Electronic Supplementary Information

Pyrrole-bridged quinones: π-electronic systems that modulate electronic structures by tautomerism and deprotonation

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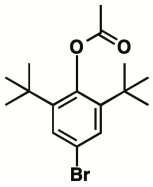
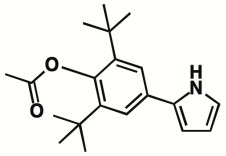
1. Synthetic procedures and spectroscopic data

General Procedures. Starting materials were purchased from FUJIFILM Wako Pure Chemical Corp, Nacalai Tesque Inc., and Sigma-Aldrich Co. and were used without further purification unless otherwise stated. NMR spectra used in the characterization of products were recorded on a JEOL ECA-600 600 MHz spectrometer. All NMR spectra were referenced to solvent. UV-visible absorption spectra were recorded on a Hitachi U-3500 spectrometer. High-resolution (HR) electrospray ionization mass spectrometries (ESI-MS) were recorded on a BRUKER microTOF using ESI-TOF method. TLC analyses were carried out on aluminum sheets coated with silica gel 60 (Merck 5554). Column chromatography was performed on Wakogel C-300 and Merck silica gel 60.

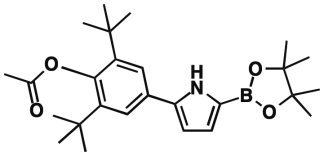
1-Acetoxy-4-bromo-2,6-di-*tert*-butylbenzene, s1. According to the literature procedure,[S1] to 4-bromo-2,6-di-*tert*-butylphenol (5.70 g, 20.0 mmol) in acetic anhydride (26 mL) was added conc. H_2SO_4 (50 μL). The mixture was heated at 80 °C for 3 h and was cooled, and acetic anhydride was removed. The residue was recrystallized from ethanol/water (2:1) to give **s1** (5.72 g, 17.5 mmol, 88%) as a white solid. R_f = 0.72 (CH_2Cl_2:*n*-hexane = 1:3). ^{1}H NMR (600 MHz, $CDCl_3$, 20 °C): δ (ppm) 7.40 (s, 2H, Ar-H), 2.32 (s, 3H, CH_3), 1.30 (s, 18H, $C(CH_3)_3$). ^{13}C NMR (151 MHz, $CDCl_3$, 20 °C): δ (ppm) 170.93, 147.34, 144.86, 129.59, 119.63, 35.73, 31.39, 22.72. ESI-TOF-MS (HR): 349.0763. Calcd for $C_{16}H_{22}BrNaO_2$ ([M + Na]$^+$): 349.0774.



2-(4-Acetoxy-3,5-di-*tert*-butylphenyl)pyrrole, s2. A round-bottomed flask placed with **s1** (3.30 g, 10.0 mmol), *N*-Boc-pyrrolyl-2-boronic acid[S2] (2.37 g, 11.0 mmol), $Pd(PPh_3)_4$ (1.73 g, 1.50 mmol), and K_2CO_3 (2.76 g, 20.0 mmol) was flushed with N_2 and was charged with a mixture of degassed 1,4-dioxane (100 mL) and water (30 mL). The mixture was heated at 80 °C for 15 h, was cooled, and then was partitioned between water and CH_2Cl_2. The combined organic extracts were dried over anhydrous Na_2SO_4 and was evaporated. This crude product was dissolved in ethylene glycol and was heated at 180 °C for 30 min, followed by cooling and partitioning between water and CH_2Cl_2. The combined organic extracts were dried over anhydrous Na_2SO_4 and was evaporated. The residue was then chromatographed over silica gel column (Wakogel C-300, eluent: CH_2Cl_2:*n*-hexane = 1:3) to give **s2** (2.51 g, 8.00 mmol, 80%) as a white solid. R_f = 0.32 (CH_2Cl_2:*n*-hexane = 1:3). ^{1}H NMR (600 MHz, $CDCl_3$, 20 °C): δ (ppm) 8.37 (s, 1H, NH), 7.39 (s, 2H, Ar-H), 6.83 (ddd, J = 2.4, 2.4, and 1.2 Hz, 1H, pyrrole-H), 6.42 (ddd, J = 3.6, 2.4, and 1.2 Hz, 1H, pyrrole-H), 6.27 (ddd, J = 3.6, 2.4, and 2.4 Hz, 1H, pyrrole-H), 2.34 (s, 3H, CH_3), 1.36 (s, 18H, $C(CH_3)_3$). ^{13}C NMR (151 MHz, $CDCl_3$, 20 °C): δ (ppm) 171.34, 146.81, 143.00, 132.74, 130.40, 122.75, 118.66, 110.02, 105.96, 35.60, 31.57, 22.81. ESI-TOF-MS (HR): 348.1736. Calcd for $C_{20}H_{26}NO_2$ ([M – H]$^-$): 348.1725.

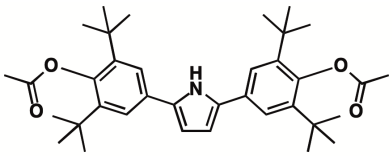


5-(4-Acetoxy-3,5-di-*tert*-butylphenyl)pyrrol-2-yl-4,4,5,5-tetramethyl-1,3,2-dioxaborolane, s3. According to the literature procedure,[S3] a round-bottomed flask placed with **s2** (626.9 mg, 2.00 mmol), bis(pinacolato)diboron (516.3 mg, 2.03 mmol), $[Ir(cod)OMe]_2$ (20.0 mg, 0.031 mmol), and 4,4′-di-*tert*-butyl-2,2′-dipyridyl (32.2 mg, 0.12 mmol) was flushed with N_2 and was charged with *n*-hexane (15 mL). The mixture was heated at 80 °C for 15 h, was cooled, and then was partitioned between water and CH_2Cl_2. The combined organic extracts were dried over anhydrous Na_2SO_4 and was evaporated. The residue was then chromatographed over silica gel column (Wakogel C-300, eluent: 10% EtOAc: *n*-hexane) to give **s3** (806.3 mg, 1.84 mmol, 92%) as a white solid. R_f = 0.19 (CH_2Cl_2:*n*-hexane = 1:3). ^{1}H NMR (600 MHz, CD_3CN, 20 °C): δ (ppm) 9.81 (s, 1H, NH), 7.53 (s, 2H, Ar-H), 6.70 (s, 1H, pyrrole-H), 6.52 (s, 1H, pyrrole-H), 2.33 (s, 3H, $COCH_3$), 1.36 (s, 18H, $C(CH_3)_3$), 1.32 (s, 12H, pinacolato-CH_3). ^{13}C NMR (151 MHz, CD_3CN, 20 °C): δ (ppm) 172.26, 148.22, 144.18, 138.10, 130.63, 124.12, 122.51, 108.46, 84.41, 36.29, 31.79, 25.23, 22.97 (one signal was missing probably due to the coupling with ^{10}B/^{11}B). ESI-TOF-MS (HR): 440.2971. Calcd for $C_{26}H_{37}NO_4$ ([M + H]$^+$): 440.2967.

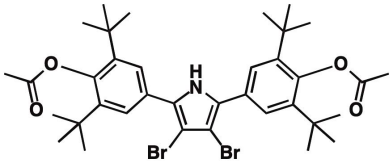


2,5-Bis(4-acetoxy-3,5-di-*tert*-butylphenyl)pyrrole, 1a. A round-bottomed flask placed with **s1** (326.4 mg, 1.00 mmol), **s3** (348.2 mg, 1.06 mmol), $Pd(PPh_3)_4$ (259.7 mg, 0.22 mmol), and K_2CO_3 (317.6 mg, 2.29 mmol) was flushed with N_2 and was charged with a mixture of degassed 1,4-dioxane (10 mL) and water (3 mL). The mixture was heated at 80 °C for 15 h, was cooled, and then was partitioned between water and CH_2Cl_2. The combined organic extracts were dried over anhydrous Na_2SO_4 and was evaporated. The residue was then chromatographed over silica gel column (Wakogel C-300, eluent: CH_2Cl_2:*n*-hexane = 1:3) to give **1a** (294.6 mg, 0.53 mmol, 53%) as a white solid. R_f = 0.26

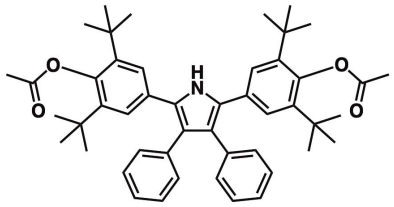
(CH_2Cl_2:*n*-hexane = 1:3). ^{1}H NMR (600 MHz, $CDCl_3$, 20 °C): δ (ppm) 8.32 (s, 1H, NH), 7.36 (s, 4H, Ar-H), 6.39 (d, J = 2.4 Hz, 2H, pyrrole-H), 2.29 (s, 6H, $COCH_3$), 1.31 (s, 36H, $C(CH_3)_3$). ^{13}C NMR (151 MHz, $CDCl_3$, 20 °C): δ (ppm) 171.34, 147.06, 143.16, 133.58, 130.33, 122.95, 107.76, 35.64, 31.57, 22.83. UV/vis (CH_2Cl_2, λ_{max}[nm] (ε, 10^5 $M^{-1}cm^{-1}$)): 324 (0.31). ESI-TOF-MS (HR): 594.3357. Calcd for $C_{36}H_{48}NO_4$ ([M – H]$^-$): 594.3356.



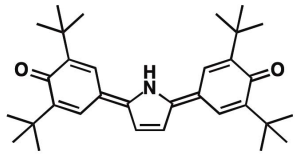
2,5-Bis(4-acetoxy-3,5-di-*tert*-butylphenyl)-3,4-dibromopyrrole, 1b. According to the literature procedure,[S3] to a solution of **1b** (100.0 mg, 0.179 mmol) in THF (30 mL) under N_2 was added *N*-bromosuccinimide (82.6 mg, 0.464 mmol) at –40 °C. The mixture was stirred for 3 h and was quenched with Na_2SO_3 aq., followed by warming to 20 °C and partitioning between water and CH_2Cl_2. The combined organic extracts were dried over anhydrous Na_2SO_4 and was evaporated. The residue was then chromatographed over flash silica gel column (Merck silica gel 60, eluent: CH_2Cl_2:*n*-hexane = 1:3) to give **1b** (106.8 mg, 0.142 mmol, 79%) as a white solid. R_f = 0.37 (CH_2Cl_2:*n*-hexane = 1:3). ^{1}H NMR (600 MHz, $CDCl_3$, 20 °C): δ (ppm) 8.41 (s, 1H, NH), 7.50 (s, 4H, Ar-H), 2.29 (s, 6H, $COCH_3$), 1.31 (s, 36H, $C(CH_3)_3$). ^{13}C NMR (151 MHz, $CDCl_3$, 20 °C): δ (ppm) 171.32, 147.95, 143.25, 130.10, 128.43, 125.58, 99.44, 35.83, 31.56, 22.79. UV/vis (CH_2Cl_2, λ_{max}[nm] (ε, 10^5 $M^{-1}cm^{-1}$)): 305 (0.23). ESI-TOF-MS (HR): 735.3935. Calcd for $C_{36}H_{46}Br_2ClNO_4$ ([M + Cl]$^-$): 735.3934.



2,5-Bis(4-acetoxy-3,5-di-*tert*-butylphenyl)-3,4-diphenylpyrrole, 1c. A round-bottomed flask placed with **1b** (31.0 mg, 0.043 mmol), phenylboronic acid (16.1 mg, 0.132 mmol), $Pd(PPh_3)_4$ (15.3 mg, 0.013 mmol), and K_2CO_3 (36.4 mg, 0.26 mmol) was flushed with N_2 and was charged with a mixture of degassed 1,4-dioxane (2.0 mL) and water (0.7 mL). The mixture was heated at 100 °C for 15 h, was cooled, and then was partitioned between water and CH_2Cl_2. The combined organic extracts were dried over anhydrous Na_2SO_4 and was evaporated. The residue was then chromatographed over silica gel column (Wakogel C-300, eluent: CH_2Cl_2:*n*-hexane = 1:3) to give **1c** (12.1 mg, 0.017 mmol, 40%) as a white solid. R_f = 0.35 (CH_2Cl_2:*n*-hexane = 1:3). ^{1}H NMR (600 MHz, $CDCl_3$, 20 °C): δ (ppm) 8.36 (s, 1H, NH), 7.19 (s, 4H, Ar-H), 7.18–7.15 (m, 4H, Ph-H), 7.12–7.09 (m, 6H, Ph-H), 2.34 (s, 6H, $COCH_3$), 1.22 (s, 36 H, $C(CH_3)_3$). ^{13}C NMR (151 MHz, $CDCl_3$, 20 °C): δ (ppm) 171.34, 146.81, 143.00, 132.74, 130.40, 122.75, 118.66, 110.02, 105.96, 35.60, 31.57, 22.81. UV/vis (CH_2Cl_2, λ_{max}[nm] (ε, 10^5 $M^{-1}cm^{-1}$)): 311 (0.25). ESI-TOF-MS (HR): 746.3982. Calcd for $C_{48}H_{57}ClNO_4$ ([M + Cl]$^-$): 746.3982. This compound was further characterized by single-crystal X-ray diffraction analysis.

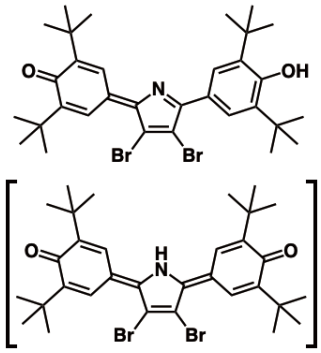


2,5-Bis(3,5-di-*tert*-butyl-4-oxocyclohexa-2,5-dienylidene)-1*H*-pyrrole, 2a. To a solution of **1a** (55.5 mg, 0.10 mmol) in CH_2Cl_2 (30 mL) under N_2 was added $FeCl_3$ (486.6 mg, 3.00 mmol) at 20 °C. The mixture was stirred at 20 °C for 5 min. To the mixture were added MeOH, CH_2Cl_2, and water for separation. Organic phase was dried over anhydrous Na_2SO_4 and was evaporated. The residue was then chromatographed over flash silica gel column (Merck silica gel 60, eluent: CH_2Cl_2) to give **2a** (31.3 mg, 0.066 mmol, 66%) as a blue solid with metallic luster. R_f = 0.56 (CH_2Cl_2). ^{1}H NMR (600 MHz, CD_3CN, 20 °C; observed as a quinoidal (NH) form **2a**$_{NH}$): 9.59 (s, 1H, NH), 7.55 (d, J = 2.4 Hz, 2H, quinone methide CH), 7.51 (d, J = 1.8 Hz, 2H, quinone methide CH), 7.41 (d, J = 2.4 Hz, 2H, pyrrole-H), 1.29 (s, 18H, $C(CH_3)_3$), 1.25 (s, 18H, $C(CH_3)_3$). ^{13}C NMR (151 MHz, CD_3CN, 20 °C): δ (ppm) 185.95, 150.27, 149.28, 147.08, 129.05, 128.40, 126.50, 116.43, 36.68, 36.11, 30.11, 29.84. UV/vis (CH_2Cl_2, λ_{max}[nm] (ε, 10^5 $M^{-1}cm^{-1}$)): 625 (0.82). ESI-TOF-MS (HR): 472.3216. Calcd for $C_{32}H_{42}NO_2$ ([M – H]$^-$): 472.3221. This compound was further characterized by single-crystal X-ray diffraction analysis.

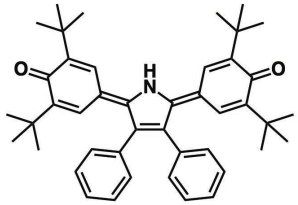


3,4-Dibromo-2,5-bis(3,5-di-*tert*-butyl-4-oxocyclohexa-2,5-dienylidene)-1*H*-pyrrole, 2b. To a solution of **1b** (87.2 mg, 0.12 mmol) in CH_2Cl_2 (50 mL) under N_2 was added $FeCl_3$ (486.7 mg, 3.00 mmol) at 20 °C. The mixture was stirred at 20 °C for 5 min and was added to MeOH. The suspension was washed with water and was extracted with CH_2Cl_2. Organic phase was dried over anhydrous Na_2SO_4 and was evaporated. The residue was then chromatographed over silica gel column (Wakogel C-300, eluent: CH_2Cl_2:*n*-hexane = 1:3) to give **2b** (56.8 mg, 0.090 mmol, 74%) as a dark brown solid. R_f = 0.77 (CH_2Cl_2:*n*-hexane = 1:3). ^{1}H NMR (600 MHz, $CDCl_3$, 20 °C; observed as a phenol (OH) form **2b**$_{OH}$): δ (ppm) 8.69 (d, J = 2.4 Hz, 1H, quinone methide CH), 8.53 (d, J = 2.4 Hz, 1H, quinone methide CH), 8.24 (s, 2H, phenol CH), 5.74 (s, 1H, OH), 1.51 (s, 18H, $C(CH_3)_3$), 1.38 (s, 9H, $C(CH_3)_3$), 1.37 (s, 9H, $C(CH_3)_3$). ^{13}C NMR (151 MHz, $CDCl_3$, 20 °C): δ (ppm) 186.98,

165.36, 157.99, 153.22, 151.67, 151.46, 136.39, 134.88, 129.81, 127.23, 127.21, 126.50, 124.14, 123.63, 36.78, 36.30, 34.74, 30.29, 29.96, 29.76. UV/vis (CH_2Cl_2, λ_{max}[nm] (ε, 10^5 $M^{-1}cm^{-1}$)): 462 (0.33). ESI-TOF-MS (HR): 628.1426. Calcd for $C_{32}H_{40}Br_2NO_2$ ([M – H]$^-$): 628.1431. This compound was further characterized in the form of the anion **2b**$^-$ as an ion pair with tetrapropylammonium (TPA) cation by single-crystal X-ray diffraction analysis.



2,5-Bis(3,5-di-*tert*-butyl-4-oxocyclohexa-2,5-dienylidene)-3,4-diphenyl-1*H*-pyrrole, 2c. To a solution of **1c** (81.2 mg, 0.11 mmol) in CH_2Cl_2 (80 mL) under N_2 was added $FeCl_3$ (546.2 mg, 3.37 mmol) at 20 °C. The mixture was stirred at 20 °C for 5 min. To the mixture were added MeOH, CH_2Cl_2, and water for separation. Organic phase was dried over anhydrous Na_2SO_4 and was evaporated. The residue was then chromatographed over silica gel column (Wakogel C-300, eluent: CH_2Cl_2) to give **2c** (51.4 mg, 0.082 mmol, 72%) as a dark green solid with metallic luster. R_f = 0.47 (CH_2Cl_2). ^{1}H NMR (600 MHz, CD_3CN, 20 °C; observed as a quinoidal (NH) form **2c**$_{NH}$): δ (ppm) 9.64 (s, 1H, NH), 7.64 (d, J = 2.4 Hz, 2H, quinone methide CH), 7.33–7.31 (m, 4H, Ph-H), 7.27–7.24 (m, 6H, Ph-H), 6.87 (d, J = 2.4 Hz, 2H, quinone methide CH), 1.38 (s, 18H, $C(CH_3)_3$), 0.85 (s, 18H, $C(CH_3)_3$). ^{13}C NMR (151 MHz, CD_3CN, 50 °C): δ (ppm) 186.04, 149.13, 147.68, 146.52, 144.14, 135.47, 131.12, 129.73, 129.43, 129.20, 127.75, 36.81, 35.98, 30.26, 29.69 (a signal was overlapped with other signals). UV/vis (CH_2Cl_2, λ_{max}[nm] (ε, 10^5 $M^{-1}cm^{-1}$)): 645 (0.40). ESI-TOF-MS (HR): 624.3848. Calcd for $C_{44}H_{50}NO_2$ ([M – H]$^-$): 624.3847. This compound was further characterized by single-crystal X-ray diffraction analysis.



[S1] K. Tamura, Y. Kato, A. Ishikawa, Y. Kato, M. Himori, M. Yoshida, Y. Takashima, T. Suzuki, Y. Kawabe, O. Cynshi, T. Kodama, E. Niki and M. Shimizu, *J. Med. Chem*., 2003, **46**, 3083–3093.

[S2] T. A. Kelly, V. U. Fuchs, C. W. Perry and R. J. Snow, *Tetrahedron*, 1993, **49**, 1009–1016.

[S3] T. Ishiyama, J. Takagi, Y. Yonekawa, J. F. Hartwig and N. Miyaura, *Adv. Synth. Catal*., 2003, **345**, 1103–1106.

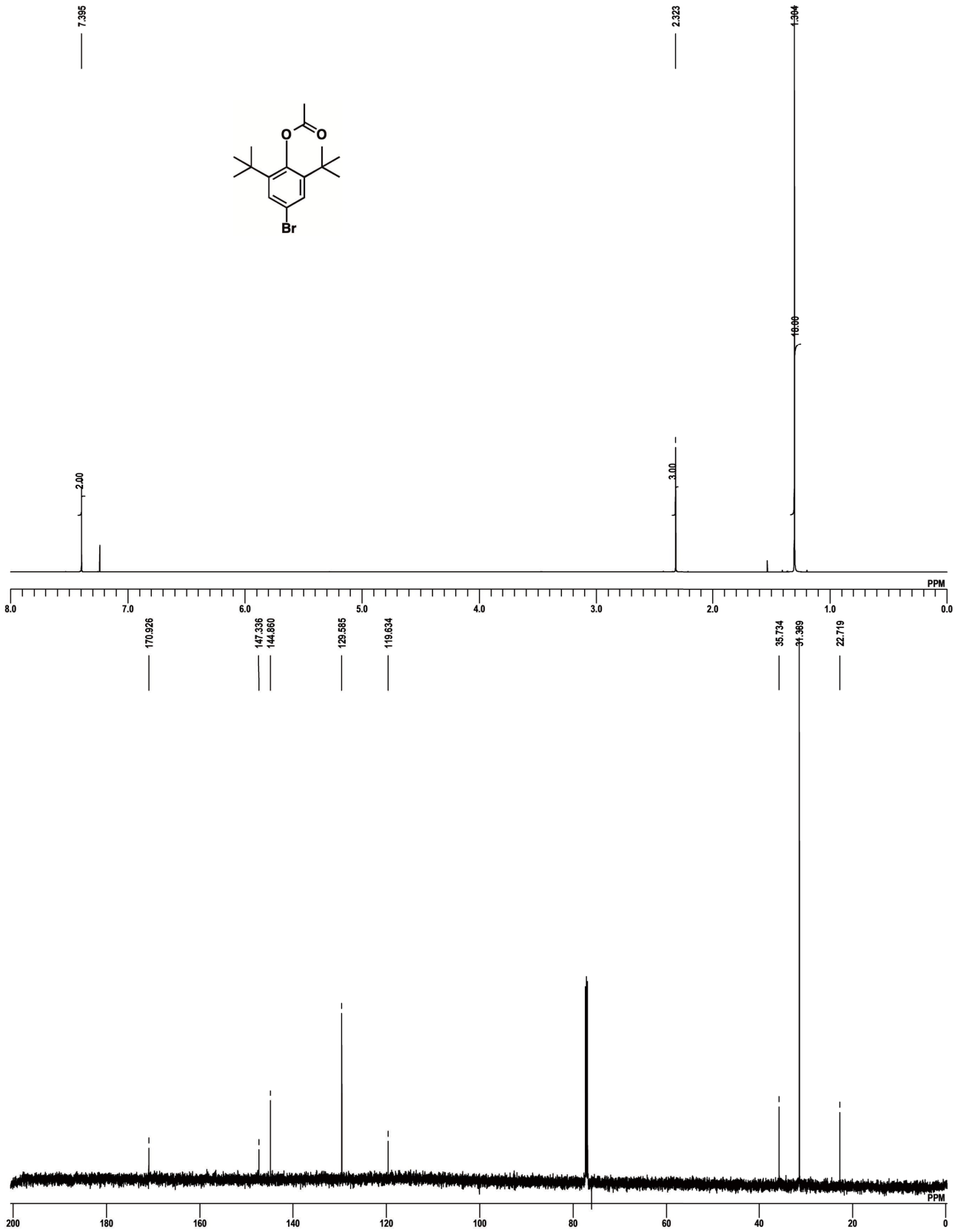


Fig. S1 ^{1}H NMR (top) and ^{13}C NMR (bottom) spectra of **s1** in $CDCl_3$.

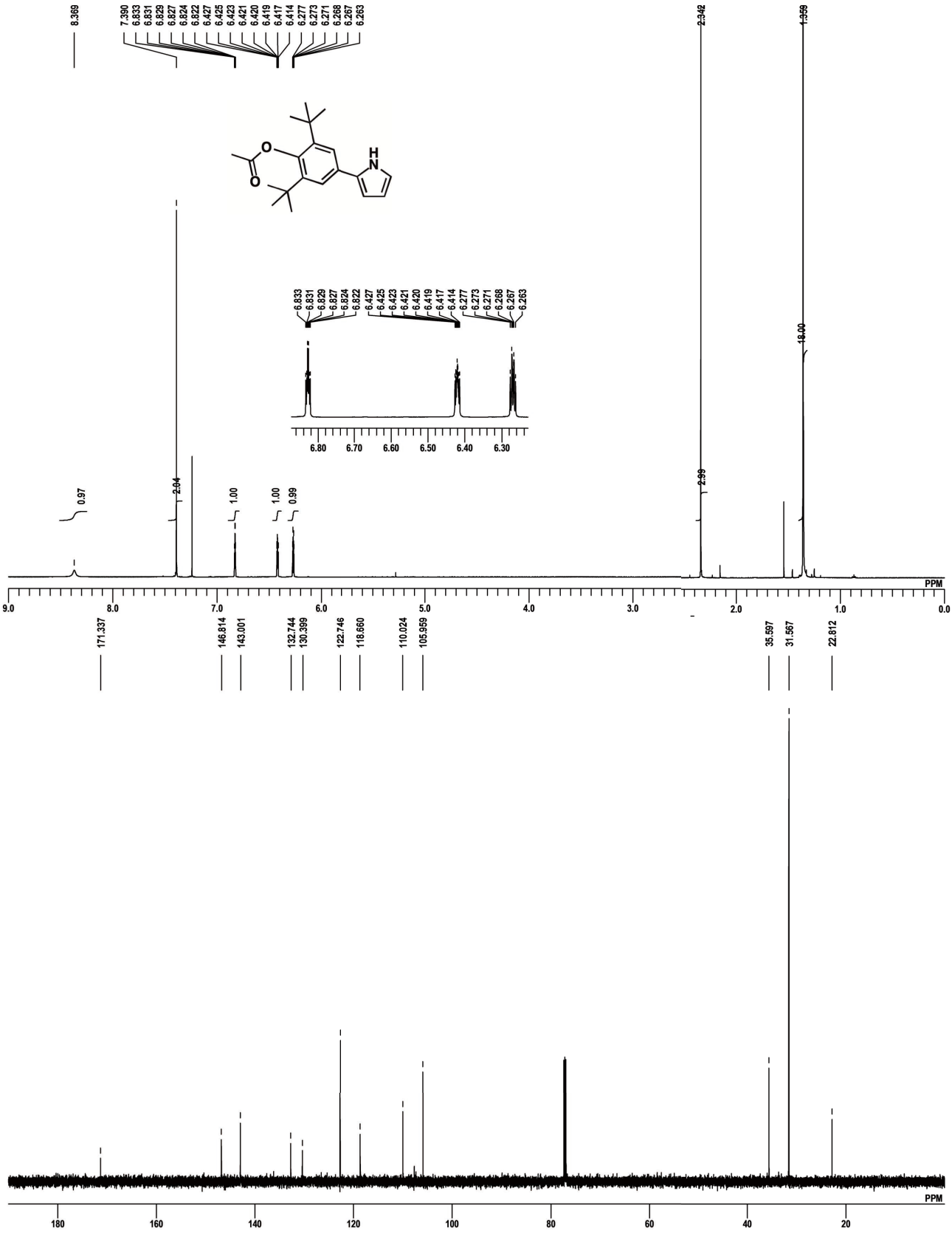


Fig. S2 ^{1}H NMR (top) and ^{13}C NMR (bottom) spectra of **s2** in $CDCl_3$.

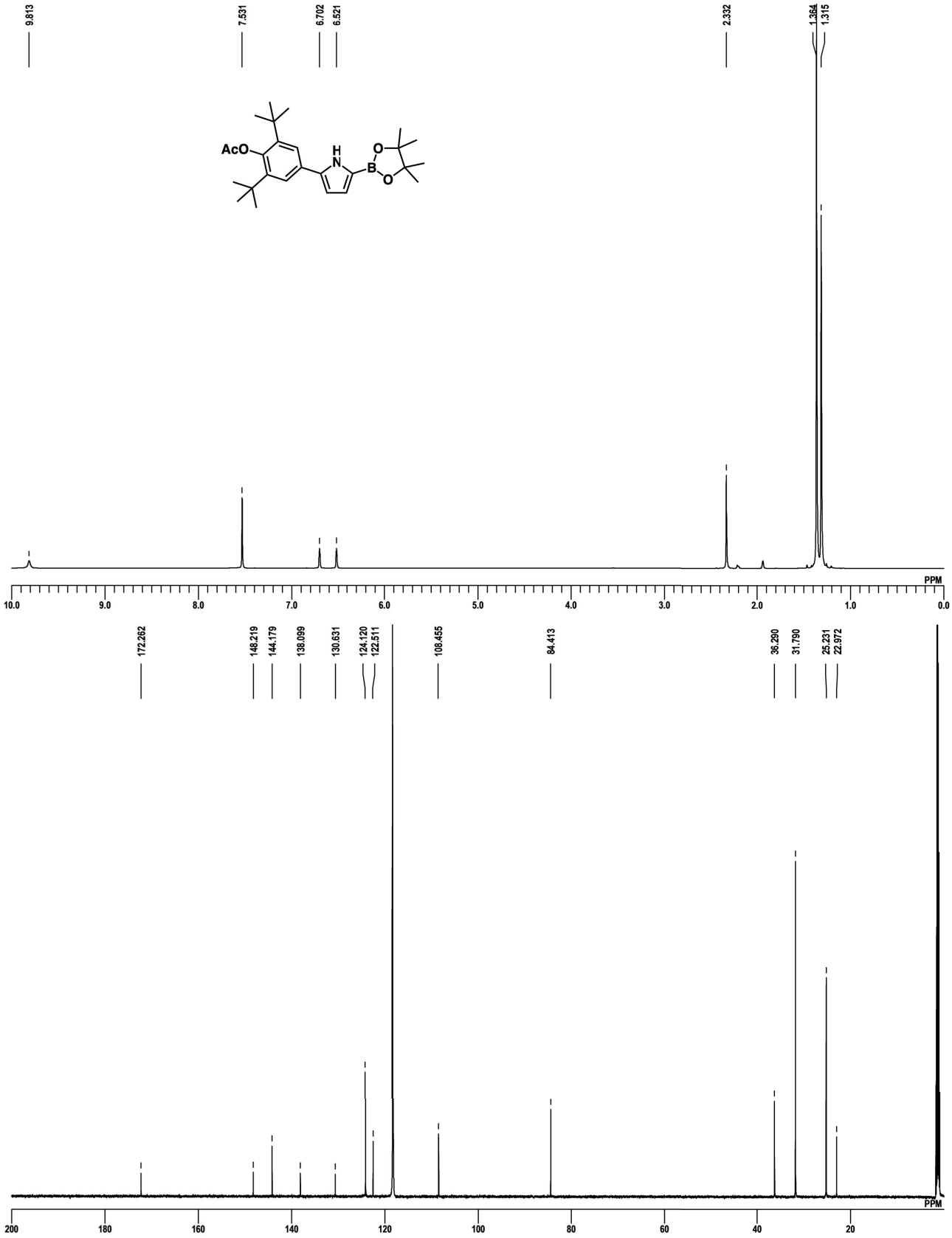


Fig. S3 ^{1}H NMR (top) and ^{13}C NMR (bottom) spectra of **s3** in CD_3CN.

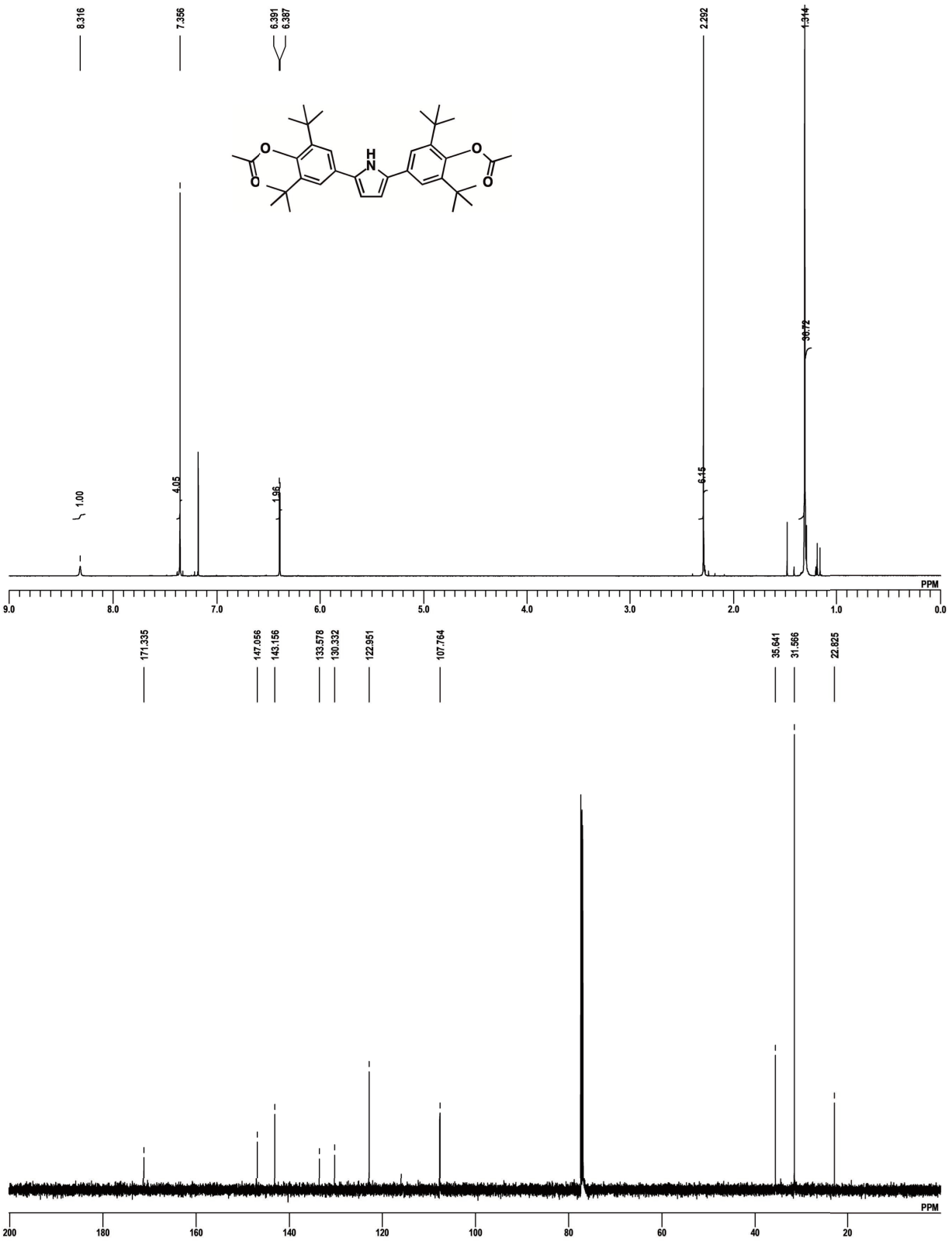


Fig. S4 ^{1}H NMR (top) and ^{13}C NMR (bottom) spectra of **1a** in $CDCl_3$.

