a	λ_{abs} [nm]	ϵ_{max} [M ⁻¹ cm ⁻¹]	Peak 1	Peak 2	I_1^b [10 ⁵ cps]	I_1/I_2^b	$\Delta\nu$ [cm ⁻¹] ^c
				λ_{em1} [nm]	λ_{em2} [nm]			
Toluene	2.38	533, 572	2,700	583	635	7.44	1.21	330
CHCl ₃	4.81	530, 568	2,110	579	630	7.44	1.27	340
EtOAc	6.09	527, 565	2,540	580	629	4.03	1.16	460
THF	7.58	528, 566	2,320	580	628	3.58	1.13	430
CH ₂ Cl ₂	8.93	531, 569	2,300	581	633	4.59	1.22	360
DMF	36.71	525, 564	2,590	580	631	2.52	1.05	490

^a Dielectric constant. ^b I_1 : Intensity of the peak 1, I_2 : Intensity of the peak 2. ^c Stokes shift.

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1. General

^1H (400 MHz) and $^{13}\text{C}\{^1\text{H}\}$ (100 MHz) NMR spectra were recorded on JEOL JNM-EX400 or JNM-AL400 spectrometers. For 5AP-B (5), $^{13}\text{C}\{^1\text{H}\}$ (151 MHz) NMR spectrum was recorded on JEOL JNM-ECA600P spectrometer. ^1H spectra were recorded by using tetramethylsilane (TMS) as an internal standard in DMSO- d_6 , CD_2Cl_2 and CDCl_3 . $^{13}\text{C}\{^1\text{H}\}$ spectra were recorded by using the residual solvent as an internal standard in DMSO- d_6 , CD_2Cl_2 and CDCl_3 . $^{11}\text{B}\{^1\text{H}\}$ NMR spectra were referenced externally by $\text{BF}_3\cdot\text{OEt}_2$ in CDCl_3 . High-resolution mass spectra (HRMS) were obtained on a Thermo Fisher EXACTIVE for electron spray ionization (ESI). UV-vis absorption spectra were recorded on a Shimadzu UV-3600 spectrophotometer. Fluorescence spectra were recorded on a HORIBA JOBIN YVON Fluoromax-4P spectrofluorometer. The wavelength dependency of the detection sensitivity was corrected by the built-in program of Fluoromax-4P. All reactions were performed under argon atmosphere. X-ray crystallographic analysis was carried out by Rigaku XtaLAB P 200 Cu $\text{K}\alpha$ radiation diffractometer (monochromated by multi-layer mirror optics) with PILATUS 200K Hybrid Photon Counting area detector. The structure was solved by SHELXT^[1] and refined by SHELXL^[2]. Details of the structure refinement are described in the CIF file. The programs Olex2^[3] and Mercury^[4] were used to generate the X-ray structural image.

2. Materials

Reagent (methyl *N*-cyanoacetimidate, 2,6-diaminopyridine, benzoyl chloride, 2-bromobenzoyl chloride, *n*-butyllithium *n*-hexane solution (1.6 M), and dimesitylfluoroborane) and solvent (dehydrated pyridine) was purchased from commercial sources and used without further purification. 2-bromo-5-methoxybenzoyl chloride and 2-bromo-5-trifluoromethylbenzoyl chloride were prepared according to the literature procedure.^[5] Glyme (1,2-dimethoxyethane) was purchased from commercial source and degassed by Ar bubbling before use. For the synthesis of 5c, dehydrated glyme was purchased from commercial source and used as received. Tetrahydrofuran (THF) was purified using a two-column solid-state purification system (Glasscontour System, Joerg Meyer, Irvine, CA).

3. Synthetic procedures

- *N*-Cyano-*N'*-(6-amino-2-pyridyl)acetamidine (**2**).

The synthesis was performed according to the previous literatures.^[5,6] A solution of 2,6-diaminopyridine (25 g, 0.23 mol) and methyl *N*-cyanoacetimidate (25 g, 0.26 mol) in 100 mL of degassed glyme was stirred at room temperature for 24 h. A part of the product was precipitated after stirring overnight. After filtration, the precipitate was washed repeatedly with chloroform and ethanol. The filtrate was evaporated *in vacuo*. Then, the residue was washed repeatedly with chloroform and ethanol. The crude product was obtained as an off-white powder (21.5 g, 0.12 mol, 54%). ¹H NMR (DMSO-*d*₆, ppm): δ 10.56 (s, 1H, NH), 7.41 (t, *J* = 7.9 Hz, 1H, Ar), 7.21 (d, *J* = 7.7 Hz, 1H, Ar), 6.27 (d, *J* = 8.2 Hz, 1H, Ar), 5.89 (s, 2H, NH₂), 2.42 (s, 3H, Me). ¹³C NMR (DMSO-*d*₆, ppm): δ 170.6, 158.5, 148.7, 138.8, 116.5, 105.1, 102.9, 21.6. HRMS (ESI-orbitrap) *m/z*: [M+H]⁺ calcd. for C₈H₉N₅+H 176.0932; Found 176.0931.

- 2-Methyl-5-phenyl-1,3,4,6,9b-pentaazaphenalene (**3**, 5AP-Ph)

The synthesis was performed according to the previous literature.^[6,7] A slurry of **2** (0.175 g, 1 mmol) and dehydrated pyridine (0.0791 g, 0.081 mL, 1 mmol) in 2 mL of degassed glyme was stirred. Then, benzoyl chloride (0.28 mL, 2.4 mmol) was added dropwise. After the mixture was refluxed for 13 h, the reaction was quenched by slowly adding saturated aqueous sodium hydrogen carbonate. The mixture was extracted with 3 × 20 mL of dichloromethane. The combined organic layers were washed with water (3 × 50 mL) and brine, and then dried over magnesium sulfate. After filtration, the solvent was removed *in vacuo*. The crude product was purified with column chromatography on silica gel using chloroform/ethyl acetate (1:1) as an eluent. Removing the solvent gave 5AP-Ph as a blue powder (0.136 g, 0.52

mmol, 52%). ^1H NMR (CD_2Cl_2 , ppm): δ 8.17 (d, $J = 8.35$ Hz, H, Ar), 8.16 (d, $J = 8.53$ Hz, 1H, Ar), 7.54 (t, $J = 7.4$ Hz, 1H, Ar), 7.42 (t, $J = 7.6$ Hz, 2H, Ar), 7.31 (t, $J = 8.4$ Hz, 1H, Ar), 6.23 (d, $J = 8.3$, 1H), 6.08 (d, $J = 8.4$ Hz, 1H, Ar), 2.02 (s, 3H, CH_3). ^{13}C NMR (CDCl_3 , ppm): δ 177.6, 171.3, 160.6, 155.1, 154.6, 145.7, 134.4, 133.1, 129.1, 128.3, 111.9, 110.7, 25.90. HRMS (ESI-orbitrap) m/z : $[\text{M}+\text{H}]^+$ calcd. for $\text{C}_{15}\text{H}_{11}\text{N}_5+\text{H}$ 262.1087; Found 262.1083.

• 2-(2-Bromophenyl)-5-methyl-1,3,4,6,9b-pentaazaphenalene (**4a**)

The synthesis was performed according to the previous literature.^[5,6] A slurry of **2** (5.26 g, 30 mmol) and dehydrated pyridine (2.37 g, 2.4 mL, 30 mmol) in 50 mL of degassed glyme was stirred. Then, 2-bromobenzoyl chloride (9.4 mL, 72 mmol) was added dropwise. After the mixture was refluxed for 18 h, the reaction was quenched by slowly adding saturated aqueous sodium hydrogen carbonate. The mixture was extracted with 3×100 mL of dichloromethane. The combined organic layers were washed with water (3×200 mL) and brine, and then dried over magnesium sulfate. After filtration, the solvent was removed *in vacuo*. The crude product was purified with column chromatography on silica gel using chloroform/ethyl acetate (1:1) as an eluent. Recrystallization from chloroform and methanol gave **4a** as a purple powder (4.67 g, 14 mmol, 46%). ^1H NMR (CD_2Cl_2 , ppm): δ 7.65 (d, $J = 7.7$ Hz, 1H, Ar), 7.61 (d, $J = 8.0$ Hz, 1H, Ar), 7.35 (dd, $J = 7.5$ Hz, 1H, Ar), 7.29 (t, $J = 8.4$ Hz, 1H, Ar), 7.28 (dd, $J = 7.9$ Hz, 1H, Ar), 6.16 (d, $J = 8.3$, 1H), 6.10 (d, $J = 8.4$ Hz, 1H, Ar), 1.99 (s, 3H, CH_3). ^{13}C NMR (CDCl_3 , ppm): δ 178.2, 173.9, 160.8, 154.9, 154.7, 145.9, 136.8, 134.1, 131.7, 130.6, 127.1, 121.1, 111.7, 111.7, 25.74. HRMS (ESI-orbitrap) m/z : $[\text{M}+\text{H}]^+$ calcd. for $\text{C}_{15}\text{H}_{10}\text{BrN}_5+\text{H}$ 340.0192; Found 340.0193.

• 2-(2'-Bromo-5'-methoxyphenyl)-5-methyl-1,3,4,6,9b-pentaazaphenalene (**4b**)

A slurry of **1** (1.51 g, 8.6 mmol), dehydrated pyridine (0.68 g, 0.69 mL, 8.6 mmol) and 2-bromo-5-methoxybenzoyl chloride (5.16 g, 20.7 mmol) in THF (15 mL) was refluxed for 19 h, the reaction mixture was cooled to room temperature and diluted with CHCl₃ (300 mL) and H₂O (150 mL). The organic layer was separated and the aqueous layer was extracted by CHCl₃ (2 × 100 mL). The combined organic layer was washed by sat. NaHCO₃ aqueous solution (1 × 100 mL), brine (1 × 50 mL), and then dried over magnesium sulfate. After filtration, the solvent was removed *in vacuo*. The crude product was passed through silica plug (eluent: CHCl₃). Recrystallization from chloroform and methanol gave **4b** as a purple powder (1.57 g, 4.25 mmol, 47% isolated yield). ¹H NMR (400 MHz; CDCl₃) δ 7.47 (d, *J* = 8.8 Hz, 1H), 7.31 (t, *J* = 8.3 Hz, 1H), 7.23 (d, *J* = 3.1 Hz, 1H), 6.82 (dd, *J* = 8.8, 3.1 Hz, 1H), 6.22 (d, *J* = 8.3 Hz, 1H), 6.13 (d, *J* = 8.3 Hz, 1H), 3.79 (s, 3H), 2.05 (s, 3H). ¹³C{¹H} NMR (101 MHz; CDCl₃) δ 178.1, 173.6, 160.9, 158.7, 154.8, 154.5, 146.0, 137.3, 134.9, 118.7, 115.2, 111.9, 111.8, 111.5, 77.5, 77.2, 76.8, 55.7, 25.8. HRMS (ESI-orbitrap) *m/z*: [M+Na]⁺ calcd. for C₁₆H₁₂BrN₅O+Na 392.0117; Found 392.0103.

• 2-(2'-Bromo-5'-trifluoromethylphenyl)-5-methyl-1,3,4,6,9b-pentaazaphenalene (**4c**)

A slurry of **1** (1.40 g, 8.01 mmol), dehydrated pyridine (0.61 g, 0.63 mL, 7.8 mmol) and 2-bromo-5-methoxybenzoyl chloride (prepared from 5 g (18.6 mmol) of corresponding carboxylic acid, crude) in dehydrated glyme (15 mL) was refluxed for 18 h, the reaction mixture was cooled to room temperature and diluted with CHCl₃ (100 mL) and H₂O (100 mL). The organic layer was separated, and the aqueous layer was extracted by CHCl₃ (2 × 100 mL). The combined organic layer was washed by H₂O (1 × 100 mL), brine (1 × 50 mL), and then dried over magnesium sulfate. After filtration, the solvent was removed *in vacuo*. The crude product was passed through silica plug (eluent: CHCl₃ / EtOAc = 1:1 (v/v)). Reprecipitation

from chloroform into hexane and then trituration by MeOH gave **4c** as a purple powder (0.402 g, 0.985 mmol, 12% isolated yield). ^1H NMR (400 MHz; CDCl_3) δ 7.97 (d, J = 2.1 Hz, 1H), 7.74 (d, J = 8.3 Hz, 1H), 7.49 (dd, J = 8.4, 2.1 Hz, 1H), 7.34 (t, J = 8.3 Hz, 1H), 6.23 (dd, J = 8.3, 1.0 Hz, 1H), 6.17 (dd, J = 8.4, 1.0 Hz, 1H), 2.06 (s, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz; CDCl_3) δ 178.4, 172.7, 161.0, 155.0, 154.5, 146.2, 137.5, 134.9 (br q), 130.0 (q, J = 34 Hz), 128.1 (br q), 127.7 (br q), 125.2, 123.6 (q, J = 271 Hz), 112.4 (br q), 112.0 (br q), 25.9.

• 2-Methyl-5-(2'-dimesitylborylphenyl)-1,3,4,6,9b-pentaazaphenalene (**5a**, 5AP-B)

To a THF (30 mL) solution of **4a** (0.13g, 0.40 mmol) was slowly added *n*-BuLi (1.64 M in hexane, 0.24 mL, 0.40 mmol) at -78°C . After stirred for 1 h, dimesitylfluoroborane (0.54 g, 2.0 mmol) was slowly added to the mixture. The reaction mixture was stirred for an additional 10 min at -78°C and then was allowed to warm to room temperature. After stirring for 13 h at room temperature, the reaction was quenched by slowly addition of methanol and subsequent saturated aqueous sodium hydrogen carbonate. The mixture was extracted with 3×30 mL of chloroform. The combined organic layers were washed with water (3×30 mL) and brine, and then dried over magnesium sulfate. After filtration, the solvent was removed *in vacuo*. The crude product was purified with column chromatography on silica gel using hexane/ethyl acetate (1:1) as an eluent. Reprecipitation from chloroform/hexane gave the desired product as a red solid (0.027 mmol, 7%). ^1H NMR (CDCl_3 , ppm): δ 7.88 (d, J = 7.6 Hz, 1H, Ar), 7.73 (d, J = 7.7 Hz, 1H, Ar), 7.58 (dd, J = 8.1 Hz, 1H, Ar), 7.37 (t, J = 7.5 Hz, 1H, Ar), 7.20 (dd, J = 7.4 Hz, 1H, Ar), 6.67 (s, 5H, Ar), 6.65 (d, J = 8.9 Hz, 1H, Ar), 6.49 (d, J = 8.3 Hz, 1H, Ar), 2.19 (s, 3H, 5AP-CH₃), 1.97-2.15 (br, 18H, Ph-CH₃). ^{11}B NMR (CDCl_3 , ppm): δ 4.69. ^{13}C NMR (CDCl_3 , ppm): δ 175.9, 171.3, 169.4, 154.0, 152.9, 151.6, 146.2, 141.7, 135.1, 133.7, 132.3, 130.1, 129.8, 125.7, 125.3, 113.3, 113.2, 25.8, 25.4, 20.8. A peak adjacent to boron atom were probably overlapped with a broad peak at 141.7 ppm and

therefore could not be observed. HRMS (APCI-orbitrap) m/z : $[M+H]^+$ calcd. for $C_{33}H_{32}BN_5+H$ 510.2824; Found 510.2812.

- 2-Methyl-5-(2'-dimesitylboryl-5'-methoxyphenyl)-1,3,4,6,9b-pentaazaphenalene (**5b**, 5AP-B-OMe)

To a THF (2 mL) solution of **4b** (0.15 g, 0.40 mmol) was slowly added *n*-BuLi (1.64 M in hexane, 0.24 mL, 0.40 mmol) at $-78\text{ }^{\circ}\text{C}$. After stirred for 1 h, dimesitylfluoroborane (0.54 g, 2.0 mmol) in THF (2 mL) was slowly added to the mixture. The reaction mixture was then allowed to warm to room temperature. After stirring for 13 h at room temperature, the reaction was quenched by slowly addition of methanol and subsequent saturated aqueous sodium hydrogen carbonate. The organic layer was diluted by CHCl_3 and washed with water three times and brine, and then dried over magnesium sulfate. After filtration, the solvent was removed *in vacuo*. The crude product was purified with column chromatography on silica gel using hexane/ethyl acetate (1:1) as an eluent. Reprecipitation from chloroform/hexane gave the desired product as a red solid (0.082 g, 0.015 mmol, 4%). ^1H NMR (400 MHz; CDCl_3) δ 7.61 (d, $J = 8.4$ Hz, 1H), 7.57 (t, $J = 8.3$ Hz, 1H), 7.32 (d, $J = 1.7$ Hz, 1H), 7.01 (dd, $J = 8.4$, 2.6 Hz, 1H), 6.67 (s, 5H), 6.49 (dd, $J = 8.3$, 1.0 Hz, 1H), 3.82 (s, 3H), 2.19 (s, 6H), 2.12 (br, 12H). $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz; CDCl_3) δ 175.9, 169.4, 164.7, 158.4, 154.4, 153.0, 151.4, 146.2, 141.6, 133.7, 133.1, 131.2, 129.9, 125.2, 113.2, 112.8, 106.4, 55.5, 25.8, 25.5, 20.9. A peak adjacent to the boron atom was not observed probably due to quadrupolar coupling. HRMS (ESI-orbitrap) m/z : $[M+H]^+$ calcd. for $C_{34}H_{34}BN_5O+H$ 540.2929; Found 540.2927.

- 2-Methyl-5-(2'-dimesitylboryl-5'-trifluoromethylphenyl)-1,3,4,6,9b-pentaazaphenalene (**5c**, 5AP-B-CF₃)

To a THF (1.5 mL) solution of **4c** (0.11 g, 0.26 mmol) was slowly added *n*-BuLi (1.64 M in hexane, 0.16 mL, 0.26 mmol) at −78 °C. After stirred for 1 h, dimesitylfluoroborane (0.35 g, 1.3 mmol) in THF (1 mL) was slowly added to the mixture. The reaction mixture was then allowed to warm to room temperature. After stirring for 17 h at room temperature, the reaction was quenched by slowly addition of methanol and subsequent saturated aqueous sodium hydrogen carbonate. The organic layer was diluted by CHCl₃ and washed with water three times and brine, and then dried over magnesium sulfate. After filtration, the solvent was removed *in vacuo*. The crude product was purified with column chromatography on silica gel using hexane/ethyl acetate (2:1) as an eluent. Reprecipitation from chloroform/hexane gave the desired product as a red solid (0.0108 g, 0.019 mmol, 7%). ¹H NMR (400 MHz; CDCl₃) δ 8.12 (s, 1H), 7.86 (d, *J* = 8.3 Hz, 1H), 7.63 (t, *J* = 7.6 Hz, 1H), 7.56 (d, *J* = 8.3 Hz, 1H), 6.68 (s, 4H), 6.55 (dd, *J* = 8.3, 1.2 Hz, 1H), 2.19 (s, 6H), 2.08 (d, *J* = 0.4 Hz, 12H). Because of the complicated coupling involving the fluorine atoms and the boron atom, ¹³C NMR spectrum of this compound could not be recorded. HRMS (ESI-orbitrap) *m/z*: [M+H]⁺ calcd. for C₃₄H₃₁BF₃N₅+H 578.2697; Found 578.2687.

