Supporting Information for

Stabilizing Fleeting Intermediates of Stilbene Photocyclization with Amino-Borane Functionalization: The Rare Isolation of Persistent Dihydrophenanthrenes and Their [1,5] H-Shift Isomers

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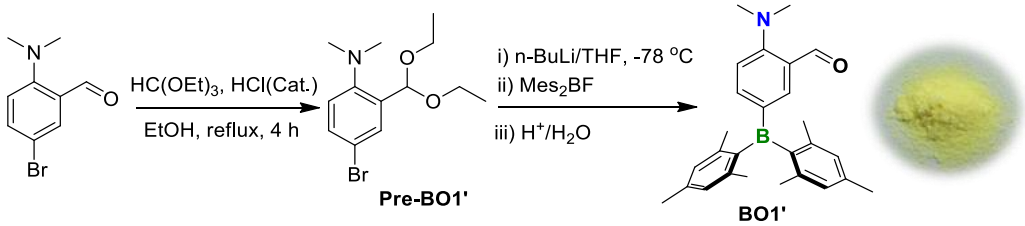
Contents

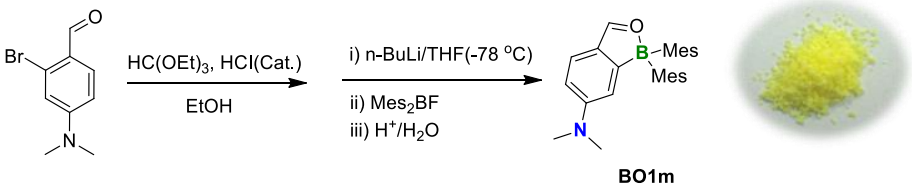
S1. Starting Material Synthesis

1.1 Synthesis of pre-*E*-8a



5-bromo-2-(dimethylamino)benzaldehyde (0.5 g, 2.19 mmol) and triethyl orthoformate (1.2 mL, 7.23 mmol) were dissolved in ethanol (10 mL), and then a catalytic amount of concentrated HCl (31 μL) was added to it. The resultant solution was refluxed for 4 h. After all the starting compound had been consumed, the reaction mixture was brought to room temperature and extracted with a water/ethyl acetate mixture. The combined organic layer was washed with brine and dried over anhydrous Na_2SO_4. Removing the volatiles under reduced pressure afforded 4-bromo-2-(diethoxymethyl)-N,N-dimethylaniline as a pale yellow liquid. Yield: 0.658 g, 99%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 (s, 1H), 7.37 (d, J = 8.5 Hz, 1H), 6.99 (d, J = 8.5 Hz, 1H), 5.76 (s, 1H), 3.72 – 3.63 (m, 2H), 3.55 – 3.46 (m, 2H), 2.70 (s, 6H), 1.22 (t, J = 7.0 Hz, 6H). To an oven-dried Schlenk flask was added 4-bromo-2-(diethoxymethyl)-N,N-dimethylaniline (0.65 g, 2.15 mmol) and the flask was evacuated and back-filled with N_2 three times, and then dried THF (10 mL) was injected into the mixture, then cooled to −78 °C (acetone and liquid N_2). n-BuLi [1.5 mL (1.6 M solution in hexane), 2.37 mmol] was added over 30 min. After 1 h, a solution of Mes_2BF (0.636 g, 2.37 mmol) in 4 mL of dry THF was added over 10 min. The reaction mixture was allowed to warm to room temperature, and stirring was continued for 12 h. After 12 h, 8 mL of 1 N HCl was added and stirring was continued for an additional 4 h and extracted with ether. The combined organic layers were washed with a brine solution and dried over anhydrous Na_2SO_4. After removing the solvents at reduced pressure, the crude product was purified by silica gel chromatography (PE/EA = 10/1). Compound **BO1'** as a yellow soild in 58 % yield (0.501 g, 1.3 mmol). ^{1}H NMR (400 MHz, C_6D_6) δ 9.71 (s, 1H), 8.21 (s, 1H), 7.69 (d, J = 8.5 Hz, 1H), 6.85 (s, 4H), 6.45 (d, J = 8.5 Hz, 1H), 2.39 (s, 6H), 2.22 (s, 18H). ^{13}C NMR (101 MHz, C_6D_6) δ 189.19, 155.60, 146.18, 143.12, 142.13, 140.98, 138.58, 134.46, 128.93, 124.83, 115.33, 43.42, 23.83, 21.32. ^{11}B NMR (225 MHz, C_6D_6) δ 71.39. HR-ESIMS (m/z): $[M+H]^+$ calcd. for C27H33BNO, 398.2650; found 398.2658.

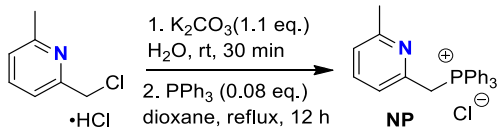
1.2 Synthesis of pre-*E*-9a



2-bromo-4-(dimethylamino)-benzaldehyde (1.415 g, 6.21 mmol), and triethyl orthoformate (3.4 mL, 20.49 mmol) were dissolved in ethanol (28 mL), and then a catalytic amount of concentrated HCl (90 μL) was added to it. The resultant solution was refluxed for 4 h. After the removal of the solvent, the product was dissolved in THF (120 mL) and n-BuLi (1.6 M solution in hexane, 4.27 mL, 6.83 mmol) was added dropwise at -78 °C. The mixture was stirred for 1 h at -78 °C and $BMes_2F$(1.83 g, 6.83 mmol) in THF (30 mL) was added, the solution was stirred at -78 °C for 1

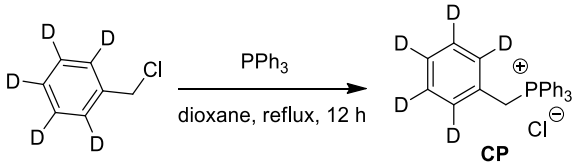
hrs, then warmed to room temperature and stirred for 12 hrs. The HCl (3 mL, 1 M) was added to the mixture, and the solution was stirred at room temperature for 4 hrs and extracted with ethyl acetate. The combined organic layers were washed with a brine solution and dried over anhydrous Na_2SO_4. After removing the solvents at reduced pressure, the crude product was purified by silica gel chromatography (PE/EA = 10/1). Compound **BO1m** as a yellow soild in 54 % yield (1.34 g, 3.38 mmol). ^{1}H NMR (400 MHz, CD_2Cl_2) δ 9.05 (s, 1H), 7.80 (d, J = 8.9 Hz, 1H), 7.06 (s, 1H), 6.67 (d, J = 8.9 Hz, 1H), 6.61 (s, 4H), 3.11 (s, 6H), 2.17 (s, 6H), 2.02 (s, 12H). ^{13}C NMR (101 MHz, CD_2Cl_2) δ 188.63, 156.05, 141.00, 134.29, 131.21, 129.50, 129.08, 112.94, 112.10, 40.58, 24.65, 20.81. ^{11}B NMR (225 MHz, CD_2Cl_2) δ 13.61. HR-ESIMS (m/z): $[M+H]^+$ calcd. for $C_{27}H_{33}BNO$, 398.2650; found 398.2666.

1.2 Synthesis of Compound NP



(Chloromethyl)pyrdine hydrochloride[1] (1.164 g, 6.5 mmol) was dissolved in water (3 mL). Potassium carbonate (0.948 g, 6.86 mmol) was added portionwise and the solution was stirred for 30 minutes. The solution was diluted by the addition of Et_2O and the biphasic system was extracted with Et_2O (× 3). The organic layers were combined, dried (Na_2SO_4), and concentrated in vacuo. The resulting crude product was dissolved in dioxane (8 mL) and triphenylphosphine (1.36 g, 5.2 mmol) was added. The solution was heated at reflux for 12 hours then cooled to room temperature. The solution was filtered and the solid was then dried under high vacuum for 1 hour to afford the corresponding ylide compound **NP**.

1.3 Synthesis of Compound CP



1-(Chloromethyl)benzene-2,3,4,5,6-d_5[2] (0.091 g, 0.69 mmol) was dissolved in dioxane (2 mL) and triphenylphosphine (0.181 g, 0.69 mmol) was added. The solution was heated at reflux for 12 hours then cooled to room temperature. The solution was filtered and the solid was then dried under high vacuum for 1 hour to afford the corresponding ylide compound **CP**.

S2. NMR Photo- and Thermal Isomerization Data of *E*-1a – *E*-9a

2.1 NMR Photo/Thermal Isomerization Data of *E*-1a

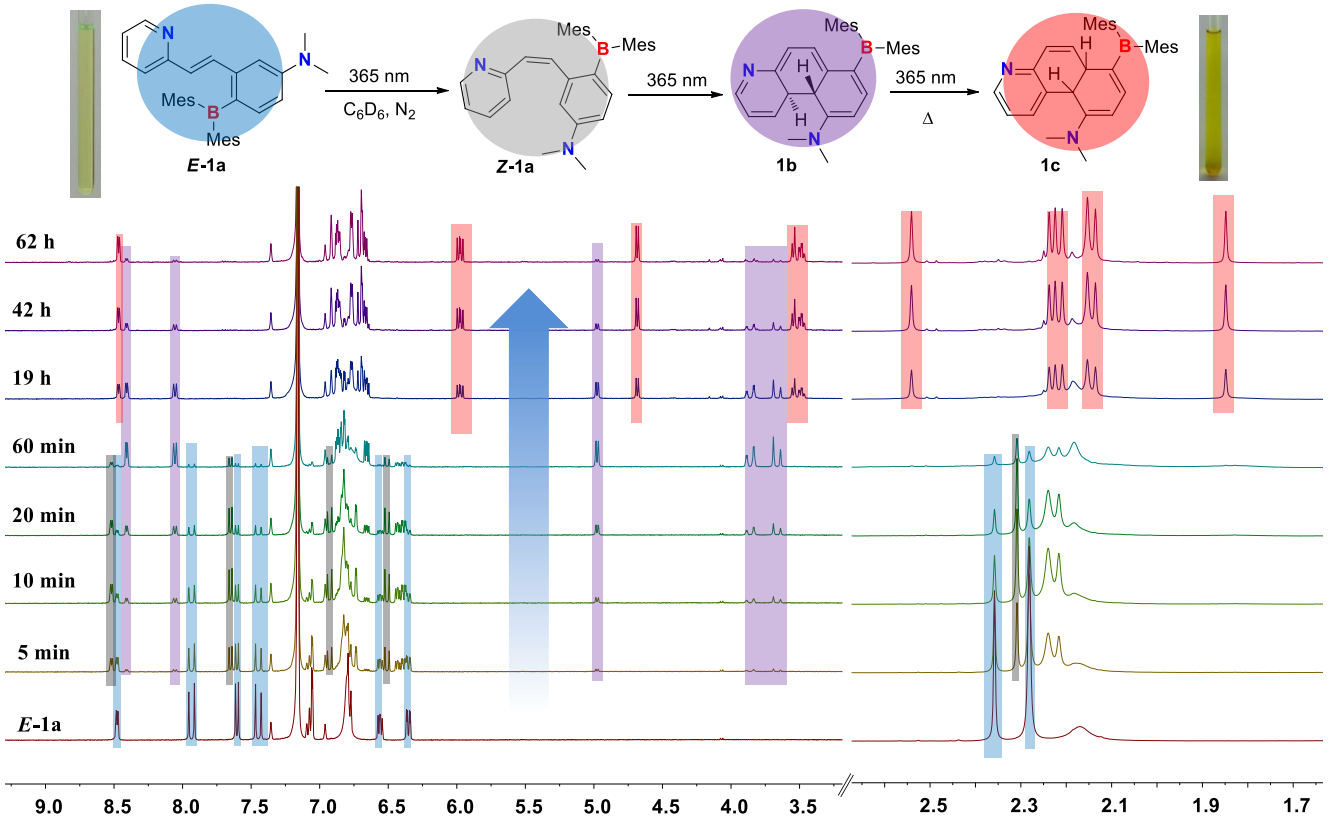


Figure S1. ^{1}H NMR spectra showing the clean conversion of ***E*-1a** (blue highlight) to **1c** (red highlight) in C_6D_6 under 365 nm irradiation (70 °C).

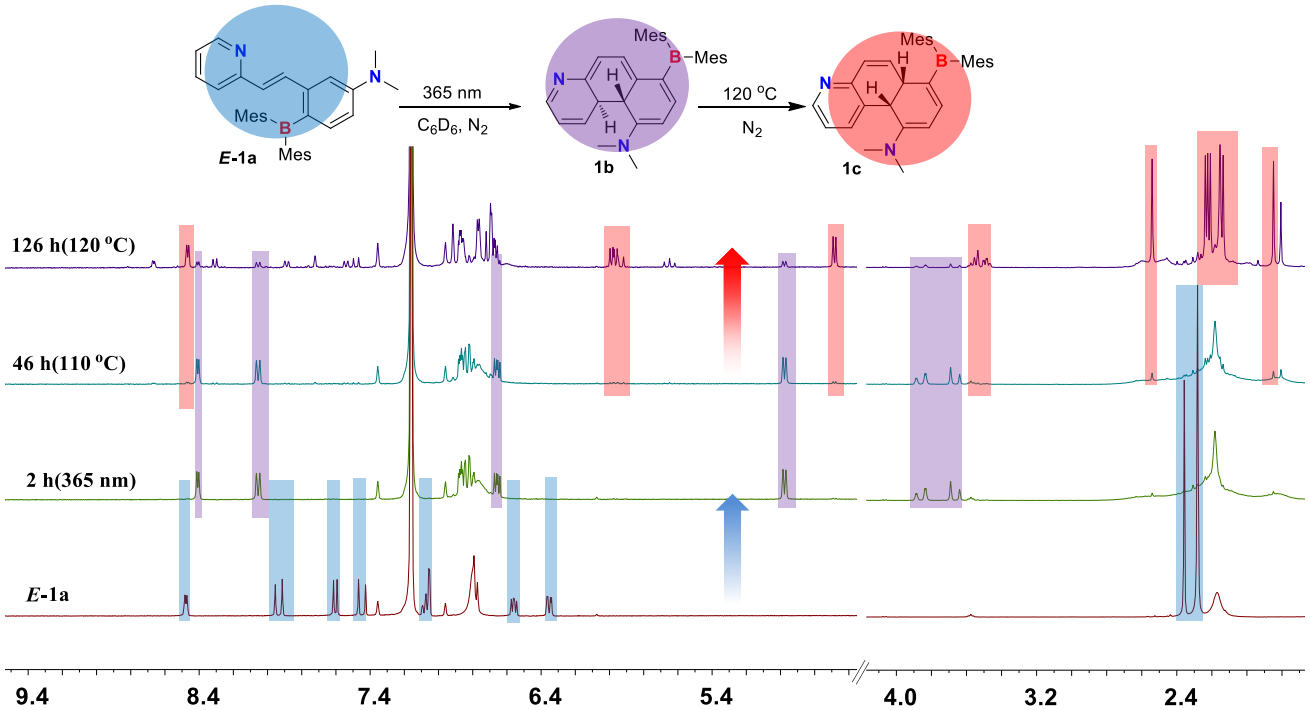


Figure S2. ^{1}H NMR spectra showing the clean conversion of ***E*-1a** (blue highlight) to **1c** (purple highlight) in C_6D_6 first under 365 nm irradiation, followed by heating to 120 °C.

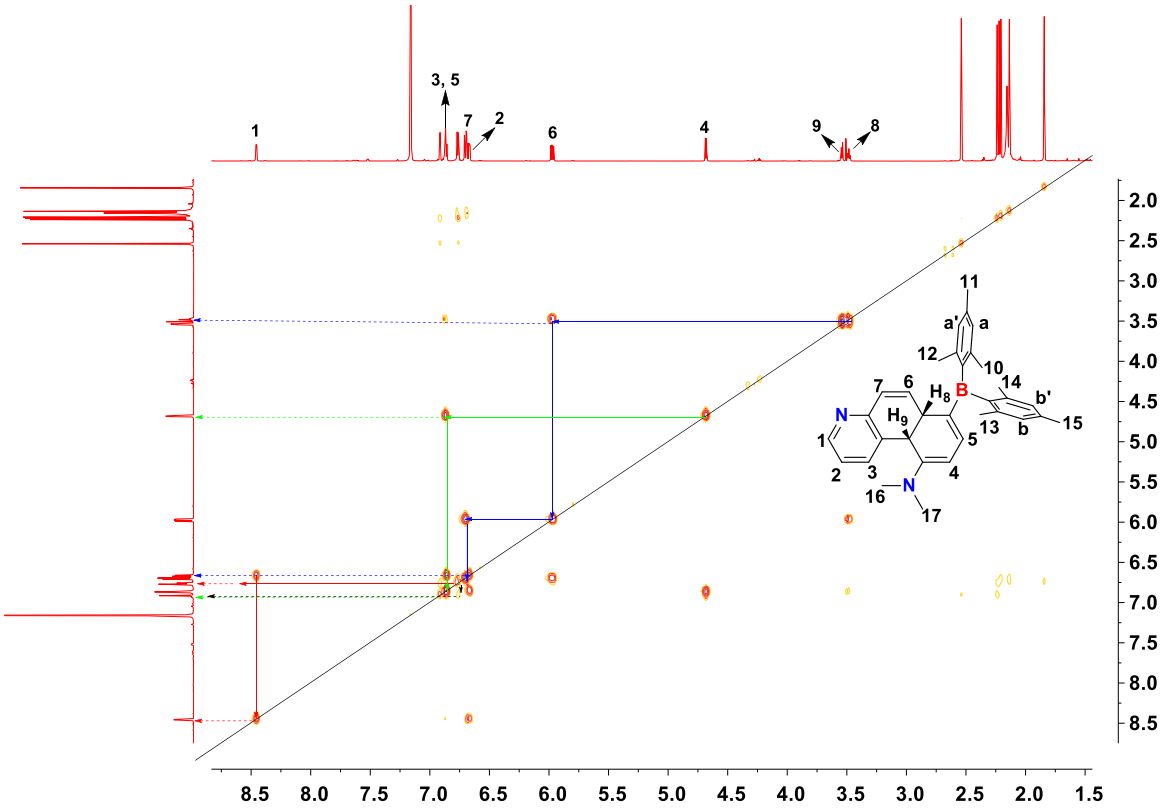


Figure S3. Partial ^{1}H- ^{1}H COSY NMR spectrum of **1c** in C_6D_6 at r.t.

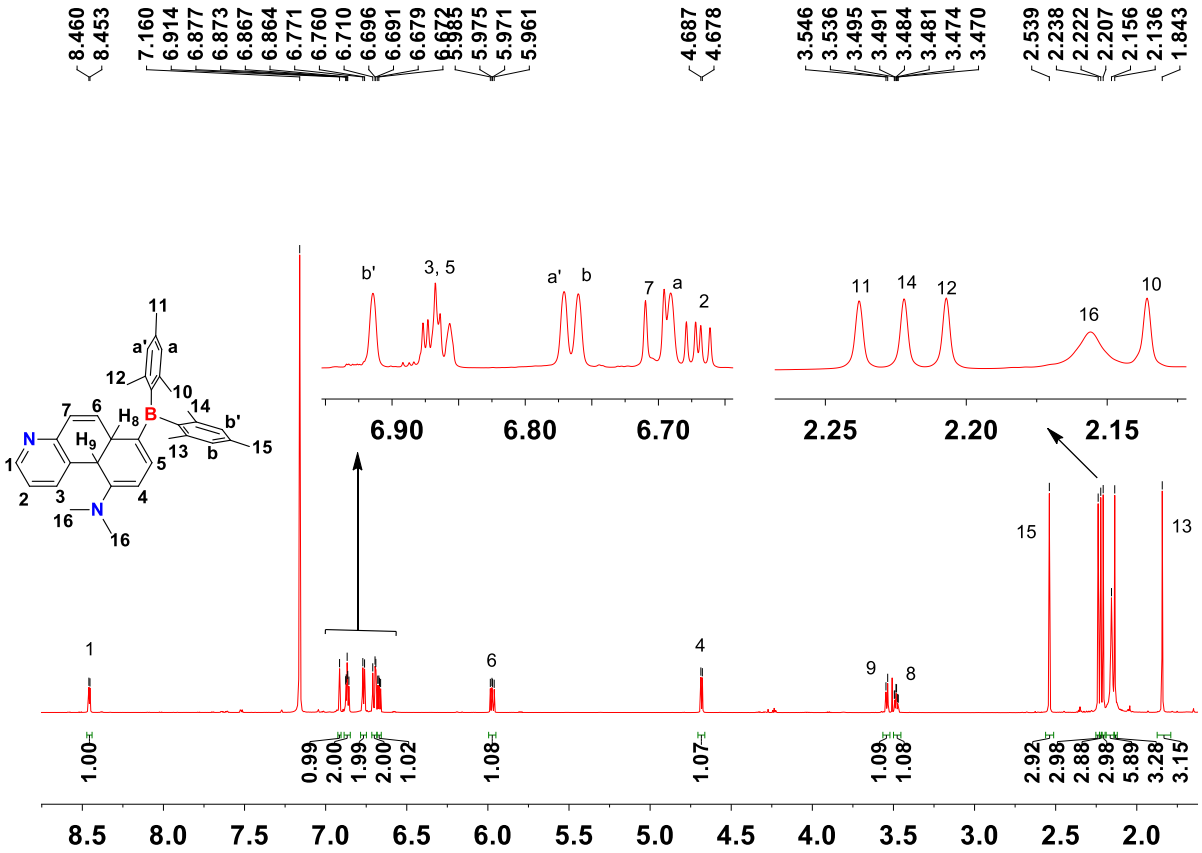


Figure S4. ^{1}H NMR (C_6D_6, 700 MHz) spectra of compound **1c**.

2.2 NMR Photo/Thermal Isomerization Data of *E*-2a

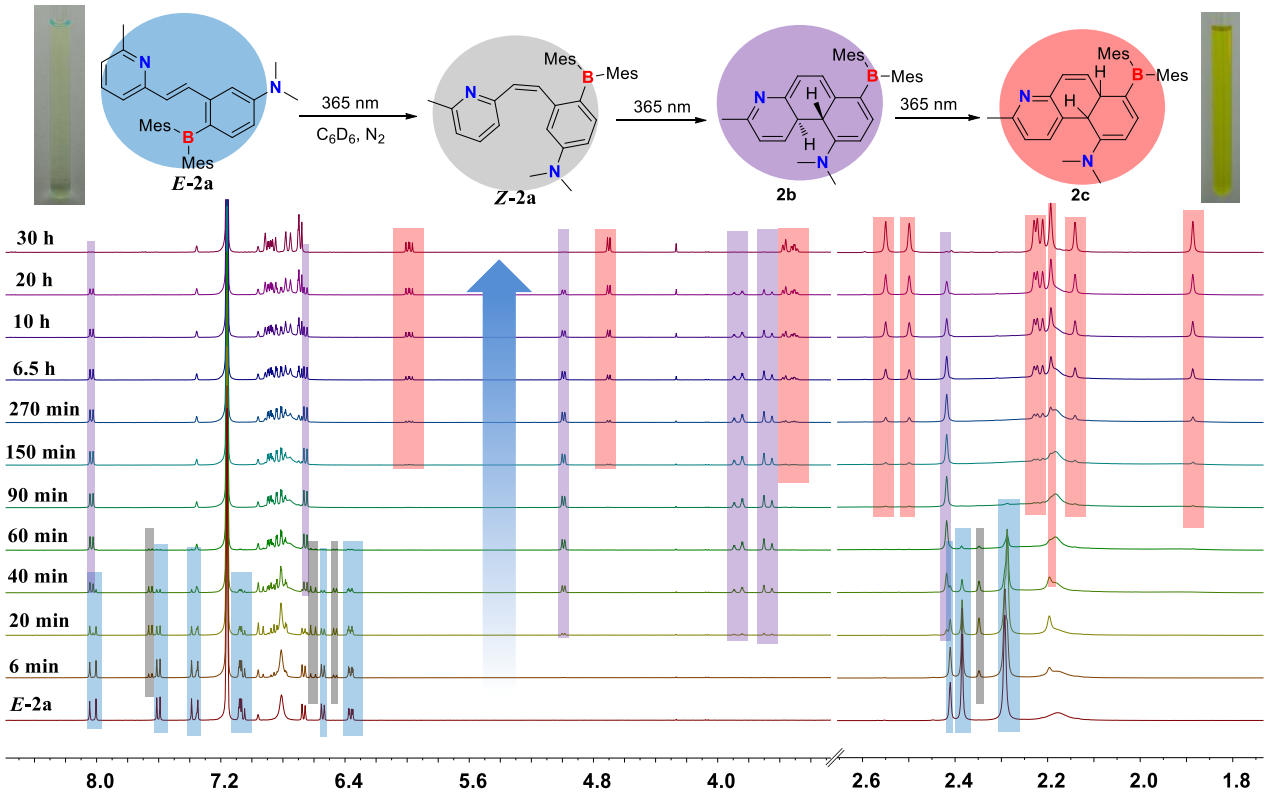


Figure S5. ^{1}H NMR spectra showing the clean conversion of ***E*-2a** (blue highlight) to **2c** (red highlight) in C_6D_6 under 365 nm irradiation (70 °C).

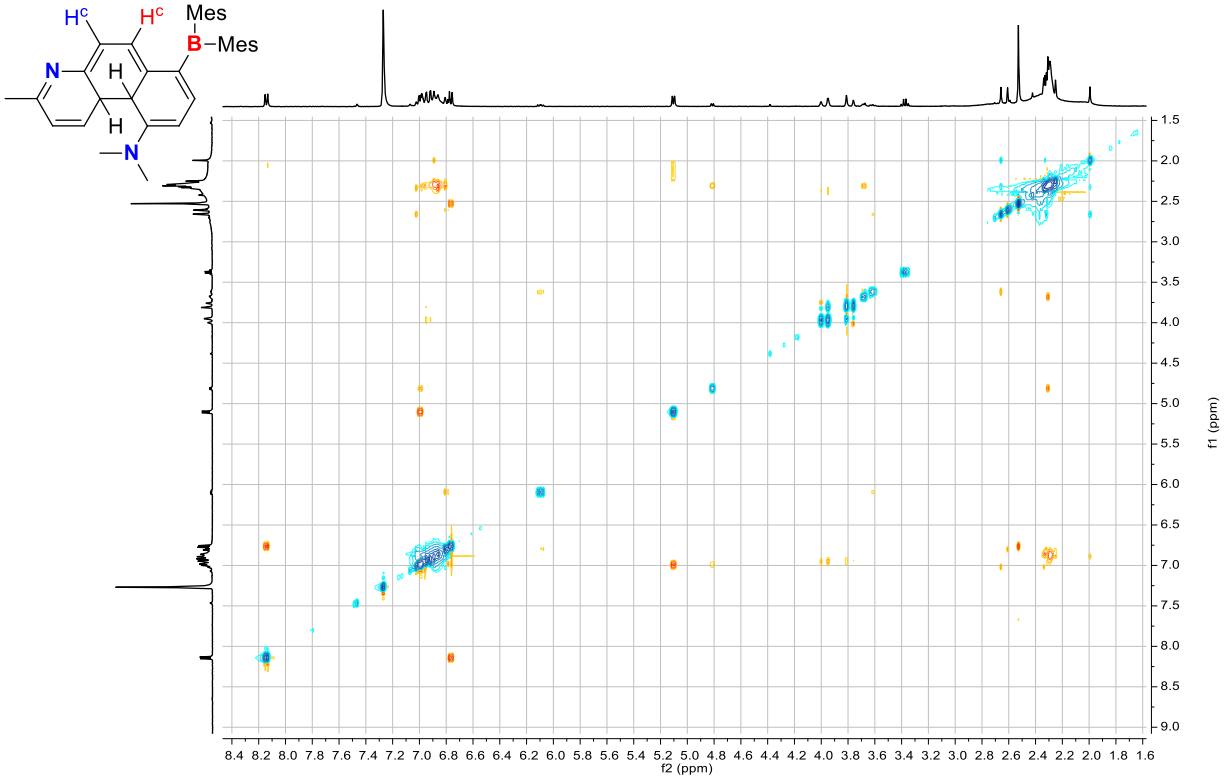


Figure S6. Full ^{1}H-^{1}H NOSEY NMR spectrum of **2b** in C_6D_6 (600 MHz).

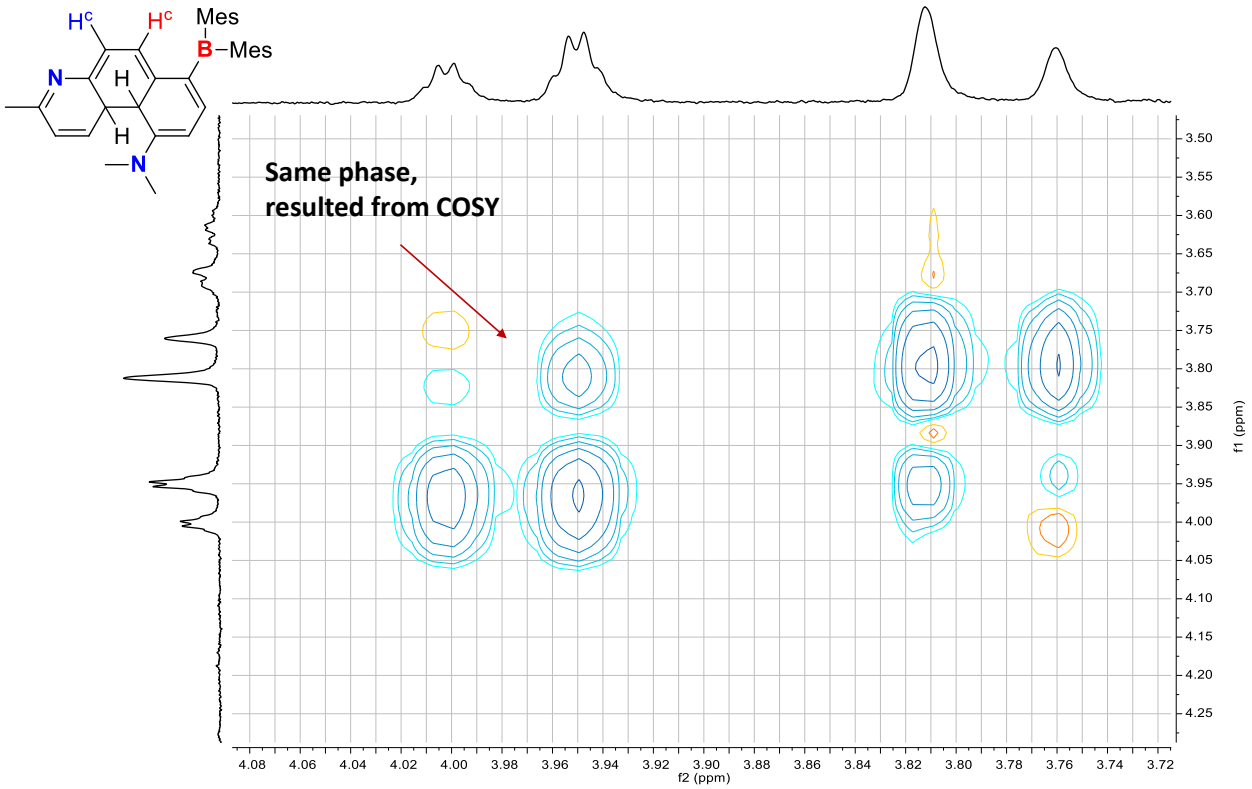


Figure S7. Partial ^{1}H-^{1}H NOSEY NMR spectrum of **2b** in C_6D_6 (600 MHz) establishing its *trans*-configuration.

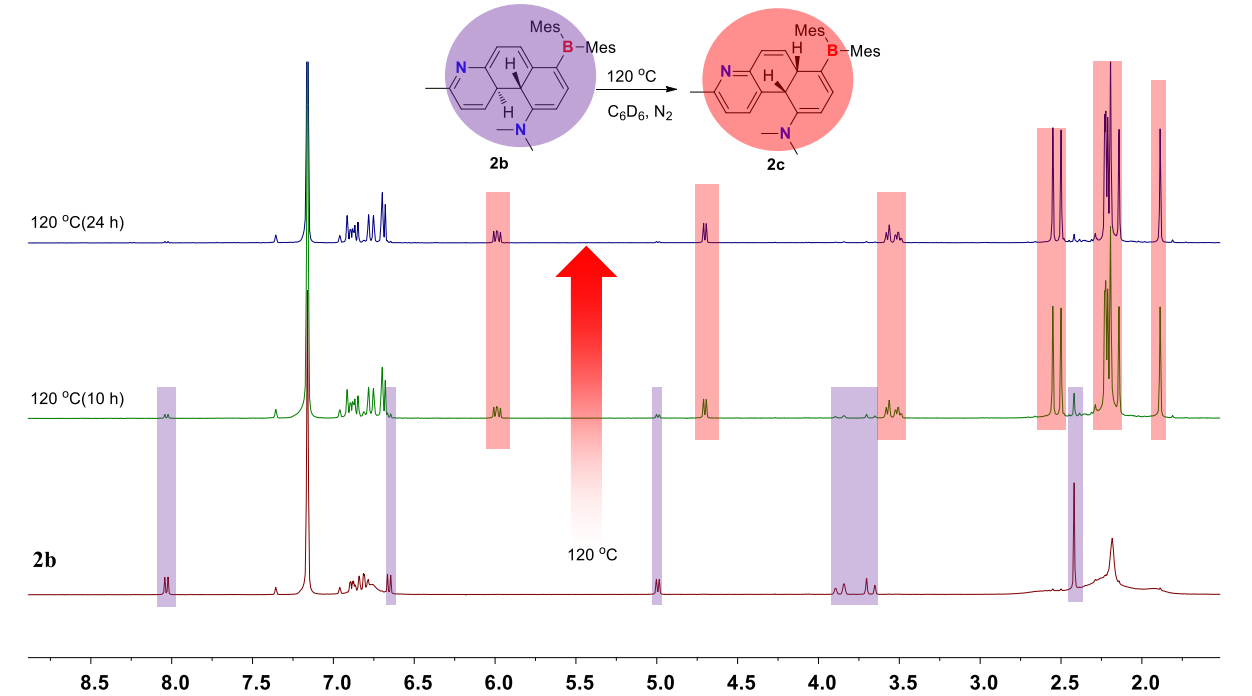


Figure S8. ^{1}H NMR spectra showing the clean conversion of **2b** (blue highlight) to **2c** (top spectrum, red highlight) in C_6D_6 (120 °C).

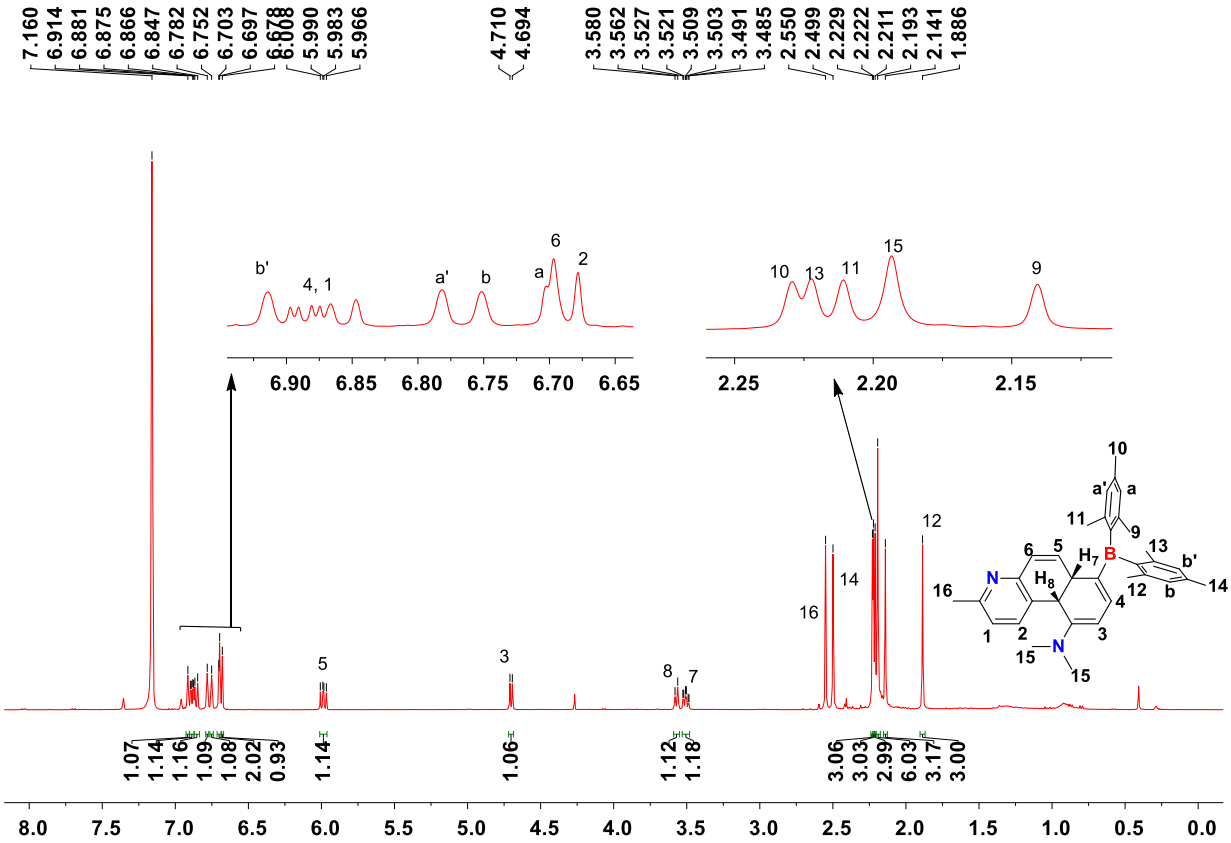


Figure S9. ^{1}H NMR (C_6D_6, 400 MHz) spectra of compound **2c**.

2.3 NMR Photo/Thermal Isomerization Data of *E*-3a

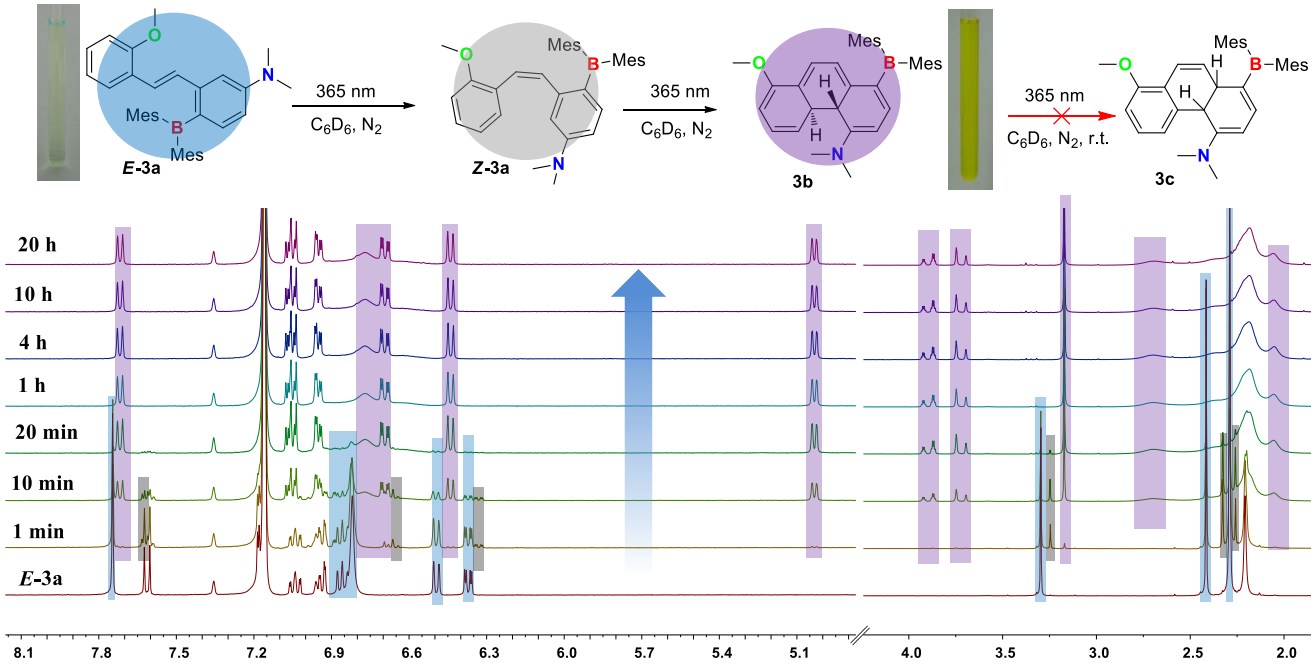


Figure S10. ^{1}H NMR spectra showing the clean conversion of ***E*-3a** (blue highlight) to **3b** (purple highlight) in C_6D_6 under 365 nm irradiation (room temperature).

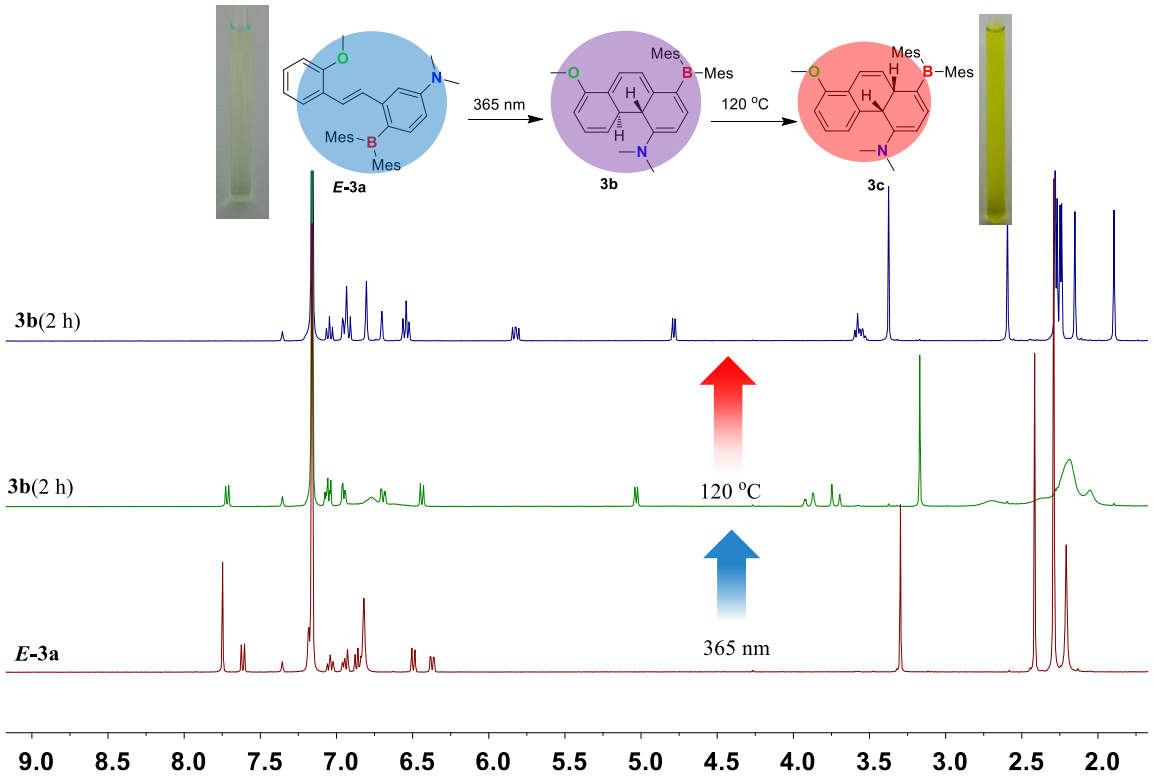


Figure S11. ^{1}H NMR spectra showing the clean conversion of ***E*-3b** (purple highlight) to **3c** (red highlight) in C_6D_6 (120 °C).

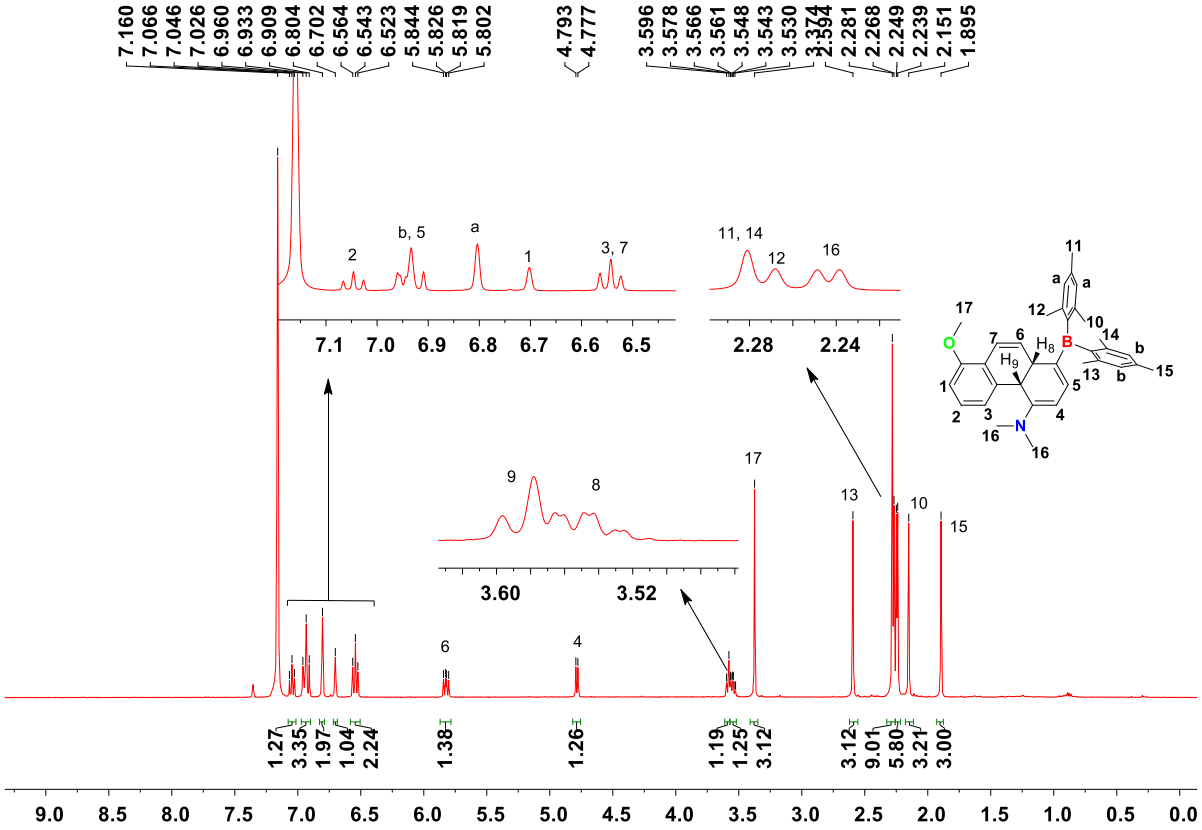


Figure S12. ^{1}H NMR (C_6D_6, 400 MHz) spectra of compound **3c**.

2.4 NMR Photo/Thermal Isomerization Data of *E*-4a

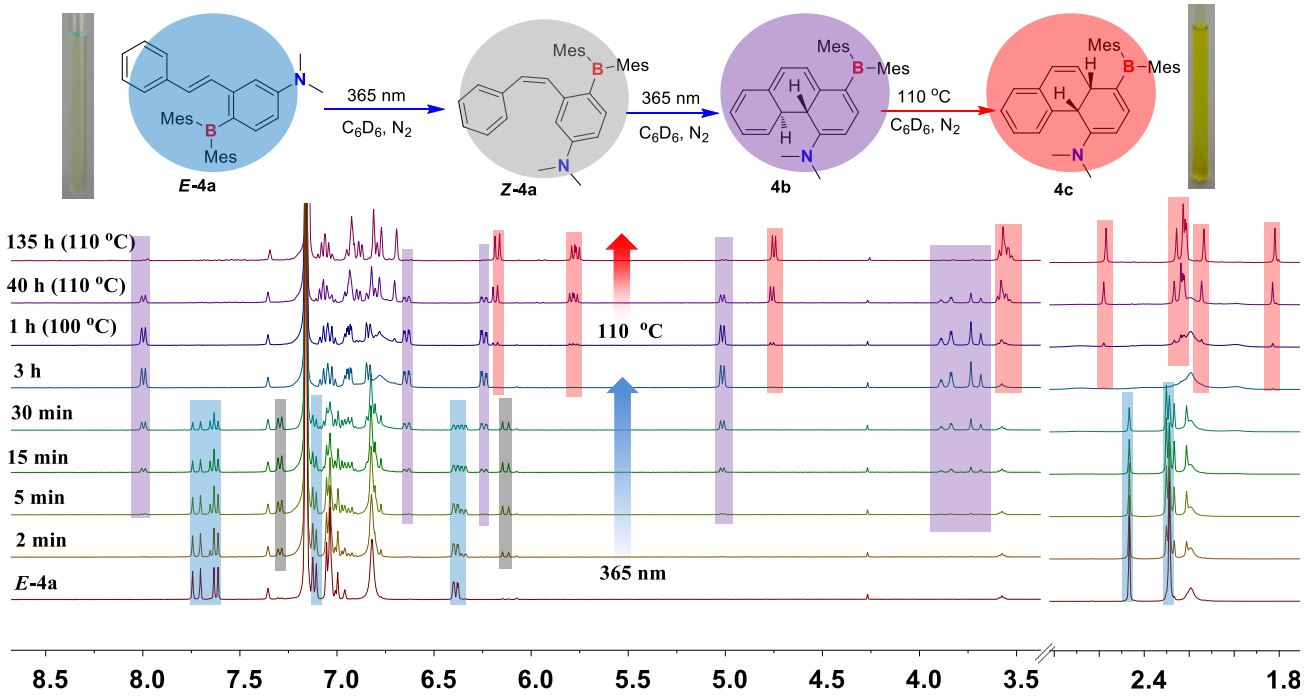


Figure S13. ^{1}H NMR spectra showing the clean conversion of ***E*-4a** (blue highlight) to **4c** (red highlight) in C_6D_6 first under 365 nm irradiation, followed by heating at 110 °C.

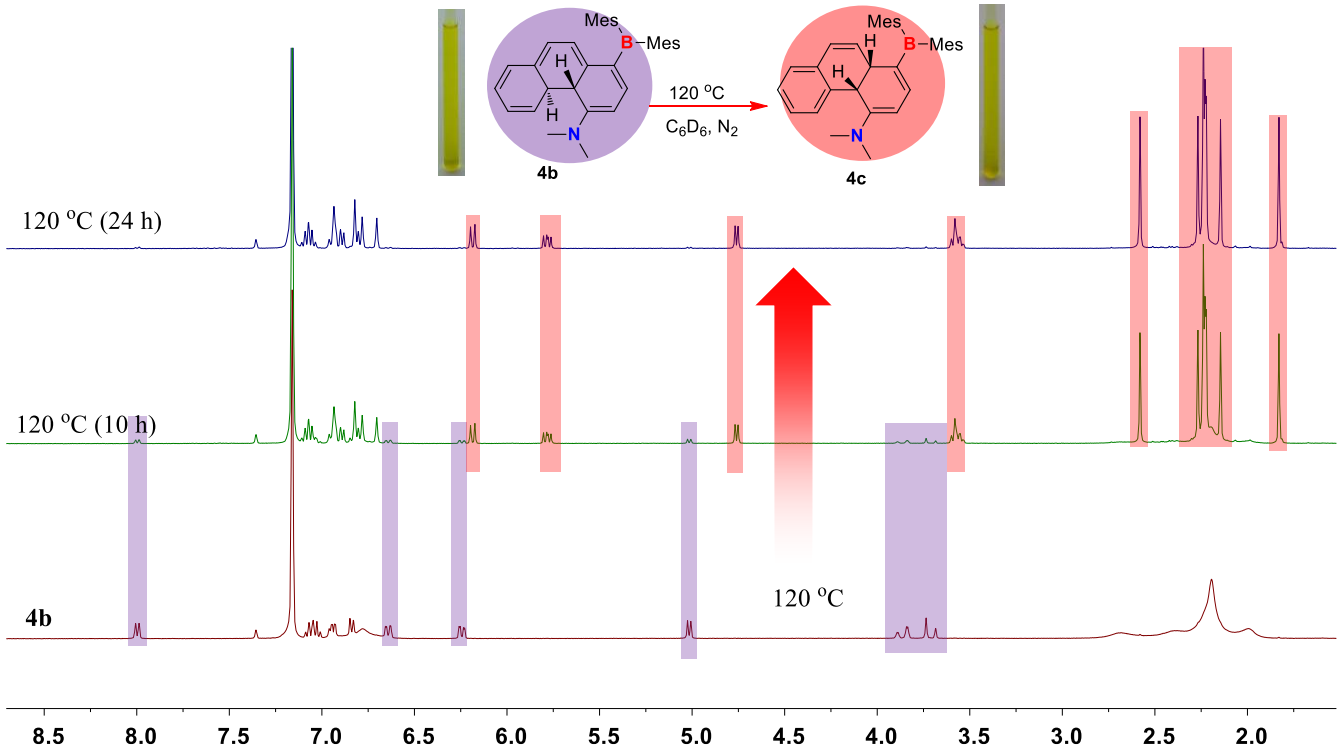


Figure S14. ^{1}H NMR spectra showing the clean conversion of **4b** (1 mg, 0.6 mL C_6D_6, bottom spectrum, blue highlight) to **4c** (top spectrum, red highlight) in C_6D_6 (120 °C).

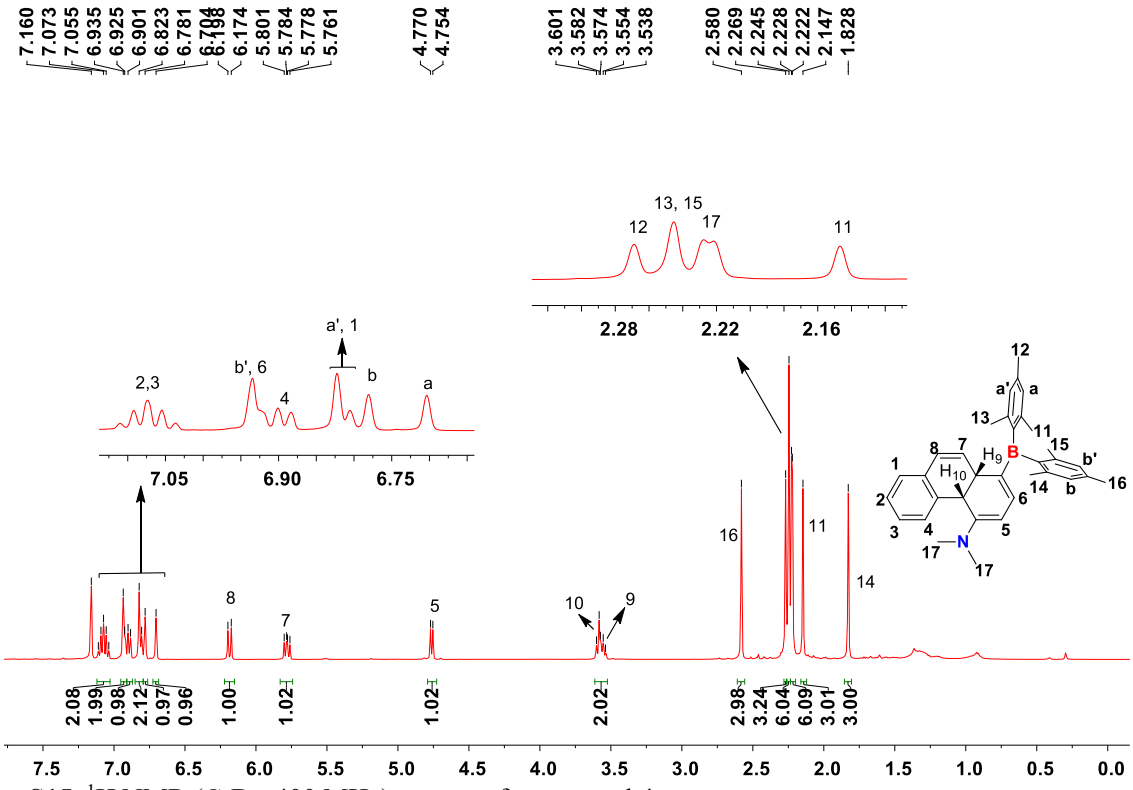


Figure S15. ^{1}H NMR (C_6D_6, 400 MHz) spectra of compound **4c**.