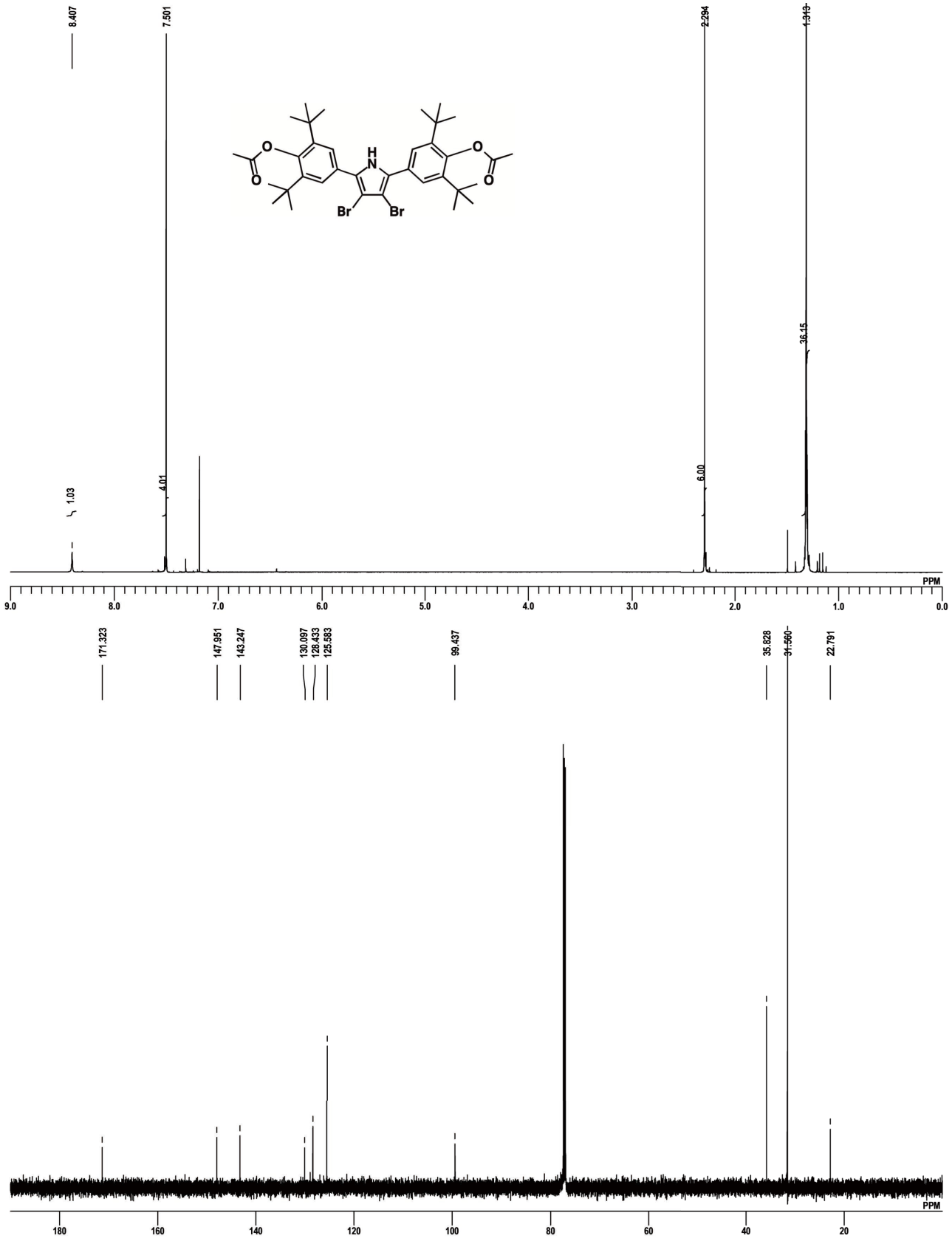


Fig. S5 ^{1}H NMR (top) and ^{13}C NMR (bottom) spectra of **1b** in $CDCl_3$.

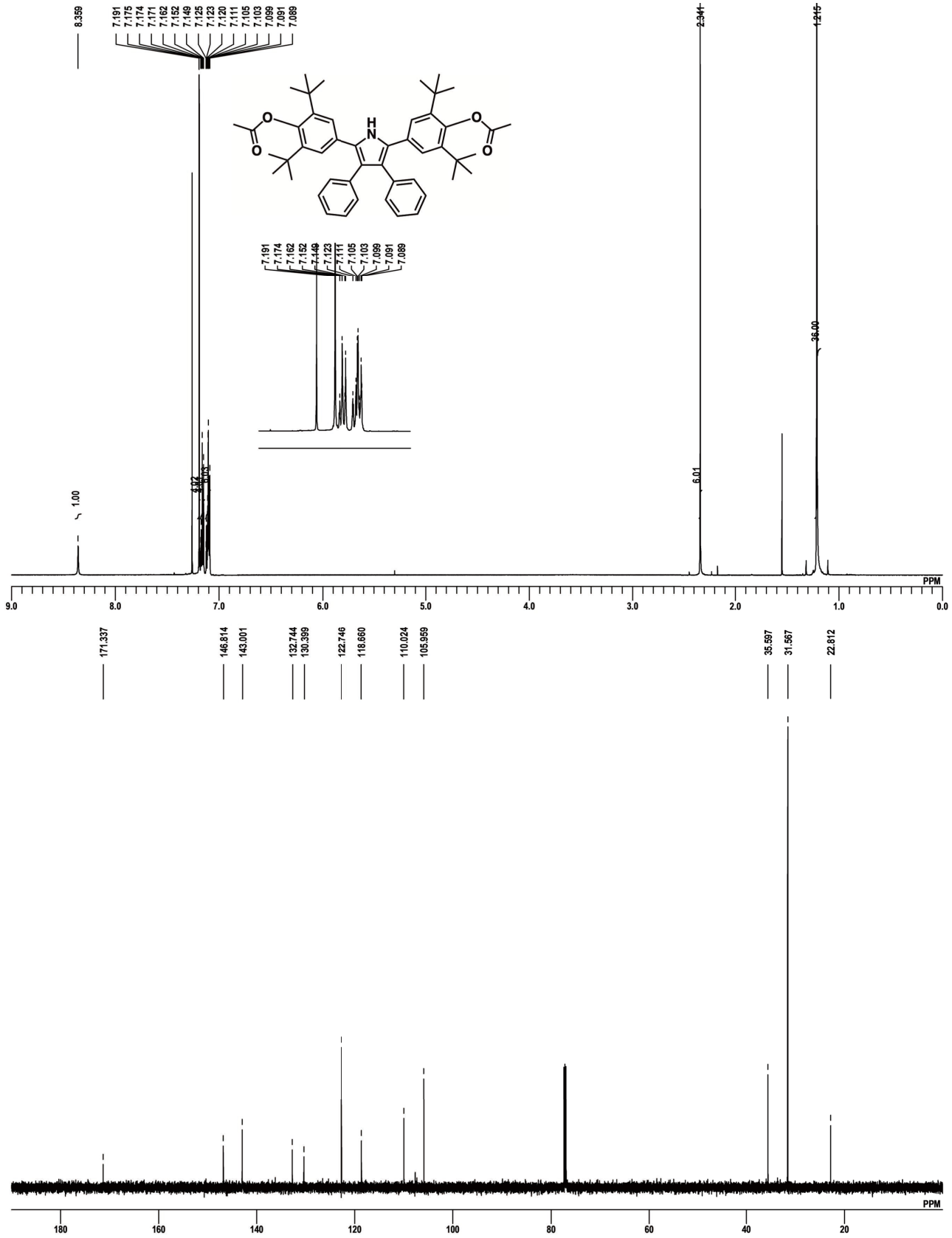


Fig. S6 ^{1}H NMR (top) and ^{13}C NMR (bottom) spectra of **1c** in $CDCl_3$.

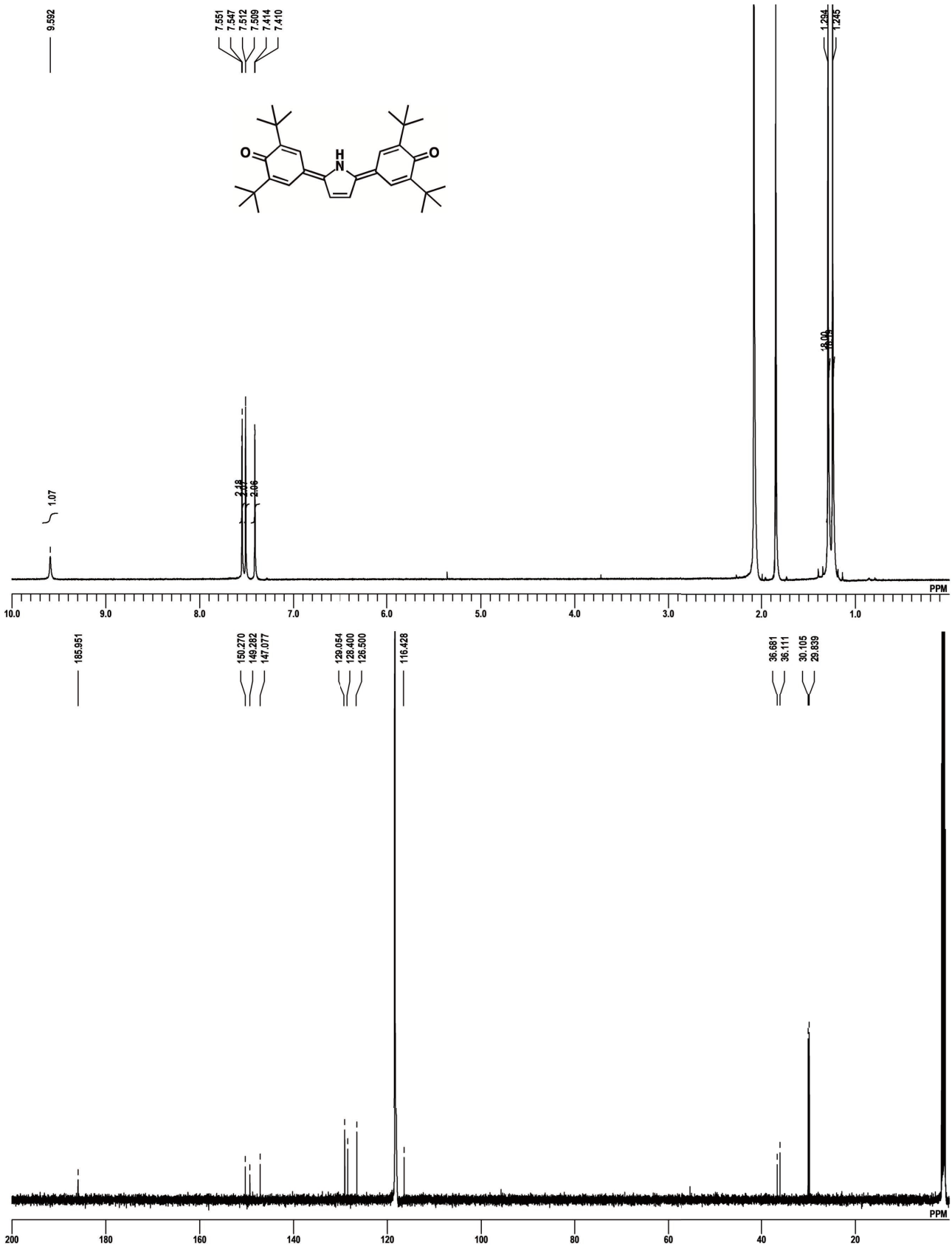


Fig. S7 ^{1}H NMR (top) and ^{13}C NMR (bottom) spectra of **2a** (**2a**$_{NH}$) in CD_3CN.

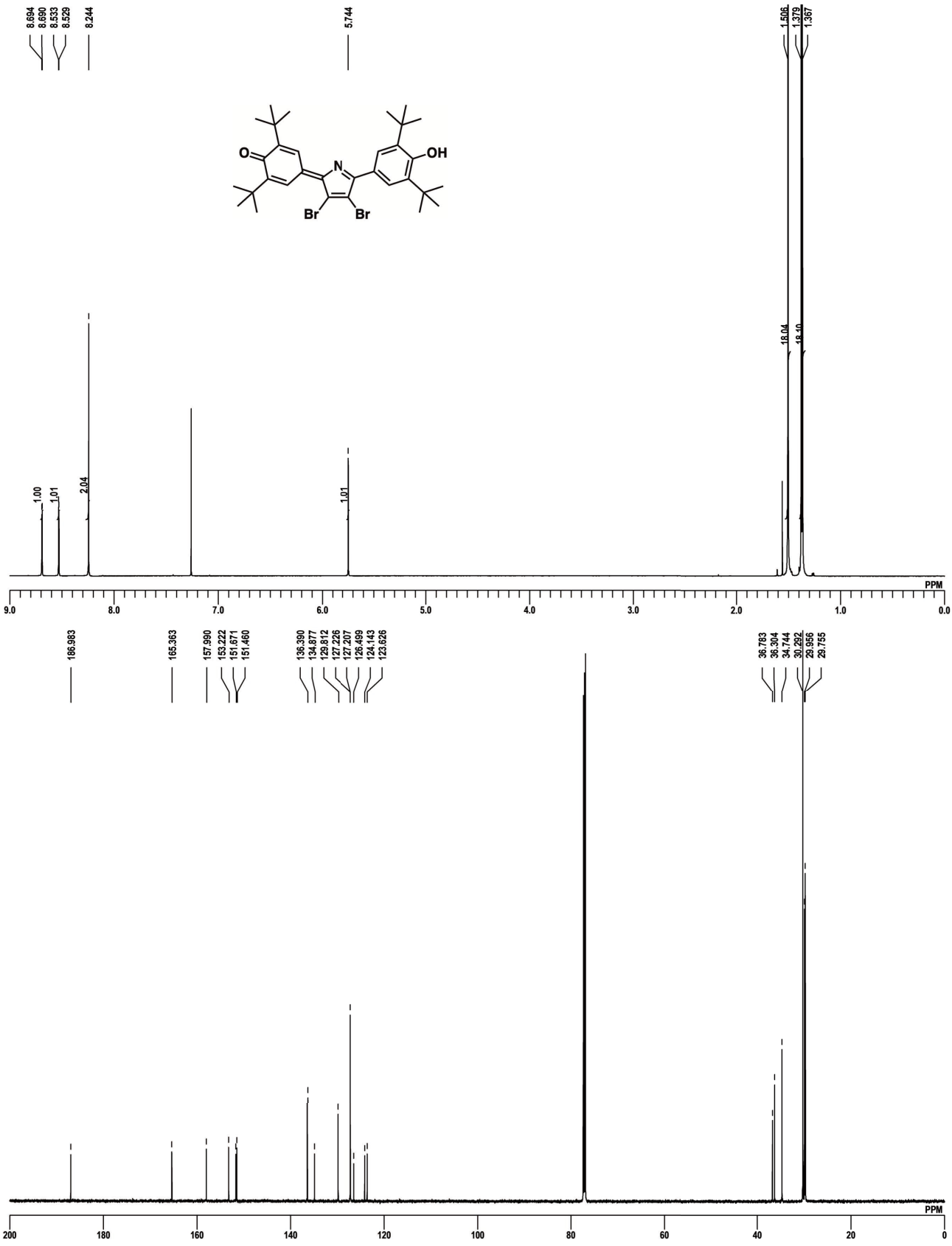


Fig. S8 ^{1}H NMR (top) and ^{13}C NMR (bottom) spectra of **2b** (**2b**$_{OH}$) in $CDCl_3$.

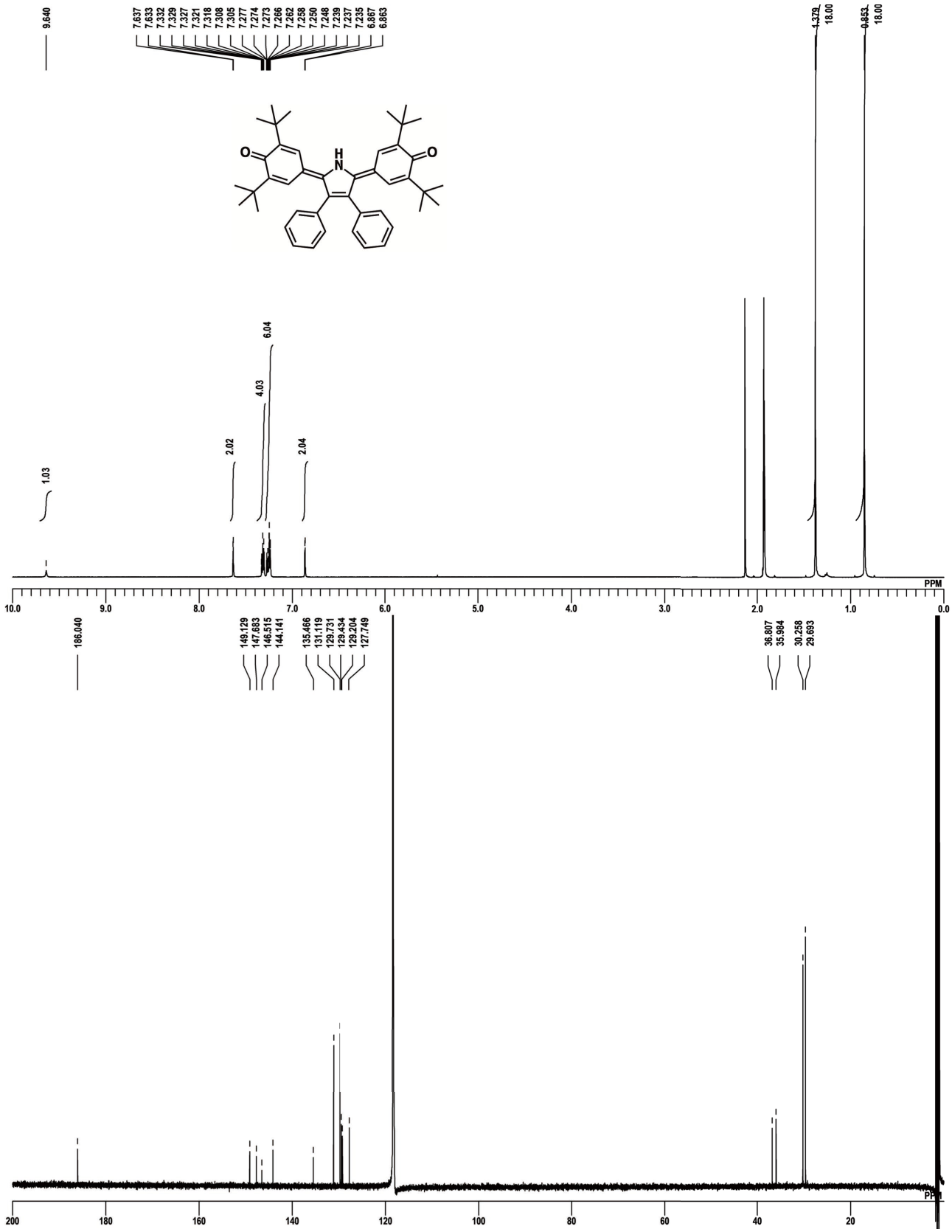


Fig. S9 ^{1}H NMR (top) and ^{13}C NMR (bottom) spectra of **2c** (**2c**$_{NH}$) in CD_3CN.

2. X-ray crystallographic data

Method for single-crystal X-ray analysis. Crystallographic data are summarized in Table S1. A single crystal of **1c** was obtained by vapor diffusion of *n*-hexane into a CH_2Cl_2 solution of **1c**. The data crystal was a colorless block of approximate dimensions 0.50 mm × 0.20 mm × 0.20 mm. A single crystal of **2a** was obtained by vapor diffusion of *n*-hexane into a diisopropyl ether solution of **2a**. The data crystal was a blue plate of approximate dimensions 0.30 mm × 0.30 mm × 0.05 mm. A single crystal of **2c** was obtained by vapor diffusion of *n*-hexane into a CH_2Cl_2 solution of **2c**. The data crystal was a purple prism of approximate dimensions 0.50 mm × 0.30 mm × 0.20 mm. A single crystal of **2b**$^-$-TPA$^+$ was obtained by vapor diffusion of *n*-hexane into a CH_2Cl_2 solution of the 1:1 mixture of **2b** and tetrapropylammonium hydroxide (TPAOH). The data crystal was a red prism of approximate dimensions 0.60 mm × 0.30 mm × 0.30 mm. A single crystal of **2c**$^-$-TPA$^+$ was obtained by vapor diffusion of *n*-hexane into an acetone solution of the 1:1 mixture of **2c** and TPAOH. The data crystal was a brown block crystal of approximate dimensions 0.60 mm × 0.10 mm × 0.10 mm. All the data was collected at 90 K on a Bruker D8 goniometer with graphite monochromated MoKα radiation (λ = 0.71073 Å). The structures were refined by a full-matrix least-squares method using a SHELXL 2014[S4] (Yadokari-XG).[S5] For **2c**$^-$-TPA$^+$, the disordered acetone was removed using the SQUEEZE protocol included in PLATON.[S6] CIF files (CCDC- 2076439–2076443) can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Table S1 Crystallographic details.

	1c	**2a**	**2c**	**2b**$^-$-TPA$^+$	**2c**$^-$-TPA$^+$
formula	$C_{48}H_{57}NO_4 \cdot 0.55C_6H_{14} \cdot 2.63O$ [a]	$C_{32}H_{43}NO_2 \cdot 1.5C_6H_{14} \cdot H_2O$	$C_{44}H_{51}NO_2 \cdot H_2O$	$C_{32}H_{40}Br_2NO_2 \cdot C_{12}H_{28}N$	$C_{44}H_{50}NO_2 \cdot C_{12}H_{28}N \cdot C_3H_6O$
fw	802.47	620.94	643.87	816.82	869.28
crystal size, mm	0.50 × 0.20 × 0.20	0.30 × 0.30 × 0.05	0.50 × 0.30 × 0.20	0.60 × 0.30 × 0.20	0.20 × 0.20 × 0.15
crystal system	trigonal	monoclinic	monoclinic	orthorhombic	triclinic
space group	*R*-3 (no. 148)	$P2_1/n$ (no. 14)	$P2_1/n$ (no. 14)	$P2_12_12_1$ (no. 19)	*P*-1 (no. 2)
a, Å	47.954(2)	13.569(3)	13.767(2)	15.404(2)	11.902(3)
b, Å	47.954(2)	10.997(2)	9.1739(16)	15.899(2)	13.335(3)
c, Å	13.5821(10)	28.205(5)	29.862(5)	17.995(2)	18.233(4)
α, °	90	90	90	90	80.776(7)
β, °	90	102.296(6)	92.477(6)	90	82.656(9)
γ, °	120	90	90	90	70.927(8)
V, Å^3	27049(3)	4112.2(14)	3768.1(11)	4406.9(10)	2690.8(11)
ρ_{calcd}, gcm^{-3}	0.887	1.003	1.135	1.231	1.073
Z	12	4	4	4	2
T, K	90	90	90	90	90
μ, mm^{-1} (MoKα)	0.058	0.061	0.070	1.875	0.064
no. of reflns	89696	30242	37105	68939	22449
no. of unique reflns	10357	7239	12194	17335	9076
variables	562	417	453	467	557
λ, Å (MoKα)	0.71073	0.71073	0.71073	0.71073	0.71073
R_1 ($I > 2\sigma(I)$)	0.1069	0.1186	0.1054	0.0547	0.0901
wR_2 ($I > 2\sigma(I)$)	0.2897	0.2448	0.2580	0.1223	0.2354
GOF	1.035	1.166	1.028	1.025	1.050

[a] The total formula in the cif file is represented as $C_{51.37}H_{64.89}NO_{6.63}$ because two *tert*-butyl groups are disordered with the occupancy ratios of 0.495:0.323:0.185 and 0.399:0.350:0.266, containing standard deviations of 0.01.

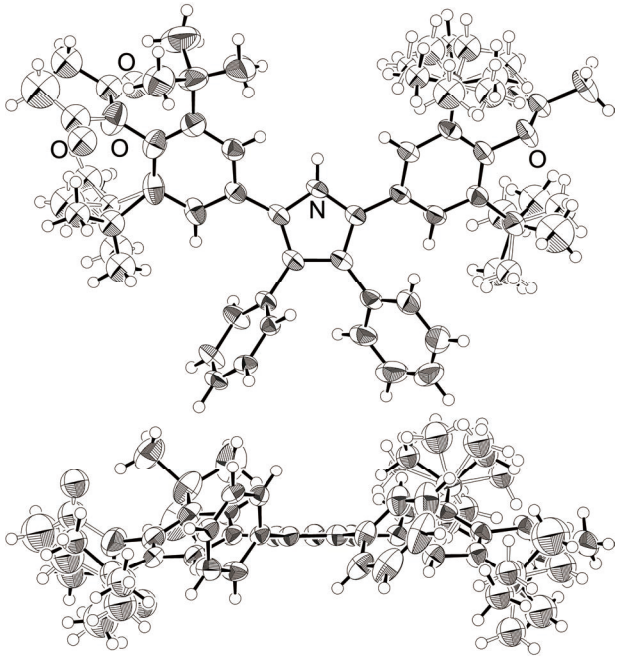


Fig. S10 Ortep drawing of single-crystal X-ray structure (top and side views) of **1c**. Thermal ellipsoids are scaled to the 50% probability level. Disordered structures are represented by black and white bonds for major and minor structures, respectively, in the ratios of 49.5:32.3:18.5, 39.9:35.0:26.6 (as described in the footnote of Table S1), 53.2:46.8, and 51.6:48.4. Solvent molecules are omitted for clarity.

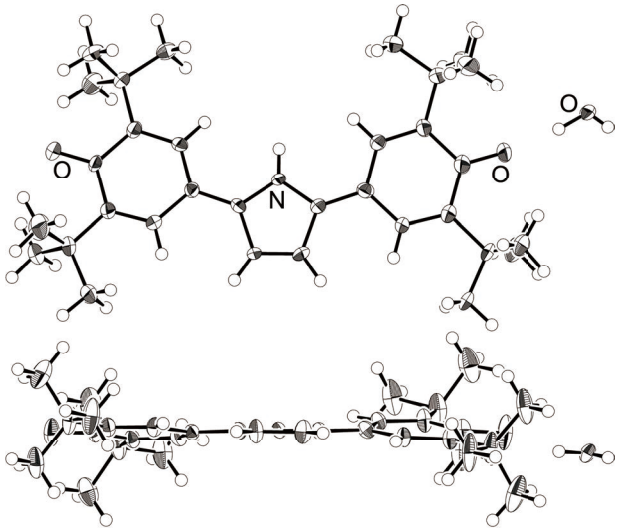


Fig. S11 Ortep drawing of single-crystal X-ray structure (top and side views) of **2a**. Thermal ellipsoids are scaled to the 50% probability level. Solvent molecules are omitted for clarity.

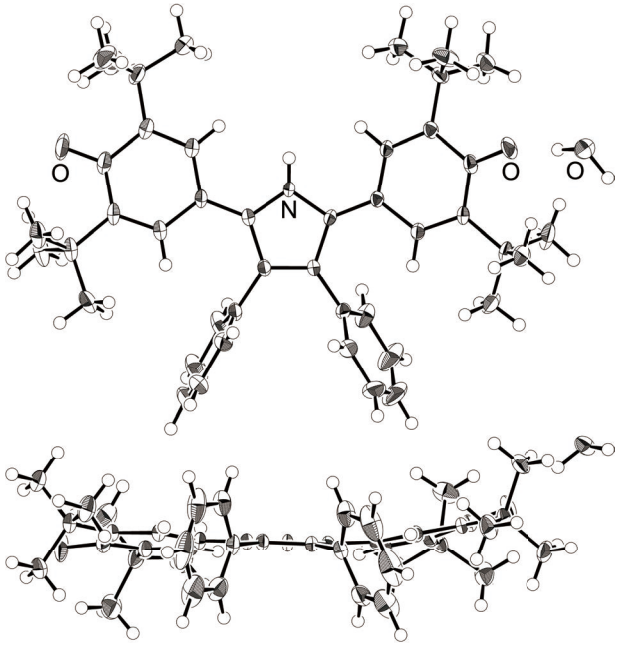


Fig. S12 Ortep drawing of single-crystal X-ray structure (top and side views) of **2c**. Thermal ellipsoids are scaled to the 50% probability level.

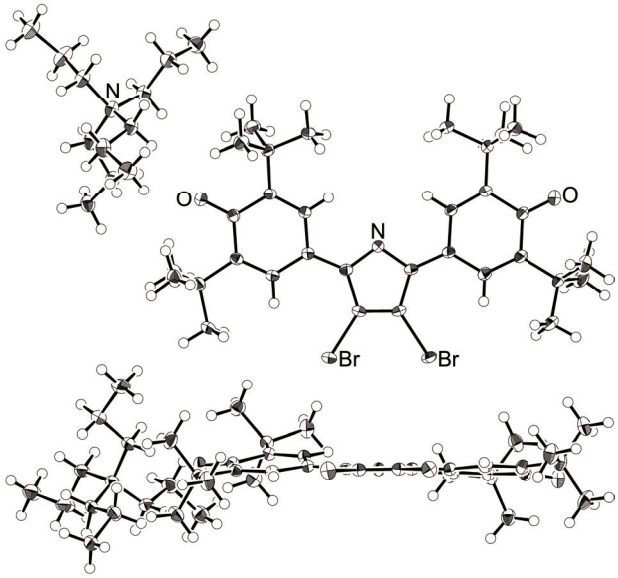


Fig. S13 Ortep drawing of single-crystal X-ray structure (top and side views) of **2b**$^{-}$-TPA^{+}. Thermal ellipsoids are scaled to the 50% probability level.

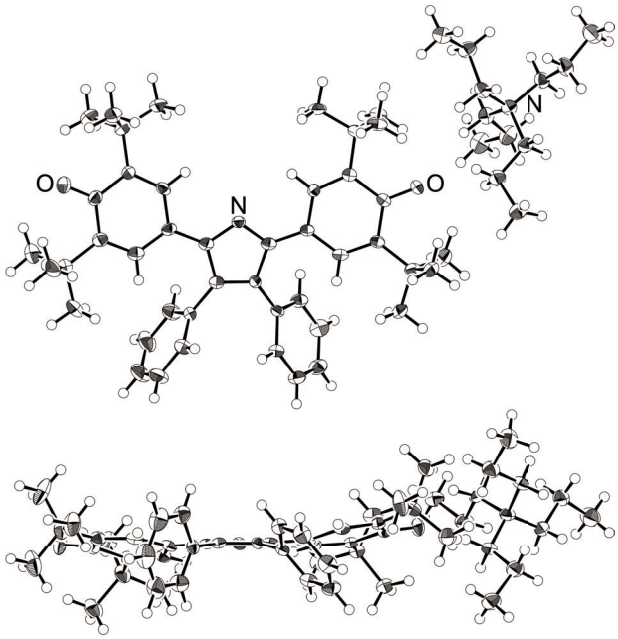


Fig. S14 Ortep drawing of single-crystal X-ray structure (top and side views) of **2c**$^{-}$-TPA^{+}. Thermal ellipsoids are scaled to the 50% probability level. Solvent molecules are omitted for clarity.

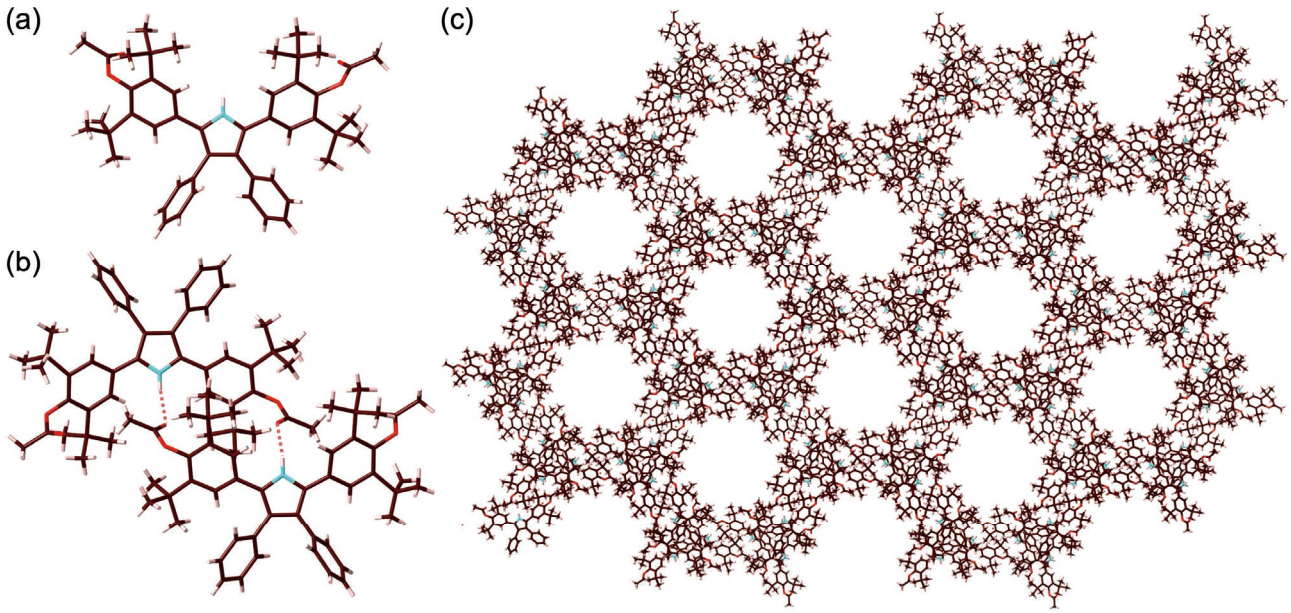


Fig. S15 Single-crystal X-ray structure of **1c**: (a)(i) top view, (b) a hydrogen-bonding dimer with an N(–H)···O distance of 2.98 Å, and (c) packing diagram. Atom color code: brown, pink, blue, and red refer to carbon, hydrogen, nitrogen, and oxygen, respectively. Solvent molecules are omitted for clarity.