4. Copies of NMR spectra

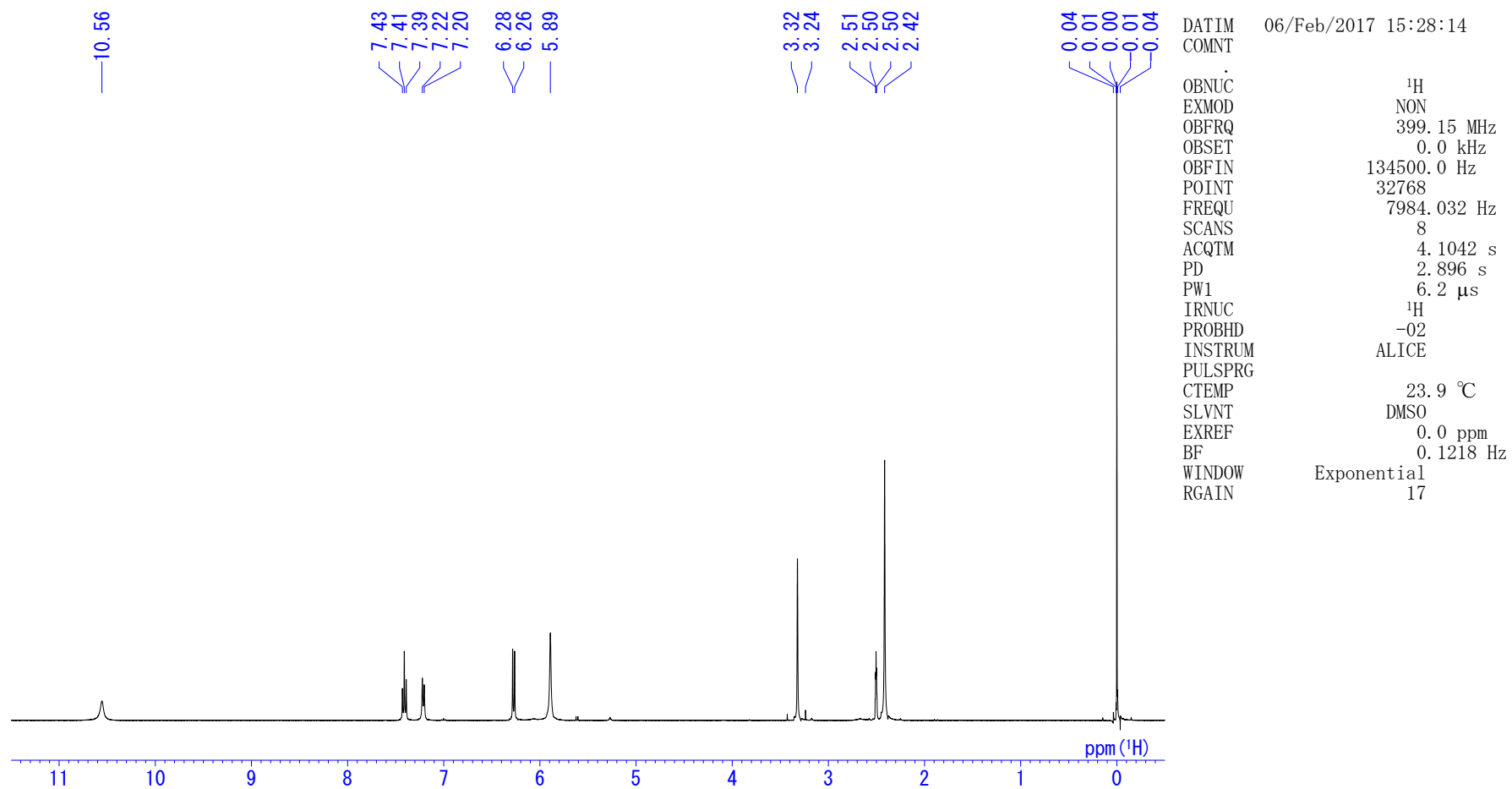


Figure S1. ¹H NMR spectrum of *N*-Cyano-*N'*-(6-amino-2-pyridyl)acetamidine (**2**).

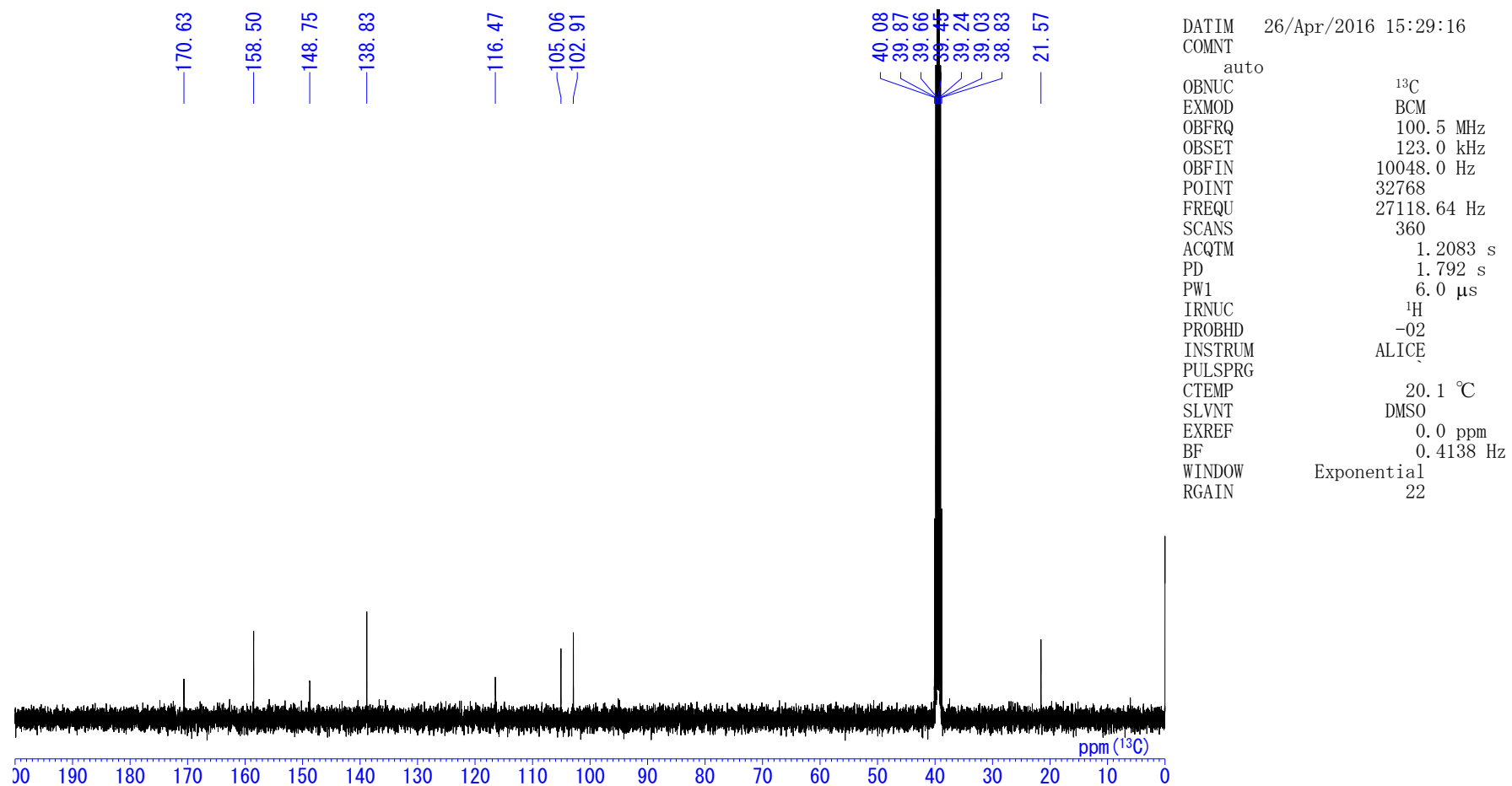


Figure S2. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of *N*-Cyano-*N'*-(6-amino-2-pyridyl)acetamidine (**2**).

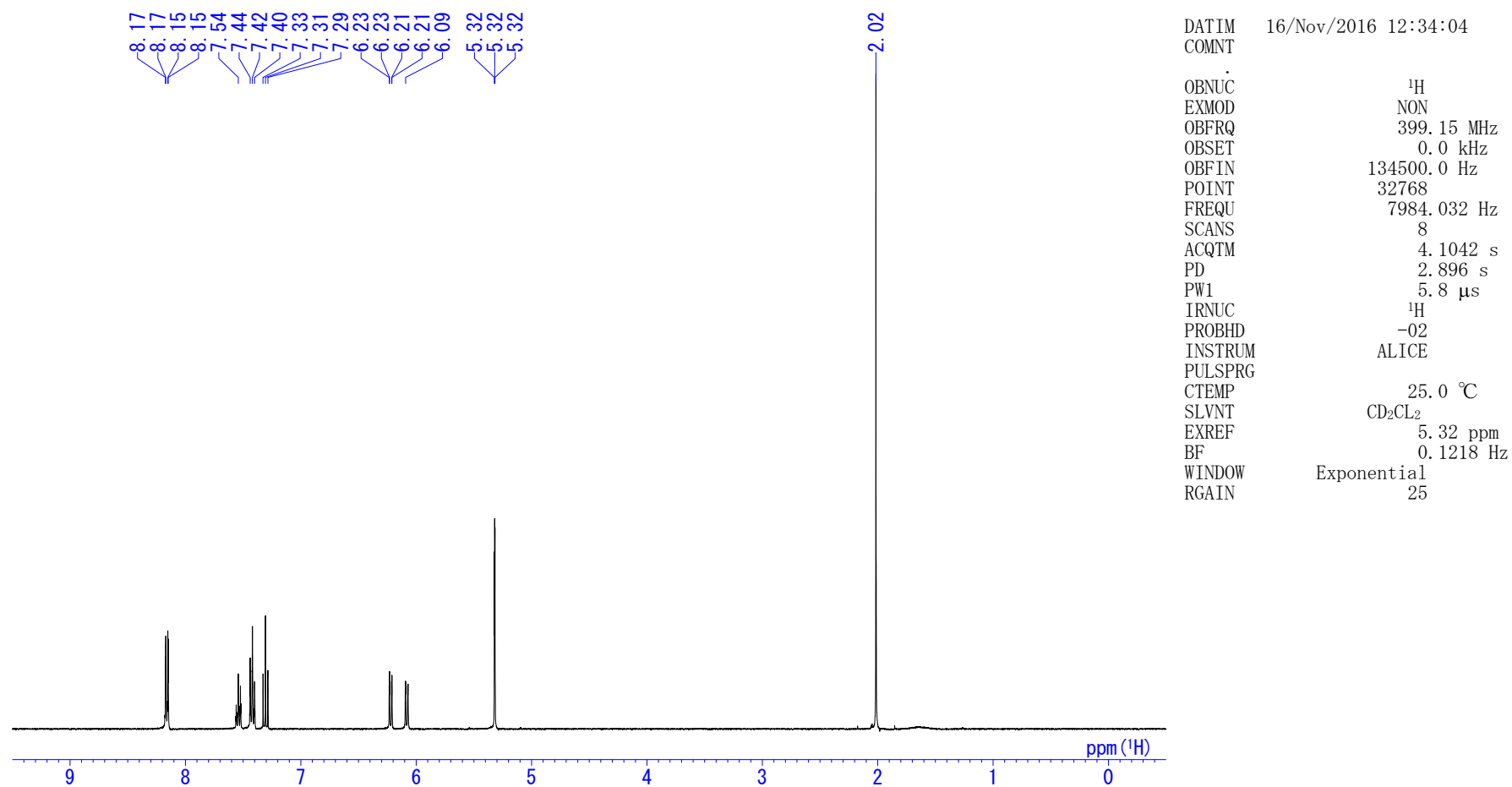


Figure S3. ¹H NMR spectrum of 2-Methyl-5-phenyl-1,3,4,6,9b-pentaazaphenalene (**3**).

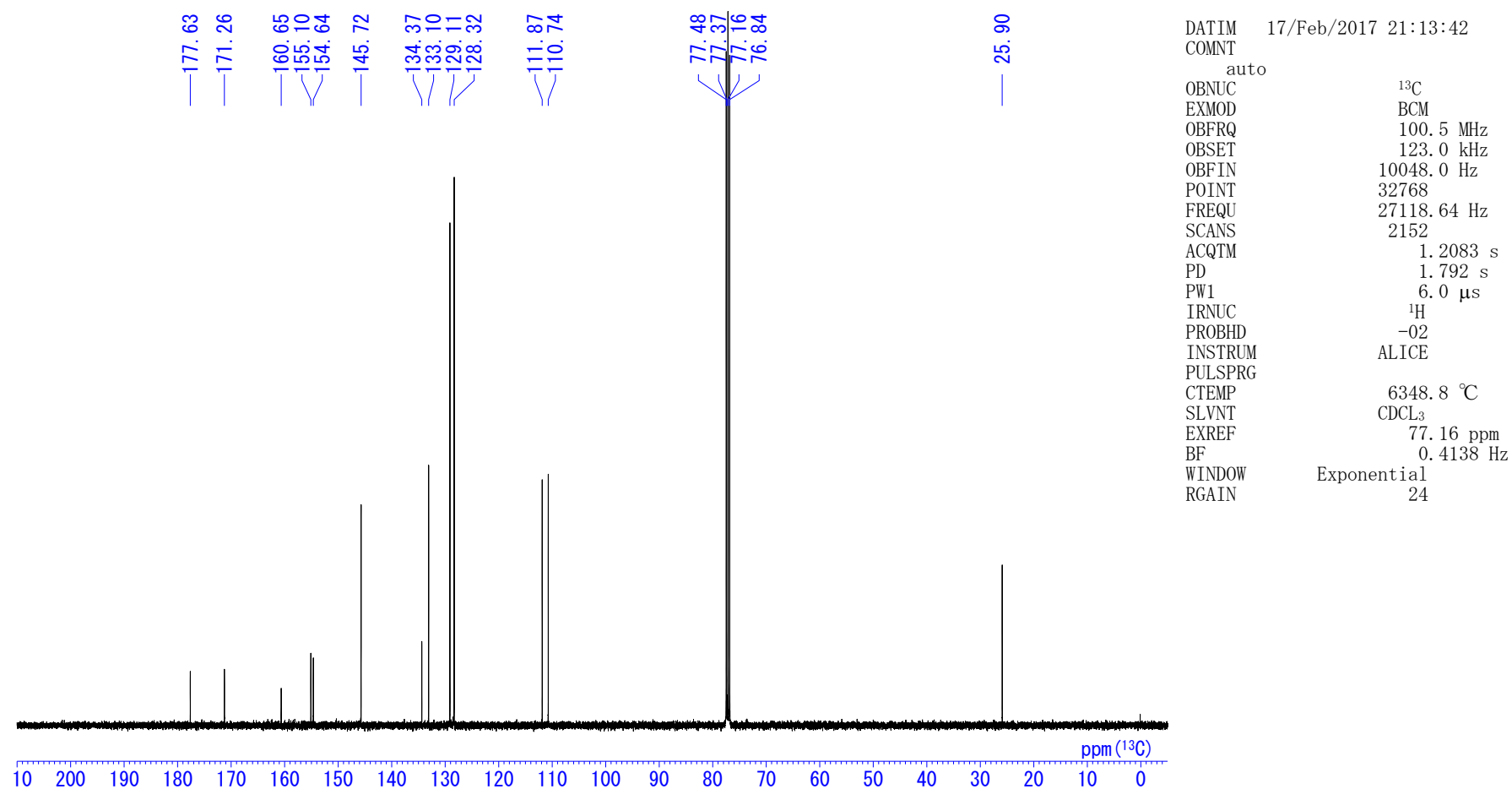


Figure S4. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of 2-Methyl-5-phenyl-1,3,4,6,9b-pentaazaphenalene (**3**).

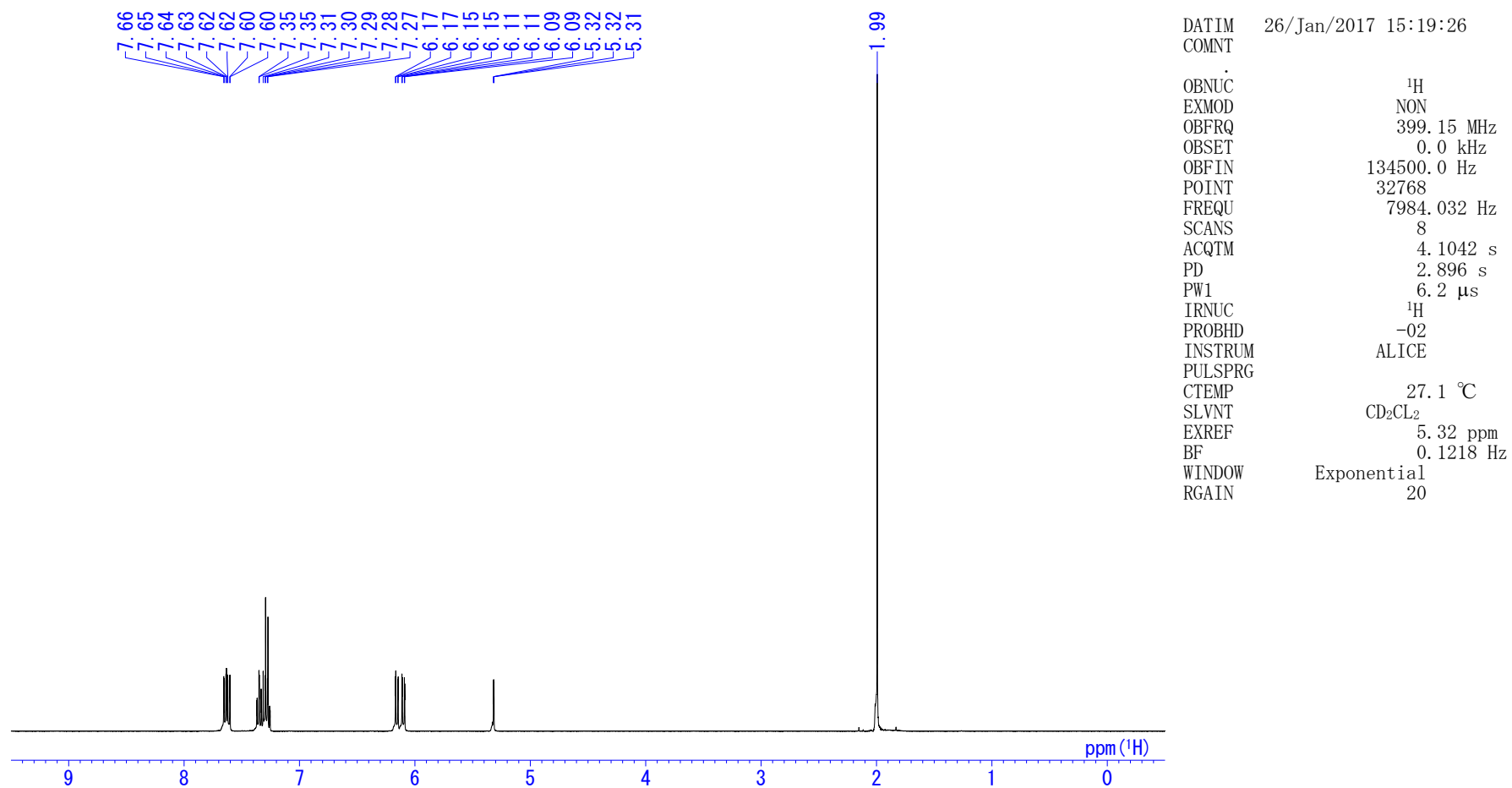


Figure S5. ^1H NMR spectrum of 2-(2-Bromophenyl)-5-methyl-1,3,4,6,9b-pentaazaphenalene (**4a**).