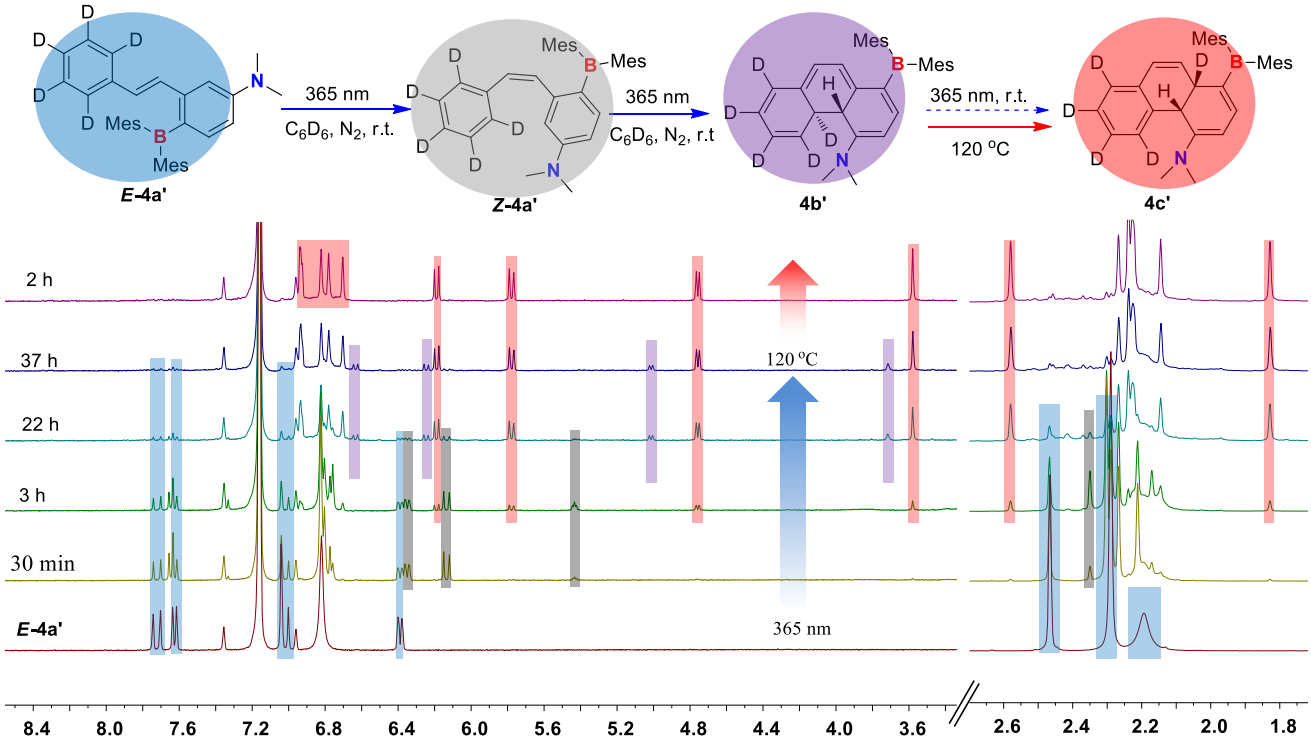


Figure S16. ^{1}H NMR spectra showing the clean conversion of ***E*-4a'** (blue highlight) to **4c'** (red highlight) in C_6D_6 first under 365 nm irradiation, followed by heating at 110 °C.

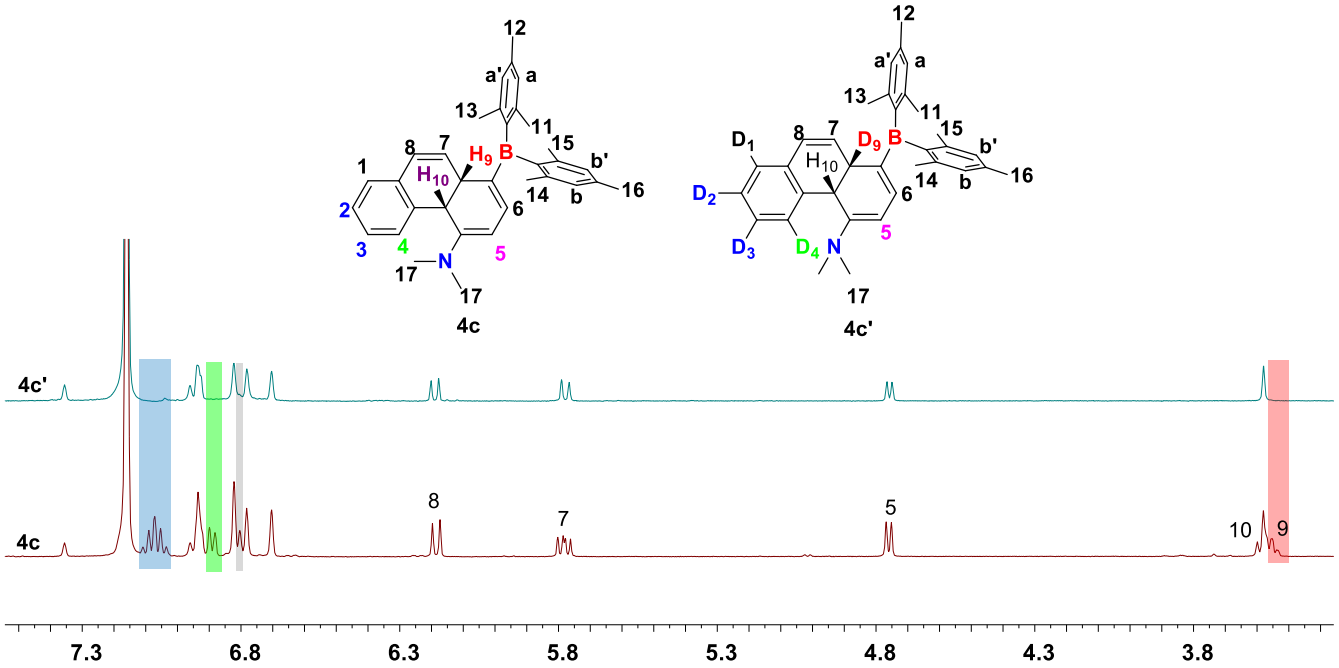


Figure S17. Stacked ^{1}H-NMR spectra comparing **4c** (bottom) and **4c′** (top) with the deuterated protons highlighted.

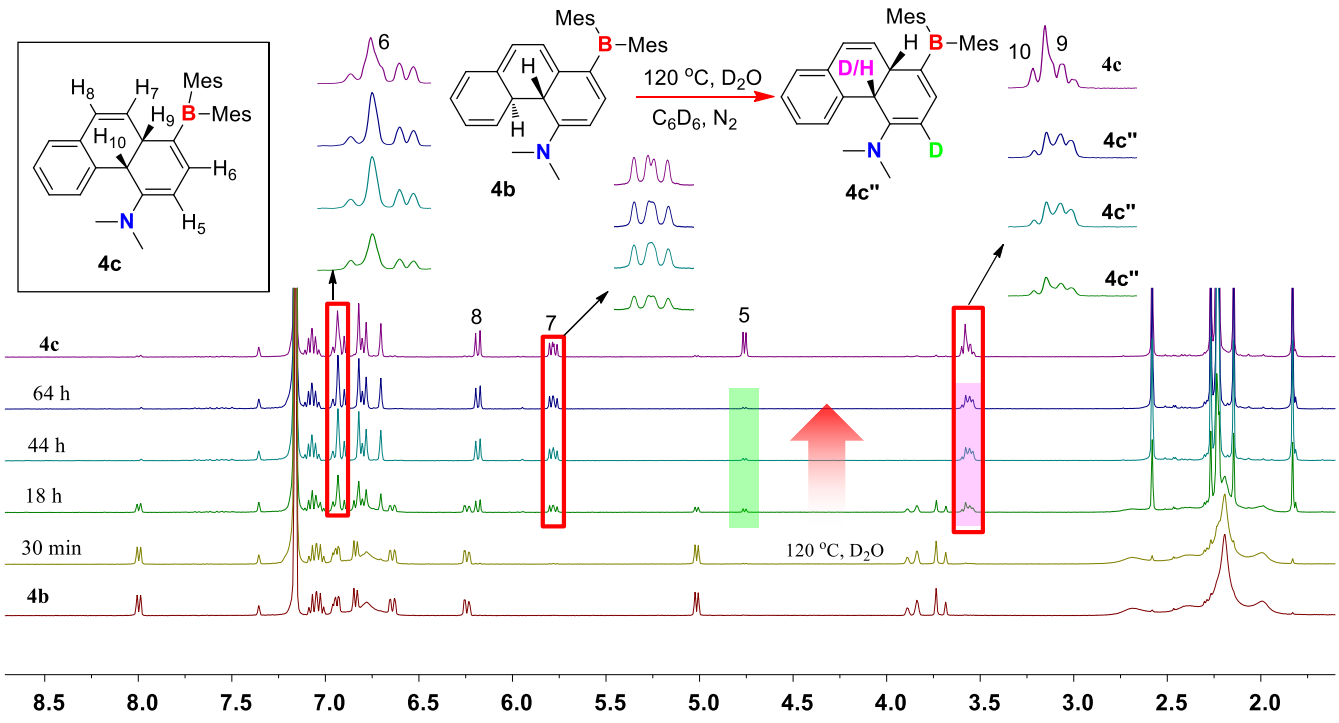


Figure S18. ^{1}H NMR spectra showing the clean conversion of **4b** to **4c"** with heating at 120 °C in the prescence of D_2O. The top specrum shows pure **4c**.

2.5 NMR Photo/Thermal Isomerization Data of *E*-5a

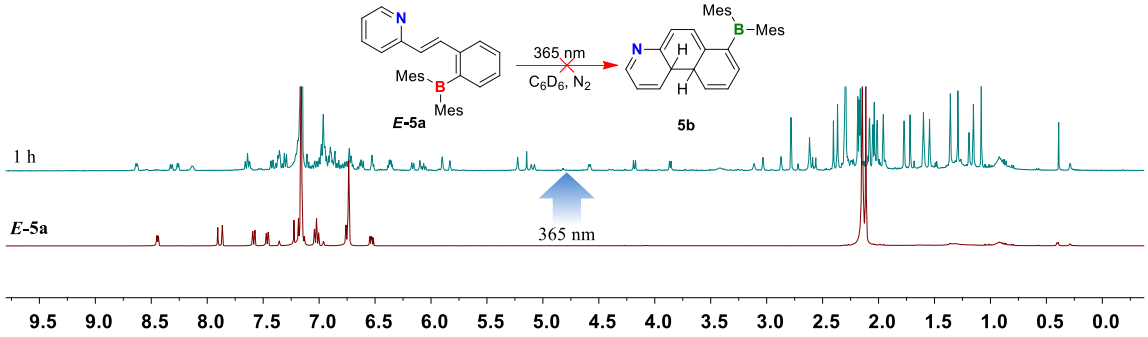


Figure S19. ^{1}H NMR spectra of ***E*-5a** in C_6D_6 (1 mg, 0.6 mL) under 365 nm irradiation.

2.6 NMR Photo/Thermal Isomerization Data of *E*-6a

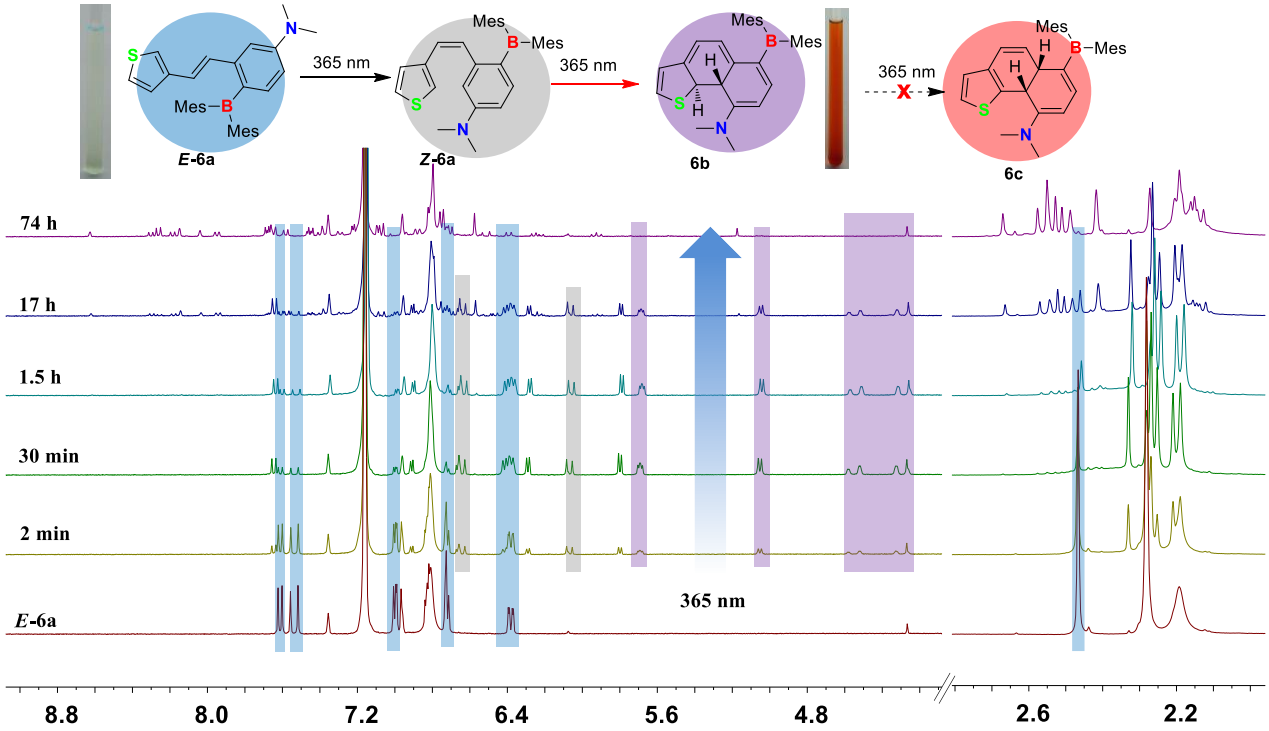


Figure S20. ^{1}H NMR spectra showing the clean conversion of ***E*-6a** (blue highlight) to **6b** (purple highlight) in C_6D_6 under 365 nm irradiation.

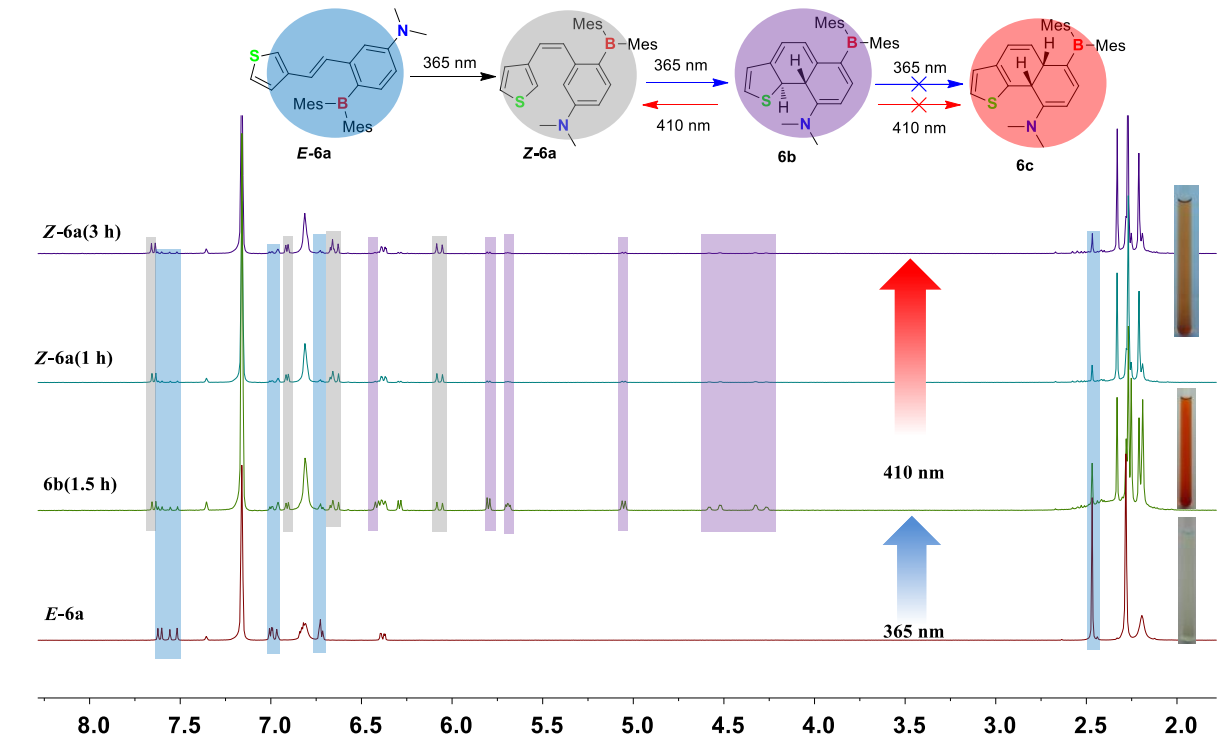


Figure S21. Time-lapsed ^{1}H NMR spectra of ***E*-6a** in C_6D_6.

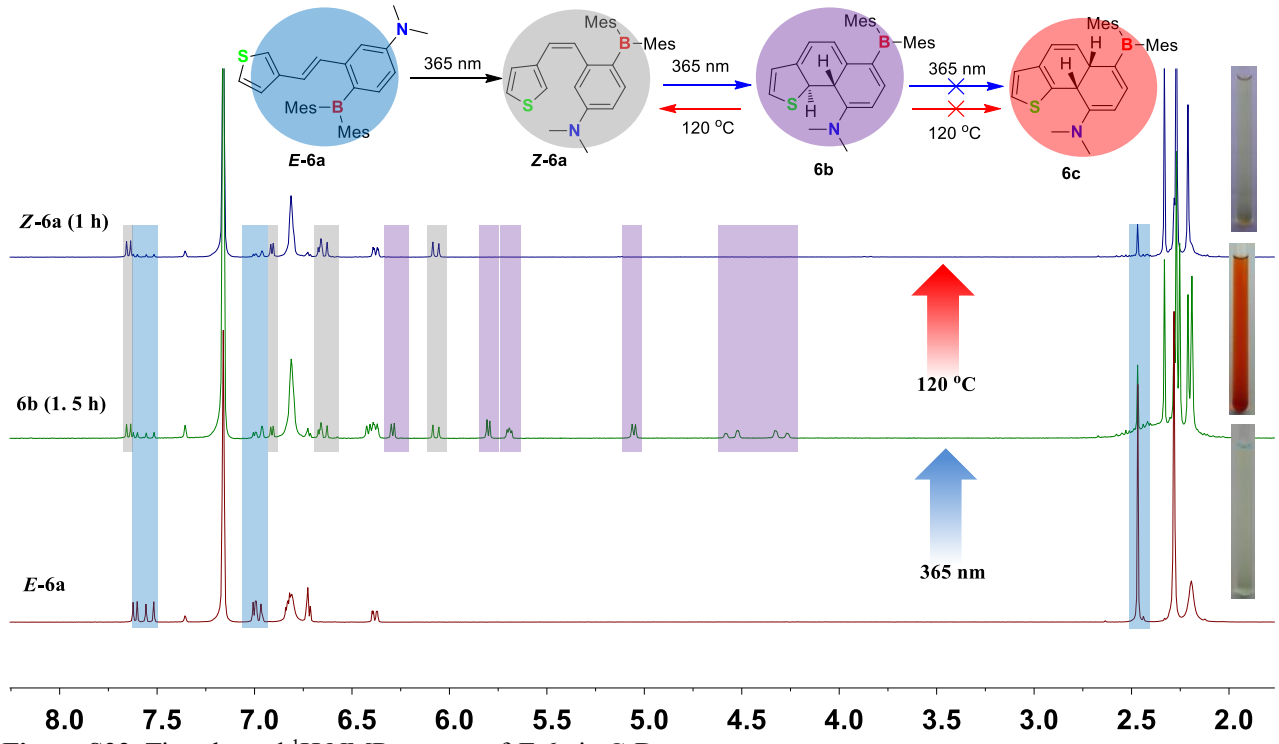


Figure S22. Time-lapsed ^{1}H NMR spectra of ***E*-6a** in C_6D_6.

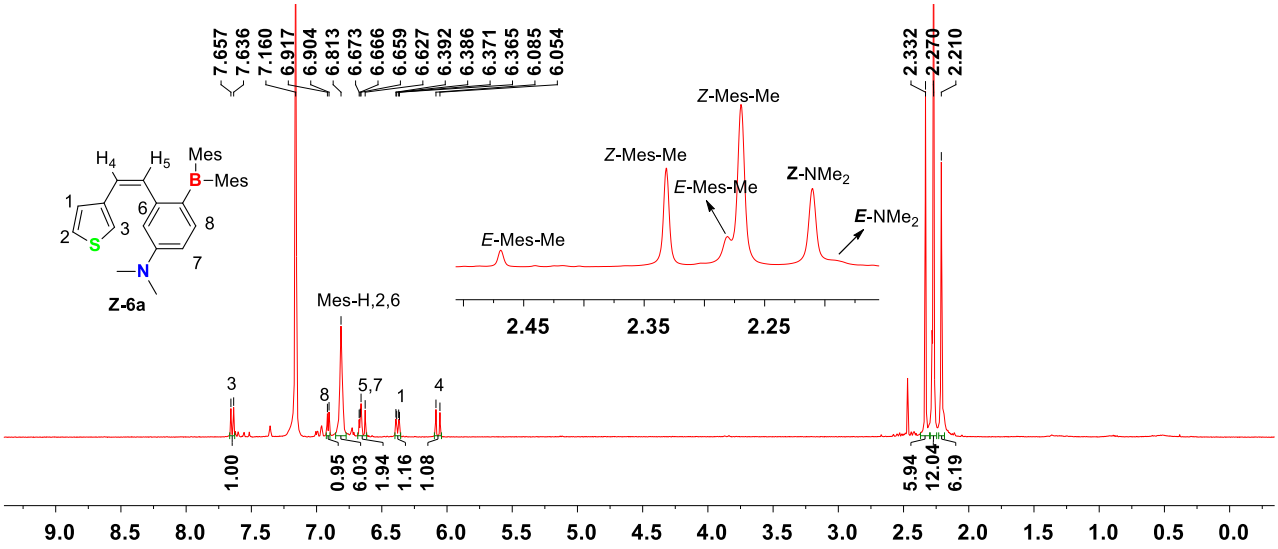


Figure S23. ^{1}H NMR spectrum of ***Z*-6a** in C_6D_6.

2.7 NMR Photo/Thermal Isomerization Data of *E*-7a

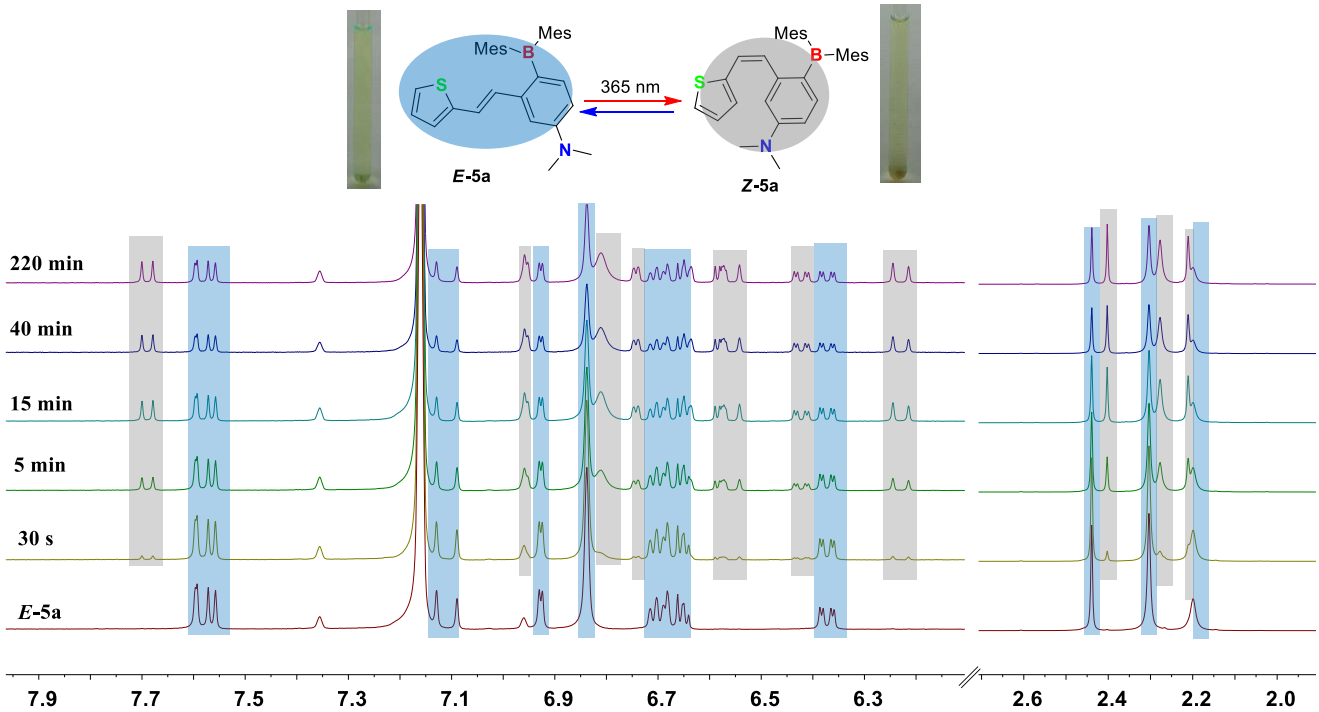


Figure S24. ^{1}H NMR spectra showing the conversion of ***E*-7a** (blue highlight) to ***Z*-7a** (purple highlight) in C_6D_6 under 365 nm irradiation.

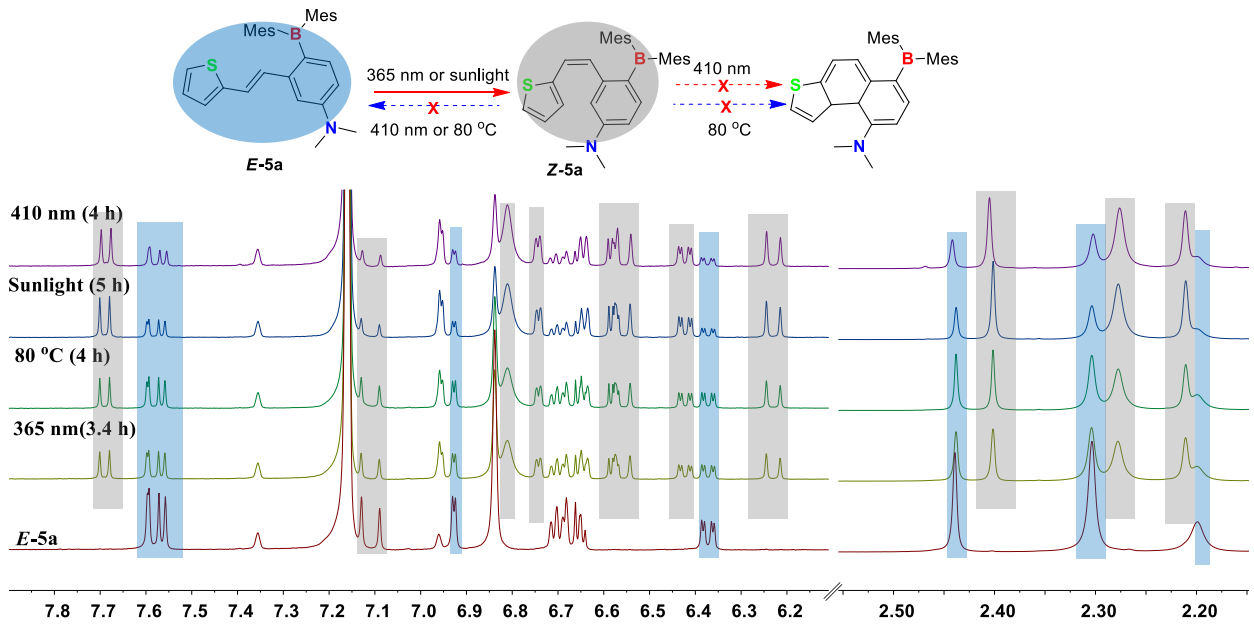


Figure S25. Time-lapsed ^{1}H NMR spectra from ***E*-7a** to ***Z*-7a** in C_6D_6, r.t. or 80 °C.

2.8 NMR Photo/Thermal Isomerization Data of *E*-8a

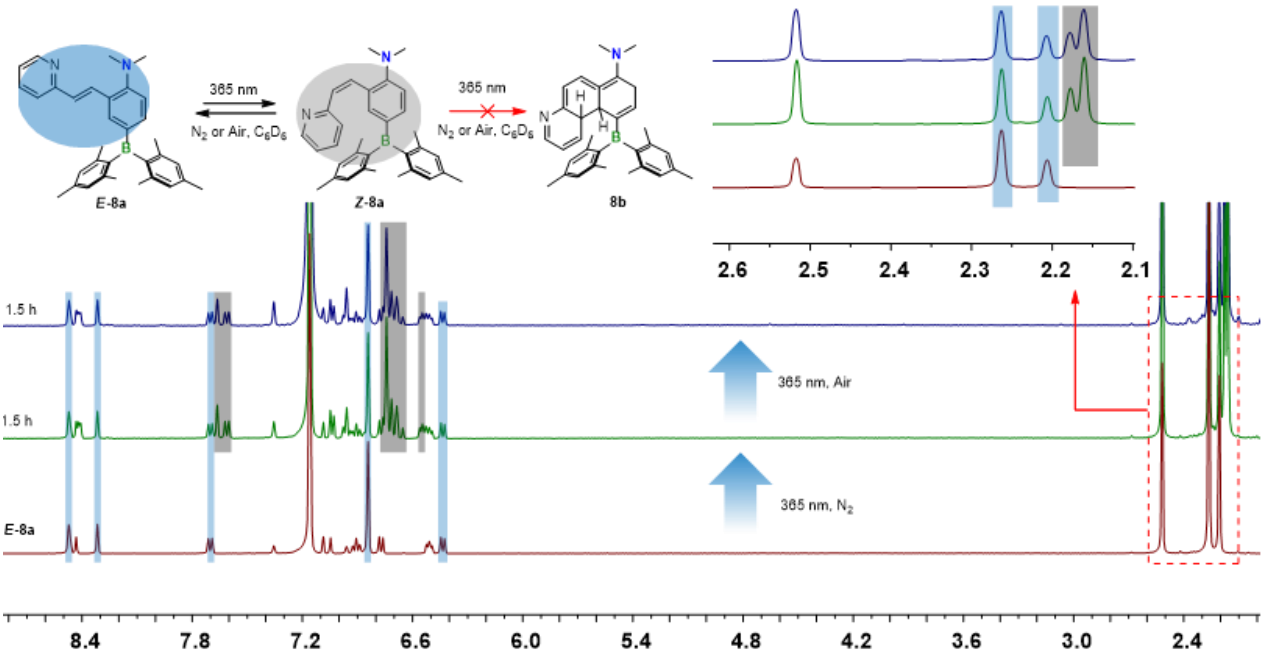


Figure S26. ^{1}H NMR spectra showing the conversion of ***E*-8a** (blue highlight) to ***Z*-8a** (black highlight) in C_6D_6 under 365 nm irradiation.

2.9 NMR Photo/Thermal Isomerization Data of *E*-9a

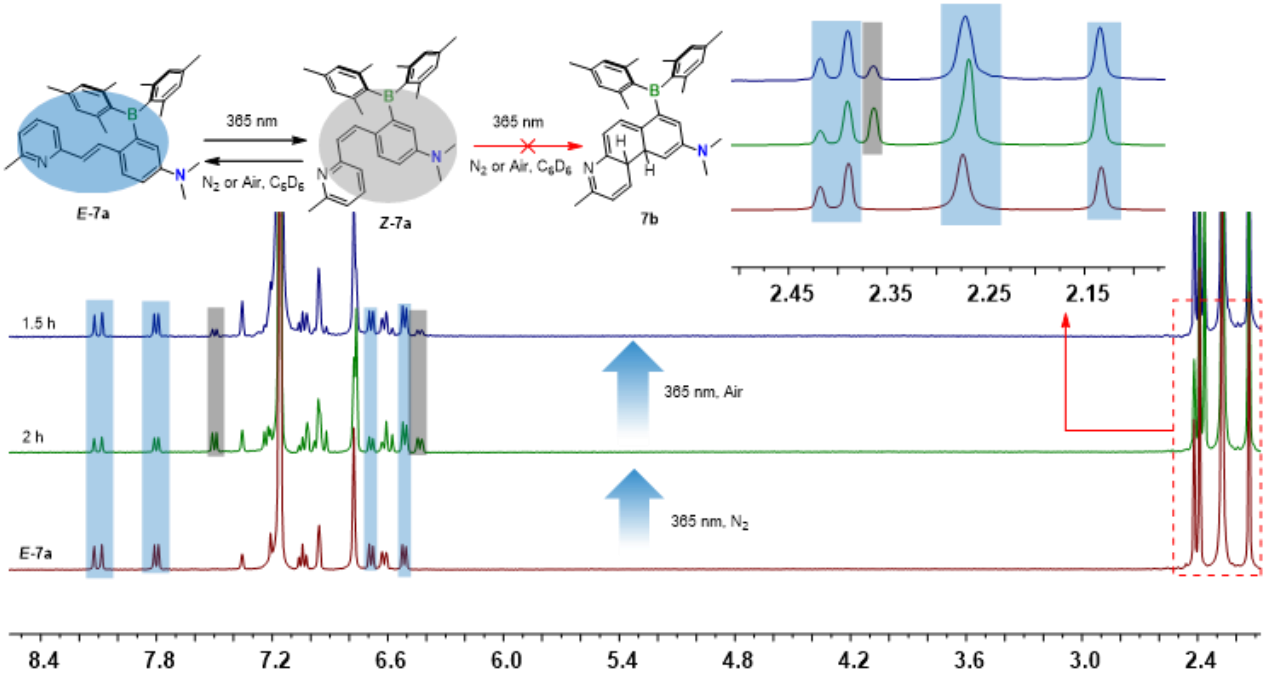


Figure S27. ^{1}H NMR spectra showing the conversion of ***E*-9a** (blue highlight) to ***Z*-9a** (black highlight) in C_6D_6 under 365 nm irradiation.

S3: Stability of 1b – 4b Under Ambient Conditions

General procedure:

Following conversion (according to the procedure outlined previously) to their cyclized products in J-Young NMR tubes, **1b** – **4b** were exposed to air by means of removing their Teflon caps. The samples were then monitored by NMR for the allotted time listed.

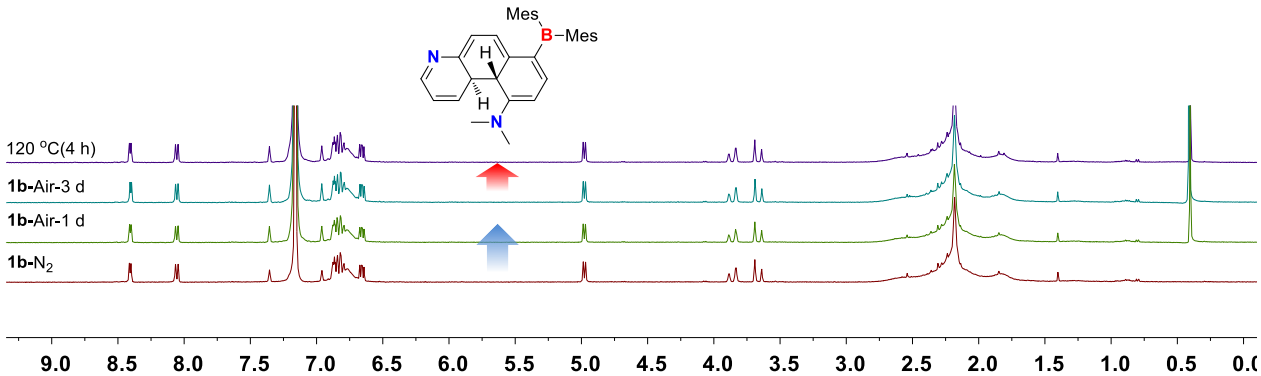


Figure S28. ^{1}H NMR tracking of compound **1b** upon exposure to the air.

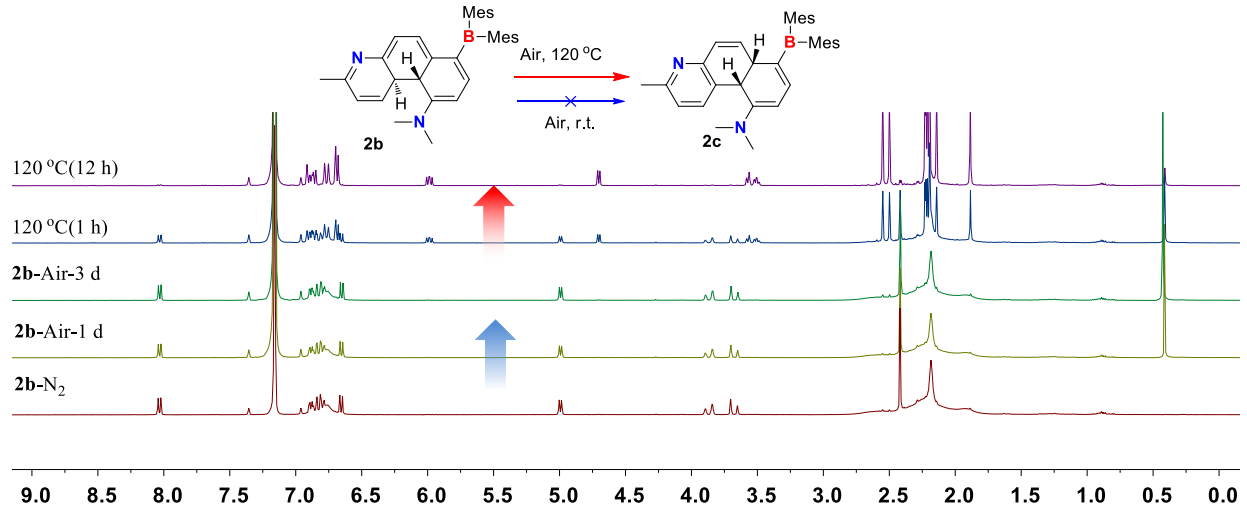


Figure S29. ^{1}H NMR tracking of compound **2b** under exposed to the air.

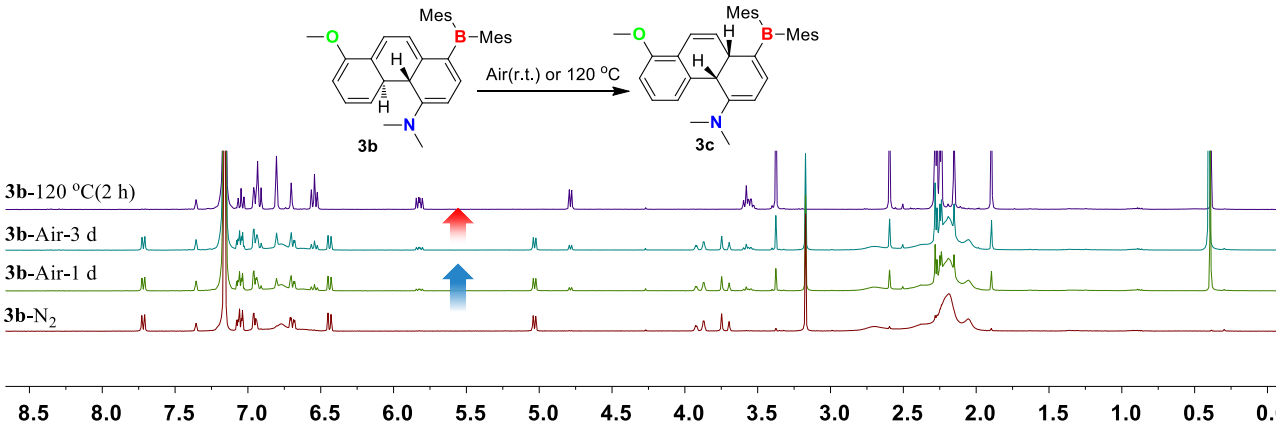


Figure S30. ^{1}H NMR tracking of compound **3b** under exposed to the air.

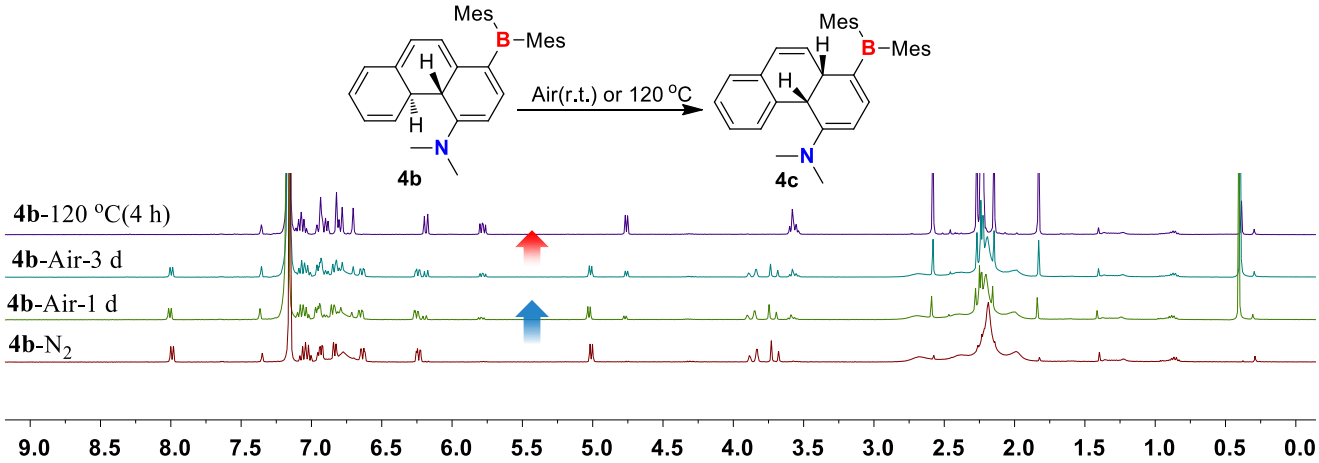


Figure S31. ^{1}H NMR tracking of compound **4b** under exposed to the air.

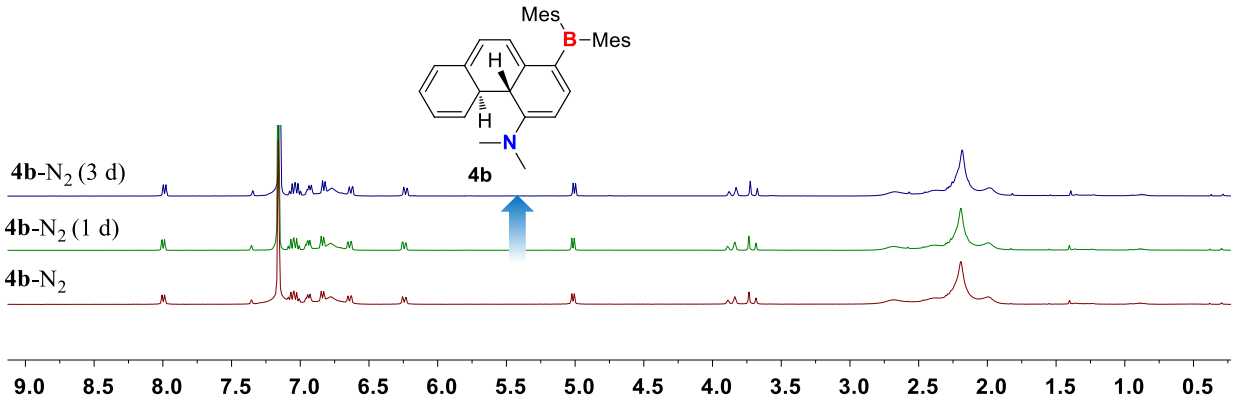


Figure S32. ^{1}H NMR tracking of compound **4b** under the N_2.

S4: Stability of 1c – 4c Under Ambient Conditions

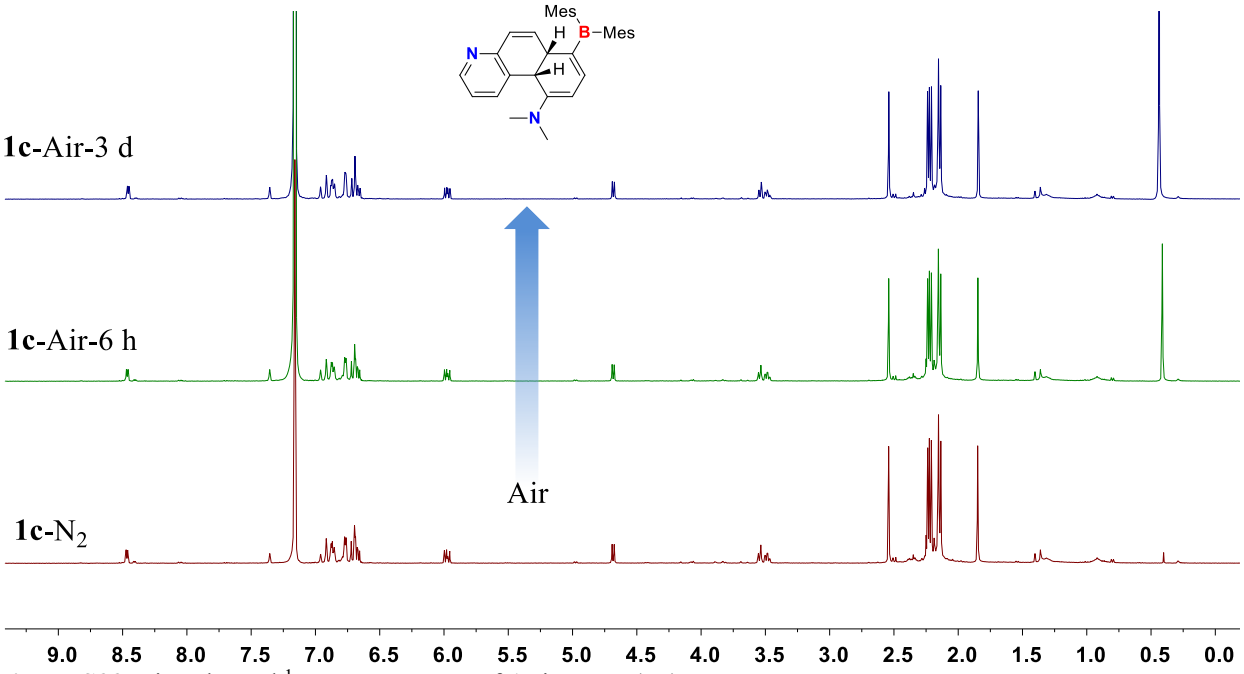


Figure S33. Time-lapsed ^{1}H NMR spectra of **1c** in C_6D_6 (r.t.).

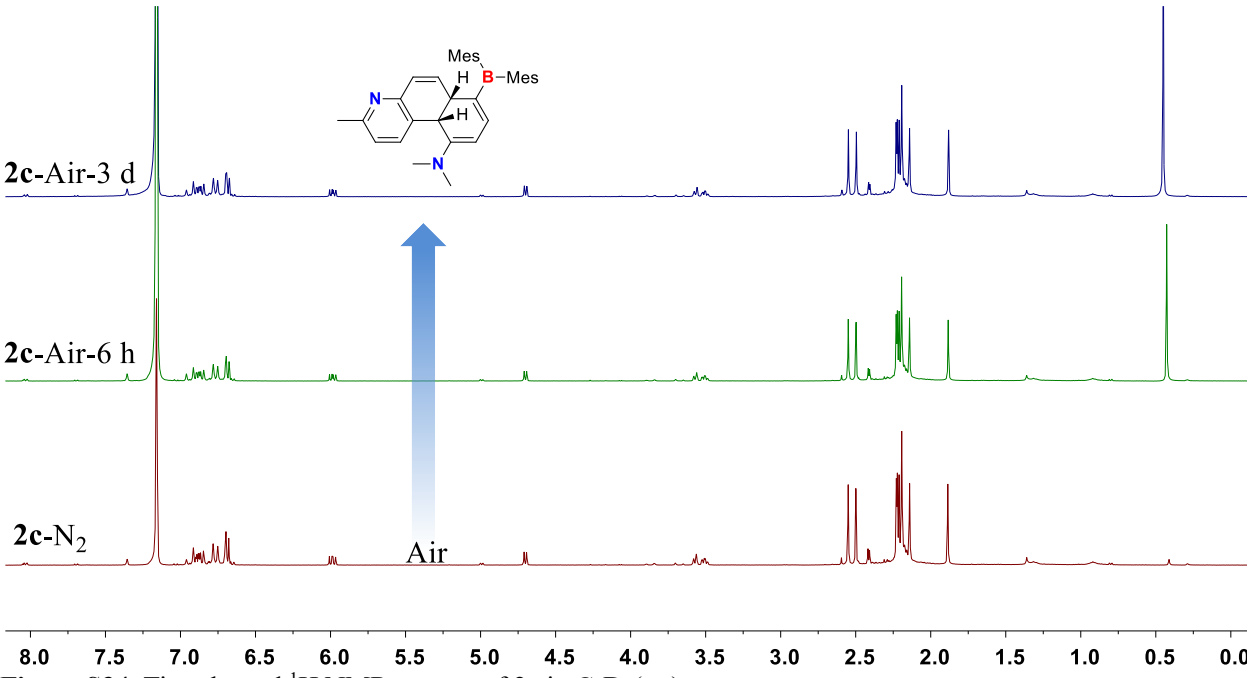


Figure S34. Time-lapsed ^{1}H NMR spectra of **2c** in C_6D_6(r.t.).

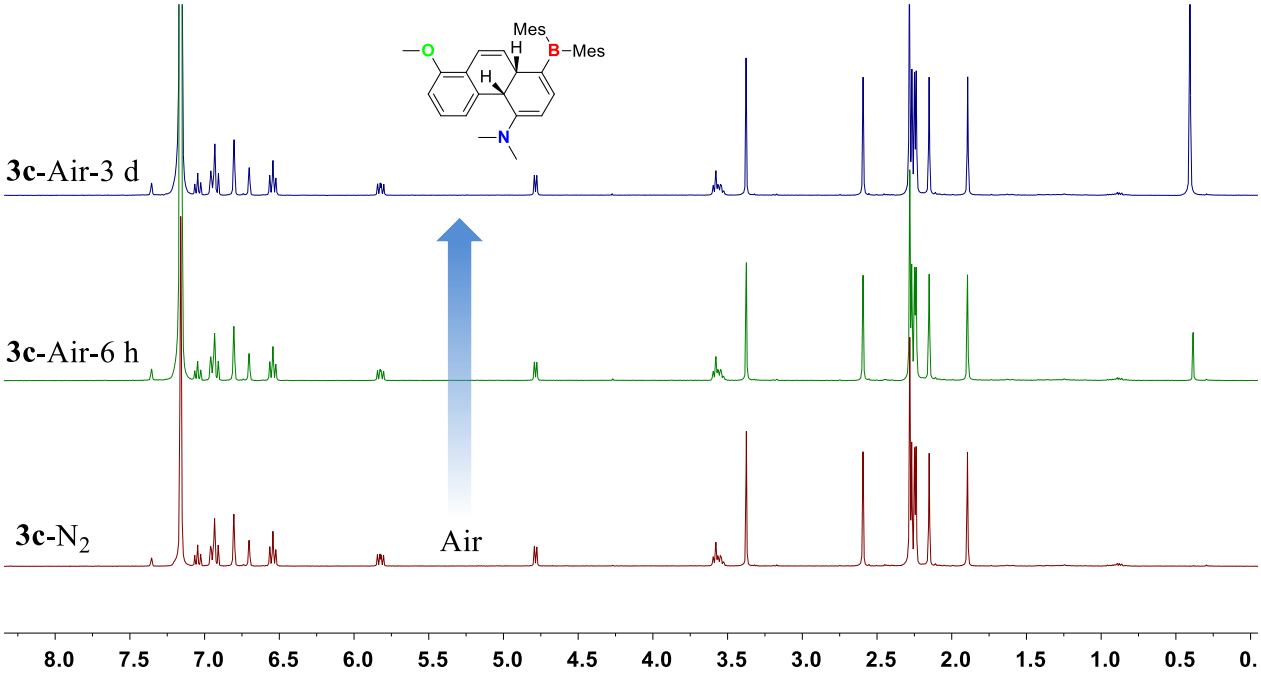


Figure S35. Time-lapsed ^{1}H NMR spectra of **3c** in C_6D_6(r.t.).

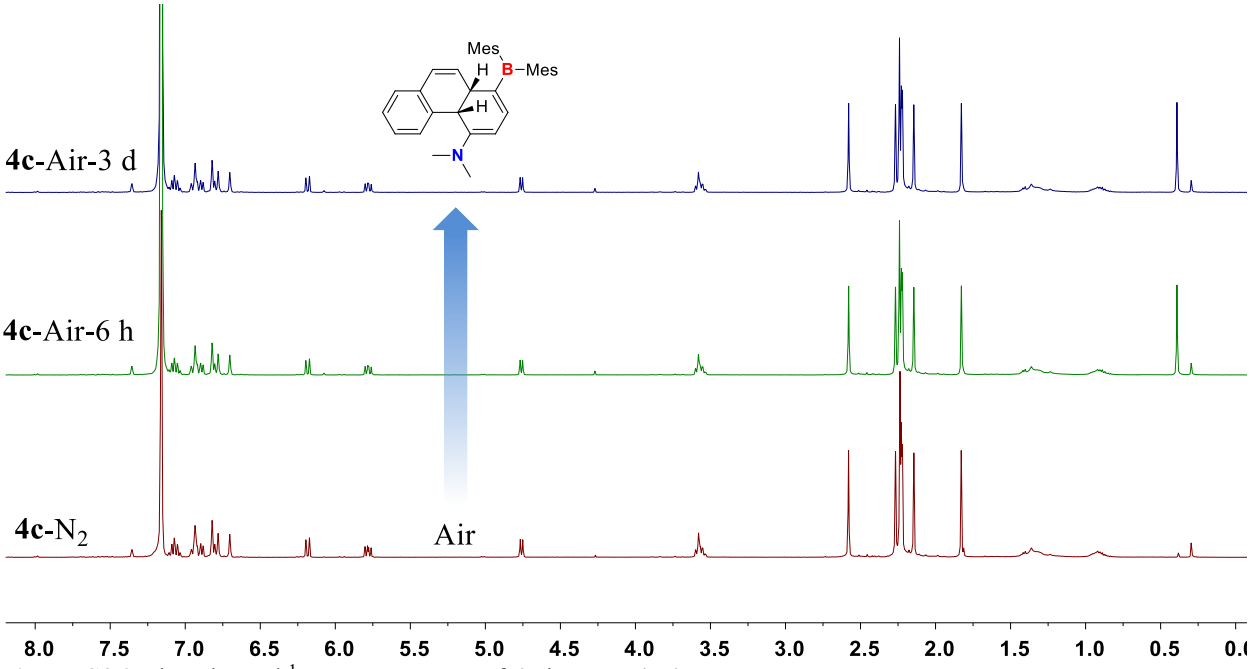


Figure S36. Time-lapsed ^{1}H NMR spectra of **4c** in C_6D_6 (r.t.).