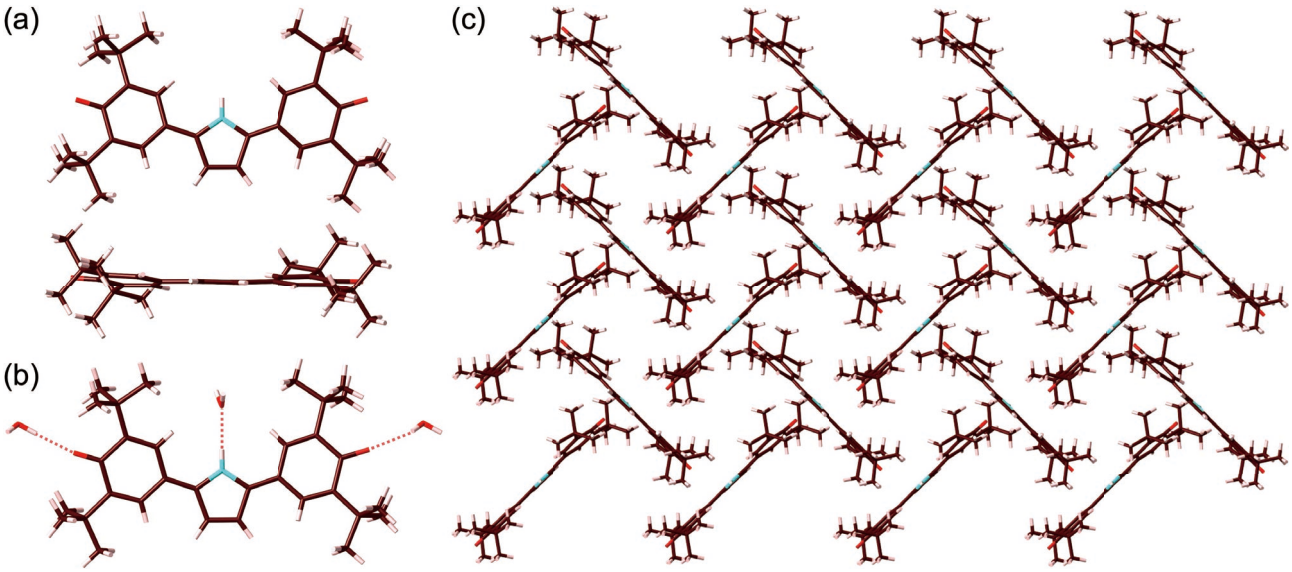


Fig. S16 Single-crystal X-ray structure of **2a**: (a) top and side views, (b) hydrogen-bonding structure for water molecules with N(–H)···O and O(–H)···O distances of 2.77 and 2.72/2.75 Å, respectively, and (c) packing diagram. Atom color code: brown, pink, blue, and red refer to carbon, hydrogen, nitrogen, and oxygen, respectively. Water molecules represented in (b), wherein *n*-hexane was omitted for clarity, were adventitiously contained in the crystal, whereas solvents are omitted for clarity for (a,c).

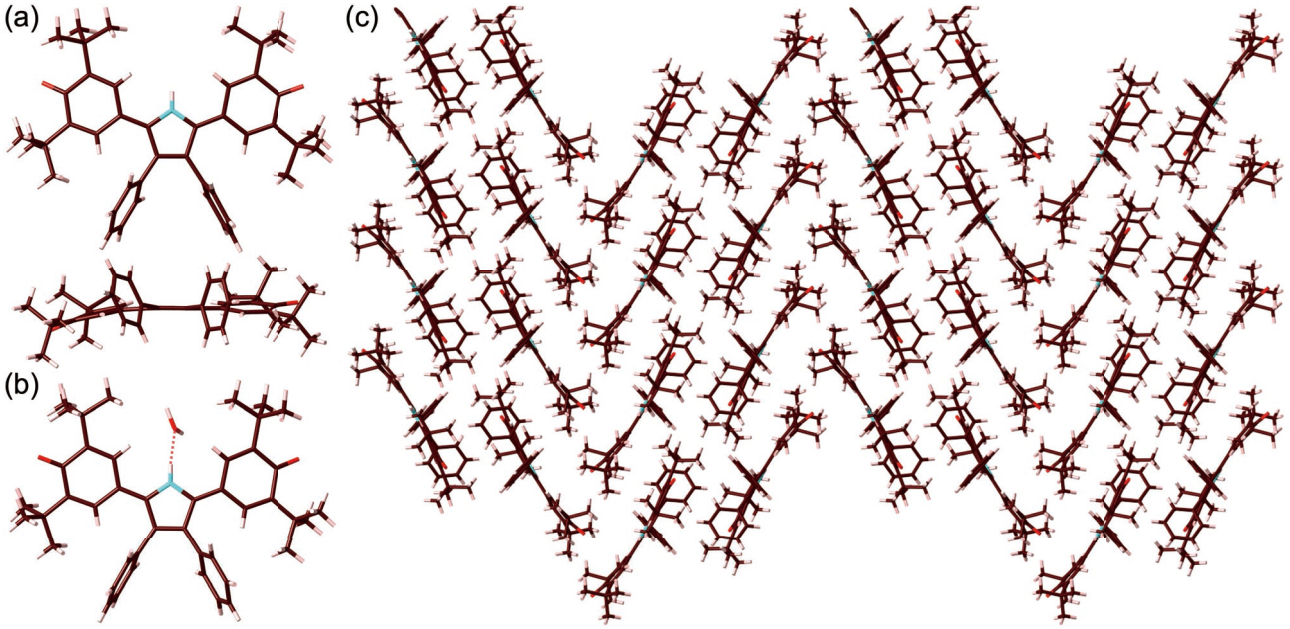


Fig. S17 Single-crystal X-ray structure of **2c**: (a)(i) top and side views, (b) hydrogen-bonding structure for water molecules with N(–H)···O and O(–H)···O distances of 2.87 and 2.74 Å, respectively, and (c) packing diagram. Atom color code: brown, pink, blue, and red refer to carbon, hydrogen, nitrogen, and oxygen, respectively. Water molecules represented in (b) were adventitiously contained in the crystal, whereas solvents are omitted for clarity for (a,c).

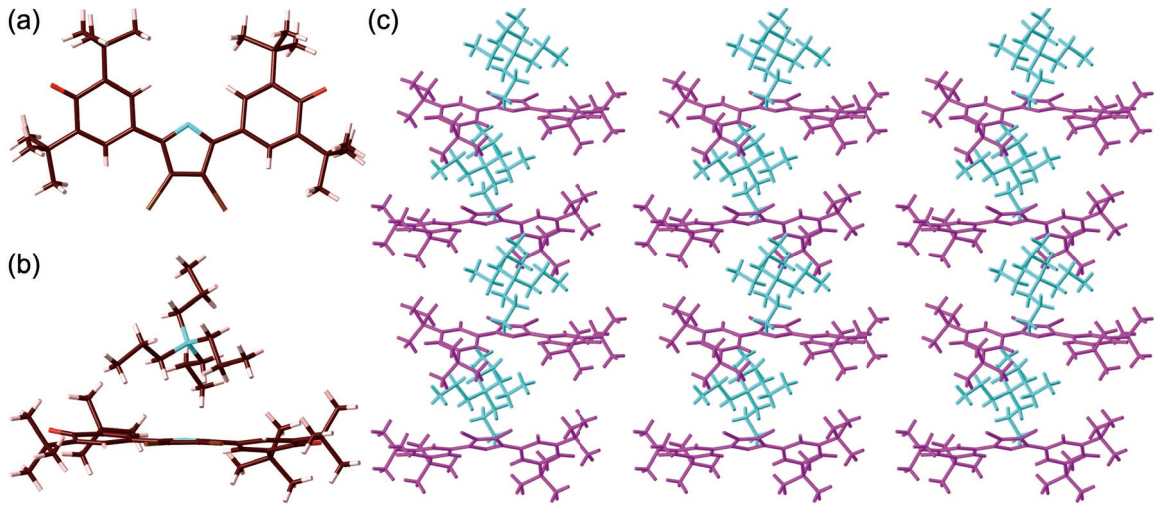


Fig. S18 Single-crystal X-ray structure of **2b**$^{-}$-TPA: (a) top view of **2b**$^{-}$, (b) side view, and (c) packing diagram (magenta: **2b**$^{-}$, cyan: TPA^{+}). Atom color code in (a,b): brown, pink, light brown, blue, and red refer to carbon, hydrogen, bromine, nitrogen, and oxygen, respectively.

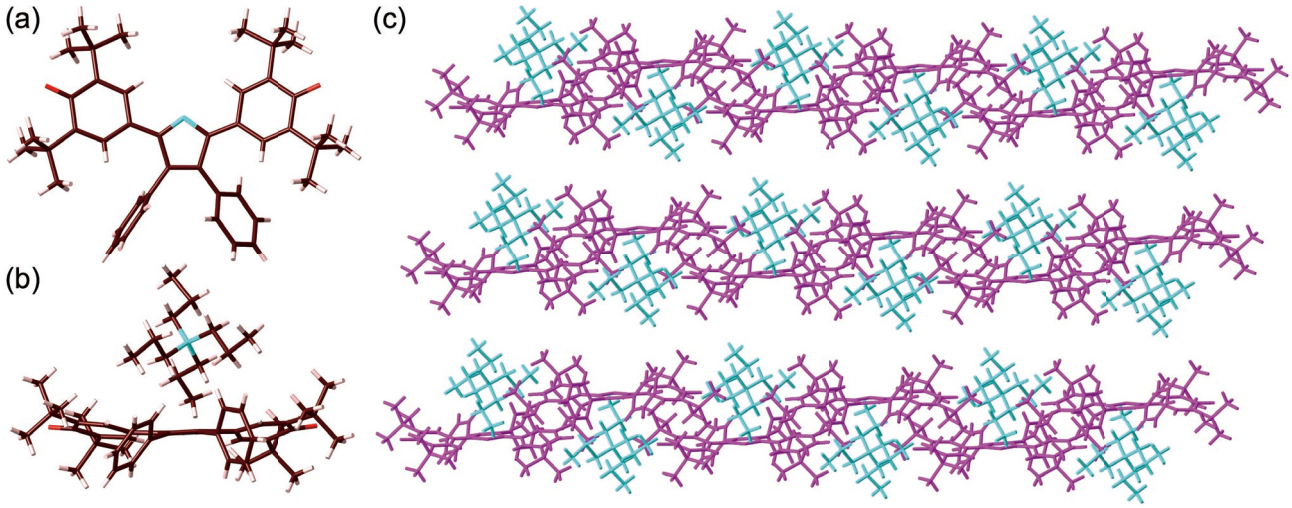


Fig. S19 Single-crystal X-ray structure of **2c**$^{-}$-TPA: (a) top view of **2c**$^{-}$, (b) side view, and (c) packing diagram (magenta: **2c**$^{-}$, cyan: TPA^{+}). Atom color code in (a,b): brown, pink, blue, and red refer to carbon, hydrogen, nitrogen, and oxygen, respectively. Solvent molecules are omitted for clarity.

[S4] G. M. Sheldrick, *Acta Crystallogr. Sect. A*, 2008, **64**, 112–122.
[S5] (a) *Yadokari-XG*, Software for Crystal Structure Analyses, K. Wakita, 2001; (b) C. Kabuto, S. Akine, T. Nemoto and E. Kwon, *J. Cryst. Soc. Jpn.*, 2009, **51**, 218–224.
[S6] A. L. Spek, *Acta Crystallogr. Sect. D*, 2009, **65**, 148–155.

3. Theoretical study

DFT calculations. DFT calculations of the geometrical optimizations were carried out using the *Gaussian 09* program.[S7]

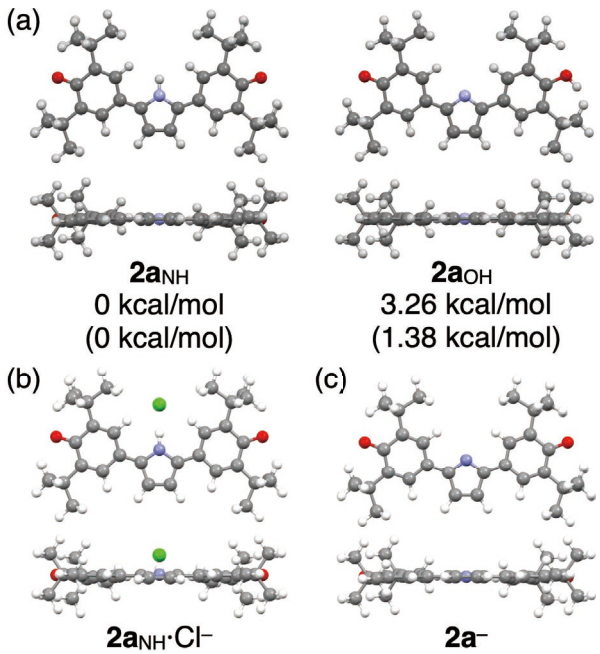


Fig. S20 Optimized structures (top and side views) of (a) **2a**$_{NH}$: quinoidal (NH) form (left) and **2a**$_{OH}$: phenol (OH) form (right), (b) **2a**$_{NH}$·Cl^-, and (c) **2a**$^-$ estimated at B3LYP/6-31+G(d,p). The relative energies estimated at PCM-B3LYP/6-31+G(d,p)(CH_2Cl_2)//B3LYP/6-31+G(d,p) in (a) are shown in the parentheses.

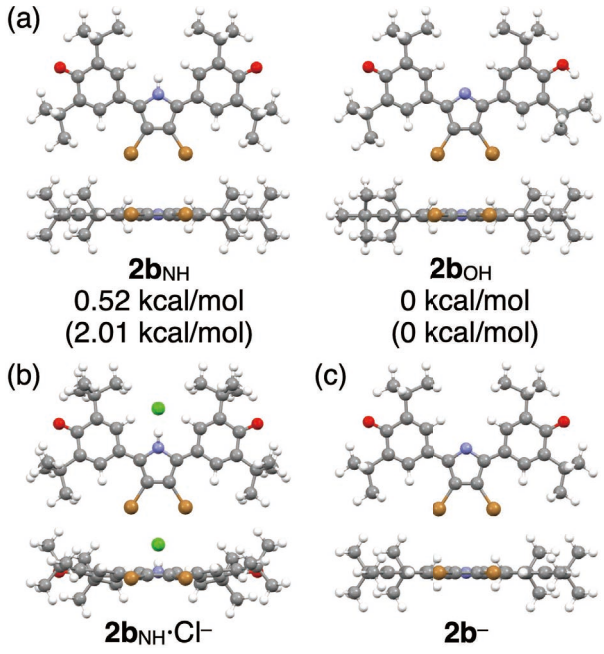


Fig. S21 Optimized structures (top and side views) of (a) **2b**$_{NH}$ (left) and **2b**$_{OH}$ (right), (b) **2b**$_{NH}$·Cl^-, and (c) **2b**$^-$ estimated at B3LYP/6-31+G(d,p). The relative energies estimated at PCM-B3LYP/6-31+G(d,p)(CH_2Cl_2)//B3LYP/6-31+G(d,p) in (a) are shown in the parentheses.

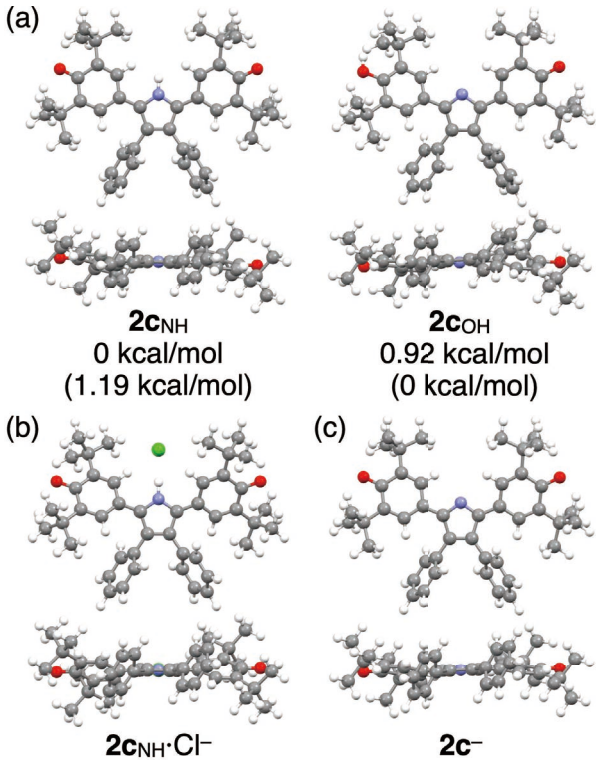


Fig. S22 Optimized structures (top and side views) of (a) $\mathbf{2c}_{NH}$ (left) and $\mathbf{2c}_{OH}$ (right), (b) $\mathbf{2c}_{NH}\cdot Cl^-$, and (c) $\mathbf{2c}^-$estimated at B3LYP/6-31+G(d,p). The relative energies estimated at PCM-B3LYP/6-31+G(d,p)(CH_2Cl_2)//B3LYP/ 6-31+G(d,p) in (a) are shown in the parentheses.

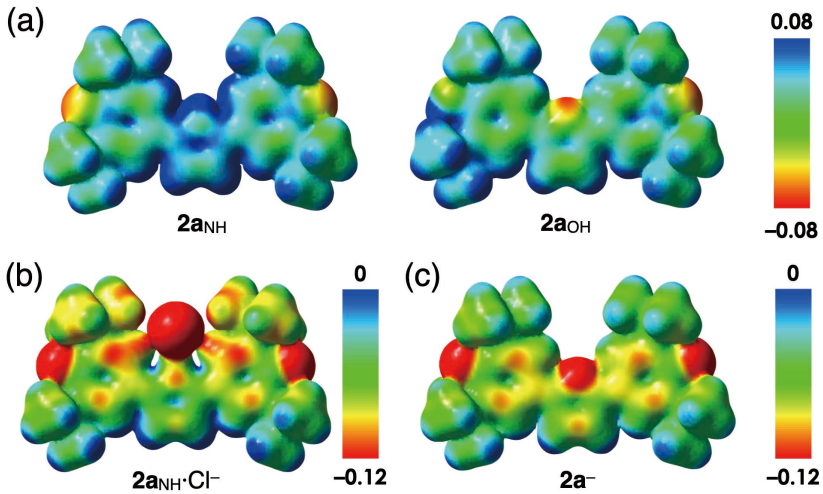


Fig. S23 Electrostatic potential (ESP) mapping of (a) $\mathbf{2b}_{NH}$ (left) and $\mathbf{2b}_{OH}$ (right), (b) $\mathbf{2b}_{NH}\cdot Cl^-$, and (c) $\mathbf{2b}^-$ estimated by electrostatic potential mapped onto the electron density isosurface ($\delta = 0.01$) calculated at B3LYP/6-31+G(d,p).

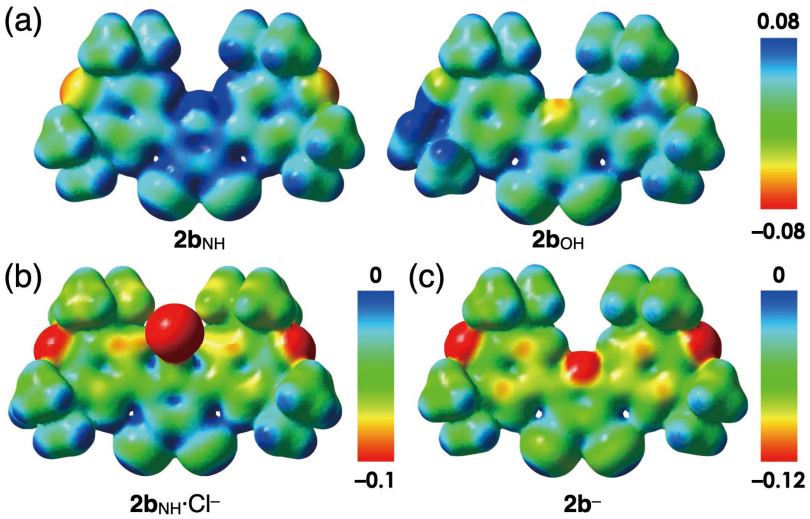


Fig. S24 Electrostatic potential (ESP) mapping of (a) **2b**$_{NH}$ (left) and **2b**$_{OH}$ (right), (b) **2b**$_{NH}$·Cl^-, and (c) **2b**$^-$ estimated by electrostatic potential mapped onto the electron density isosurface (δ = 0.01) calculated at B3LYP/6-31+G(d,p).

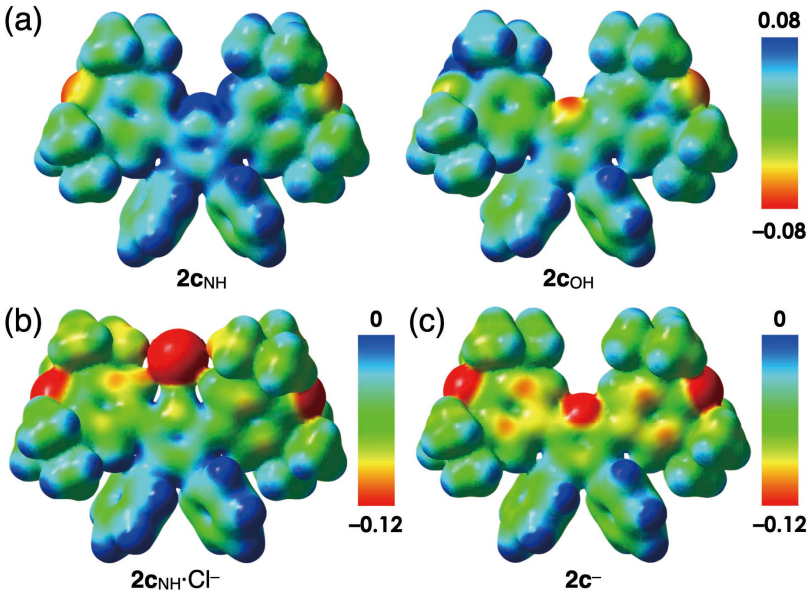


Fig. S25 Electrostatic potential (ESP) mapping of (a) **2c**$_{NH}$ (left) and **2c**$_{OH}$ (right), (b) **2c**$_{NH}$·Cl^-, and (c) **2c**$^-$ estimated by electrostatic potential mapped onto the electron density isosurface (δ = 0.01) calculated at B3LYP/6-31+G(d,p).

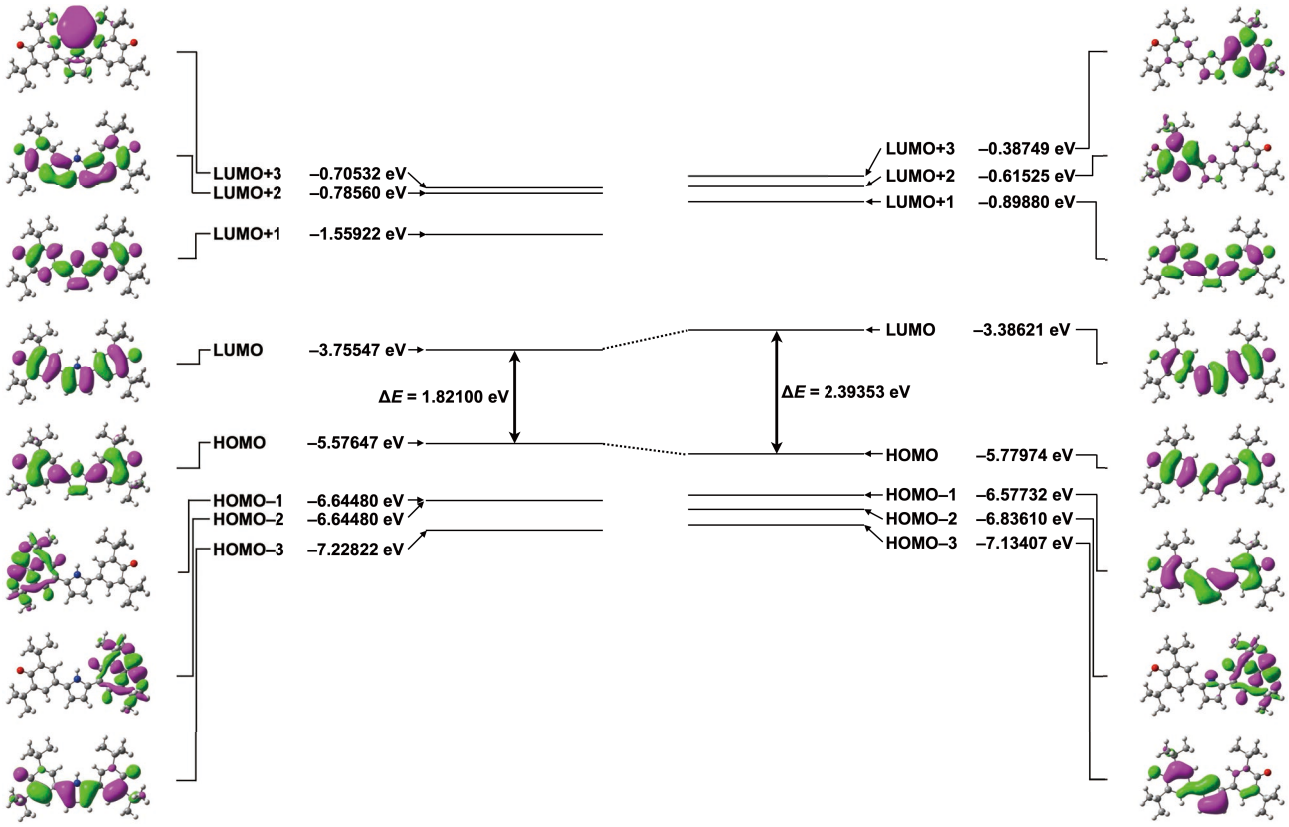


Fig. S26 Molecular orbitals (HOMO/LUMO) of $\mathbf{2a}_{NH}$ (left) and $\mathbf{2a}_{OH}$ (right) estimated at B3LYP/6-31+G(d,p).

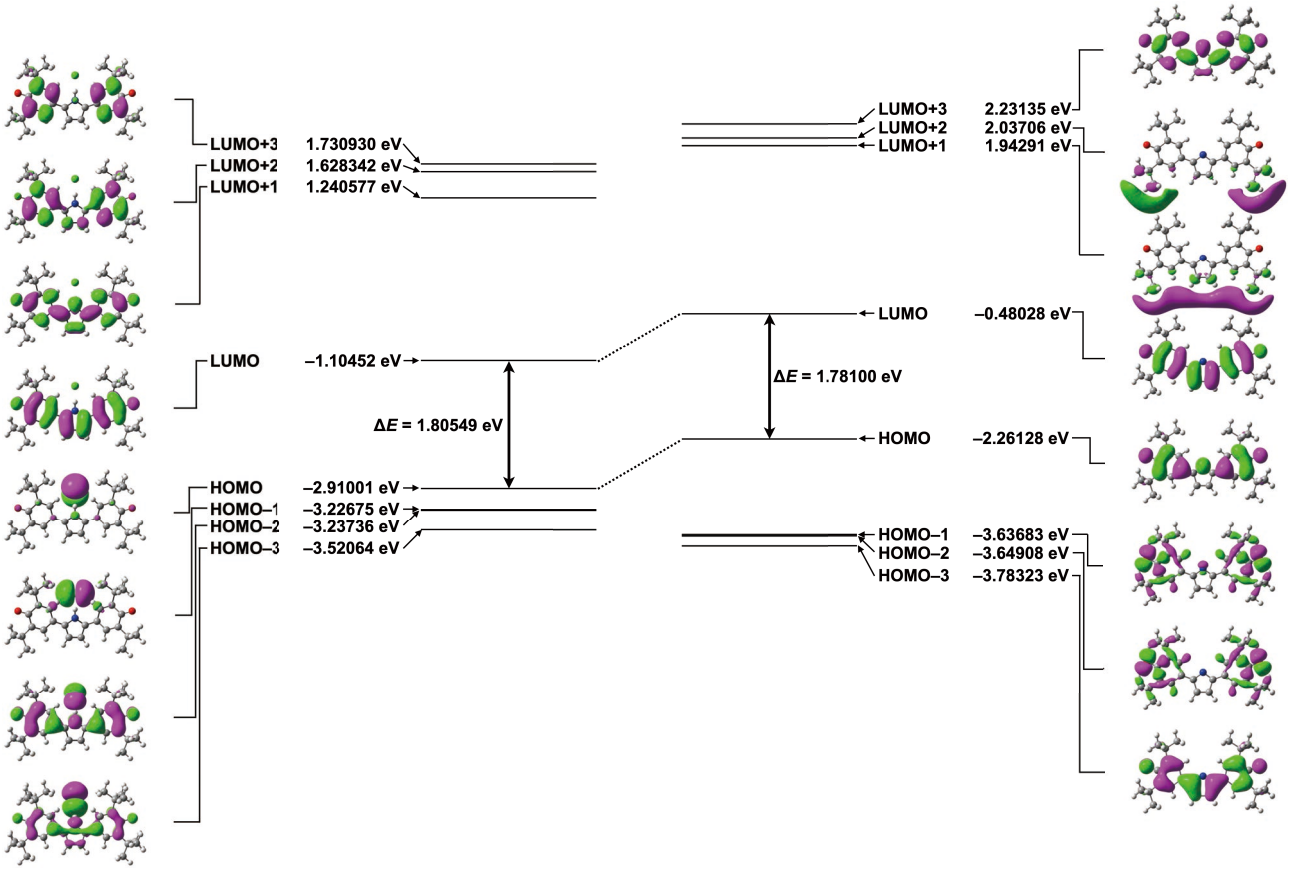


Fig. S27 Molecular orbitals (HOMO/LUMO) of $\mathbf{2a}_{NH}\cdot Cl^-$ (left) and $\mathbf{2a}^-$ (right) estimated at B3LYP/6-31+G(d,p).

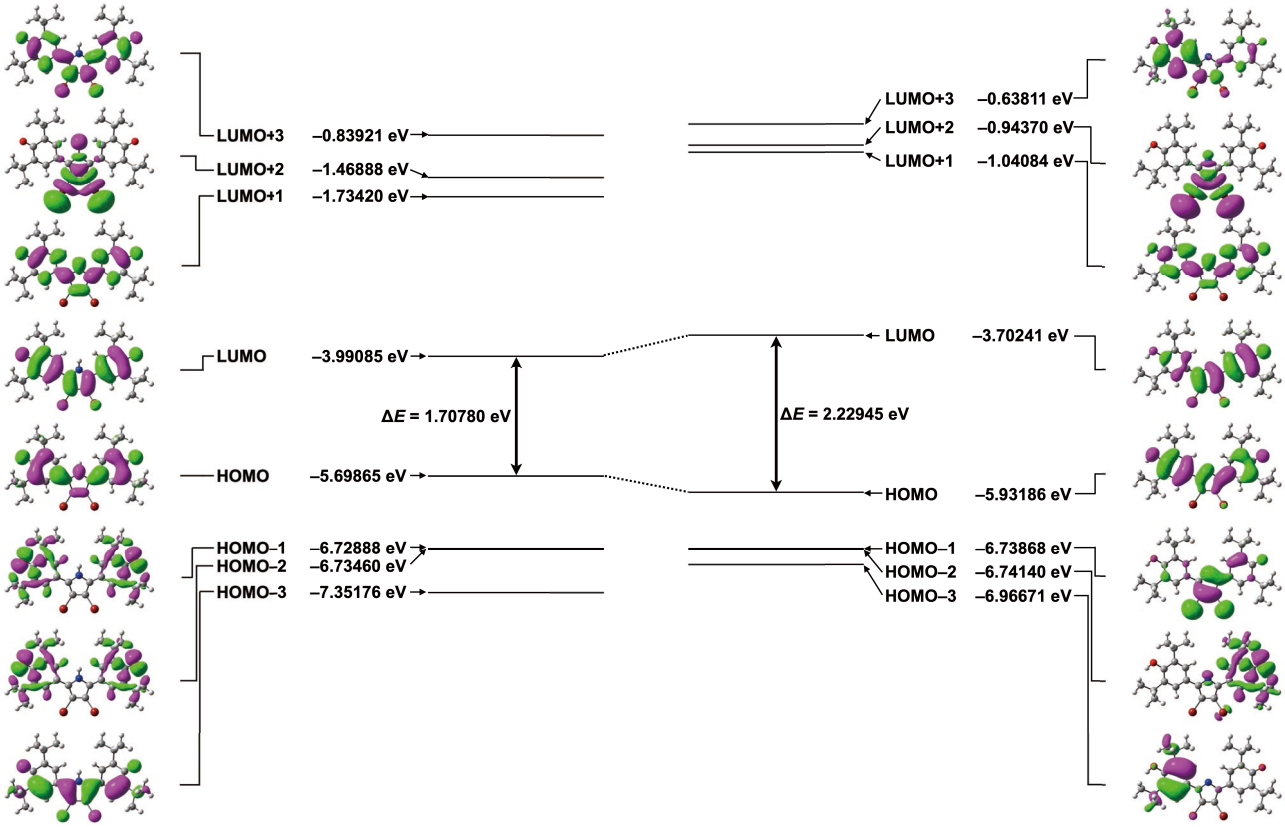


Fig. S28 Molecular orbitals (HOMO/LUMO) of $\mathbf{2b}_{NH}$ (left) and $\mathbf{2b}_{OH}$ (right) estimated at B3LYP/6-31+G(d,p).