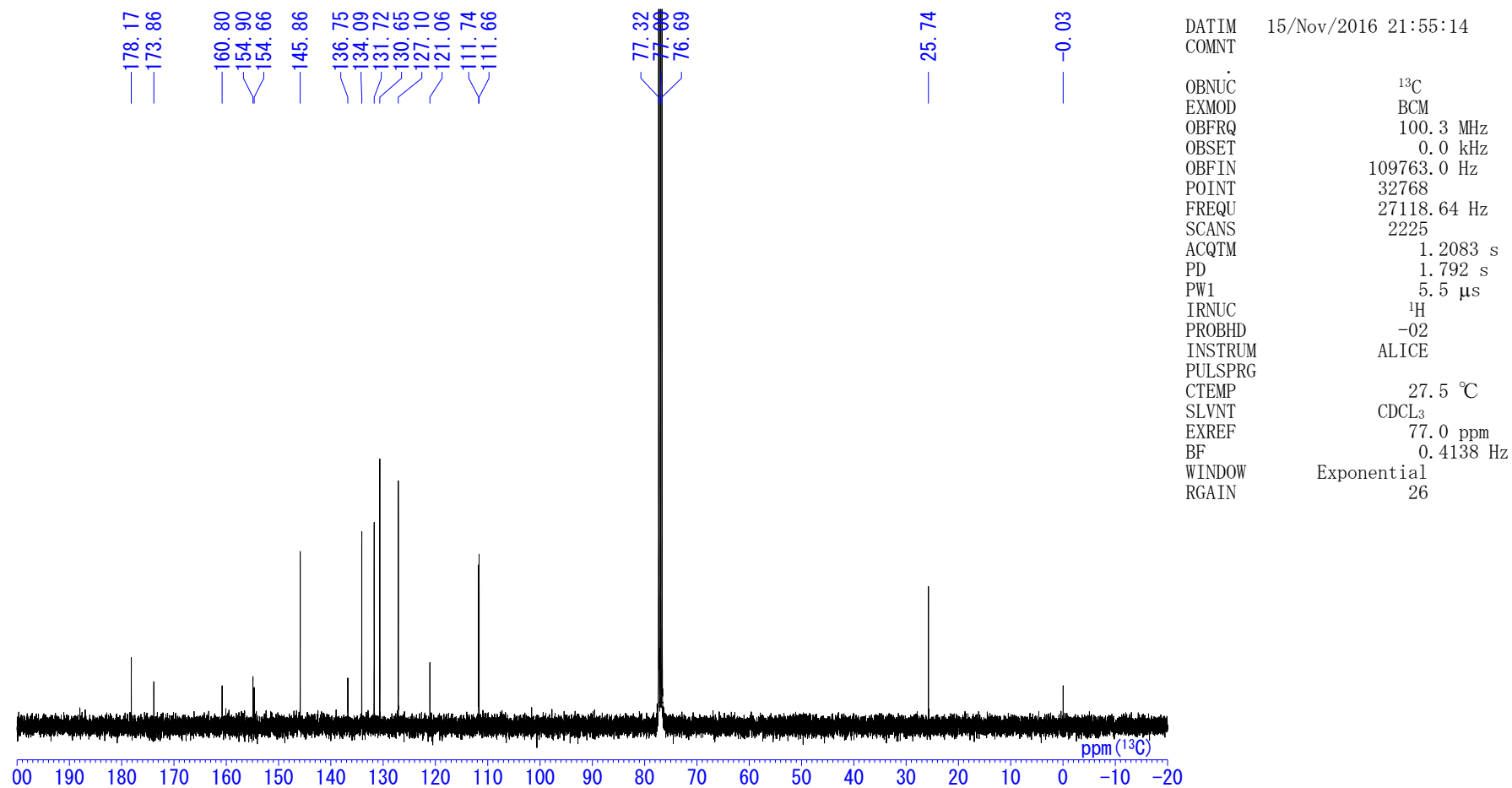


Figure S6. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of 2-(2-Bromophenyl)-5-methyl-1,3,4,6,9b-pentaazaphenalene (**4a**).

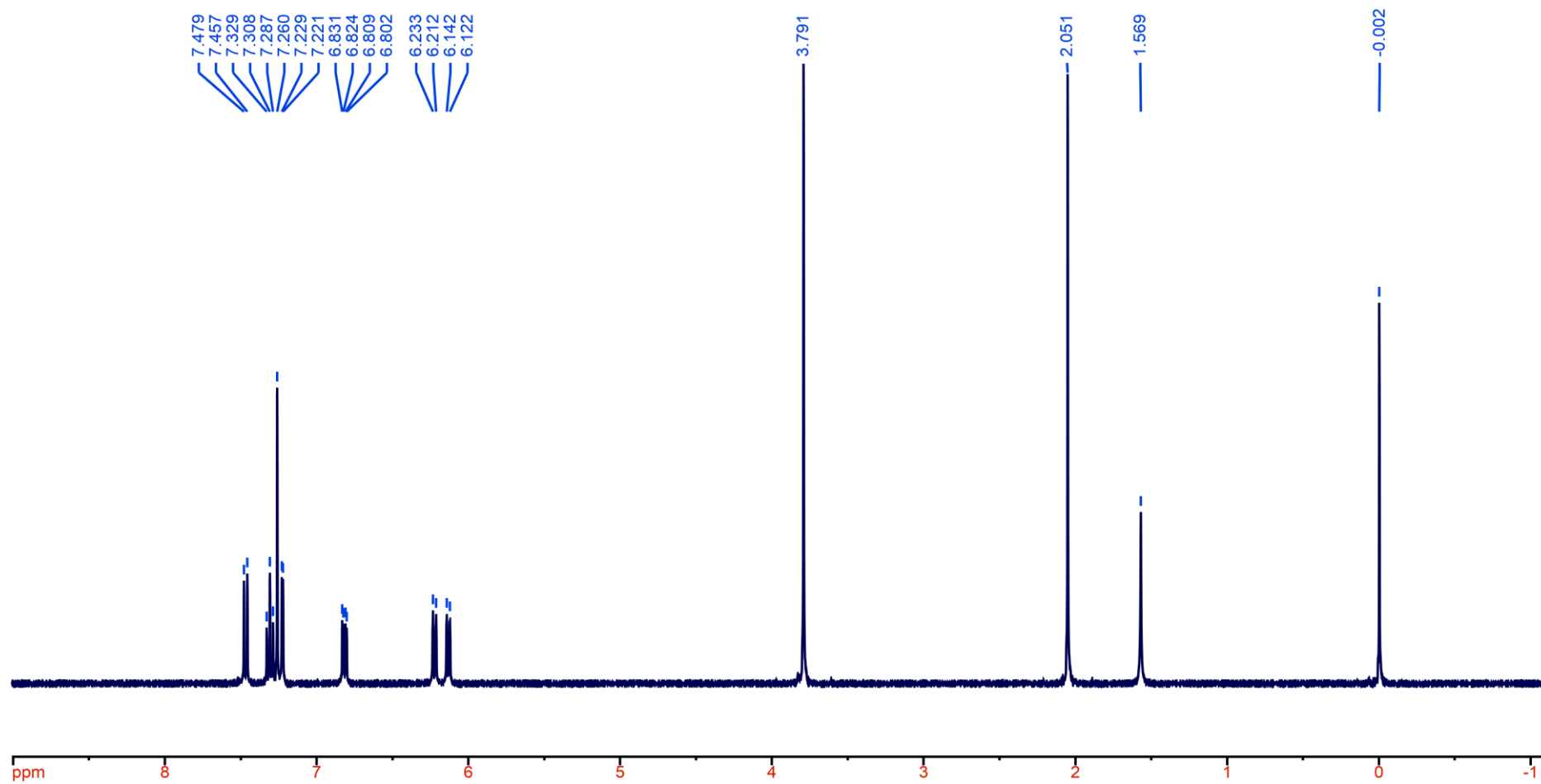


Figure S7. ¹H NMR spectrum of 2-(2-Bromophenyl)-5-methyl-1,3,4,6,9b-pentaazaphenalene (**4b**).

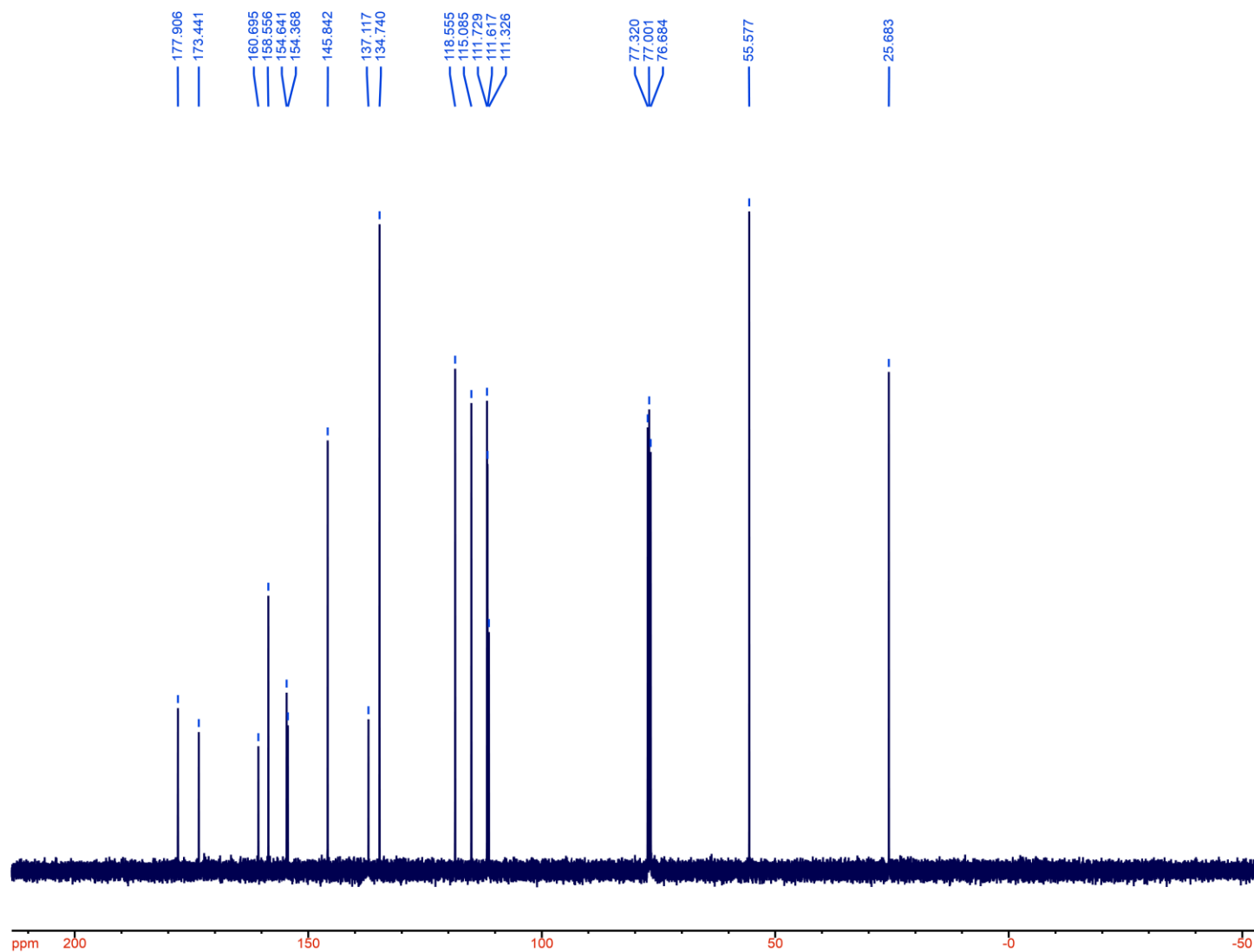


Figure S8. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of 2-(2-Bromophenyl)-5-methyl-1,3,4,6,9b-pentaazaphenalene (**4b**).

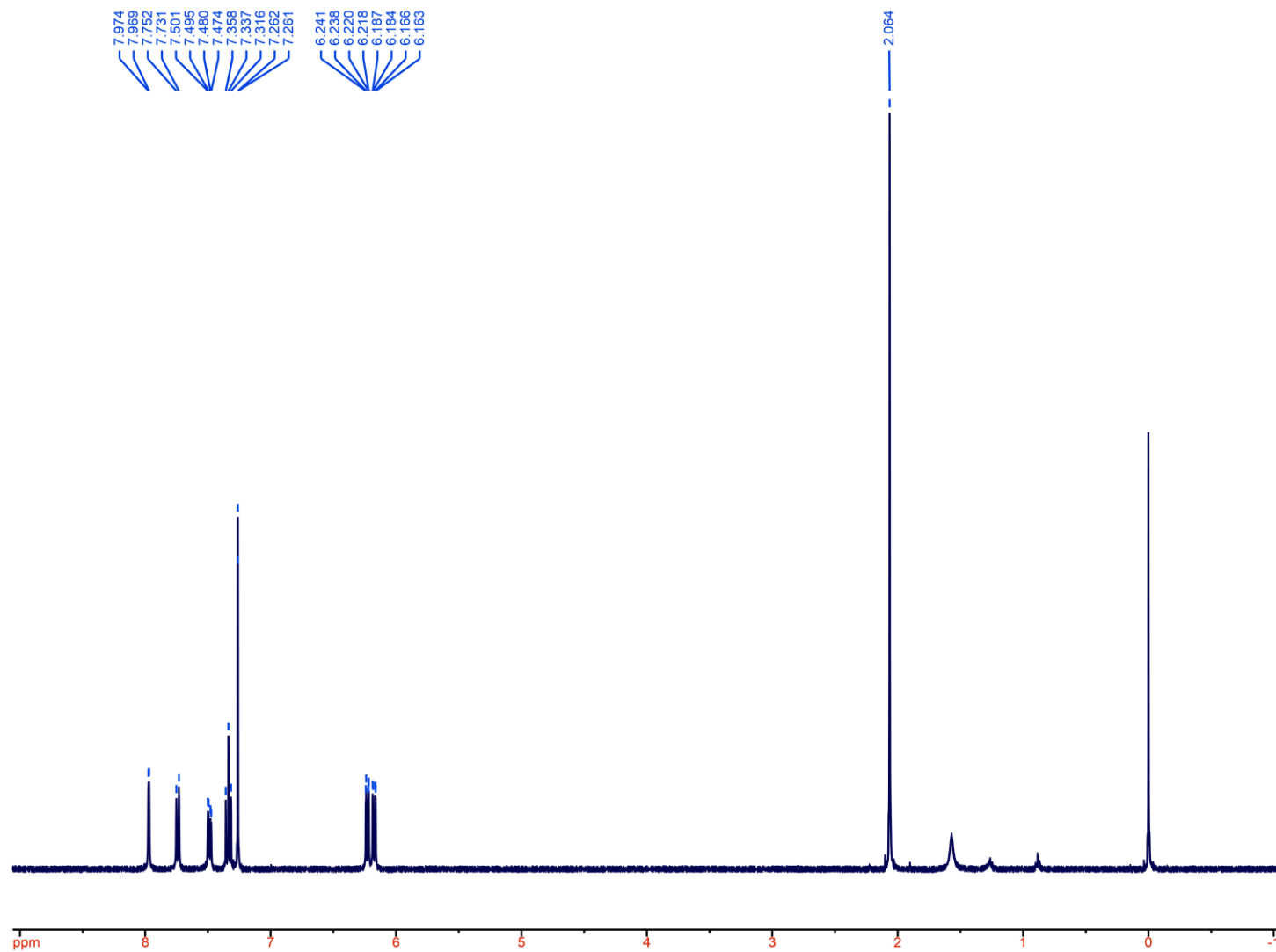


Figure S9. ^1H NMR spectrum of 2-(2'-Bromo-5'-trifluoromethylphenyl)-5-methyl-1,3,4,6,9b-pentaazaphenalene (**4c**).

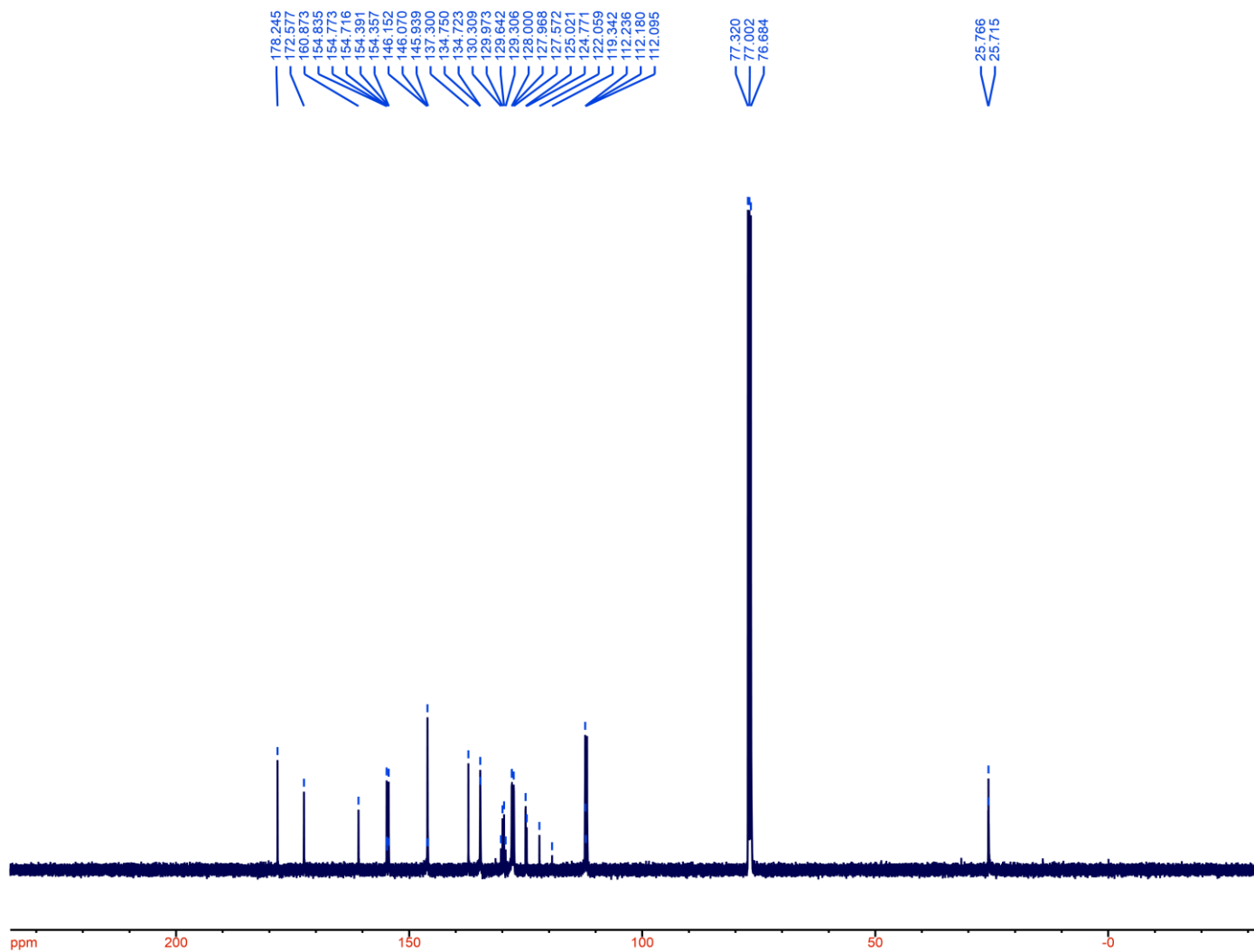


Figure S10. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of 2-(2'-Bromo-5'-trifluoromethylphenyl)-5-methyl-1,3,4,6,9b-pentaazaphenalene (**4c**).