S5: UV-Vis/Fluorescence Photoisomerization Data of *E*-1a–*E*-9a, 1d–4d, 6d

General procedure:

In a N_2 filled glovebox, compounds ***E*-1a** – ***E*-9a** were added to quartz cuvettes to achieve concentrations of 1×10^{-5} M in THF (2.8 mL), after which the completed samples were tightly sealed with their teflon caps and removed from the glovebox. Photoisomerization experiments were performed in a 360 nm Uv lamp (room temperature) and monitored periodically by UV-vis and fluorescence spectrometer until no additional spectral change was observed.

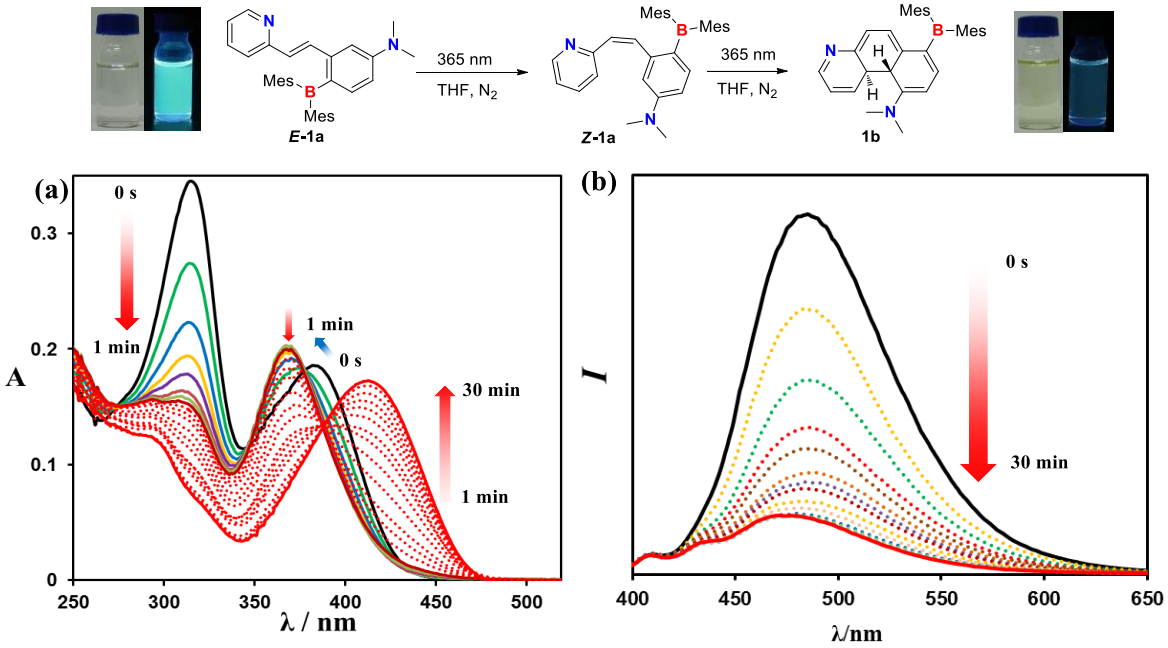


Figure S37. Absorption (a) and emission (b) spectra of ***E*-1a→*Z*-1a→1b** in THF (1× 10^{-5} M) under 365 nm irradiation. Excitation wavelength was 382 nm.

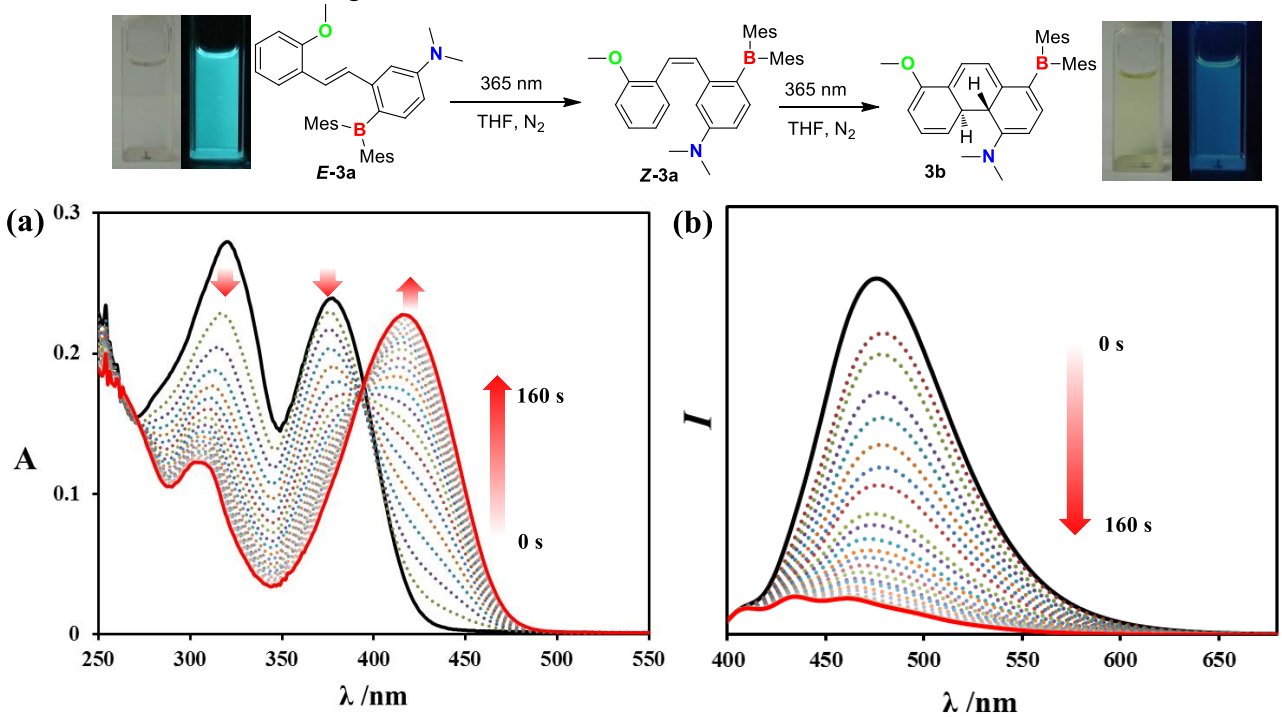


Figure S38. Absorption (a) and emission (b) spectra of ***E*-3a→*Z*-3a→3b** in THF (1 × 10^{-5} M) under 365 nm irradiation. Excitation wavelength was 379 nm.

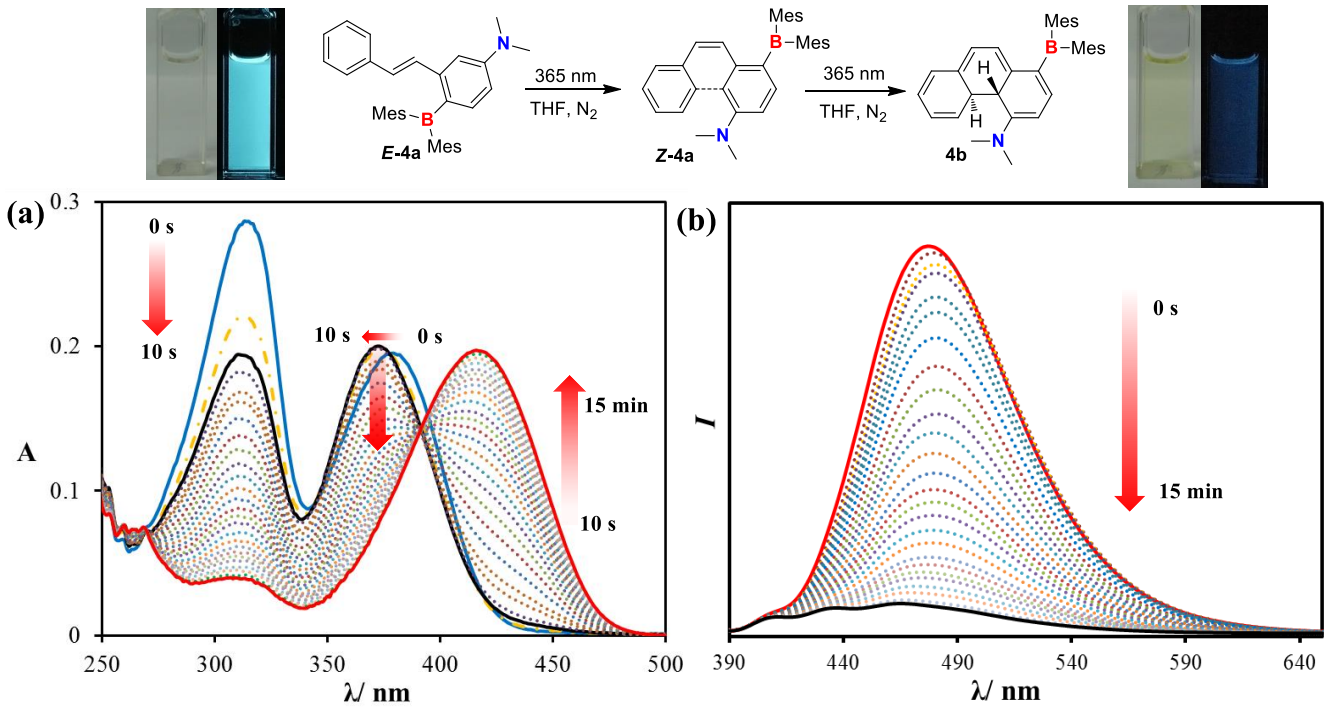


Figure S39. Absorption (a) and emission (b) spectra of ***E*-4a→*Z*-4a→4b** in THF (1×10^{-5} M) under 365 nm irradiation. Excitation wavelength was 382 nm.

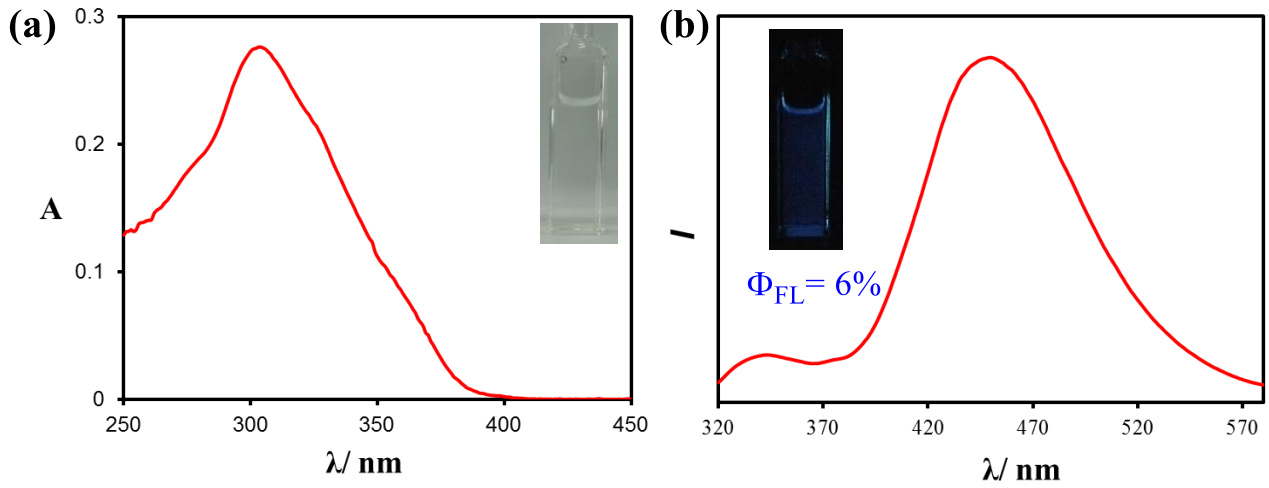


Figure S40. Absorption (a) and emission (b) spectra of ***E*-5a** in THF (1×10^{-5} M) under 365 nm irradiation. Excitation wavelength was 307 nm.

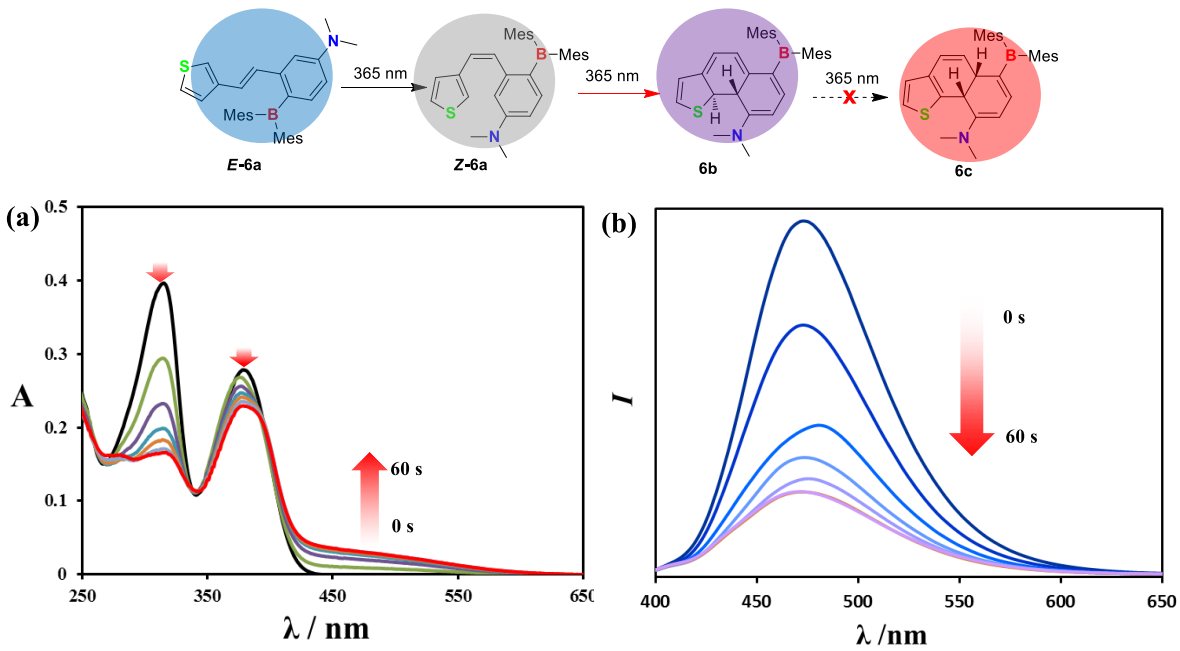


Figure S41. Absorption (a) and emission (b) spectra of ***E*-6a** to **6b** in THF (1×10^{-5} M) under 365 nm irradiation.

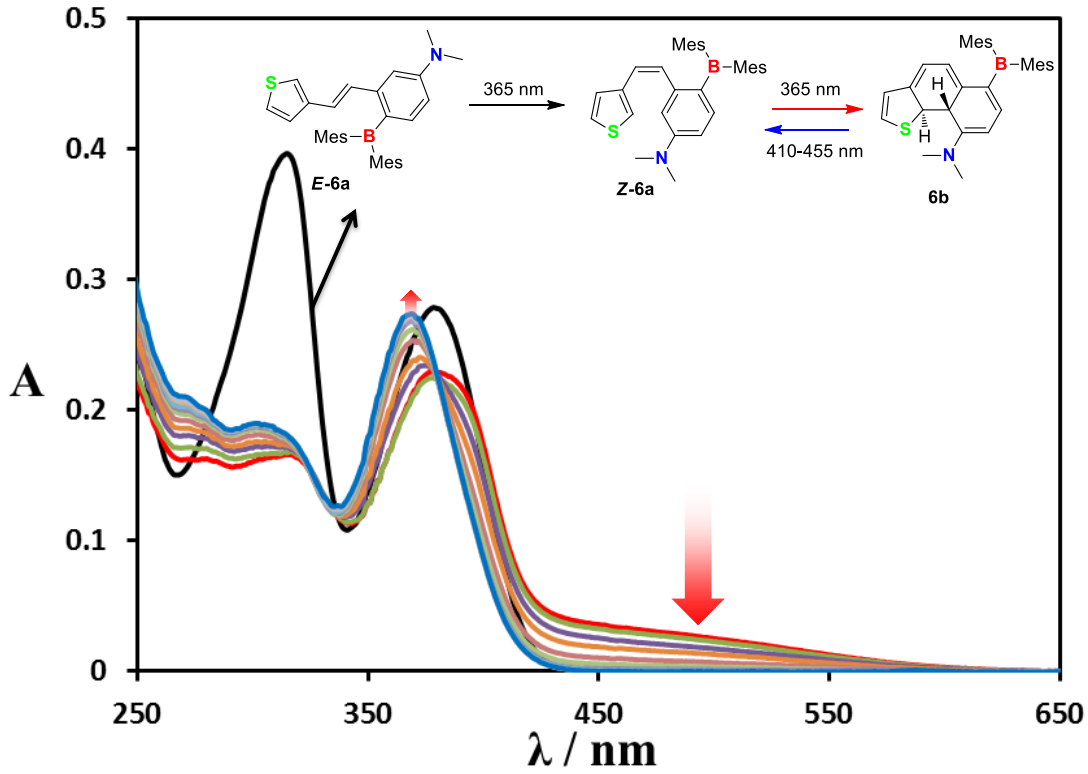


Figure S42. Absorption spectra of **6b** to ***Z*-6a** in THF (1×10^{-5} M) under 455 nm irradiation.

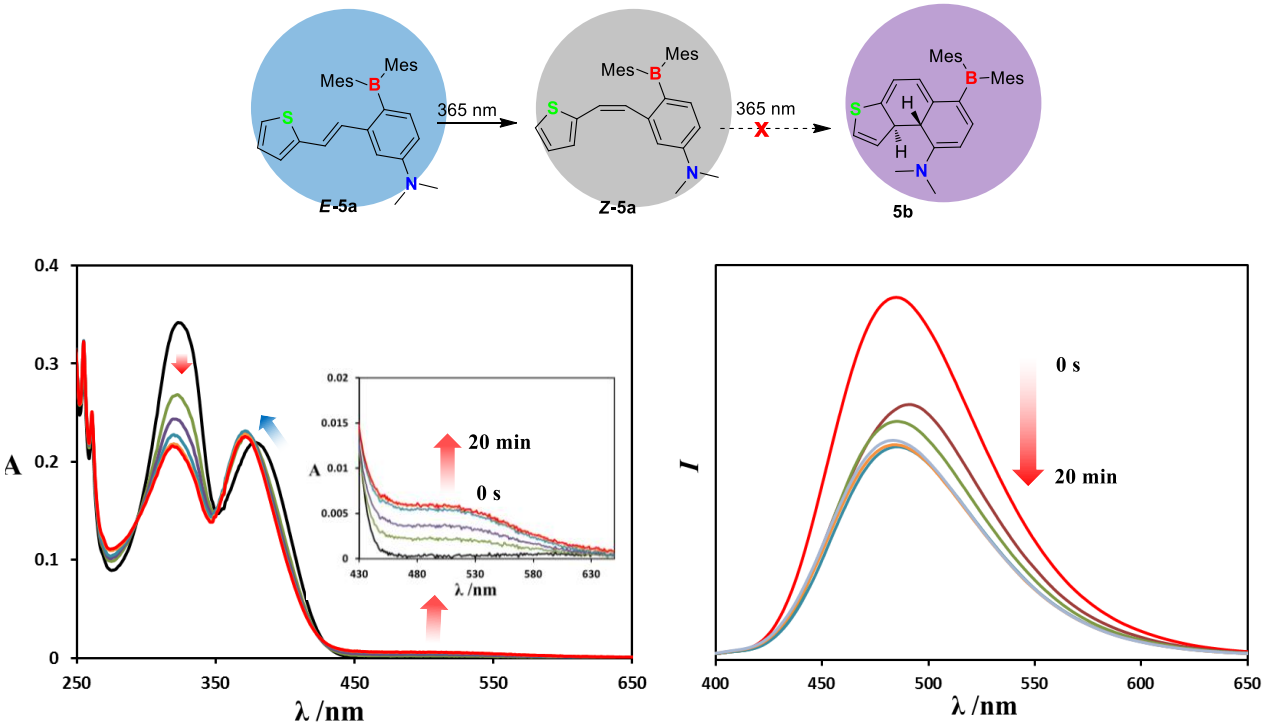


Figure S43. Absorption (a) and emission (b) spectra of ***E*-7a** to ***Z*-7a** in THF (1 × 10^{-5} M) under 365 nm irradiation. Excitation wavelength was 380 nm.

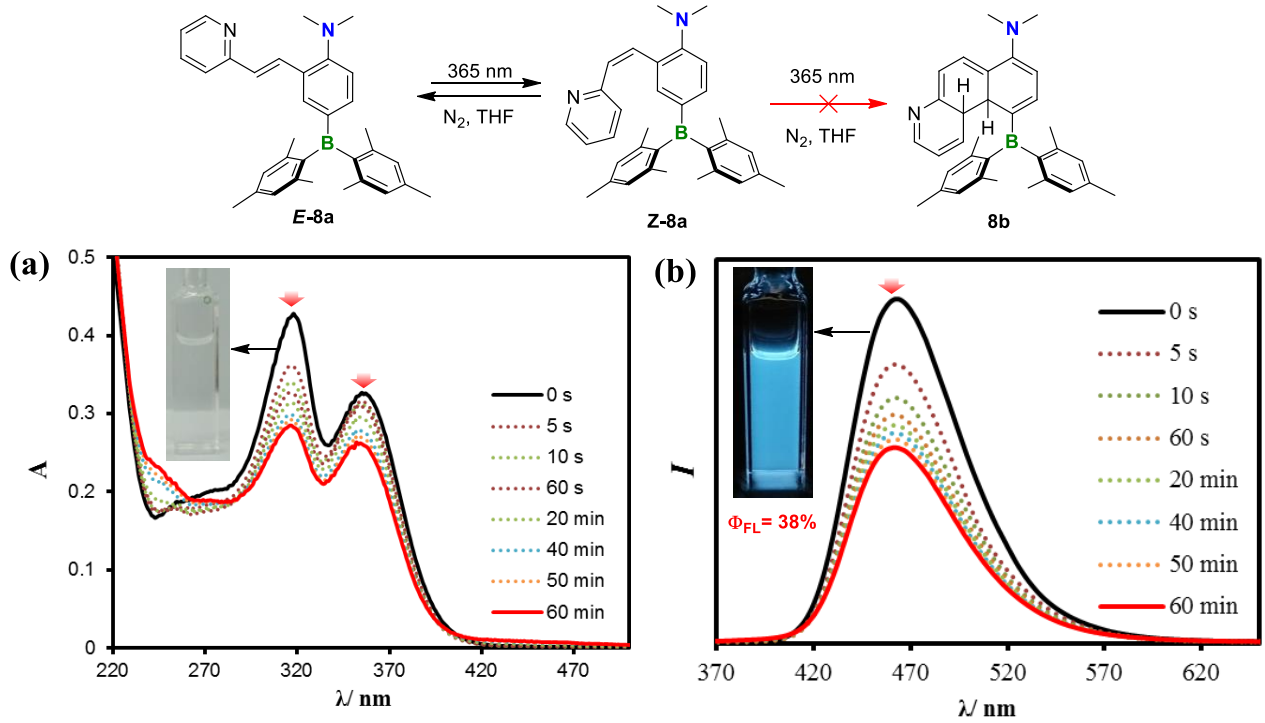


Figure S44. Absorption(a) and emission(b) spectra of ***E*-8a** in THF (1×10^{-5} M) under 365 nm irradiation. Excitation wavelength was 356 nm.

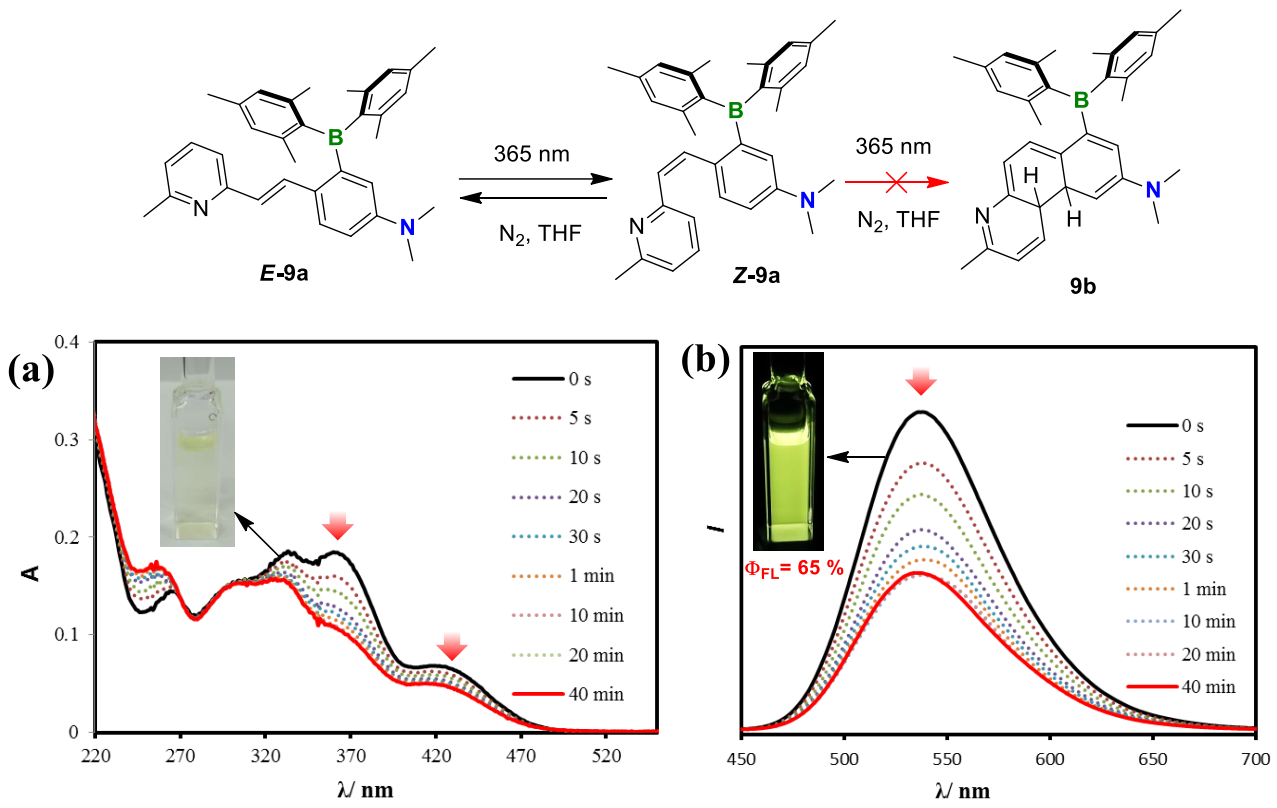


Figure S45. Absorption(a) and emission(b) spectra of ***E*-9a** in THF (1×10^{-5} M) under 365 nm irradiation. Excitation wavelength was 420 nm.

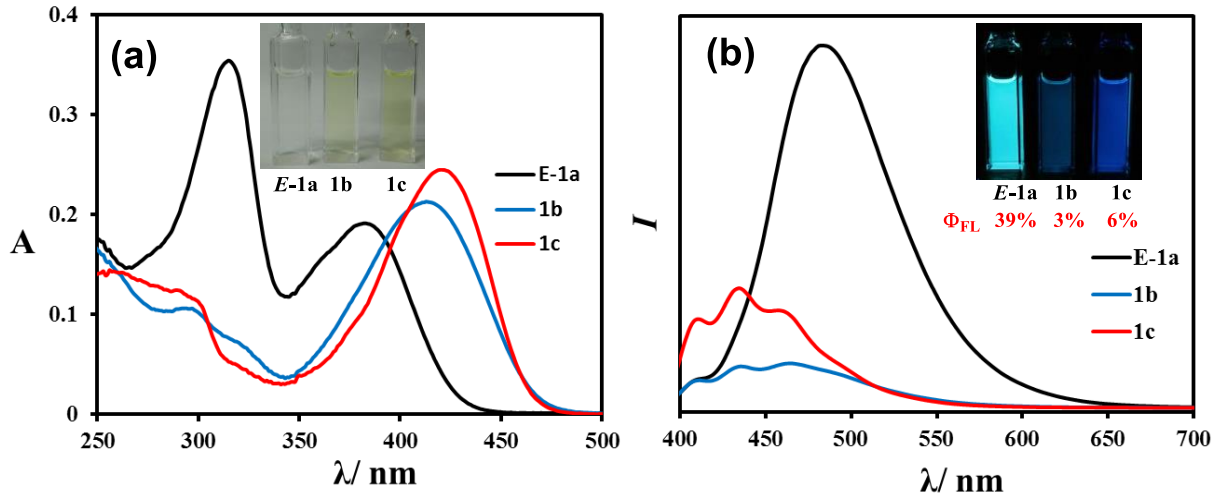


Figure S46. Absorption (a) and emission (b) spectra of ***E*-1a**, **1b** and **1c** in THF (1×10^{-5} M). Excitation wavelength was 382 nm.

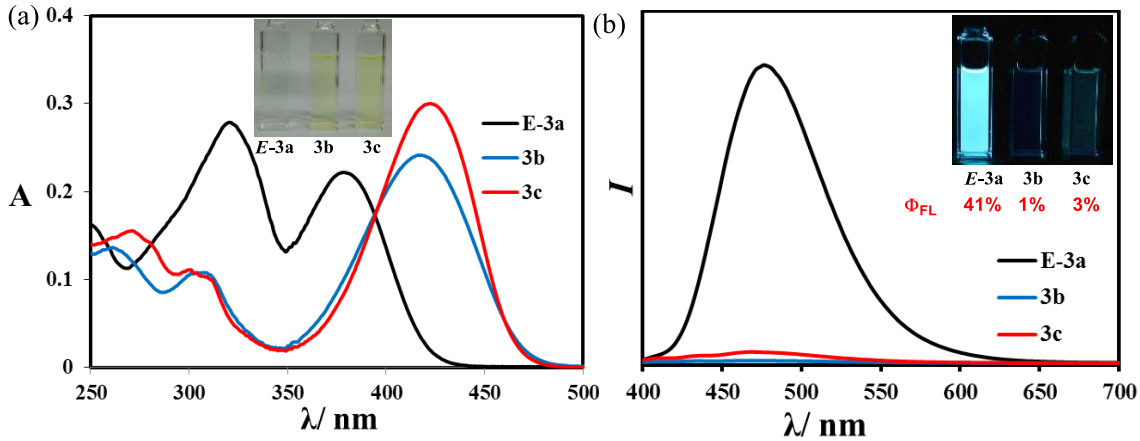


Figure S47. Absorption (a) and emission (b) spectra of ***E*-3a**, **3b** and **3c** in THF (1×10^{-5} M). Excitation wavelength was 379 nm.

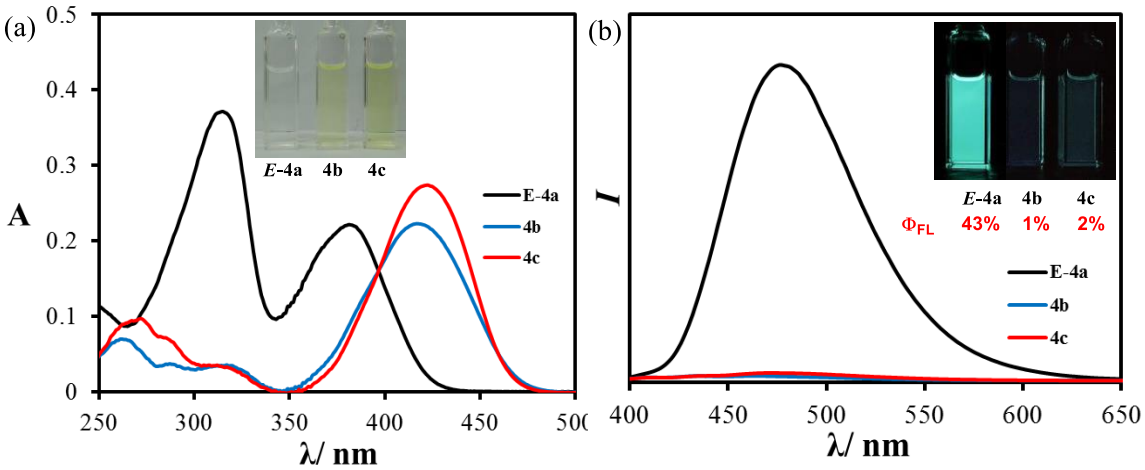


Figure S48. Absorption (a) and emission (b) spectra of ***E*-4a**, **4b** and **4c** in THF (1×10^{-5} M). Excitation wavelength was 382 nm.

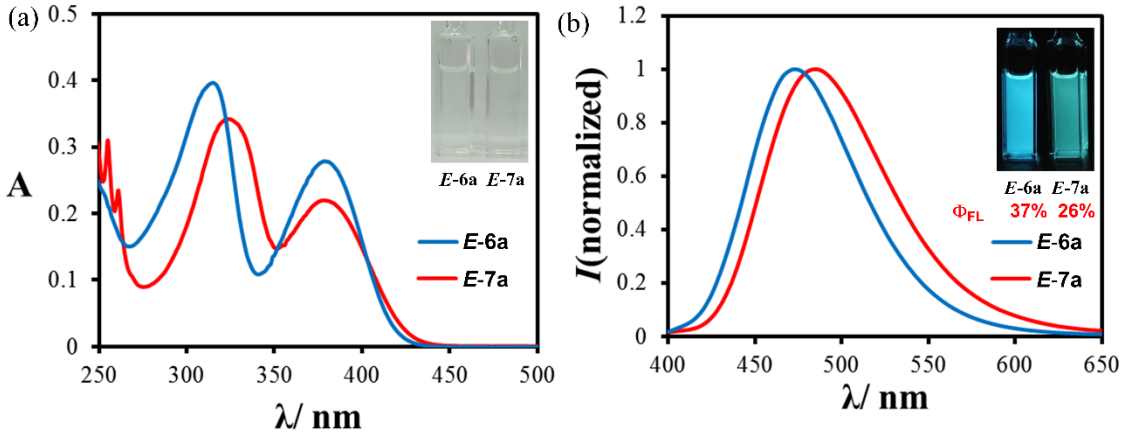


Figure S49. Absorption (a) and emission (b) spectra of ***E*-6a** and ***E*-7a** in THF (1×10^{-5} M). Excitation wavelength was 380 nm.

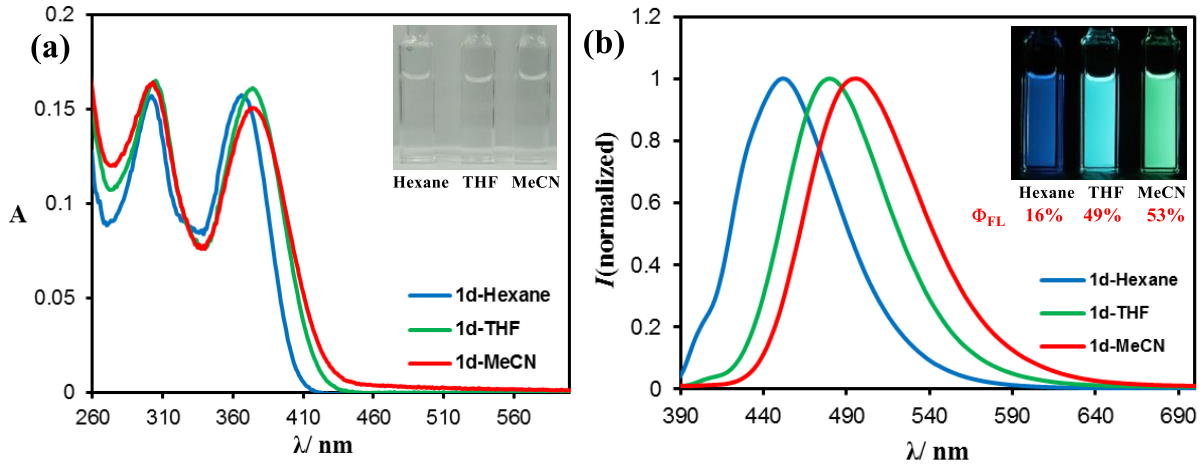


Figure S50. Absorption (a) and emission spectra (b) of **1d** in various solvents (1×10^{-5} M). The fluorescence spectra were recorded at λ_{max} of absorption.

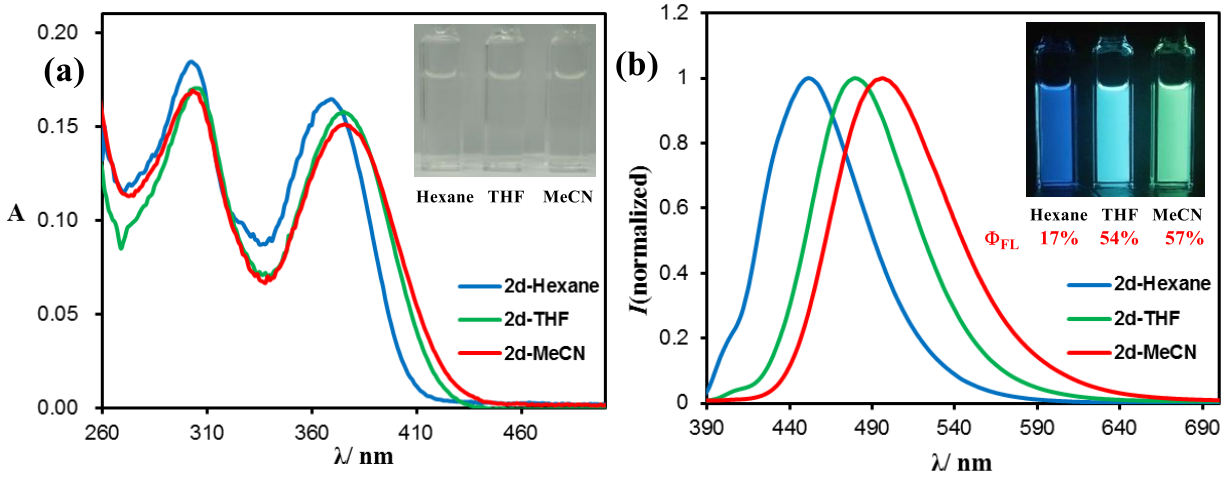


Figure S51. Absorption (a) and emission spectra (b) of **2d** in various solvents (1×10^{-5} M). The fluorescence spectra were recorded at λ_{max} of absorption.

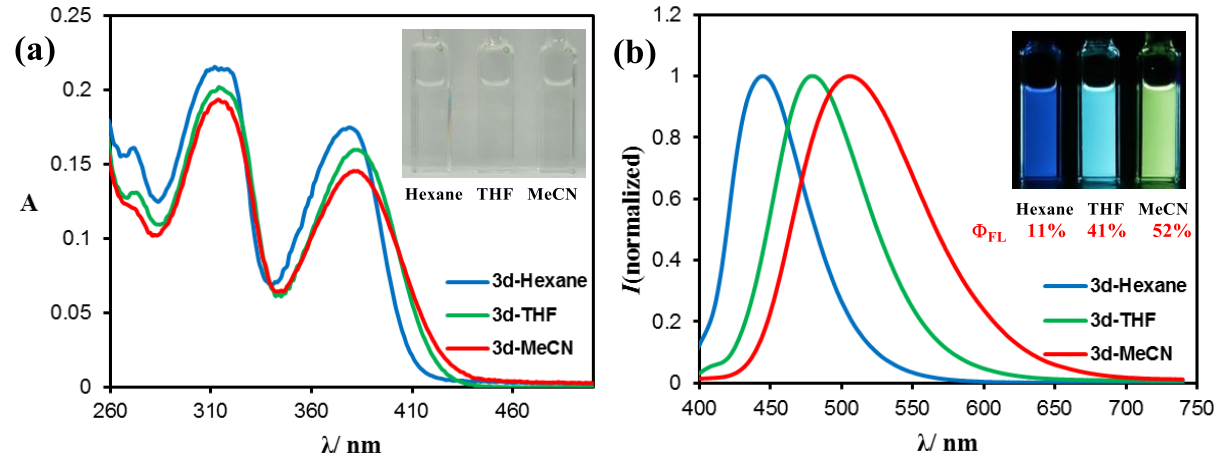


Figure S52. Absorption (a) and emission spectra (b) of **3d** in various solvents (1×10^{-5} M). The fluorescence spectra were recorded at λ_{max} of absorption.

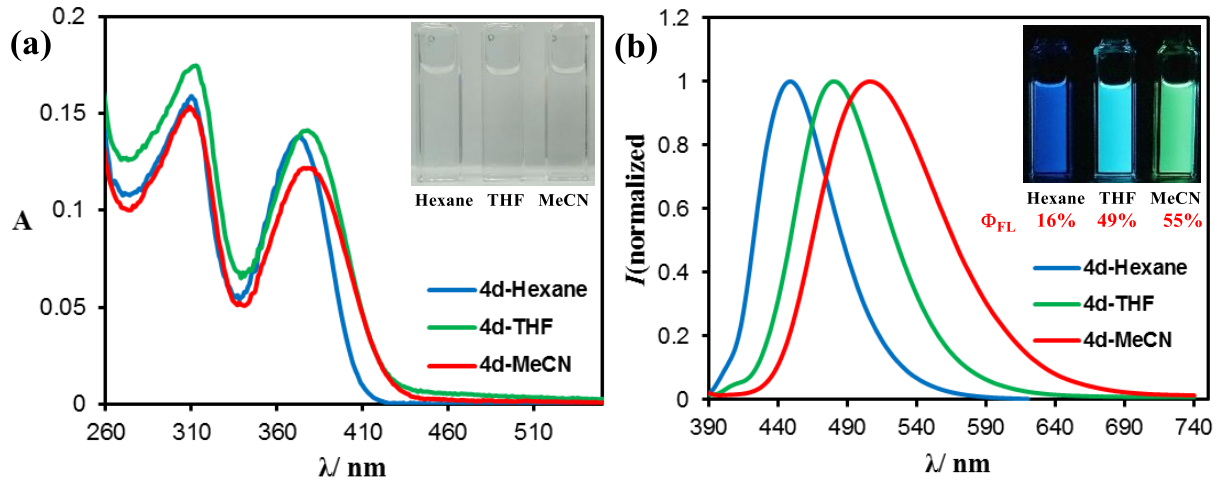


Figure S53. Absorption (a) and emission spectra (b) of **4d** in various solvents (1×10^{-5} M). The fluorescence spectra were recorded at λ_{max} of absorption.

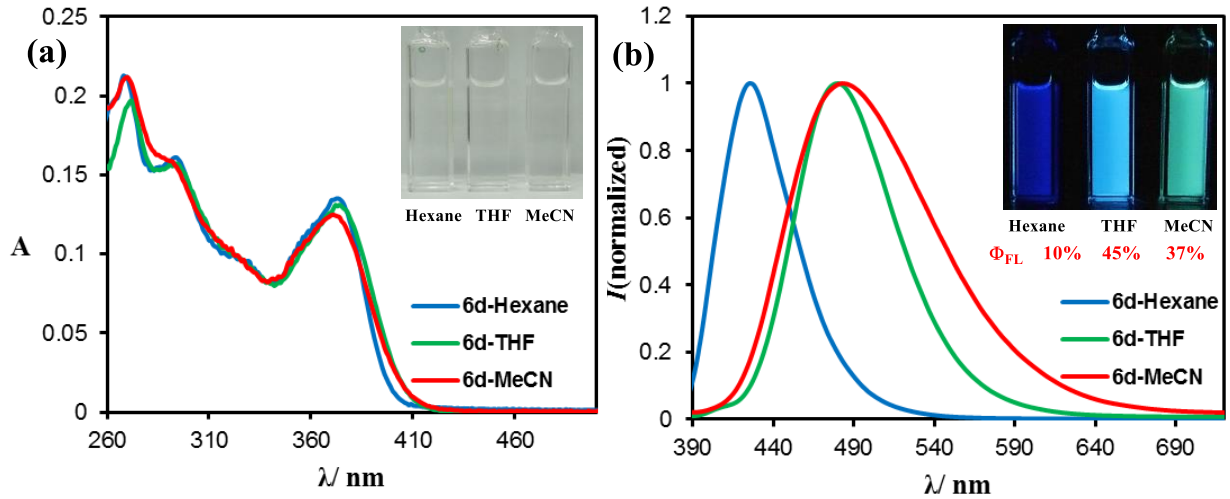


Figure S54. Absorption (a) and emission spectra (b) of **6d** in various solvents (1×10^{-5} M). The fluorescence spectra were recorded at λ_{max} of absorption.

S6: H/D Exchange and Kinetic Data

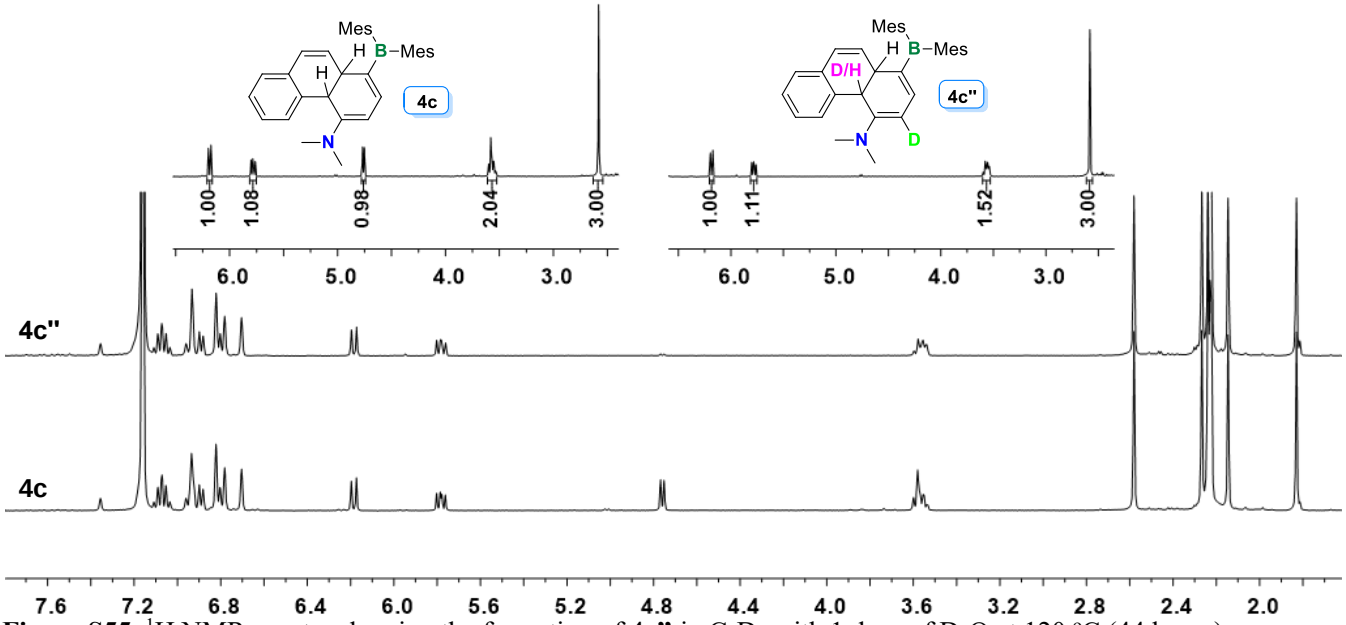
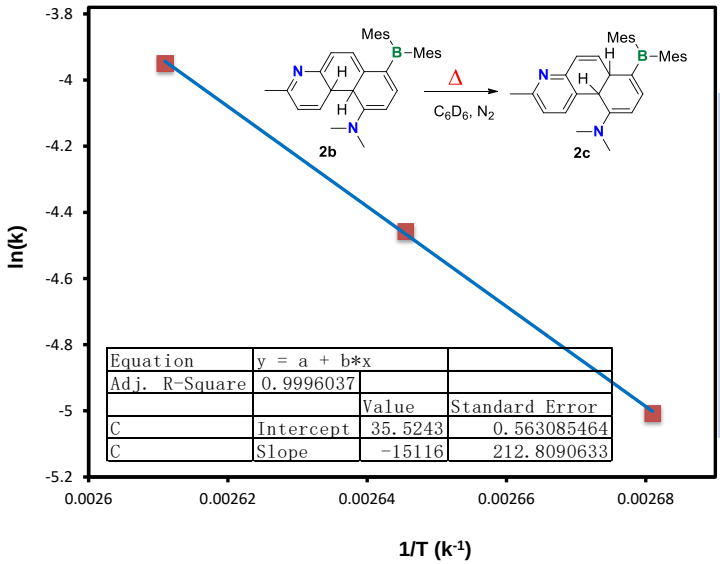


Figure S55. ^{1}H NMR spectra showing the formation of **4c"** in C_6D_6 with 1 drop of D_2O at 120 °C (44 hours).



$-E_a/R = -1.5116 \times 10^4$ K

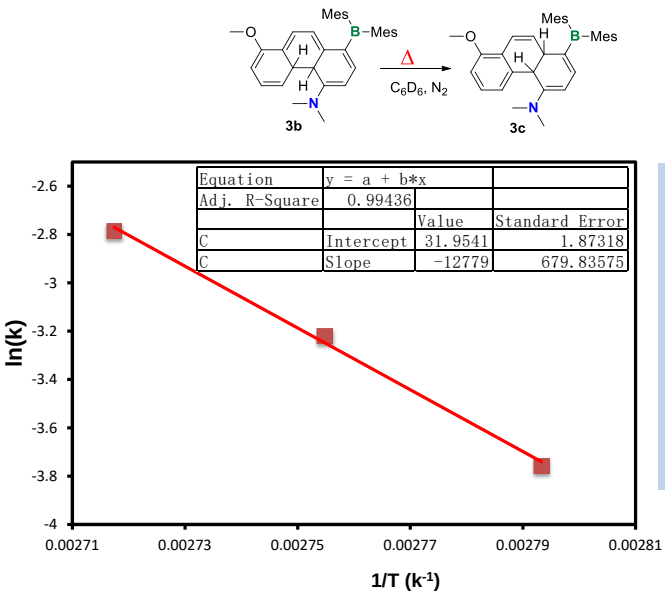
R=8.3138462≈8.314 J/(mol·K)

E_a = 125674.424 J·mol^{-1}

E_a = 30051.27 cal·mol^{-1}

≈ 30.0(4) kcal·mol^{-1}

Figure S56. Arrhenius plot of the rate constants for **2b** to **2c**.



$-E_a/R = -1.2779 \times 10^4$ K

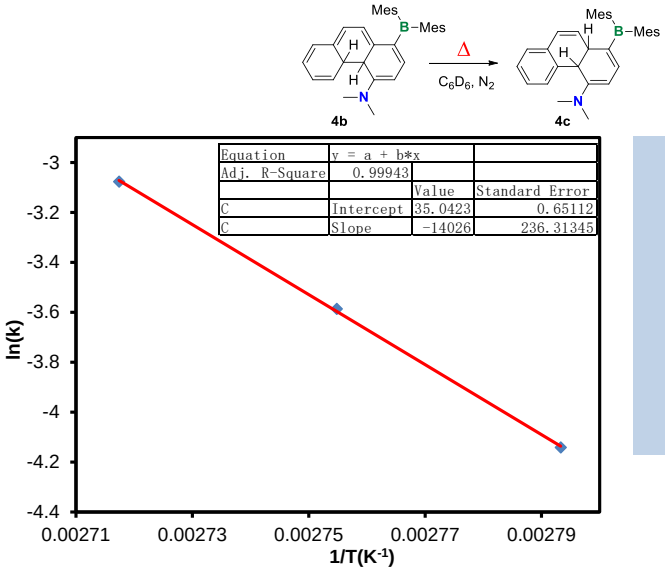
R=8.3138462≈8.314 J/(mol·K)

E_a = 106244.61 J·mol^{-1}

E_a = 25405.21 cal·mol^{-1}

≈ 25(1) kcal·mol^{-1}

Figure S57. Arrhenius plot of the rate constants for **3b** to **3c**.



$-E_a/R = -1.4026 \times 10^4$ K

R=8.3138462≈8.314 J/(mol·K)

E_a = 116612.16 J·mol^{-1}

E_a = 27884.30 cal·mol^{-1}

≈ 27.9(5) kcal·mol^{-1}

Figure S58. Arrhenius plot of the rate constants for **4b** to **4c**.

S7: Characterization Data

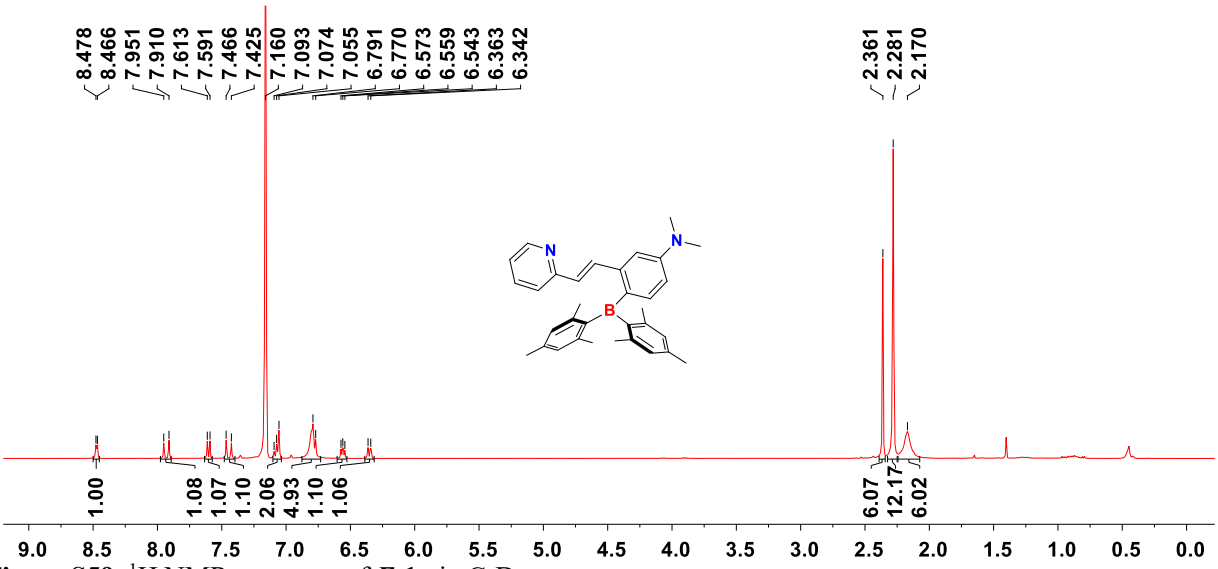


Figure S59. ^{1}H NMR spectrum of ***E*-1a** in C_6D_6.