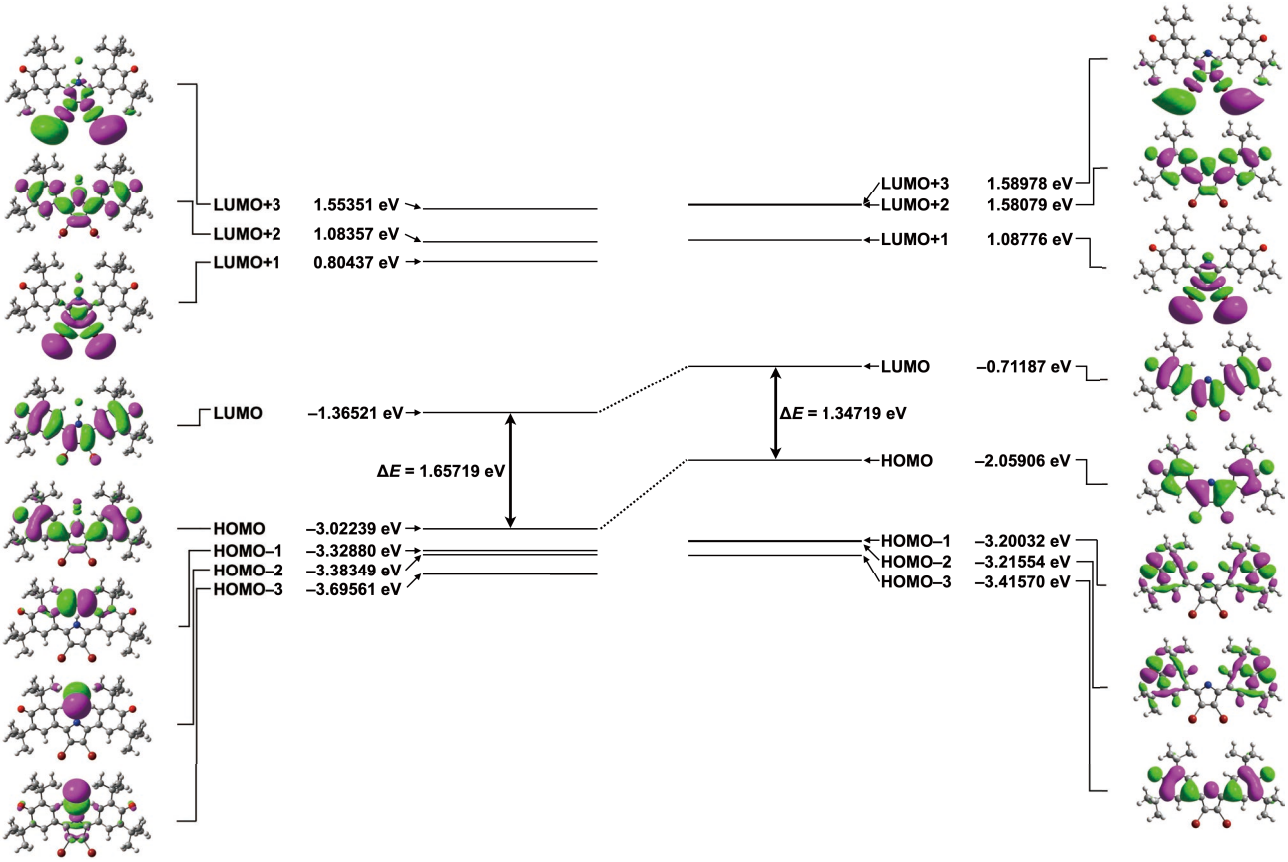


Fig. S29 Molecular orbitals (HOMO/LUMO) of $\mathbf{2b}_{NH}\cdot Cl^-$ (left) and $\mathbf{2b}^-$ (right) estimated at B3LYP/6-31+G(d,p).

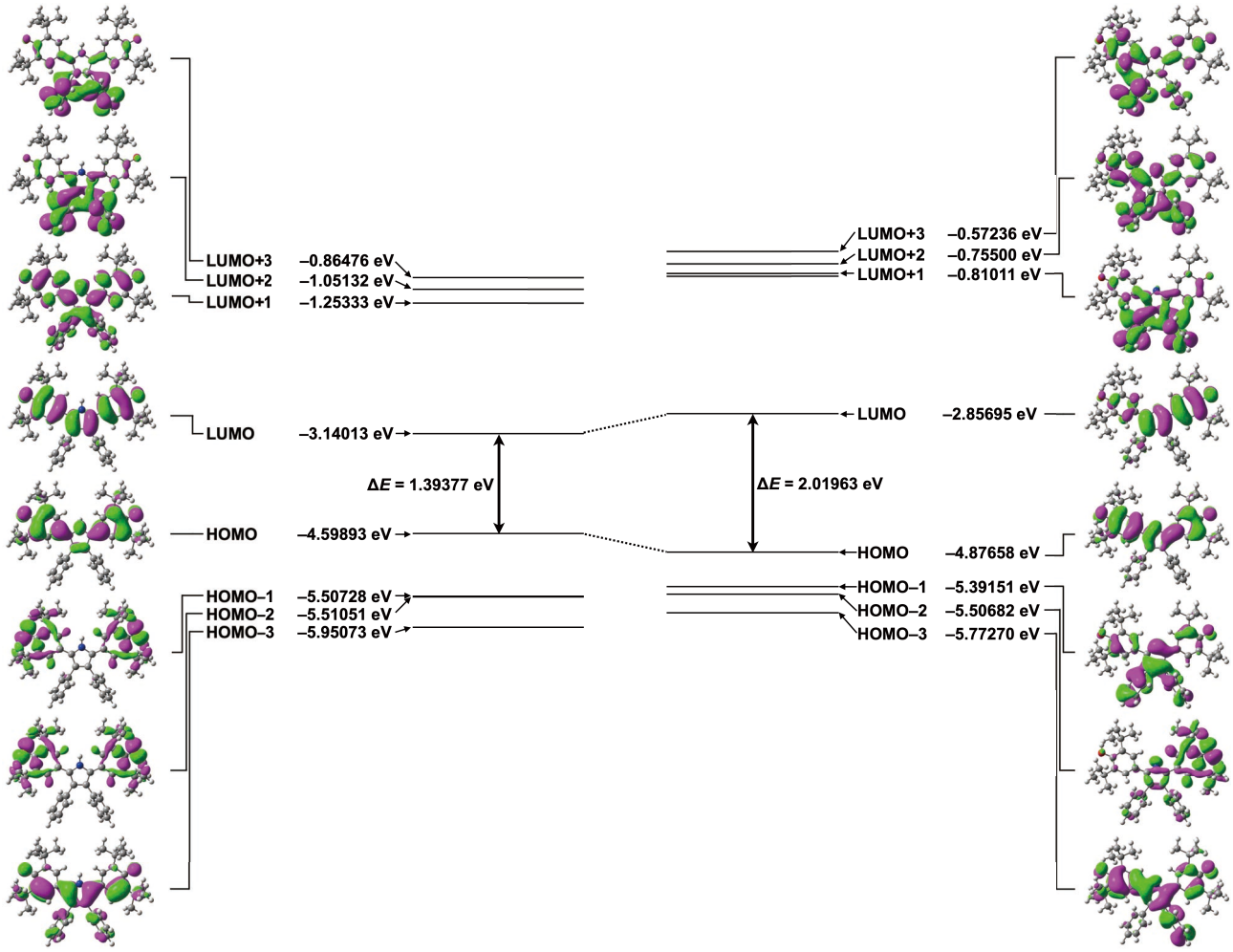


Fig. S30 Molecular orbitals (HOMO/LUMO) of $\mathbf{2c}_{NH}$ (left) and $\mathbf{2c}_{OH}$ (right) estimated at B3LYP/6-31+G(d,p).

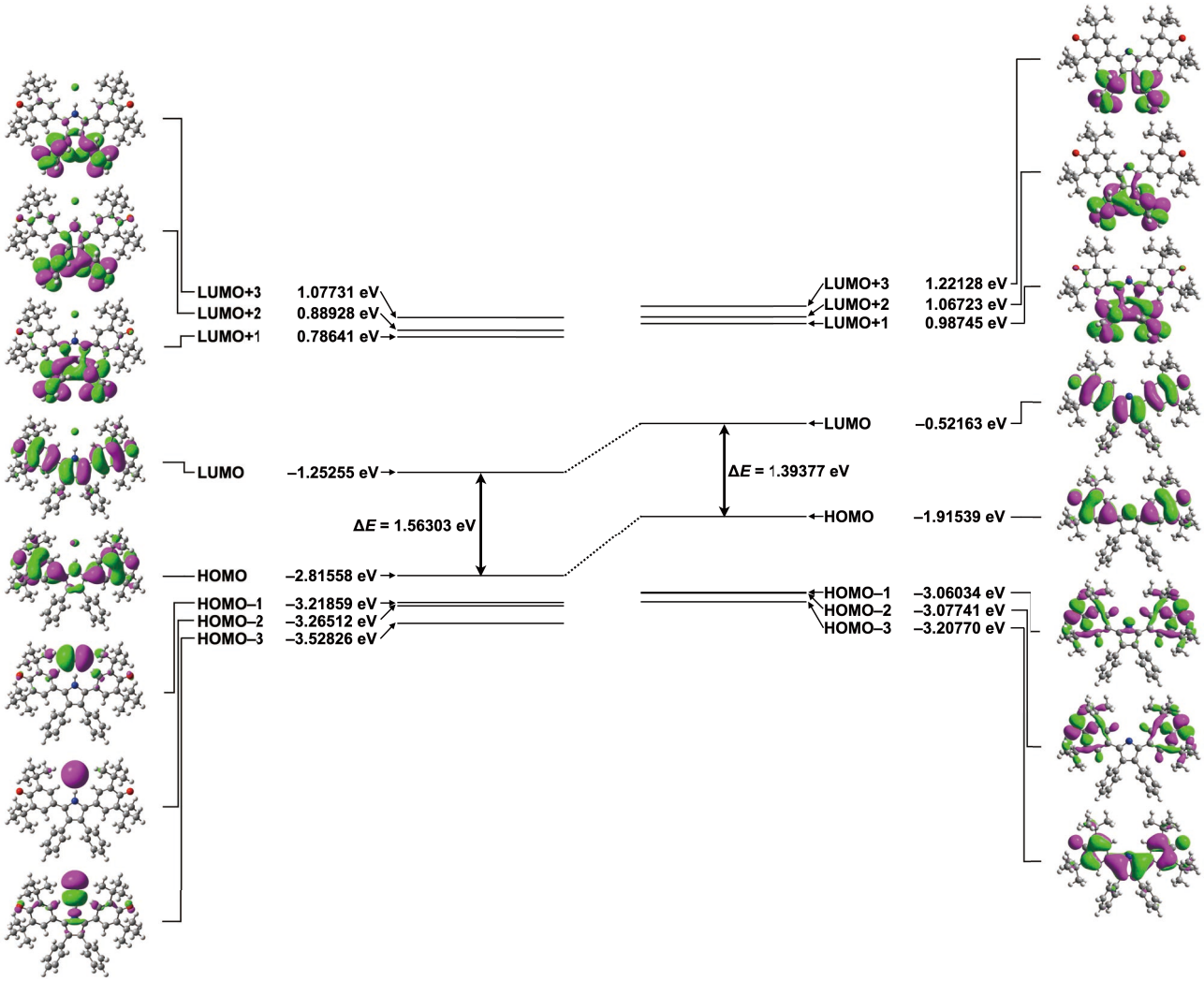


Fig. S31 Molecular orbitals (HOMO/LUMO) of $\mathbf{2c}_{NH}\cdot Cl^-$ (left) and $\mathbf{2c}^-$ (right) estimated at B3LYP/6-31+G(d,p).

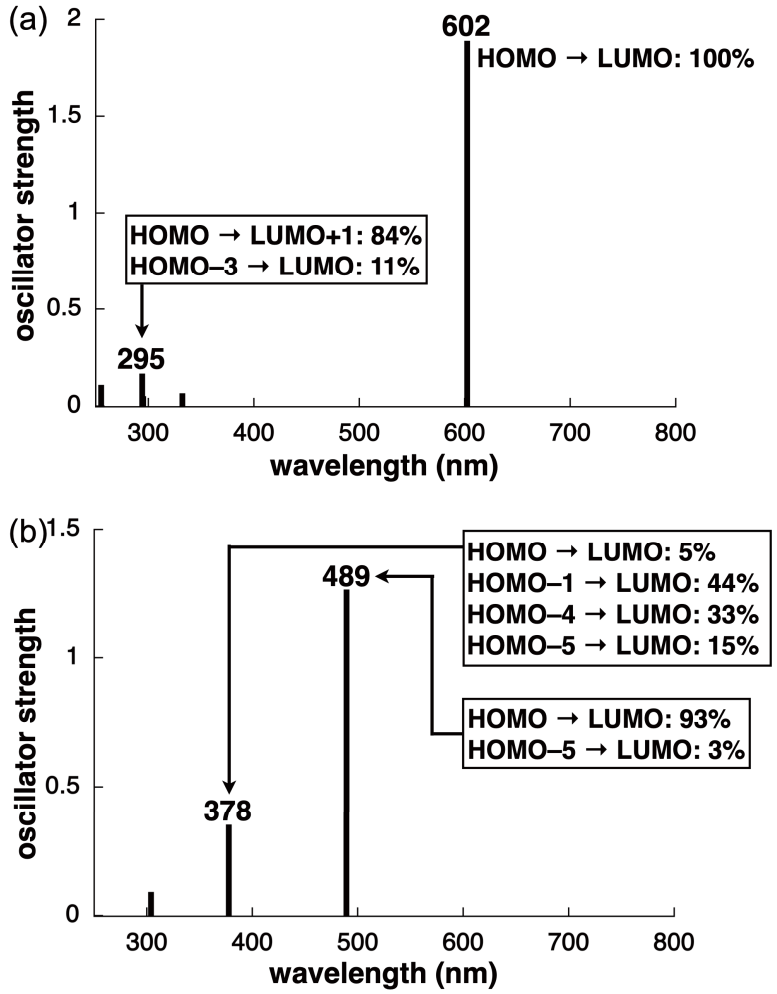


Fig. S32 TD-DFT-based UV/vis absorption stick spectra of (a) $\mathbf{2a}_{NH}$ and (b) $\mathbf{2a}_{OH}$ with the transitions correlated with molecular orbitals estimated at PCM-CAM-B3LYP/6-31+G(d,p)(CH_2Cl_2)//B3LYP/6-31+G(d,p).

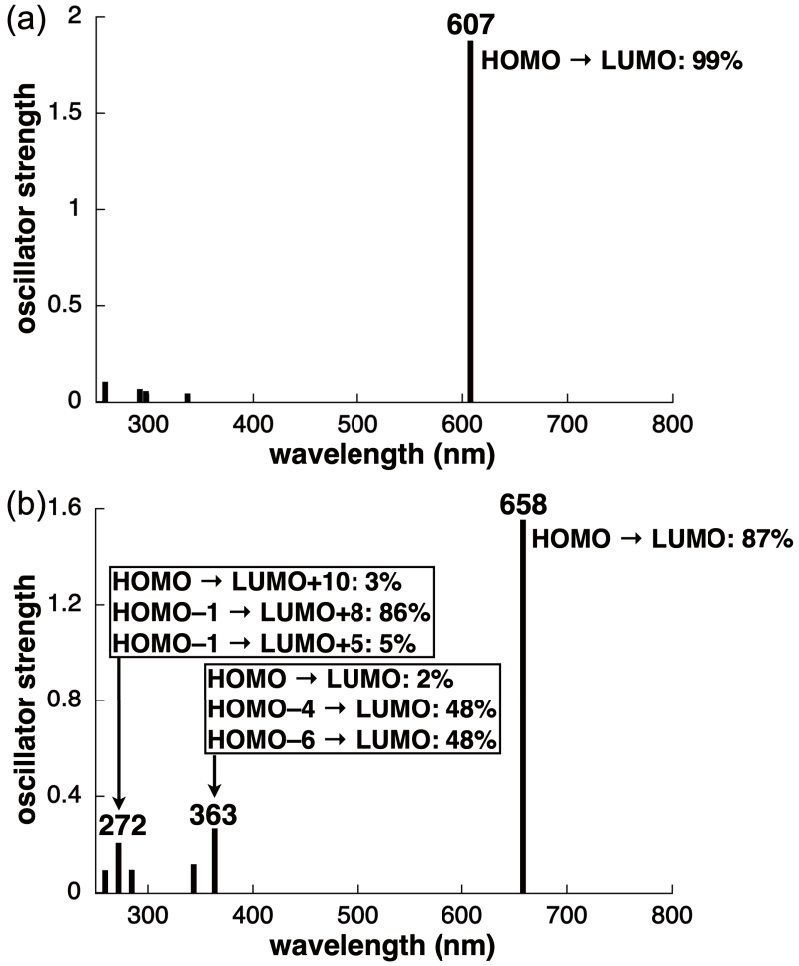


Fig. S33 TD-DFT-based UV/vis absorption stick spectra of (a) $\mathbf{2a}_{NH}\cdot Cl^-$ and (b) $\mathbf{2a}^-$ with the transitions correlated with molecular orbitals estimated at PCM-CAM-B3LYP/6-31+G(d,p)(CH_2Cl_2)//B3LYP/6-31+G(d,p).

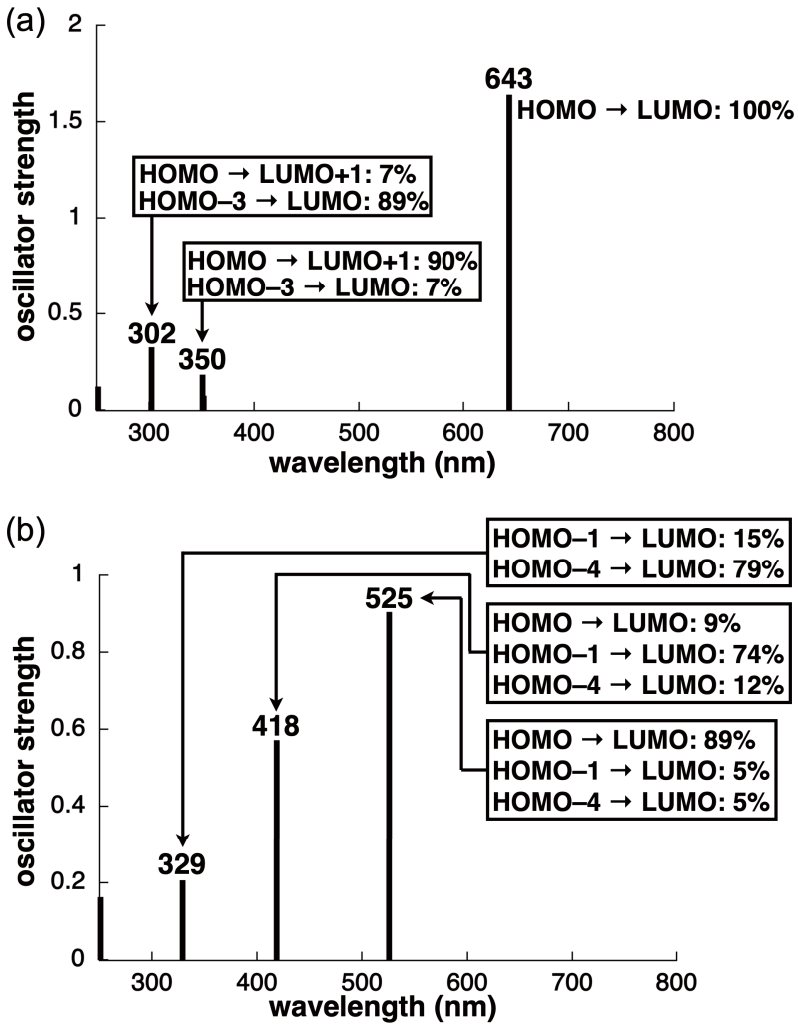


Fig. S34 TD-DFT-based UV/vis absorption stick spectra of (a) $\mathbf{2b}_{NH}$ and (b) $\mathbf{2b}_{OH}$ with the transitions correlated with molecular orbitals estimated at PCM-CAM-B3LYP/6-31+G(d,p)(CH_2Cl_2)//B3LYP/6-31+G(d,p).

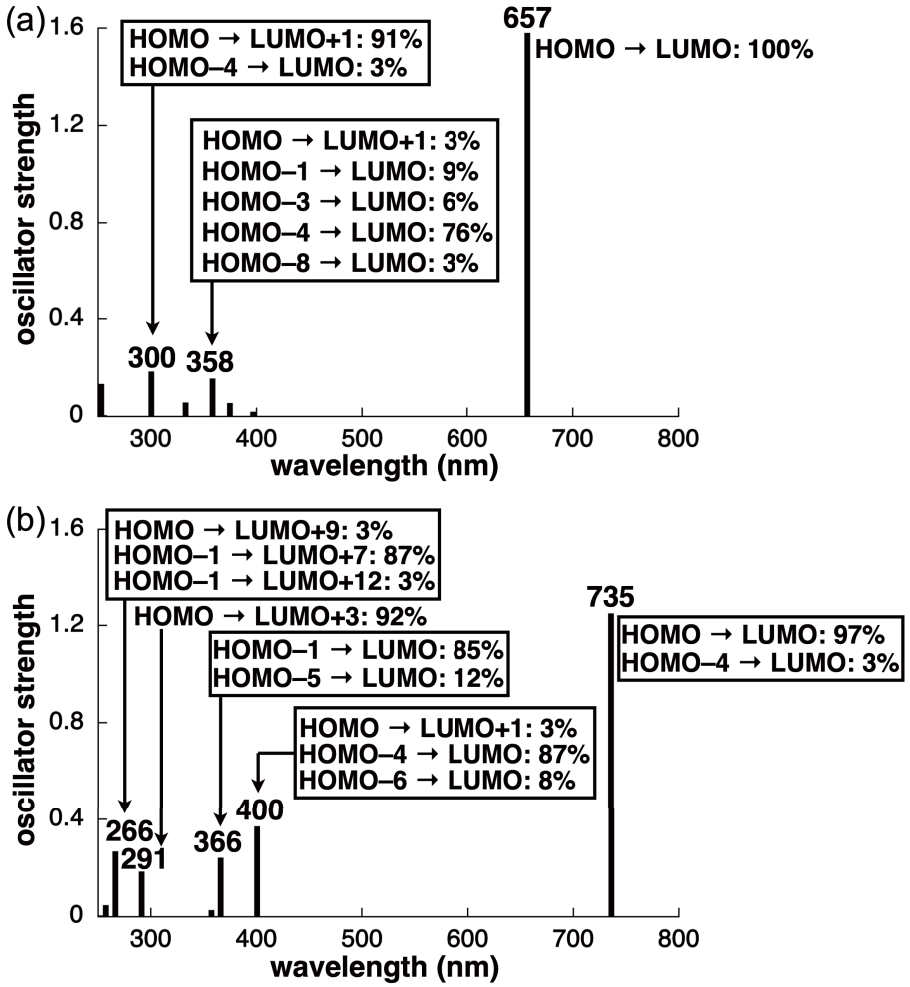


Fig. S35 TD-DFT-based UV/vis absorption stick spectra of (a) $\mathbf{2b}_{NH}\cdot Cl^-$ and (b) $\mathbf{2b}^-$ with the transitions correlated with molecular orbitals estimated at PCM-CAM-B3LYP/6-31+G(d,p)(CH_2Cl_2)//B3LYP/6-31+G(d,p).

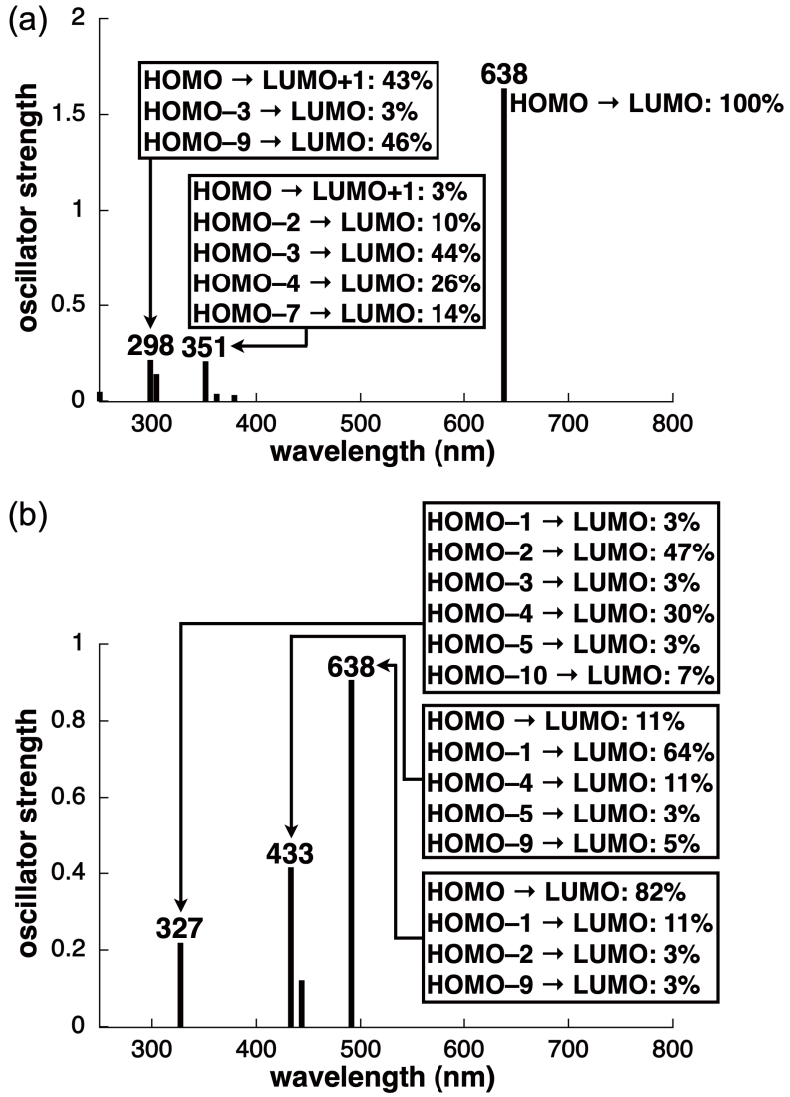


Fig. S36 TD-DFT-based UV/vis absorption stick spectra of (a) **2c**$_{NH}$ and (b) **2c**$_{OH}$ with the transitions correlated with molecular orbitals estimated at PCM-CAM-B3LYP/6-31+G(d,p)(CH_2Cl_2)//B3LYP/6-31+G(d,p).

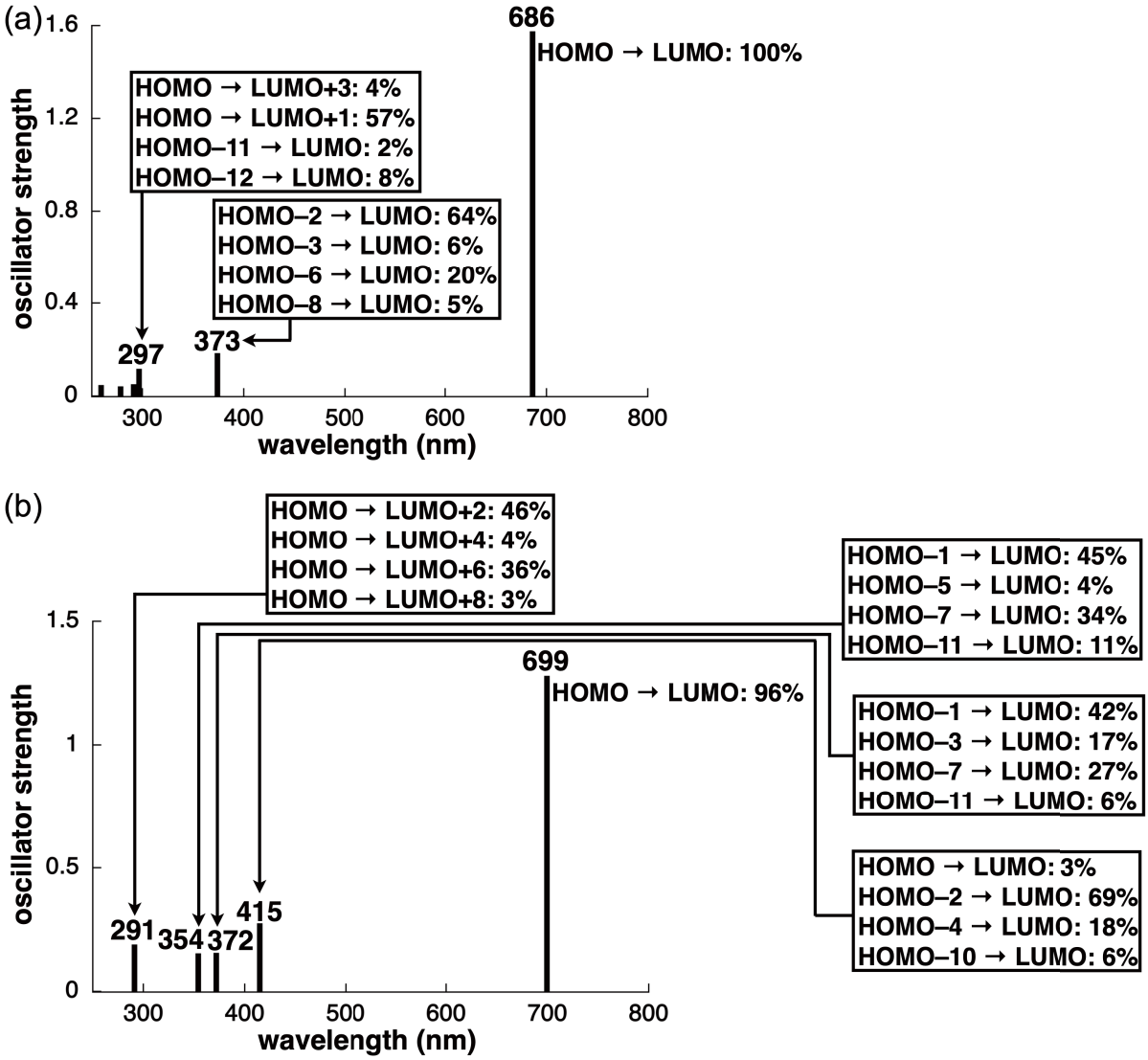


Fig. S37 TD-DFT-based UV/vis absorption stick spectra of (a) $\mathbf{2c}_{NH}\cdot Cl^-$ and (b) $\mathbf{2c}^-$ with the transitions correlated with molecular orbitals estimated at PCM-CAM-B3LYP/6-31+G(d,p)(CH_2Cl_2)//B3LYP/6-31+G(d,p).

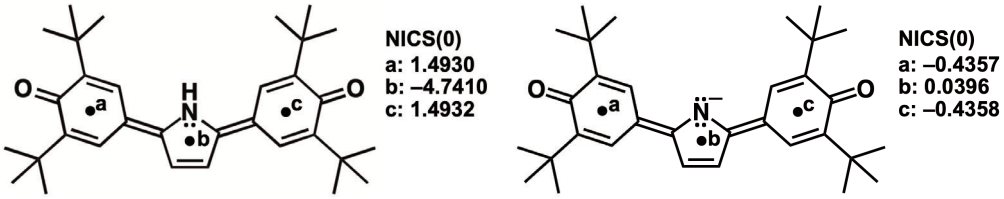


Fig. S38 NICS(0) values of **2a** (left) and $\mathbf{2a}^-$ (right) estimated at B3LYP/6-31+G(d,p). It is not easy to see the correlation of the ^{1}H NMR spectral changes showing the downfield shifts for $\mathbf{2a}^-$, especially those of pyrrole β-CH and their proximal quinone methide CH (Fig. S58), with the theoretically speculated aromaticity of the constituent rings and also with the C=C double bond characters at the pyrrole β C=C and quinone methide C=C moieties. The details will be reported elsewhere.