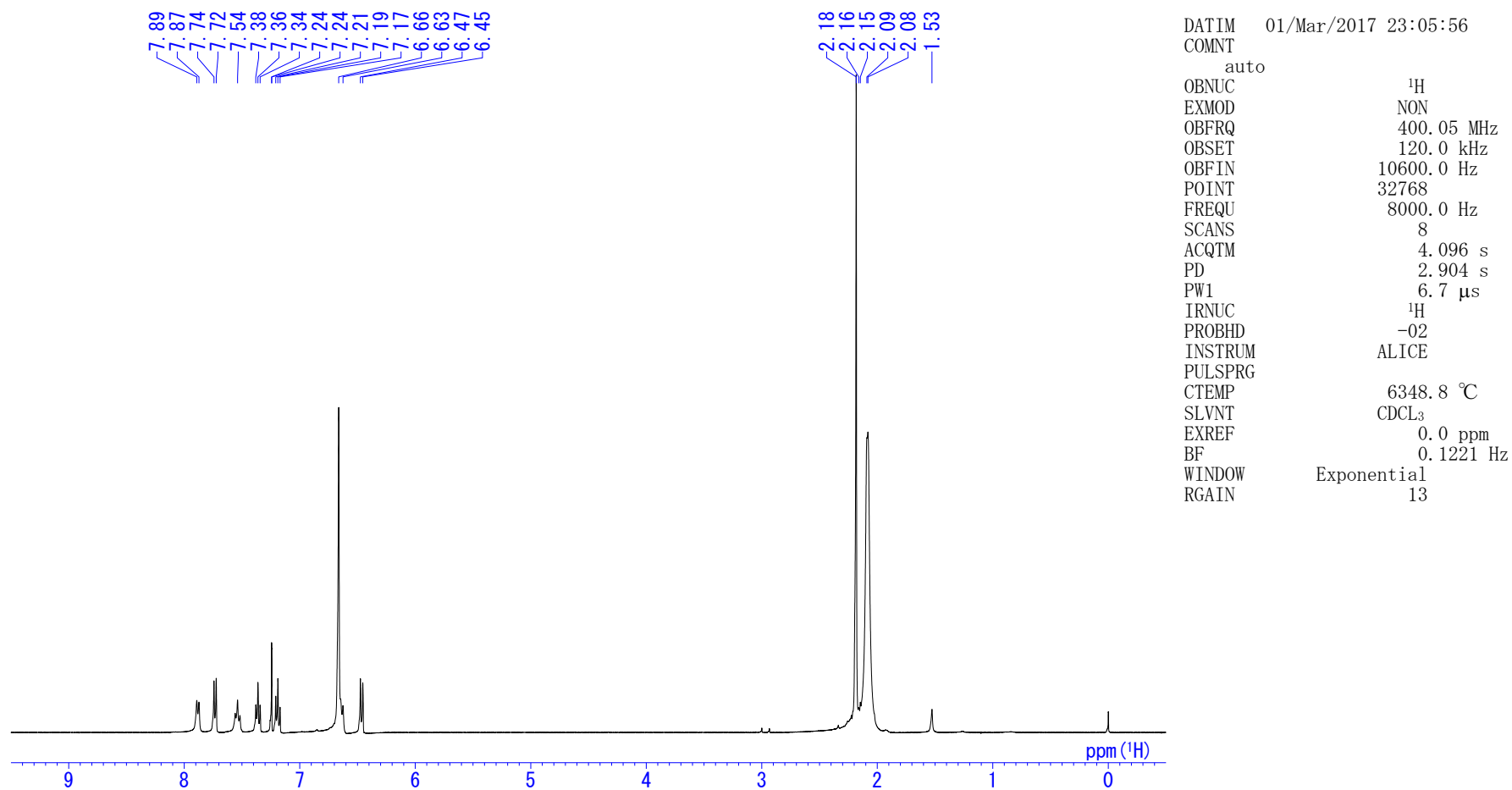


Figure S7. ¹H NMR spectrum of 2-Methyl-5-(2'-dimesitylborylphenyl)-1,3,4,6,9b-pentaazaphenalene (5, 5AP-B).

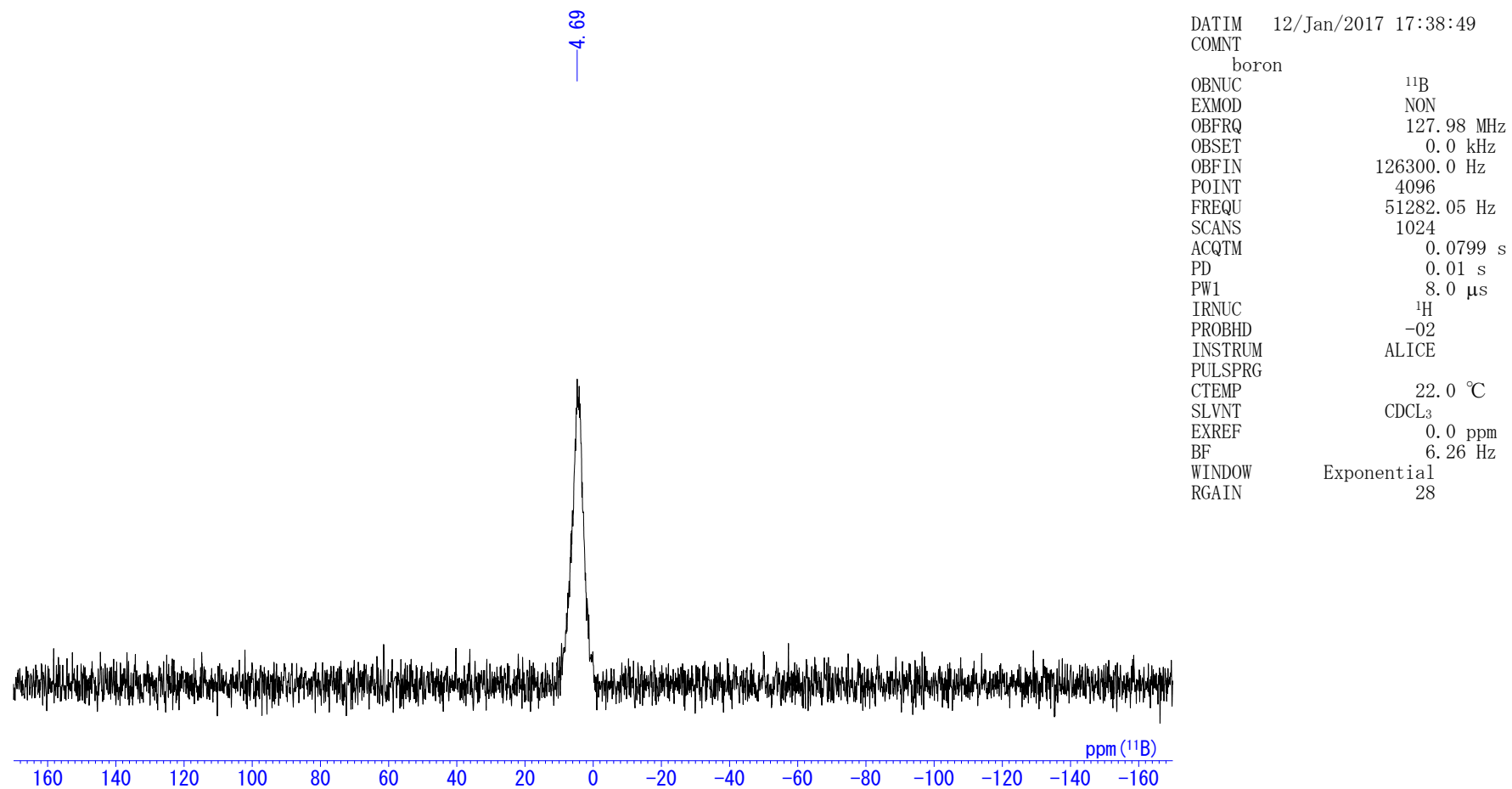


Figure S8. ¹¹B{¹H} NMR spectrum of 2-Methyl-5-(2'-dimesitylborylphenyl)-1,3,4,6,9b-pentaazaphenalene (**5**, 5AP-B).

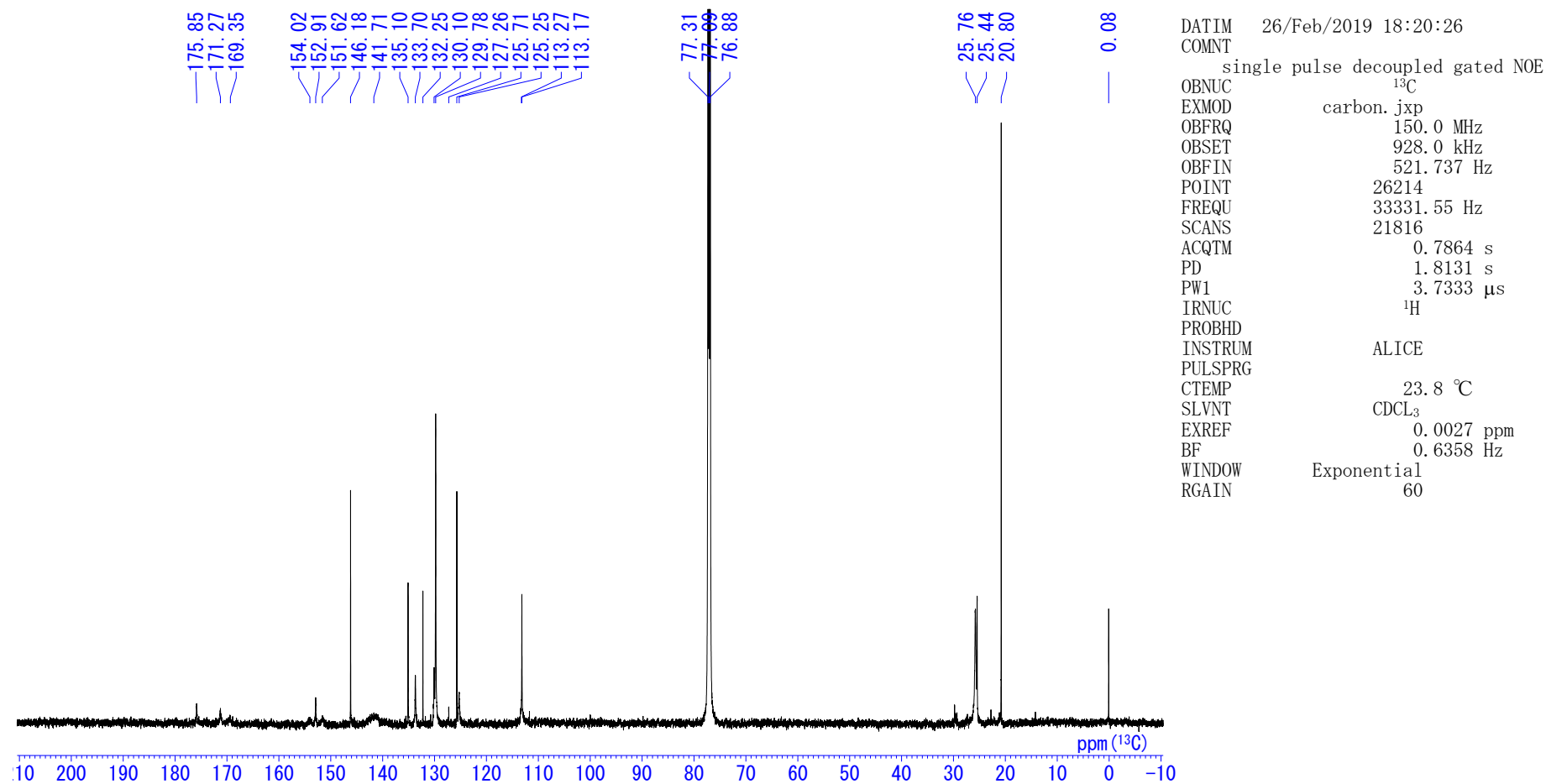


Figure S9. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of 2-Methyl-5-(2'-dimesitylborylphenyl)-1,3,4,6,9b-pentaazaphenalene (**5**, 5AP-B).

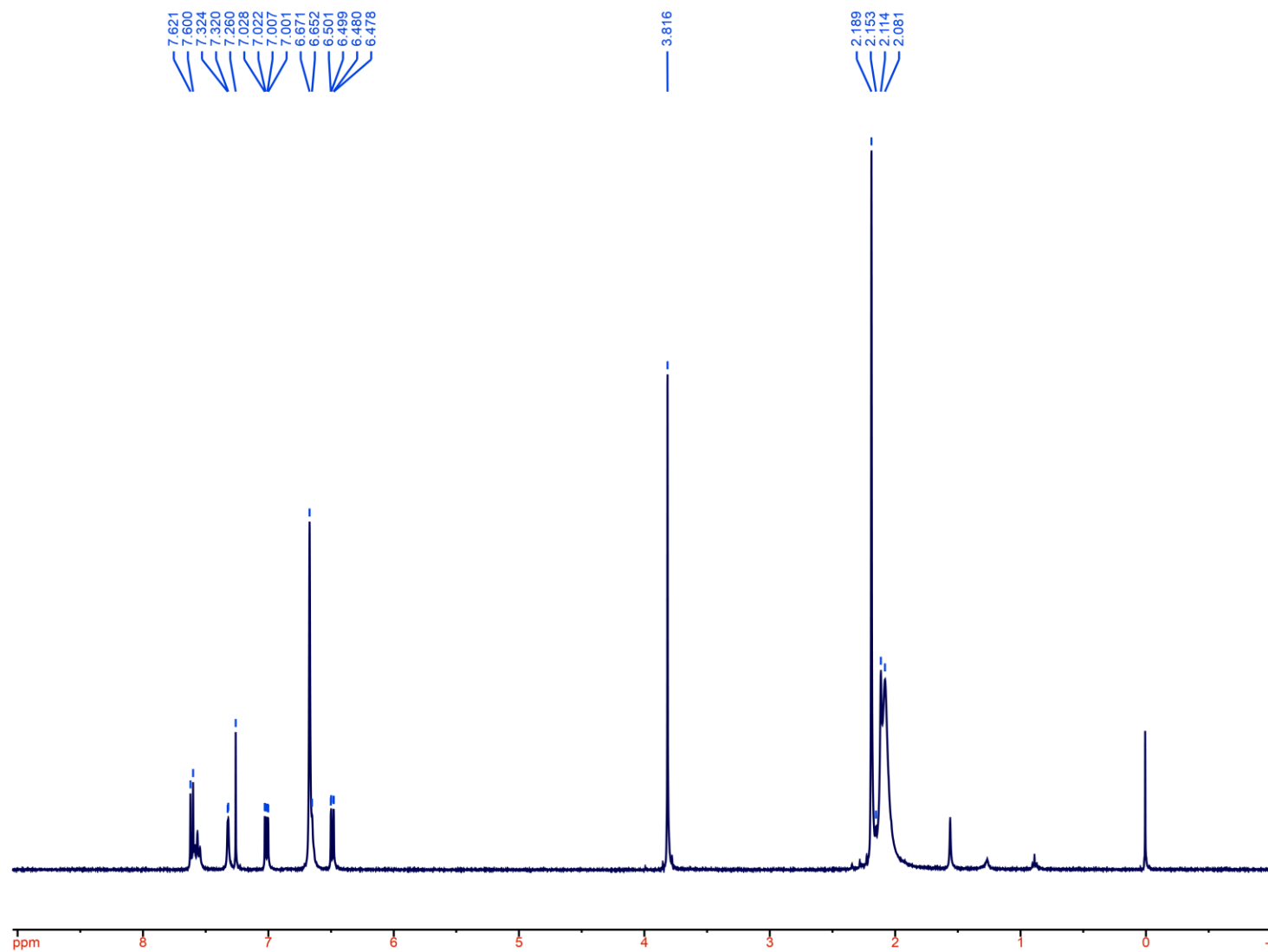


Figure S7. ^1H NMR spectrum of 2-Methyl-5-(2'-dimesitylborylphenyl)-1,3,4,6,9b-pentaazaphenalene (**5b**, 5AP-B-OMe).