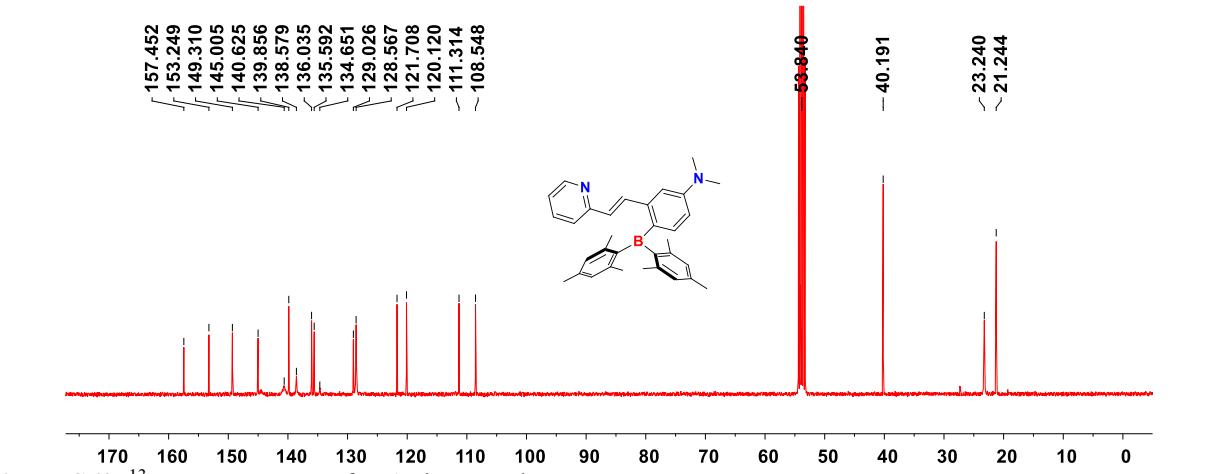


Figure S60. ^{13}C NMR spectra of ***E*-1a** in CD_2Cl_2.

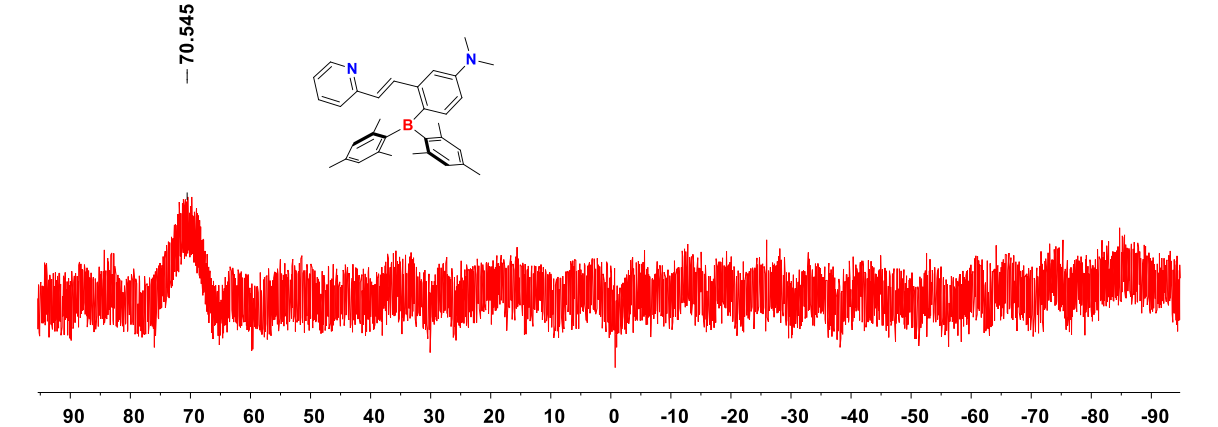


Figure S61. ^{11}B NMR spectrum of ***E*-1a** in C_6D_6.

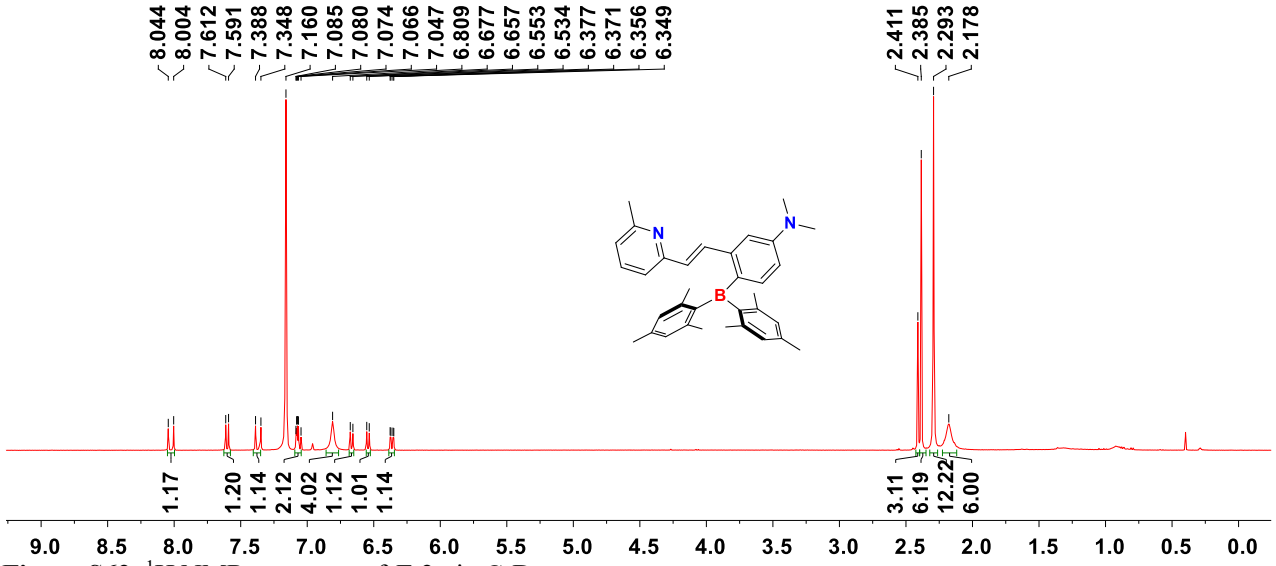


Figure S62. ^{1}H NMR spectrum of ***E*-2a** in C_6D_6.

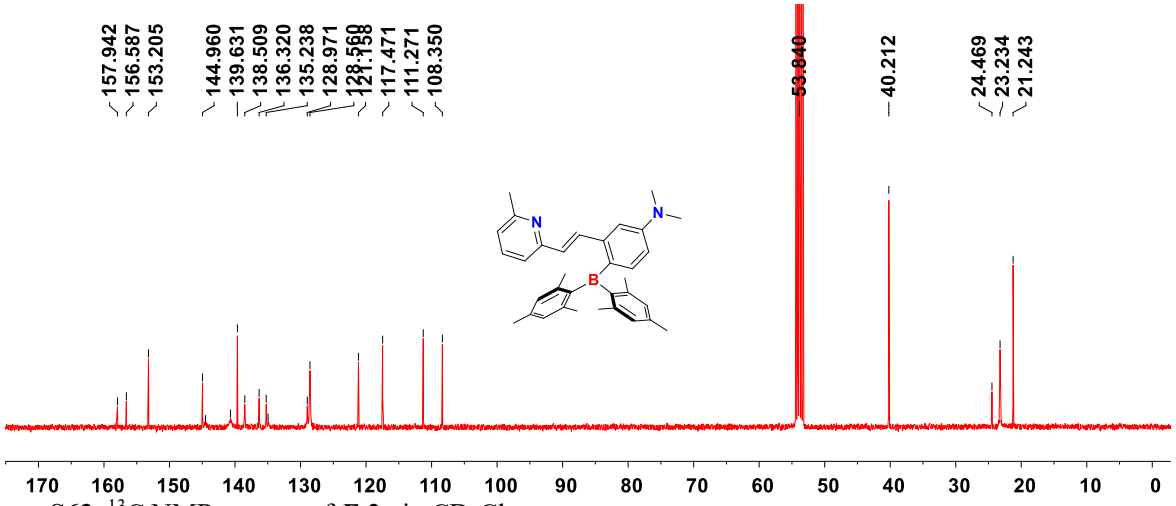


Figure S63. ^{13}C NMR spectra of ***E*-2a** in CD_2Cl_2.

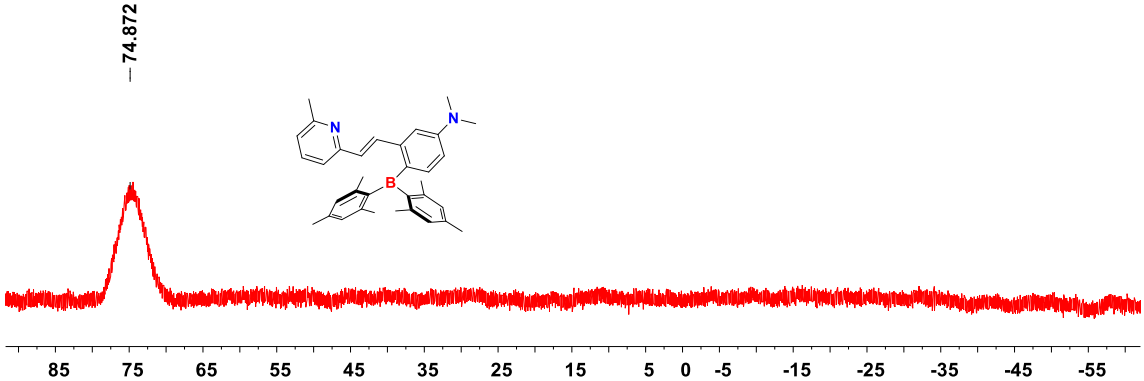


Figure S64. ^{11}B NMR spectrum of ***E*-2a** in C_6D_6.

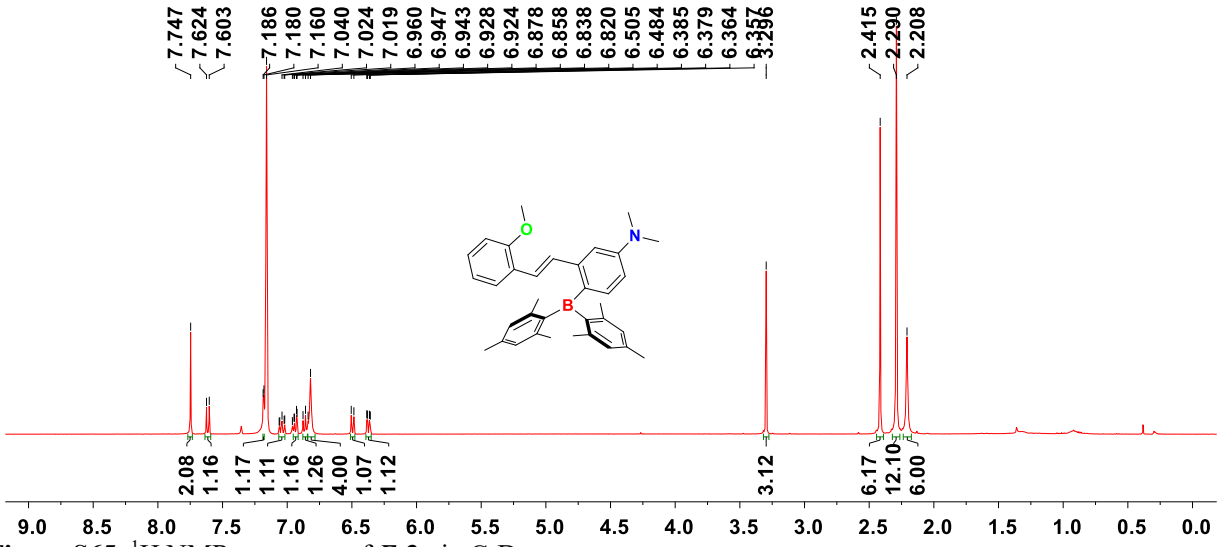


Figure S65. ^{1}H NMR spectrum of ***E*-3a** in C_6D_6.

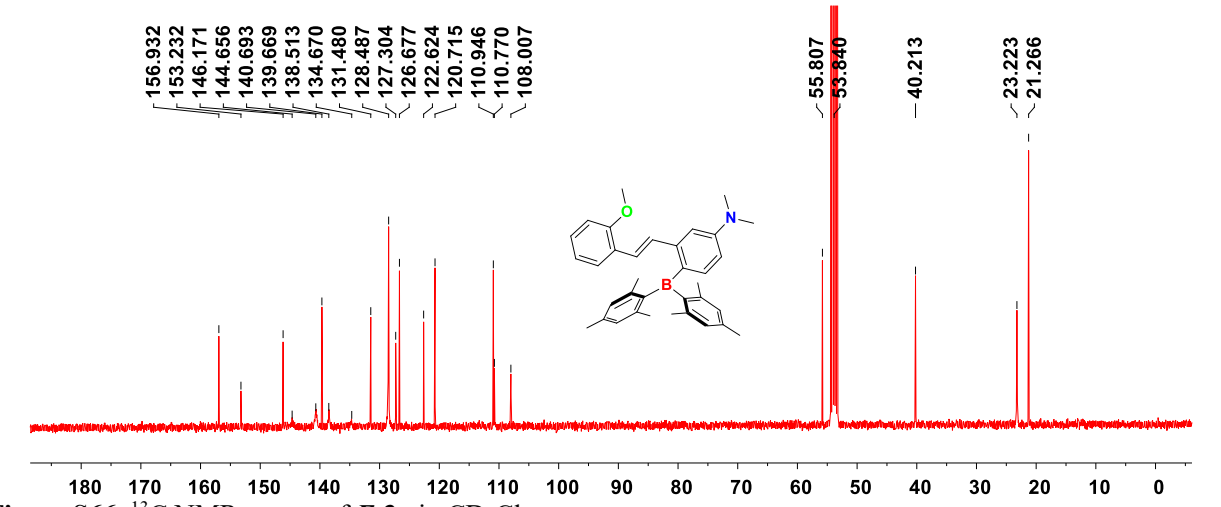


Figure S66. ^{13}C NMRspectra of ***E*-3a** in CD_2Cl_2.

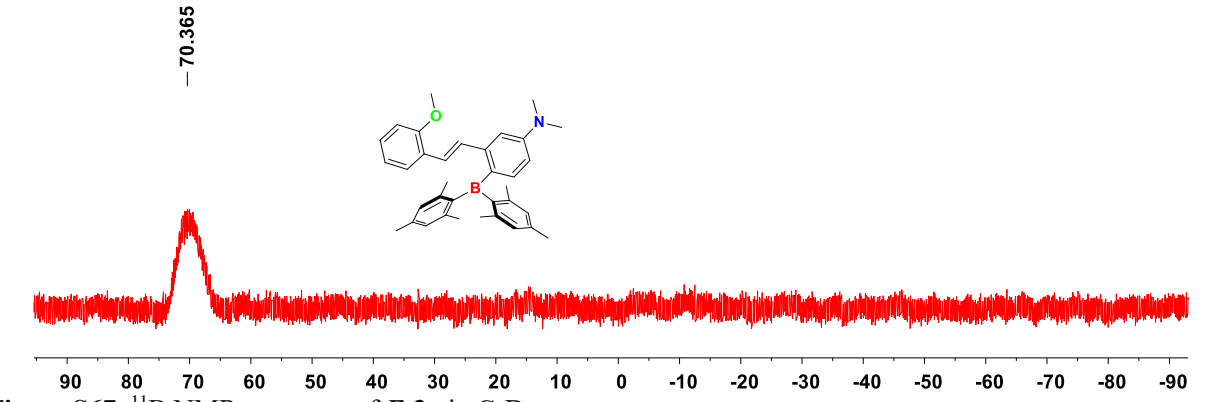


Figure S67. ^{11}B NMR spectrum of ***E*-3a** in C_6D_6.

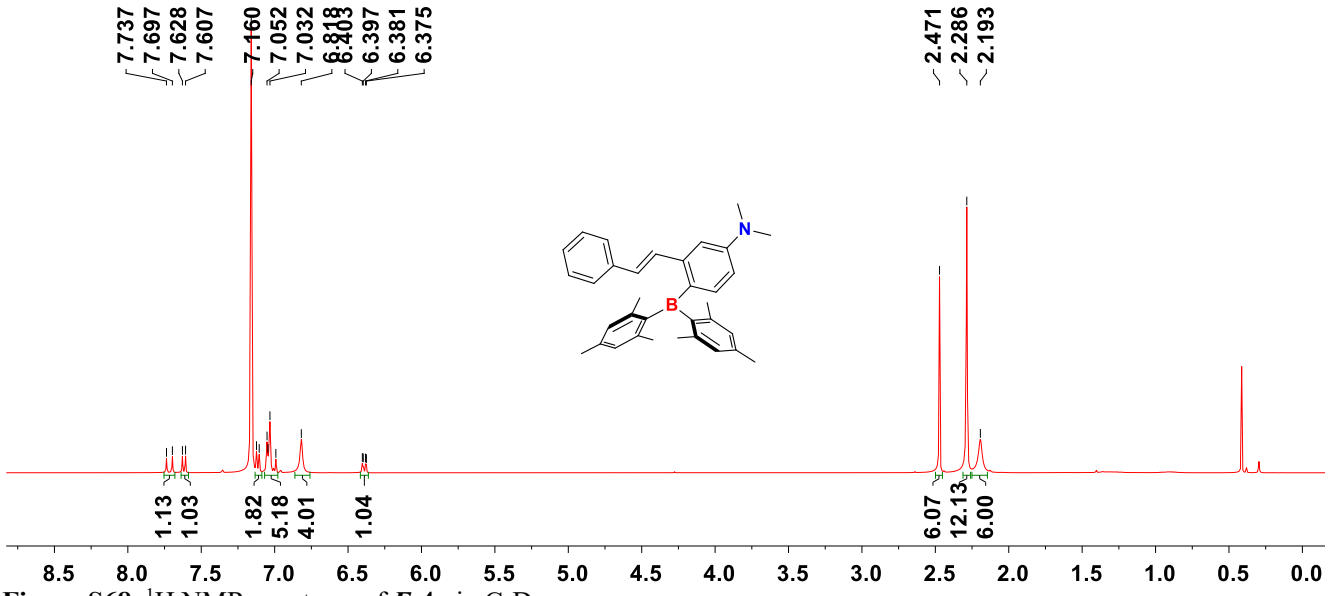


Figure S68. ^{1}H NMR spectrum of ***E*-4a** in C_6D_6.

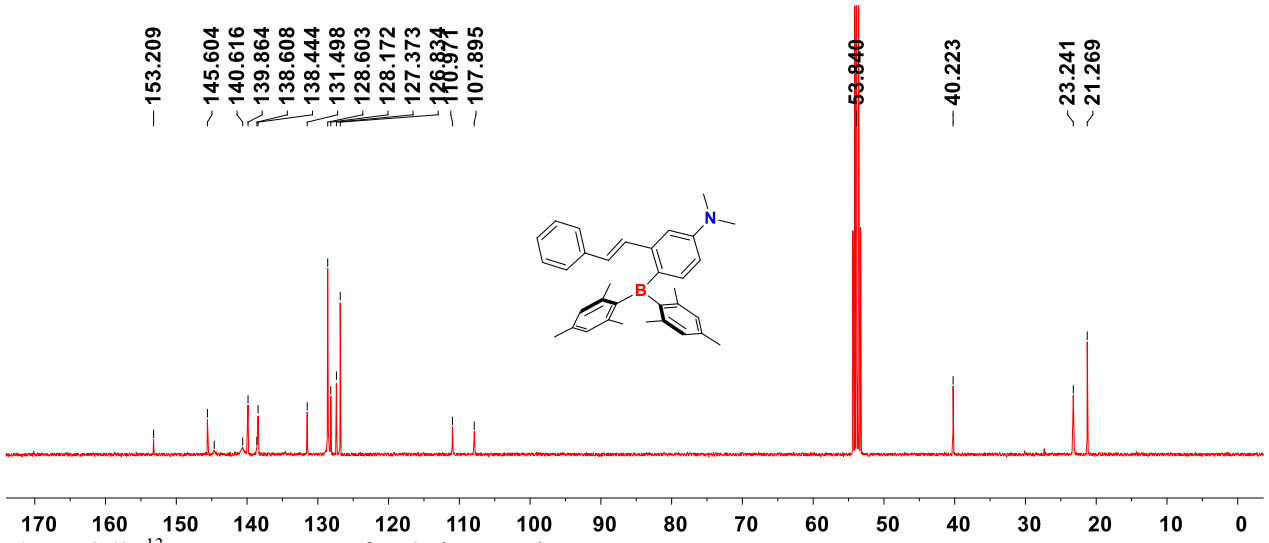


Figure S69. ^{13}C NMR spectra of ***E*-4a** in CD_2Cl_2.

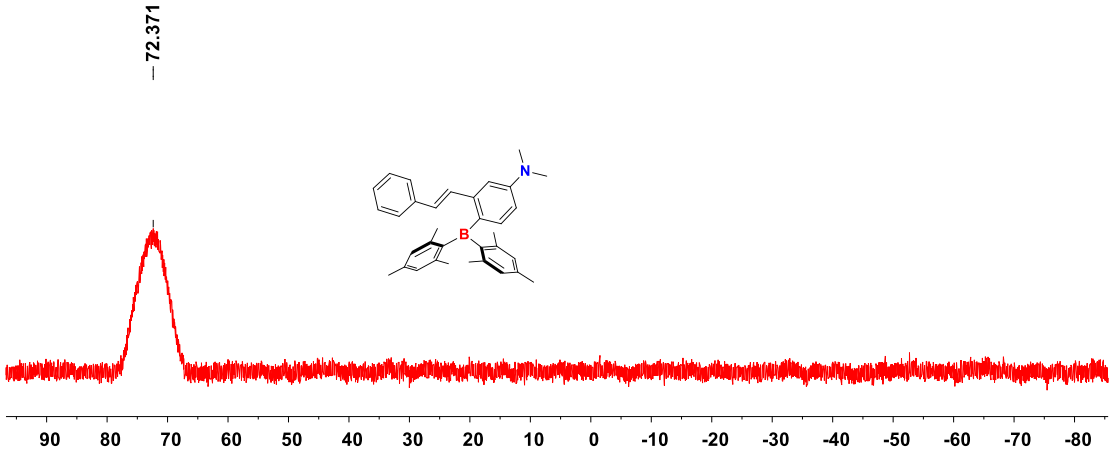


Figure S70. ^{11}B NMR spectra of ***E*-4a** in CD_2Cl_2.

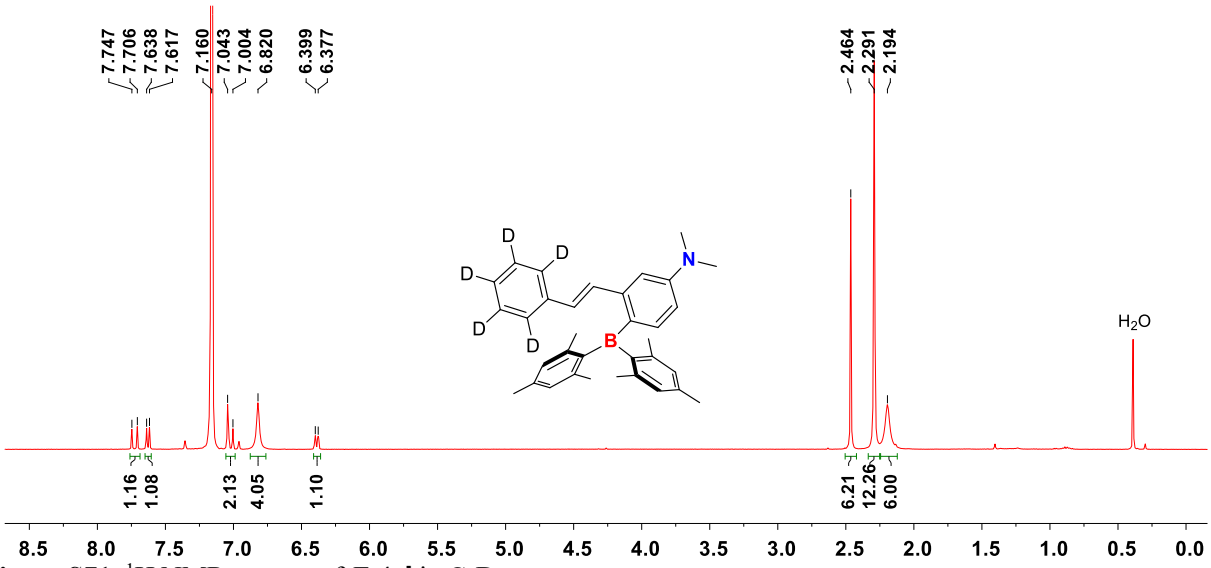


Figure S71. ^{1}H NMR spectra of ***E*-4a'** in C_6D_6.

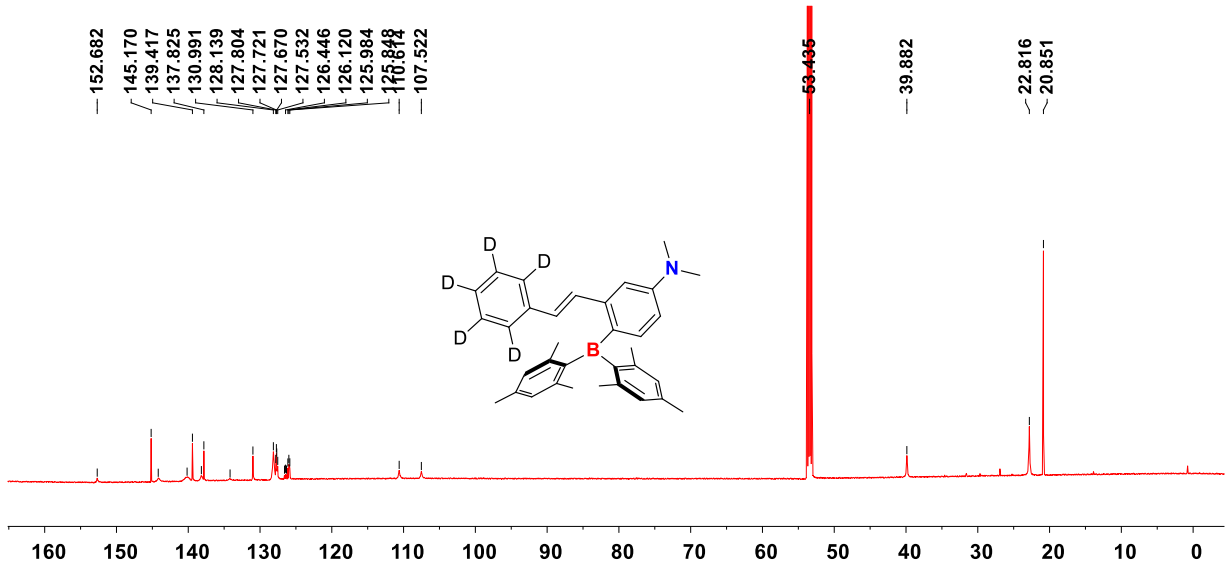


Figure S72. ^{13}C NMR spectra of ***E*-4a'** in CD_2Cl_2.

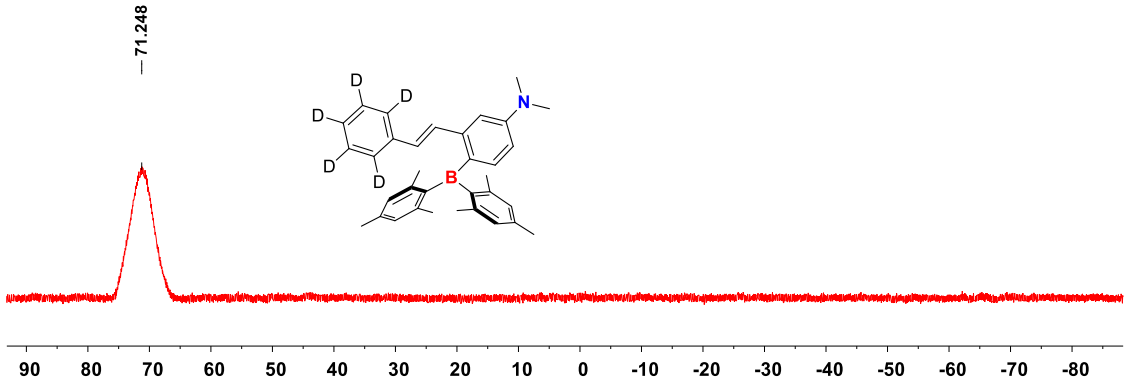


Figure S73. ^{11}B NMR spectra of ***E*-4a'** in CD_2Cl_2.

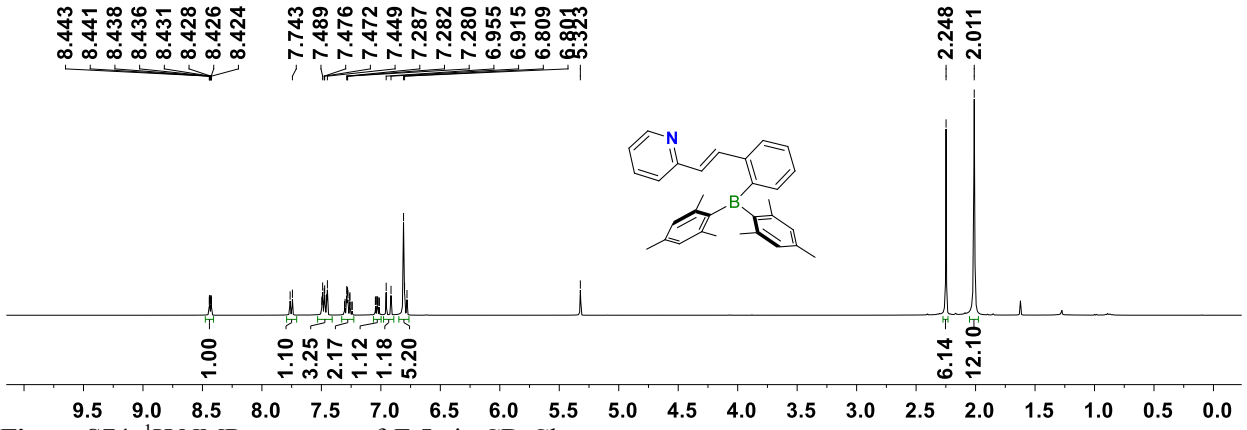


Figure S74. ^{1}H NMR spectrum of ***E*-5a** in CD_2Cl_2.

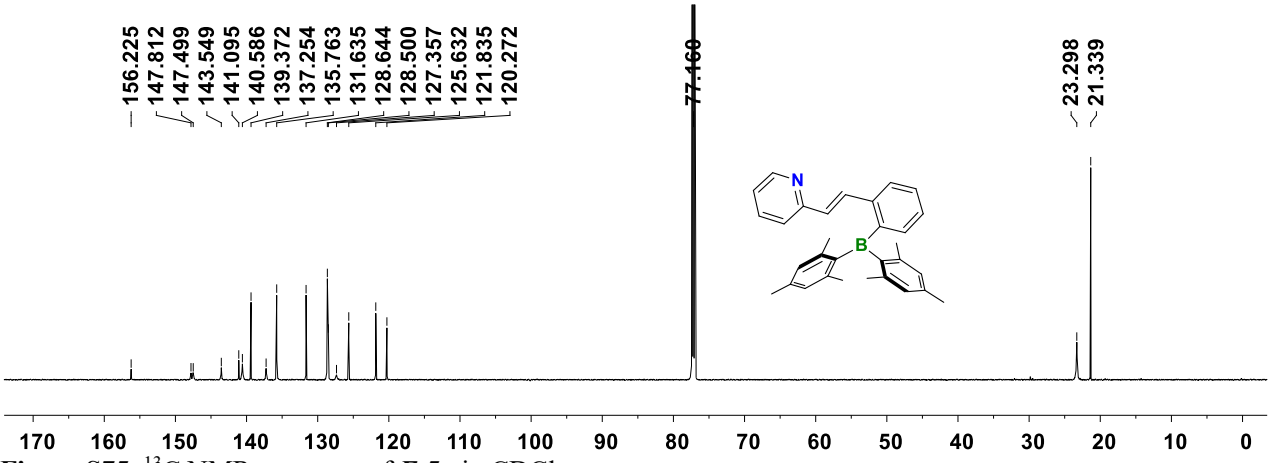


Figure S75. ^{13}C NMR spectrum of ***E*-5a** in $CDCl_3$.

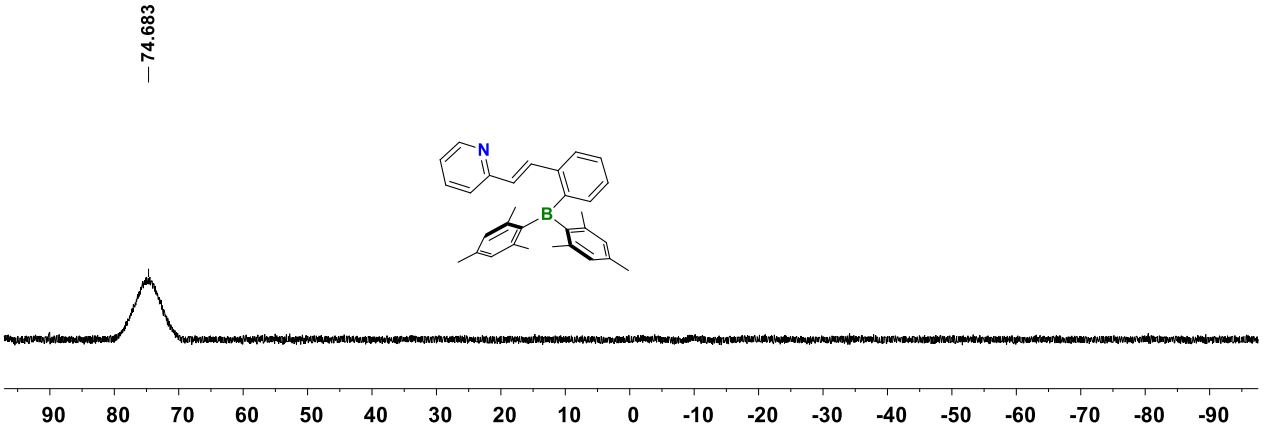


Figure S76. ^{11}B NMR spectrum of ***E*-5a** in C_6D_6.

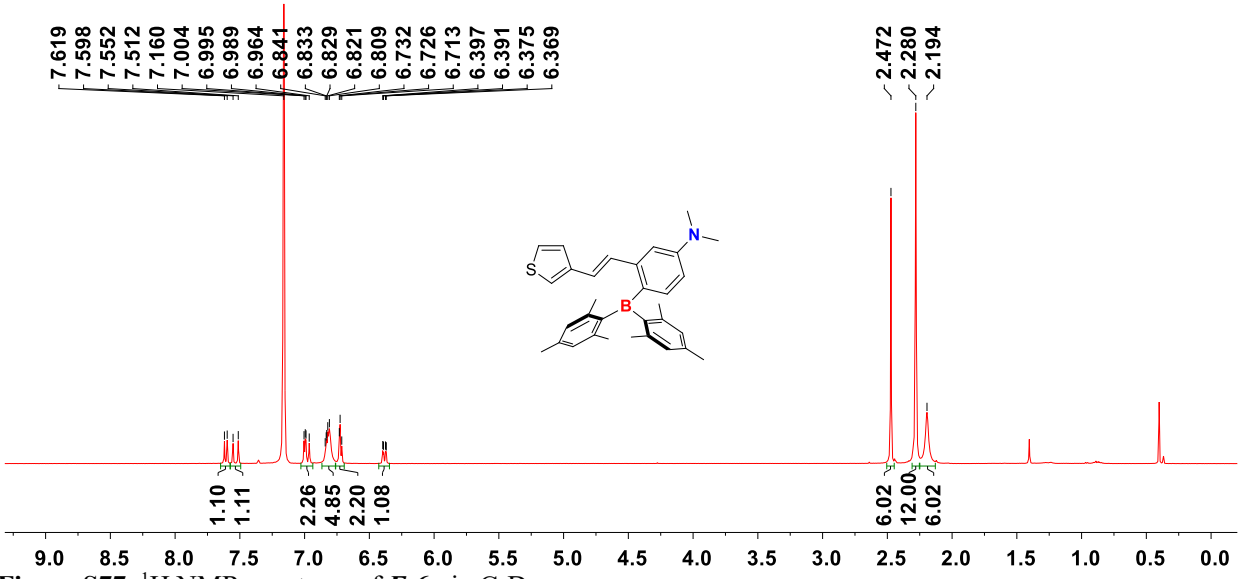


Figure S77. ^{1}H NMR spectrum of ***E*-6a** in C_6D_6.

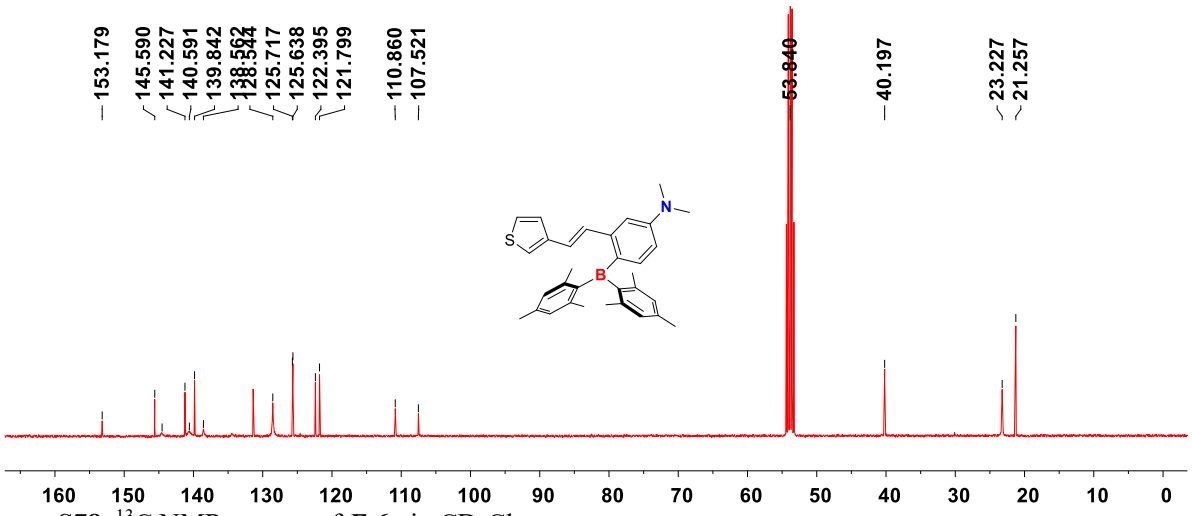


Figure S78. ^{13}C NMR spectra of ***E*-6a** in CD_2Cl_2.

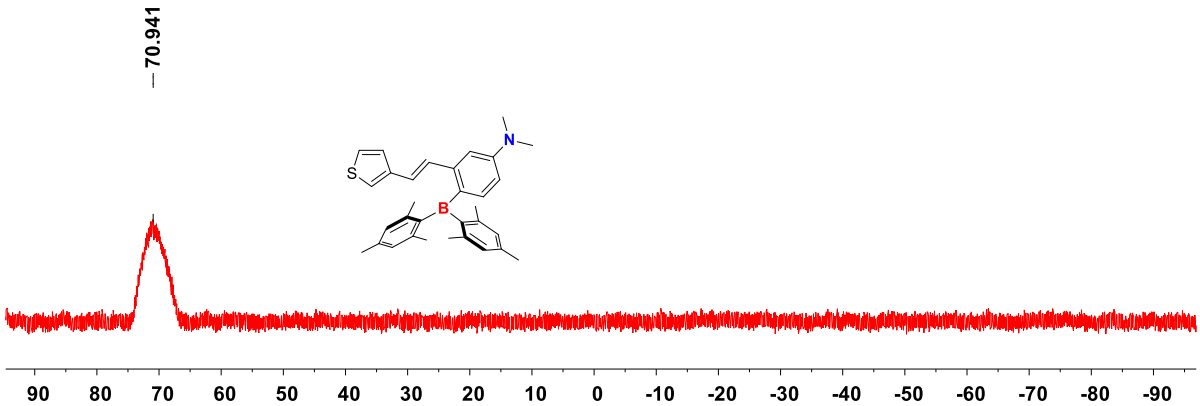


Figure S79. ^{11}B NMR spectrum of ***E*-6a** in C_6D_6.

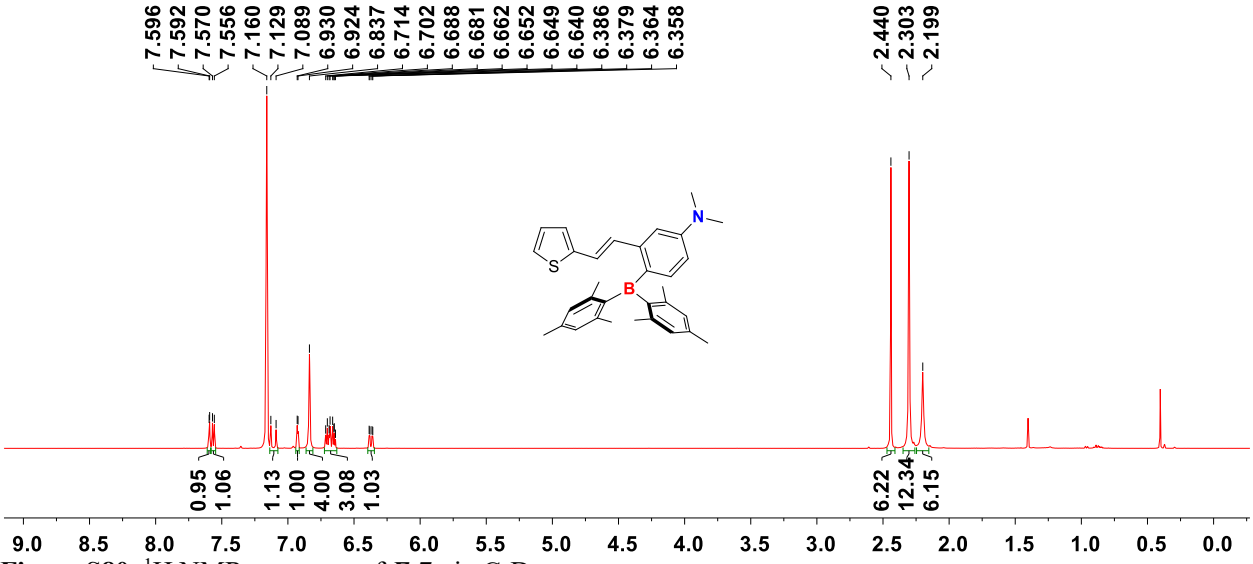


Figure S80. ^{1}H NMR spectrum of ***E*-7a** in C_6D_6.

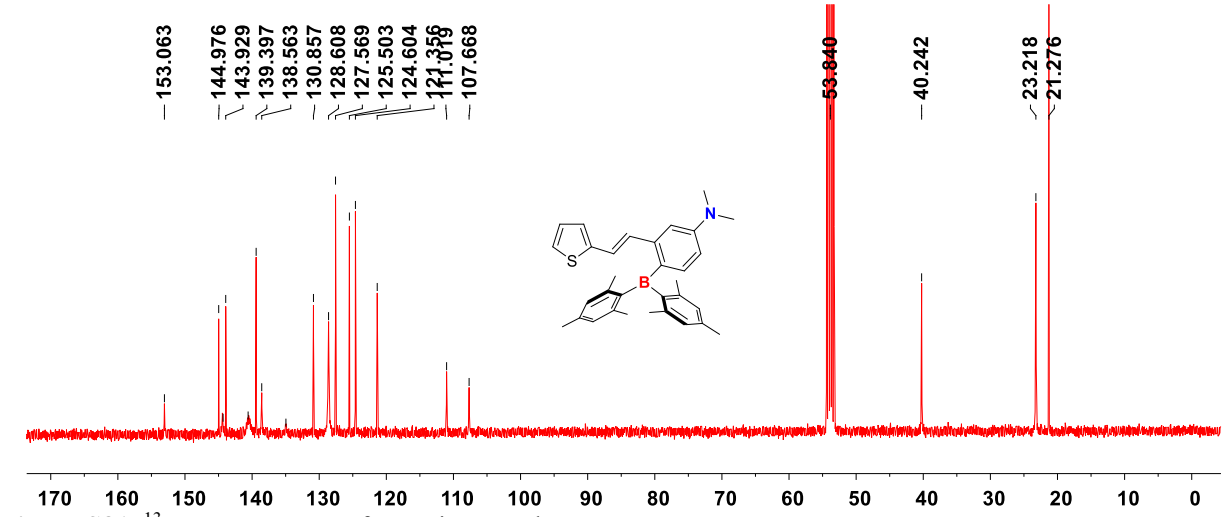


Figure S81. ^{13}C NMR spectra of ***E*-7a** in CD_2Cl_2.

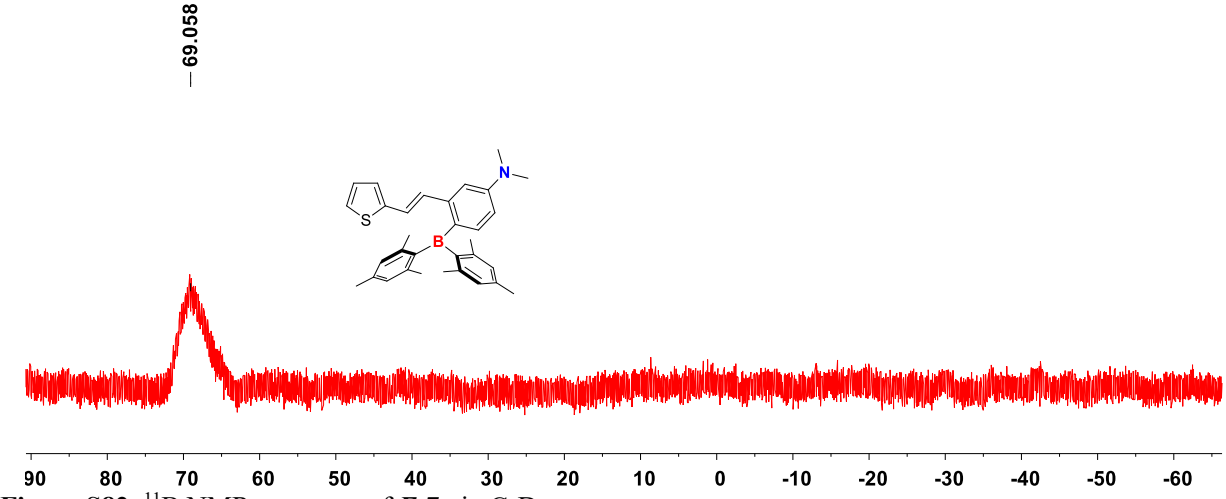


Figure S82. ^{11}B NMR spectrum of ***E*-7a** in C_6D_6.

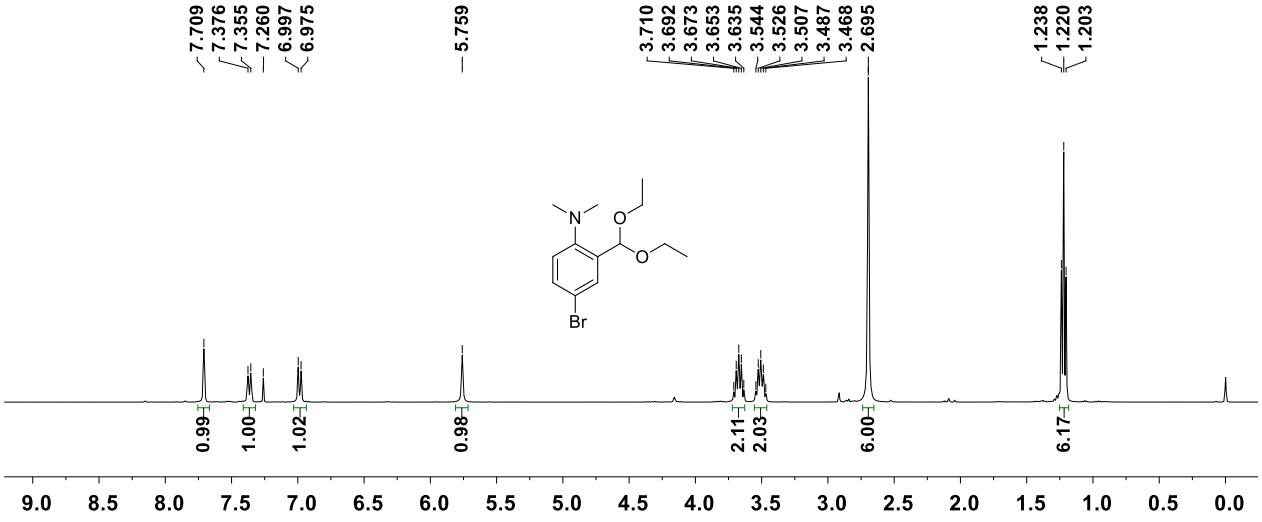


Figure S83. ^{1}H NMR spectra of **Pre-BO1'** in $CDCl_3$.

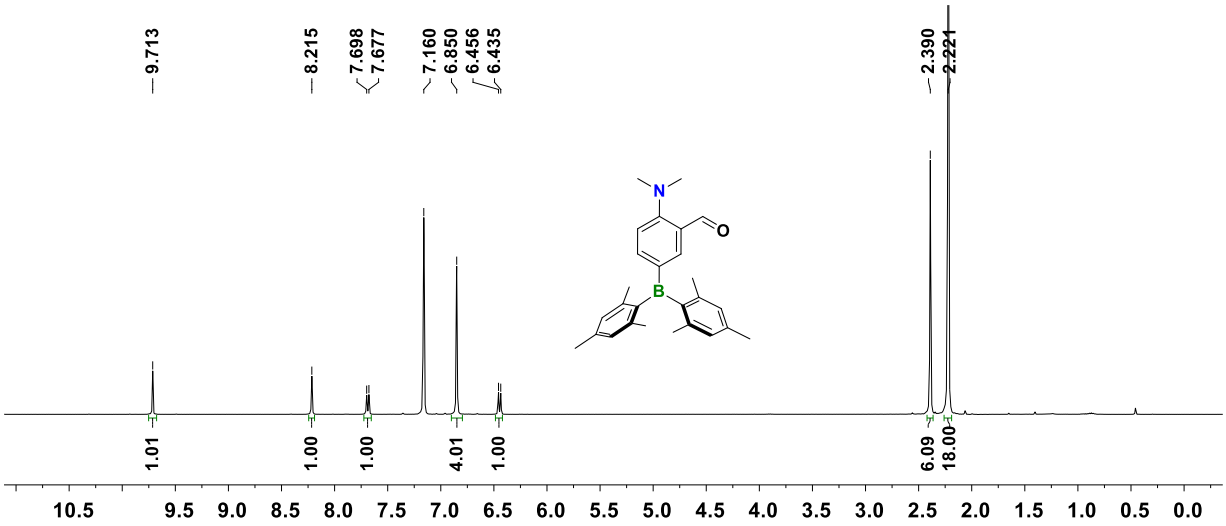


Figure S84. ^{1}H NMR spectra of **BO1'** in C_6D_6.

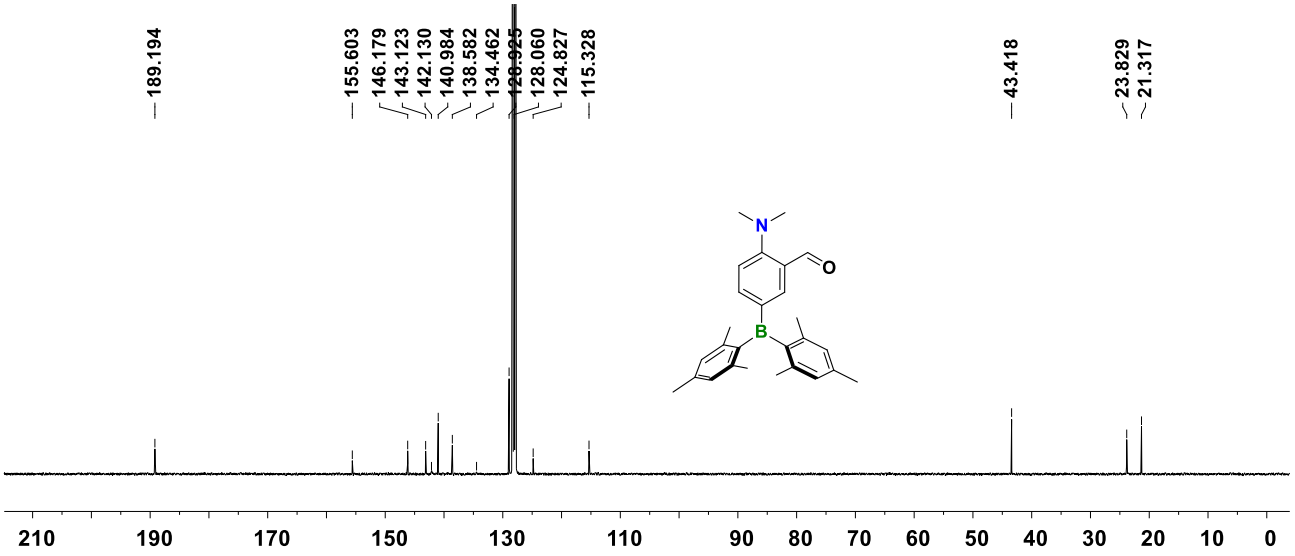


Figure S85. ^{13}C NMR spectra of **BO1'** in C_6D_6.

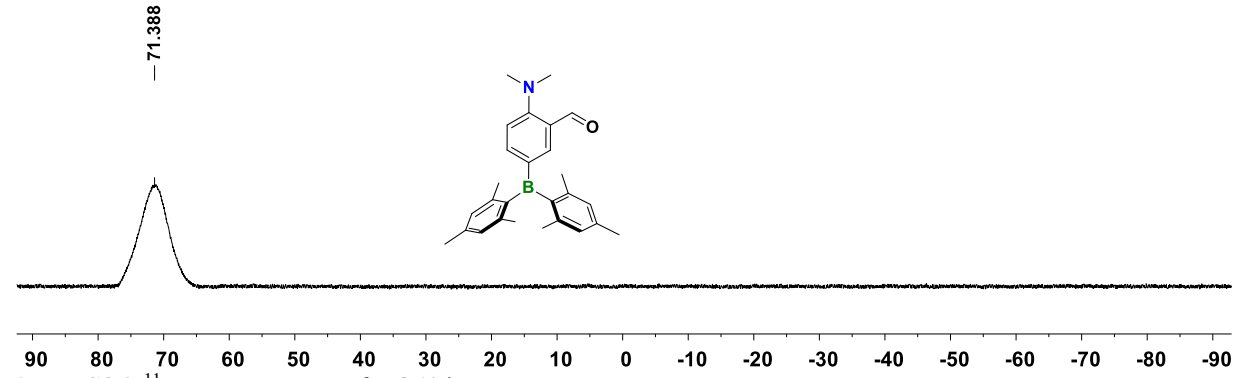


Figure S86. ^{11}B NMR spectra of **BO1'** in C_6D_6.