Cartesian Coordination of $\mathbf{2a}_{NH}$

-1450.604972 hartree

C,-0.6819753296,1.2403887037,0.0469218718
C,0.6812532152,1.2408463234,-0.027906308
C,1.1460197449,-0.1258536558,-0.0541063167
C,-1.1463689101,-0.1265926932,0.0632232571
C,2.4535929277,-0.6185755302,-0.115983976
C,3.5634643941,0.2897416242,-0.2074713303
C,2.7342703508,-2.0267075402,-0.0928136745
C,4.8610931808,-0.1240461208,-0.2852278547
H,3.3424445261,1.3487374211,-0.2221770152
C,3.9988028768,-2.5358339443,-0.1563270095
H,1.9004466622,-2.7144166796,-0.0122796943
C,5.1446212518,-1.5849835987,-0.2668257319
C,-2.4538140067,-0.6201015158,0.1214314288
C,-2.7340949037,-2.0281138801,0.0883455207
C,-3.5639561486,0.2872403555,0.2190982938
C,-3.9985001836,-2.5380258467,0.1479619769

H,-1.9000539419,-2.7150157895,0.0033062014
C,-4.8614873388,-0.1274398547,0.2936477527
H,-3.3432375158,1.3461688074,0.2412953188
C,-5.144619455,-1.5882881642,0.2647690706
O,-6.3097744994,-2.0129067436,0.335958609
O,6.3098611897,-2.0087781677,-0.3414767355
N,-0.0000647107,-0.9003546637,0.0018381794
H,0.0000540002,-1.9066392812,-0.0022320697
H,-1.3200187244,2.1105662436,0.0834087633
H,1.3190639457,2.11143931,-0.0579915672
C,4.2772762987,-4.0479901467,-0.1179090111
C,2.9790862475,-4.8720940998,0.0119564593
C,4.982977054,-4.4893566648,-1.4265143446
C,5.17224379,-4.390564529,1.1018598646
H,2.4342115195,-4.6457356692,0.9360387271
H,2.3052256949,-4.7207175527,-0.8394551898
H,3.2327693195,-5.9365089598,0.0380877627
H,5.9404579514,-3.982831727,-1.5499285806
H,5.1606129114,-5.5708199033,-1.4005274192
H,4.3549753503,-4.2733800568,-2.2987197545
H,5.3476950187,-5.4721618632,1.135063434
H,6.1356820278,-3.8840254208,1.0408693564
H,4.6812025364,-4.1015448106,2.0384680297
C,6.0316467889,0.8686053806,-0.3968496811
C,6.9912018719,0.6977955161,0.8094211923
C,6.804659985,0.6283357002,-1.7194239704
C,5.5449998673,2.3328927822,-0.4010943531
H,6.4649826692,0.8799374968,1.7537947202
H,7.4211718493,-0.3039458663,0.8363092938
H,7.8078107963,1.4254853569,0.7350479649
H,6.1462629404,0.7671060586,-2.5849909697
H,7.624987568,1.3509820201,-1.8030916918
H,7.2239422841,-0.3775760943,-1.7565027884
H,6.4111382122,2.9973510916,-0.4822243546
H,4.888724554,2.5483289317,-1.2522250162
H,5.0173184099,2.5966763813,0.5228361893
C,-4.2765210745,-4.0499644669,0.0989466857
C,-2.9780462268,-4.8727748395,-0.0361963582
C,-4.9825335567,-4.5006149459,1.4042194821
C,-5.1709798742,-4.3843271071,-1.1234688291
H,-2.4329608475,-4.6398836942,-0.9585294776
H,-2.3044901149,-4.7270793767,0.8164451691
H,-3.2314079672,-5.937057658,-0.0697550069
H,-5.9401475697,-3.9951489203,1.5308974268
H,-5.1599650633,-5.5819009135,1.3705862712
H,-4.3548255827,-4.290650082,2.2781017823
H,-5.3459250031,-5.4657418797,-1.164373181
H,-6.1346586377,-3.8786552837,-1.0591942291
H,-4.6798072266,-4.0884723748,-2.0578739641
C,-6.0323131536,0.864100252,0.4120716611
C,-6.9915306375,0.7017247183,-0.7956277343
C,-6.8055879666,0.6141863101,1.7327082123
C,-5.5460085242,2.3284321073,0.4269352983
H,-6.465130036,0.8907903987,-1.7385381583
H,-7.4212358042,-0.2999073391,-0.829831423
H,-7.8083479042,1.4286484957,-0.7162182623
H,-6.1474525213,0.7470017031,2.5994078959
H,-7.6261625619,1.3359636176,1.8213057063
H,-7.2245738142,-0.3920898729,1.762523704
H,-6.412321008,2.9920860189,0.5126649857
H,-4.8899520647,2.5378972926,1.2797231006
H,-5.018206843,2.5989739895,-0.4949700873

Cartesian Coordination of $2a_{OH}$

-1450.5997758 hartree

C,-0.691601579,1.3532795685,0.0465302624
C,0.661397665,1.3350598429,-0.0310662755
C,1.0540245705,-0.0887227971,-0.0520883587
C,-1.1165627898,-0.0515907157,0.073064752
C,2.4155012384,-0.6021844508,-0.1297440575
C,3.520405681,0.2600107239,-0.1840131537
C,2.646074564,-1.9894481506,-0.1507824537
C,4.834558407,-0.2090994663,-0.2564241527
H,3.343640721,1.3257367914,-0.1679734942
C,3.9241415919,-2.5336995361,-0.2228346828
H,1.7756301039,-2.6283570082,-0.1080789823
C,5.0115269464,-1.617456318,-0.2743344289
C,-2.4130795249,-0.5467126232,0.1500383556
C,-2.6413499156,-1.9718938473,0.1675065972
C,-3.5527001566,0.3366373078,0.2141257695
C,-3.8851643288,-2.516701233,0.2427403104
H,-1.7539144538,-2.5877686866,0.1170029858
C,-4.8327971176,-0.1166075739,0.2906305448
H,-3.3583975178,1.4008506079,0.1991017666
C,-5.0631553474,-1.5966978823,0.3095773079
O,-6.2133591082,-2.0500018315,0.3795043613
N,-0.0048453847,-0.8795595465,0.0097712972
H,-1.3306810115,2.22449338,0.0820483567
H,1.3212499152,2.1911919903,-0.0705251931
C,4.1395730416,-4.0660431145,-0.2449652333
C,2.7972816611,-4.8270882332,-0.1809044885
C,4.8440389902,-4.4952903591,-1.5573146335
C,4.9753342592,-4.513265924,0.9814558835
H,2.2428098711,-4.6126605625,0.7387242263
H,2.1505749187,-4.5996661069,-1.0348674831
H,2.9986588928,-5.9031491938,-0.1992066187
H,5.8349733729,-4.0505890492,-1.6556320453
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H,5.9710548943,-4.0683694467,0.983838576
H,4.4698535596,-4.2369772701,1.9136971851
C,6.025507294,0.7842520769,-0.3125711761
C,6.9562054541,0.6095370926,0.9196685017
C,6.8235793066,0.6251849961,-1.6365819611
C,5.5473830256,2.2534351373,-0.2787550045
H,6.3953697191,0.7765740341,1.8447354615
H,7.4185604019,-0.3791776322,1.0077351288
H,7.7708198513,1.3409036893,0.8786545024
H,6.170130718,0.8028074429,-2.496605544
H,7.6381873366,1.3568523477,-1.6710974161
H,7.2741187527,-0.3619180269,-1.7839374283
H,6.418929308,2.914424076,-0.3201696328
H,4.9096356101,2.4975466923,-1.1342055602
H,5.002309489,2.4867681435,0.6413138517
C,-4.1162960638,-4.0368174314,0.2609906148
C,-2.7853805499,-4.8135076983,0.1843116433
C,-4.8277833874,-4.451314123,1.5751318189
C,-4.9779891432,-4.4587137724,-0.9573835576
H,-2.2352914624,-4.6000711272,-0.7387008889

H,-2.1300481114,-4.5950016342,1.0345534063
H,-2.9972510411,-5.8876925731,0.1999432463
H,-5.8086559924,-3.9830044111,1.6630522553
H,-4.9591213158,-5.5395847718,1.5925518209
H,-4.2251276292,-4.1729163184,2.4474711744
H,-5.1096839582,-5.547069957,-0.9531435667
H,-5.9627123644,-3.9909458603,-0.9312185465
H,-4.4830134008,-4.1851610233,-1.8964484461
C,-6.0412918351,0.8319614123,0.3574625822
C,-6.9739588956,0.5899559476,-0.8577742115
C,-6.8255542907,0.6011645926,1.6754025467
C,-5.608635529,2.3128141,0.325568851
H,-6.438326157,0.7602581583,-1.7989537429
H,-7.3693587239,-0.4261727466,-0.8595982988
H,-7.8159865809,1.2911096403,-0.819947115
H,-6.1836079721,0.7788410872,2.5460663097
H,-7.6661535421,1.3028983161,1.7302307813
H,-7.2181627869,-0.4144683723,1.7321441813
H,-6.4999678522,2.9465390756,0.3749655291
H,-4.9727753208,2.5766523386,1.178388946
H,-5.0768135859,2.5687296392,-0.59795334
O,6.2592075317,-2.177626206,-0.3431658712
H,6.933668931,-1.4914152503,-0.3734342326

Cartesian Coordination of $2a_{NH}{\cdot}Cl^{-}$

-1910.934883 hartree
C,-0.6799901148,2.321040226,0.1885607413
C,0.6799989252,2.321036222,0.188098516
C,1.1346780308,0.9554669484,0.0093298024
C,-1.1348159109,0.9554993019,0.0099213359
C,2.4679941894,0.5112372834,-0.0100610263
C,3.5275891092,1.4829973623,0.0078470703
C,2.8279385622,-0.8788935599,-0.0155654123
C,4.8507200727,1.1483568442,-0.0107966486
H,3.2481990151,2.527920412,0.0151959125
C,4.131553433,-1.2993924536,0.0033060956
H,2.0234580733,-1.6049401608,-0.049776046
C,5.219308355,-0.2895702346,-0.0385767998
C,-2.4681134572,0.5112119391,-0.0087977071
C,-2.8278934589,-0.8789520073,-0.0142858046
C,-3.5278340578,1.4828358834,0.0098712693
C,-4.1314302022,-1.2996368763,0.0050591119
H,-2.0233370863,-1.6048938689,-0.0489069078
C,-4.8509301294,1.1480167049,-0.0082519543
H,-3.2485961415,2.5277922011,0.0174539589
C,-5.2193327788,-0.2899596401,-0.0364207974
O,-6.4194884481,-0.6334296222,-0.0959927333
O,6.4195052494,-0.6328968431,-0.0982209122
N,-0.0001018569,0.1764259579,-0.0868635108
H,-1.3182341691,3.1792324183,0.335851423
H,1.3183684319,3.179207432,0.3349900236
C,4.5009367627,-2.7943610339,0.0458746009
C,3.255068033,-3.6919294601,0.1860280633
C,5.2293248738,-3.1909513254,-1.2644196948
C,5.4209143357,-3.0848523485,1.2606985435
H,2.7136589154,-3.4910905282,1.1179511944
H,2.543999674,-3.5779520382,-0.6371229113
H,3.5760165607,-4.7401122347,0.2120736282
H,6.1443550164,-2.6112139104,-1.3998008257
H,5.4903448277,-4.2565456354,-1.2324657362
H,4.5750021386,-3.0325570901,-2.1287850169
H,5.6474906663,-4.1580483731,1.2971512659
H,6.3581055876,-2.5303626908,1.1988394402
H,4.915476367,-2.8200918135,2.1975983997
C,5.9634994256,2.2132237663,-0.0168089925
C,6.8845462148,2.0309338941,1.2168811412
C,6.8042796324,2.0967098999,-1.314242627
C,5.3948596226,3.6467014406,0.0394742567
H,6.3118263018,2.1383738607,2.1459794297
H,7.3570080541,1.0479499796,1.2097684439
H,7.6681763667,2.7995554332,1.213014121
H,6.1742745076,2.255222926,-2.1975932387
H,7.5912309438,2.8621983892,-1.3188581434
H,7.2697852559,1.1132862638,-1.3899923765
H,6.2245451348,4.3624909869,0.0415078549
H,4.7661620328,3.8758057973,-0.8286164367
H,4.8072584933,3.8211957375,0.9484114717
C,-4.5005074424,-2.794676727,0.0476212543
C,-3.2544092143,-3.6919782928,0.1875159831
C,-5.420167744,-3.0854478698,1.262615884
C,-5.229033635,-3.1913834195,-1.2625654431
H,-2.5435998915,-3.5780243558,-0.6358712275
H,-2.7127811342,-3.4908482785,1.1192659139
H,-3.5751512464,-4.7402200353,0.2138477352
H,-6.3574822849,-2.5311394879,1.2010376407
H,-5.6465351105,-4.1586902162,1.2990099268
H,-4.9145557923,-2.8206956706,2.1994259535
H,-5.4897333274,-4.2570554248,-1.2306269731
H,-6.1442667541,-2.6119172421,-1.3977599184
H,-4.5749164338,-3.0327436902,-2.1270382124
C,-5.9638686262,2.2127284605,-0.0133744085
C,-6.8049573704,2.0968204527,-1.3106570186
C,-6.884590005,2.0296096162,1.2204369117
C,-5.3954488485,3.646264786,0.0435851304
H,-6.1751892299,2.2558852485,-2.1940779022
H,-7.2703605957,1.1133791762,-1.3868123195
H,-7.5920013988,2.862218039,-1.3146649984
H,-6.3116622896,2.1365660298,2.1494613474
H,-7.6683145772,2.7981367316,1.2172112842
H,-7.3569326093,1.0465722068,1.2128626571
H,-6.2252560468,4.3619121947,0.046272889
H,-4.8076172559,3.8203218257,0.9524581781
H,-4.7670386283,3.8759879123,-0.8245487379
H,-0.0002173246,-0.8108928562,-0.4709130488
Cl,-0.0004744037,-2.5784834064,-1.4105628272

Cartesian Coordination of $2a^{-}$

-1450.094532 hartree
C,-0.6771042136,2.5588866777,0.0025943363
C,0.6771185673,2.5588852755,-0.0026911499
C,1.090513943,1.1415455646,-0.0010229996
C,-1.0905024448,1.1415477583,0.0009583324
C,2.422813442,0.6651535262,0.0043332115
C,3.5402711025,1.5550051255,-0.0249718109
C,2.6898982353,-0.7386521066,0.0378984657
C,4.8425351855,1.1221299954,-0.0272774727
H,3.3333690984,2.6174707512,-0.0519449055
C,3.9594916261,-1.2559397197,0.0464227859
H,1.8194559338,-1.3816650038,0.0598285237
C,5.1146065892,-0.330582621,0.0110676905

C,-2.4228030518,0.6651587359,-0.004387062
C,-2.6898920975,-0.7386469552,-0.0379283528
C,-3.5402582459,1.5550138357,0.0249115303
C,-3.9594866639,-1.2559318623,-0.046439698
H,-1.8194517457,-1.3816636108,-0.0598469815
C,-4.8425229523,1.1221397861,0.0272280301
H,-3.3333523467,2.6174783788,0.0518726882
C,-5.1145991658,-0.3305697223,-0.0110932468
O,-6.2940182389,-0.7662374097,-0.0129608787
O,6.294021114,-0.7662627218,0.0130778214
N,0.0000049441,0.3361277242,-0.0000270605
H,-1.3285323364,3.4226054826,0.0038260346
H,1.3285483919,3.422602755,-0.0039422058
C,4.2161786517,-2.7749451194,0.0909102385
C,2.9023588469,-3.5830859741,0.1295676681
C,5.0010503764,-3.2193931553,-1.1697218441
C,5.0271329535,-3.141038064,1.3604247237
H,2.3005062424,-3.3501198155,1.0148679853
H,2.2840989616,-3.4068339647,-0.7574015775
H,3.1391037057,-4.6531650307,0.1615414639
H,5.9622170916,-2.7067120826,-1.2296585886
H,5.1778940964,-4.3027606381,-1.1379971691
H,4.4265018289,-2.9986574694,-2.0773911513
H,5.202065947,-4.2246809772,1.3928045718
H,5.9897683657,-2.6277323286,1.3680117121
H,4.4723418207,-2.8625287016,2.2645601637
C,6.0279254475,2.106441265,-0.0738665479
C,6.9150605525,1.9361481339,1.1860125565
C,6.8795704843,1.8524486571,-1.3439401773
C,5.5629530748,3.5774850137,-0.1160749781
H,6.3373347147,2.1451189677,2.0945867682
H,7.3080579056,0.920352777,1.2481079458
H,7.7566915422,2.6409321334,1.1512124429
H,6.2768764155,2.0040067194,-2.2476655126
H,7.723240179,2.554907836,-1.3787067493
H,7.2686147027,0.8332701214,-1.3505431594
H,6.4416132919,4.2321765476,-0.1499305718
H,4.9573035271,3.7925398434,-1.0040472365
H,4.9814850877,3.8518153952,0.7718142816
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C,-2.9023347071,-3.583070487,-0.1293251093
C,-5.0011935767,-3.2193245087,1.1696783191
C,-5.026952271,-3.1411129429,-1.3604791465
H,-2.3003696967,-3.350144093,-1.0145595812
H,-2.2841904144,-3.4067670018,0.7577145761
H,-3.1390666814,-4.6531529959,-0.161273866
H,-5.9623714411,-2.7066466692,1.2294681465
H,-5.1780275151,-4.3026945636,1.1379886256
H,-4.4267606681,-2.9985376966,2.0774084799
H,-5.2018587611,-4.2247612113,-1.3928254323
H,-5.9895965161,-2.6278271744,-1.3682169196
H,-4.472051204,-2.8626398806,-2.264558537
C,-6.0279236215,2.1064354615,0.0738355492
C,-6.9149291969,1.9363067866,-1.1861562754
C,-6.8796950361,1.8522256955,1.3437794895
C,-5.562985359,3.5774839974,0.1163089962
H,-6.3371182404,2.14542715,-2.0946417734
H,-7.3078930435,0.9205099878,-1.2484428048
H,-7.7565811333,2.6410646223,-1.1513343894
H,-6.2771063999,2.0036813883,2.2475919707
H,-7.7234016058,2.5546398936,1.3785536056
H,-7.2686927904,0.8330269658,1.3501948895
H,-6.4416632167,4.2321517522,0.1501643151
H,-4.9574380215,3.7924243697,1.0043785597
H,-4.9814271305,3.8519561111,-0.7714771329

Cartesian Coordination of $2b_{NH}$

-6592.8449688 hartree

C,0.6877304415,2.8436502871,-0.0123202593
C,-0.6877316802,2.8436485499,0.0110803558
C,-1.1626168215,1.4753426382,0.0193961622
C,1.162623891,1.4753431319,-0.0202324055
C,-2.4386111447,0.8879955984,0.0412161198
C,-3.6514242641,1.6582953528,0.0619693163
C,-2.5667567172,-0.5469429207,0.043439927
C,-4.8953455398,1.0960206008,0.0833139125
H,-3.5623230603,2.7312692145,0.0604132799
C,-3.7643908219,-1.1981293477,0.0640083963
H,-1.668091555,-1.1505566393,0.0279859458
C,-5.0152028412,-0.3852574937,0.0854451105
C,2.4386169877,0.8879837152,-0.0418287865
C,2.5667390399,-0.5469568081,-0.043942693
C,3.651448799,1.6582613289,-0.0623437745
C,3.7643677059,-1.1981656624,-0.0641109303
H,1.6680558986,-1.1505528682,-0.0288305398
C,4.8953672853,1.095963185,-0.0832433098
H,3.562367035,2.7312361521,-0.0609156088
C,5.0152009011,-0.385316907,-0.085174318
O,6.1262567831,-0.939293438,-0.1038463827
O,-6.12626151,-0.9392138331,0.1045444088
N,0.0000050799,0.7254409717,-0.0003356294
C,-3.8629838116,-2.7326323758,0.0657183723
C,-2.4737888049,-3.4033870061,0.0418999478
C,-4.591934565,-3.2142013438,1.3474567716
C,-4.6354722881,-3.214240086,-1.1902497134
H,-1.9039709674,-3.147500929,-0.8592261376
H,-1.8734128435,-3.1474816115,0.9229546182
H,-2.6028914647,-4.4901721438,0.0441254656
H,-5.6077129289,-2.8215596422,1.397649558
H,-4.6405853334,-4.309258665,1.3513868079
H,-4.0480883448,-2.8998249231,2.2458730618
H,-4.684190026,-4.3093002526,-1.192504366
H,-5.6523912053,-2.8216415642,-1.2055424797
H,-4.1227936969,-2.8998449164,-2.1068011749
C,-6.1726871223,1.9524478775,0.1051826985
C,-7.0336641951,1.6500182574,-1.1487441807
C,-6.9902115421,1.6501384967,1.3878820209
C,-5.8535504145,3.461866695,0.099643492
H,-6.4771682597,1.8757065016,-2.0658468097
H,-7.3435778273,0.6049126128,-1.1753962389
H,-7.9314549168,2.2791205022,-1.1384746851
H,-6.4026415186,1.8759226267,2.2853698686
H,-7.8878382818,2.2792299853,1.4083092403
H,-7.299024909,0.6050359649,1.4252445124
H,-6.7927070809,4.0240866167,0.1157033699
H,-5.2747317504,3.766346015,0.9790939183
H,-5.3051953364,3.7662617967,-0.7991460045
C,3.8629332697,-2.7326706091,-0.0657604148
C,2.4737185855,-3.4033994991,-0.0423751517
C,4.5922941948,-3.2142829363,-1.347248717

C,4.6350032384,-3.2142626363,1.1904715534
H,1.9036213844,-3.1474903541,0.858567786
H,1.8736252393,-3.1474952926,-0.9236225055
H,2.6028020458,-4.4901870404,-0.0445395572
H,5.6081083621,-2.8216901776,-1.3970983011
H,4.6408953885,-4.3093422017,-1.3511531282
H,4.0487700981,-2.8998878722,-2.2458533053
H,4.6837306626,-4.3093226678,1.1927507464
H,5.6519125388,-2.8216527199,1.2061072528
H,4.1220087611,-2.8998665166,2.1068460158
C,6.1727313882,1.9523654281,-0.1047712321
C,7.0332594482,1.6500637263,1.1494948469
C,6.9907040758,1.6498935222,-1.3871461851
C,5.8536206904,3.4617908131,-0.0995246467
H,6.4764322769,1.8758385348,2.0663750105
H,7.3431659521,0.6049612603,1.1763610567
H,7.9310505547,2.2791691544,1.1394862018
H,6.4034669231,1.8756142064,-2.2848678822
H,7.8883651171,2.2789449363,-1.4073131464
H,7.2994888007,0.6047750121,-1.4242936651
H,6.7927931479,4.0239915191,-0.1153326196
H,5.2751098331,3.7661682423,-0.9792126547
H,5.3049625648,3.7663109073,0.799037728
H,0.0000120655,-0.2793921816,0.0000324369
Br,-1.7004385066,4.4201873686,0.0280182237
Br,1.7004166127,4.4201971364,-0.0298033971

Cartesian Coordination of 2b$_{OH}$

-6592.8458003 hartree

C,-0.6712643435,-1.9340354564,-0.189959554
C,0.6922594593,-1.9531085545,-0.1705095312
C,1.1278902014,-0.5560884734,-0.0850475474
C,-1.0820575331,-0.5175685462,-0.1161627875
N,-0.0036161904,0.2448044403,-0.0568412875
C,2.3963578489,0.0235607351,-0.0331981221
C,3.6224695517,-0.7364218445,-0.0577055421
C,2.4865235147,1.4660594593,0.0496725095
C,4.8515833124,-0.1554859076,-0.0064150966
H,3.5424172049,-1.8090452654,-0.1195073344
C,3.6694574198,2.1324440207,0.1051226104
H,1.5442331577,1.9938137546,0.0653469407
C,4.9361874649,1.3371892276,0.0792371113
C,-2.4152541805,0.0806687426,-0.1025028424
C,-2.5185073354,1.4860653597,-0.0246028534
C,-3.6015299077,-0.6564001184,-0.162146899
C,-3.7378858376,2.1459578569,-0.0057453044
H,-1.5943757472,2.0425663824,0.0208588075
C,-4.8725109528,-0.0677132431,-0.1481261626
H,-3.5385282233,-1.7308890966,-0.2219353962
C,-4.9198492804,1.3449983846,-0.0689429513
Br,-1.7187277447,-3.4962471565,-0.2939766515
Br,1.7040568778,-3.5375903063,-0.2447025821
O,6.0360654199,1.9009448882,0.127661419
C,6.1466177071,-0.9819287458,-0.0336471645
C,6.9603073848,-0.7352377927,1.2638061704
C,5.8561299241,-2.4945018303,-0.1234563486
C,6.9983187581,-0.5920690926,-1.2701548668
H,7.2552360906,0.3102672208,1.3578945333
H,6.3773305967,-1.0176946071,2.1480000494
H,7.8663149701,-1.3521537102,1.2494432173
H,5.3108930697,-2.7580543112,-1.0365469936
H,6.8060873128,-3.0381805439,-0.1399559576
H,5.2843352698,-2.8582749432,0.7374697542
H,7.904470149,-1.2082924475,-1.298348211
H,6.4424648548,-0.7720477869,-2.1975574722
H,7.2942566845,0.4568545845,-1.2369830216
C,3.7453289031,3.6650349199,0.1929227777
C,4.4679725731,4.0874892386,1.4988002696
C,4.506167111,4.2307429899,-1.034717053
C,2.3414368917,4.303819193,0.2078782526
H,3.9349312716,3.7078412181,2.3781583137
H,5.4943406849,3.7200639857,1.5257959501
H,4.4889281161,5.1813681321,1.5672041474
H,4.0004327987,3.9535184877,-1.9668765394
H,4.5272952508,5.3253224793,-0.9787408035
H,5.5335116474,3.8669767181,-1.0720954499
H,2.4465806783,5.3916931993,0.2709008501
H,1.7757637137,4.0798762429,-0.703122982
H,1.7490740009,3.9797133425,1.0705037156
C,-3.8018943944,3.6905163884,0.0806622153
C,-4.5430457907,4.1324797589,1.3686363705
C,-2.3908507033,4.315023618,0.1372893542
C,-4.5047145855,4.2761358856,-1.1709792928
H,-5.5759210794,3.7839094474,1.3883254891
H,-4.0307244852,3.7488527779,2.2582437271
H,-4.5497101035,5.2268741316,1.4326539581
H,-1.8003305547,4.0877249102,-0.7564944219
H,-2.4894960268,5.4036577258,0.1974358514
H,-1.8270632116,3.987311455,1.0170483203
H,-4.5112895785,5.3707798482,-1.1113808164
H,-3.9652232996,3.9943649178,-2.082351372
H,-5.5359416611,3.933781023,-1.2608949866
C,-6.0707111073,-1.0644873199,-0.2226174847
C,-5.9593263191,-1.8813774893,-1.5359174183
C,-5.9979174499,-2.0240002373,0.9933247573
C,-7.4931564287,-0.4539778379,-0.2099183804
H,-6.0219519342,-1.2248301266,-2.4105825458
H,-5.0177047111,-2.4317581023,-1.5999442643
H,-6.7760251709,-2.609969328,-1.5971861715
H,-6.0882279161,-1.4698097625,1.9339263683
H,-6.8148575022,-2.7534549421,0.9474605352
H,-5.057734381,-2.5796992317,1.0236689922
H,-8.2241786384,-1.2666287588,-0.2670611828
H,-7.7197558886,0.0821751738,0.7207450413
H,-7.6920889433,0.1840218451,-1.0807316055
O,-6.0933745396,2.0438786399,-0.0471309061
H,-6.8464151652,1.4453681656,-0.0923382217

Cartesian Coordination of 2b$_{NH}$·Cl$^-$

-7053.1770396 hartree

C,0,-0.685469,-1.970356,0.1564
C,0,0.685484,-1.97035,0.156481
C,0,1.147973,-0.599863,0.044971
C,0,-1.147949,-0.599868,0.044906
C,0,2.441919,-0.043929,0.0424
C,0,3.623299,-0.841699,-0.133134
C,0,2.613694,1.374449,0.207546
C,0,4.881089,-0.311138,-0.174762
H,0,3.498131,-1.902701,-0.267958
C,0,3.838556,1.981041,0.214455

H,0,1.724233,1.974742,0.330929
C,0,5.050957,1.154052,-0.001449
C,0,-2.441882,-0.043917,0.042307
C,0,-2.613668,1.37446,0.207539
C,0,-3.623229,-0.841685,-0.133389
C,0,-3.838561,1.980981,0.21468
H,0,-1.724198,1.974794,0.330714
C,0,-4.881051,-0.311181,-0.174843
H,0,-3.497992,-1.902642,-0.268545
C,0,-5.050978,1.153938,-0.001042
O,0,-6.188049,1.668978,-0.035643
O,0,6.187977,1.669168,-0.036554
N,0,0.000015,0.167593,-0.018409
C,0,3.98869,3.498514,0.426325
C,0,2.629533,4.180032,0.687518
C,0,4.900944,3.781976,1.647745
C,0,4.601003,4.141277,-0.845599
H,0,1.92642,4.045352,-0.140468
H,0,2.158001,3.804865,1.604129
H,0,2.793134,5.255712,0.821678
H,0,5.903563,3.377579,1.50229
H,0,4.976755,4.865743,1.803378
H,0,4.47326,3.343727,2.557996
H,0,4.699548,5.224368,-0.698393
H,0,5.587528,3.727177,-1.061517
H,0,3.946778,3.97705,-1.708493
C,0,6.123398,-1.191756,-0.401238
C,0,6.859178,-0.754028,-1.693921
C,0,7.085598,-1.074907,0.809229
C,0,5.754687,-2.681735,-0.558115
H,0,6.202477,-0.857308,-2.56569
H,0,7.187385,0.283806,-1.62561
H,0,7.737452,-1.392367,-1.855048
H,0,6.590602,-1.406909,1.729709
H,0,7.963148,-1.714473,0.64917
H,0,7.420998,-0.045881,0.944438
H,0,6.669847,-3.262605,-0.71896
H,0,5.262605,-3.08049,0.336183
H,0,5.097574,-2.856819,-1.417419
C,0,-3.988746,3.498445,0.426622
C,0,-2.629578,4.180029,0.687556
C,0,-4.601348,4.141173,-0.84518
C,0,-4.900764,3.781855,1.648235
H,0,-2.157894,3.804935,1.60412
H,0,-1.926584,4.045311,-0.140521
H,0,-2.793181,5.255715,0.821667
H,0,-5.587886,3.727005,-1.060916
H,0,-4.699949,5.224256,-0.697951
H,0,-3.947271,3.976999,-1.708196
H,0,-4.976622,4.865623,1.803844
H,0,-5.903379,3.37737,1.503035
H,0,-4.472821,3.343675,2.558398
C,0,-6.123332,-1.191769,-0.401566
C,0,-7.085376,-1.075536,0.809096
C,0,-6.859308,-0.753479,-1.693944
C,0,-5.754572,-2.681653,-0.55918
H,0,-6.590227,-1.407965,1.72934
H,0,-7.420786,-0.046586,0.944841
H,0,-7.962923,-1.71506,0.648855
H,0,-6.202725,-0.856342,-2.565851
H,0,-7.737585,-1.391768,-1.855245
H,0,-7.187535,0.284316,-1.625116
H,0,-6.669718,-3.26248,-0.720265
H,0,-5.097494,-2.856297,-1.418599
H,0,-5.262439,-3.080823,0.334904
Br,0,1.695777,-3.54388,0.364672
Br,0,-1.695722,-3.543909,0.364587
H,0,0.000008,1.0966,-0.559024
Cl,0,-0.000165,2.628051,-1.755138

Cartesian Coordination of 2b^{-}

-6592.3473129 hartree

C,-0.6813249647,-2.897387957,-0.002727749
C,0.6813082034,-2.8973912844,0.002642219
C,1.1107266026,-1.4875995263,0.004361579
C,-1.1107366764,-1.487594103,-0.004409006
C,2.4102062292,-0.9162676691,0.0094893704
C,3.6240027559,-1.670551607,0.0143135868
C,2.5213286459,0.512917063,0.0099050431
C,4.8664808908,-1.0884498073,0.0192474657
H,3.5477546185,-2.7455547847,0.0140229472
C,3.7207798347,1.172952136,0.0146437091
H,1.5867314178,1.0567774746,0.0061945867
C,4.9742632738,0.3857091504,0.0196463547
C,-2.4102136295,-0.9162559469,-0.0095207074
C,-2.5213296506,0.512929264,-0.0098993397
C,-3.6240136288,-1.6705340123,-0.0143630497
C,-3.7207779192,1.1729697703,-0.0146179412
H,-1.5867299614,1.0567854146,-0.0061771627
C,-4.8664891307,-1.088426929,-0.0192793075
H,-3.5477710858,-2.7455378029,-0.0141016039
C,-4.9742652019,0.385733073,-0.0196361715
O,-6.0946300231,0.9526702119,-0.024078008
O,6.094631715,0.9526390405,0.0241006327
N,-0.0000031735,-0.7120278143,-0.000013172
C,3.7995439663,2.7114817737,0.0149323059
C,2.4013422957,3.3629183226,0.0093517324
C,4.5397422911,3.2064874626,1.2840421047
C,4.5498312856,3.2064493891,-1.2482532732
H,1.8223052739,3.0899453494,-0.8796382128
H,1.8152009251,3.0898920183,0.8936572087
H,2.5139004993,4.4532970287,0.0098362351
H,5.5549597684,2.8090410671,1.324101032
H,4.5885414448,4.3033891034,1.2840228541
H,4.003435041,2.8942098678,2.1882010656
H,4.5986269933,4.3033508372,-1.2478778585
H,5.5653363223,2.8090040723,-1.2802082537
H,4.0207487616,2.8941434021,-2.1566491932
C,6.1542291242,-1.9341922913,0.0243926039
C,6.9988416656,-1.6247453337,-1.2382195186
C,6.988727747,-1.6247296161,1.2937117218
C,5.8563792591,-3.4482465655,0.0232112944
H,6.4367631376,-1.8716226484,-2.1469370583
H,7.2735657134,-0.5695761558,-1.2726353168
H,7.9153728867,-2.2296519853,-1.2337559774
H,6.4194005018,-1.8715833714,2.197911633
H,7.9052604186,-2.2296433244,1.2965861803
H,7.2631746563,-0.5695616456,1.3303012671
H,6.8040194816,-3.9993432514,0.0269390683
H,5.2893241835,-3.7584195014,0.9081820571

H,5.2963110953,-3.7584034366,-0.8662039519
C,-3.7995350506,2.7114995633,-0.0148682009
C,-2.4013301278,3.3629292485,-0.009286698
C,-4.5397449889,3.2065388713,-1.2839580697
C,-4.549806905,3.206439742,1.2483373495
H,-1.8222854488,3.0899330674,0.8796911373
H,-1.8151989494,3.0899203731,-0.8936043298
H,-2.5138830636,4.4533084921,-0.0097449715
H,-5.5549644392,2.8090972636,-1.3240158287
H,-4.5885400453,4.3034406784,-1.2839116166
H,-4.0034486551,2.8942812031,-2.1881303767
H,-4.5985984869,4.3033413823,1.2479886966
H,-5.565313062,2.8089973906,1.2802938643
H,-4.0207157026,2.8941100442,2.1567200543
C,-6.1542370332,-1.9341695602,-0.0244449876
C,-6.9988495642,-1.6247587668,1.2381763497
C,-6.9887372056,-1.6246812693,-1.2937571618
C,-5.8563788419,-3.4482219313,-0.0233009819
H,-6.4367680354,-1.8716548855,2.1468869666
H,-7.2735806998,-0.569592416,1.2726186268
H,-7.9153766934,-2.2296715205,1.2336993486
H,-6.4194084554,-1.8715103692,-2.1979629157
H,-7.9052661787,-2.2296005611,-1.2966461956
H,-7.2631907459,-0.5695143304,-1.3303218571
H,-6.804015924,-3.9993238649,-0.0270381263
H,-5.2893252122,-3.7583702686,-0.9082813501
H,-5.296305007,-3.7583965679,0.8661045868
Br,-1.7077225391,-4.4854754274,-0.0067982995
Br,1.7076981699,-4.4854837325,0.0066712515