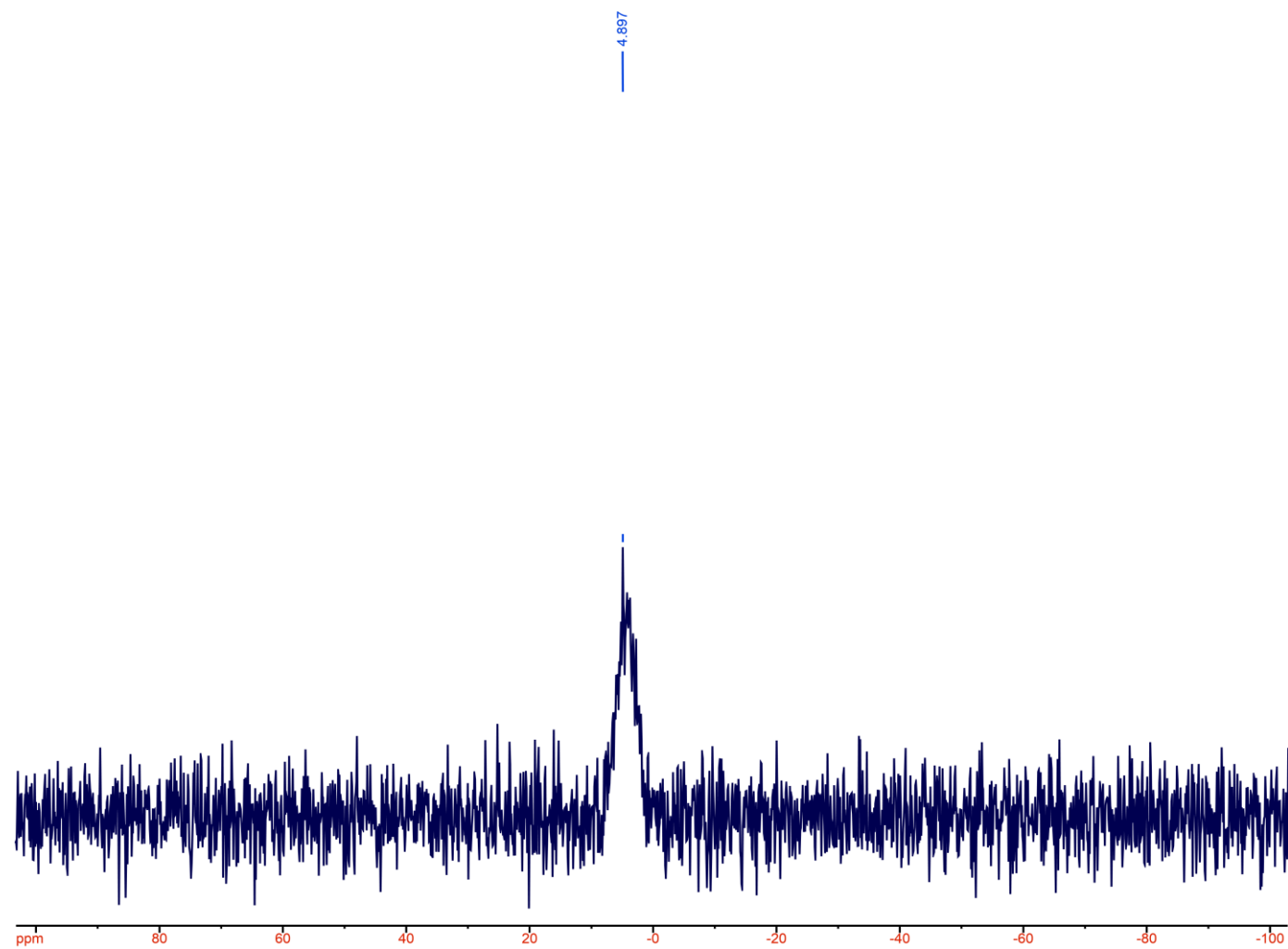


Figure S8. $^{11}\text{B}\{^1\text{H}\}$ NMR spectrum of 2-Methyl-5-(2'-dimesitylborylphenyl)-1,3,4,6,9b-pentaazaphenalene (**5b**, 5AP-B-OMe).

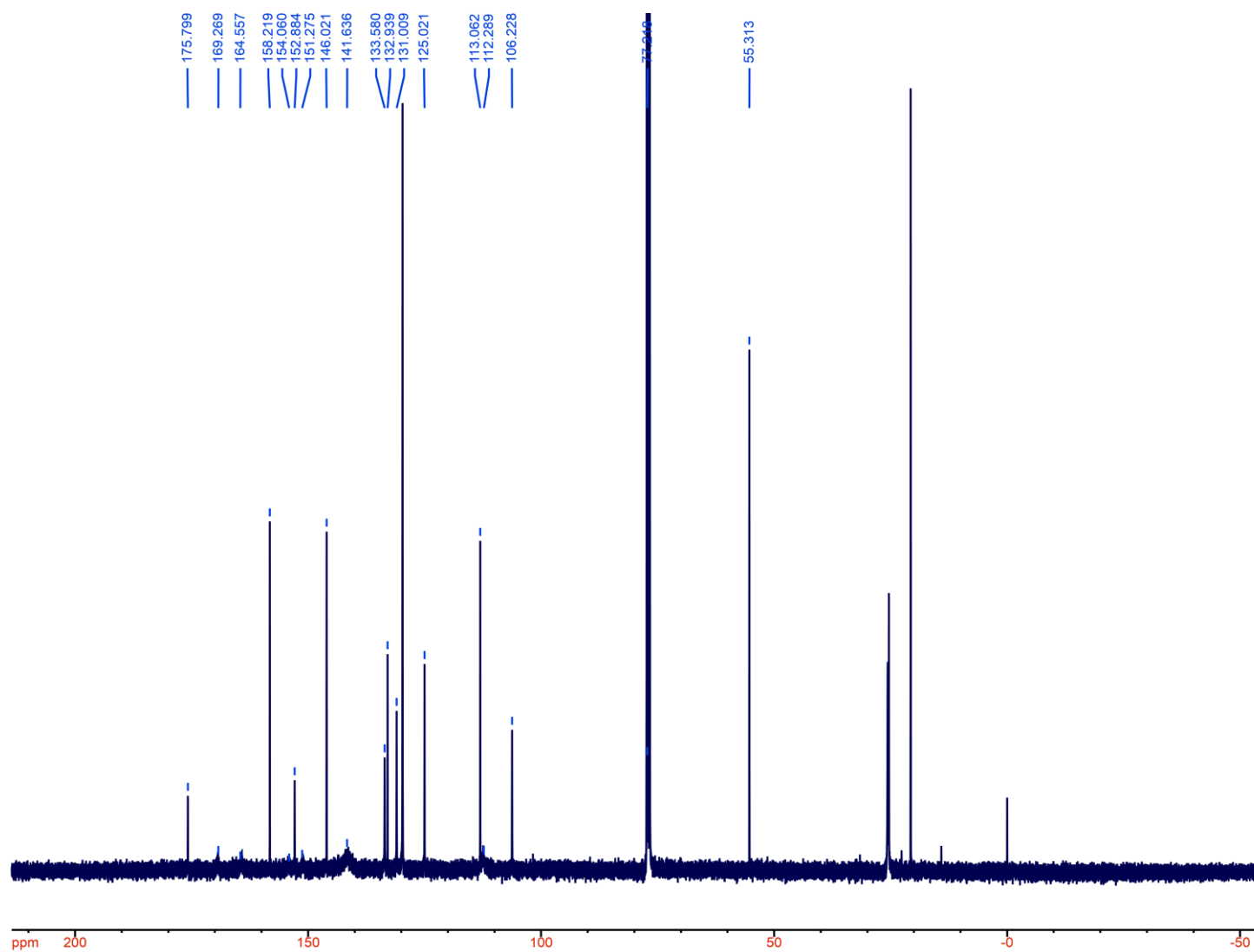


Figure S9. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of 2-Methyl-5-(2'-dimesitylborylphenyl)-1,3,4,6,9b-pentaazaphenalene (**5b**, 5AP-B-OMe).

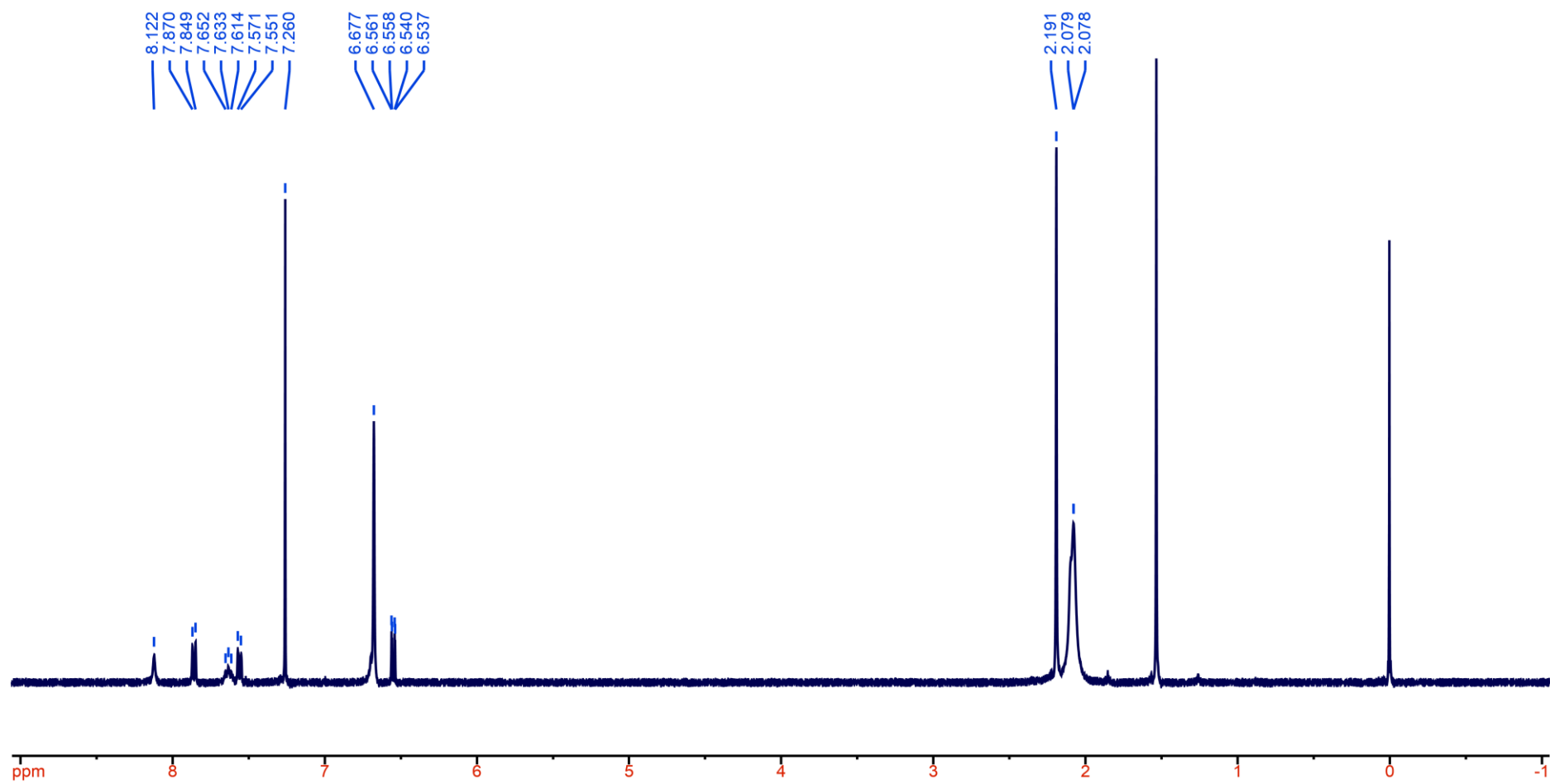


Figure S7. ^1H NMR spectrum of 2-Methyl-5-(2'-dimesitylborylphenyl)-1,3,4,6,9b-pentaazaphenalene (5, 5AP-B-CF₃).

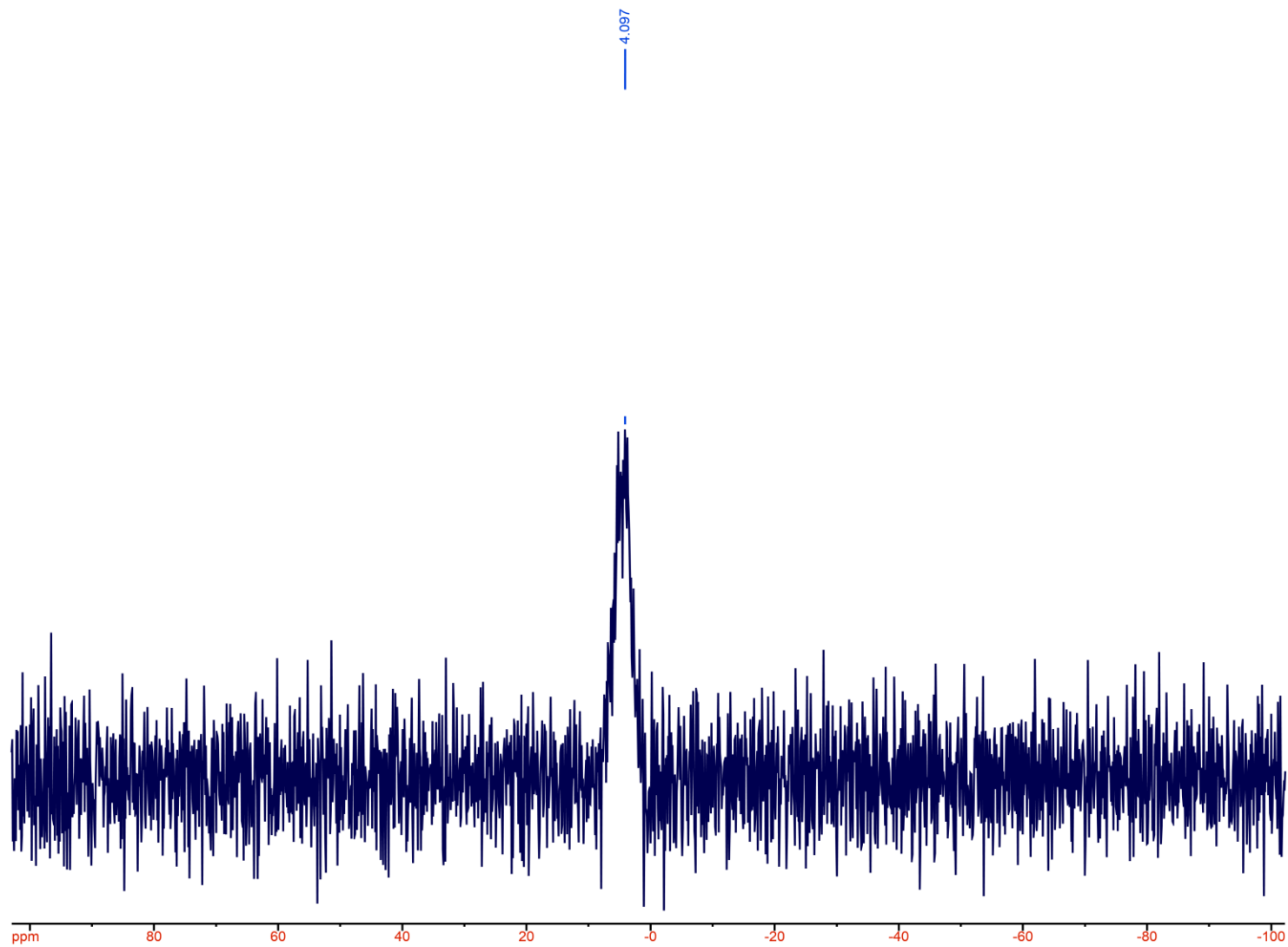


Figure S8. $^{11}\text{B}\{^1\text{H}\}$ NMR spectrum of 2-Methyl-5-(2'-dimesitylborylphenyl)-1,3,4,6,9b-pentaazaphenalene (**5**, 5AP-B- CF_3).

5. Discussion on the selective complexation with the boron atom of 3-nitrogen atom

As we described in the paper, the complexation of the boron atom occurred not at 1-nitrogen atom (Figure S10, complex A) but at 3-nitrogen atom (complex B). During the purification process, we did not observed formation of the formation of the complex A. We calculated the electrostatic surface potential (ESP) of 5AP-Ph at B3LYP/6-31+G(d,p) level of theory using Gaussian 16 A.03 package. Figure S11 is the calculated ESP of 5AP-Ph. It was suggested that the lone pair of the 3-nitrogen atom is more negatively charged compared to that of the 1-nitrogen atom. It is probably because of the polarized nature of 5AP originating from the electronegative nitrogen atoms which induces the dipole moment. We would think that the more negatively charged 3-nitrogen atom sufficiently stabilizes the boron complex during and after the complexation step.

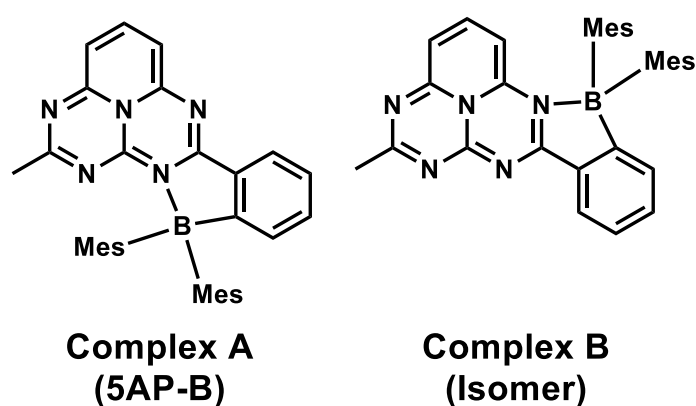


Figure S10. Chemical structures of isomers of 5AP-B.

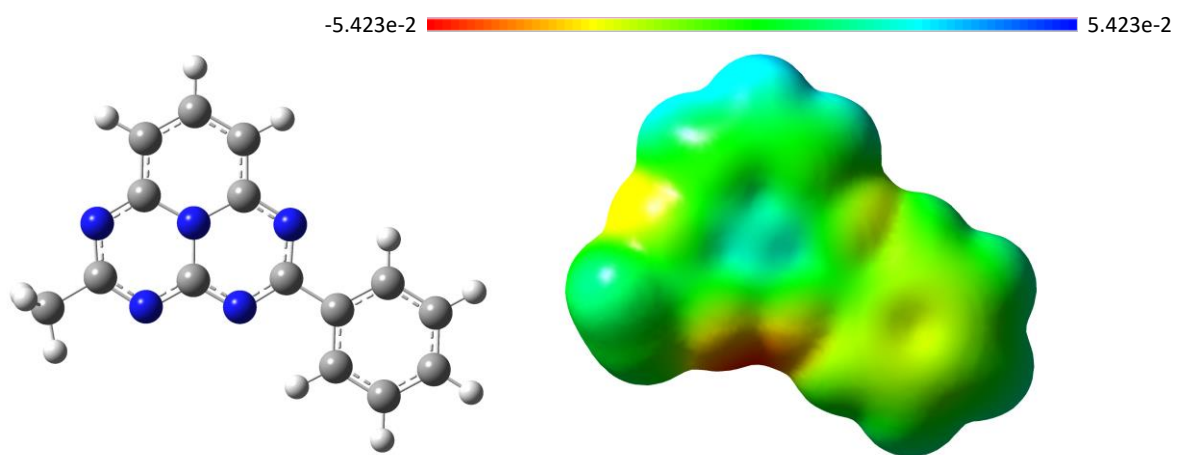


Figure S11. The calculated electrostatic potential mapping of 5AP-Ph. The ESP is mapped on the cube of the total electron density (isovalue 0.0004).