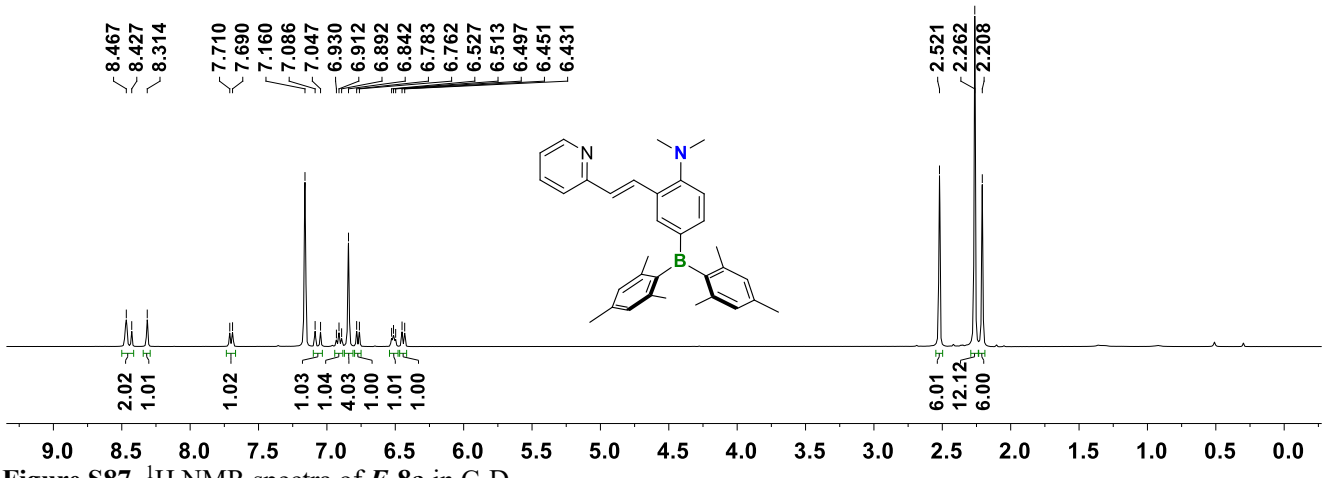


Figure S87. ^{1}H NMR spectra of ***E*-8a** in C_6D_6.

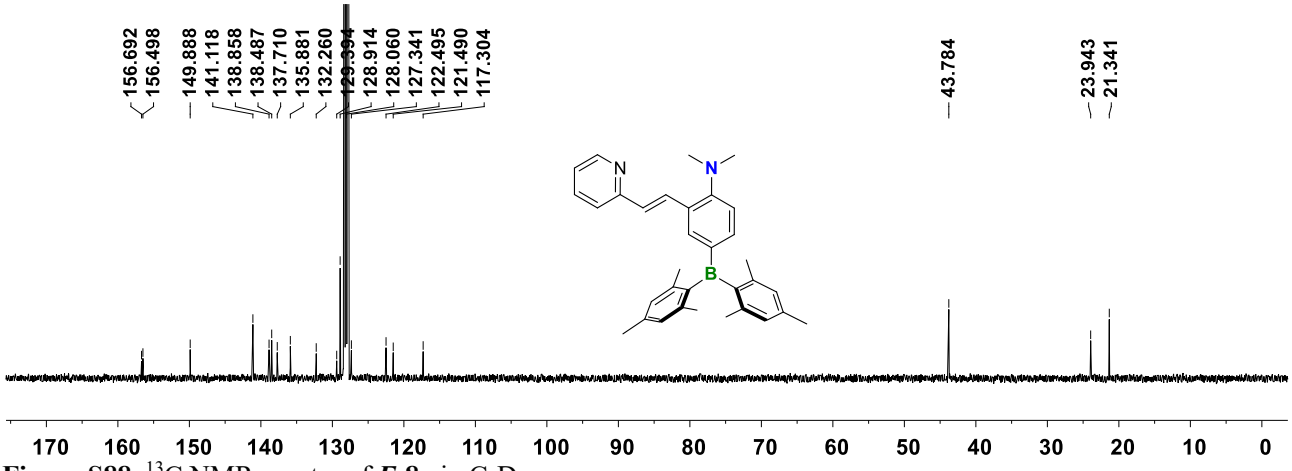


Figure S88. ^{13}C NMR spectra of ***E*-8a** in C_6D_6.

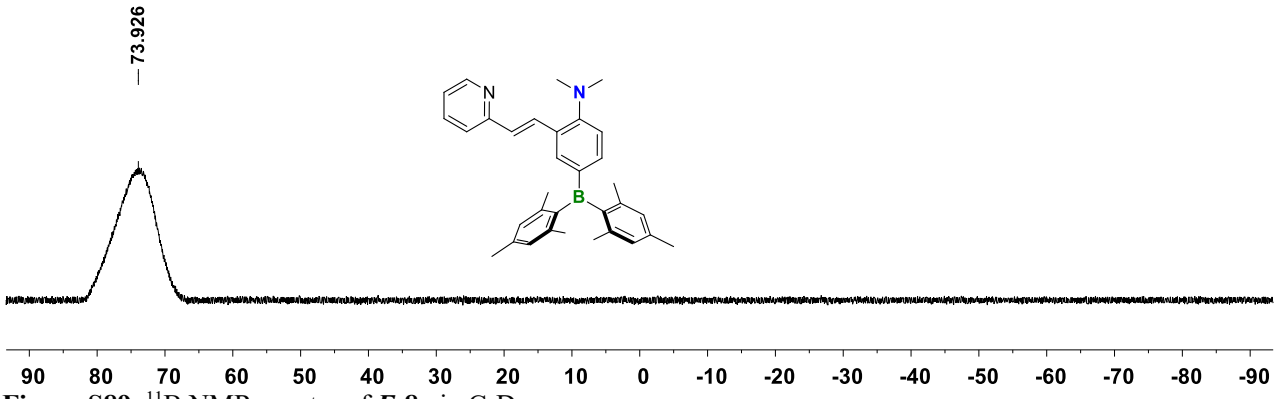


Figure S89. ^{11}B NMR spectra of ***E*-8a** in C_6D_6.

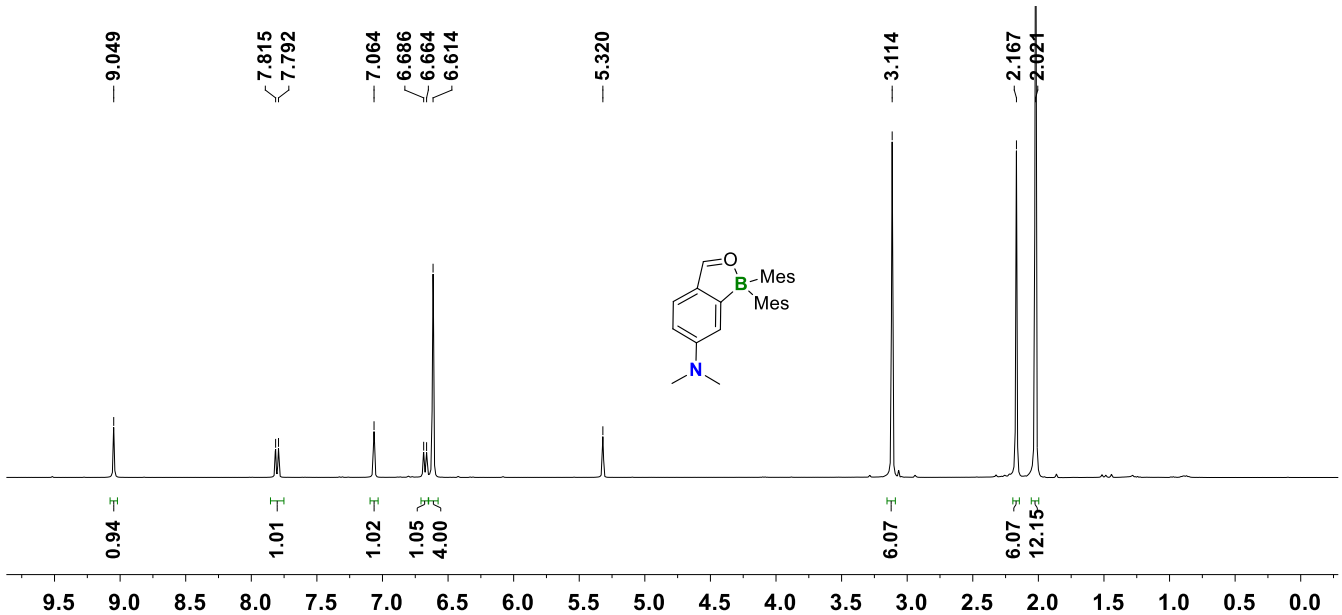


Figure S90. ^{1}H NMR spectra of **BO1m** in CD_2Cl_2.

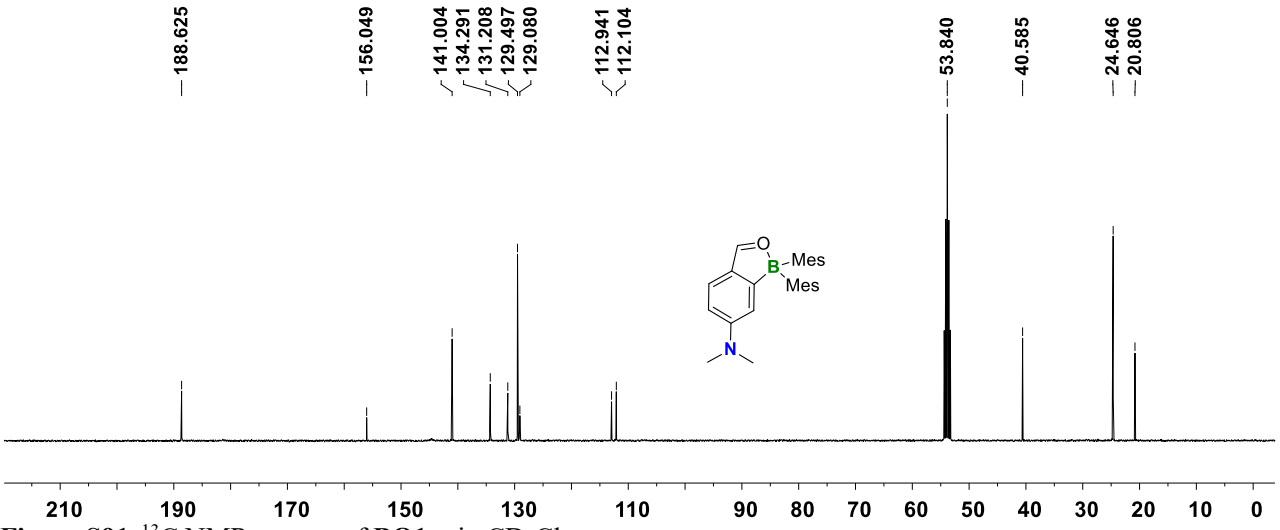


Figure S91. ^{13}C NMR spectra of **BO1m** in CD_2Cl_2.

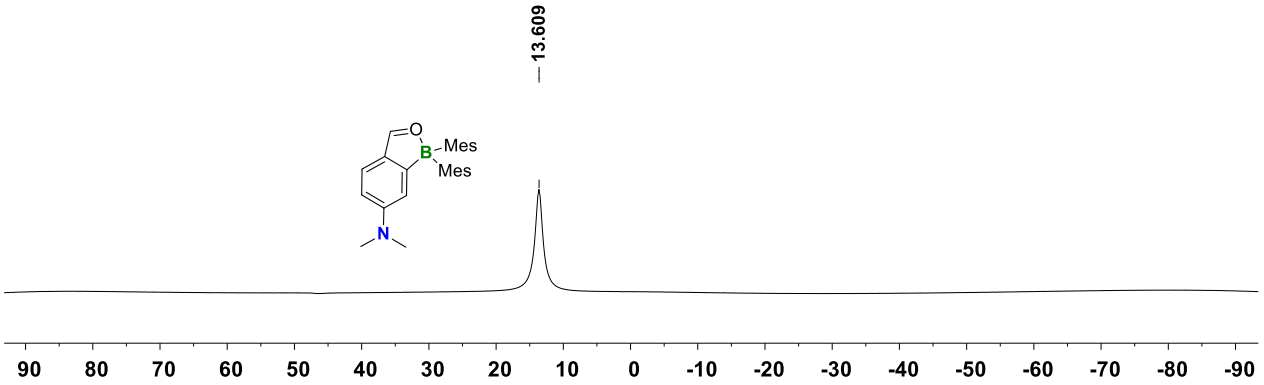


Figure S92. ^{11}B NMR spectra of **BO1m** in CD_2Cl_2.

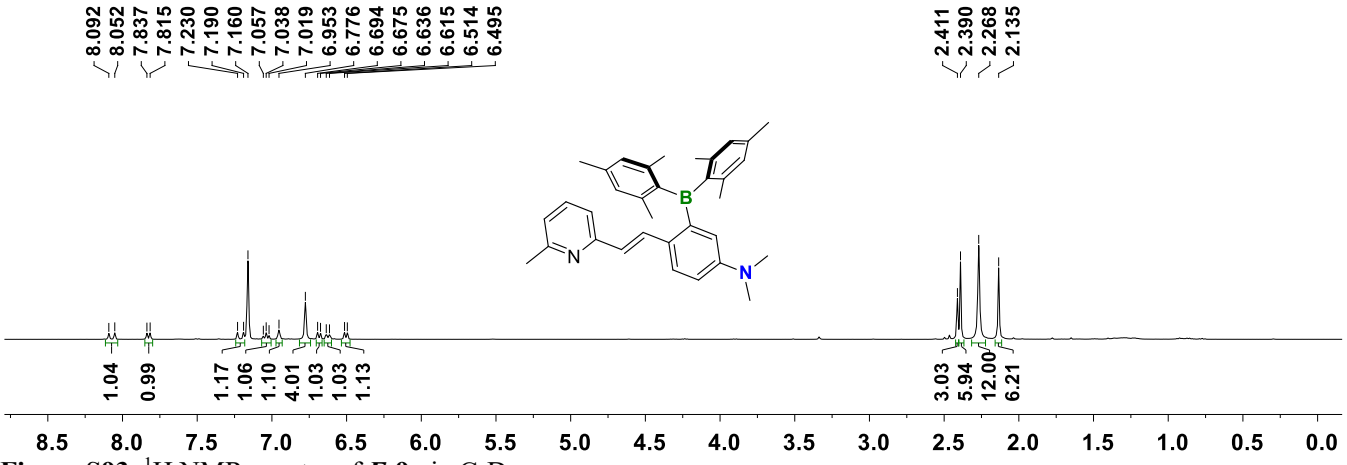


Figure S93. ^{1}H NMR spectra of ***E*-9a** in C_6D_6.

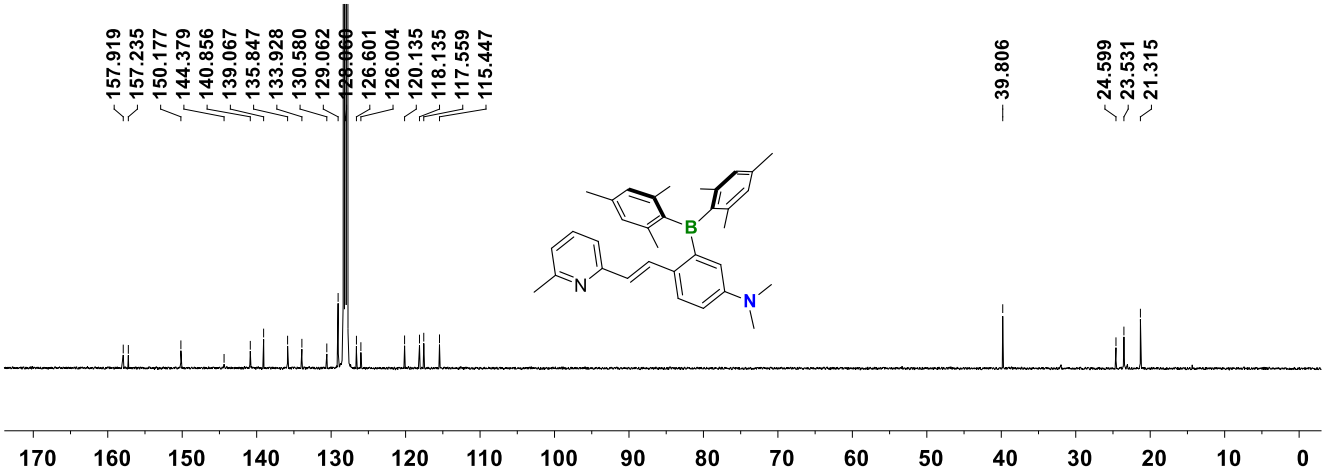


Figure S94. ^{13}C NMR spectra of ***E*-9a** in C_6D_6.

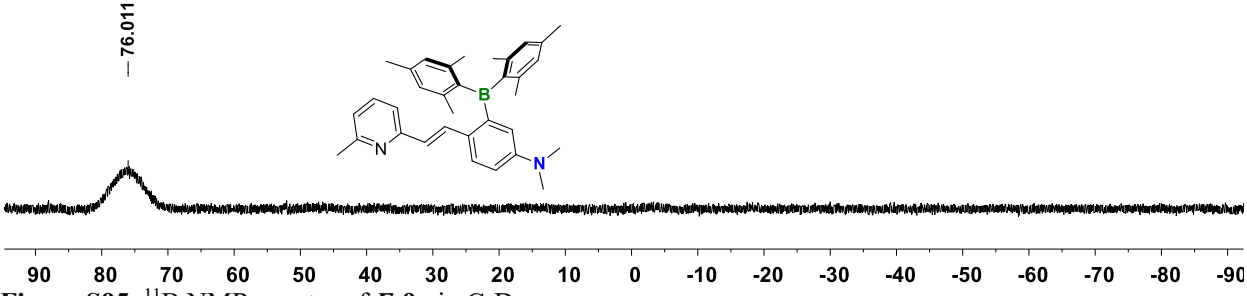


Figure S95. ^{11}B NMR spectra of ***E*-9a** in C_6D_6.

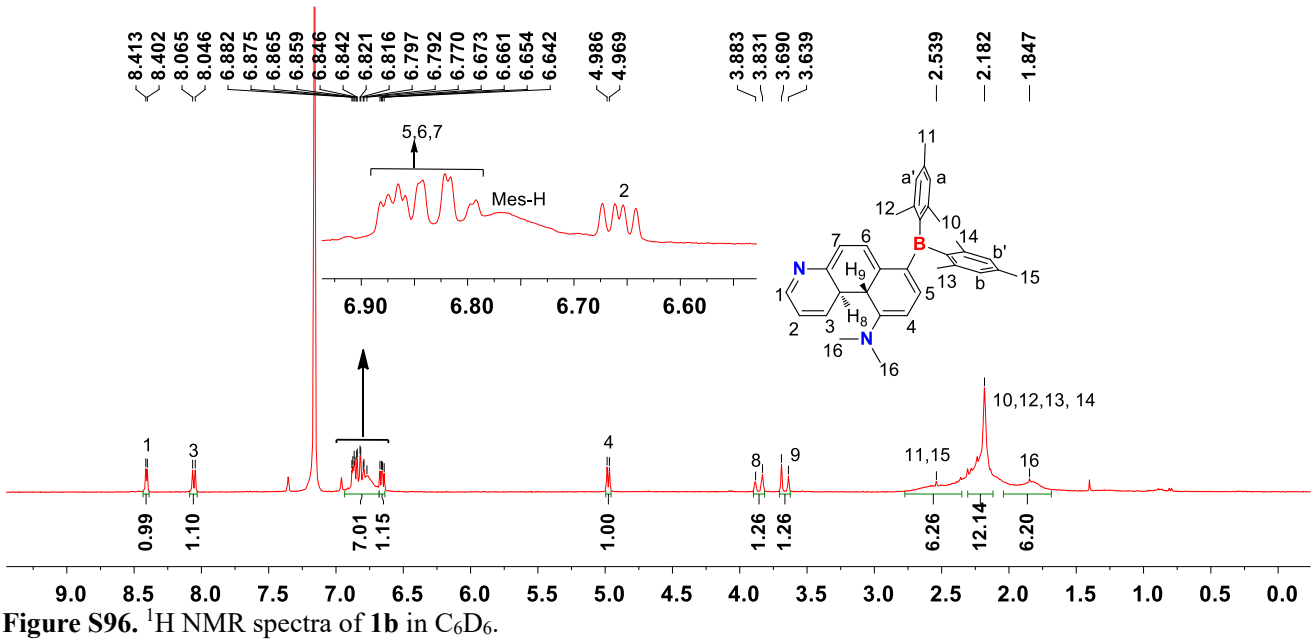


Figure S96. ^{1}H NMR spectra of **1b** in C_6D_6.

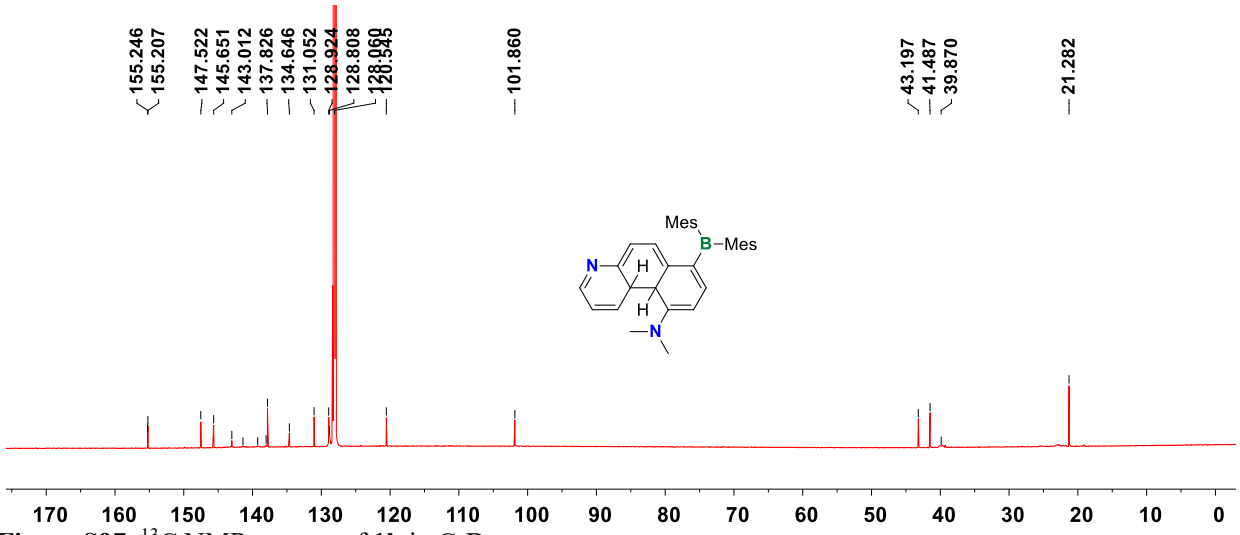


Figure S97. ^{13}C NMR spectra of **1b** in C_6D_6.

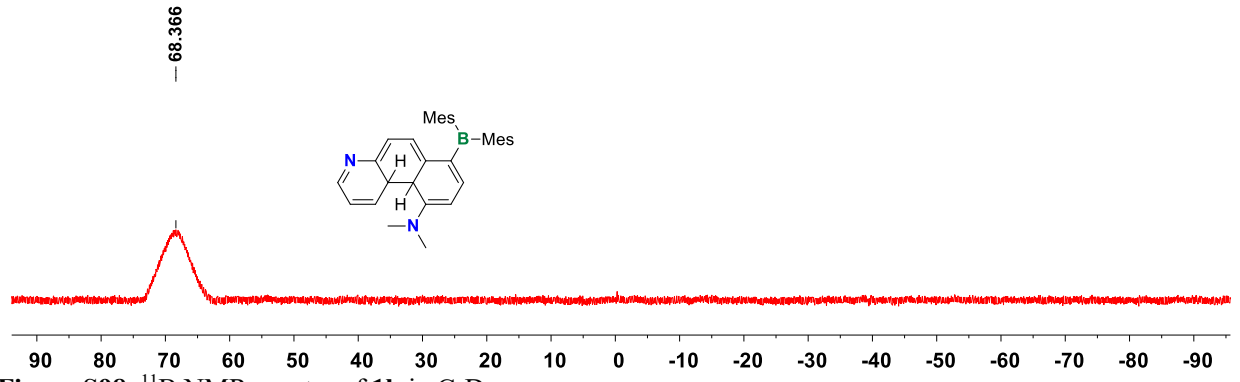


Figure S98. ^{11}B NMR spectra of **1b** in C_6D_6.

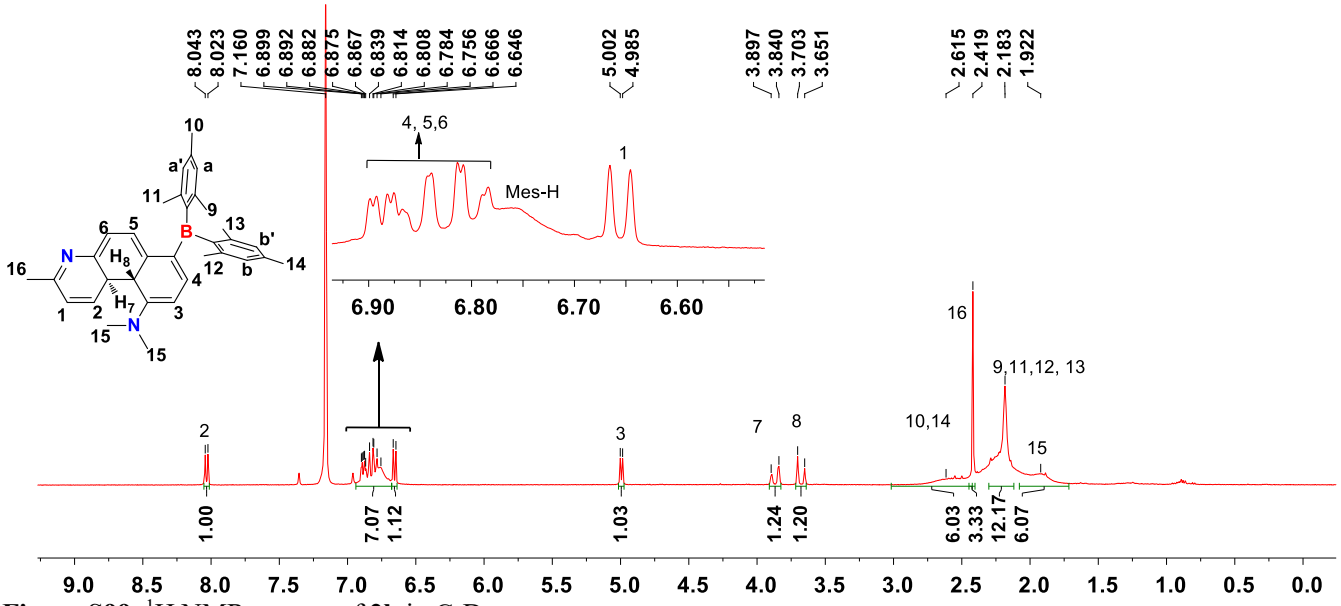


Figure S99. ^{1}H NMR spectra of **2b** in C_6D_6.

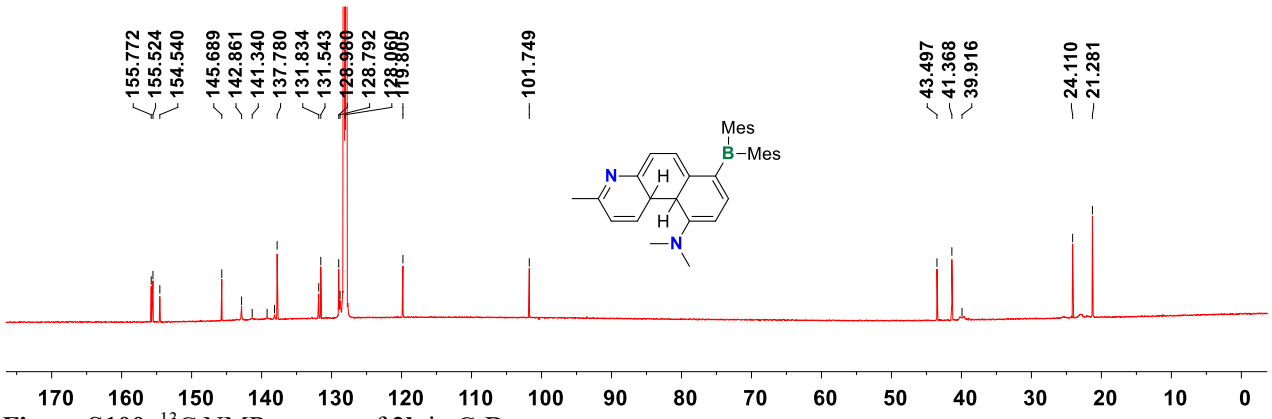


Figure S100. ^{13}C NMR spectra of **2b** in C_6D_6.

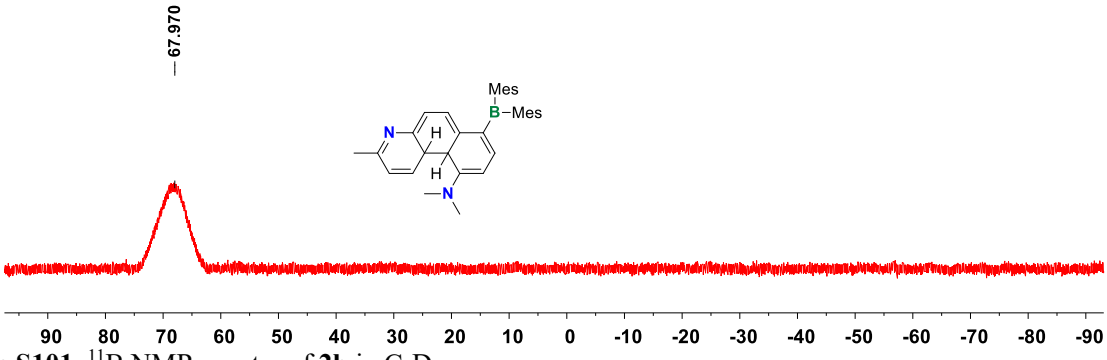


Figure S101. ^{11}B NMR spectra of **2b** in C_6D_6.

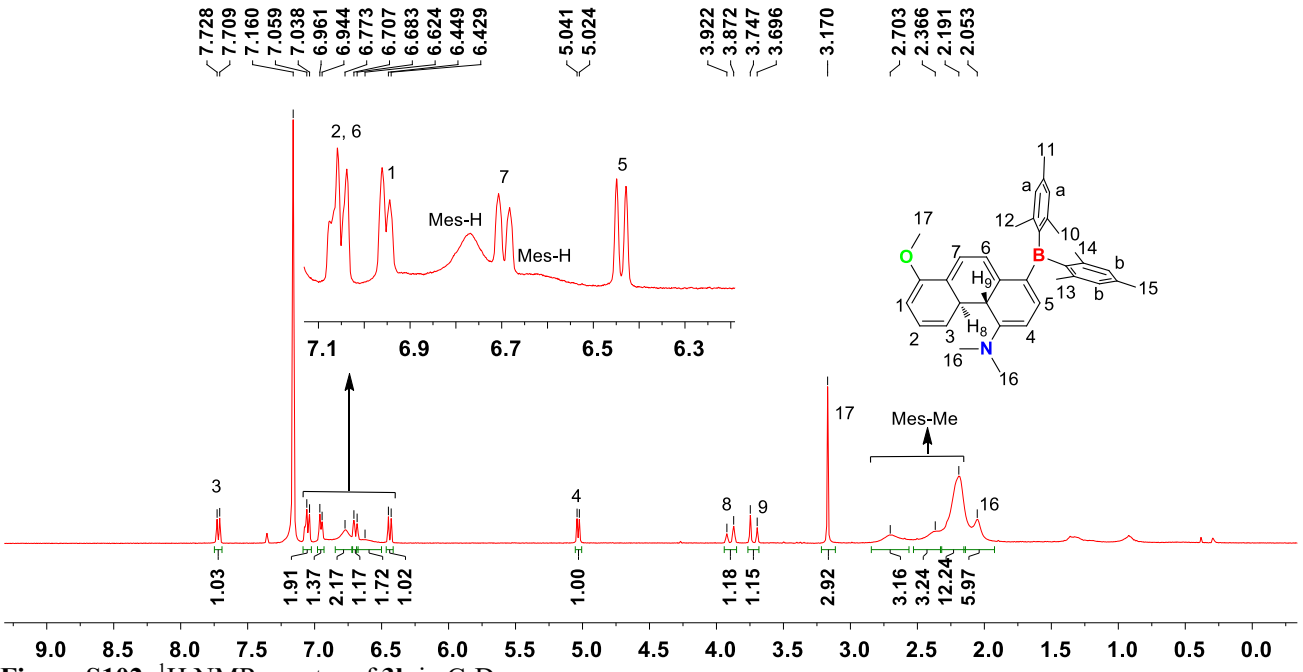


Figure S102. ^{1}H NMR spectra of **3b** in C_6D_6.

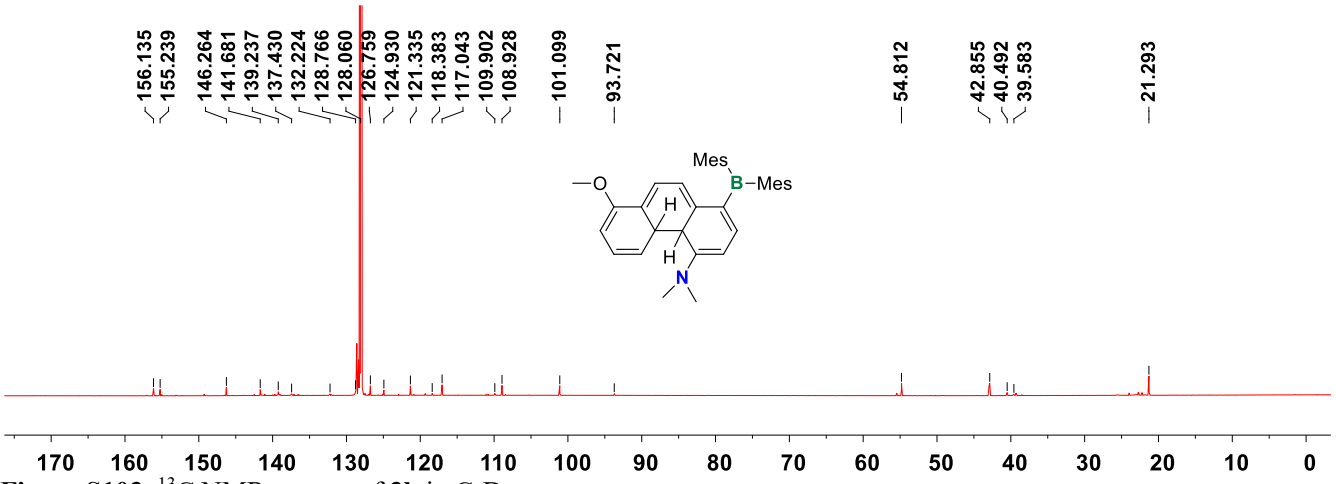


Figure S103. ^{13}C NMR spectra of **3b** in C_6D_6.

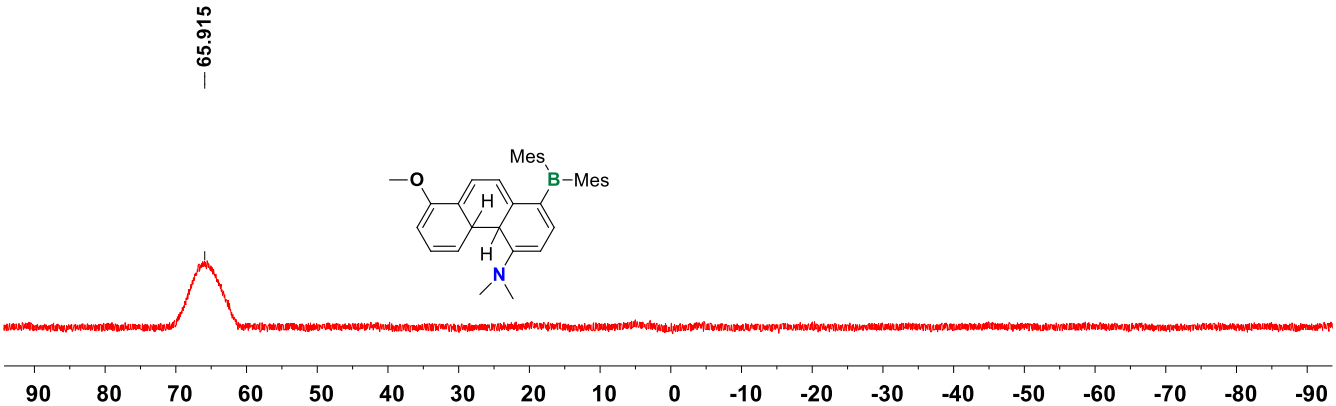


Figure S104. ^{11}B NMR spectra of **3b** in C_6D_6.

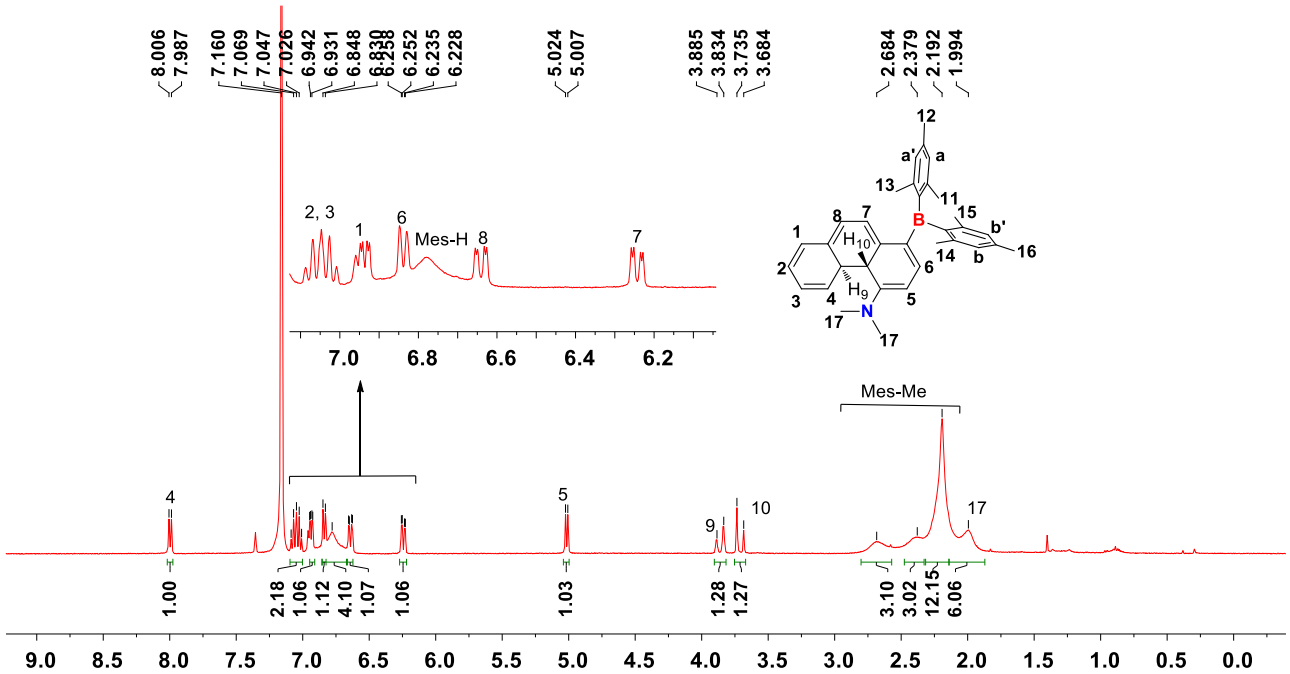


Figure S105. ^{1}H NMR spectra of **4b** in C_6D_6.

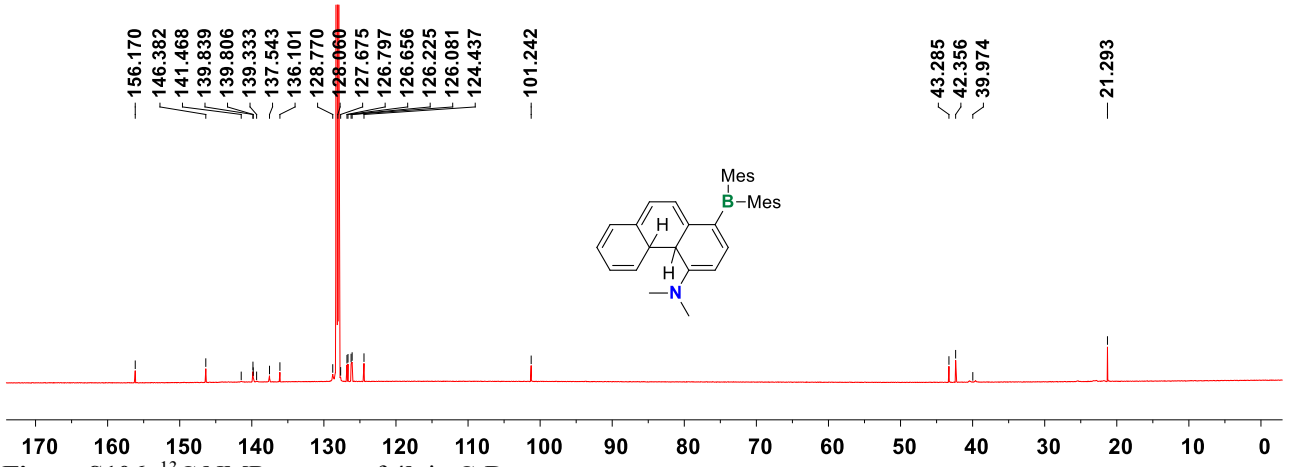


Figure S106. ^{13}C NMR spectra of **4b** in C_6D_6.

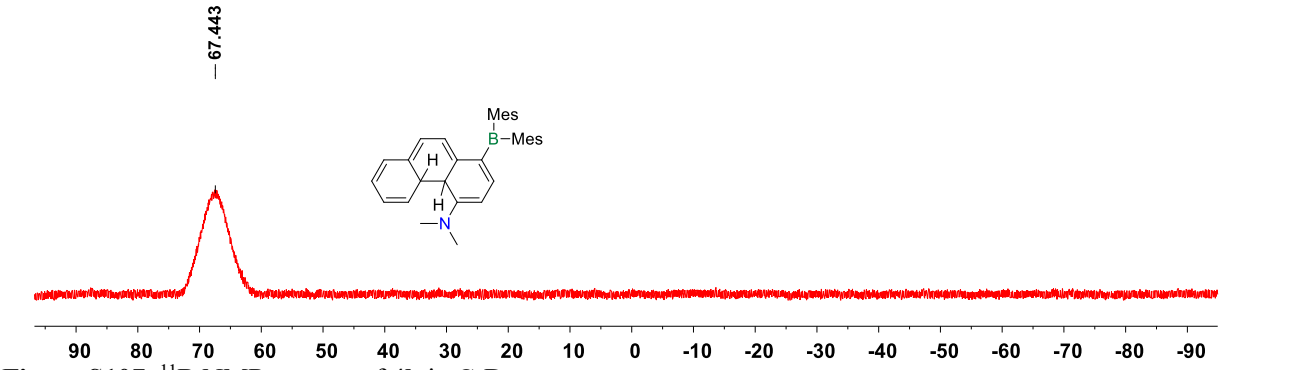


Figure S107. ^{11}B NMR spectra of **4b** in C_6D_6.

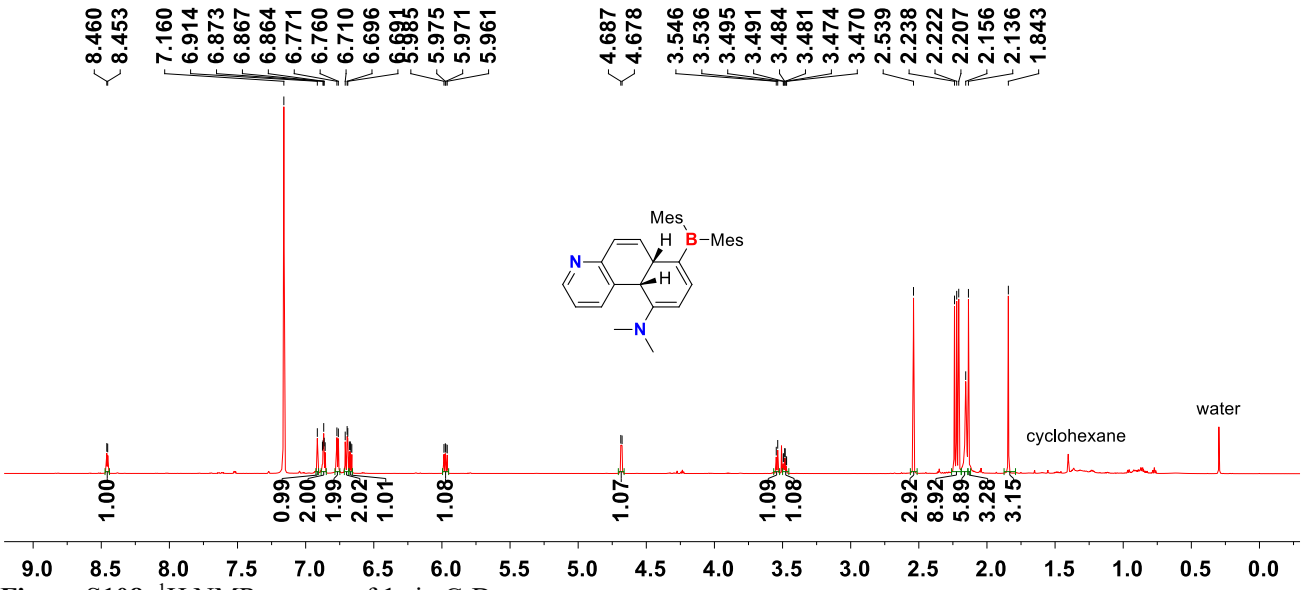


Figure S108. ^{1}H NMR spectra of **1c** in C_6D_6.

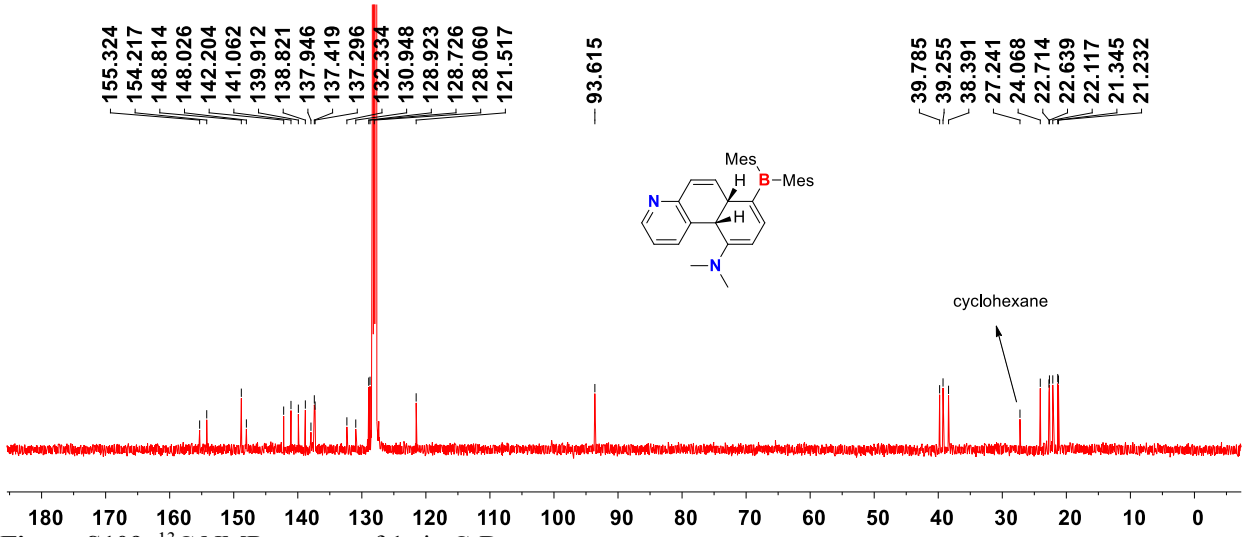


Figure S109. ^{13}C NMR spectra of **1c** in C_6D_6.

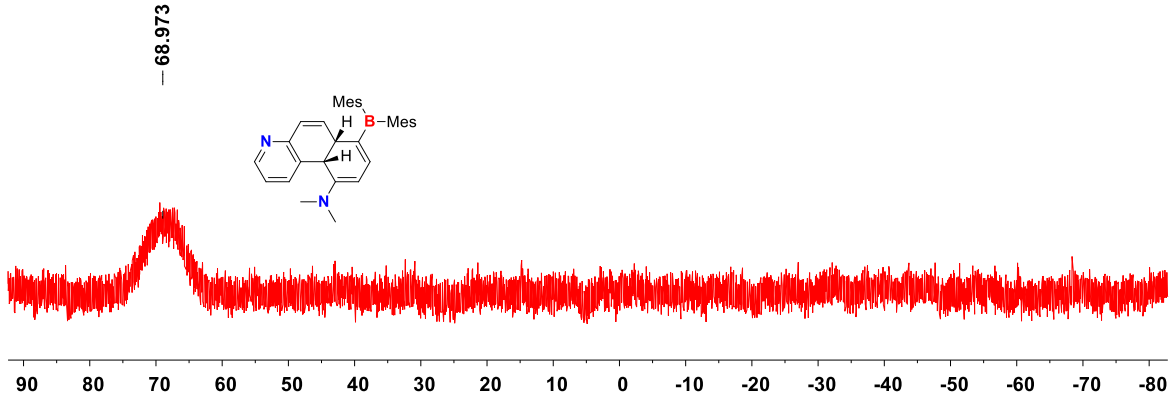


Figure S110. ^{11}B NMR spectra of **1c** in C_6D_6.

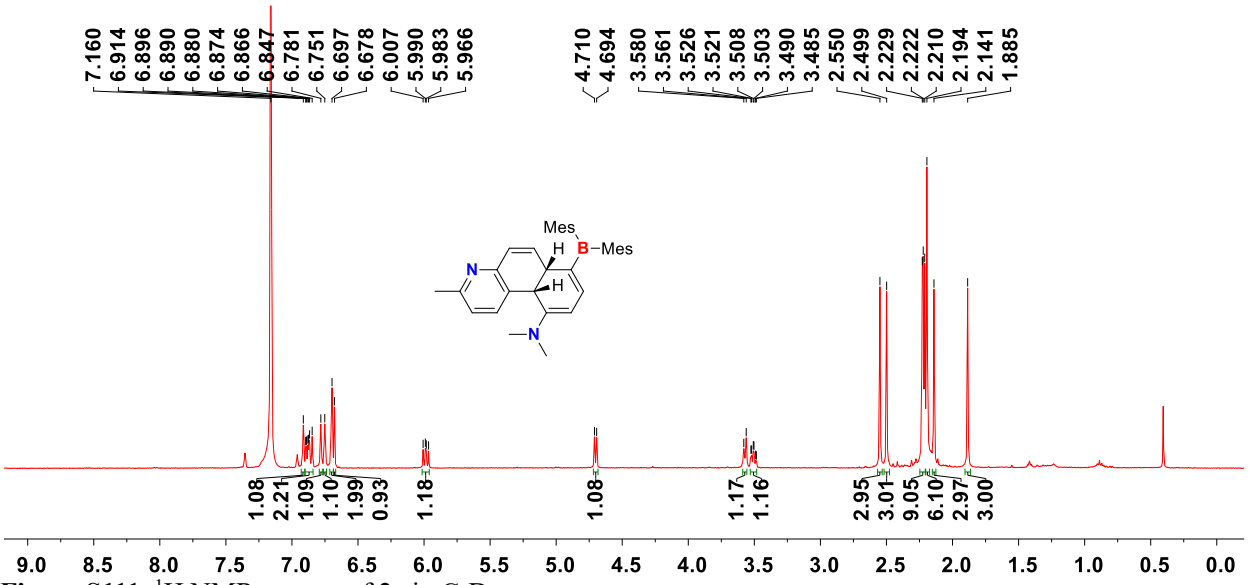


Figure S111. ^{1}H NMR spectra of **2c** in C_6D_6.

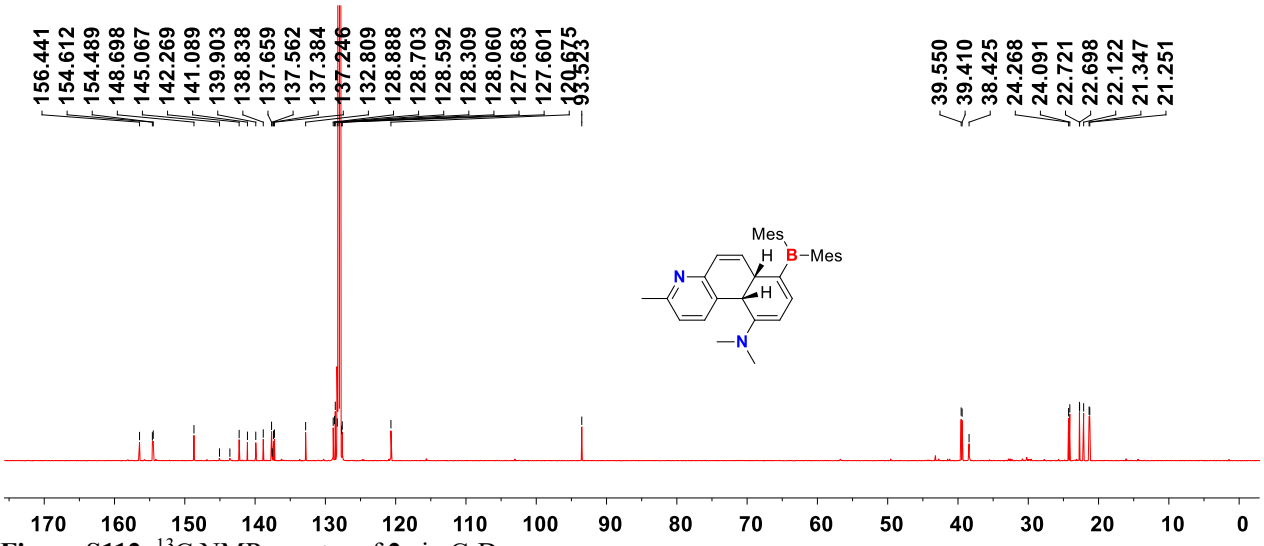


Figure S112. ^{13}C NMR spectra of **2c** in C_6D_6.