Cartesian Coordination of 2c$_{NH}$

-1912.7318895 hartree
C,0.6927184368,-1.5444632023,0.0062150167
C,-0.6927183447,-1.5444633142,-0.006213972
C,-1.1516296789,-0.1644638608,-0.0046416408
C,1.1516295928,-0.1644637335,0.0046425383
C,-2.4348431771,0.410994515,0.0005632929
C,-2.5945932307,1.8210840292,-0.238227433
C,-3.6178137379,-0.3527050348,0.2882738034
C,-3.803119543,2.4546394427,-0.2306314352
H,-1.715151514,2.4027392094,-0.4868414775
C,-4.8652687045,0.2022595851,0.354087505
H,-3.4919794593,-1.4031383444,0.5016666832
C,-5.0233763158,1.6516508517,0.0662492893
C,2.4348431171,0.4109945281,-0.0005622748
C,2.5945933597,1.8210842408,0.2382271744
C,3.617813615,-0.3527055476,-0.2882716068
C,3.8031197913,2.4546394186,0.2306309051
H,1.7151516096,2.402739989,0.4868397982
C,4.8652688233,0.2022585911,-0.3540845995
H,3.4919791376,-1.4031389787,-0.5016638921
C,5.0233766527,1.6516500607,-0.0662474798
O,6.1452578707,2.1876110601,-0.0698000379
O,-6.1452577479,2.1876114342,0.0697985858
N,-0.0000000833,0.5962971559,0.0000002909
C,-6.1090252316,-0.6263679844,0.7233540685
C,-5.7526513786,-2.09443822,1.0324142497
C,-6.7852774503,-0.03493614,1.9872535195
C,-7.1136321297,-0.6253783007,-0.4582770875
H,-5.3047897003,-2.6043539636,0.172978171
H,-5.0663128842,-2.1829712851,1.8820363485
H,-6.667928059,-2.6357061322,1.2939511586
H,-7.1145335609,0.9911548141,1.8210784297
H,-7.6585986019,-0.6415667226,2.254899699
H,-6.0946181767,-0.049665419,2.8387084111
H,-7.9908412535,-1.2291432308,-0.1966589394
H,-7.4460310095,0.3856004284,-0.6959568999
H,-6.6586133749,-1.0660074767,-1.3532235451
C,-3.9436599792,3.9564654909,-0.5315828872
C,-4.833413393,4.1644587182,-1.784858271
C,-4.5745169322,4.6809599871,0.6861284168
C,-2.5805995951,4.6218736817,-0.8139947655
H,-4.3906535793,3.6755073951,-2.6605474098
H,-5.8355976515,3.7641817835,-1.6296728852
H,-4.9145050037,5.2356099485,-2.0042912483
H,-3.9466121285,4.562378369,1.5769765515
H,-4.6563655667,5.753311807,0.4735167996
H,-5.5693384313,4.2924221836,0.9050181957
H,-2.7378503123,5.6860172153,-1.0163144396
H,-1.8996936687,4.5521879239,0.0425972882
H,-2.0839811288,4.1948394357,-1.6930793472
C,3.9436601895,3.9564659743,0.531579828
C,2.580599952,4.6218740152,0.8139927054
C,4.8334154387,4.1644613937,1.784853556
C,4.5745149498,4.6809589286,-0.6861335372
H,1.8996924847,4.5521857754,-0.0425979205
H,2.0839833695,4.1948415687,1.693079224
H,2.737850408,5.6860181208,1.0163095751
H,5.8355995565,3.764184455,1.6296672617
H,4.9145071315,5.2356129873,2.0042847156
H,4.3906570903,3.6755113364,2.6605441429
H,4.6563630477,5.753311166,-0.4735238089
H,5.5693364435,4.2924215481,-0.9050240461
H,3.9466089902,4.5623753709,-1.5769806007
C,6.109025102,-0.6263693907,-0.7233509847
C,6.7852870845,-0.0349271378,-1.9872402998
C,7.1136246088,-0.6253947063,0.4582865276
C,5.7526484309,-2.0944354535,-1.0324277527
H,6.0946331491,-0.0496458754,-2.8386996999
H,7.1145452784,0.9911611958,-1.8210529198
H,7.6586081404,-0.6415576424,-2.2548869399
H,6.6585983961,-1.0660302771,1.3532260476
H,7.9908328437,-1.2291609198,0.1966683285
H,7.446026224,0.3855803944,0.6959777665
H,6.667925,-2.6357037927,-1.2939641657
H,5.3047796414,-2.6043581113,-0.1729994842
H,5.0663150235,-2.1829580171,-1.8820550548
H,-0.0000001471,1.6019028798,0.0000003412
C,-1.5283167853,-2.7716103539,-0.0711425766
C,-1.5799153697,-3.6630645305,1.0111531012
C,-2.2300955683,-3.0903978839,-1.2458289977
C,-2.3190679375,-4.8450180337,0.9227590636
H,-1.0389073692,-3.4293088454,1.9228804936
C,-2.9644033775,-4.2741563866,-1.3347654229
H,-2.1964229893,-2.4085014238,-2.0908194008
C,-3.0106911012,-5.1554902984,-0.2504501258
H,-2.350896699,-5.5231701576,1.7704427194
H,-3.4986920025,-4.5076736126,-2.2511105376
H,-3.583059487,-6.0757873865,-0.3195870921
C,1.5283171923,-2.7716100535,0.0711432689

C,2.2300962917,-3.0903975912,1.2458294933
C,1.5799160972,-3.663063831,-1.0111527196
C,2.964404641,-4.2741557971,1.3347654715
H,2.1964235762,-2.4085013511,2.090820071
C,2.3190691639,-4.8450170546,-0.9227591098
H,1.0389079503,-3.4293080576,-1.922880007
C,3.0106926011,-5.1554893684,0.250449909
H,3.4986935128,-4.5076730477,2.2511104366
H,2.3508981426,-5.5231688987,-1.7704429814
H,3.5830614014,-6.0757862247,0.3195865288

Cartesian Coordination of $2c_{OH}$

-1912.7304307 hartree

C,-0.7211329403,-1.620805004,0.0590556493
C,0.6487433127,-1.599108597,0.1434904608
C,1.0412640521,-0.1674479115,0.0333355395
C,-1.141322851,-0.207348825,-0.0520158017
C,2.3919169394,0.401258821,0.0167575152
C,2.5700334385,1.7324399206,0.425768982
C,3.5087017727,-0.3091368098,-0.4521056406
C,3.8141487842,2.3618558185,0.4074804124
H,1.6903381665,2.2603098482,0.7649571934
C,4.781799544,0.259955086,-0.5225035004
H,3.3666495692,-1.3233075728,-0.7939982481
C,4.9138187352,1.5974637313,-0.0701138304
C,-2.4109433462,0.3703294795,-0.0819215748
C,-2.5102535832,1.8046505085,-0.259577014
C,-3.6349883337,-0.378411353,0.0894880948
C,-3.6959479211,2.4652427626,-0.3259841952
H,-1.5693444166,2.3261678606,-0.3576226552
C,-4.8652669018,0.2046723777,0.0647154959
H,-3.5487808303,-1.4387875806,0.2696963091
C,-4.9573597181,1.6758095966,-0.1963704638
O,-6.0613667193,2.2269732363,-0.3013964247
N,-0.0151697381,0.6086295488,-0.0807475571
C,5.9854018249,-0.54213302,-1.0747658947
C,5.5682708357,-1.9586064819,-1.5258296293
C,6.5883454674,0.1681977913,-2.3137820625
C,7.0688996998,-0.7127841666,0.0208328856
H,5.1642183039,-2.5571384788,-0.7031406523
H,4.8265204377,-1.9335906993,-2.3314778987
H,6.4501368421,-2.4816942363,-1.9099968054
H,6.9648362375,1.1630415449,-2.0737708783
H,7.4200285766,-0.4260658115,-2.7100729685
H,5.8377456403,0.2641601584,-3.1065844819
H,7.9025413327,-1.3054665368,-0.3739093888
H,7.4632132006,0.2460906607,0.3593345646
H,6.6598777063,-1.2448576493,0.8871295465
C,3.9617940919,3.8298253706,0.8878771695
C,4.9106803332,3.9235865544,2.1146619628
C,4.4569969101,4.7441263416,-0.2671307336
C,2.6094004299,4.4183472659,1.3476542654
H,4.5193727246,3.3238221226,2.9426326512
H,5.9324941725,3.575548906,1.9312029659
H,4.9815824996,4.9632993634,2.4524034425
H,3.7490259091,4.7153809714,-1.1014405282
H,4.5296417885,5.7799605514,0.0821654872
H,5.435805871,4.4742672336,-0.6773927846
H,2.7616886029,5.4519280171,1.6751349944
H,1.8720223897,4.4325797699,0.5395009767
H,2.1864604854,3.8637868019,2.1908614903
C,-3.778286305,3.9857083728,-0.5420279318
C,-2.3767622176,4.625627371,-0.6218637002
C,-4.5135668598,4.2944638566,-1.8720644098
C,-4.5314296507,4.6505999161,0.6393515709
H,-1.8000984098,4.4707793923,0.2968146307
H,-1.7930871276,4.2382996869,-1.4640112732
H,-2.4854213193,5.705776888,-0.7652786813
H,-5.5369740091,3.9181441191,-1.8580614814
H,-4.5433155484,5.3787966449,-2.0317772595
H,-3.984909166,3.8450051513,-2.7206549996
H,-4.5602641188,5.7364930503,0.4909305973
H,-5.5558812466,4.2848113243,0.7163259292
H,-4.0162455537,4.4556334751,1.5872315981
C,-6.1592041927,-0.5956760905,0.2901240301
C,-6.9445458405,-0.0115126843,1.4935796228
C,-7.0423052522,-0.546712668,-0.984533831
C,-5.8680088538,-2.0776728011,0.6023061135
H,-6.3395839429,-0.0486753174,2.4071650506
H,-7.2447991563,1.0211274676,1.3140577504
H,-7.8464663423,-0.6104637202,1.6657918733
H,-6.5119062858,-0.9795146392,-1.8407855803
H,-7.952225553,-1.1361662221,-0.8213122194
H,-7.3303713735,0.4756329545,-1.2313407281
H,-6.8162568828,-2.6003060951,0.7656433671
H,-5.3524190645,-2.5836061737,-0.2202370551
H,-5.2662111997,-2.1977139015,1.5097980411
C,1.5395066834,-2.7602566303,0.3633963033
C,1.5251327248,-3.8664076843,-0.5037855049
C,2.4017497511,-2.7920640658,1.4750899224
C,2.3467259607,-4.970324893,-0.2668874351
H,0.868410397,-3.8571434699,-1.3676630081
C,3.217029917,-3.8989028666,1.7153290063
H,2.425295128,-1.9462828954,2.1558862808
C,3.193669097,-4.9925002351,0.8443593162
H,2.3233017001,-5.8134386844,-0.951421155
H,3.869962231,-3.9072773384,2.5835331192
H,3.830414596,-5.8526833872,1.0296731588
C,-1.557706109,-2.8478578882,0.0839402671
C,-2.1977522994,-3.3020729915,-1.0824834294
C,-1.677043399,-3.6116362343,1.2561963239
C,-2.935266704,-4.4876266987,-1.0760985997
H,-2.1104735635,-2.7226918933,-1.997553971
C,-2.4189824439,-4.7952553262,1.2636310482
H,-1.1833528981,-3.2749242655,2.1628423134
C,-3.0483075902,-5.2387529479,0.0977442218
H,-3.4191266607,-4.8250523834,-1.988363694
H,-2.5014119452,-5.3719182855,2.1805002673
H,-3.6226674931,-6.1605274363,0.1032891159
O,6.1789352355,2.1246087124,-0.1206976448
H,6.1737461882,3.0350147341,0.1916730011

Cartesian Coordination of $2c_{NH}\cdot Cl^-$

-1912.2213567 hartree

C,-0.6849108217,-1.5894877825,-0.0339611318
C,0.6849110673,-1.5894882249,0.0339632053
C,1.0968591962,-0.1595784908,0.03394795
C,-1.0968580708,-0.1595778968,-0.0339466861
C,2.4053497877,0.3971425064,0.0437344576
C,2.5474283149,1.8074215394,0.2528089474

C,3.597213243,-0.3552992155,-0.1963784426
C,3.7596368003,2.445361398,0.2804529359
H,1.6257984441,2.3513158912,0.4093126698
C,4.8479272898,0.2130119703,-0.223360611
H,3.4925524624,-1.4101892119,-0.4022980858
C,4.9907587134,1.6573895645,0.0546972893
C,-2.4053485314,0.3971433102,-0.0437339583
C,-2.547427083,1.807422336,-0.2528084775
C,-3.5972120354,-0.355298728,0.1963775478
C,-3.7596356633,2.4453620001,-0.2804531265
H,-1.6257971919,2.3513168087,-0.4093116079
C,-4.8479262036,0.2130122029,0.2233588638
H,-3.4925512069,-1.410188909,0.4022963987
C,-4.990757569,1.6573900399,-0.0546978758
O,-6.1239264887,2.2004444271,-0.0930678104
O,6.1239276104,2.200444028,0.0930667823
N,0.0000007685,0.6289858071,0.000000669
C,6.1100100513,-0.6147095434,-0.5387518496
C,5.7788746826,-2.0876192698,-0.8542856164
C,6.8358541398,-0.0289818203,-1.7771299537
C,7.0705792582,-0.6023771739,0.6783343028
H,5.3010766835,-2.5968703974,-0.0108664635
H,5.1220374779,-2.1839459827,-1.7261662247
H,6.7082731423,-2.6236860681,-1.0804898338
H,7.1298902476,1.0069907002,-1.6034932771
H,7.7345463814,-0.620062517,-1.9990784094
H,6.1829044581,-0.0665274703,-2.6576649113
H,7.9707098954,-1.1900549302,0.4529653305
H,7.3676024193,0.4174136392,0.9274017623
H,6.5856982622,-1.051506359,1.5537087052
C,3.8737648187,3.9591669116,0.5448770102
C,4.7066932018,4.2137488834,1.8274541496
C,4.5533532161,4.6588123179,-0.6601213646
C,2.4937833276,4.6179118531,0.7475509217
H,4.2218573504,3.754330393,2.6973919983
H,5.7114107054,3.8002697405,1.7274873019
H,4.7834030278,5.2930254737,2.0156895913
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H,4.6289611562,5.7380941727,-0.4723655351
H,5.5544665934,4.2588073923,-0.8276552588
H,2.6302030999,5.6907754851,0.9274432742
H,1.8513096375,4.5077462751,-0.1327589736
H,1.9616393722,4.2022687038,1.6102405661
C,-3.8737638702,3.9591675322,-0.5448770293
C,-2.493782318,4.6179133792,-0.7475476096
C,-4.7066894927,4.2137494509,-1.8274559681
C,-4.5533554807,4.6588121018,0.660120011
H,-1.8513108469,4.5077486987,0.1327640124
H,-1.9616358127,4.2022702109,-1.6102356738
H,-2.6302024004,5.6907768301,-0.9274408079
H,-5.7114070214,3.8002697976,-1.7274915107
H,-4.7833994026,5.2930260588,-2.0156912847
H,-4.2218514436,3.754331441,-2.6973928467
H,-4.6289639273,5.7380939337,0.4723642629
H,-5.5544688908,4.2588062771,0.8276516109
H,-3.9600789258,4.5163894512,1.5713684324
C,-6.1100090839,-0.6147097783,0.5387483796
C,-6.8358585382,-0.0289782901,1.7771215566
C,-7.0705737628,-0.6023833304,-0.6783414134
C,-5.7788729722,-2.0876178956,0.8542888661
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H,-7.1298946299,1.0069934467,1.6034801081
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H,-6.7082717956,-2.6236855638,1.08048952
H,-5.3010692421,-2.5968709017,0.0108740754
H,-5.1220406065,-2.1839406693,1.7261735506
C,1.5276241958,-2.805681324,0.1458818454
C,1.5896120232,-3.7474466521,-0.8946273359
C,2.2398688417,-3.0734886624,1.3290562689
C,2.3377596899,-4.919339476,-0.7583897476
H,1.0448605581,-3.5558319143,-1.8139859193
C,2.9849205947,-4.2457048944,1.4674978102
H,2.2054610813,-2.3526085689,2.1408376582
C,3.0363439739,-5.1755134424,0.4241242154
H,2.3723732277,-5.6326148849,-1.5776413839
H,3.5269793482,-4.4317196483,2.3909529158
H,3.6186883492,-6.086677461,0.5306700406
C,-1.5276251051,-2.8056802112,-0.1458783237
C,-2.2398719383,-3.0734870181,-1.3290515402
C,-1.5896126579,-3.7474450122,0.8946313495
C,-2.9849253558,-4.2457023776,-1.4674915512
H,-2.2054646461,-2.352607154,-2.1408331557
C,-2.3377618987,-4.9193370035,0.7583952565
H,-1.0448597008,-3.5558305399,1.8139891078
C,-3.0363482295,-5.1755105451,-0.4241175914
H,-3.5269857798,-4.4317167565,-2.3909457529
H,-2.3723751151,-5.6326120686,1.5776472052
H,-3.618693868,-6.0866738955,-0.5306622321

Cartesian Coordination of 2c^{-}

- 2373.0557597 hartree

C,0,0.69091066,-1.51572347,-0.01293315
C,0,-0.69092688,-1.51571047,0.01304134
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C,0,1.1374182,-0.12833237,-0.00776501
C,0,-2.46201422,0.37011911,-0.03088956
C,0,-2.76939854,1.66896681,-0.56120273
C,0,-3.54731642,-0.42513565,0.47371116
C,0,-4.05472681,2.13467418,-0.66713095
H,0,-1.94458641,2.27961098,-0.90842993
C,0,-4.84327775,0.00987134,0.49643291
H,0,-3.30225335,-1.37853555,0.91714309
C,0,-5.16390135,1.32786798,-0.10260273
C,0,2.46203584,0.37007296,0.03099502
C,0,2.76946465,1.66890495,0.56131878
C,0,3.5472985,-0.42517609,-0.47369893
C,0,4.0548041,2.13459976,0.66717158
H,0,1.94467898,2.27954913,0.90861026
C,0,4.84326064,0.0098214,-0.49650392
H,0,3.30219989,-1.3785586,-0.91715084
C,0,5.16394138,1.32778499,0.10258279
O,0,6.34258251,1.74554615,0.12019459
O,0,-6.3425814,1.74550622,-0.12050824
N,0,0.00001286,0.64527873,0.0000777
C,0,-5.97183082,-0.82051888,1.13683219
C,0,-5.45136923,-2.14416128,1.73379478
C,0,-6.63441704,-0.0209817,2.28836635

C,0,-7.04034404,-1.17676354,0.0711711
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H,0,-4.71524558,-1.97480673,2.5277751
H,0,-6.2917753,-2.69178307,2.17567606
H,0,-7.06380215,0.91253464,1.9227642
H,0,-7.43149091,-0.62130881,2.74598233
H,0,-5.89923437,0.21224735,3.06775095
H,0,-7.83834894,-1.77578101,0.52930287
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H,0,-6.59606836,-1.77053141,-0.73671919
C,0,-4.38029761,3.4804138,-1.34329128
C,0,-5.40794134,3.27101874,-2.48680713
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H,0,-5.1943751,5.4216419,-0.77638108
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H,0,-2.34470152,4.34188604,-1.23012153
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C,0,5.40819852,3.27093075,2.48672012
C,0,4.96227988,4.46326362,0.29410431
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[S7 (the complete form of ref. 16)] *Gaussian 09*, revision D.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Ö. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski and D. J. Fox, Gaussian, Inc., Wallingford CT, 2013.

4. Solution-state properties

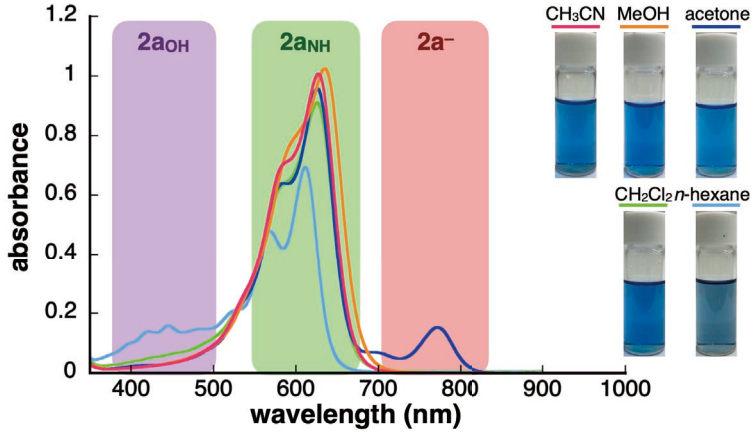

Fig. S39 UV/vis absorption spectra of **2a** (1.0×10^{-5} M) in CH_3CN (dielectric constant ε_r: 35.94; red), MeOH (ε_r: 32.66; orange), acetone (ε_r: 20.56; blue), CH_2Cl_2 (ε_r: 8.93; green), and *n*-hexane (ε_r: 1.88; light blue) and photographs under visible light.

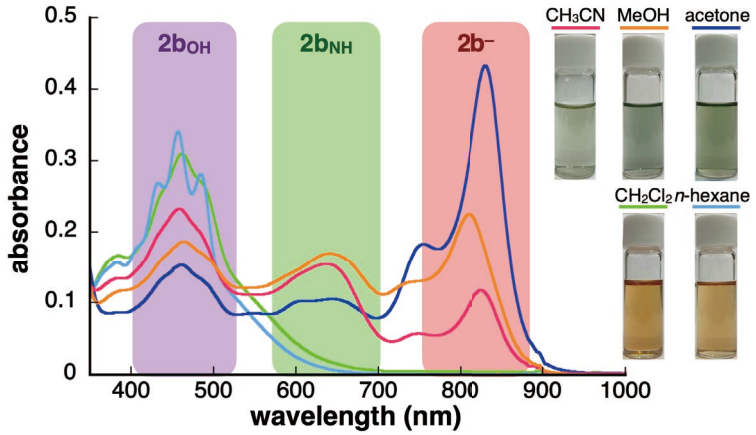

Fig. S40 UV/vis absorption spectra of **2b** (1.0×10^{-5} M) in CH_3CN (red), acetone (blue), MeOH (orange), CH_2Cl_2 (green), and *n*-hexane (light blue) and photographs under visible light. In non-polar solvents, such as CH_2Cl_2 and *n*-hexane, **2b** formed phenol (OH) form **2b**$_{OH}$ and in polar solvents, such as MeOH and CH_3CN, quinoidal (NH) form **2b**$_{NH}$ was exhibited around 650 nm. In acetone, **2b** showed a near-infrared absorption (λ_{max} = 830 nm), which was also observed in MeOH and CH_3CN, suggesting the deprotonation of **2b** (see Fig. S57).

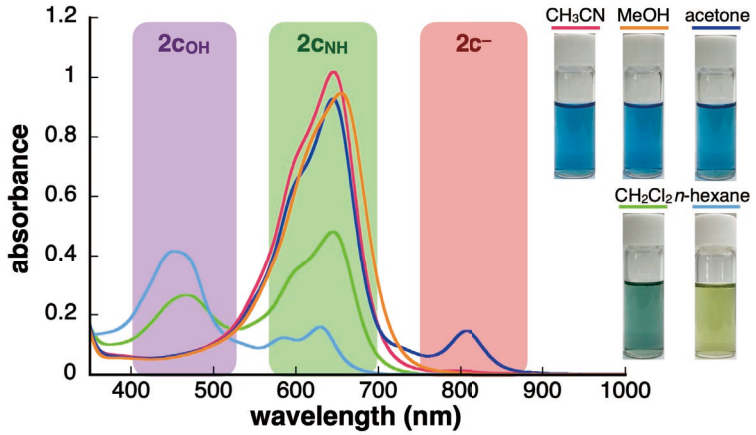

Fig. S41 UV/vis absorption spectra of **2c** (1.0×10^{-5} M) in CH_3CN (red), MeOH (orange), acetone (blue), CH_2Cl_2 (green), and *n*-hexane (light blue) and photographs under visible light (inset).

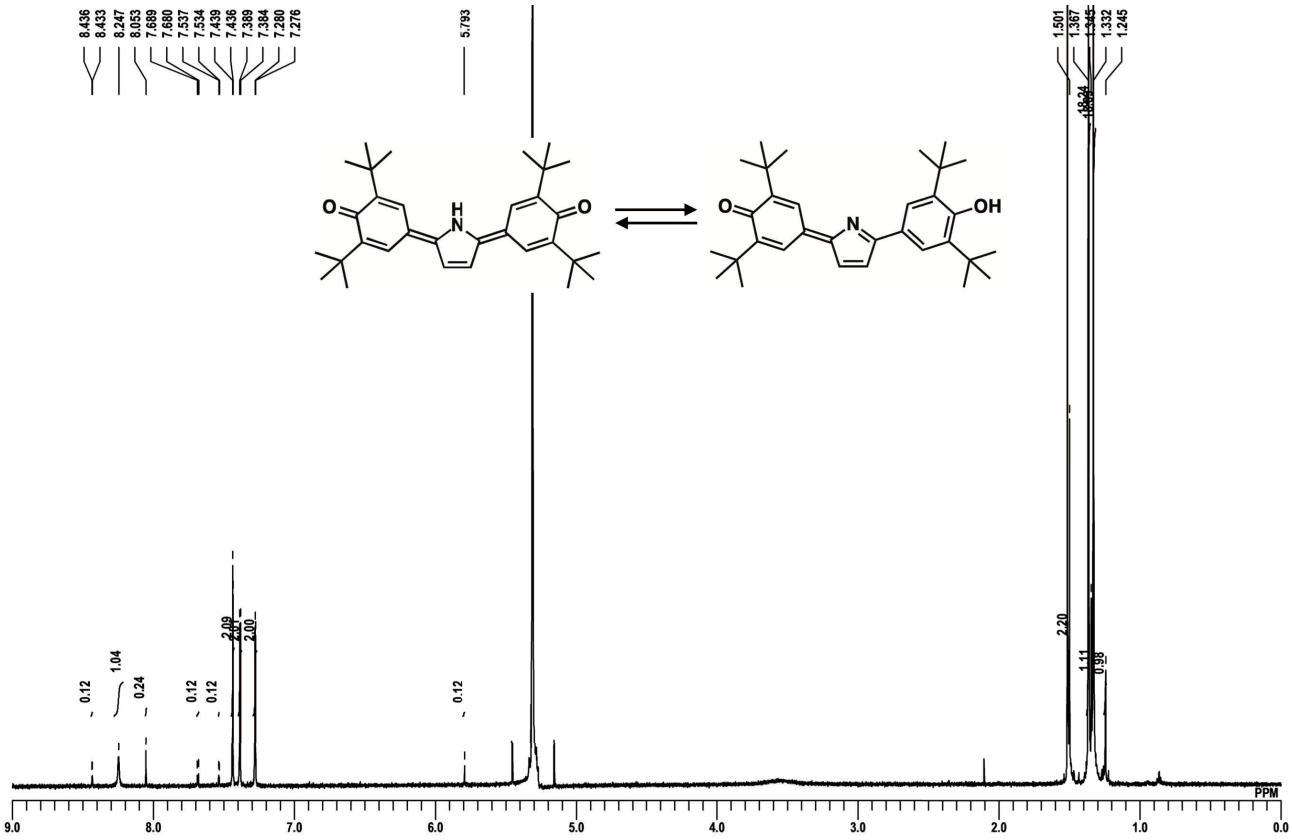

Fig. S42 ^{1}H NMR of **2a** in CD_2Cl_2, wherein **2a** was observed as a mixture of NH and OH tautomers (**2a**$_{NH}$ and **2a**$_{OH}$) in the ratio of 89:11. Therefore, the Gibbs energy for the NH/OH tautomerization of **2a** was estimated as 1.23 kcal/mol at 293 K. Chemical shift: δ (ppm) quinoidal (NH) form 8.25 (s, 1H, NH), 7.44 (d, J = 1.8 Hz, 2H, pyrrole-H), 7.39 (d, J = 3.0 Hz, 2H, quinone methide CH), 7.28 (d, J = 2.4 Hz, 2H, quinone methide CH), 1.37 (s, 18H, $C(CH_3)_3$), 1.33 (s, 18H, $C(CH_3)_3$); phenol (OH) form 8.43 (d, J = 1.8 Hz, 1H, quinone methide CH), 8.05 (s, 2H, phenol CH), 7.68 (d, J = 7.2 Hz, 1H, pyrrole-H), 7.54 (d, J = 1.8 Hz, 1H, quinone methide CH), 5.79 (s, 1H, phenol OH), 1.50 (s, 18H, $C(CH_3)_3$), 1.35 (s, 9H, $C(CH_3)_3$), 1.25 (s, 9H, $C(CH_3)_3$). The other pyrrole-H signal of **2a**$_{OH}$ is overlapped with that of **2a**$_{NH}$. In contrast to the spectrum, the ^{1}H NMR in CD_3CN (Fig. S7) shows only **2a**$_{NH}$.

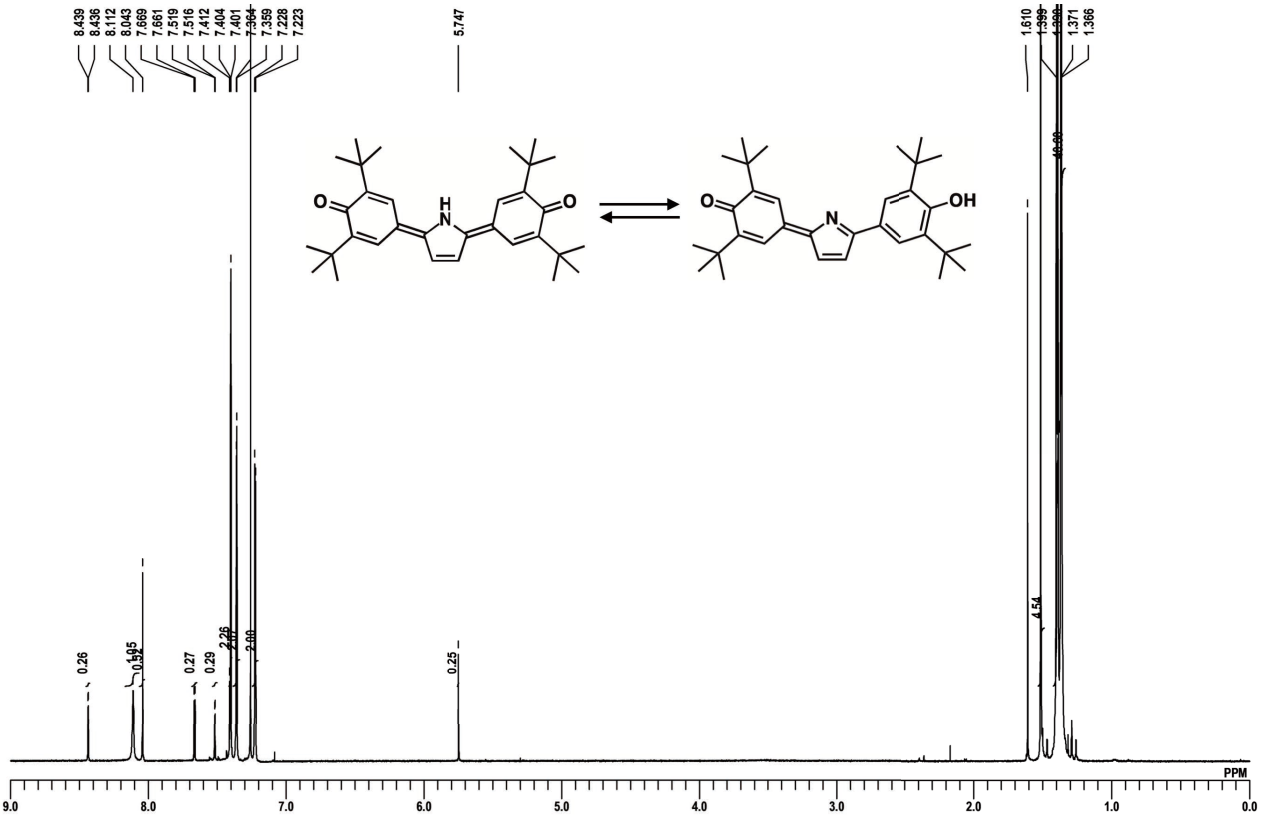

Fig. S43 ^{1}H NMR spectrum of **2a** in $CDCl_3$ at 20 °C, wherein **2a** was observed as a mixture of NH and OH tautomers (**2a**$_{NH}$ and **2a**$_{OH}$) in the ratio of 79:21. Therefore, the Gibbs energy for the NH/OH tautomerization of **2a** was estimated as 0.78 kcal/mol at 293 K. Chemical shift: δ (ppm) quinoidal (NH) form 8.11 (s, 1H, NH), 7.40 (d, J = 1.8 Hz, 2H, pyrrole-H), 7.36 (d, J = 3.0 Hz, 2H, quinone methide CH), 7.23 (d, J = 3.0 Hz, 2H, quinone methide CH), 1.40 (s, 18H, $C(CH_3)_3$), 1.37 (s, 18H, $C(CH_3)_3$); phenol (OH) form 8.44 (d, J = 1.8 Hz, 1H, quinone methide CH), 8.04 (s, 2H, phenol CH), 7.67(d, J = 4.2 Hz, 1H, pyrrole-H), 7.52 (d, J = 1.8 Hz, 1H, quinone methide CH), 7.41 (d, J = 1.8 Hz, 1H, Ar-H), 5.75 (s, 1H, phenol OH), 1.61 (s, 18H, $C(CH_3)_3$), 1.39 (s, 9H, $C(CH_3)_3$), 1.37 (s, 9H, $C(CH_3)_3$). The other pyrrole-H signal of **2a**$_{OH}$ is overlapped with that of **2a**$_{NH}$.