6. Theoretical calculation

All calculations were performed using Gaussian 16 A.03 package.^[8]

6-1. Ground state calculation

The ground-state optimized structure was obtained at B3LYP/6-31+G(d,p) level of theory. For the calculation of 5AP-Ph, opt=calcall option was employed because opt freq job gave one imaginary frequency mode. We performed the frequency calculation at this structure to confirm that the optimized structure was at the local minimum because no imaginary frequencies were found. The single-point ground-state calculation (CAM-B3LYP/6-311+G(2d,p) level of theory) was performed at the optimized structure. Kohn-Sham orbitals of 5AP-Ph and 5AP-B were generated from the single-point calculation using GaussView 6 (isovalue: 0.02, Figure 4) The following tables describe the optimized Cartesian coordinates and the total energies of 5AP-Ph and 5AP-B at the ground state.

Table S1. Cartesian coordinate of the optimized structure of 5AP-Ph

Number of imaginary frequency: 0

Total energy: -851.794922138 (CAM-B3LYP/6-311+G(2d,p), hartree)

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	0.652064	1.521826	-0.000011
2	6	0	0.928844	-0.887414	-0.000061
3	6	0	-1.147916	0.101588	-0.000020
4	6	0	1.240051	2.794781	0.000020
5	6	0	2.902503	0.523177	-0.000010
6	6	0	3.053267	-1.761907	-0.000101
7	1	0	0.572713	3.646670	0.000035
8	1	0	4.960898	-2.740098	0.000001
9	6	0	2.623930	2.925084	0.000036
10	7	0	1.720947	-1.958540	-0.000135
11	1	0	3.065148	3.917435	0.000060
12	6	0	3.455307	1.808496	0.000020
13	6	0	3.901973	-2.998891	0.000145
14	7	0	-0.395027	-1.015245	-0.000033
15	6	0	-5.398508	-0.439916	0.000034
16	6	0	-4.549905	-1.551551	0.000009
17	7	0	1.505769	0.407687	-0.000027
18	1	0	-3.044852	2.024803	0.000026
19	1	0	4.534898	1.882104	0.000027
20	1	0	-6.476121	-0.577910	0.000048
21	1	0	3.664971	-3.608185	-0.878453
22	1	0	-5.514328	1.715735	0.000059
23	6	0	-3.475687	1.030231	0.000021
24	7	0	3.674597	-0.586673	-0.000042
25	6	0	-2.617397	-0.083270	-0.000003
26	1	0	-4.966508	-2.554513	0.000004
27	6	0	-3.166540	-1.377302	-0.000009
28	1	0	-2.496646	-2.229376	-0.000029
29	7	0	-0.682139	1.352453	-0.000018
30	6	0	-4.857733	0.850575	0.000040
31	1	0	3.665280	-3.607484	0.879359

Table S2. Cartesian coordinate of the optimized structure of 5AP-B

Number of imaginary frequency: 0

Total energy: -1575.00743245 (CAM-B3LYP/6-311+G(2d,p), hartree)

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	7	0	-3.029274	-0.671304	-0.504826
2	6	0	-1.734810	-0.114370	-0.598434
3	7	0	-0.756458	-0.665757	0.148102
4	6	0	-1.062719	-1.748813	0.944489
5	7	0	-2.246700	-2.331298	1.015159
6	6	0	-3.252600	-1.803265	0.297477
7	6	0	-4.544153	-2.341066	0.328815
8	6	0	-5.566535	-1.759022	-0.411448
9	6	0	-5.331184	-0.636784	-1.199801
10	6	0	-4.052706	-0.076814	-1.262374
11	7	0	-3.795312	1.004813	-2.031974
12	6	0	-2.545647	1.435770	-2.080495
13	7	0	-1.502452	0.895615	-1.406738
14	6	0	-2.233219	2.618382	-2.942816
15	6	0	0.074480	-2.154411	1.726554
16	6	0	1.145484	-1.247015	1.573661
17	6	0	2.304068	-1.535502	2.317349
18	6	0	2.353520	-2.640768	3.166369
19	6	0	1.259962	-3.517689	3.300437
20	6	0	0.104930	-3.277272	2.572803
21	5	0	0.829901	-0.116890	0.423766
22	6	0	0.643868	1.477196	0.832395
23	6	0	0.894377	2.541204	-0.087133
24	6	0	0.743516	3.880941	0.306619
25	6	0	0.338652	4.251567	1.587594
26	6	0	0.043773	3.218151	2.475399
27	6	0	0.176819	1.865526	2.124535
28	6	0	-0.227967	0.880331	3.207786
29	6	0	1.328821	2.355531	-1.531803
30	6	0	0.233076	5.702102	1.997582
31	6	0	1.943438	-0.494197	-0.746307
32	6	0	1.737749	-1.375791	-1.846980
33	6	0	2.786066	-1.696681	-2.722242
34	6	0	4.081134	-1.205368	-2.556338
35	6	0	4.296586	-0.369297	-1.463597
36	6	0	3.274318	-0.014939	-0.570371
37	6	0	3.716381	0.932897	0.537919
38	6	0	0.408065	-2.034583	-2.170881

39	6	0	5.201607	-1.598179	-3.491368
40	1	0	-4.697187	-3.211631	0.953340
41	1	0	-6.563733	-2.186743	-0.373793
42	1	0	-6.104123	-0.161256	-1.789093
43	1	0	-3.129007	2.965220	-3.457634
44	1	0	-1.820075	3.421397	-2.323200
45	1	0	-1.459326	2.352093	-3.670263
46	1	0	3.179261	-0.901841	2.244572
47	1	0	3.259604	-2.832192	3.735840
48	1	0	1.326204	-4.374583	3.963858
49	1	0	-0.760499	-3.928833	2.640880
50	1	0	0.949783	4.661226	-0.424752
51	1	0	-0.309411	3.466041	3.474891
52	1	0	-0.624841	1.418557	4.073653
53	1	0	-1.008377	0.188081	2.876827
54	1	0	0.608645	0.268887	3.555762
55	1	0	0.873638	1.484814	-1.996894
56	1	0	1.045069	3.239450	-2.113680
57	1	0	2.413510	2.245744	-1.625788
58	1	0	0.007093	6.345229	1.140567
59	1	0	-0.549249	5.850505	2.749449
60	1	0	1.174899	6.060211	2.433464
61	1	0	2.580490	-2.363567	-3.557964
62	1	0	5.295589	0.030540	-1.292562
63	1	0	3.860646	1.947859	0.147277
64	1	0	3.010571	1.022183	1.359735
65	1	0	4.682035	0.610336	0.944343
66	1	0	0.041791	-2.661867	-1.351963
67	1	0	-0.366960	-1.300806	-2.413066
68	1	0	0.516253	-2.684159	-3.044218
69	1	0	4.839939	-1.728253	-4.516994
70	1	0	5.993245	-0.842028	-3.505606
71	1	0	5.661481	-2.547283	-3.186250

6-2. Excited state calculation

Time-dependent (TD) DFT single point calculations (CAM-B3LYP/6-311+G(2d,p) level of theory) were performed at the ground-state optimized structures to obtain the assignment of the absorption spectra (Table S3 and S4). TD-DFT optimization calculations were performed at B3LYP/6-31+G(d,p) level of theory. The frequency calculations were also performed at this level, which confirmed that the obtained structures were local minima. At these excited-state optimized structures (Table S5 and S6), TD-DFT single point calculations (CAM-B3LYP/6-311+G(2d,p) level of theory) were performed to obtain the assignment of the emission spectra (Table S7 and S8). From Table S3, S4, S7 and S8, information on the excited state 1 (S_1) was selected and described in Table 1.

Table S3. Result of TD-DFT single point calculation at the S₀ optimized structure (3, 5AP-Ph)

		Excitation Energy	Wavelength	Oscillator Strength	Assignment (Weight)
Excited State	1	2.5128 eV	493.41 nm	0.0136	HOMO→LUMO(0.68248)
Excited State	2	4.0515 eV	306.02 nm	0.1942	HOMO→LUMO+1(0.66397) HOMO→LUMO+2(-0.19676)
Excited State	3	4.1346 eV	299.87 nm	0	HOMO-4→LUMO(0.43605) HOMO-4→LUMO+1(-0.12035) HOMO-3→LUMO(0.51114) HOMO-3→LUMO+1(-0.10327)
Excited State	4	4.3179 eV	287.14 nm	0	HOMO-4→LUMO(0.46527) HOMO-4→LUMO+2(0.22785) HOMO-3→LUMO(-0.38931) HOMO-3→LUMO+2(-0.23438)
Excited State	5	4.3561 eV	284.62 nm	0.5413	HOMO-1→LUMO(-0.18203) HOMO→LUMO(-0.11216) HOMO→LUMO+1(0.17142) HOMO→LUMO+2(0.63048)
Excited State	6	4.5951 eV	269.82 nm	0.4690	HOMO-2→LUMO(0.14803) HOMO-1→LUMO(0.61694) HOMO-1→LUMO+1(-0.17760) HOMO→LUMO+2(0.16200)
Excited State	7	4.6790 eV	264.98 nm	0.0768	HOMO-2→LUMO(0.56972) HOMO-2→LUMO+1(-0.22013) HOMO-2→LUMO+7(0.14504) HOMO-1→LUMO(-0.15899) HOMO-1→LUMO+4(0.21012) HOMO→LUMO+2(-0.10104)
Excited State	8	5.2029 eV	238.30 nm	0.0006	HOMO-7→LUMO(0.15011) HOMO-4→LUMO+1(-0.22528) HOMO-4→LUMO+7(-0.10207) HOMO-3→LUMO+1(0.57850)

					HOMO-3→LUMO+2(-0.16829) HOMO-3→LUMO+7(0.10903)
Excited State	9	5.2282 eV	237.14 nm	0.0001	HOMO-4→LUMO+1(0.11694) HOMO→LUMO+3(0.61757) HOMO→LUMO+6(-0.18657) HOMO→LUMO+8(0.12001) HOMO→LUMO+9(0.10431) HOMO→LUMO+10(0.11559)
Excited State	10	5.2387 eV	236.67 nm	0.0029	HOMO-8→LUMO(-0.13448) HOMO-4→LUMO+1(0.49810) HOMO-4→LUMO+2(-0.28456) HOMO-3→LUMO+1(0.13625) HOMO-3→LUMO+2(-0.27829) HOMO→LUMO+3(-0.10520)
Excited State	11	5.6542 eV	219.28 nm	0.0002	HOMO-8→LUMO(0.30769) HOMO-7→LUMO(-0.28277) HOMO-4→LUMO(0.20865) HOMO-4→LUMO+2(-0.28996) HOMO-3→LUMO(-0.14419) HOMO-3→LUMO+1(0.18585) HOMO-3→LUMO+2(0.32246)
Excited State	12	5.6609 eV	219.02 nm	0.0324	HOMO-5→LUMO(0.11431) HOMO-2→LUMO(0.13654) HOMO-1→LUMO(0.15107) HOMO-1→LUMO+1(0.57790) HOMO-1→LUMO+2(-0.16521) HOMO-1→LUMO+4(-0.12404)
Excited State	13	5.7371 eV	216.11 nm	0.0003	HOMO-7→LUMO(0.40630) HOMO-7→LUMO+2(0.16101) HOMO-4→LUMO(0.10055) HOMO-4→LUMO+1(0.27914) HOMO-4→LUMO+2(0.22935) HOMO-3→LUMO+2(0.35281)
Excited State	14	5.8268 eV	212.78 nm	0.0001	HOMO→LUMO+3(0.23778) HOMO→LUMO+5(0.24374)

					HOMO→LUMO+6(0.54301)
					HOMO→LUMO+8(-0.17334)
					HOMO→LUMO+9(-0.11121)
					HOMO→LUMO+10(-0.13031)
					HOMO-5→LUMO(-0.35946)
					HOMO-2→LUMO(0.13440)
Excited State	15	5.8424 eV	212.21 nm	0.0634	HOMO-2→LUMO+4(-0.11573)
					HOMO-1→LUMO+2(-0.36186)
					HOMO→LUMO+7(0.38503)
					HOMO-6→LUMO(0.19334)
					HOMO-5→LUMO(0.10679)
					HOMO-2→LUMO(-0.11081)
Excited State	16	5.8806 eV	210.84 nm	0.0464	HOMO-1→LUMO+1(0.16100)
					HOMO-1→LUMO+2(0.28330)
					HOMO-1→LUMO+4(0.15650)
					HOMO→LUMO+4(0.13696)
					HOMO→LUMO+7(0.47710)
					HOMO-5→LUMO(0.34997)
					HOMO-2→LUMO(0.24120)
					HOMO-2→LUMO+1(0.17255)
Excited State	17	5.9586 eV	208.07 nm	0.1102	HOMO-2→LUMO+7(-0.15859)
					HOMO-1→LUMO+1(-0.14665)
					HOMO-1→LUMO+4(-0.27317)
					HOMO→LUMO+4(-0.26151)
					HOMO→LUMO+7(0.22080)
					HOMO-8→LUMO(0.17097)
					HOMO-7→LUMO(-0.33123)
Excited State	18	5.9611 eV	207.99 nm	0	HOMO-4→LUMO+1(0.22536)
					HOMO-4→LUMO+2(0.43551)
					HOMO-3→LUMO(0.18379)
					HOMO-3→LUMO+1(0.15865)
					HOMO-6→LUMO(-0.11876)
Excited State	19	6.1054 eV	203.07 nm	0.0817	HOMO-5→LUMO(0.25456)
					HOMO-2→LUMO+1(0.15491)
					HOMO-1→LUMO+2(-0.13656)

					HOMO→LUMO+4(0.56163)
					HOMO→LUMO+5(-0.29849)
					HOMO→LUMO+6(0.27623)
Excited State	20	6.1210 eV	202.56 nm	0.0053	HOMO→LUMO+8(0.50890)
					HOMO→LUMO+10(-0.14961)
					HOMO→LUMO+15(-0.10926)

Table S4. Result of TD-DFT single point calculation at the S₀ optimized structure (5, 5AP-B)

		Excitation Energy	Wavelength	Oscillator Strength	Assignment (Weight)
					HOMO-5→LUMO(-0.13605)
					HOMO-4→LUMO(0.62783)
Excited State	1	2.7221 eV	455.47 nm	0.0417	HOMO-3→LUMO(0.15309)
					HOMO-2→LUMO(-0.11326)
					HOMO→LUMO(-0.10913)
Excited State	2	3.2243 eV	384.53 nm	0.0394	HOMO→LUMO(0.65579)
					HOMO→LUMO+1(0.16654)
Excited State	3	3.4008 eV	364.58 nm	0.0147	HOMO-2→LUMO(0.28719)
					HOMO-1→LUMO(0.61145)
					HOMO-1→LUMO+1(0.12300)
Excited State	4	3.6702 eV	337.81 nm	0.0099	HOMO-4→LUMO(0.15762)
					HOMO-3→LUMO(-0.11754)
					HOMO-2→LUMO(0.59847)
					HOMO-2→LUMO+1(0.10521)
					HOMO-1→LUMO(-0.28772)
Excited State	5	3.8578 eV	321.39 nm	0.0008	HOMO-4→LUMO(-0.13897)
					HOMO-3→LUMO(0.65489)
					HOMO-3→LUMO+1(0.11586)
					HOMO-2→LUMO(0.13456)
Excited State	6	4.0059 eV	309.51 nm	0.1874	HOMO-6→LUMO(-0.16352)
					HOMO-5→LUMO(0.53936)
					HOMO-5→LUMO+1(0.20171)
					HOMO-4→LUMO(0.14818)
					HOMO-4→LUMO+2(-0.15227)

					HOMO-3→LUMO(0.10567) HOMO→LUMO(0.12322)
Excited State	7	4.0805 eV	303.85 nm	0.1333	HOMO-4→LUMO+1(0.48994) HOMO-4→LUMO+2(0.23994) HOMO-3→LUMO+1(0.15561) HOMO-2→LUMO+1(-0.11977) HOMO→LUMO+1(-0.29859) HOMO→LUMO+2(-0.16148)
Excited State	8	4.1696 eV	297.35 nm	0.0459	HOMO-5→LUMO(0.16966) HOMO-4→LUMO+1(0.19589) HOMO-4→LUMO+2(0.16412) HOMO-1→LUMO+1(0.39220) HOMO-1→LUMO+2(0.19613) HOMO→LUMO+1(0.35516) HOMO→LUMO+2(0.16300)
Excited State	9	4.2579 eV	291.18 nm	0.0104	HOMO-9→LUMO(-0.11620) HOMO-6→LUMO(-0.21494) HOMO-4→LUMO+1(0.21090) HOMO-2→LUMO+1(-0.20208) HOMO-2→LUMO+2(-0.12738) HOMO-1→LUMO+1(-0.22398) HOMO-1→LUMO+2(-0.22846) HOMO→LUMO+1(0.41420)
Excited State	10	4.3026 eV	288.16 nm	0.2937	HOMO-9→LUMO(-0.22362) HOMO-9→LUMO+2(-0.12609) HOMO-6→LUMO(0.33201) HOMO-5→LUMO(0.16997) HOMO-4→LUMO+1(-0.22528) HOMO-4→LUMO+2(0.27222) HOMO-2→LUMO+2(-0.11355) HOMO-1→LUMO+2(-0.15432) HOMO→LUMO+1(0.11165) HOMO→LUMO+2(-0.21304)
Excited State	11	4.3467 eV	285.24 nm	0.1449	HOMO-9→LUMO(-0.24557) HOMO-9→LUMO+2(-0.14233)

					HOMO-6→LUMO(-0.31185)
					HOMO-6→LUMO+1(-0.10340)
					HOMO-5→LUMO(-0.10820)
					HOMO-2→LUMO+1(0.16981)
					HOMO-1→LUMO+1(0.35063)
					HOMO→LUMO+2(-0.31066)
					HOMO-9→LUMO(-0.35090)
					HOMO-9→LUMO+2(-0.18142)
					HOMO-6→LUMO(0.20417)
Excited State	12	4.3964 eV	282.01 nm	0.0654	HOMO-4→LUMO+2(-0.16189)
					HOMO-1→LUMO+1(0.11215)
					HOMO→LUMO+1(-0.13225)
					HOMO→LUMO+2(0.38982)
					HOMO-6→LUMO(-0.26862)
					HOMO-6→LUMO+2(0.10550)
					HOMO-4→LUMO+1(-0.16199)
					HOMO-4→LUMO+2(0.41062)
Excited State	13	4.4590 eV	278.05 nm	0.1331	HOMO-3→LUMO+2(0.10986)
					HOMO-2→LUMO+2(-0.18220)
					HOMO-1→LUMO+2(0.11270)
					HOMO→LUMO+1(-0.14447)
					HOMO→LUMO+2(0.29956)
					HOMO-4→LUMO+1(0.17999)
					HOMO-4→LUMO+2(0.13506)
					HOMO-3→LUMO+1(-0.18469)
Excited State	14	4.5247 eV	274.02 nm	0.0051	HOMO-2→LUMO+1(0.52503)
					HOMO-2→LUMO+2(0.21573)
					HOMO-1→LUMO+1(-0.22092)
					HOMO-1→LUMO+2(-0.10249)
					HOMO-9→LUMO(-0.24391)
					HOMO-9→LUMO+2(-0.13323)
Excited State	15	4.5659 eV	271.54 nm	0.0022	HOMO-8→LUMO(0.10050)
					HOMO-2→LUMO+2(0.22014)
					HOMO-1→LUMO+1(-0.21266)
					HOMO-1→LUMO+2(0.51614)