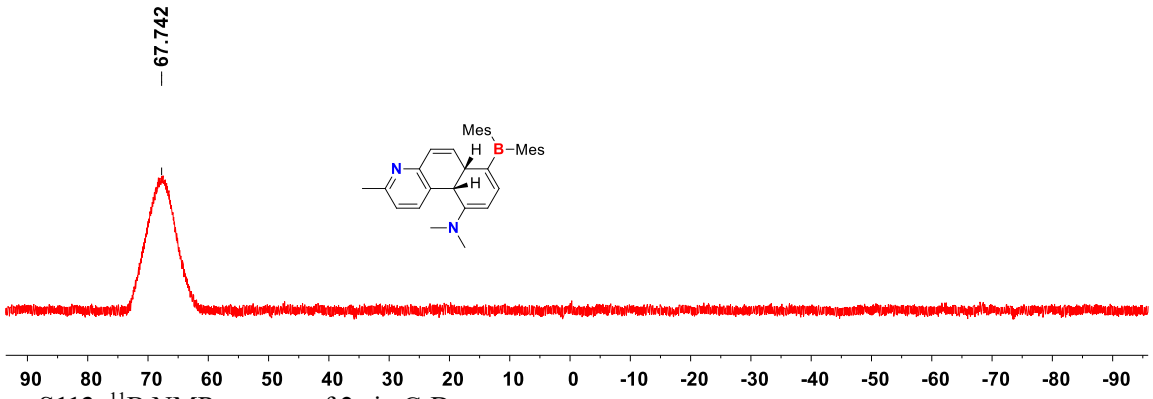


Figure S113. ^{11}B NMR spectra of **2c** in C_6D_6.

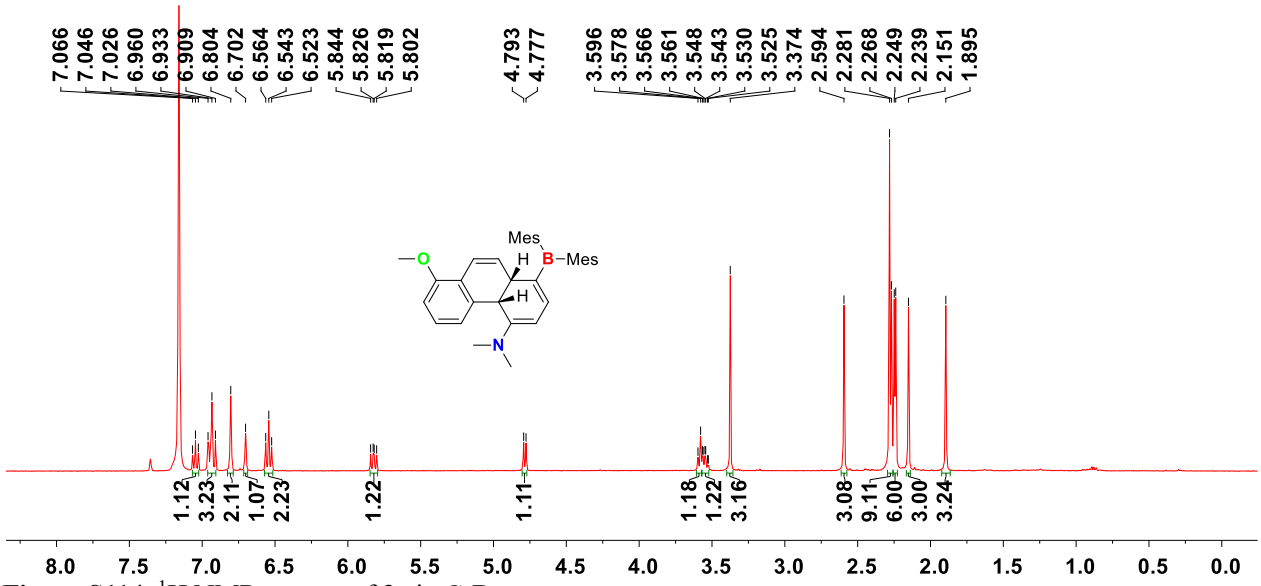


Figure S114. ^{1}H NMR spectra of **3c** in C_6D_6.

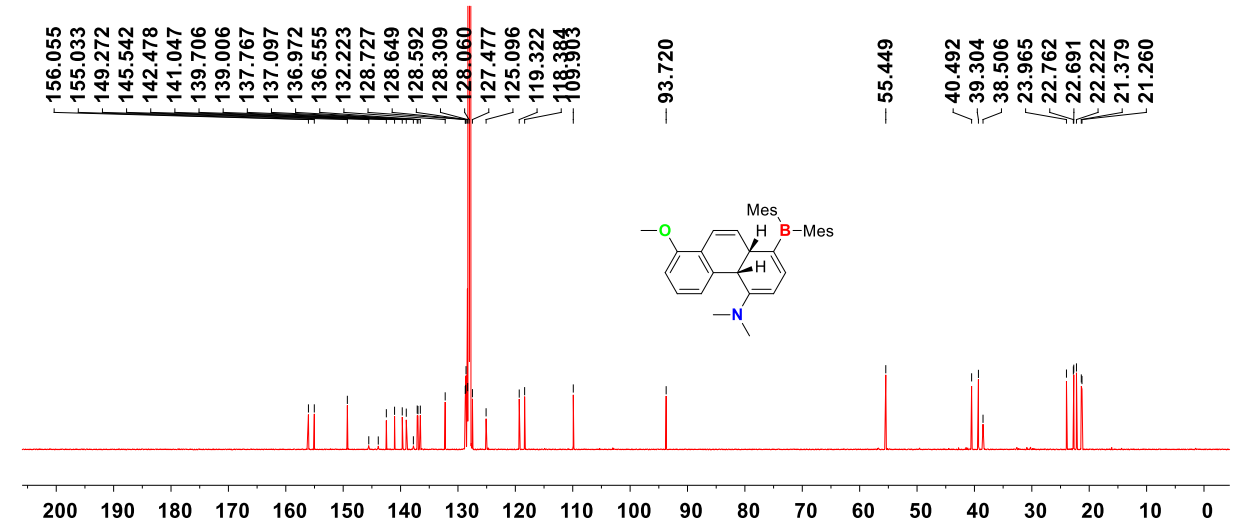


Figure S115. ^{13}C NMR spectra of **3c** in C_6D_6.

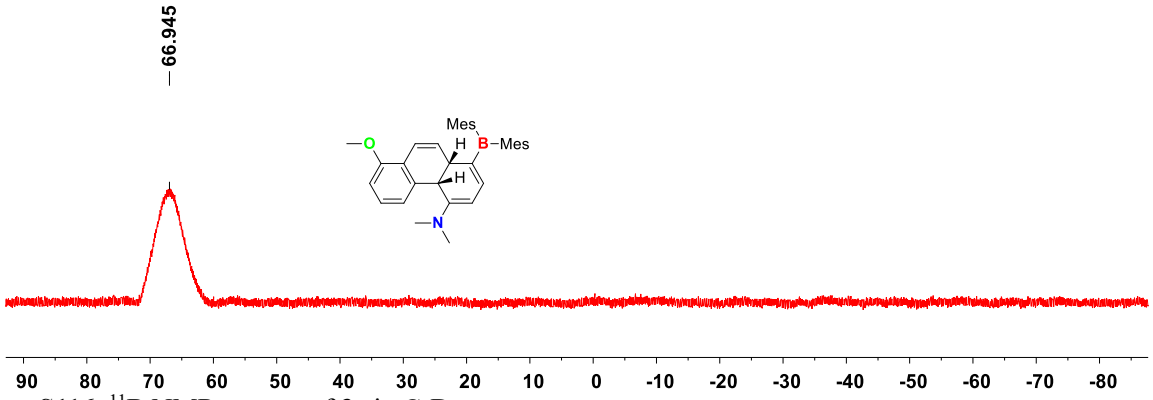


Figure S116. ^{11}B NMR spectra of **3c** in C_6D_6.

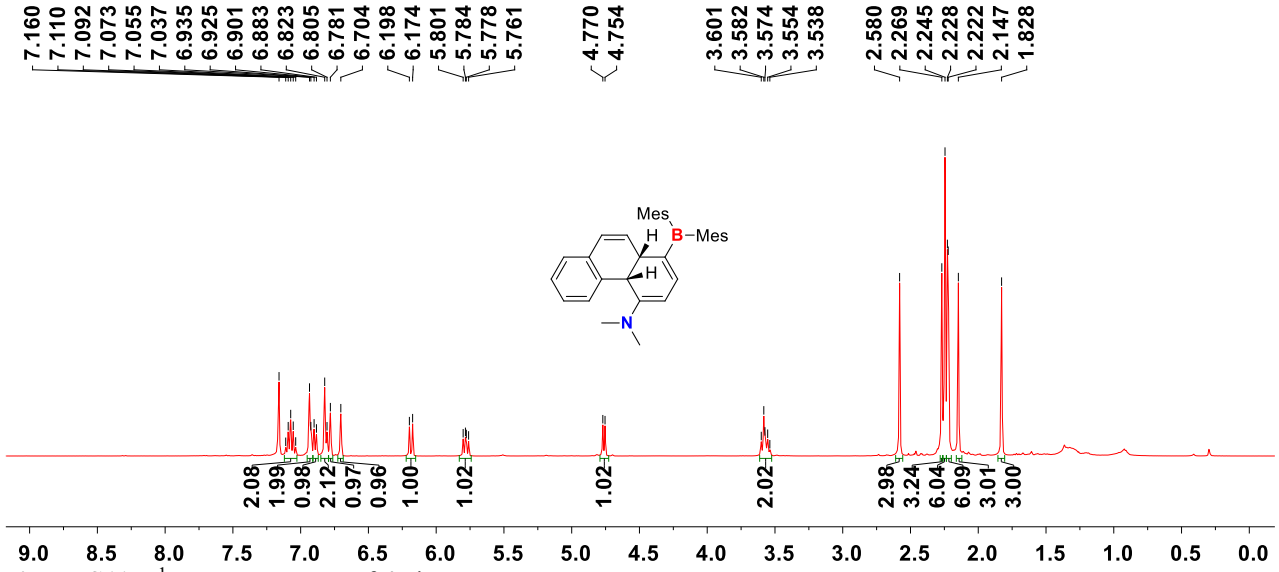


Figure S117. ^{1}H NMR spectra of **4c** in C_6D_6.

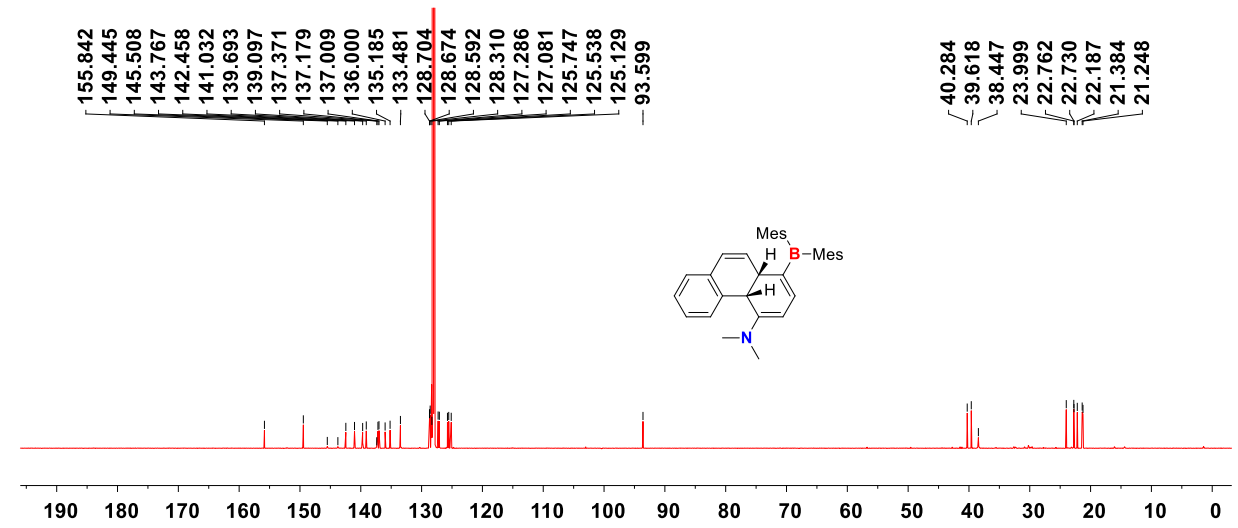


Figure S118. ^{13}C NMR spectra of **4c** in C_6D_6.

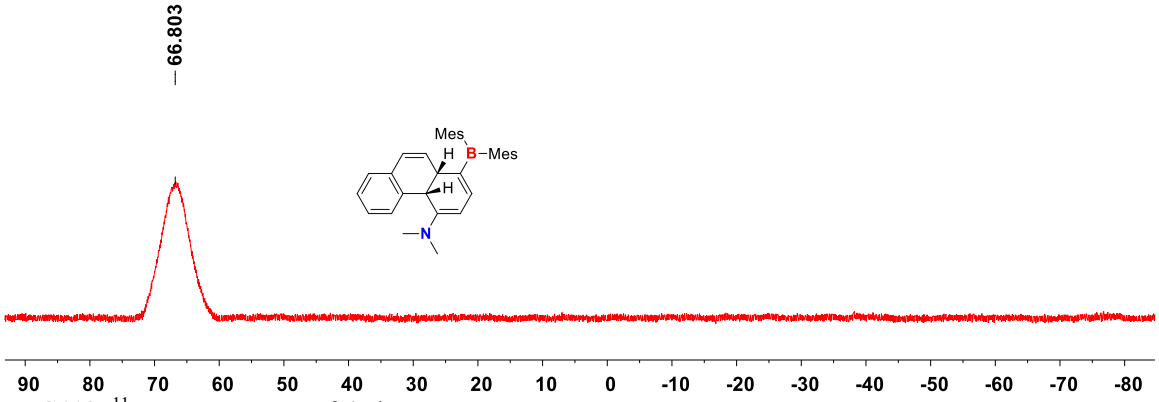


Figure S119. ^{11}B NMR spectra of **4c** in C_6D_6.

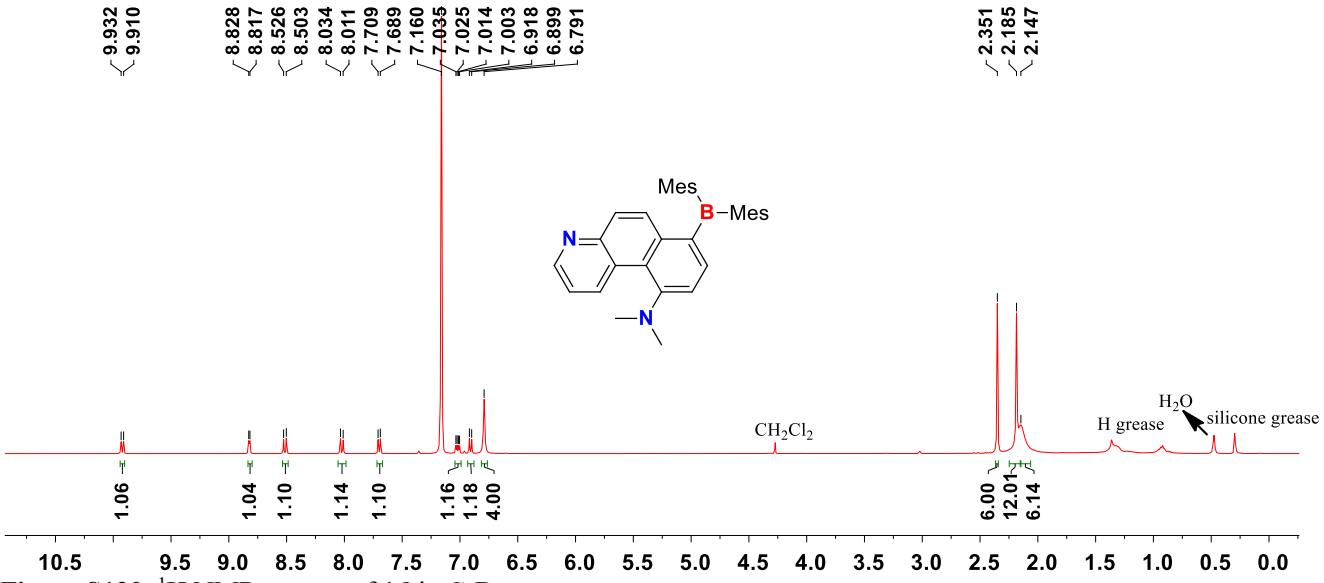


Figure S120. ^{1}H NMR spectra of **1d** in C_6D_6.

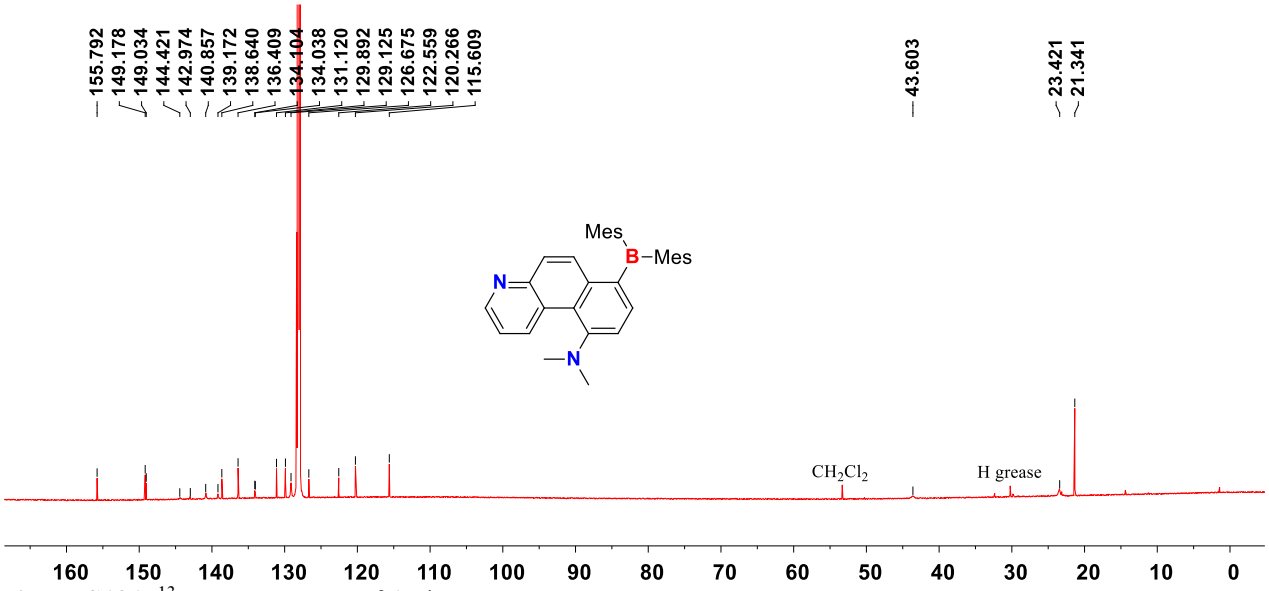


Figure S121. ^{13}C NMR spectra of **1d** in C_6D_6.

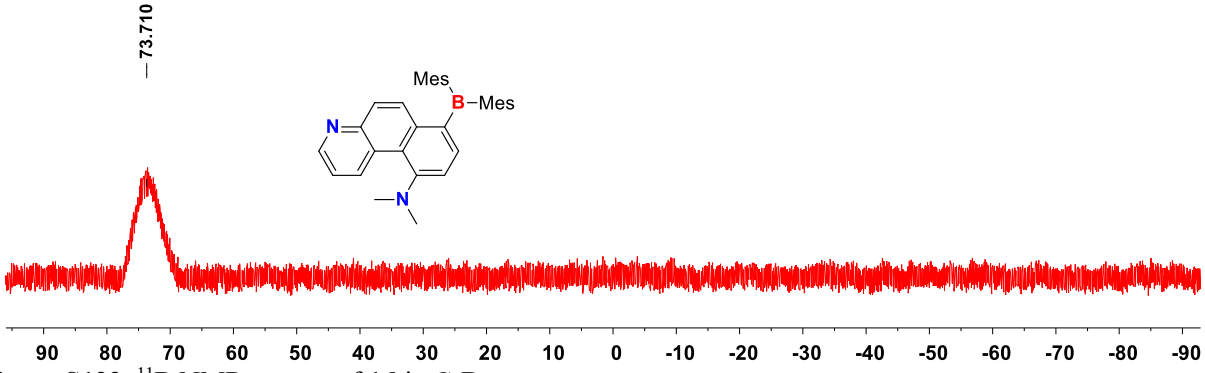


Figure S122. ^{11}B NMR spectra of **1d** in C_6D_6.

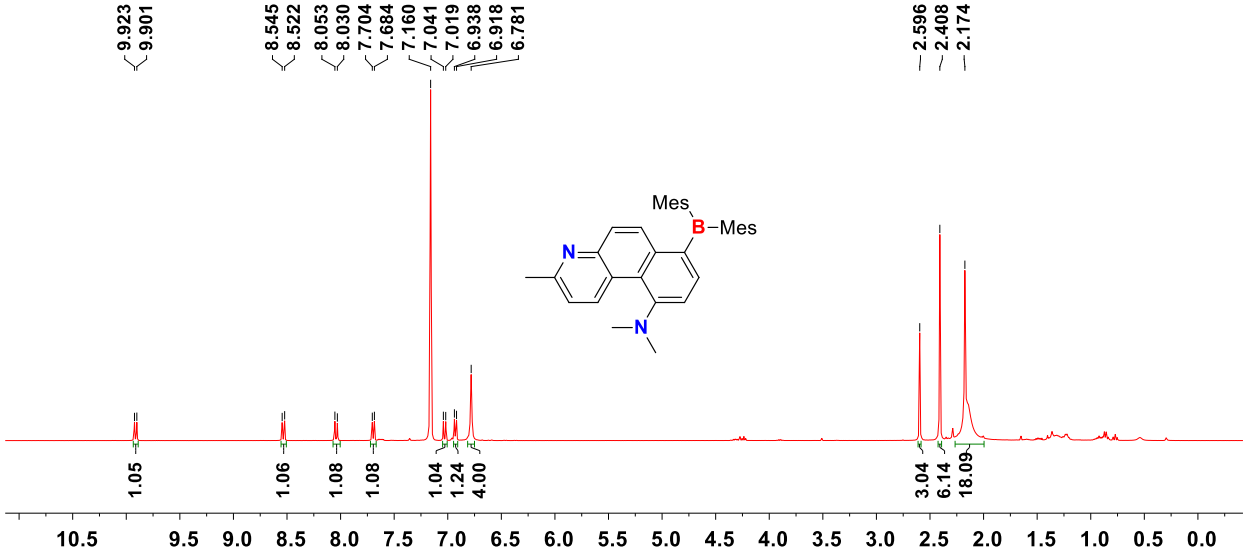


Figure S123. ^{1}H NMR spectra of **2d** in C_6D_6.

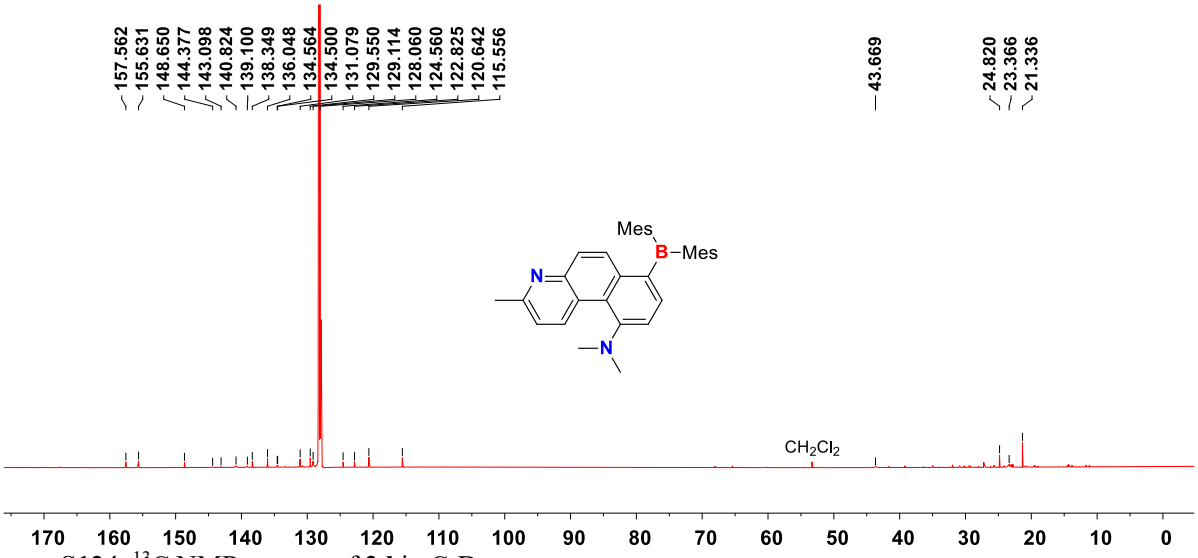


Figure S124. ^{13}C NMR spectra of **2d** in C_6D_6.

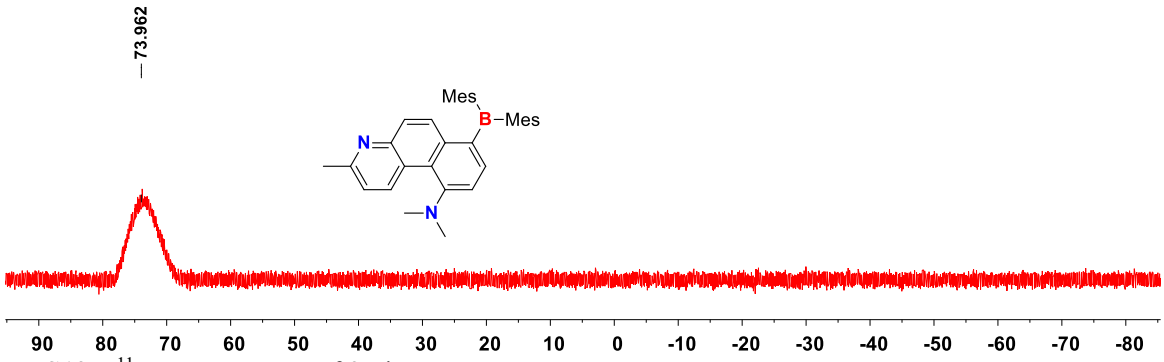


Figure S125. ^{11}B NMR spectra of **2d** in C_6D_6.

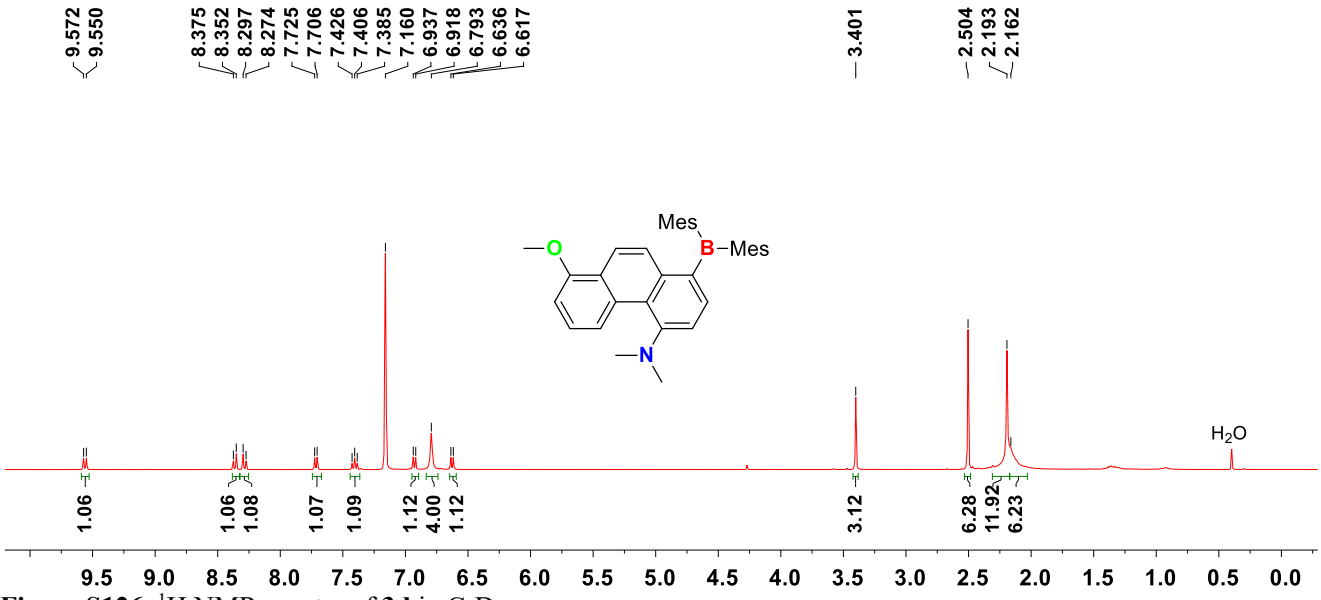


Figure S126. ^{1}H NMR spectra of **3d** in C_6D_6.

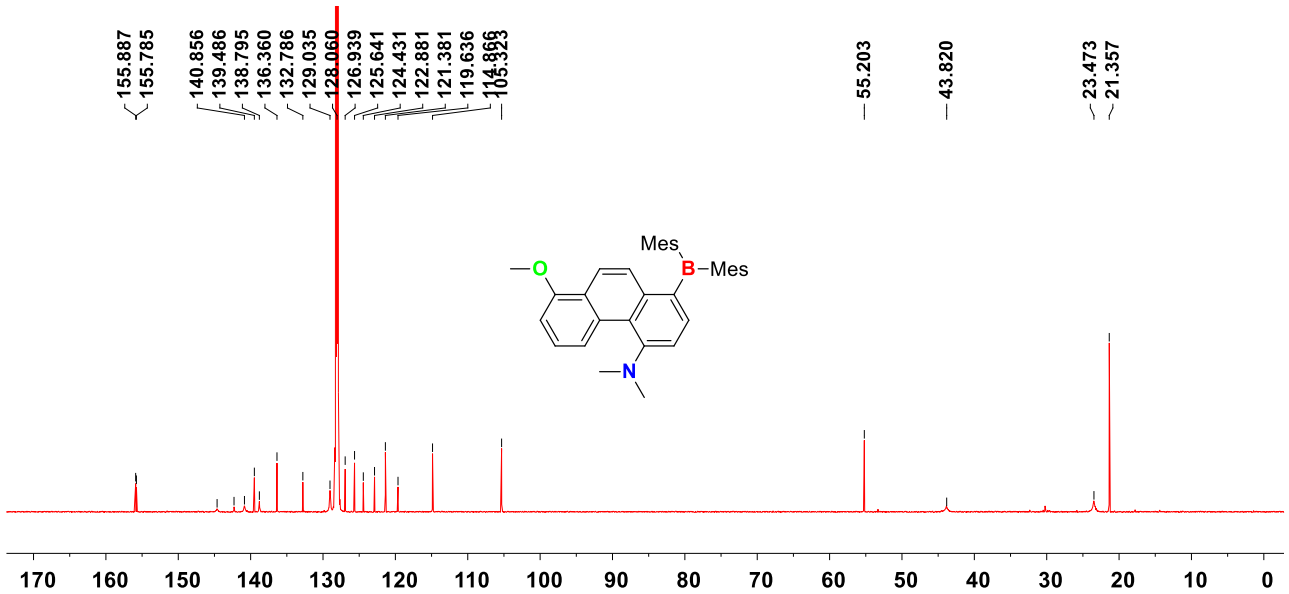


Figure S127. ^{13}C NMR spectra of **3d** in C_6D_6.

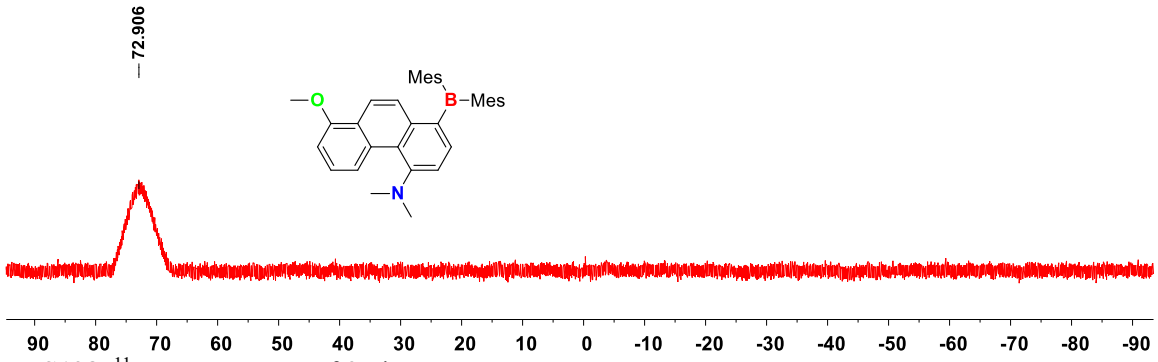


Figure S128. ^{11}B NMR spectra of **3d** in C_6D_6.

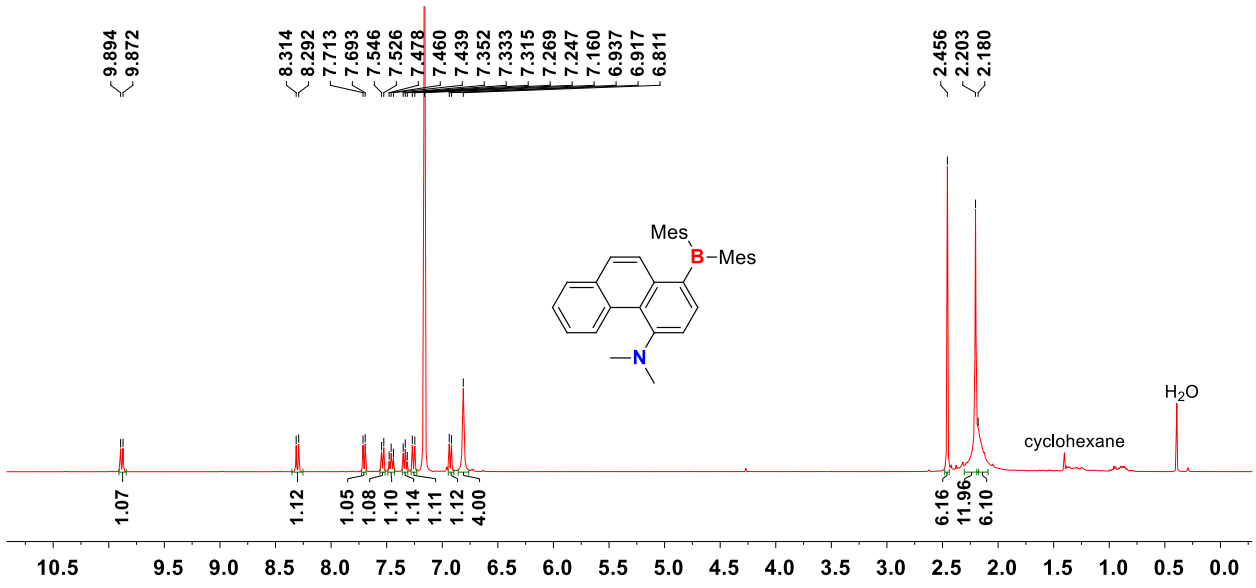


Figure S129. ^{1}H NMR spectra of **4d** in C_6D_6.

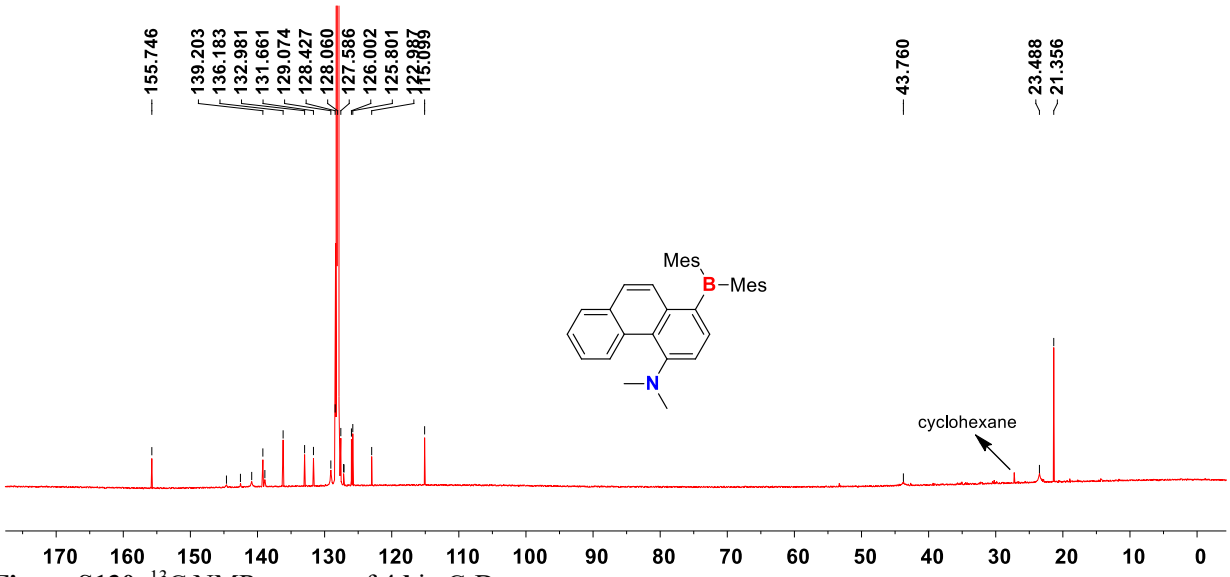


Figure S130. ^{13}C NMR spectra of **4d** in C_6D_6.

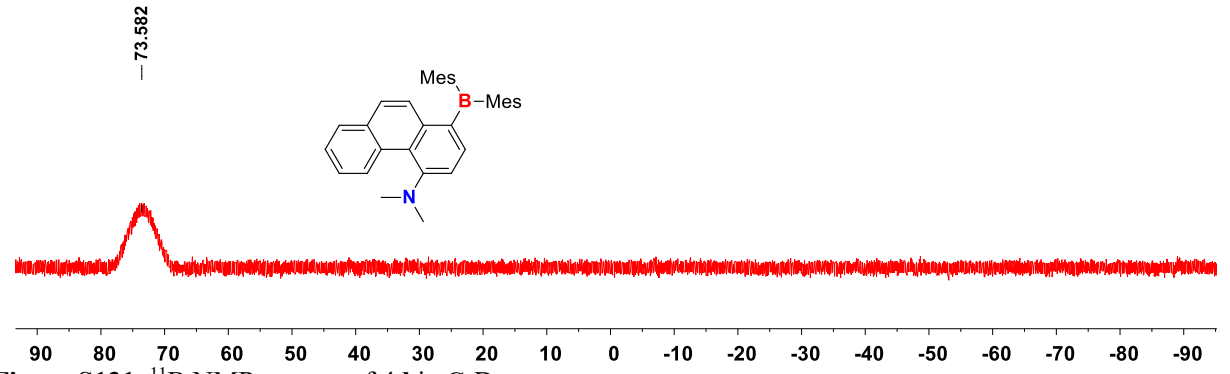


Figure S131. ^{11}B NMR spectra of **4d** in C_6D_6.

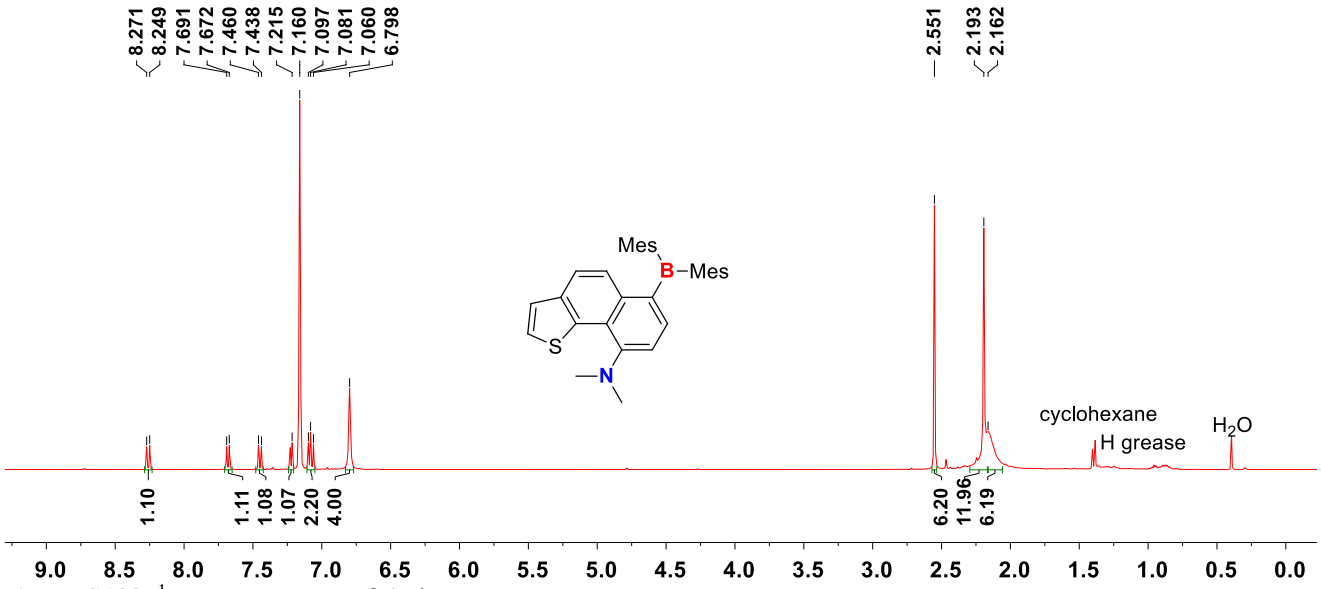


Figure S132. ^{1}H NMR spectra of **6d** in C_6D_6.

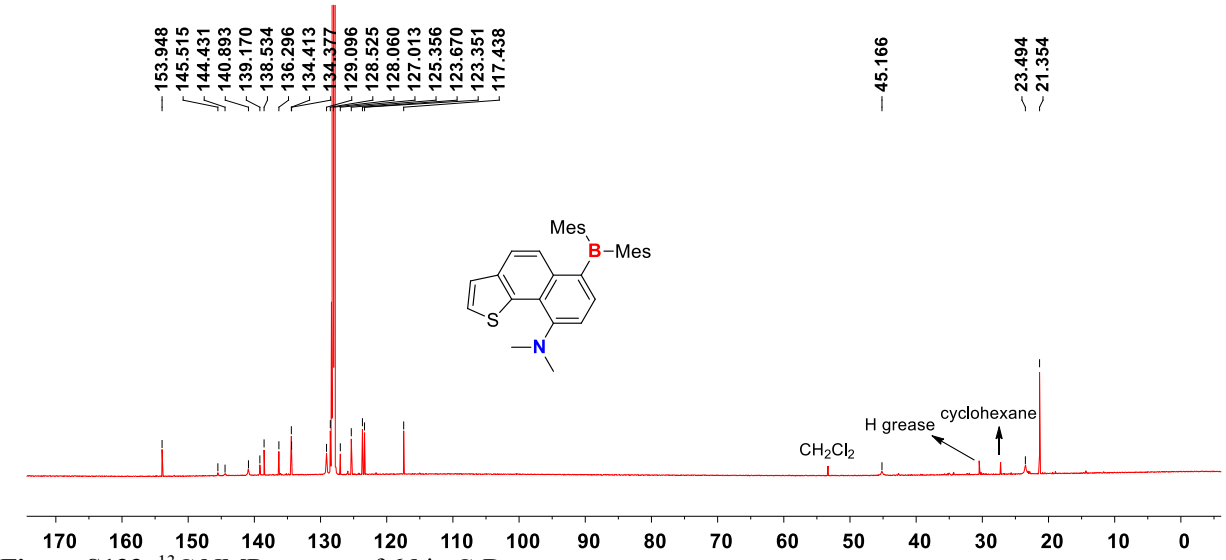


Figure S133. ^{13}C NMR spectra of **6d** in C_6D_6.

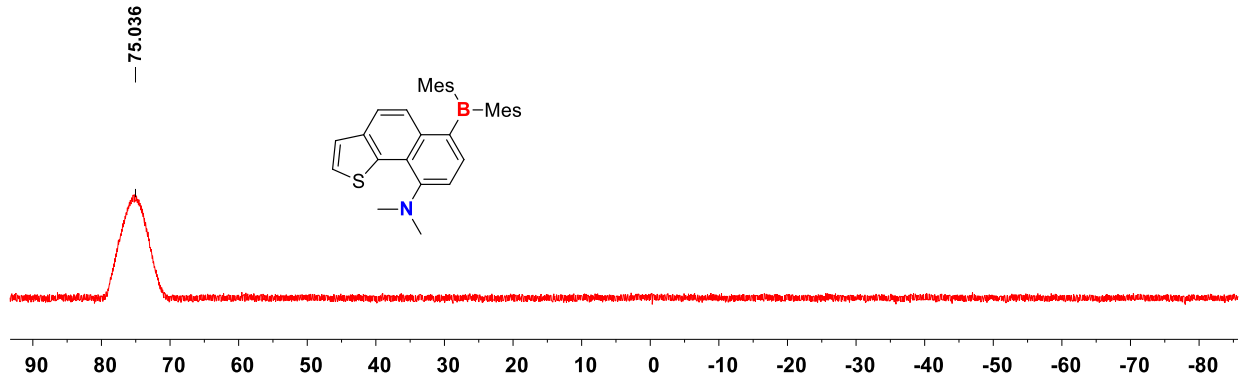


Figure S134. ^{11}B NMR spectra of **6d** in C_6D_6.

S8: DFT Calculation Data of *E*-1a-*E*-9a, 1b-4b, 1c-4c, 1d-4d, and 6d

Table S1. TD-DFT calculated electronic transitions for ***E*-1a** along with their corresponding excitation energies and oscillator strengths.

Compound	Spin State	Transition Configuration	Excitation Energy (nm, eV)	Oscillator Strength
***E*-1a**	S_1	HOMO → LUMO (96%)	386.34 (3.21)	0.2616
	S_2	HOMO-1 → LUMO (50%)	358.99 (3.45)	0.0243
		HOMO → LUMO+1 (46%)		
	S_3	HOMO-2 → LUMO (91%)	341.42 (3.63)	0.0653
		HOMO-2 → LUMO+1 (5%)		
	S_4	HOMO-1 → LUMO (37%)	329.19 (3.77)	0.3698
		HOMO-1 → LUMO+1 (13%)		
		HOMO → LUMO+1 (47%)		
	S_5	HOMO-3 → LUMO (89%)	321.93 (3.85)	0.0027
		HOMO-3 → LUMO+1 (4%)		
		HOMO-6 → LUMO+1 (20%)		

Table S2. TD-DFT calculated electronic transitions for ***Z*-1a** along with their corresponding excitation energies and oscillator strengths.

Compound	Spin State	Transition Configuration	Excitation Energy (nm, eV)	Oscillator Strength
***Z*-1a**	S_1	HOMO → LUMO (90%)	362.44 (3.42)	0.3078
		HOMO-2 → LUMO (3%)		
	S_2	HOMO-1 → LUMO (39%)	340.67 (3.64)	0.0500
		HOMO → LUMO+1 (56%)		
	S_3	HOMO-2 → LUMO (20%)	338.53 (3.66)	0.0748
		HOMO-1 → LUMO (42%)		
		HOMO → LUMO+1 (31%)		
	S_4	HOMO-2 → LUMO (72%)	321.00 (3.86)	0.0592
		HOMO-1 → LUMO (12%)		
		HOMO → LUMO+1 (10%)		
	S_5	HOMO-4 → LUMO (18%)	315.95 (3.92)	0.0126
		HOMO-3 → LUMO (76%)		
		HOMO → LUMO+2 (74%)		
		HOMO-3 → LUMO+1 (2%)		
		HOMO-1 → LUMO+1 (4%)		

Table S3. TD-DFT calculated electronic transitions for **1b** along with their corresponding excitation energies and oscillator strengths.

Compound	Spin State	Transition Configuration	Excitation Energy (nm, eV)	Oscillator Strength
1b	S_1	HOMO → LUMO (100%)	649.57 (1.91)	0.0520
	S_2	HOMO-1 → LUMO (6%)	473.25 (2.62)	0.1469
		HOMO → LUMO+1 (92%)		
	S_3	HOMO-1 → LUMO (81%)	393.14 (3.15)	0.1830
		HOMO → LUMO+2 (11%)		

		HOMO → LUMO+1 (5%)		
	S_4	HOMO-2 → LUMO (85%)	376.17 (3.30)	0.0479
		HOMO → LUMO+2 (9%)		
	S_5	HOMO-4 → LUMO (12%)	360.22 (3.44)	0.0061
		HOMO-3 → LUMO (64%)		
		HOMO → LUMO+2 (12%)		
		HOMO-2 → LUMO (4%)		
		HOMO-1 → LUMO (3%)		

Table S4. TD-DFT calculated electronic transitions for **1c** along with their corresponding excitation energies and oscillator strengths.

Compound	Spin State	Transition Configuration	Excitation Energy (nm, eV)	Oscillator Strength
1c	S_1	HOMO → LUMO (92%)	377.20 (3.29)	0.4413
		HOMO → LUMO+1 (3%)		
	S_2	HOMO → LUMO (2%)	366.71 (3.38)	0.0163
		HOMO → LUMO+1 (97%)		
	S_3	HOMO-1 → LUMO (98%)	346.16 (3.58)	0.0403
	S_4	HOMO-2 → LUMO (94%)	327.22 (3.79)	0.0082
		HOMO-5 → LUMO (2%)		
	S_5	HOMO-3 → LUMO (96%)	321.22 (3.86)	0.0112

Table S5. TD-DFT calculated electronic transitions for **1d** along with their corresponding excitation energies and oscillator strengths.

Compound	Spin State	Transition Configuration	Excitation Energy (nm, eV)	Oscillator Strength
1d	S_1	HOMO → LUMO (94%)	378.83 (3.27)	0.2957
	S_2	HOMO-2 → LUMO (18%)	348.57 (3.56)	0.0150
		HOMO → LUMO+1 (73%)		
		HOMO-3 → LUMO (3%)		
	S_3	HOMO-1 → LUMO (94%)	345.25 (3.59)	0.0910
		HOMO-2 → LUMO (2%)		
	S_4	HOMO-4 → LUMO (11%)	326.12 (3.80)	0.0198
		HOMO-3 → LUMO (27%)		
		HOMO-2 → LUMO (49%)		
		HOMO-5 → LUMO (3%)		
		HOMO → LUMO+1 (6%)		
	S_5	HOMO-5 → LUMO (53%)	320.34 (3.87)	0.0275
		HOMO-4 → LUMO (17%)		
		HOMO-3 → LUMO (18%)		
		HOMO-2 → LUMO (7%)		
		HOMO → LUMO+1 (2%)		

Table S6. TD-DFT calculated electronic transitions for ***E*-2a** along with their corresponding excitation energies and oscillator strengths.

Compound	Spin State	Transition Configuration	Excitation Energy (nm, eV)	Oscillator Strength

***E*-2a**	S_1	HOMO → LUMO (95%)	385.45 (3.22)	0.2828
	S_2	HOMO-1 → LUMO (58%) HOMO → LUMO+1 (38%)	359.34 (3.45)	0.0252
	S_3	HOMO-2 → LUMO (92%) HOMO-2 → LUMO+1 (4%)	341.11 (3.63)	0.0665
	S_4	HOMO-1 → LUMO (31%) HOMO-1 → LUMO+1 (12%) HOMO → LUMO+1 (54%)	329.03 (3.77)	0.3733
	S_5	HOMO-3 → LUMO (87%) HOMO-4 → LUMO (4%) HOMO-3 → LUMO+1 (3%) HOMO-6 → LUMO+1 (18%) HOMO-2 → LUMO+1 (10%)	321.45 (3.86)	0.0035

Table S7. TD-DFT calculated electronic transitions for ***Z*-2a** along with their corresponding excitation energies and oscillator strengths.

Compound	Spin State	Transition Configuration	Excitation Energy (nm, eV)	Oscillator Strength
***Z*-2a**	S_1	HOMO → LUMO (89%) HOMO-3 → LUMO (2%) HOMO-2 → LUMO (4%)	360.93 (3.44)	0.3159
	S_2	HOMO-1 → LUMO (74%) HOMO → LUMO+1 (12%) HOMO-3 → LUMO (2%) HOMO-2 → LUMO (7%)	340.14 (3.65)	0.0869
	S_3	HOMO-2 → LUMO (29%) HOMO → LUMO+1 (66%)	335.79 (3.69)	0.0328
	S_4	HOMO-2 → LUMO (56%) HOMO-1 → LUMO (19%) HOMO → LUMO+1 (20%)	322.71 (3.84)	0.0602
	S_5	HOMO-4 → LUMO (18%) HOMO-3 → LUMO (77%) HOMO → LUMO+2 (84%) HOMO-7→ LUMO (3%)	316.13 (3.92)	0.0141

Table S8. TD-DFT calculated electronic transitions for **2b** along with their corresponding excitation energies and oscillator strengths.

Compound	Spin State	Transition Configuration	Excitation Energy (nm, eV)	Oscillator Strength
2b	S_1	HOMO → LUMO (100%)	638.53 (1.94)	0.0584
	S_2	HOMO → LUMO+1 (94%) HOMO-1 → LUMO (4%)	475.60 (2.61)	0.1537
	S_3	HOMO-1 → LUMO (78%) HOMO → LUMO+2 (15%) HOMO → LUMO+1 (3%)	388.07 (3.19)	0.1985
	S_4	HOMO-2 → LUMO (81%) HOMO → LUMO+2 (12%)	369.94 (3.35)	0.0394

		HOMO-2 → LUMO+1 (3%)		
	S_5	HOMO-3 → LUMO (24%)	355.77 (3.48)	0.0546
		HOMO → LUMO+2 (45%)		
		HOMO-6 → LUMO (2%)		
		HOMO-4→ LUMO (6%)		
		HOMO-2 → LUMO (9%)		
		HOMO-1 → LUMO (9%)		

Table S9. TD-DFT calculated electronic transitions for **2c** along with their corresponding excitation energies and oscillator strengths.

Compound	Spin State	Transition Configuration	Excitation Energy (nm, eV)	Oscillator Strength
2c	S_1	HOMO → LUMO (94%)	377.45 (3.28)	0.4504
	S_2	HOMO → LUMO+1 (99%)	361.96 (3.43)	0.0033
	S_3	HOMO-1 → LUMO (97%)	348.01 (3.56)	0.0396
	S_4	HOMO-2 → LUMO (93%)	328.27 (3.78)	0.0115
		HOMO-5 → LUMO (3%)		
	S_5	HOMO-3 → LUMO (95%)	321.64 (3.85)	0.0134

Table S10. TD-DFT calculated electronic transitions for **2d** along with their corresponding excitation energies and oscillator strengths.

Compound	Spin State	Transition Configuration	Excitation Energy (nm, eV)	Oscillator Strength
2d	S_1	HOMO → LUMO (95%)	380.91 (3.25)	0.3013
	S_2	HOMO-2 → LUMO (20%)	346.25 (3.58)	0.0220
		HOMO-1 → LUMO (13%)		
		HOMO → LUMO+1 (59%)		
		HOMO-3 → LUMO (2%)		
		HOMO-2 → LUMO+2 (2%)		
	S_3	HOMO-2 → LUMO (11%)	344.93 (3.59)	0.0750
		HOMO-1 → LUMO (81%)		
		HOMO → LUMO+1 (5%)		
	S_4	HOMO-3 → LUMO (37%)	326.01 (3.80)	0.0278
		HOMO-2 → LUMO (37%)		
		HOMO-4 → LUMO (8%)		
		HOMO → LUMO+1 (9%)		
	S_5	HOMO-5 → LUMO (23%)	320.11 (3.87)	0.0458
		HOMO-4 → LUMO (48%)		
		HOMO-2 → LUMO (11%)		
		HOMO-4 → LUMO (7%)		
		HOMO → LUMO+1 (6%)		

Table S11. TD-DFT calculated electronic transitions for ***E*-3a** along with their corresponding excitation energies and oscillator strengths.