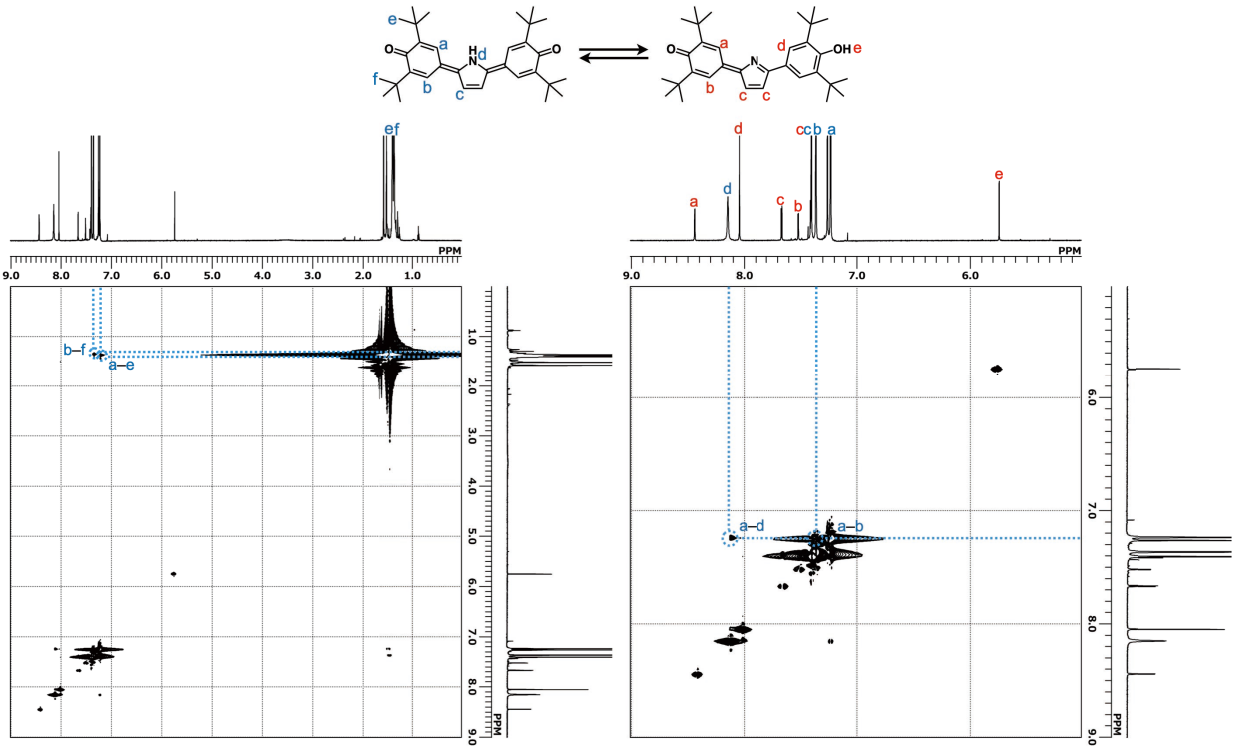

Fig. S44 NOESY of **2a** (overview chart (left) and enlarged version (right)) in $CDCl_3$ at 20 °C. The quinone methide CH signal of $\mathbf{2a}_{OH}$ at the pyrrole N side shifted downfield due to the hydrogen bonding with pyrrole N.

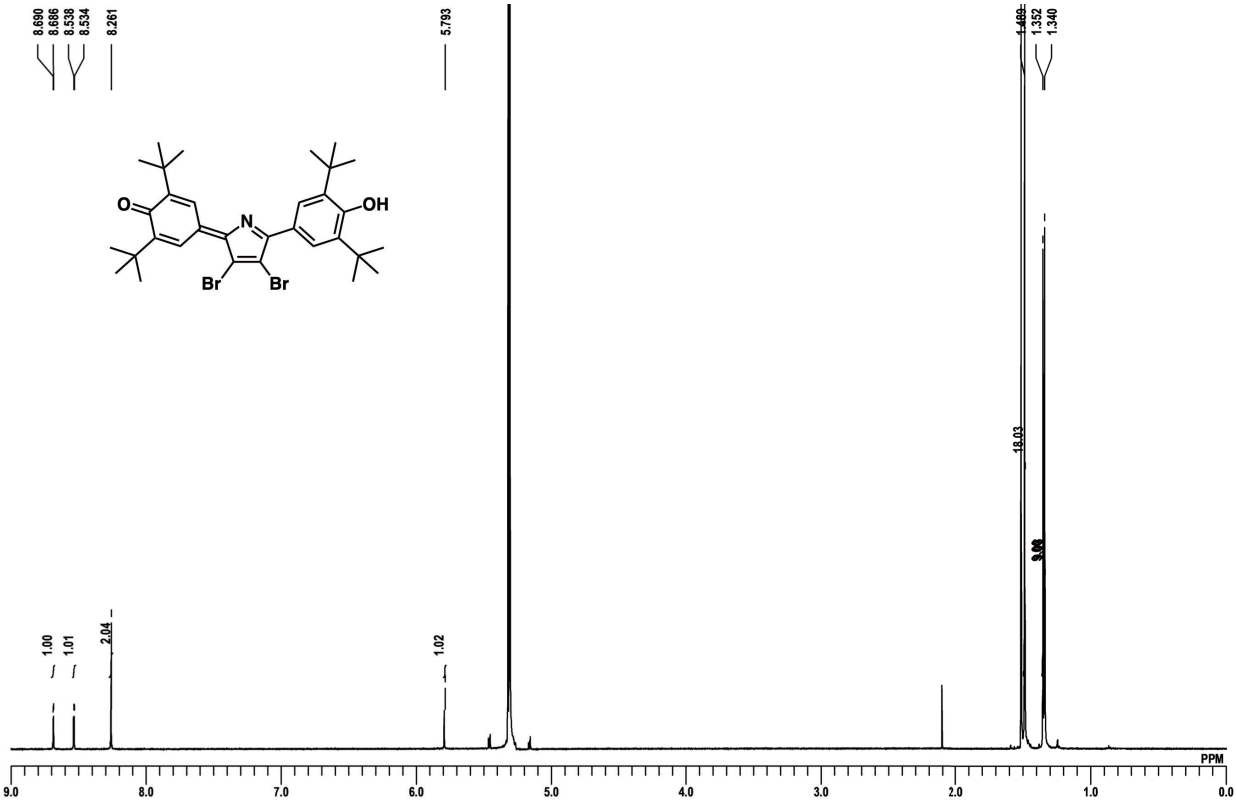

Fig. S45 ^{1}H NMR of **2b** in CD_2Cl_2 at 20 °C. Chemical shift: δ (ppm); phenol (OH) form: δ (ppm) 8.69 (d, J = 2.4 Hz, 1H, quinone methide CH), 8.54 (d, J = 2.4 Hz, 1H, quinone methide CH), 8.26 (s, 2H, phenol CH), 5.79 (s, 1H, OH), 1.49 (s, 18H, $C(CH_3)_3$), 1.35 (s, 9H, $C(CH_3)_3$), 1.34 (s, 9H, $C(CH_3)_3$). The signals of two kinds of quinone methide CH could not be distinguished by the NOESY, as the appropriate hydrogens for the correlation, such as NH and β-CH, are missing. The ^{1}H NMR in $CDCl_3$, showing the similar feature, is shown in Fig. S8.

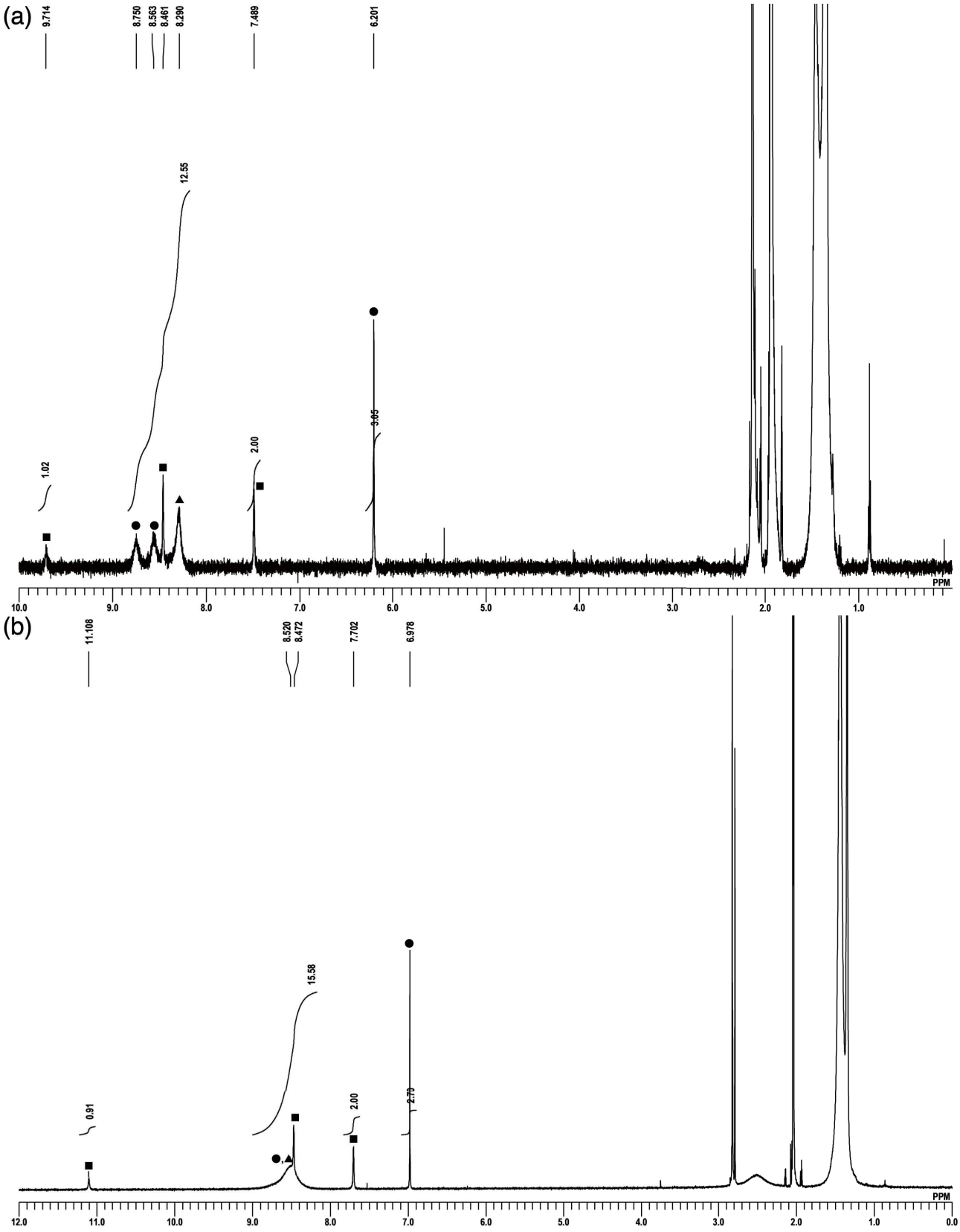

Fig. S46 ^{1}H NMR of **2b** in (a) CD_3CN and (b) acetone-d_6 showing the signals derived from the mixture of $\mathbf{2b}_{NH}$, $\mathbf{2b}_{OH}$, and $\mathbf{2b}^-$. Square, circle, and triangle marks represent $\mathbf{2b}_{NH}$, $\mathbf{2b}_{OH}$, and $\mathbf{2b}^-$, respectively. The relative amounts of $\mathbf{2b}_{NH}$ and $\mathbf{2b}_{OH}$ were estimated from their integral ratios at 7.49 and 6.21 ppm for CD_3CN and at 7.70 and 6.98 ppm for acetone-d_6. Moreover, those of $\mathbf{2b}^-$ were obtained by subtracting the integrals of the other forms from the broad signals at 8.75–8.29 ppm (CD_3CN) and 8.52 ppm (acetone-d_6), providing the ratios of $\mathbf{2b}_{NH}$, $\mathbf{2b}_{OH}$, and $\mathbf{2b}^-$ as 1:1.53:1.87 (CD_3CN) and 1:1.35:2.72 (acetone-d_6).

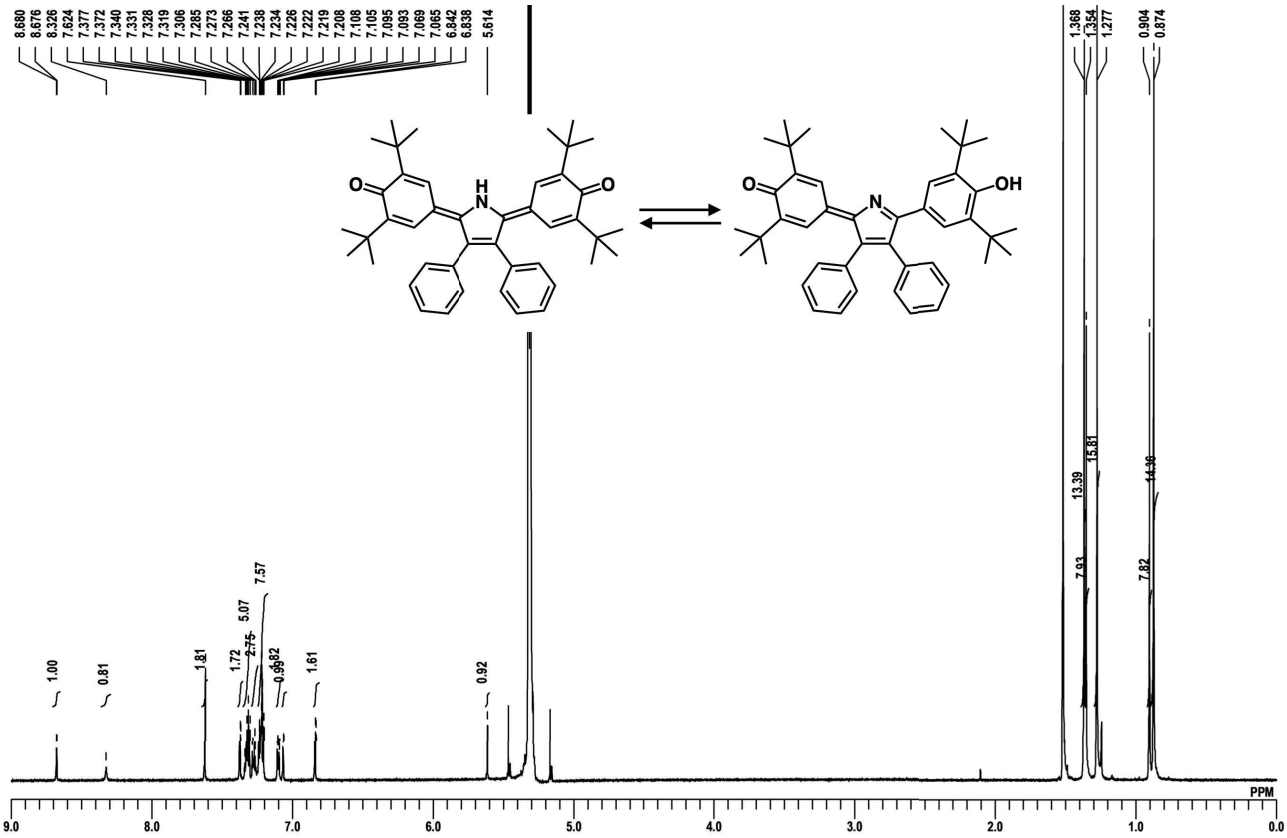

Fig. S47 ^{1}H NMR of **2c** in CD_2Cl_2, wherein **2c** was observed as a mixture of NH and OH tautomers in the ratio of 45:55. Therefore, the Gibbs energy for the NH/OH tautomerization of **2c** was estimated as –0.13 kcal/mol at 293 K. Chemical shift: δ (ppm) quinoidal (NH) form 8.33 (s, 1H, NH), 7.37 (d, J = 3.0 Hz, 2H, quinone methide CH), 7.34–7.21/7.11–7.09 (m, 10H, Ph-H), 6.84 (d, J = 2.4 Hz, 2H, quinone methide CH), 1.37 (s, 18H, $C(CH_3)_3$), 0.87 (s, 18H, $C(CH_3)_3$); phenol (OH) form 8.68 (d, J = 2.4 Hz, 1H, quinone methide CH), 7.62 (s, 2H, phenol CH), 7.34–7.21 and 7.11–7.09 (m, 10H, Ph-H), 7.07 (d, J = 2.4 Hz, 1H, quinone methide CH), 5.61 (s, 1H, phenol OH), 1.35 (s, 9H, $C(CH_3)_3$), 1.28 (s, 18H, $C(CH_3)_3$), 0.90 (s, 9H, $C(CH_3)_3$). In contrast to the spectrum, the ^{1}H NMR in CD_3CN (Fig. S9) shows only $\mathbf{2c}_{NH}$.

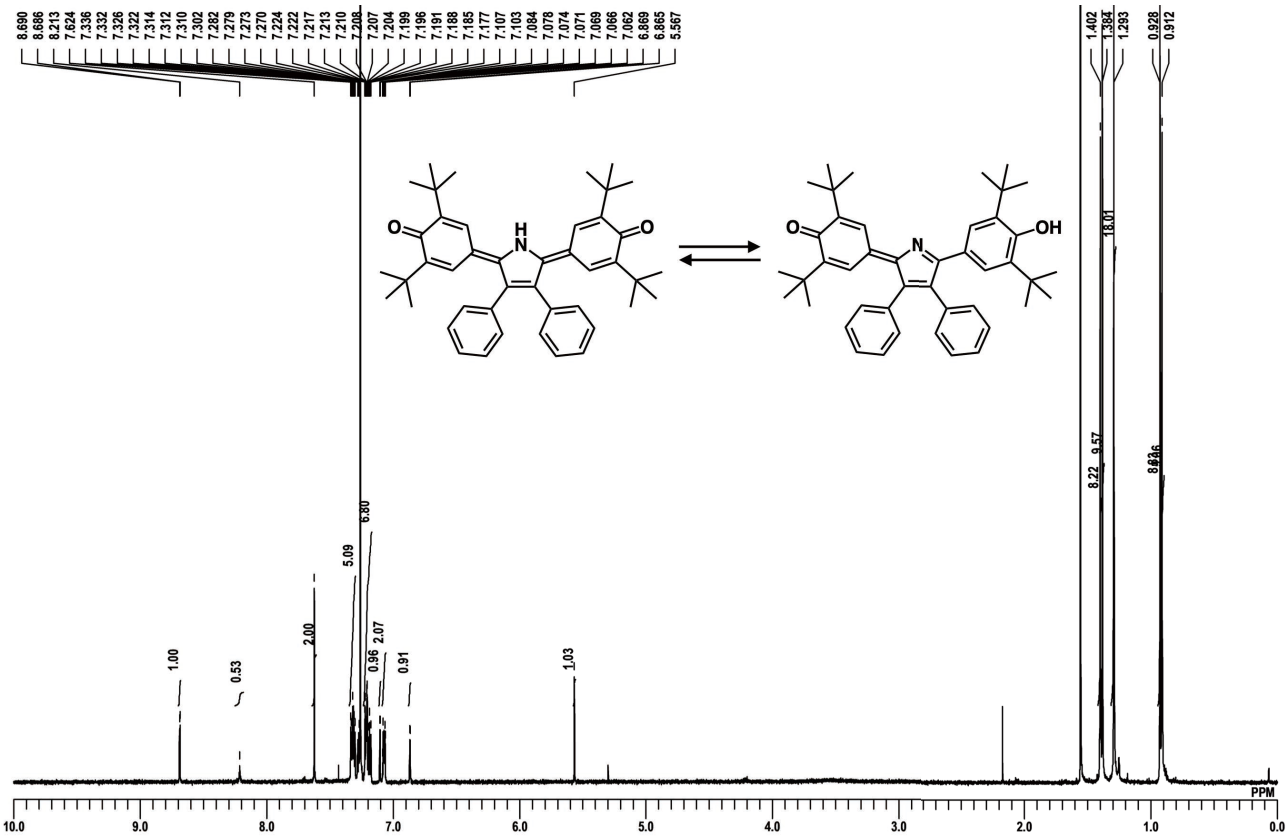

Fig. S48 ^{1}H NMR spectrum of **2c** in $CDCl_3$ at 20 °C, wherein **2c** was observed as a mixture of NH and OH tautomers in the ratio of 31:69. Therefore, the Gibbs energy for the NH/OH tautomerization of **2c** was estimated as –0.46 kcal/mol at 293 K. Chemical shift: δ (ppm) quinoidal (NH) form 8.69 (s, 1H, NH), 7.62–7.18/7.08–7.06 (m, 12H, Ph-H and quinone methide CH), 6.87 (d, J = 2.4 Hz, 2H, quinone methide CH), 1.39 (s, 18H, $C(CH_3)_3$), 0.91 (s, 18H, $C(CH_3)_3$); phenol (OH) form 8.69 (d, J = 2.4 Hz, 1H, quinone methide CH), 7.62 (s, 2H, phenol CH), 7.62–7.18 and 7.08–7.06 (m, 10H, Ph-H), 7.11 (d, J = 2.4 Hz, 1H, quinone methide CH), 5.57 (s, 1H, phenol OH), 1.40 (s, 9H, $C(CH_3)_3$), 1.29 (s, 18H, $C(CH_3)_3$), 0.93 (s, 9H, $C(CH_3)_3$).

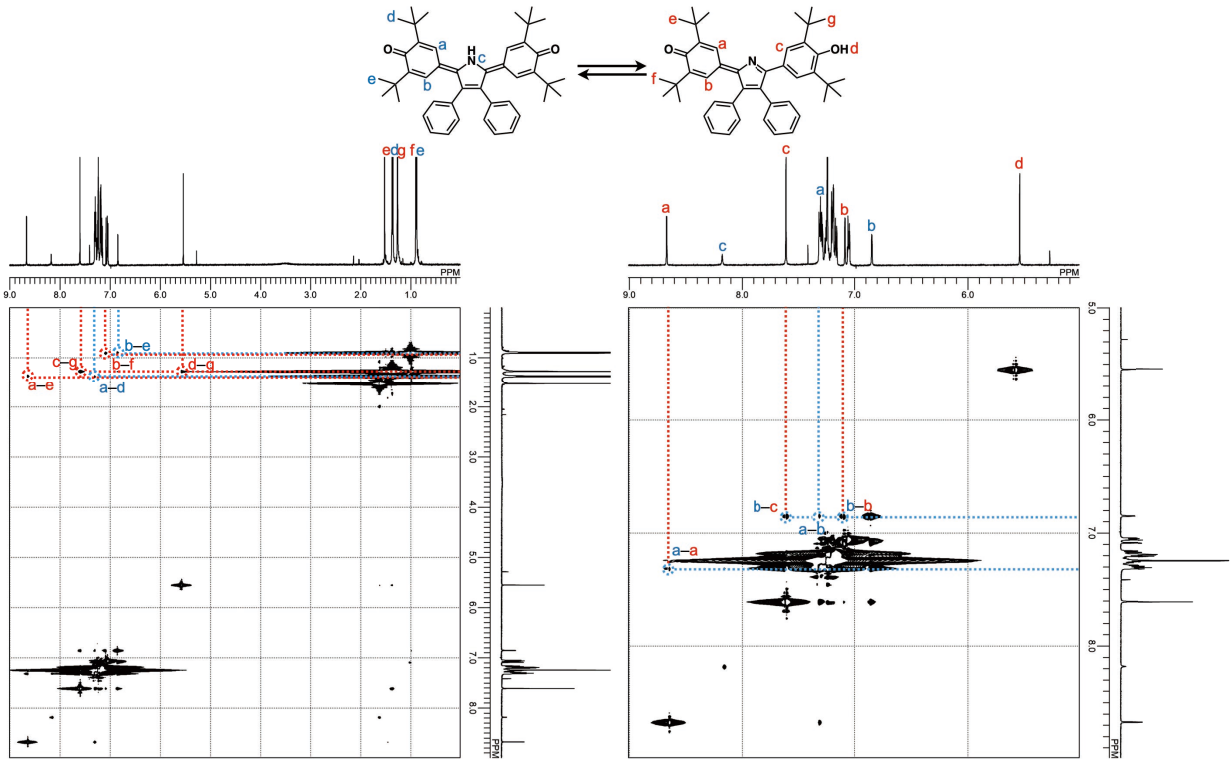

Fig. S49 NOESY of **2c** (overview chart (left) and enlarged version (right)) in $CDCl_3$ at 20 °C. The quinone methide CH signal of $\mathbf{2c}_{OH}$ at the pyrrole N side shifted downfield due to the hydrogen bonding with pyrrole N, whereas the quinone methide CH signals of $\mathbf{2c}_{OH}$ and $\mathbf{2c}_{NH}$ at the phenyl side shifted upfield due to the aromatic ring current effect of β-phenyl units.

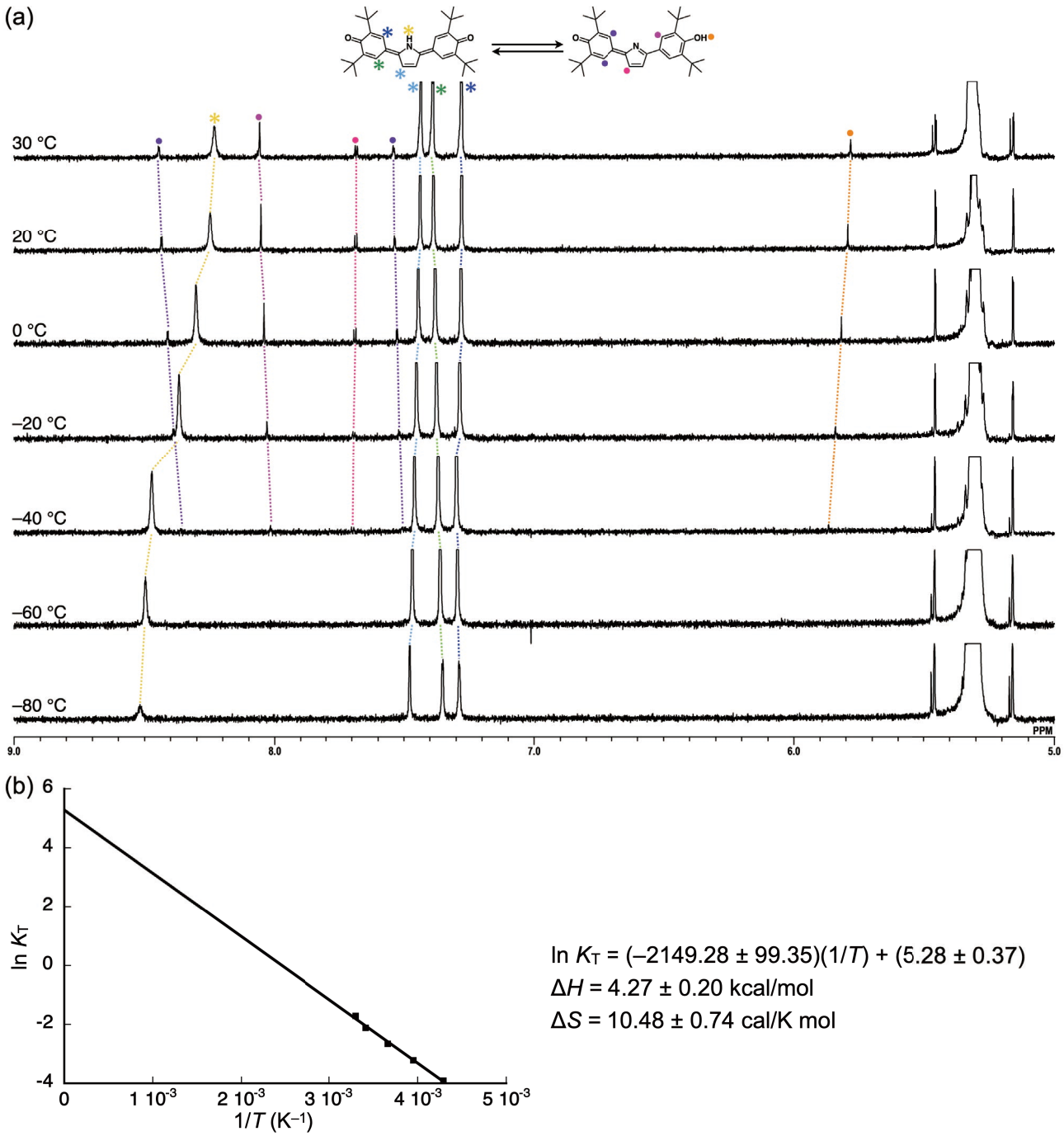

Fig. S50 (a) VT ^{1}H NMR of **2a** in CD_2Cl_2 (1×10^{-3} M) and (b) van't Hoff plot (R = 0.997).

Table S2 Tautomeric ratios and ln K_T values of **2a** at various temperatures. Tautomeric ratios were estimated from the corresponding ^{1}H NMR integrals.

T (K)	$\mathbf{2a}_{NH}$:$\mathbf{2a}_{OH}$	ln K_T
303	1:0.18	–1.71
293	1:0.12	–2.12
273	1:0.07	–2.66
253	1:0.04	–3.22
233	1:0.02	–3.91
213	1:0	–
193	1:0	–

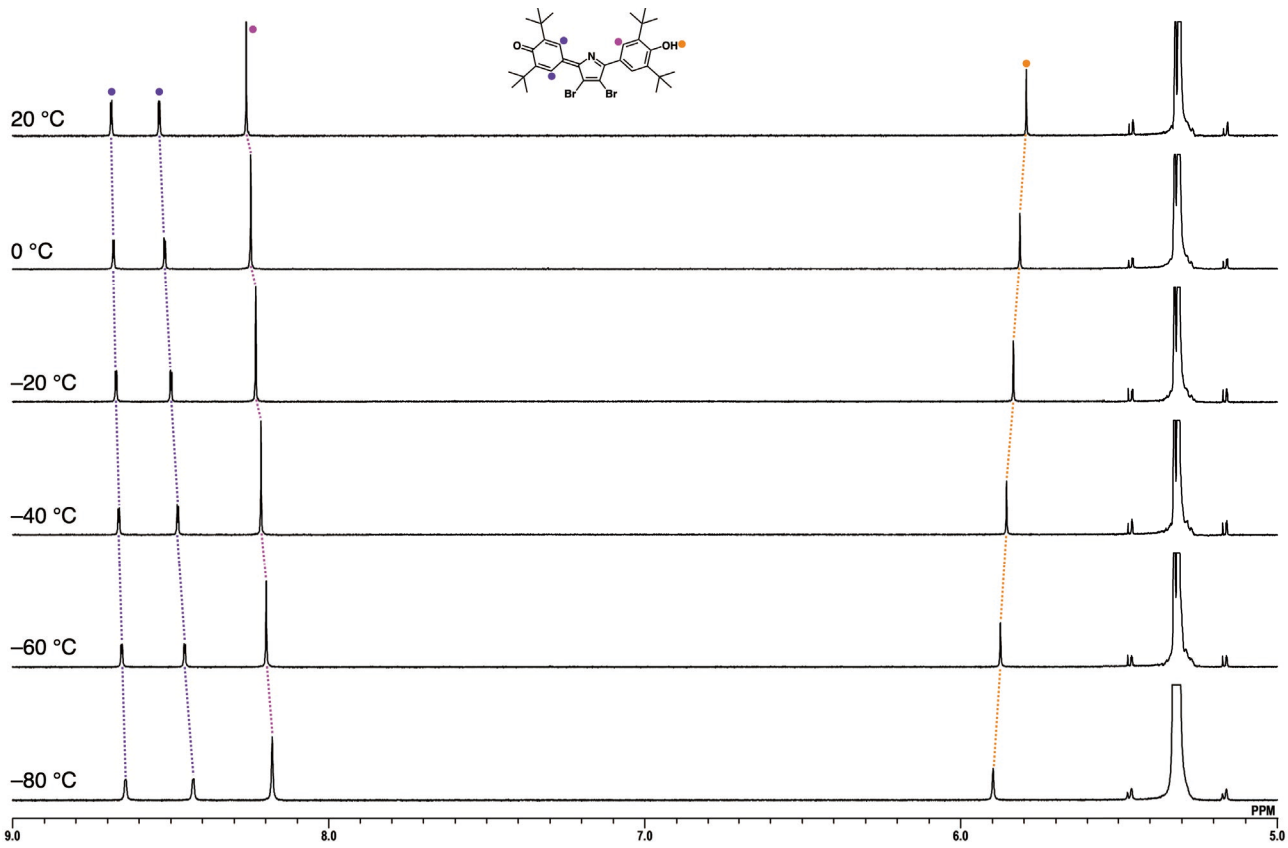

Fig. S51 VT ^{1}H NMR of **2b** in CD_2Cl_2 (1×10^{-3} M), wherein only $\mathbf{2b}_{OH}$ was observed.

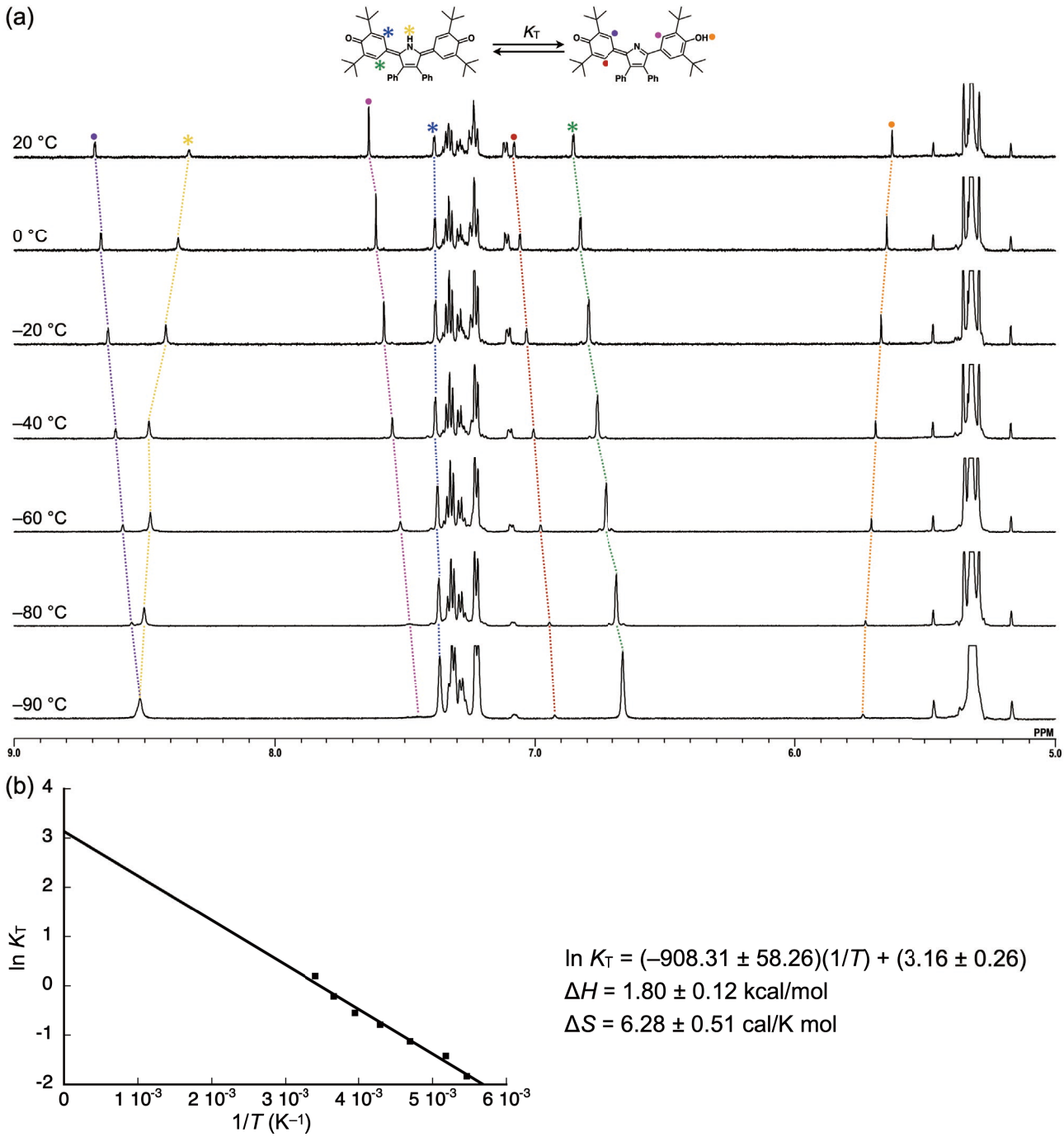

Fig. S52 (a) VT ^{1}H NMR of **2c** in CD_2Cl_2 (1×10^{-3} M) and (b) van't Hoff plot (R = 0.990).