					HOMO→LUMO+2(-0.10878)
Excited State	16	4.7358 eV	261.80 nm	0.0070	HOMO-4→LUMO+2(0.20220)
					HOMO-3→LUMO+2(-0.17639)
					HOMO-2→LUMO+1(-0.27990)
					HOMO-2→LUMO+2(0.50034)
					HOMO-1→LUMO+1(0.12781)
					HOMO-1→LUMO+2(-0.19316)
Excited State	17	4.7690 eV	259.98 nm	0.0005	HOMO-4→LUMO+1(-0.12069)
					HOMO-3→LUMO+1(0.58080)
					HOMO-3→LUMO+2(0.20332)
					HOMO-2→LUMO+1(0.12858)
					HOMO-2→LUMO+2(0.19372)
Excited State	18	4.8582 eV	255.21 nm	0.0058	HOMO-14→LUMO(0.17181)
					HOMO-13→LUMO(0.32972)
					HOMO-10→LUMO(-0.31787)
					HOMO-9→LUMO(-0.16552)
					HOMO-9→LUMO+2(0.16396)
					HOMO-8→LUMO(-0.24938)
					HOMO-7→LUMO(-0.21167)
Excited State	19	4.8948 eV	253.30 nm	0.0010	HOMO-4→LUMO+2(-0.10538)
					HOMO-3→LUMO+1(-0.20848)
					HOMO-3→LUMO+2(0.43770)
					HOMO-3→LUMO+5(0.12626)
					HOMO-2→LUMO+5(0.11371)
					HOMO→LUMO+7(-0.10517)
					HOMO→LUMO+10(0.15868)
					HOMO→LUMO+12(0.10593)
					HOMO→LUMO+13(-0.12370)
					HOMO→LUMO+16(-0.11388)
					HOMO→LUMO+17(0.11846)
Excited State	20	4.9316 eV	251.41 nm	0.0102	HOMO-13→LUMO(0.11961)
					HOMO-10→LUMO(-0.18605)
					HOMO-7→LUMO(0.54191)
					HOMO-7→LUMO+1(0.16732)
					HOMO-5→LUMO(-0.10671)

HOMO-5→LUMO+1(0.12609)

Table S5. Cartesian coordinate of the optimized structure at the excited state 1 of 5AP-Ph

Number of imaginary frequency: 0

Total energy: -851.783680480 (CAM-B3LYP/6-311+G(2d,p), hartree)

Total energy of S₁: -851.704190958 (TD-CAM-B3LYP/6-311+G(2d,p), hartree)

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	-0.630742	1.511209	0.000074
2	6	0	-0.918559	-0.905565	0.000110
3	6	0	1.172739	0.062420	0.000252
4	6	0	-1.244565	2.806803	0.000055
5	6	0	-2.909060	0.518115	-0.000116
6	6	0	-3.046711	-1.785574	-0.000066
7	1	0	-0.574859	3.657883	0.000138
8	1	0	-4.604739	-2.963350	0.879185
9	6	0	-2.623091	2.945299	-0.000058
10	7	0	-1.733231	-1.975237	0.000096
11	1	0	-3.062747	3.937344	-0.000070
12	6	0	-3.458881	1.819552	-0.000131
13	6	0	-3.950016	-2.980688	-0.000050
14	7	0	0.389231	-1.035784	0.000242
15	6	0	5.418340	-0.418668	-0.000198
16	6	0	4.578339	-1.541541	-0.000103
17	7	0	-1.503804	0.402678	-0.000068
18	1	0	3.035351	2.018184	0.000037
19	1	0	-4.538867	1.896293	-0.000180
20	1	0	6.497315	-0.542154	-0.000311
21	1	0	-3.361486	-3.898656	0.001397
22	1	0	5.496799	1.738243	-0.000217
23	6	0	3.471290	1.026141	-0.000005
24	7	0	-3.668320	-0.557953	-0.000104
25	6	0	2.614625	-0.099936	0.000104
26	1	0	5.007466	-2.539664	-0.000140
27	6	0	3.196571	-1.390574	0.000042
28	1	0	2.546468	-2.258073	0.000118
29	7	0	0.661255	1.358260	0.000179
30	6	0	4.854049	0.862197	-0.000146
31	1	0	-4.602569	-2.964936	-0.880952

Table S6. Cartesian coordinate of the optimized structure at the excited state of 5AP-B

Number of imaginary frequency: 0

Total energy: -1574.99020932 (CAM-B3LYP/6-311+G(2d,p), hartree)

Total energy of S₁: -1574.89546252 (TD-CAM-B3LYP/6-311+G(2d,p), hartree)

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	7	0	-2.962479	-0.743576	-0.683053
2	6	0	-1.662269	-0.107924	-0.717421
3	7	0	-0.644469	-0.756559	-0.099888
4	6	0	-0.868872	-2.014385	0.478088
5	7	0	-2.046838	-2.633543	0.449130
6	6	0	-3.131760	-2.021378	-0.097908
7	6	0	-4.404865	-2.599790	-0.095019
8	6	0	-5.485260	-1.930249	-0.658834
9	6	0	-5.321606	-0.677501	-1.232594
10	6	0	-4.063850	-0.057210	-1.253938
11	7	0	-3.869555	1.172904	-1.804572
12	6	0	-2.633793	1.691465	-1.861878
13	7	0	-1.531797	1.049315	-1.370099
14	6	0	-2.415477	3.024332	-2.475614
15	6	0	0.322446	-2.505458	1.129325
16	6	0	1.334922	-1.524321	1.178129
17	6	0	2.546383	-1.843015	1.784761
18	6	0	2.721988	-3.107701	2.333631
19	6	0	1.705544	-4.074035	2.286281
20	6	0	0.494796	-3.778679	1.680553
21	5	0	0.820856	-0.222394	0.341086
22	6	0	0.493365	1.183904	1.092174
23	6	0	0.516310	2.391357	0.380399
24	6	0	0.080426	3.573958	0.994975
25	6	0	-0.374626	3.567419	2.308863
26	6	0	-0.380600	2.370596	3.020621
27	6	0	0.054497	1.184384	2.420719
28	6	0	0.019771	-0.034772	3.285446
29	6	0	0.994693	2.549957	-1.027287
30	6	0	-0.850611	4.823133	2.960955
31	6	0	2.066088	-0.125847	-0.704872
32	6	0	2.027901	-0.752636	-1.952487
33	6	0	3.136421	-0.691985	-2.807377
34	6	0	4.292398	-0.024243	-2.420570
35	6	0	4.340631	0.582753	-1.167544
36	6	0	3.239788	0.534409	-0.306283

37	6	0	3.419362	1.246764	0.997911
38	6	0	0.849241	-1.519082	-2.463615
39	6	0	5.478806	0.034746	-3.324507
40	1	0	-4.519203	-3.583950	0.365065
41	1	0	-6.477008	-2.396215	-0.648554
42	1	0	-6.159848	-0.139146	-1.681742
43	1	0	-3.331478	3.426033	-2.938919
44	1	0	-2.074380	3.750463	-1.709719
45	1	0	-1.620747	2.988442	-3.242427
46	1	0	3.361199	-1.120669	1.812767
47	1	0	3.670940	-3.360861	2.807118
48	1	0	1.874600	-5.053471	2.723331
49	1	0	-0.311703	-4.509553	1.623840
50	1	0	0.101640	4.505595	0.439352
51	1	0	-0.728474	2.361247	4.049123
52	1	0	-0.341378	0.180249	4.299430
53	1	0	-0.643005	-0.809780	2.881982
54	1	0	1.022500	-0.471836	3.401308
55	1	0	0.741434	1.686911	-1.663733
56	1	0	0.562680	3.428226	-1.519144
57	1	0	2.088440	2.654353	-1.064260
58	1	0	-0.828855	5.685692	2.284163
59	1	0	-1.883975	4.716938	3.319783
60	1	0	-0.228336	5.076547	3.830964
61	1	0	3.092645	-1.175059	-3.778407
62	1	0	5.243847	1.099143	-0.859344
63	1	0	3.127414	2.304798	0.900380
64	1	0	2.803927	0.845975	1.815413
65	1	0	4.460201	1.225434	1.341963
66	1	0	0.557687	-2.319276	-1.771490
67	1	0	-0.006462	-0.854557	-2.635069
68	1	0	1.057707	-2.009641	-3.425284
69	1	0	5.241619	-0.271343	-4.351480
70	1	0	5.898035	1.048151	-3.378476
71	1	0	6.276904	-0.630447	-2.964474

Table S7. Result of TD-DFT optimization calculation (3, 5AP-Ph)

		Excitation Energy	Wavelength	Oscillator Strength	Assignment (Weight)
Excited State	1	2.1630 eV	573.20 nm	0.0125	HOMO→LUMO(0.67304) HOMO→LUMO+1(0.15878)
Excited State	2	3.8154 eV	324.96 nm	0	HOMO-4→LUMO(0.68596)
Excited State	3	3.8428 eV	322.64 nm	0.1364	HOMO→LUMO(-0.11696) HOMO→LUMO+1(0.59907) HOMO→LUMO+2(-0.32337)

Table S8. Result of TD-DFT optimization calculation (5, 5AP-B)

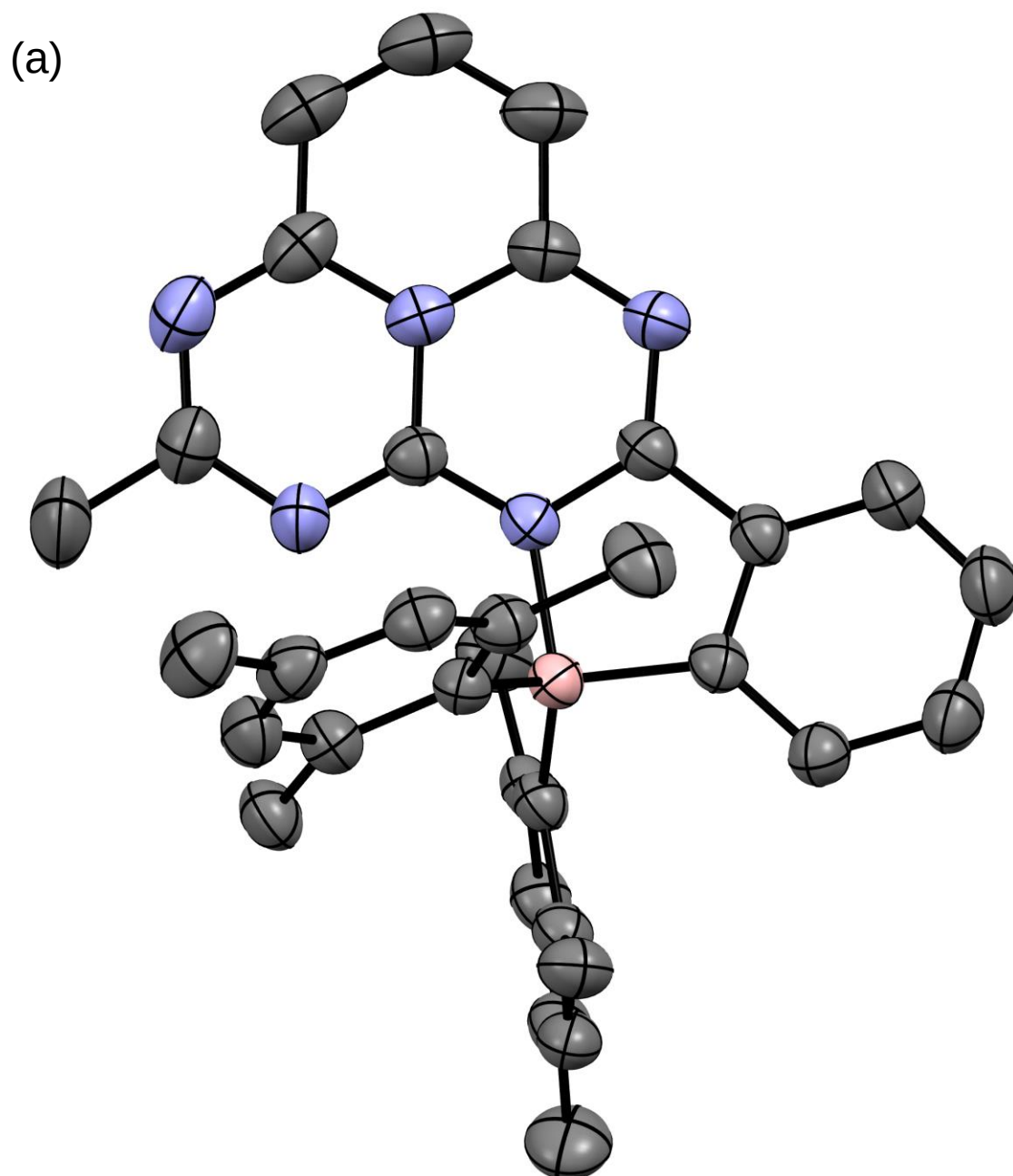
		Excitation Energy	Wavelength	Oscillator Strength	Assignment (Weight)
Excited State	1	2.5782 eV	480.90 nm	0.0094	HOMO→LUMO(0.67267) HOMO→LUMO+1(0.15380)
Excited State	2	2.6936 eV	460.30 nm	0.0528	HOMO-6→LUMO(-0.12923) HOMO-5→LUMO(0.25539) HOMO-4→LUMO(0.59138) HOMO-2→LUMO(-0.14675)
Excited State	3	3.1930 eV	388.29 nm	0.0065	HOMO-2→LUMO(0.11456) HOMO-1→LUMO(0.67504) HOMO-1→LUMO+1(0.11191)

7. Single crystal X-ray crystallographic analysis of 5AP-B.

7-1. Experimental details

A needle single crystal of 5AP-B suitable for X-ray analysis was obtained by the recrystallization from the mixed solvent of CHCl_3 and *n*-hexane. X-ray crystallographic analysis was carried out at Rigaku Analysis Center with the generous support by Rigaku Corp. (Dr. Hiroyasu Sato and Dr. Takashi Kikuchi). The measurement was carried out by Rigaku XtaLAB P 200 Cu $\text{K}\alpha$ radiation diffractometer (monochromated by multi-layer mirror optics) with PILATUS 200K Hybrid Photon Counting area detector. The structure was solved by SHELXT^[1] and refined by SHELXL^[2]. Details of the structure refinement are described in the CIF file. The programs Olex2^[3] and Mercury^[4] were used to generate the table of crystallographic information and the X-ray structural images.

7-2. Single crystal X-ray structure of 5AP-B.



(b)