Compound	Spin State	Transition Configuration	Excitation Energy (nm, eV)	Oscillator Strength
***E*-3a**	S_1	HOMO → LUMO (92%)	392.35 (3.16)	0.2679

		HOMO → LUMO+1 (3%)		
	S_2	HOMO-1 → LUMO (77%)	363.99 (3.41)	0.0801
		HOMO → LUMO+1 (16%)		
		HOMO → LUMO (4%)		
	S_3	HOMO-2 → LUMO (94%)	337.14 (3.68)	0.0672
		HOMO-2 → LUMO+1 (3%)		
	S_4	HOMO-1 → LUMO (15%)	331.13 (3.74)	0.4143
		HOMO-1 → LUMO+1 (12%)		
		HOMO → LUMO+1 (65%)		
	S_5	HOMO-3 → LUMO (81%)	317.48 (3.91)	0.0208
		HOMO-4 → LUMO (5%)		
		HOMO-1 → LUMO+1 (4%)		
		HOMO-3 → LUMO+1 (3%)		
		HOMO-2 → LUMO+1 (91%)		

Table S12. TD-DFT calculated electronic transitions for ***Z*-3a** along with their corresponding excitation energies and oscillator strengths.

Compound	Spin State	Transition Configuration	Excitation Energy (nm, eV)	Oscillator Strength
***Z*-3a**	S_1	HOMO → LUMO (87%)	368.27 (3.37)	0.3220
		HOMO-3 → LUMO (2%)		
		HOMO-1 → LUMO (6%)		
	S_2	HOMO-1 → LUMO (84%)	351.77 (3.52)	0.0551
		HOMO → LUMO+1 (6%)		
		HOMO → LUMO (5%)		
	S_3	HOMO-2 → LUMO (91%)	333.28 (3.72)	0.0837
		HOMO → LUMO (2%)		
		HOMO → LUMO+1 (3%)		
	S_4	HOMO-2 → LUMO (3%)	325.83 (3.81)	0.0536
		HOMO-1 → LUMO (8%)		
		HOMO → LUMO+1 (85%)		
	S_5	HOMO-4 → LUMO (19%)	313.07 (3.96)	0.0088
		HOMO-3 → LUMO (76%)		

Table S13. TD-DFT calculated electronic transitions for **3b** along with their corresponding excitation energies and oscillator strengths.

Compound	Spin State	Transition Configuration	Excitation Energy (nm, eV)	Oscillator Strength
3b	S_1	HOMO → LUMO (100%)	628.02 (1.97)	0.0430
	S_2	HOMO → LUMO+1 (92%)	472.19 (2.63)	0.1525
		HOMO-1 → LUMO (7%)		
	S_3	HOMO-1 → LUMO (84%)	404.80 (3.06)	0.2173
		HOMO → LUMO+1 (6%)		
		HOMO → LUMO+2 (8%)		
	S_4	HOMO-2 → LUMO (93%)	361.60 (3.43)	0.0168
		HOMO-2 → LUMO+1 (4%)		
	S_5	HOMO-3 → LUMO (48%)	346.52 (3.58)	0.0659

		HOMO-1 → LUMO+1 (38%)		
		HOMO-4 → LUMO (3%)		
		HOMO-3→ LUMO+1 (3%)		
		HOMO→ LUMO+2 (5%)		

Table S14. TD-DFT calculated electronic transitions for **3c** along with their corresponding excitation energies and oscillator strengths.

Compound	Spin State	Transition Configuration	Excitation Energy (nm, eV)	Oscillator Strength
3c	S_1	HOMO → LUMO (92%)	380.29 (3.26)	0.4099
		HOMO-1 → LUMO (4%)		
	S_2	HOMO-1 → LUMO (93%)	358.86 (3.45)	0.0625
		HOMO → LUMO (4%)		
	S_3	HOMO → LUMO+1 (99%)	349.94 (3.54)	0.0032
	S_4	HOMO-2 → LUMO (94%)	331.81 (3.74)	0.0333
	S_5	HOMO-3 → LUMO (94%)	319.33 (3.88)	0.0133

Table S15. TD-DFT calculated electronic transitions for **3d** along with their corresponding excitation energies and oscillator strengths.

Compound	Spin State	Transition Configuration	Excitation Energy (nm, eV)	Oscillator Strength
3d	S_1	HOMO → LUMO (93%)	393.94 (3.15)	0.2312
		HOMO-1 → LUMO (4%)		
	S_2	HOMO-1 → LUMO (87%)	368.77 (3.36)	0.0771
		HOMO → LUMO (4%)		
		HOMO → LUMO+1 (4%)		
		HOMO → LUMO+2 (3%)		
	S_3	HOMO-2 → LUMO (97%)	340.53 (3.64)	0.0902
	S_4	HOMO-1 → LUMO+1 (12%)	324.20 (3.82)	0.0670
		HOMO → LUMO+1 (52%)		
		HOMO → LUMO+2 (13%)		
		HOMO-6 → LUMO (5%)		
		HOMO-1 → LUMO (7%)		
		HOMO-1 → LUMO+2 (7%)		
	S_5	HOMO-4 → LUMO (11%)	321.24 (3.86)	0.0009
		HOMO-3 → LUMO (85%)		

Table S16. TD-DFT calculated electronic transitions for ***E*-4a** along with their corresponding excitation energies and oscillator strengths.

Compound	Spin State	Transition Configuration	Excitation Energy (nm, eV)	Oscillator Strength
***E*-4a**	S_1	HOMO → LUMO (91%)	387.19 (3.20)	0.2721
		HOMO-1 → LUMO (5%)		
	S_2	HOMO-1 → LUMO (79%)	360.91 (3.44)	0.0750
		HOMO-2 → LUMO (3%)		
		HOMO → LUMO (5%)		
		HOMO → LUMO+1 (9%)		

	S_3	HOMO-2 → LUMO (89%)	344.43 (3.60)	0.0820
		HOMO → LUMO+1 (7%)		
	S_4	HOMO-4 → LUMO (15%)	326.72 (3.79)	0.0034
		HOMO-3 → LUMO (77%)		
		HOMO-5 → LUMO (4%)		
	S_5	HOMO-5 → LUMO (13%)	320.67 (3.87)	0.0059
		HOMO-4 → LUMO (65%)		
		HOMO-3 → LUMO (17%)		

Table S17. TD-DFT calculated electronic transitions for ***Z*-4a** along with their corresponding excitation energies and oscillator strengths.

Compound	Spin State	Transition Configuration	Excitation Energy (nm, eV)	Oscillator Strength
***Z*-4a**	S_1	HOMO → LUMO (91%)	365.86 (3.39)	0.3342
		HOMO-3 → LUMO (2%)		
		HOMO-2 → LUMO (3%)		
	S_2	HOMO-1 → LUMO (75%)	343.75 (3.61)	0.0292
		HOMO → LUMO+1 (20%)		
		HOMO-2 → LUMO (2%)		
	S_3	HOMO-2 → LUMO (83%)	334.66 (3.70)	0.0793
		HOMO → LUMO+1 (12%)		
		HOMO → LUMO (2%)		
	S_4	HOMO-1 → LUMO (22%)	325.54 (3.81)	0.0643
		HOMO → LUMO+1 (66%)		
		HOMO-2 → LUMO (9%)		
	S_5	HOMO-4 → LUMO (18%)	314.45 (3.94)	0.0101
		HOMO-3 → LUMO (77%)		

Table S18. TD-DFT calculated electronic transitions for **4b** along with their corresponding excitation energies and oscillator strengths.

Compound	Spin State	Transition Configuration	Excitation Energy (nm, eV)	Oscillator Strength
4b	S_1	HOMO → LUMO (100%)	641.11 (1.93)	0.0495
	S_2	HOMO → LUMO+1 (92%)	479.48 (2.59)	0.1491
		HOMO-1 → LUMO (7%)		
	S_3	HOMO-1 → LUMO (79%)	396.21 (3.13)	0.2224
		HOMO → LUMO+2 (15%)		
		HOMO → LUMO+1 (5%)		
	S_4	HOMO-2 → LUMO (91%)	365.46 (3.39)	0.0191
		HOMO-2 → LUMO+1 (3%)		
		HOMO → LUMO+2 (3%)		
	S_5	HOMO-3 → LUMO (69%)	349.08 (3.55)	0.0328
		HOMO → LUMO+2 (14%)		
		HOMO-4 → LUMO (5%)		
		HOMO-3→ LUMO+1 (2%)		
		HOMO-1→ LUMO (2%)		
		HOMO-1→ LUMO+1 (4%)		

Table S19. TD-DFT calculated electronic transitions for **4c** along with their corresponding excitation energies and oscillator strengths.

Compound	Spin State	Transition Configuration	Excitation Energy (nm, eV)	Oscillator Strength
4c	S_1	HOMO → LUMO (94%)	378.92 (3.27)	0.4471
	S_2	HOMO → LUMO+1 (99%)	350.93 (3.53)	0.0057
	S_3	HOMO-1 → LUMO (97%)	346.91 (3.57)	0.0438
	S_4	HOMO-2 → LUMO (92%)	327.31 (3.79)	0.0194
		HOMO-4 → LUMO (4%)		
	S_5	HOMO-3 → LUMO (94%)	318.94 (3.89)	0.0161

Table S20. TD-DFT calculated electronic transitions for **4d** along with their corresponding excitation energies and oscillator strengths.

Compound	Spin State	Transition Configuration	Excitation Energy (nm, eV)	Oscillator Strength
4d	S_1	HOMO → LUMO (94%)	384.43 (3.23)	0.2877
	S_2	HOMO-1 → LUMO (74%)	354.02 (3.50)	0.0059
		HOMO → LUMO+1 (21%)		
	S_3	HOMO-2 → LUMO (97%)	341.69 (3.63)	0.0888
	S_4	HOMO-3 → LUMO (21%)	324.42 (3.82)	0.0751
		HOMO-1 → LUMO (17%)		
		HOMO → LUMO+1 (49%)		
		HOMO-1 → LUMO+1 (4%)		
	S_5	HOMO-4 → LUMO (25%)	320.41 (3.87)	0.0247
		HOMO-3 → LUMO (52%)		
		HOMO → LUMO+1 (12%)		
		HOMO-1 → LUMO (5%)		

Table S21. TD-DFT calculated electronic transitions for ***E*-5a** along with their corresponding excitation energies and oscillator strengths.

Compound	Spin State	Transition Configuration	Excitation Energy (nm, eV)	Oscillator Strength
***E*-5a**	S_1	HOMO → LUMO (90%)	377.45 (3.28)	0.1421
		HOMO → LUMO+1 (7%)		
	S_2	HOMO-1 → LUMO (94%)	350.06 (3.54)	0.0898
		HOMO-1 → LUMO+1 (3%)		
	S_3	HOMO-2 → LUMO (80%)	330.64 (3.75)	0.0408
		HOMO → LUMO+1 (10%)		
		HOMO-3 → LUMO (4%)		
	S_4	HOMO-3 → LUMO (82%)	326.55 (3.80)	0.0506
		HOMO-3 → LUMO+1 (2%)		
		HOMO-2 → LUMO (7%)		
		HOMO → LUMO+1 (5%)		
	S_5	HOMO-4 → LUMO (96%)	320.45 (3.87)	0.0161

Table S22. TD-DFT calculated electronic transitions for ***Z*-5a** along with their corresponding excitation

energies and oscillator strengths.

Compound	Spin State	Transition Configuration	Excitation Energy (nm, eV)	Oscillator Strength
***Z*-5a**	S_1	HOMO → LUMO (84%)	352.04 (3.52)	0.0784
		HOMO-2 → LUMO (2%)		
		HOMO-1 → LUMO (12%)		
	S_2	HOMO-1 → LUMO (86%)	350.38 (3.54)	0.0892
		HOMO → LUMO (11%)		
	S_3	HOMO-2 → LUMO (89%)	326.37 (3.80)	0.0167
		HOMO → LUMO (2%)		
		HOMO-3 → LUMO (5%)		
	S_4	HOMO-2 → LUMO (4%)	321.28 (3.86)	0.0625
		HOMO-3 → LUMO (91%)		
	S_5	HOMO-4 → LUMO (97%)	319.13 (3.89)	0.0111

Table S23. TD-DFT calculated electronic transitions for ***E*-6a** along with their corresponding excitation energies and oscillator strengths.

Compound	Spin State	Transition Configuration	Excitation Energy (nm, eV)	Oscillator Strength
***E*-6a**	S_1	HOMO → LUMO (91%)	386.43 (3.21)	0.2679
		HOMO-1 → LUMO (4%)		
	S_2	HOMO-1 → LUMO (82%)	359.73 (3.45)	0.1118
		HOMO-2 → LUMO (2%)		
		HOMO → LUMO (5%)		
		HOMO → LUMO+1 (8%)		
	S_3	HOMO-2 → LUMO (92%)	342.75 (3.62)	0.0856
		HOMO → LUMO+1 (4%)		
	S_4	HOMO-4 → LUMO (16%)	324.58 (3.82)	0.0034
		HOMO-3 → LUMO (78%)		
		HOMO-5 → LUMO (2%)		
	S_5	HOMO-4 → LUMO (69%)	318.25 (3.90)	0.0049
		HOMO-3 → LUMO (17%)		
		HOMO-5 → LUMO (9%)		

Table S24. TD-DFT calculated electronic transitions for ***Z*-6a** along with their corresponding excitation energies and oscillator strengths.

Compound	Spin State	Transition Configuration	Excitation Energy (nm, eV)	Oscillator Strength
***Z*-6a**	S_1	HOMO → LUMO (91%)	359.77 (3.45)	0.3369
		HOMO-3 → LUMO (3%)		
		HOMO-2 → LUMO (3%)		
	S_2	HOMO-1 → LUMO (93%)	350.29 (3.54)	0.0333
		HOMO-2 → LUMO (3%)		
		HOMO → LUMO+1 (3%)		
	S_3	HOMO-2 → LUMO (84%)	331.88 (3.74)	0.0666
		HOMO → LUMO+1 (10%)		
	S_4	HOMO → LUMO+1 (84%)	324.16 (3.82)	0.0280

		HOMO-2 → LUMO (8%)		
		HOMO-1 → LUMO (5%)		
	S_5	HOMO-4 → LUMO (16%)	314.57 (3.94)	0.0147
		HOMO-3 → LUMO (79%)		

Table S25. TD-DFT calculated electronic transitions for **6b** along with their corresponding excitation energies and oscillator strengths.

Compound	Spin State	Transition Configuration	Excitation Energy (nm, eV)	Oscillator Strength
6b	S_1	HOMO → LUMO (99%)	549.33 (2.26)	0.0485
	S_2	HOMO → LUMO+1 (93%)	448.09 (2.77)	0.1378
		HOMO-1 → LUMO (5%)		
	S_3	HOMO-1 → LUMO (86%)	387.54 (3.20)	0.2812
		HOMO → LUMO+1 (4%)		
		HOMO → LUMO+2 (6%)		
	S_4	HOMO-2 → LUMO (92%)	357.98 (3.46)	0.0526
		HOMO-2 → LUMO+1 (4%)		
	S_5	HOMO-3 → LUMO (58%)	341.72 (3.63)	0.0179
		HOMO-1 → LUMO+1 (31%)		
		HOMO → LUMO+2 (6%)		

Table S26. TD-DFT calculated electronic transitions for **6d** along with their corresponding excitation energies and oscillator strengths.

Compound	Spin State	Transition Configuration	Excitation Energy (nm, eV)	Oscillator Strength
6d	S_1	HOMO → LUMO (96%)	389.28 (3.18)	0.2150
	S_2	HOMO-1 → LUMO (90%)	351.95 (3.52)	0.0125
		HOMO → LUMO+2 (4%)		
	S_3	HOMO-2 → LUMO (96%)	346.91 (3.57)	0.0986
	S_4	HOMO-4 → LUMO (15%)	326.74 (3.79)	0.0003
		HOMO-3 → LUMO (80%)		
	S_5	HOMO-5 → LUMO (47%)	321.42 (3.86)	0.0181
		HOMO-4 → LUMO (42%)		
		HOMO-3 → LUMO+1 (6%)		

Table S27. TD-DFT calculated electronic transitions for ***E*-7a** along with their corresponding excitation energies and oscillator strengths.

Compound	Spin State	Transition Configuration	Excitation Energy (nm, eV)	Oscillator Strength
***E*-7a**	S_1	HOMO → LUMO (94%)	399.25 (3.11)	0.2711
		HOMO → LUMO+1 (3%)		
	S_2	HOMO-1 → LUMO (83%)	371.70 (3.34)	0.0740
		HOMO → LUMO+1 (13%)		
	S_3	HOMO-2 → LUMO (90%)	351.15 (3.53)	0.0627
		HOMO-2 → LUMO+1 (2%)		
		HOMO → LUMO+1 (6%)		
	S_4	HOMO-4 → LUMO (15%)	333.97 (3.71)	0.0047

		HOMO-3 → LUMO (77%)		
		HOMO-5 → LUMO (3%)		
	S_5	HOMO-4 → LUMO (69%)	327.29 (3.79)	0.0232
		HOMO-3 → LUMO (16%)		
		HOMO-5 → LUMO (6%)		
		HOMO-1 → LUMO+1 (4%)		

Table S28. TD-DFT calculated electronic transitions for ***Z*-7a** along with their corresponding excitation energies and oscillator strengths.

Compound	Spin State	Transition Configuration	Excitation Energy (nm, eV)	Oscillator Strength
***Z*-7a**	S_1	HOMO-1 → LUMO (16%)	363.64 (3.41)	0.2924
		HOMO → LUMO (77%)		
		HOMO-3 → LUMO (3%)		
	S_2	HOMO-1 → LUMO (76%)	360.57 (3.44)	0.0627
		HOMO → LUMO (15%)		
		HOMO-2 → LUMO (2%)		
		HOMO → LUMO+1 (5%)		
	S_3	HOMO-2 → LUMO (27%)	338.00 (3.67)	0.0587
		HOMO → LUMO+1 (68%)		
	S_4	HOMO-2 → LUMO (66%)	332.64 (3.73)	0.0705
		HOMO → LUMO+1 (23%)		
		HOMO-1 → LUMO (3%)		
	S_5	HOMO-4 → LUMO (16%)	315.86 (3.93)	0.0159
		HOMO-3 → LUMO (77%)		

Table S29. TD-DFT calculated electronic transitions for ***E*-8a** along with their corresponding excitation energies and oscillator strengths.

Compound	Spin State	Transition Configuration	Excitation Energy (nm, eV)	Oscillator Strength
***E*-8a**	S_1	HOMO → LUMO (31%)	366.77 (3.38)	0.2379
		HOMO → LUMO+1 (62%)		
	S_2	HOMO → LUMO (65%)	357.13 (3.47)	0.2162
		HOMO → LUMO+1 (28%)		
		HOMO-2 → LUMO (3%)		
	S_3	HOMO-2 → LUMO (25%)	340.31 (3.64)	0.0883
		HOMO-1 → LUMO (61%)		
		HOMO-2 → LUMO+1 (4%)		
		HOMO-1 → LUMO+1 (7%)		
	S_4	HOMO-3 → LUMO (22%)	329.50 (3.76)	0.2213
		HOMO-2 → LUMO (49%)		
		HOMO-1 → LUMO (18%)		
		HOMO-4 → LUMO (2%)		
		HOMO-3 → LUMO+1 (3%)		
	S_5	HOMO-4 → LUMO (16%)	321.93 (3.85)	0.0972
		HOMO-3 → LUMO (58%)		
		HOMO-4 → LUMO+1 (2%)		

		HOMO-3 → LUMO+1 (6%)		
		HOMO-2 → LUMO (9%)		
		HOMO-1 → LUMO (5%)		

Table S30. TD-DFT calculated electronic transitions for ***Z*-8a** along with their corresponding excitation energies and oscillator strengths.

Compound	Spin State	Transition Configuration	Excitation Energy (nm, eV)	Oscillator Strength
***Z*-8a**	S_1	HOMO → LUMO (74%)	354.65 (3.50)	0.2437
		HOMO → LUMO+1 (26%)		
		HOMO-4 → LUMO (3%)		
		HOMO-1 → LUMO (3%)		
	S_2	HOMO-1 → LUMO (27%)	343.82 (3.61)	0.0819
		HOMO → LUMO (17%)		
		HOMO → LUMO+1 (48%)		
		HOMO-2 → LUMO (4%)		
	S_3	HOMO-2 → LUMO (10%)	341.75 (3.63)	0.1334
		HOMO-1 → LUMO (58%)		
		HOMO → LUMO+1 (22%)		
		HOMO-4 → LUMO (3%)		
		HOMO-1 → LUMO+1 (4%)		
	S_4	HOMO-2 → LUMO (74%)	330.18 (3.76)	0.0988
		HOMO-3 → LUMO (7%)		
		HOMO-1 → LUMO (2%)		
		HOMO → LUMO (6%)		
		HOMO → LUMO+1 (5%)		
	S_5	HOMO-3 → LUMO (84%)	323.77 (3.83)	0.0585
		HOMO-4 → LUMO (3%)		
		HOMO-3 → LUMO+1 (3%)		
		HOMO-2 → LUMO (5%)		

Table S31. TD-DFT calculated electronic transitions for ***E*-9a** along with their corresponding excitation energies and oscillator strengths.

Compound	Spin State	Transition Configuration	Excitation Energy (nm, eV)	Oscillator Strength
***E*-9a**	S_1	HOMO → LUMO (96%)	467.76 (2.65)	0.0858
		HOMO → LUMO+1 (3%)		
	S_2	HOMO → LUMO+1 (86%)	355.61 (3.49)	0.6315
		HOMO-3 → LUMO (3%)		
		HOMO-1 → LUMO (6%)		
		HOMO → LUMO (3%)		
	S_3	HOMO-1 → LUMO (88%)	343.00 (3.61)	0.2391
		HOMO-2 → LUMO (4%)		
		HOMO → LUMO+1 (5%)		
	S_4	HOMO-3 → LUMO (27%)	327.08 (3.79)	0.0667
		HOMO-2 → LUMO (65%)		
	S_5	HOMO-4 → LUMO (88%)	318.46 (3.89)	0.0233

		HOMO-3 → LUMO (5%) HOMO-2 → LUMO (4%)		

Table S32. TD-DFT calculated electronic transitions for ***Z*-9a** along with their corresponding excitation energies and oscillator strengths.

Compound	Spin State	Transition Configuration	Excitation Energy (nm, eV)	Oscillator Strength
***Z*-9a**	S_1	HOMO → LUMO (98%)	438.35 (2.83)	0.0410
	S_2	HOMO → LUMO (89%) HOMO-1 → LUMO (8%)	351.00 (3.53)	0.2914
	S_3	HOMO-1 → LUMO (86%) HOMO-2 → LUMO (4%) HOMO → LUMO+1 (67)	343.28 (3.61)	0.1526
	S_4	HOMO-3 → LUMO (95%)	322.19 (3.85)	0.0307
	S_5	HOMO-4 → LUMO (95%)	315.33 (3.93)	0.0573

Table S33. Primary orbitals which contribute to the calculated transitions of ***E*-1a** (iso = 0.03). Most H-atoms have been omitted for clarity.

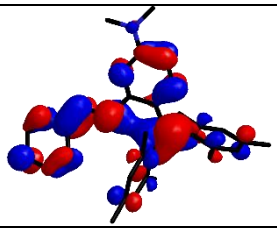
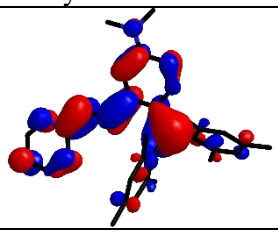
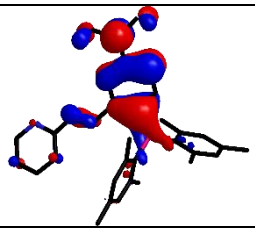
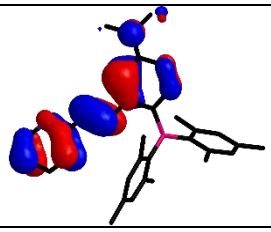
			
LUMO+1	LUMO	HOMO	HOMO-1

Table S34. Primary orbitals which contribute to the calculated transitions of ***Z*-1a** (iso = 0.03). Most H-atoms have been omitted for clarity.

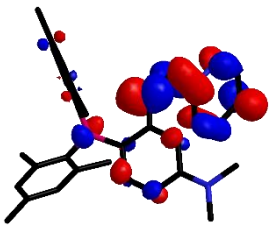
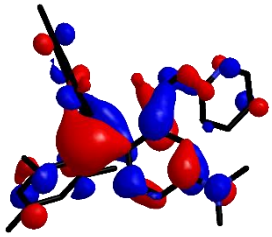
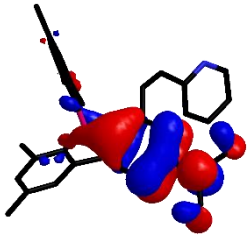
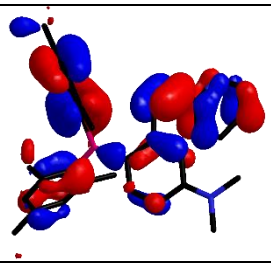
			
LUMO+1	LUMO	HOMO	HOMO-1

Table S35. Primary orbitals which contribute to the calculated transitions of **1b** (iso = 0.03). Most H-atoms have been omitted for clarity.

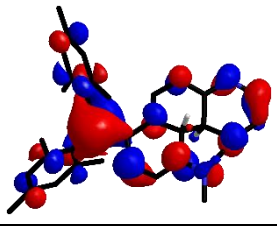
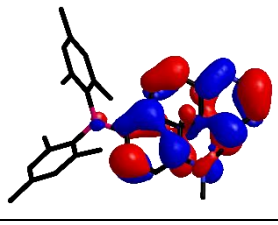
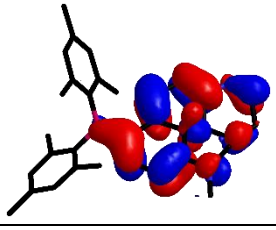
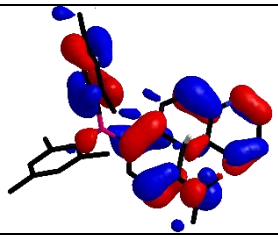
			
LUMO+1	LUMO	HOMO	HOMO-1

Table S36. Primary orbitals which contribute to the calculated transitions of **1c** (iso = 0.03). Most H-atoms have been omitted for clarity.

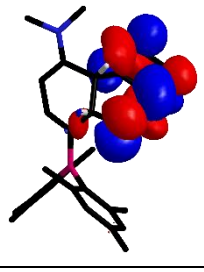
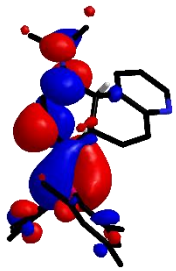
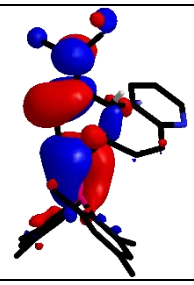
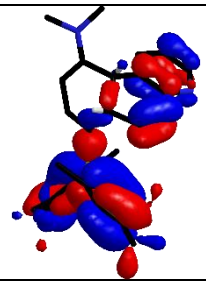
			
LUMO+1	LUMO	HOMO	HOMO-1

Table S37. Primary orbitals which contribute to the calculated transitions of **1d** (iso = 0.03). Most H-atoms have been omitted for clarity.

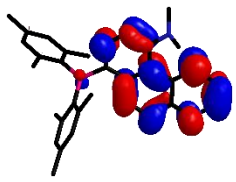
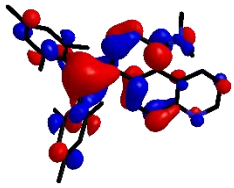
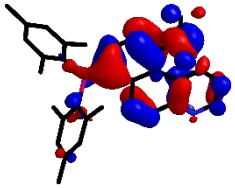
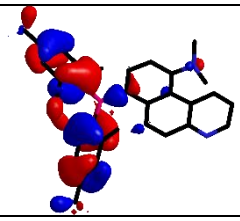
			
LUMO+1	LUMO	HOMO	HOMO-1

Table S38. Primary orbitals which contribute to the calculated transitions of ***E*-2a** (iso = 0.03). Most H-atoms have been omitted for clarity.

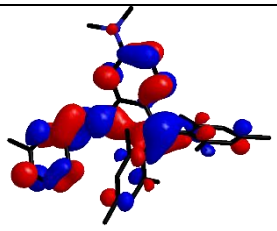
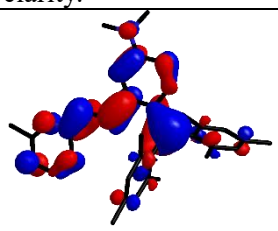
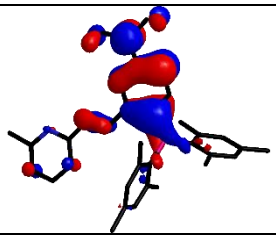
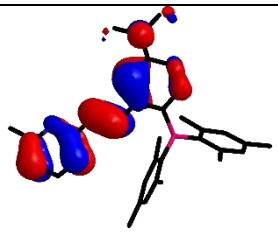
			
LUMO+1	LUMO	HOMO	HOMO-1

Table S39. Primary orbitals which contribute to the calculated transitions of ***Z*-2a** (iso = 0.03). Most H-atoms have been omitted for clarity.

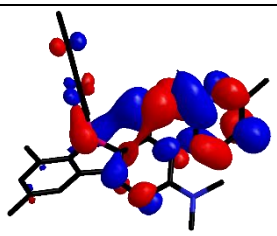
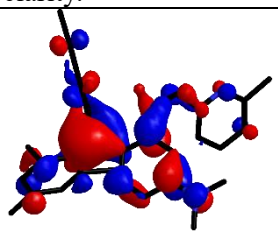
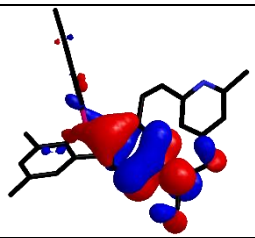
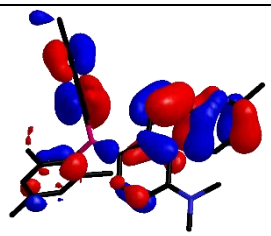
			
LUMO+1	LUMO	HOMO	HOMO-1

Table S40. Primary orbitals which contribute to the calculated transitions of **2b** (iso = 0.03). Most H-atoms have been omitted for clarity.

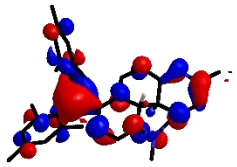
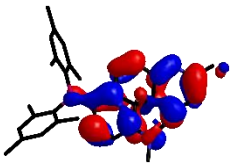
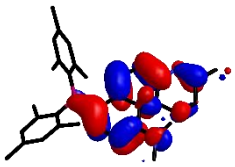
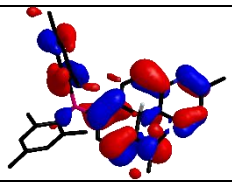
			
LUMO+1	LUMO	HOMO	HOMO-1

Table S41. Primary orbitals which contribute to the calculated transitions of **2c** (iso = 0.03). Most H-atoms have been omitted for clarity.

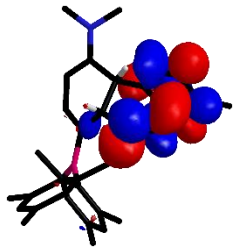
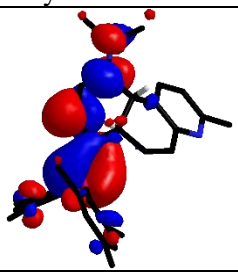
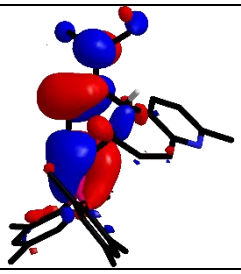
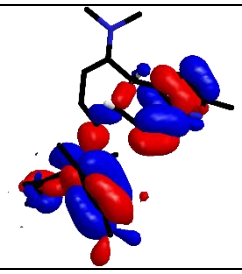
			
LUMO+1	LUMO	HOMO	HOMO-1

Table S42. Primary orbitals which contribute to the calculated transitions of **2d** (iso = 0.03). Most H-atoms have been omitted for clarity.

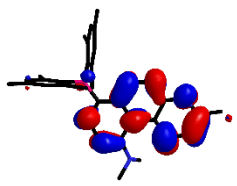
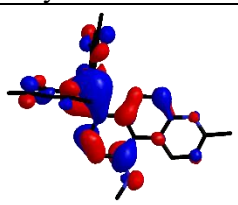
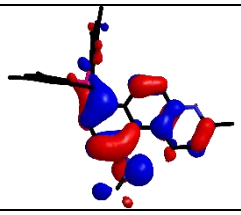
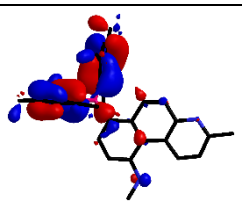
			
LUMO+1	LUMO	HOMO	HOMO-1

Table S43. Primary orbitals which contribute to the calculated transitions of ***E*-3a** (iso = 0.03). Most H-atoms have been omitted for clarity.

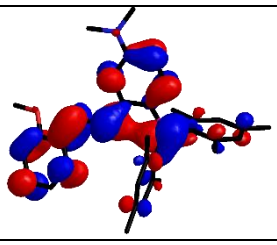
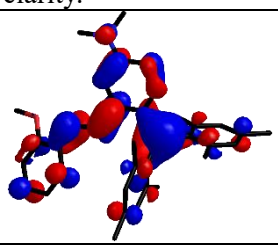
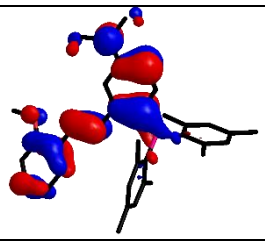
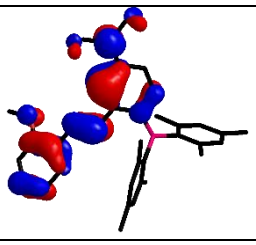
			
LUMO+1	LUMO	HOMO	HOMO-1

Table S44. Primary orbitals which contribute to the calculated transitions of ***Z*-3a** (iso = 0.03). Most H-atoms have been omitted for clarity.

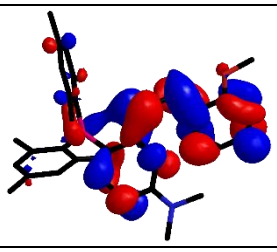
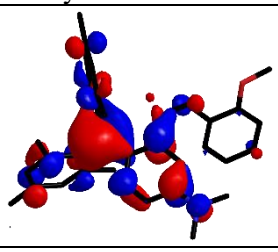
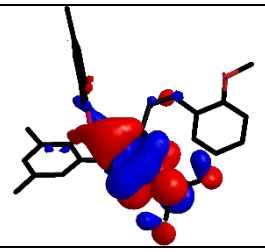
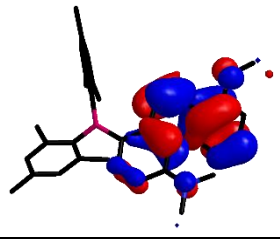
			
LUMO+1	LUMO	HOMO	HOMO-1

Table S45. Primary orbitals which contribute to the calculated transitions of **3b** (iso = 0.03). Most H-atoms have been omitted for clarity.

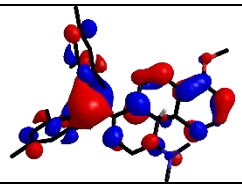
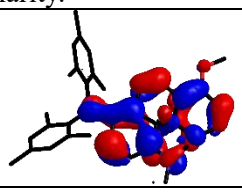
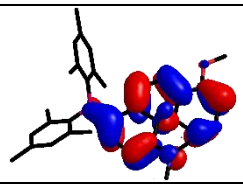
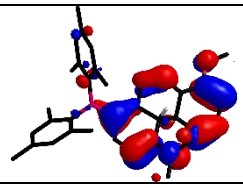
			
LUMO+1	LUMO	HOMO	HOMO-1

Table S46. Primary orbitals which contribute to the calculated transitions of **3c** (iso = 0.03). Most H-atoms have been omitted for clarity.

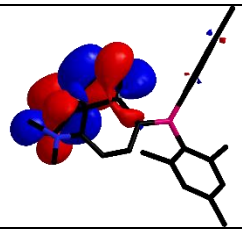
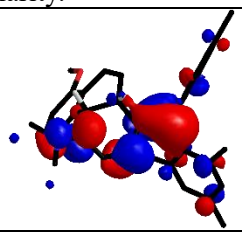
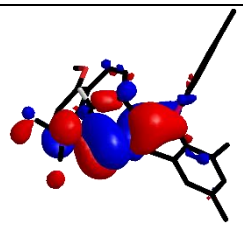
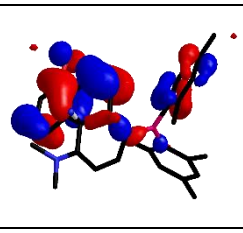
			
LUMO+1	LUMO	HOMO	HOMO-1

Table S47. Primary orbitals which contribute to the calculated transitions of **3d** (iso = 0.03). Most H-atoms have been omitted for clarity.

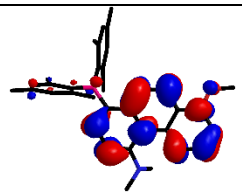
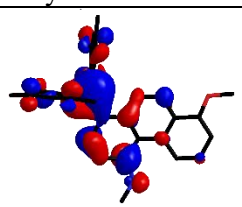
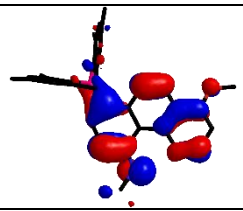
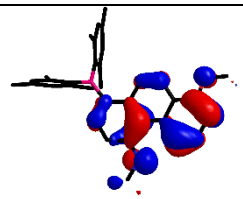
			
LUMO+1	LUMO	HOMO	HOMO-1

Table S48. Primary orbitals which contribute to the calculated transitions of ***E*-4a** (iso = 0.03). Most H-atoms have been omitted for clarity.

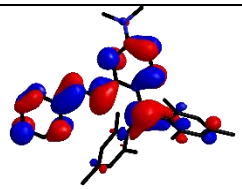
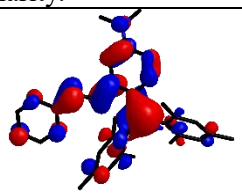
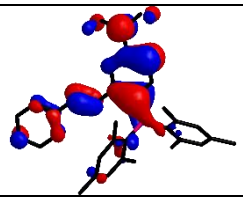
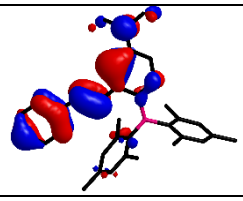
			
LUMO+1	LUMO	HOMO	HOMO-1

Table S49. Primary orbitals which contribute to the calculated transitions of ***Z*-4a** (iso = 0.03). Most H-atoms have been omitted for clarity.

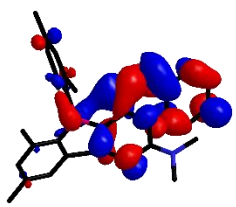
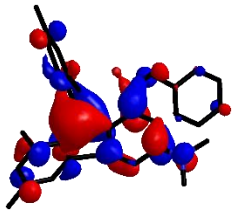
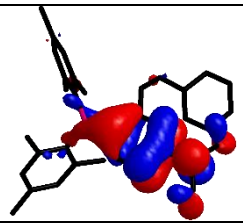
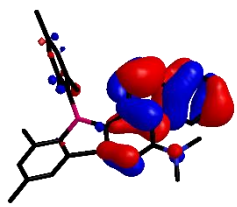
			
LUMO+1	LUMO	HOMO	HOMO-1

Table S50. Primary orbitals which contribute to the calculated transitions of **4b** (iso = 0.03). Most H-atoms have been omitted for clarity.

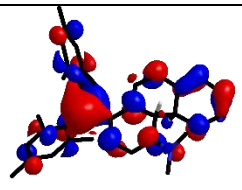
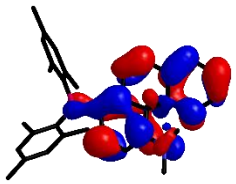
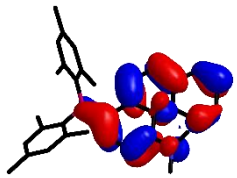
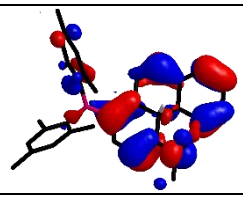
			
LUMO+1	LUMO	HOMO	HOMO-1

Table S51. Primary orbitals which contribute to the calculated transitions of **4c** (iso = 0.03). Most H-atoms have been omitted for clarity.

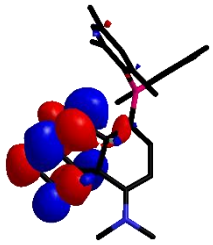
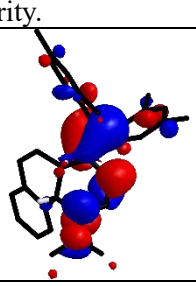
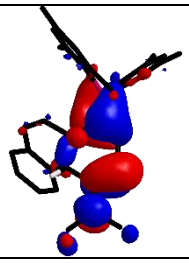
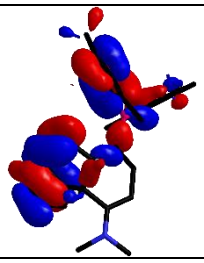
			
LUMO+1	LUMO	HOMO	HOMO-1

Table S52. Primary orbitals which contribute to the calculated transitions of **4d** (iso = 0.03). Most H-atoms have been omitted for clarity.

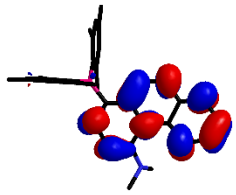
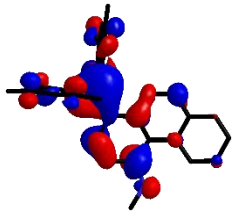
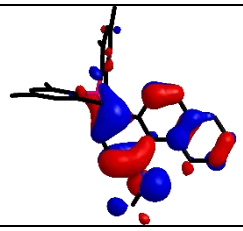
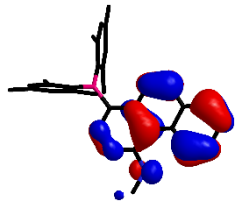
			
LUMO+1	LUMO	HOMO	HOMO-1

Table S53. Primary orbitals which contribute to the calculated transitions of ***E*-5a** (iso = 0.03). Most H-atoms have been omitted for clarity.

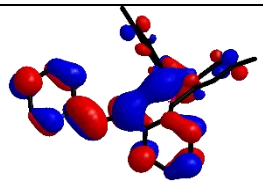
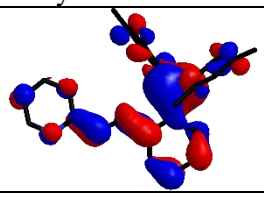
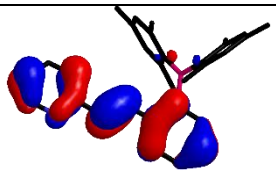
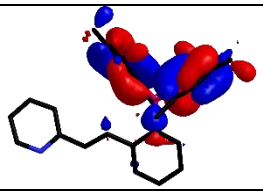
			
LUMO+1	LUMO	HOMO	HOMO-1

Table S54. Primary orbitals which contribute to the calculated transitions of ***Z*-5a** (iso = 0.03). Most H-atoms have been omitted for clarity.

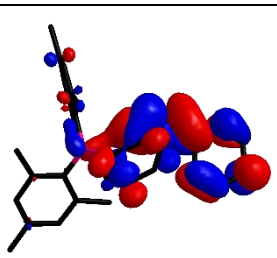
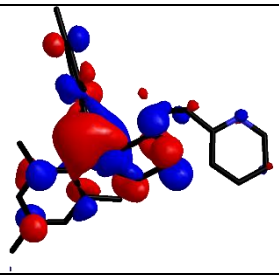
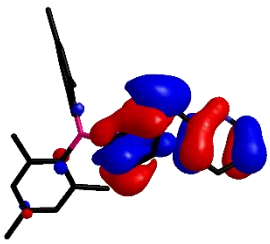
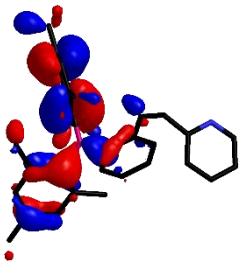
			
LUMO+1	LUMO	HOMO	HOMO-1

Table S55. Primary orbitals which contribute to the calculated transitions of ***E*-6a** (iso = 0.03). Most H-atoms have been omitted for clarity.

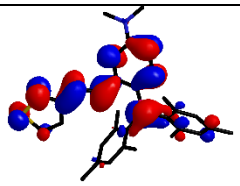
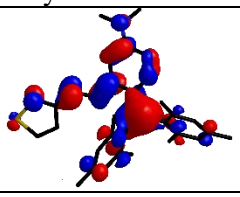
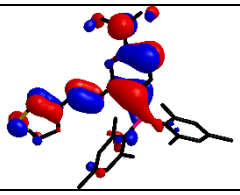
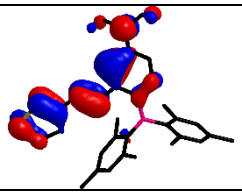
			
LUMO+1	LUMO	HOMO	HOMO-1

Table S56. Primary orbitals which contribute to the calculated transitions of ***Z*-6a** (iso = 0.03). Most H-atoms have been omitted for clarity.

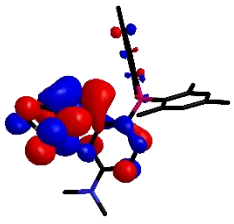
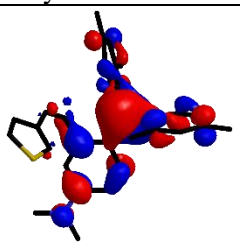
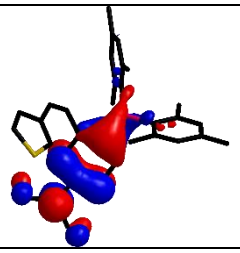
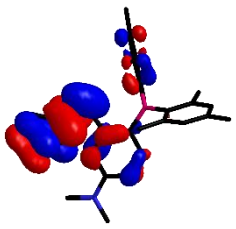
			
LUMO+1	LUMO	HOMO	HOMO-1

Table S57. Primary orbitals which contribute to the calculated transitions of **6b** (iso = 0.03). Most H-atoms have been omitted for clarity.

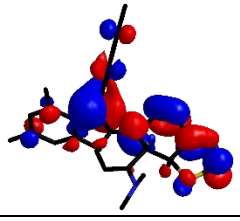
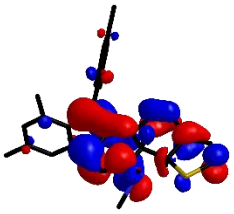
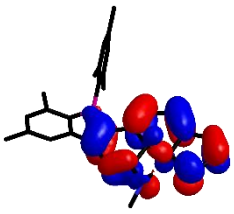
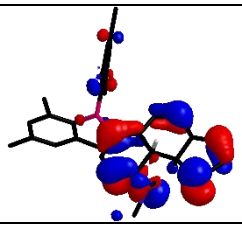
			
LUMO+1	LUMO	HOMO	HOMO-1

Table S58. Primary orbitals which contribute to the calculated transitions of **6d** (iso = 0.03). Most H-atoms have been omitted for clarity.

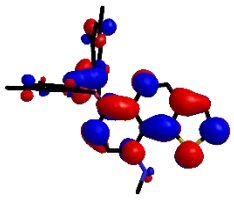
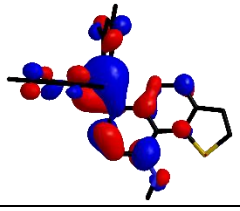
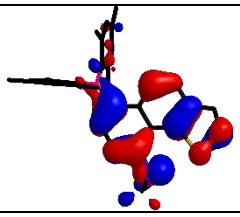
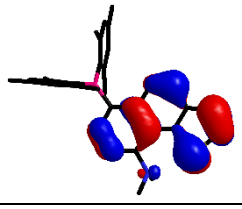
			
LUMO+1	LUMO	HOMO	HOMO-1

Table S59. Primary orbitals which contribute to the calculated transitions of ***E*-7a** (iso = 0.03). Most H-atoms have been omitted for clarity.

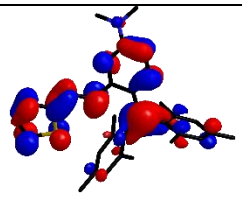
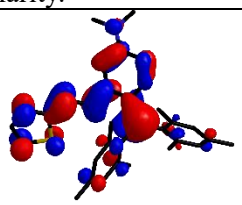
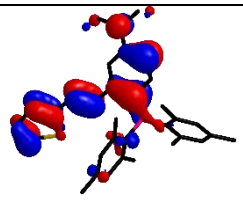
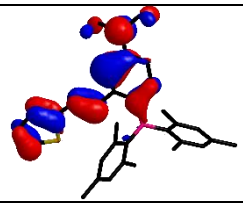
			
LUMO+1	LUMO	HOMO	HOMO-1

Table S60. Primary orbitals which contribute to the calculated transitions of ***Z*-7a** (iso = 0.03). Most H-atoms have been omitted for clarity.

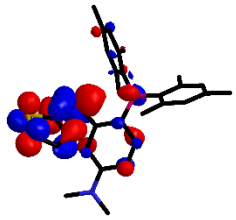
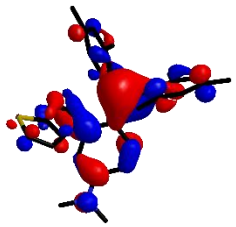
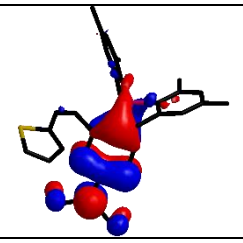
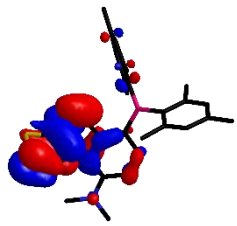
			
LUMO+1	LUMO	HOMO	HOMO-1

Table S61. Primary orbitals which contribute to the calculated transitions of ***E*-8a** (iso = 0.03). Most H-atoms have been omitted for clarity.

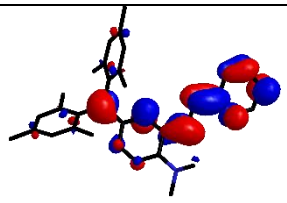
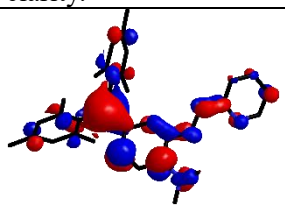
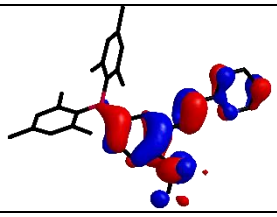
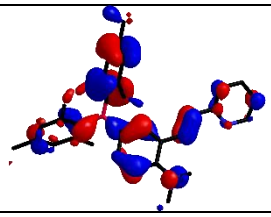
			
LUMO+1	LUMO	HOMO	HOMO-1

Table S62. Primary orbitals which contribute to the calculated transitions of ***Z*-8a** (iso = 0.03). Most H-atoms have been omitted for clarity.

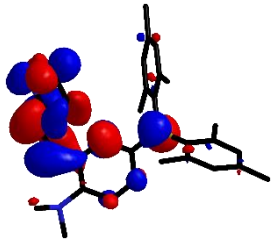
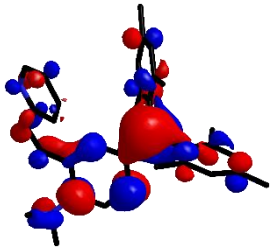
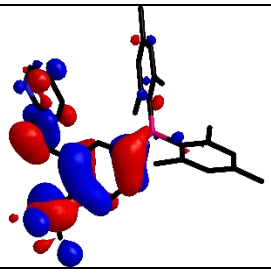
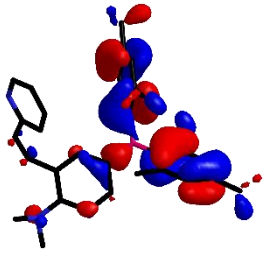
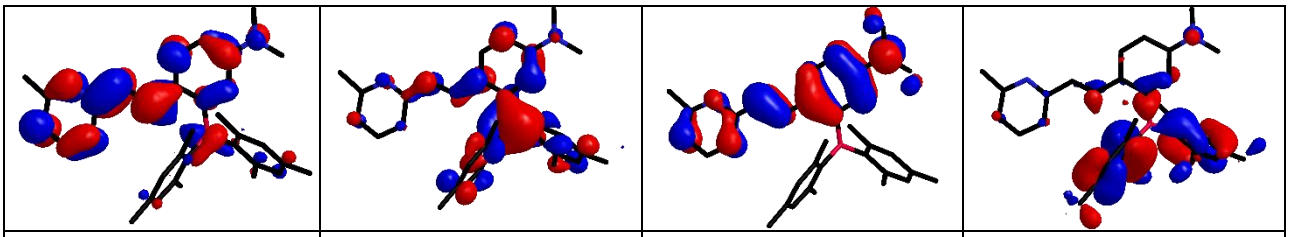
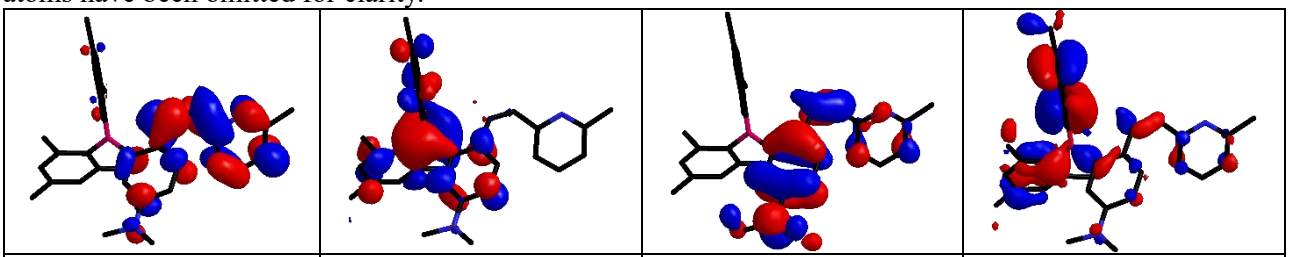
			
LUMO+1	LUMO	HOMO	HOMO-1

Table S63. Primary orbitals which contribute to the calculated transitions of ***E*-9a** (iso = 0.03). Most H-atoms have been omitted for clarity.



LUMO+1	LUMO	HOMO	HOMO-1

Table S64. Primary orbitals which contribute to the calculated transitions of ***Z*-9a** (iso = 0.03). Most H-atoms have been omitted for clarity.