Table S3 Tautomeric ratios and ln K_T values of **2c** at various temperatures. Tautomeric ratios were estimated from the corresponding ^{1}H NMR integrals.

T (K)	$\mathbf{2c}_{NH}$:$\mathbf{2c}_{OH}$	ln K_T
293	1:1.24	0.22
273	1:0.81	–0.22
253	1:0.58	–0.55
233	1:0.45	–0.79
213	1:0.32	–1.12
193	1:0.24	–1.42
183	1:0.16	–1.83

5. Anion-binding behaviors

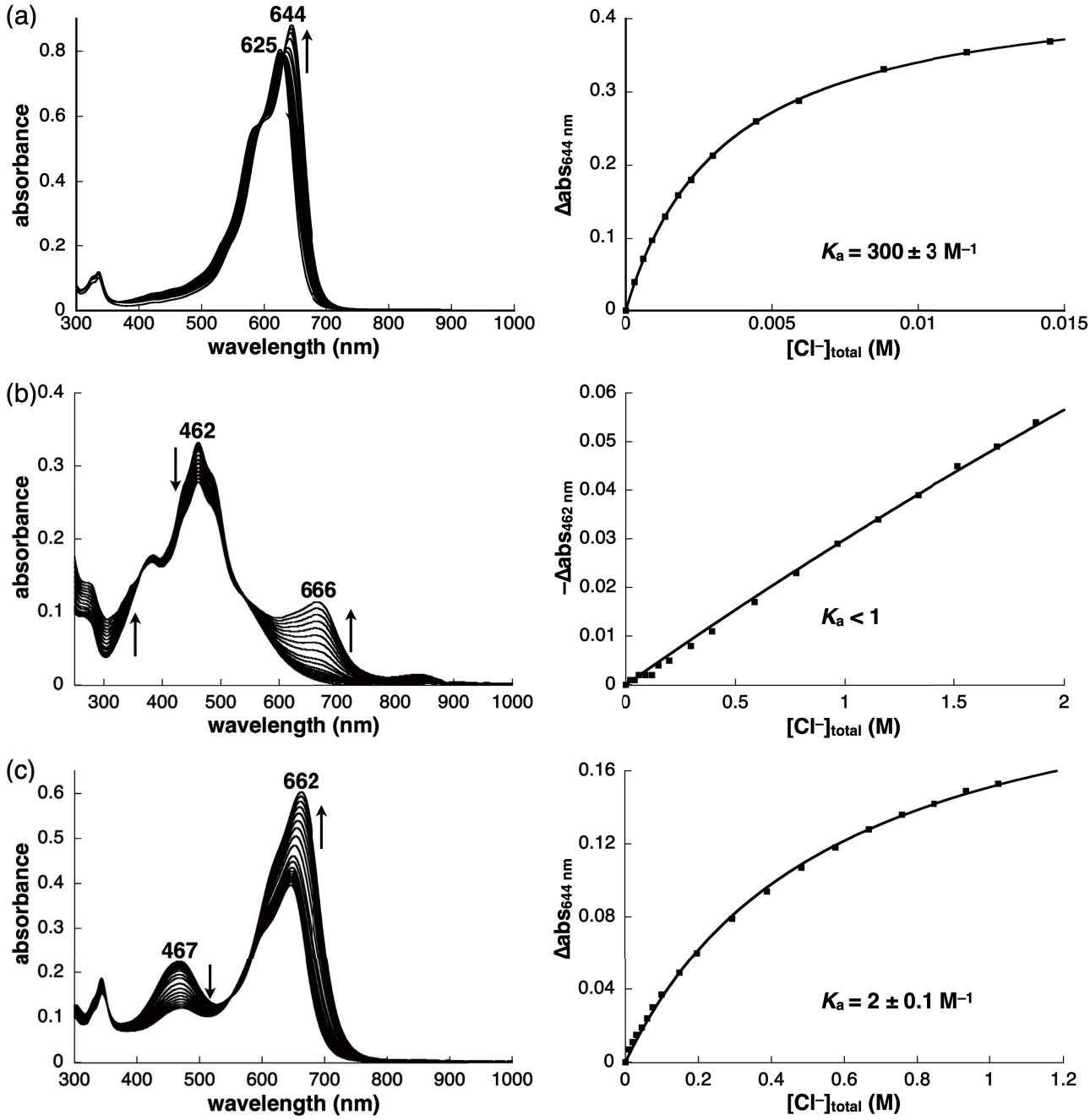

Fig. S53 UV/vis absorption spectral changes (left) and titration plots and 1:1 fitting curves (right) of (a) **2a** (R = 1.000), (b) **2b** (R = 0.999), and (c) **2c** (R = 0.999) (1.0×10^{-5} M) upon the addition of Cl^- as a tetrabutylammonium (TBA) salt in CH_2Cl_2 at 20 °C.

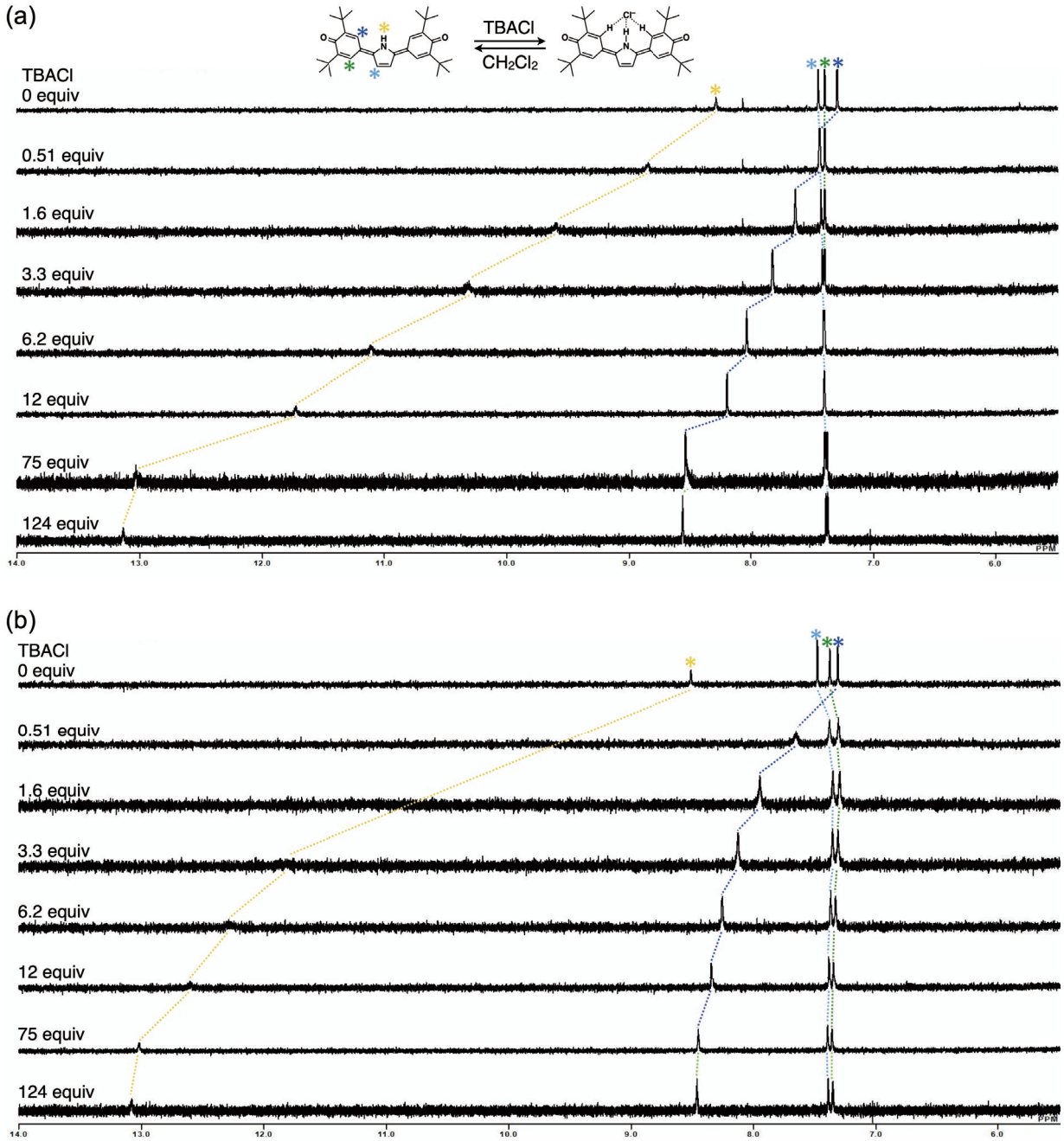

Fig. S54 ^{1}H NMR spectral changes of **2a** (1×10^{-3} M) upon the addition of Cl^- (0–124 equiv) added as a TBA salt in CD_2Cl_2 at (a) 20 °C and (b) –50 °C.

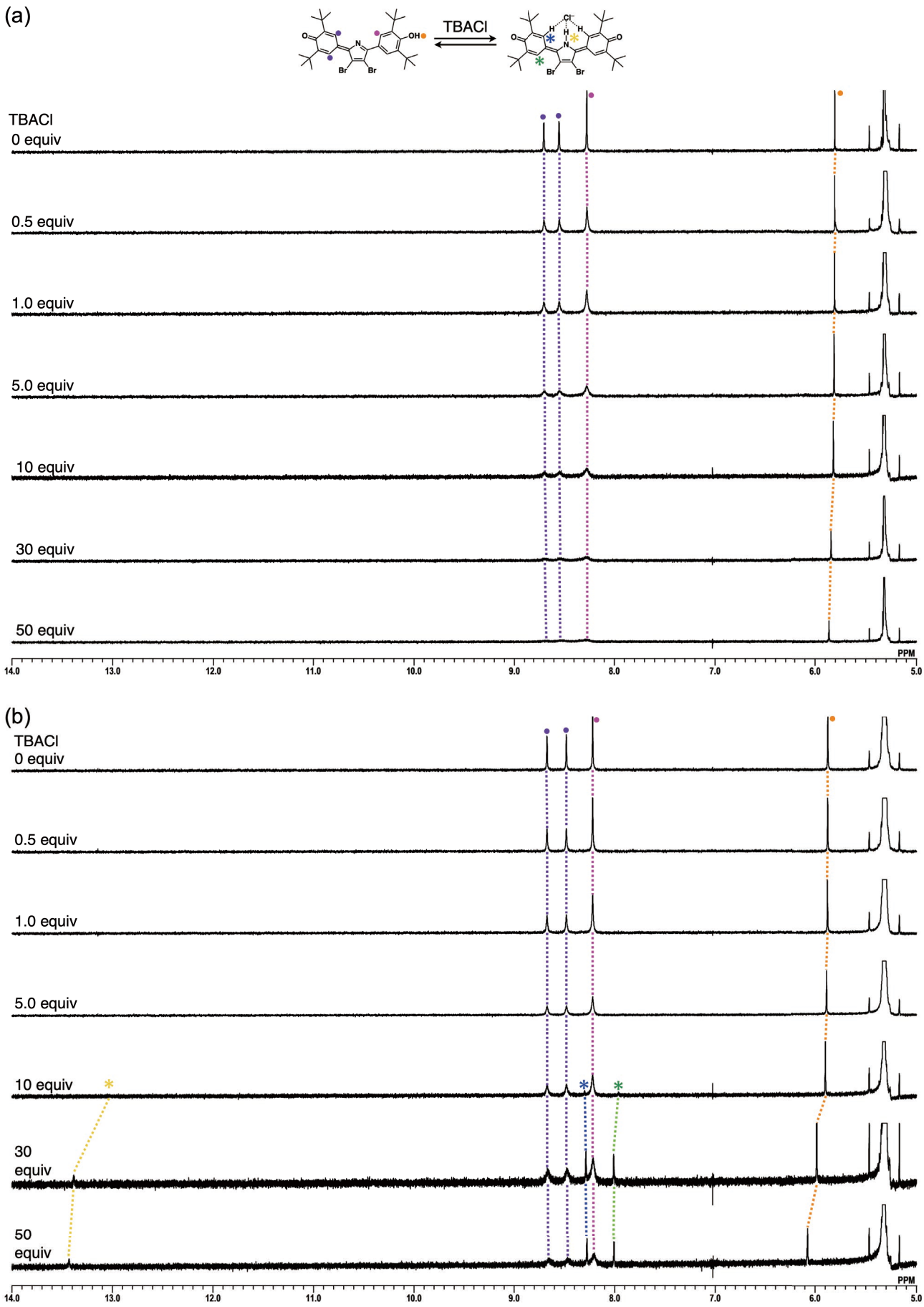

Fig. S55 ^{1}H NMR spectral changes of **2b** (1×10^{-3} M) upon the addition of Cl^{-} (0–124 equiv) added as a TBA salt in CD_2Cl_2 at (a) 20 °C and (b) –50 °C.

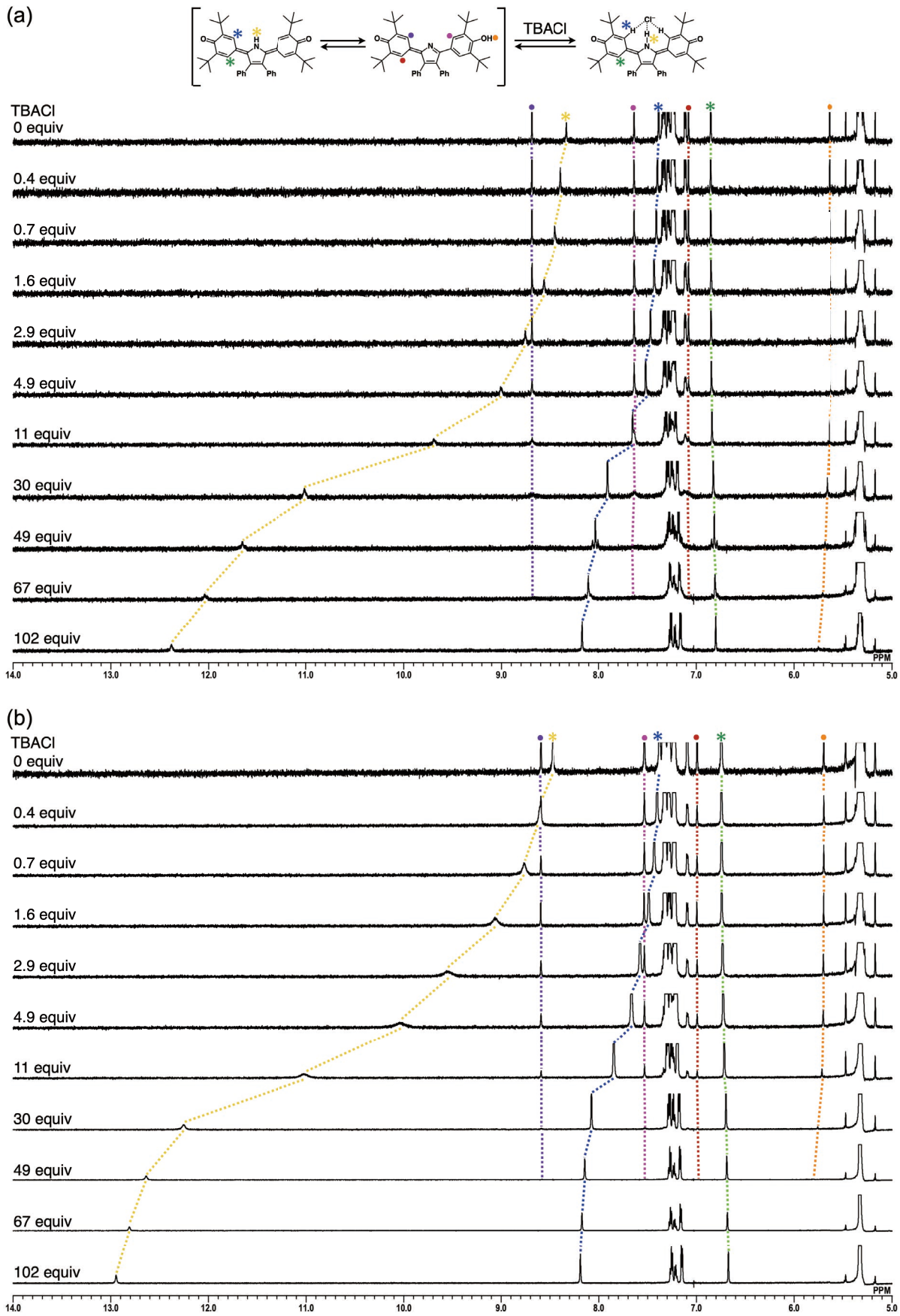

Fig. S56 ^{1}H NMR spectral changes of **2c** (1×10^{-3} M) upon the addition of Cl^- (0–124 equiv) added as a TBA salt in CD_2Cl_2 at (a) 20 °C and (b) –50 °C.

6. Deprotonation behaviors

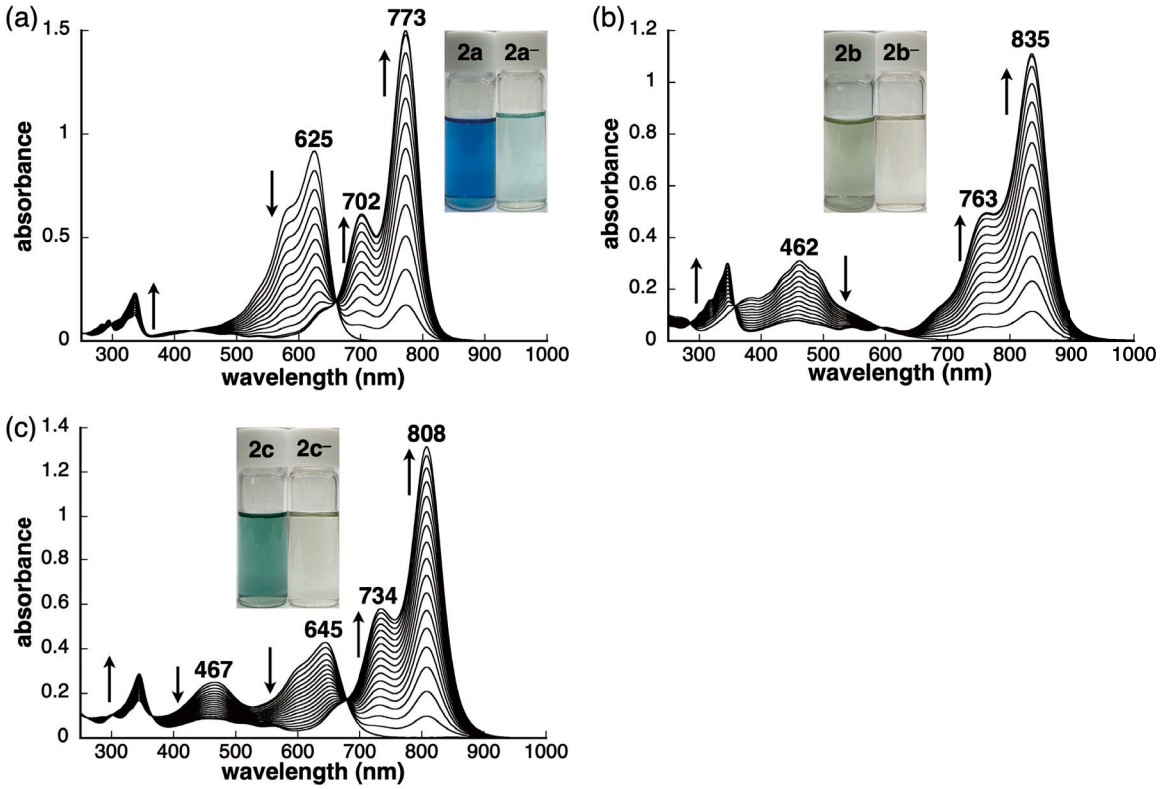

Fig. S57 UV/vis absorption spectral changes of (a) **2a**, (b) **2b**, and (c) **2c** (1.0×10^{-5} M) upon the addition of OH^- as a TBA salt in CH_2Cl_2. UV/vis absorption spectral changes of **2a** upon the addition of OAc^- as a TBA salt were similar to those of upon the addition of OH^-.

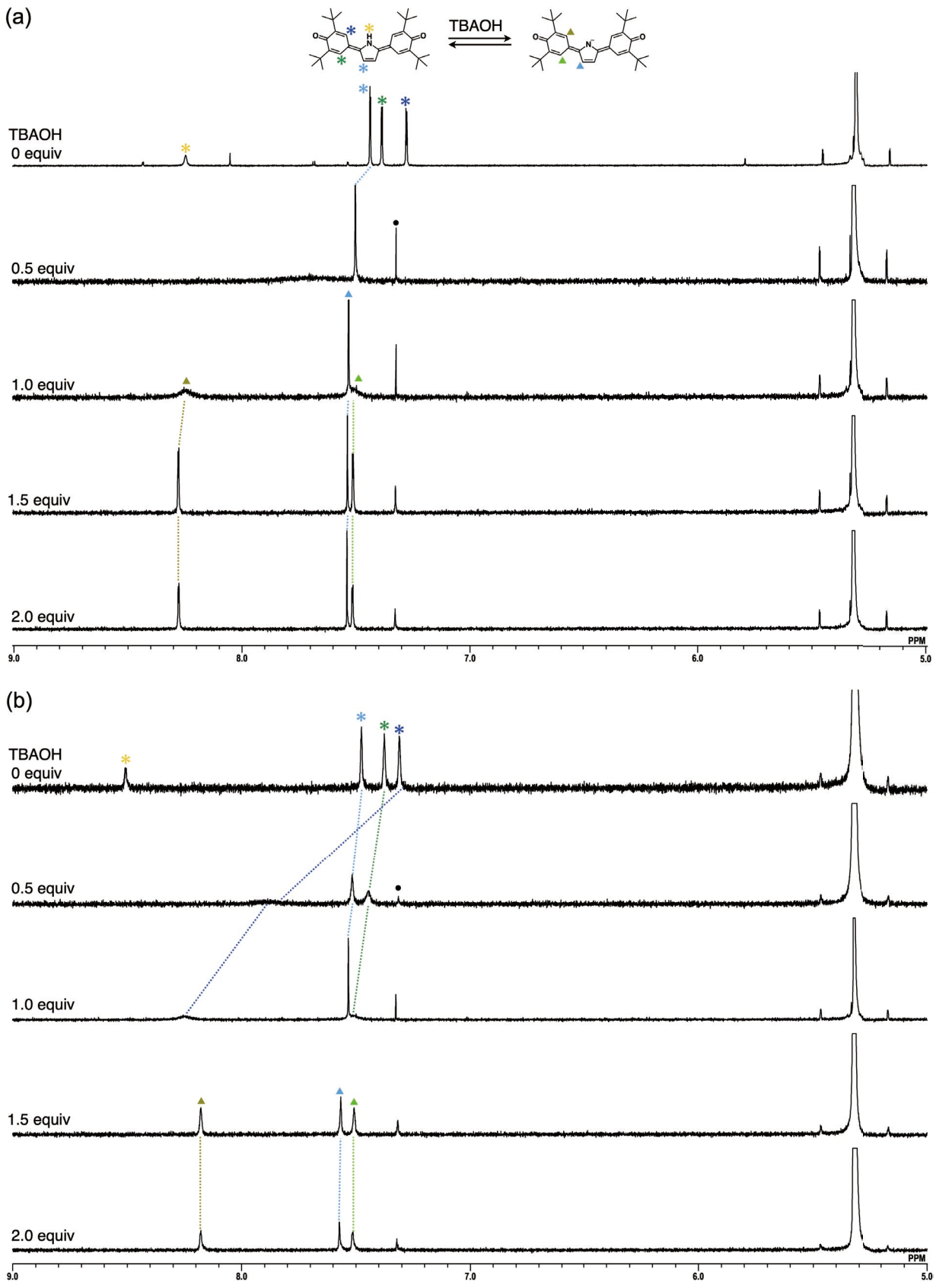

Fig. S58 ^{1}H NMR spectral changes of **2a** (1×10^{-3} M) upon the addition of OH^- (0–2.0 equiv) added as a TBA salt in CD_2Cl_2 at (a) 20 °C and (b) –50 °C. The signals labelled by black circles are derived from unidentified species in TBAOH as purchased. ^{1}H NMR spectral changes of **2a** upon the addition of OAc^- a TBA salt were similar to those of upon the addition of OH^-. The signals shifts were briefly discussed in the caption of Fig. S38. The tentative coalescence of the signals, especially those of two kinds of quinone methide CH, are derived from the fast exchange between **2a** and **2a**$^-$.

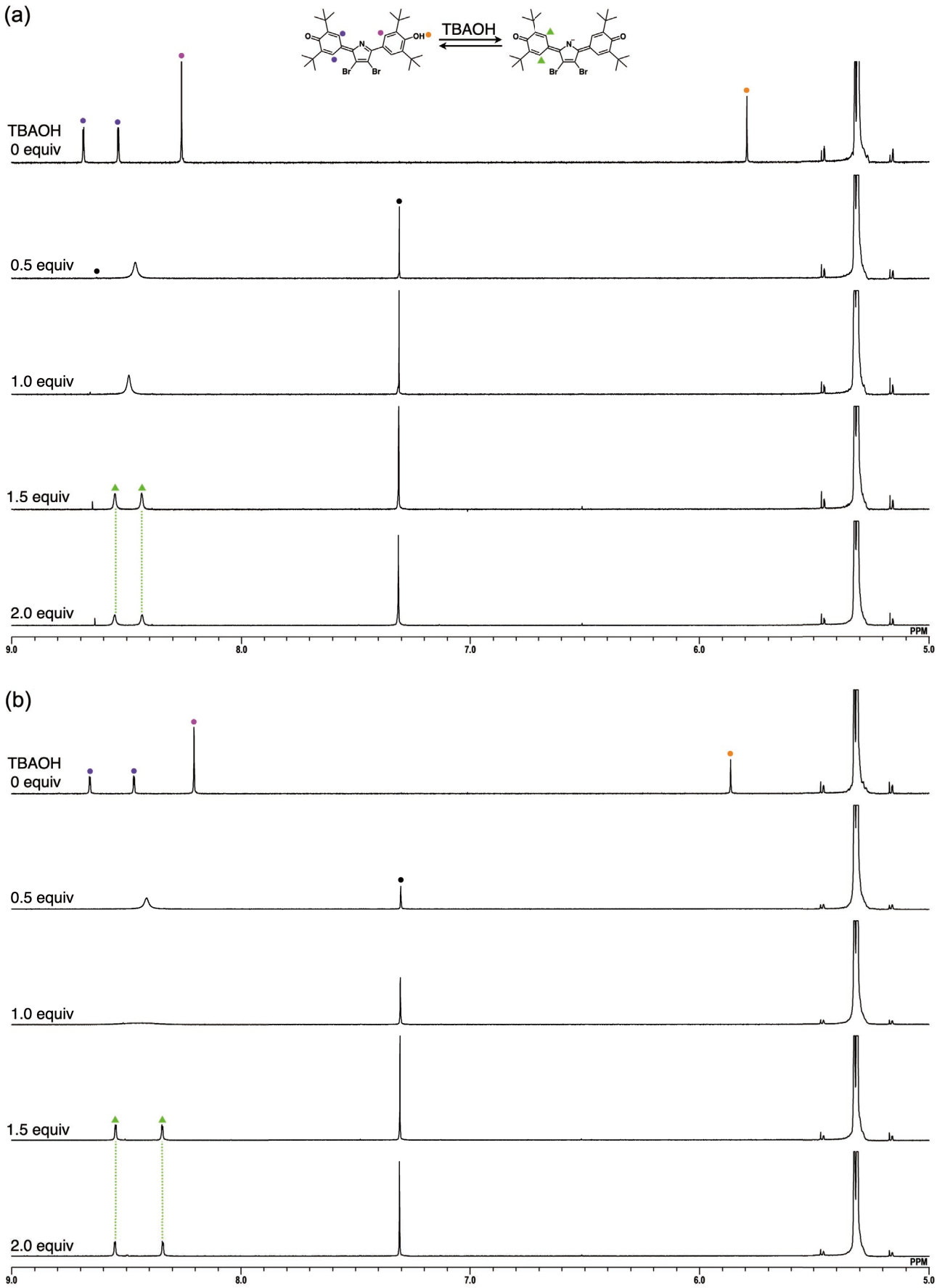

Fig. S59 ^{1}H NMR spectral changes of **2b** (1×10^{-3} M) upon the addition of OH^- (0–2.0 equiv) added as a TBA salt in CD_2Cl_2 at (a) 20 °C and (b) –50 °C. The signals labelled by black circles are derived from unidentified species in TBAOH as purchased. The tentative coalescence of the signals, especially those of quinone methide and phenol CH, are derived from the fast exchange between **2b** and **2b**$^-$.

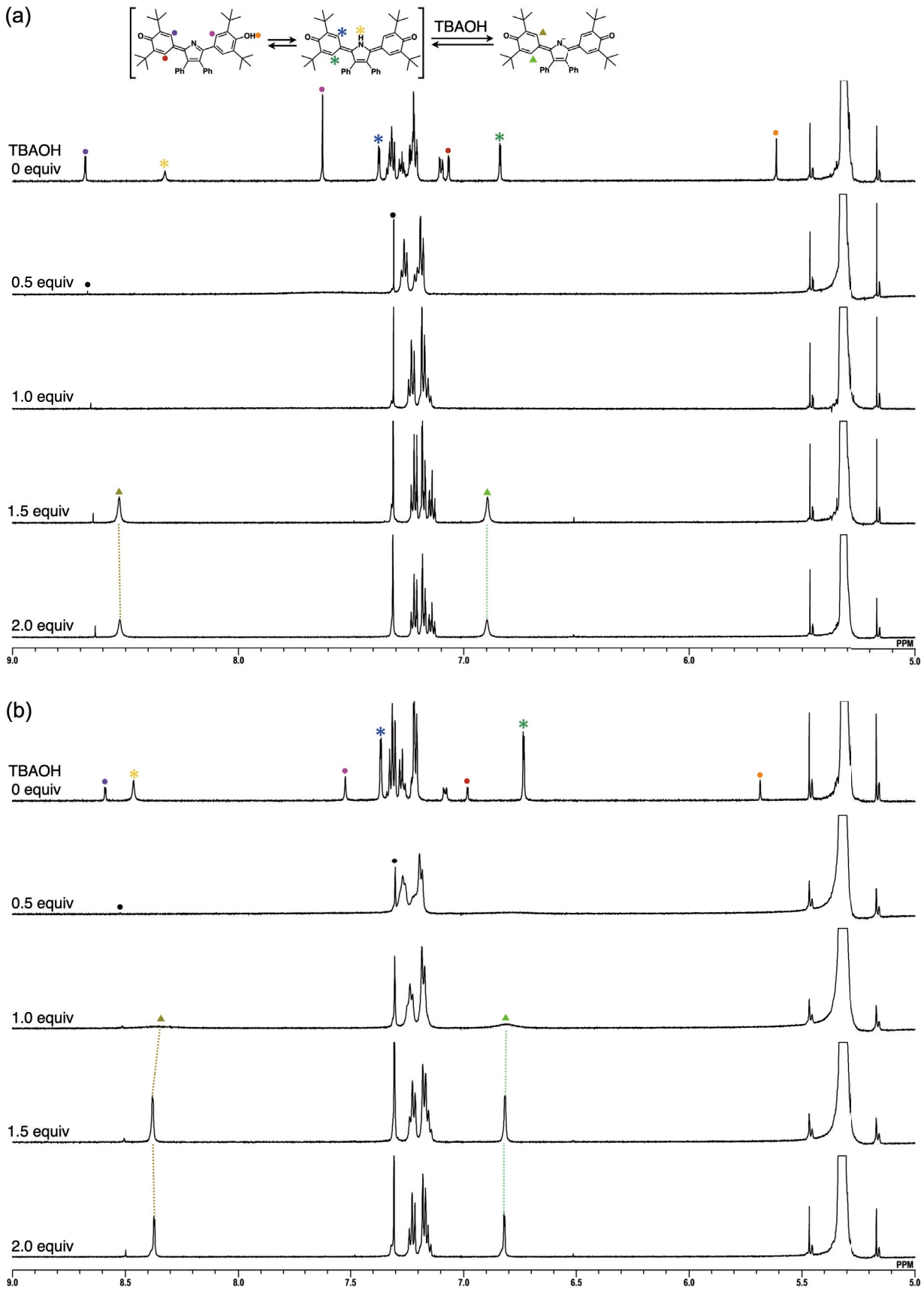

Fig. S60 ^{1}H NMR spectral changes of **2c** (1×10^{-3} M) upon the addition of OH^- (0–2.0 equiv) added as a TBA salt in CD_2Cl_2 at (a) 20 °C and (b) –50 °C. The signals labelled by black circles are derived from unidentified species in TBAOH as purchased. The tentative coalescence of the signals, especially those of quinone methide and phenol CH, are derived from the fast exchange between **2c** and **2c**$^-$. The details will be reported elsewhere.