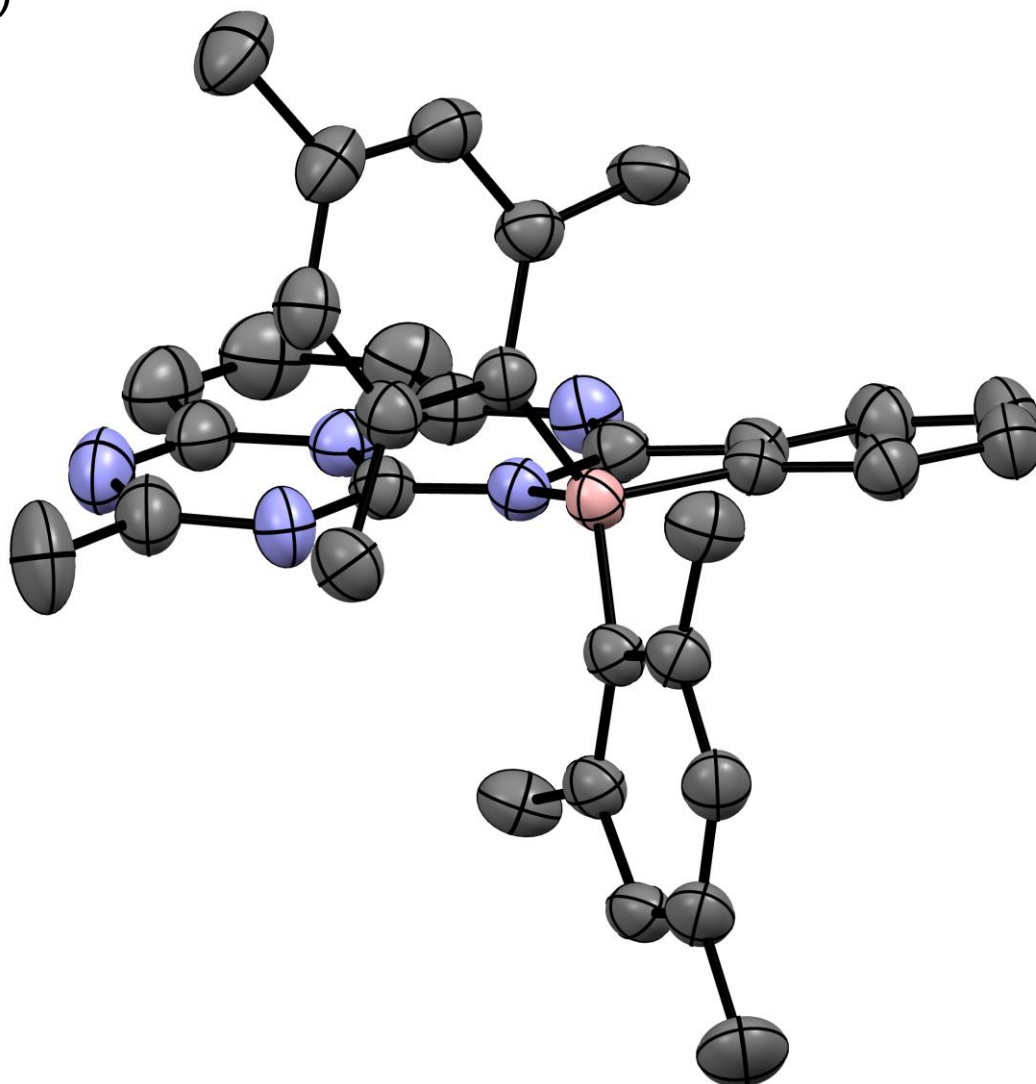
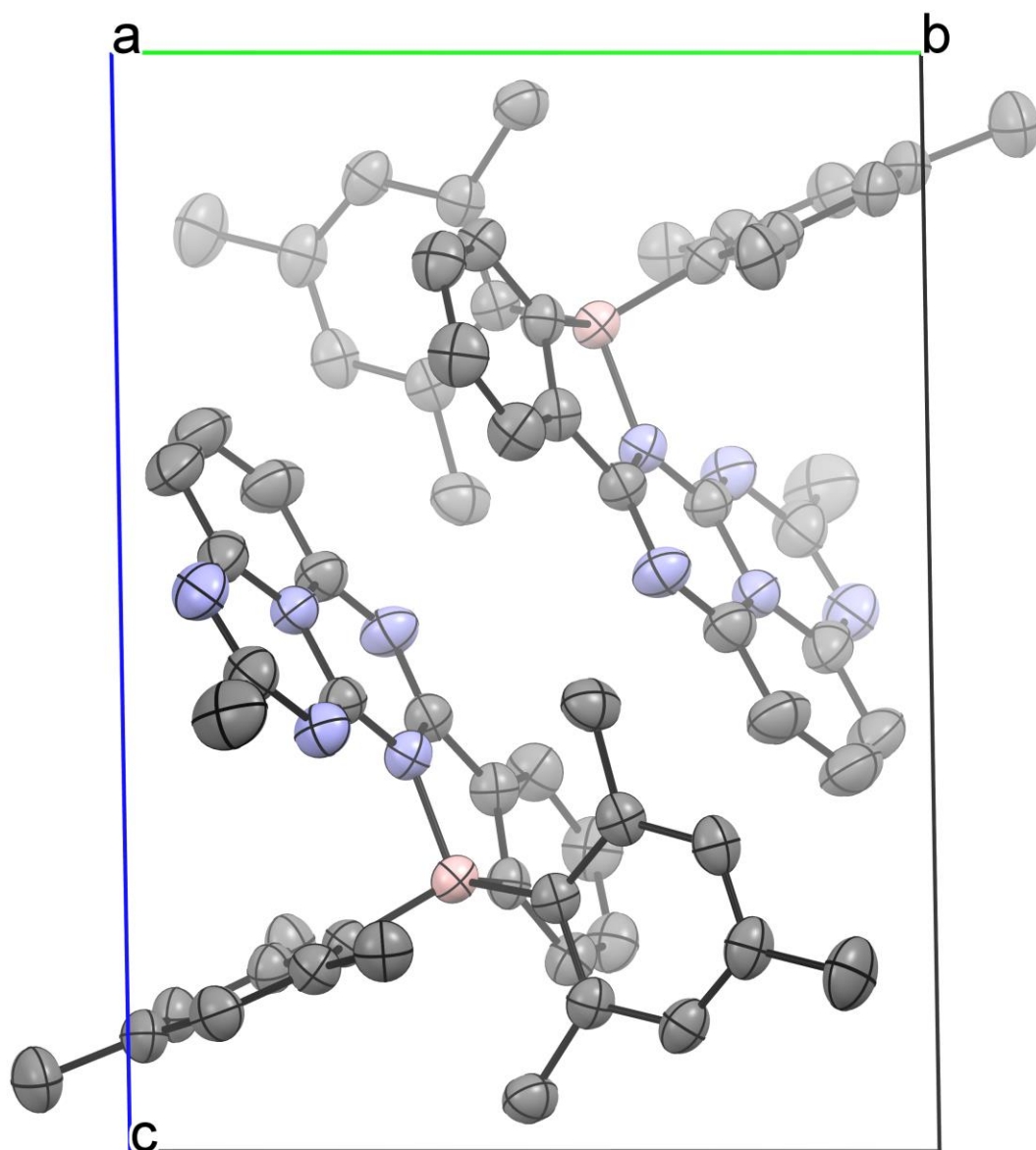
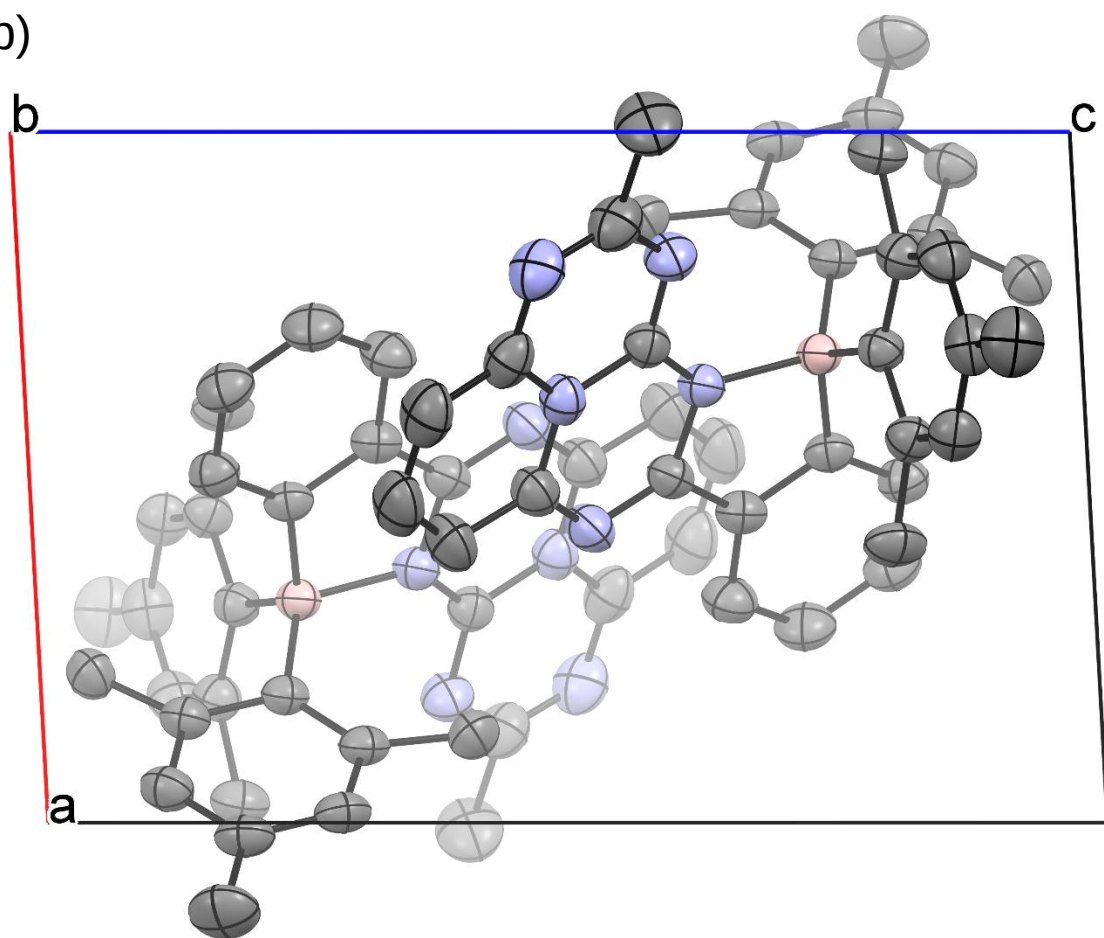


Figure S12. ORTEP (a) top and (b) side views of 5AP-B obtained by single crystal X-ray structure analysis. Thermal ellipsoid plot is shown at 50% probability level. All hydrogen atoms are omitted for clarity.

(a)



(b)



(c)

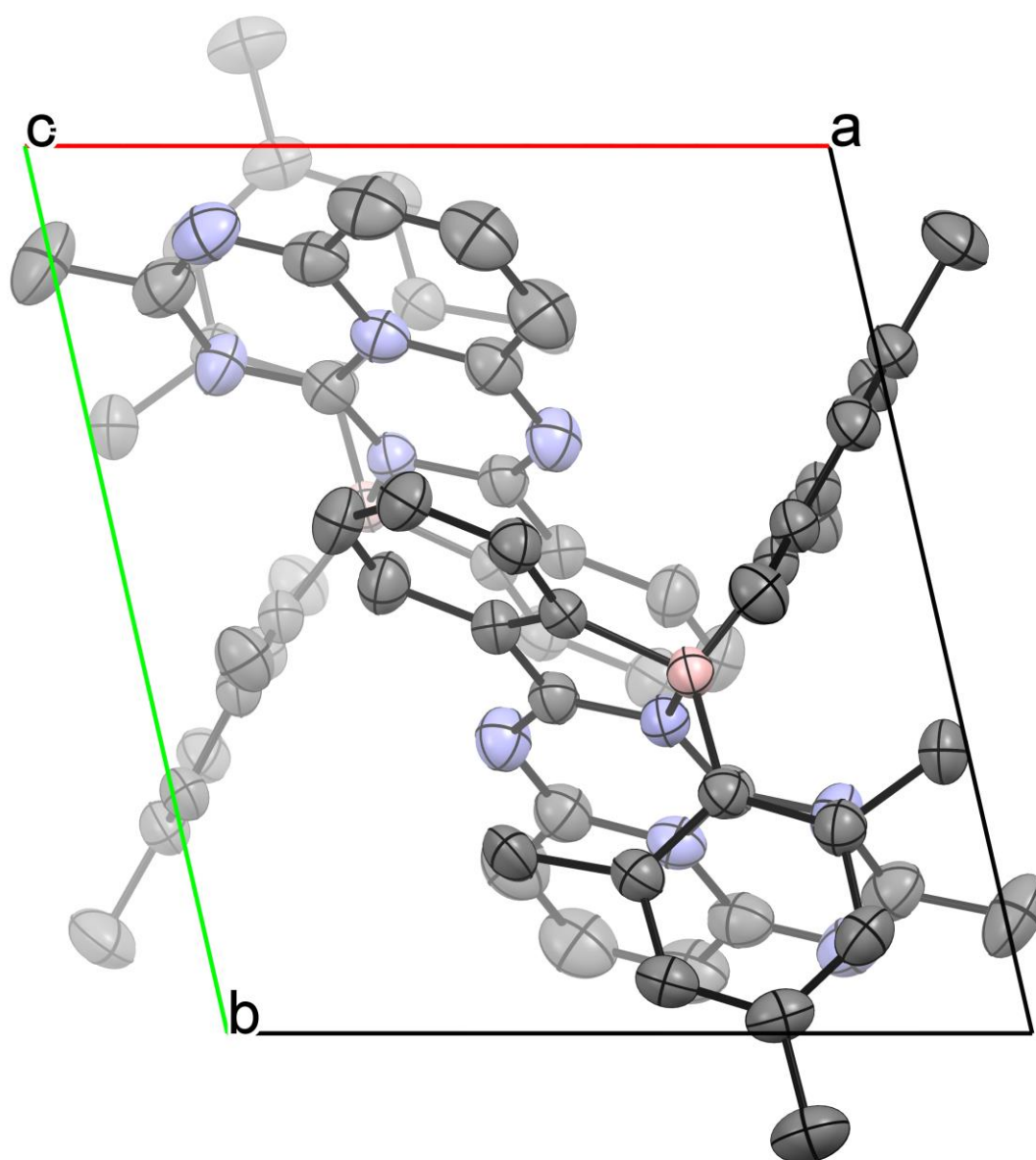


Figure S13. Packing of 5AP-B (along with (a) a (b) b and (c) c axis) of 5AP-B obtained by single crystal X-ray structure analysis. Thermal ellipsoid plot is shown at 50% probability level. All hydrogen atoms are omitted for clarity.

7-3. Crystallographic data of 5AP-B.

Table S9. Details of crystal data and structure refinement of 5AP-B.

Empirical formula	C ₃₃ H ₃₂ BN ₅
Formula weight	509.44
Temperature/K	93
Crystal system	triclinic
Space group	<i>P</i> $\bar{1}$
a/Å	9.3650(4)
b/Å	10.5772(5)
c/Å	14.0108(6)
α /°	88.287(4)
β /°	86.558(4)
γ /°	77.055(4)
Volume/Å ³	1349.95(11)
Z	2
ρ_{calc} /g/cm ³	1.253
μ /mm ⁻¹	0.577
F(000)	540.0
Crystal size/mm ³	0.165 × 0.091 × 0.034
Radiation	CuK α (λ = 1.54184)
2 Θ range for data collection/°	6.32 to 152.432
Index ranges	-11 ≤ h ≤ 11, -11 ≤ k ≤ 13, -17 ≤ l ≤ 17
Reflections collected	15122
Independent reflections	5378 [R_{int} = 0.0613, R_{sigma} = 0.0574]
Data/restraints/parameters	5378/0/359
Goodness-of-fit on F ²	1.126
Final R indexes [$I \geq 2\sigma(I)$]	R_1 = 0.0823, wR_2 = 0.2587
Final R indexes [all data]	R_1 = 0.0911, wR_2 = 0.2648
Largest diff. peak/hole / e Å ⁻³	0.34/-0.31

8. Additional optical measurements

8-1. Concentration-dependency of the emission behavior of **5AP-B**

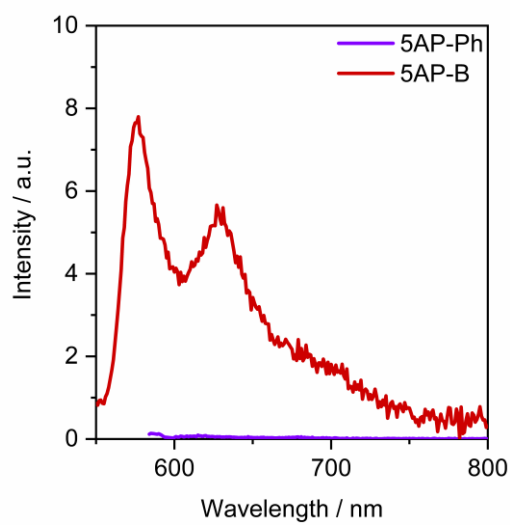


Figure S14. Emission spectra of **5AP-Ph** and **5AP-B** measured in chloroform (1.0×10^{-5} M).

8-2. Solvent-dependency of the emission behavior of **5AP-B-OMe** and **5AP-B-CF₃**

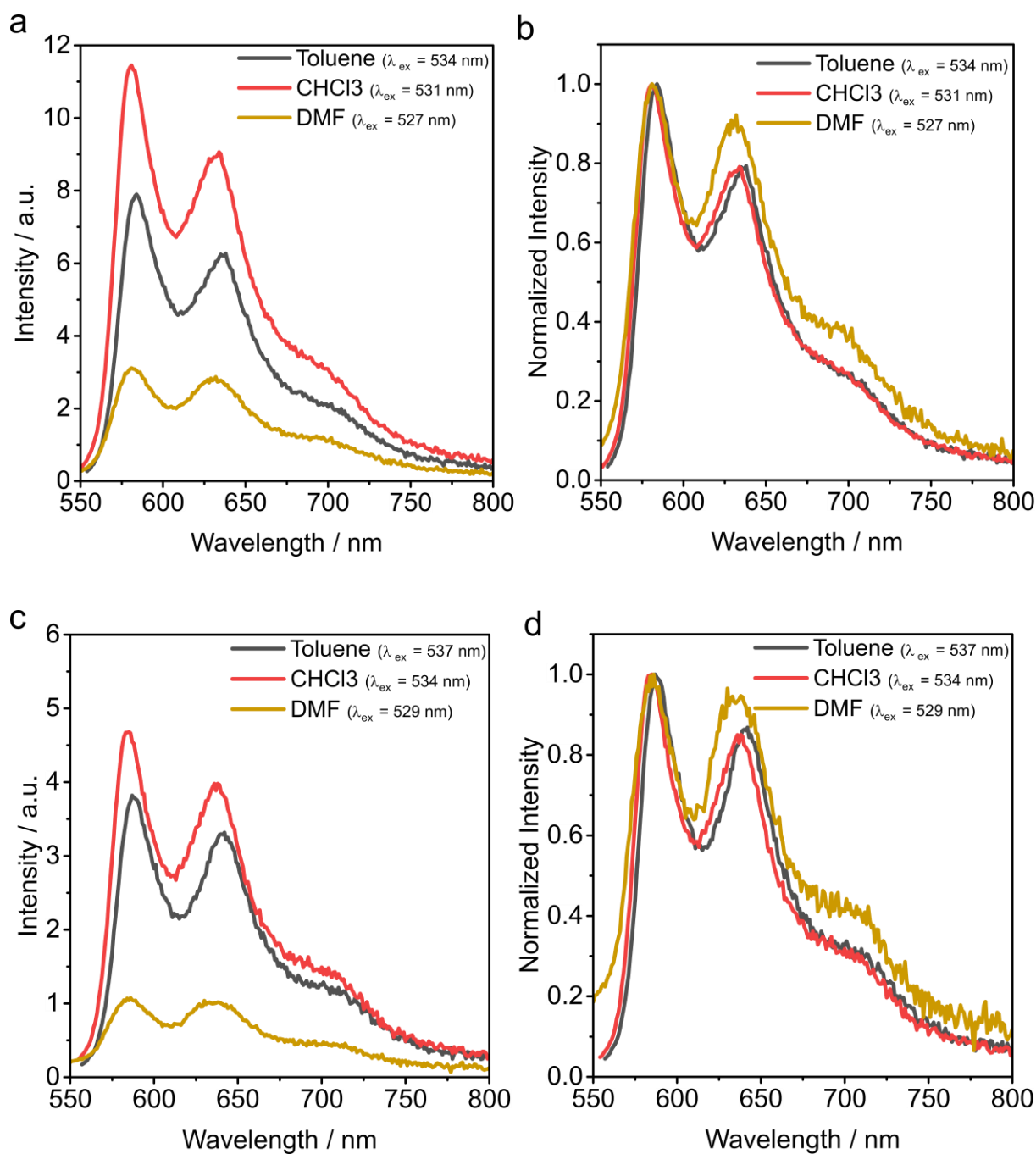


Figure S15. Solvent-dependent emission spectra of (a,b) **5AP-B-OMe** and (c,d) **5AP-B-CF₃**.

9. References

- [1] G. M. Sheldrick, *Acta Crystallogr. Sect. A Found. Adv.* **2015**, *71*, 3–8.
- [2] G. M. Sheldrick, *Acta Crystallogr. Sect. C Struct. Chem.* **2015**, *71*, 3–8.
- [3] O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard, H. Puschmann, *J. Appl. Crystallogr.* **2009**, *42*, 339–341.
- [4] C. F. Macrae, P. R. Edgington, P. McCabe, E. Pidcock, G. P. Shields, R. Taylor, M. Towler, J. van de Streek, *J. Appl. Crystallogr.* **2006**, *39*, 453–457.
- [5] P. Dai, J. Ma, W. Huang, W. Chen, N. Wu, S. Wu, Y. Li, X. Cheng, R. Tan, *ACS Catal.* **2018**, *8*, 802–806.
- [6] J. T. Shaw, M. E. O'Connor, R. C. Allen, W. M. Westler, B. D. Stefanko, *J. Heterocycl. Chem.* **1974**, *11*, 627–630.
- [7] H. Watanabe, M. Hirose, K. Tanaka, K. Tanaka, Y. Chujo, *Polym. Chem.* **2016**, *7*, 3674–3680.
- [8] Gaussian 16, Revision A.03, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. V. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, D. Williams-Young, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. J. Bearpark, J. J. Heyd, E. N. Brothers, K. N. Kudin, V. N. Staroverov, T. A. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. P. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R.

Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman, and
D. J. Fox, Gaussian, Inc., Wallingford CT, 2016.