LUMO+1	LUMO	HOMO	HOMO-1

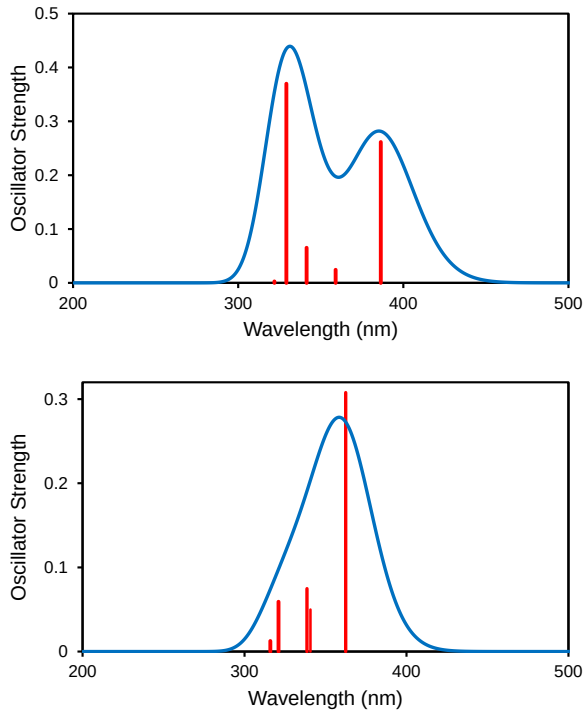


Figure S135. Predicted UV/Vis spectra of ***E*-1a** (left) and ***Z*-1a** (right) for their first five excited states.[3]

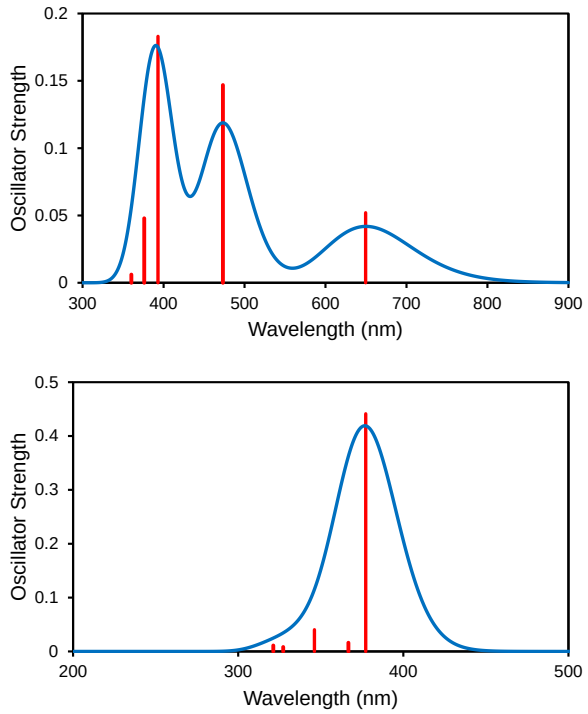


Figure S136. Predicted UV/Vis spectra of **1b** (left) and **1c** (right) for their first five excited states.[3]

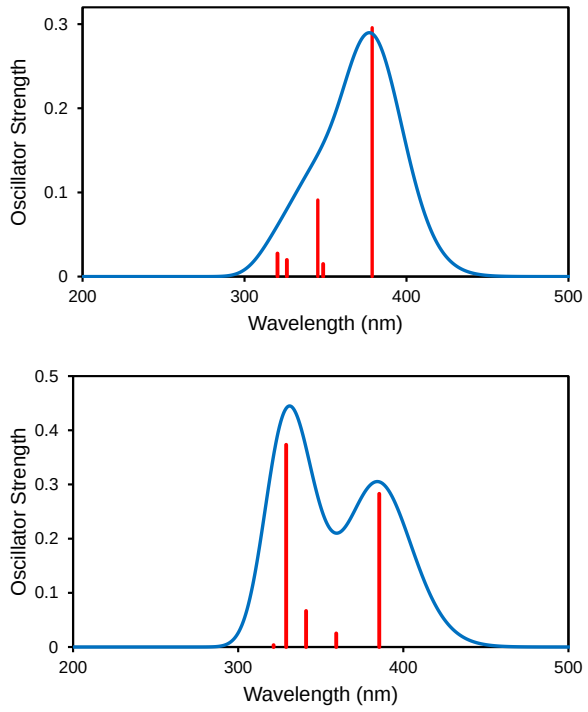


Figure S137. Predicted UV/Vis spectra of **1d** (left) and ***E*-2a** (right) for their first five excited states.[3]

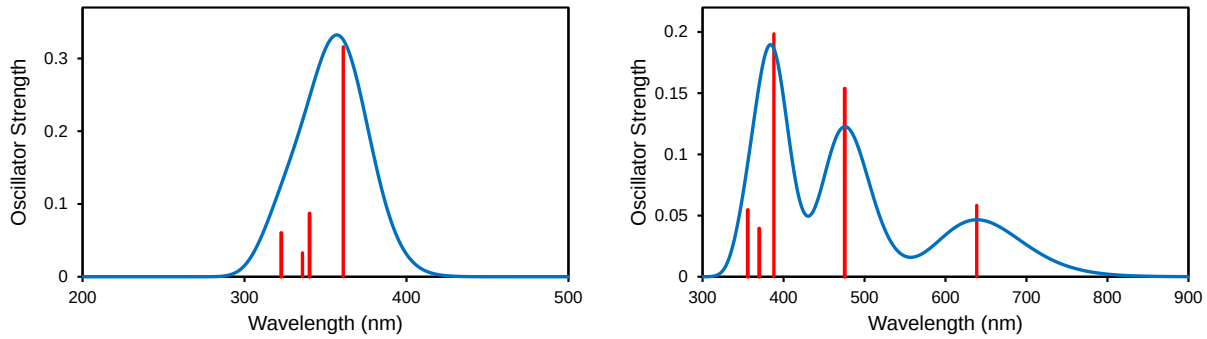


Figure S138. Predicted UV/Vis spectra of ***Z*-2a** (left) and **2b** (right) for their first five excited states.[3]

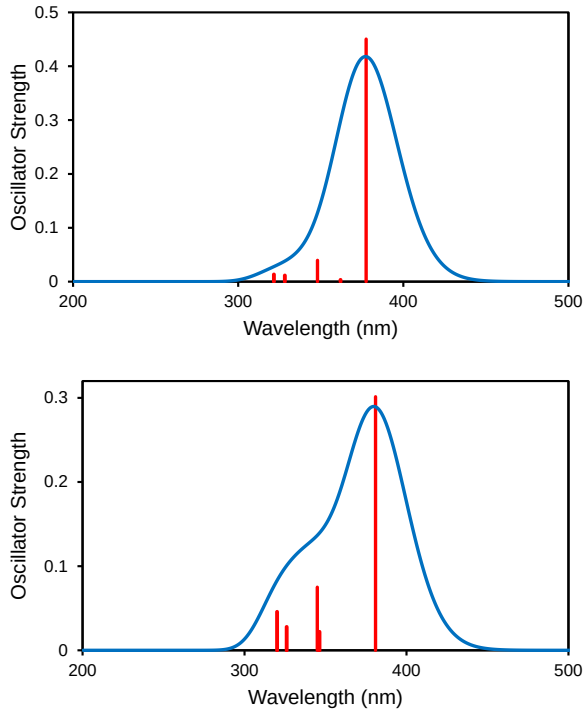
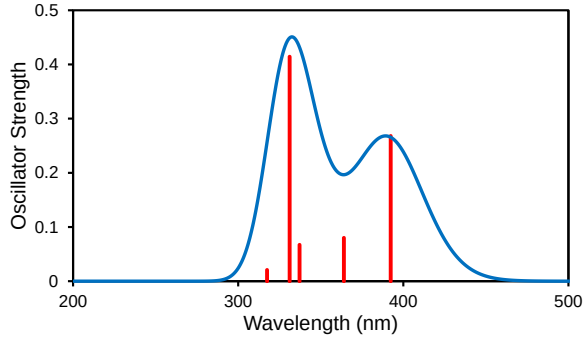


Figure S139. Predicted UV/Vis spectra of **2c** (left) and **2d** (right) for their first five excited states.[3]



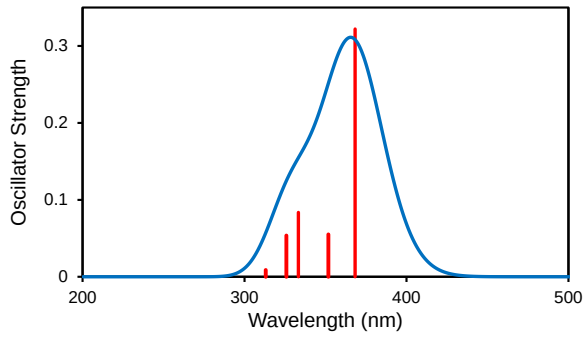


Figure S140. Predicted UV/Vis spectra of ***E*-3a** (left) and ***Z*-3a** (right) for their first five excited states.[3]

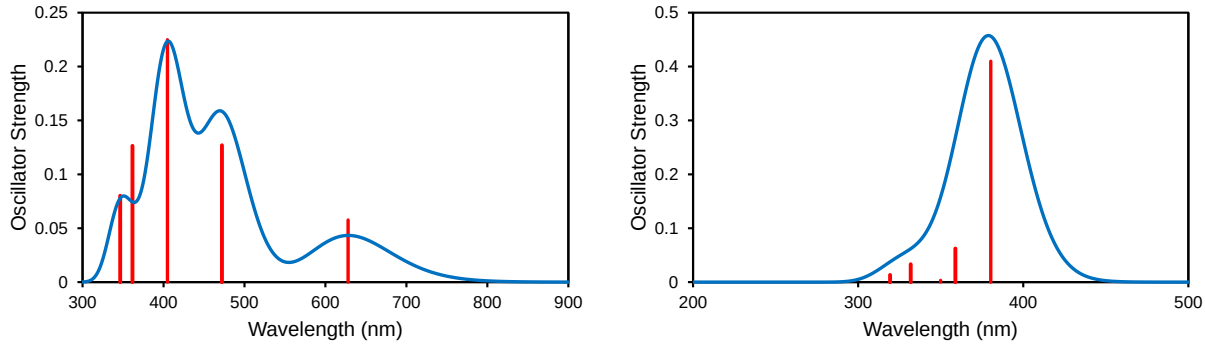


Figure S141. Predicted UV/Vis spectra of **3b** (left) and **3c** (right) for their first five excited states.[3]

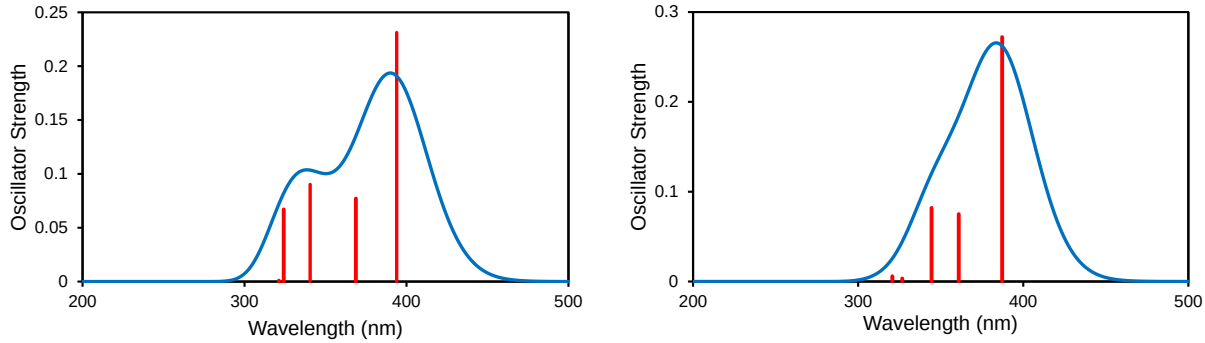


Figure S142. Predicted UV/Vis spectra of **3d** (left) and ***E*-4a** (right) for their first five excited states.[3]

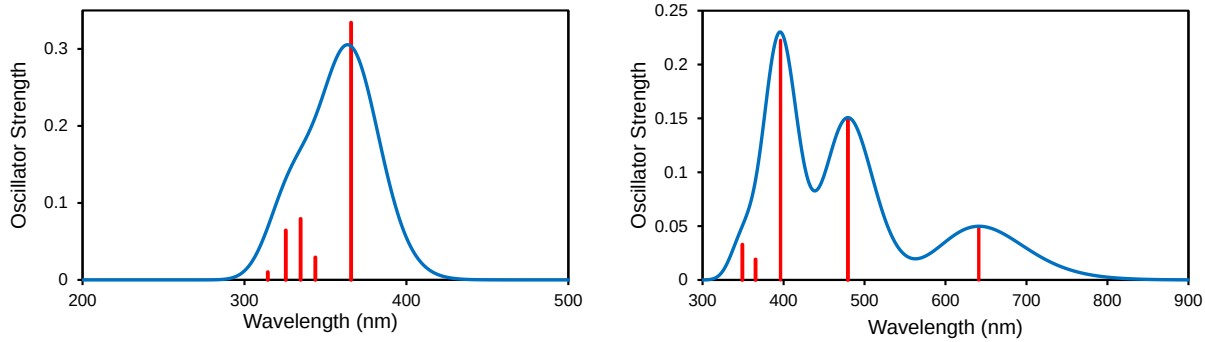


Figure S143. Predicted UV/Vis spectra of ***Z*-4a** (left) and **4b** (right) for their first five excited states.[3]

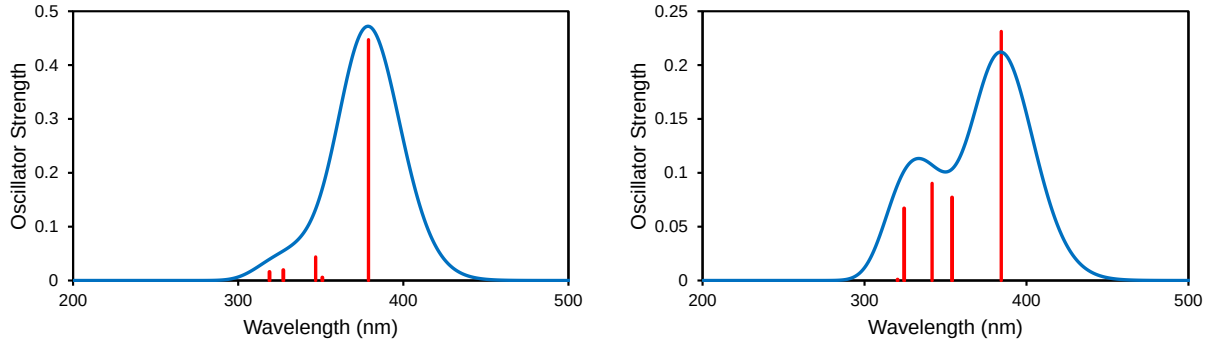


Figure S144. Predicted UV/Vis spectra of **4c** (left) and **4d** (right) for their first five excited states.[3]

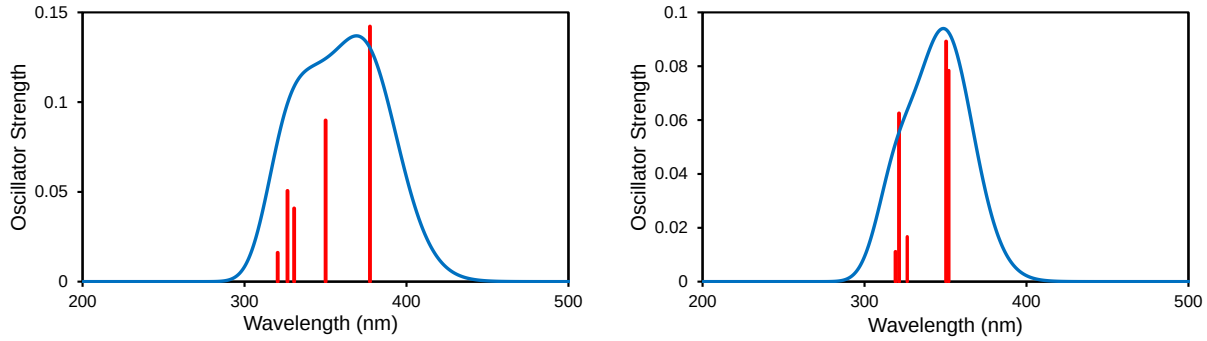


Figure S145. Predicted UV/Vis spectra of ***E*-5a** (left) and ***Z*-5a** (right) for their first five excited states.[3]

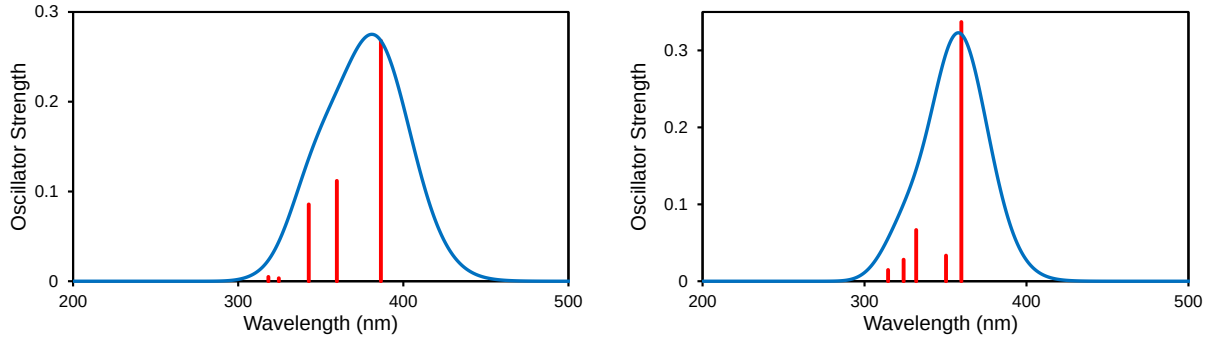


Figure S146. Predicted UV/Vis spectra of ***E*-6a** (left) and ***Z*-6a** (right) for their first five excited states.[3]

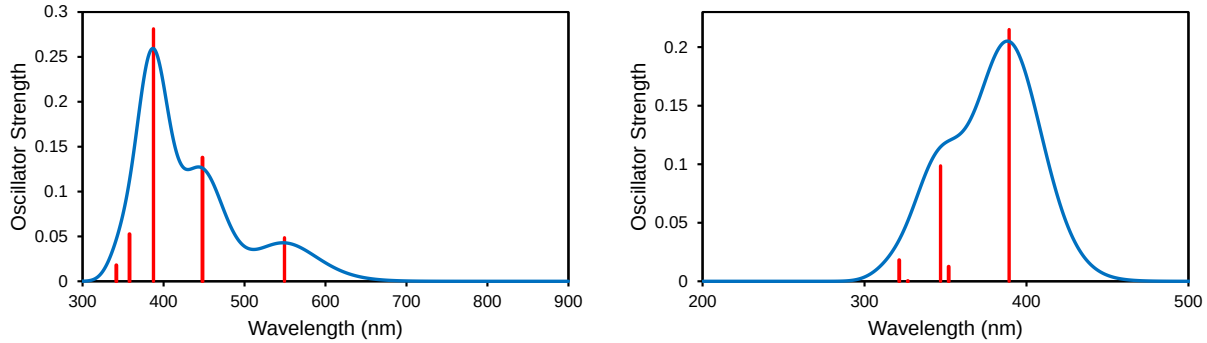


Figure S147. Predicted UV/Vis spectra of **6b** (left) and **6d** (right) for their first five excited states.[3]

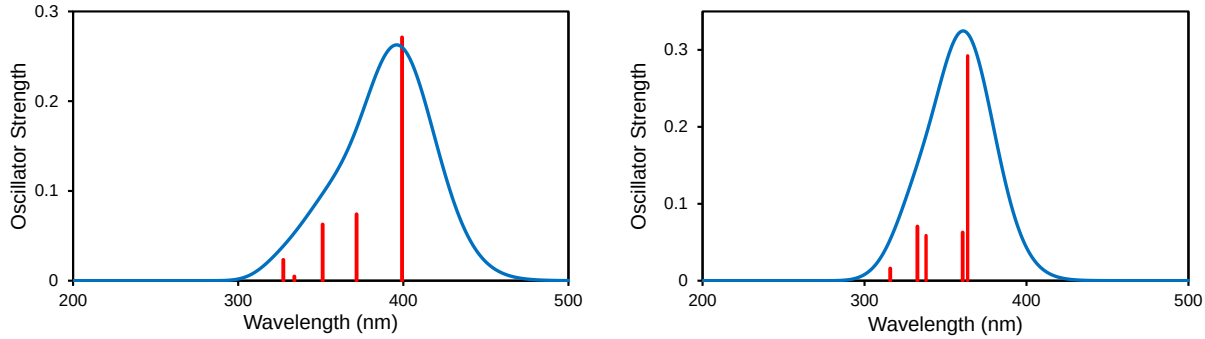


Figure S148. Predicted UV/Vis spectra of ***E*-7a** (left) and ***Z*-7a** (right) for their first five excited states.[3]

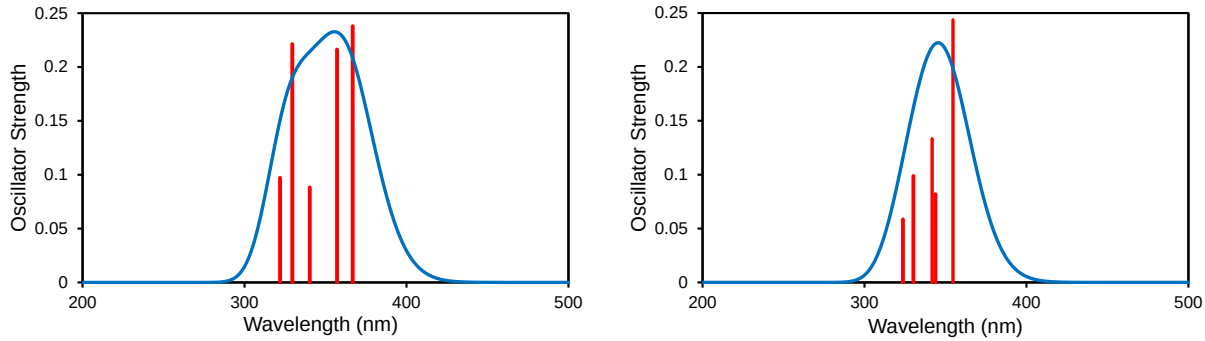


Figure S149. Predicted UV/Vis spectra of ***E*-8a** (left) and ***Z*-8a** (right) for their first five excited states.[3]

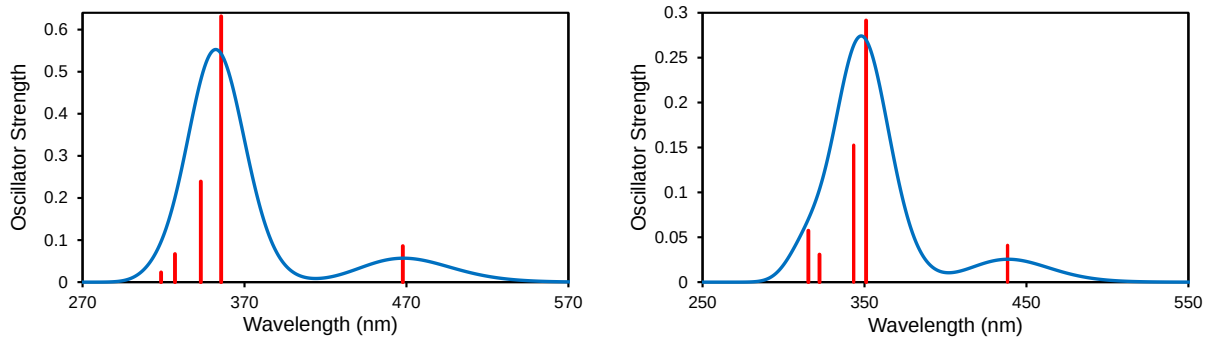


Figure S150. Predicted UV/Vis spectra of ***E*-9a** (left) and ***Z*-9a** (right) for their first five excited states.[3]

Table S65. Energies of optimized structures (kcal/mol).

	1	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**
E	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Z	5.18	5.13	4.78	4.99	4.17	3.11	2.81	3.37	3.99
b	42.22	40.74	40.70	42.24	N/A	23.88	N/A	N/A	N/A
c	9.79	9.69	9.39	9.42	N/A	N/A	N/A	N/A	N/A

Table S66. HOMO/LUMO Energies of optimized structures (eV).

	1	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**
E	-6.73/	-6.71/	-6.63/	-6.70/	-7.29/	-6.68/	-6.67/	-6.85/	-6.28/

	-1.17	-1.14	-1.05	-1.08	-1.40	-1.05	-1.12	-1.07	-1.17
Z	-6.77/ -0.91	-6.78/ -0.90	-6.64/ -0.87	-6.71/ -0.88	-7.39/ -1.11	-6.73/ -0.83	-6.73/ -0.83	-7.00/ -1.09	-6.45/ -1.06
b	-6.00/ -1.53	-5.94/ -1.40	-5.81/ -1.28	-5.82/ -1.36	N/A	-6.06/ -1.28	N/A	N/A	N/A
c	-6.51/ -0.91	-6.49/ -0.89	-6.37/ -0.78	-6.41/ -0.83	N/A	-6.46/ -0.85	N/A	N/A	N/A

S9: Crystal Structure Data

Table S67. Crystal data and structure refinement **1a**.

Identification code	**1a**	
Empirical formula	C39 H43 B N2	
Formula weight	550.56	
Temperature	180(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 8.1029(4) Å	α= 87.821(2)°.
	b = 11.3778(6) Å	β= 85.222(2)°.
	c = 18.5298(11) Å	γ = 71.032(2)°.
Volume	1609.84(15) $Å^3$	
Z	2	
Density (calculated)	1.136 Mg/m^3	
Absorption coefficient	0.065 mm^{-1}	
F(000)	592	
Crystal size	0.200 x 0.165 x 0.100 mm^3	
Theta range for data collection	2.202 to 27.876°.	
Index ranges	-10<=h<=9, -14<=k<=14, -24<=l<=24	
Reflections collected	37385	
Independent reflections	7672 [R(int) = 0.0984]	
Completeness to theta = 25.242°	99.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.994 and 0.987	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	7672 / 0 / 387	
Goodness-of-fit on F^2	1.074	
Final R indices [I>2sigma(I)]	R1 = 0.0625, wR2 = 0.1530	
R indices (all data)	R1 = 0.1148, wR2 = 0.1761	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.292 and -0.297 e.$Å^{-3}$	

Table S68. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) **1a**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
N(1)	2893(2)	6399(2)	5035(1)	36(1)
N(2)	742(2)	1010(2)	6123(1)	40(1)
C(1)	2829(2)	5262(2)	7237(1)	23(1)
C(2)	3218(2)	6334(2)	6994(1)	26(1)
C(3)	3271(2)	6712(2)	6282(1)	28(1)
C(4)	2863(2)	6033(2)	5746(1)	24(1)
C(5)	3318(3)	7503(2)	4812(1)	44(1)
C(6)	2469(3)	5693(2)	4484(1)	39(1)
C(7)	2385(2)	4991(2)	5975(1)	25(1)
C(8)	2372(2)	4597(2)	6694(1)	23(1)
C(9)	1802(2)	3517(2)	6896(1)	25(1)
C(10)	1746(2)	2636(2)	6459(1)	28(1)
C(11)	1175(2)	1570(2)	6672(1)	28(1)
C(12)	1097(2)	1144(2)	7382(1)	35(1)
C(13)	547(3)	124(2)	7536(1)	45(1)

C(14)	76(3)	-434(2)	6974(2)	47(1)
C(15)	205(3)	35(2)	6290(1)	48(1)
C(16)	3664(2)	3442(2)	8288(1)	22(1)
C(17)	2731(2)	3032(2)	8867(1)	25(1)
C(18)	1197(3)	3918(2)	9293(1)	42(1)
C(19)	3166(2)	1773(2)	9040(1)	29(1)
C(20)	4538(2)	876(2)	8672(1)	30(1)
C(21)	4965(3)	-481(2)	8869(1)	48(1)
C(22)	5484(2)	1285(2)	8121(1)	29(1)
C(23)	5085(2)	2532(2)	7922(1)	26(1)
C(24)	6249(3)	2856(2)	7325(1)	41(1)
C(25)	2885(2)	5906(2)	8613(1)	23(1)
C(26)	1249(2)	6828(2)	8760(1)	25(1)
C(27)	-337(2)	6897(2)	8364(1)	36(1)
C(28)	1020(3)	7673(2)	9311(1)	30(1)
C(29)	2369(3)	7655(2)	9728(1)	33(1)
C(30)	2056(3)	8532(2)	10354(1)	52(1)
C(31)	4281(2)	5925(2)	9015(1)	26(1)
C(32)	3997(3)	6787(2)	9561(1)	32(1)
C(33)	6109(2)	5040(2)	8844(1)	37(1)
C(34)	1885(3)	2304(3)	4239(2)	55(1)
C(35)	3020(3)	1161(3)	4402(1)	54(1)
C(36)	4325(3)	548(2)	3897(2)	53(1)
C(37)	4508(3)	1081(2)	3232(1)	49(1)
C(38)	3368(3)	2234(2)	3069(1)	48(1)
C(39)	2060(3)	2844(2)	3575(2)	55(1)
B(1)	3112(2)	4859(2)	8040(1)	22(1)

Table S69. Bond lengths [Å] and angles [°] for **1a**.

N(1)-C(4)	1.368(2)	C(10)-H(10)	0.9500
N(1)-C(5)	1.444(3)	C(11)-C(12)	1.389(3)
N(1)-C(6)	1.451(3)	C(12)-C(13)	1.384(3)
N(2)-C(15)	1.334(3)	C(12)-H(12)	0.9500
N(2)-C(11)	1.349(2)	C(13)-C(14)	1.380(3)
C(1)-C(2)	1.405(2)	C(13)-H(13)	0.9500
C(1)-C(8)	1.424(2)	C(14)-C(15)	1.367(3)
C(1)-B(1)	1.553(3)	C(14)-H(14)	0.9500
C(2)-C(3)	1.374(2)	C(15)-H(15)	0.9500
C(2)-H(2)	0.9500	C(16)-C(17)	1.413(2)
C(3)-C(4)	1.404(3)	C(16)-C(23)	1.416(2)
C(3)-H(3)	0.9500	C(16)-B(1)	1.587(3)
C(4)-C(7)	1.403(2)	C(17)-C(19)	1.390(2)
C(5)-H(5A)	0.9800	C(17)-C(18)	1.506(3)
C(5)-H(5B)	0.9800	C(18)-H(18A)	0.9800
C(5)-H(5C)	0.9800	C(18)-H(18B)	0.9800
C(6)-H(6A)	0.9800	C(18)-H(18C)	0.9800
C(6)-H(6B)	0.9800	C(19)-C(20)	1.389(3)
C(6)-H(6C)	0.9800	C(19)-H(19)	0.9500
C(7)-C(8)	1.389(2)	C(20)-C(22)	1.382(3)
C(7)-H(7)	0.9500	C(20)-C(21)	1.506(3)
C(8)-C(9)	1.473(2)	C(21)-H(21A)	0.9800
C(9)-C(10)	1.326(3)	C(21)-H(21B)	0.9800
C(9)-H(9)	0.9500	C(21)-H(21C)	0.9800
C(10)-C(11)	1.463(2)	C(22)-C(23)	1.392(3)

C(22)-H(22)	0.9500	H(5A)-C(5)-H(5B)	109.5
C(23)-C(24)	1.507(3)	N(1)-C(5)-H(5C)	109.5
C(24)-H(24A)	0.9800	H(5A)-C(5)-H(5C)	109.5
C(24)-H(24B)	0.9800	H(5B)-C(5)-H(5C)	109.5
C(24)-H(24C)	0.9800	N(1)-C(6)-H(6A)	109.5
C(25)-C(26)	1.410(2)	N(1)-C(6)-H(6B)	109.5
C(25)-C(31)	1.412(2)	H(6A)-C(6)-H(6B)	109.5
C(25)-B(1)	1.582(3)	N(1)-C(6)-H(6C)	109.5
C(26)-C(28)	1.388(3)	H(6A)-C(6)-H(6C)	109.5
C(26)-C(27)	1.512(3)	H(6B)-C(6)-H(6C)	109.5
C(27)-H(27A)	0.9800	C(8)-C(7)-C(4)	122.63(17)
C(27)-H(27B)	0.9800	C(8)-C(7)-H(7)	118.7
C(27)-H(27C)	0.9800	C(4)-C(7)-H(7)	118.7
C(28)-C(29)	1.385(3)	C(7)-C(8)-C(1)	120.45(16)
C(28)-H(28)	0.9500	C(7)-C(8)-C(9)	119.48(16)
C(29)-C(32)	1.386(3)	C(1)-C(8)-C(9)	120.02(16)
C(29)-C(30)	1.509(3)	C(10)-C(9)-C(8)	126.80(17)
C(30)-H(30A)	0.9800	C(10)-C(9)-H(9)	116.6
C(30)-H(30B)	0.9800	C(8)-C(9)-H(9)	116.6
C(30)-H(30C)	0.9800	C(9)-C(10)-C(11)	125.86(18)
C(31)-C(32)	1.388(3)	C(9)-C(10)-H(10)	117.1
C(31)-C(33)	1.511(3)	C(11)-C(10)-H(10)	117.1
C(32)-H(32)	0.9500	N(2)-C(11)-C(12)	121.72(17)
C(33)-H(33A)	0.9800	N(2)-C(11)-C(10)	115.01(17)
C(33)-H(33B)	0.9800	C(12)-C(11)-C(10)	123.26(18)
C(33)-H(33C)	0.9800	C(13)-C(12)-C(11)	119.5(2)
C(34)-C(35)	1.367(4)	C(13)-C(12)-H(12)	120.3
C(34)-C(39)	1.371(4)	C(11)-C(12)-H(12)	120.3
C(34)-H(34)	0.9500	C(14)-C(13)-C(12)	118.6(2)
C(35)-C(36)	1.373(3)	C(14)-C(13)-H(13)	120.7
C(35)-H(35)	0.9500	C(12)-C(13)-H(13)	120.7
C(36)-C(37)	1.370(4)	C(15)-C(14)-C(13)	118.30(19)
C(36)-H(36)	0.9500	C(15)-C(14)-H(14)	120.9
C(37)-C(38)	1.377(3)	C(13)-C(14)-H(14)	120.9
C(37)-H(37)	0.9500	N(2)-C(15)-C(14)	124.5(2)
C(38)-C(39)	1.374(3)	N(2)-C(15)-H(15)	117.7
C(38)-H(38)	0.9500	C(14)-C(15)-H(15)	117.7
C(39)-H(39)	0.9500	C(17)-C(16)-C(23)	117.35(15)
C(4)-N(1)-C(5)	121.23(16)	C(17)-C(16)-B(1)	121.55(15)
C(4)-N(1)-C(6)	120.60(16)	C(23)-C(16)-B(1)	121.07(15)
C(5)-N(1)-C(6)	118.16(16)	C(19)-C(17)-C(16)	120.28(16)
C(15)-N(2)-C(11)	117.35(19)	C(19)-C(17)-C(18)	117.80(16)
C(2)-C(1)-C(8)	115.38(16)	C(16)-C(17)-C(18)	121.86(16)
C(2)-C(1)-B(1)	117.43(16)	C(17)-C(18)-H(18A)	109.5
C(8)-C(1)-B(1)	126.89(15)	C(17)-C(18)-H(18B)	109.5
C(3)-C(2)-C(1)	124.35(17)	H(18A)-C(18)-H(18B)	109.5
C(3)-C(2)-H(2)	117.8	C(17)-C(18)-H(18C)	109.5
C(1)-C(2)-H(2)	117.8	H(18A)-C(18)-H(18C)	109.5
C(2)-C(3)-C(4)	119.90(16)	H(18B)-C(18)-H(18C)	109.5
C(2)-C(3)-H(3)	120.0	C(20)-C(19)-C(17)	122.43(17)
C(4)-C(3)-H(3)	120.0	C(20)-C(19)-H(19)	118.8
N(1)-C(4)-C(7)	121.90(16)	C(17)-C(19)-H(19)	118.8
N(1)-C(4)-C(3)	120.90(16)	C(22)-C(20)-C(19)	117.15(16)
C(7)-C(4)-C(3)	117.19(16)	C(22)-C(20)-C(21)	121.77(18)
N(1)-C(5)-H(5A)	109.5	C(19)-C(20)-C(21)	121.08(18)
N(1)-C(5)-H(5B)	109.5	C(20)-C(21)-H(21A)	109.5

C(20)-C(21)-H(21B)	109.5	H(30A)-C(30)-H(30B)	109.5
H(21A)-C(21)-H(21B)	109.5	C(29)-C(30)-H(30C)	109.5
C(20)-C(21)-H(21C)	109.5	H(30A)-C(30)-H(30C)	109.5
H(21A)-C(21)-H(21C)	109.5	H(30B)-C(30)-H(30C)	109.5
H(21B)-C(21)-H(21C)	109.5	C(32)-C(31)-C(25)	120.10(17)
C(20)-C(22)-C(23)	122.57(17)	C(32)-C(31)-C(33)	119.11(17)
C(20)-C(22)-H(22)	118.7	C(25)-C(31)-C(33)	120.76(17)
C(23)-C(22)-H(22)	118.7	C(29)-C(32)-C(31)	122.17(18)
C(22)-C(23)-C(16)	120.17(16)	C(29)-C(32)-H(32)	118.9
C(22)-C(23)-C(24)	117.22(16)	C(31)-C(32)-H(32)	118.9
C(16)-C(23)-C(24)	122.59(16)	C(31)-C(33)-H(33A)	109.5
C(23)-C(24)-H(24A)	109.5	C(31)-C(33)-H(33B)	109.5
C(23)-C(24)-H(24B)	109.5	H(33A)-C(33)-H(33B)	109.5
H(24A)-C(24)-H(24B)	109.5	C(31)-C(33)-H(33C)	109.5
C(23)-C(24)-H(24C)	109.5	H(33A)-C(33)-H(33C)	109.5
H(24A)-C(24)-H(24C)	109.5	H(33B)-C(33)-H(33C)	109.5
H(24B)-C(24)-H(24C)	109.5	C(35)-C(34)-C(39)	120.1(2)
C(26)-C(25)-C(31)	117.65(17)	C(35)-C(34)-H(34)	119.9
C(26)-C(25)-B(1)	120.75(15)	C(39)-C(34)-H(34)	119.9
C(31)-C(25)-B(1)	121.54(15)	C(34)-C(35)-C(36)	119.8(3)
C(28)-C(26)-C(25)	120.31(17)	C(34)-C(35)-H(35)	120.1
C(28)-C(26)-C(27)	117.39(16)	C(36)-C(35)-H(35)	120.1
C(25)-C(26)-C(27)	122.20(16)	C(37)-C(36)-C(35)	120.4(2)
C(26)-C(27)-H(27A)	109.5	C(37)-C(36)-H(36)	119.8
C(26)-C(27)-H(27B)	109.5	C(35)-C(36)-H(36)	119.8
H(27A)-C(27)-H(27B)	109.5	C(36)-C(37)-C(38)	119.7(2)
C(26)-C(27)-H(27C)	109.5	C(36)-C(37)-H(37)	120.1
H(27A)-C(27)-H(27C)	109.5	C(38)-C(37)-H(37)	120.1
H(27B)-C(27)-H(27C)	109.5	C(39)-C(38)-C(37)	119.7(2)
C(29)-C(28)-C(26)	122.00(18)	C(39)-C(38)-H(38)	120.1
C(29)-C(28)-H(28)	119.0	C(37)-C(38)-H(38)	120.1
C(26)-C(28)-H(28)	119.0	C(34)-C(39)-C(38)	120.2(2)
C(28)-C(29)-C(32)	117.62(18)	C(34)-C(39)-H(39)	119.9
C(28)-C(29)-C(30)	120.90(19)	C(38)-C(39)-H(39)	119.9
C(32)-C(29)-C(30)	121.46(19)	C(1)-B(1)-C(25)	118.01(15)
C(29)-C(30)-H(30A)	109.5	C(1)-B(1)-C(16)	121.97(16)
C(29)-C(30)-H(30B)	109.5	C(25)-B(1)-C(16)	120.00(15)

Table S70. Anisotropic displacement parameters ($Å^2 x\ 10^3$) 1a. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
N(1)	56(1)	38(1)	20(1)	6(1)	-6(1)	-25(1)
N(2)	47(1)	33(1)	45(1)	-10(1)	-1(1)	-21(1)
C(1)	24(1)	22(1)	22(1)	-1(1)	-2(1)	-6(1)
C(2)	32(1)	24(1)	23(1)	0(1)	-2(1)	-11(1)
C(3)	36(1)	24(1)	27(1)	4(1)	-3(1)	-14(1)
C(4)	26(1)	25(1)	20(1)	2(1)	-2(1)	-7(1)
C(5)	69(2)	41(1)	28(1)	11(1)	-3(1)	-25(1)
C(6)	51(1)	50(1)	21(1)	2(1)	-4(1)	-22(1)
C(7)	28(1)	25(1)	22(1)	0(1)	-4(1)	-10(1)
C(8)	21(1)	21(1)	26(1)	1(1)	-3(1)	-5(1)

C(9)	27(1)	28(1)	24(1)	4(1)	-5(1)	-11(1)
C(10)	31(1)	27(1)	28(1)	1(1)	-3(1)	-12(1)
C(11)	23(1)	23(1)	39(1)	-2(1)	-2(1)	-7(1)
C(12)	34(1)	32(1)	42(1)	6(1)	-6(1)	-13(1)
C(13)	38(1)	36(1)	58(2)	14(1)	2(1)	-13(1)
C(14)	41(1)	28(1)	77(2)	-4(1)	9(1)	-19(1)
C(15)	48(1)	36(1)	67(2)	-13(1)	2(1)	-23(1)
C(16)	25(1)	26(1)	17(1)	1(1)	-2(1)	-9(1)
C(17)	29(1)	26(1)	20(1)	2(1)	0(1)	-8(1)
C(18)	44(1)	33(1)	42(1)	2(1)	19(1)	-8(1)
C(19)	33(1)	29(1)	24(1)	4(1)	2(1)	-11(1)
C(20)	36(1)	24(1)	27(1)	3(1)	-6(1)	-8(1)
C(21)	59(1)	25(1)	52(2)	7(1)	2(1)	-6(1)
C(22)	28(1)	26(1)	26(1)	-2(1)	0(1)	0(1)
C(23)	27(1)	29(1)	20(1)	1(1)	0(1)	-7(1)
C(24)	36(1)	41(1)	37(1)	3(1)	12(1)	-6(1)
C(25)	30(1)	23(1)	18(1)	4(1)	-2(1)	-11(1)
C(26)	31(1)	23(1)	21(1)	1(1)	-2(1)	-11(1)
C(27)	30(1)	37(1)	37(1)	-6(1)	-7(1)	-6(1)
C(28)	37(1)	25(1)	27(1)	-1(1)	0(1)	-11(1)
C(29)	49(1)	31(1)	25(1)	-3(1)	-3(1)	-20(1)
C(30)	72(2)	52(1)	38(1)	-16(1)	-7(1)	-25(1)
C(31)	30(1)	28(1)	23(1)	5(1)	-4(1)	-14(1)
C(32)	41(1)	37(1)	27(1)	1(1)	-10(1)	-22(1)
C(33)	28(1)	41(1)	44(1)	0(1)	-9(1)	-12(1)
C(34)	34(1)	74(2)	54(2)	-31(1)	-3(1)	-10(1)
C(35)	46(1)	74(2)	47(2)	-6(1)	-9(1)	-24(1)
C(36)	43(1)	42(1)	71(2)	-7(1)	-15(1)	-6(1)
C(37)	30(1)	59(2)	57(2)	-21(1)	0(1)	-10(1)
C(38)	42(1)	60(2)	48(2)	-3(1)	-15(1)	-23(1)
C(39)	39(1)	47(1)	72(2)	-20(1)	-21(1)	0(1)
B(1)	19(1)	26(1)	23(1)	2(1)	0(1)	-8(1)

Table S71. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^{2}x 10^3) of **1a**.

	x	y	z	U(eq)
H(2)	3461	6829	7346	31
H(3)	3583	7433	6153	34
H(5A)	4503	7413	4938	66
H(5B)	2481	8226	5059	66
H(5C)	3257	7620	4287	66
H(6A)	2558	6087	4009	59
H(6B)	1273	5674	4591	59
H(6C)	3290	4842	4479	59
H(7)	2057	4537	5625	30
H(9)	1436	3443	7391	30
H(10)	2110	2704	5962	33
H(12)	1419	1549	7760	42
H(13)	495	-185	8018	54
H(14)	-328	-1126	7062	57
H(15)	-110	-360	5906	58
H(18A)	314	4372	8963	64

H(18B)	1592	4509	9545	64
H(18C)	686	3451	9649	64
H(19)	2501	1517	9423	34
H(21A)	3975	-757	8780	72
H(21B)	5193	-603	9382	72
H(21C)	6006	-965	8573	72
H(22)	6443	690	7869	34
H(24A)	5586	3148	6898	61
H(24B)	7253	2118	7200	61
H(24C)	6664	3513	7488	61
H(27A)	-17	6236	8003	53
H(27B)	-761	7707	8120	53
H(27C)	-1261	6791	8710	53
H(28)	-95	8282	9405	35
H(30A)	1766	9388	10170	78
H(30B)	3116	8325	10618	78
H(30C)	1084	8451	10682	78
H(32)	4951	6781	9828	39
H(33A)	6083	4185	8858	56
H(33B)	6879	5132	9203	56
H(33C)	6549	5231	8360	56
H(34)	974	2726	4585	67
H(35)	2907	791	4864	65
H(36)	5105	-251	4009	64
H(37)	5419	657	2886	59
H(38)	3484	2607	2608	57
H(39)	1275	3642	3464	66

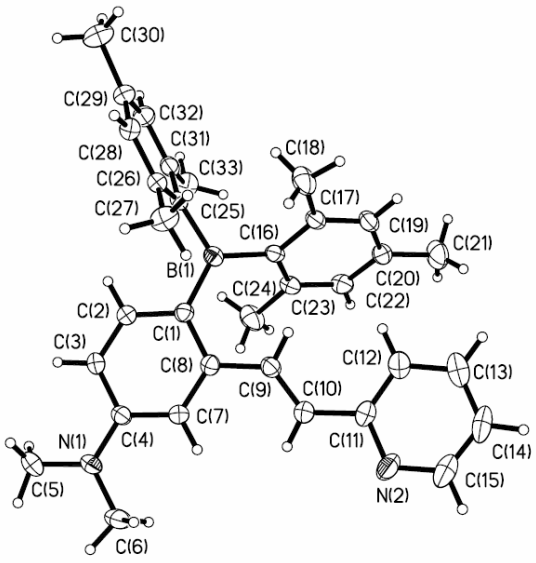


Figure S151. Structure of **1a**.

Table S72. Crystal data and structure refinement for **3a**.

Identification code	**3a**
Empirical formula	C35 H40 B N O
Formula weight	501.49
Temperature	180(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic

Space group	$P2_1/c$	
Unit cell dimensions	a = 7.2959(3) Å	α= 90°.
	b = 22.3592(8) Å	β= 92.626(2)°.
	c = 17.9840(7) Å	γ = 90°.
Volume	2930.7(2) $Å^3$	
Z	4	
Density (calculated)	1.137 Mg/m^3	
Absorption coefficient	0.066 mm^{-1}	
F(000)	1080	
Crystal size	0.358 x 0.239 x 0.164 mm^3	
Theta range for data collection	2.267 to 27.238°.	
Index ranges	-9<=h<=8, -28<=k<=28, -23<=l<=23	
Reflections collected	35189	
Independent reflections	6531 [R(int) = 0.0937]	
Completeness to theta = 25.242°	99.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.989 and 0.977	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	6531 / 0 / 352	
Goodness-of-fit on F^2	1.051	
Final R indices [I>2sigma(I)]	R1 = 0.0628, wR2 = 0.1449	
R indices (all data)	R1 = 0.1000, wR2 = 0.1614	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.257 and -0.287 e.$Å^{-3}$	

Table S73. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for **3a**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
B(1)	6237(3)	2785(1)	4306(1)	24(1)
O(1)	8384(2)	5850(1)	3860(1)	35(1)
N(1)	6377(2)	4390(1)	6815(1)	32(1)
C(1)	6478(3)	3233(1)	4954(1)	23(1)
C(2)	6035(3)	3037(1)	5668(1)	25(1)
C(3)	5980(3)	3404(1)	6280(1)	25(1)
C(4)	6414(3)	4015(1)	6219(1)	23(1)
C(5)	6933(3)	4219(1)	5520(1)	24(1)
C(6)	6951(2)	3851(1)	4900(1)	22(1)
C(7)	7555(3)	4102(1)	4193(1)	24(1)
C(8)	7503(3)	4677(1)	3999(1)	26(1)
C(9)	8060(3)	4916(1)	3284(1)	26(1)
C(10)	8124(3)	4565(1)	2647(1)	34(1)
C(11)	8675(3)	4800(1)	1979(1)	42(1)
C(12)	9170(3)	5396(1)	1941(1)	41(1)
C(13)	9090(3)	5759(1)	2558(1)	33(1)
C(14)	8522(3)	5526(1)	3226(1)	27(1)
C(15)	8806(3)	6472(1)	3843(2)	43(1)
C(16)	5981(3)	4172(1)	7551(1)	36(1)
C(17)	6843(3)	5019(1)	6755(1)	35(1)
C(18)	6466(3)	2086(1)	4456(1)	24(1)
C(19)	8084(3)	1855(1)	4814(1)	28(1)
C(20)	9607(3)	2254(1)	5125(1)	37(1)

C(21)	8344(3)	1239(1)	4882(1)	32(1)
C(22)	7025(3)	832(1)	4628(1)	31(1)
C(23)	7362(4)	166(1)	4685(1)	45(1)
C(24)	5416(3)	1057(1)	4305(1)	29(1)
C(25)	5119(3)	1670(1)	4204(1)	26(1)
C(26)	3337(3)	1860(1)	3820(1)	38(1)
C(27)	5665(3)	3000(1)	3487(1)	24(1)
C(28)	6746(3)	2866(1)	2877(1)	28(1)
C(29)	8546(3)	2537(1)	2980(1)	38(1)
C(30)	6215(3)	3067(1)	2165(1)	33(1)
C(31)	4602(3)	3378(1)	2025(1)	36(1)
C(32)	4059(4)	3597(1)	1250(1)	60(1)
C(33)	3523(3)	3499(1)	2622(1)	34(1)
C(34)	4040(3)	3330(1)	3348(1)	28(1)
C(35)	2803(3)	3506(1)	3964(1)	36(1)

Table S74. Bond lengths [Å] and angles [°] for **3a**.

B(1)-C(1)	1.541(3)	C(17)-H(17A)	0.9800
B(1)-C(27)	1.587(3)	C(17)-H(17B)	0.9800
B(1)-C(18)	1.594(3)	C(17)-H(17C)	0.9800
O(1)-C(14)	1.357(2)	C(18)-C(25)	1.413(3)
O(1)-C(15)	1.427(2)	C(18)-C(19)	1.416(3)
N(1)-C(4)	1.362(2)	C(19)-C(21)	1.396(3)
N(1)-C(16)	1.451(3)	C(19)-C(20)	1.512(3)
N(1)-C(17)	1.451(2)	C(20)-H(20A)	0.9800
C(1)-C(2)	1.408(3)	C(20)-H(20B)	0.9800
C(1)-C(6)	1.428(2)	C(20)-H(20C)	0.9800
C(2)-C(3)	1.374(3)	C(21)-C(22)	1.386(3)
C(2)-H(2)	0.9500	C(21)-H(21)	0.9500
C(3)-C(4)	1.409(2)	C(22)-C(24)	1.380(3)
C(3)-H(3)	0.9500	C(22)-C(23)	1.512(3)
C(4)-C(5)	1.405(3)	C(23)-H(23A)	0.9800
C(5)-C(6)	1.387(2)	C(23)-H(23B)	0.9800
C(5)-H(5)	0.9500	C(23)-H(23C)	0.9800
C(6)-C(7)	1.475(3)	C(24)-C(25)	1.399(3)
C(7)-C(8)	1.334(3)	C(24)-H(24)	0.9500
C(7)-H(7)	0.9500	C(25)-C(26)	1.506(3)
C(8)-C(9)	1.466(3)	C(26)-H(26A)	0.9800
C(8)-H(8)	0.9500	C(26)-H(26B)	0.9800
C(9)-C(10)	1.391(3)	C(26)-H(26C)	0.9800
C(9)-C(14)	1.411(3)	C(27)-C(34)	1.410(3)
C(10)-C(11)	1.388(3)	C(27)-C(28)	1.412(3)
C(10)-H(10)	0.9500	C(28)-C(30)	1.395(3)
C(11)-C(12)	1.383(3)	C(28)-C(29)	1.510(3)
C(11)-H(11)	0.9500	C(29)-H(29A)	0.9800
C(12)-C(13)	1.378(3)	C(29)-H(29B)	0.9800
C(12)-H(12)	0.9500	C(29)-H(29C)	0.9800
C(13)-C(14)	1.389(3)	C(30)-C(31)	1.380(3)
C(13)-H(13)	0.9500	C(30)-H(30)	0.9500
C(15)-H(15A)	0.9800	C(31)-C(33)	1.385(3)
C(15)-H(15B)	0.9800	C(31)-C(32)	1.513(3)
C(15)-H(15C)	0.9800	C(32)-H(32A)	0.9800
C(16)-H(16A)	0.9800	C(32)-H(32B)	0.9800
C(16)-H(16B)	0.9800	C(32)-H(32C)	0.9800
C(16)-H(16C)	0.9800	C(33)-C(34)	1.394(3)

C(33)-H(33)	0.9500	H(15A)-C(15)-H(15B)	109.5
C(34)-C(35)	1.513(3)	O(1)-C(15)-H(15C)	109.5
C(35)-H(35A)	0.9800	H(15A)-C(15)-H(15C)	109.5
C(35)-H(35B)	0.9800	H(15B)-C(15)-H(15C)	109.5
C(35)-H(35C)	0.9800	N(1)-C(16)-H(16A)	109.5
C(1)-B(1)-C(27)	121.42(16)	N(1)-C(16)-H(16B)	109.5
C(1)-B(1)-C(18)	120.10(17)	H(16A)-C(16)-H(16B)	109.5
C(27)-B(1)-C(18)	118.41(16)	N(1)-C(16)-H(16C)	109.5
C(14)-O(1)-C(15)	118.56(17)	H(16A)-C(16)-H(16C)	109.5
C(4)-N(1)-C(16)	121.47(16)	H(16B)-C(16)-H(16C)	109.5
C(4)-N(1)-C(17)	121.60(16)	N(1)-C(17)-H(17A)	109.5
C(16)-N(1)-C(17)	116.82(16)	N(1)-C(17)-H(17B)	109.5
C(2)-C(1)-C(6)	115.40(16)	H(17A)-C(17)-H(17B)	109.5
C(2)-C(1)-B(1)	117.73(16)	N(1)-C(17)-H(17C)	109.5
C(6)-C(1)-B(1)	126.61(16)	H(17A)-C(17)-H(17C)	109.5
C(3)-C(2)-C(1)	124.14(17)	H(17B)-C(17)-H(17C)	109.5
C(3)-C(2)-H(2)	117.9	C(25)-C(18)-C(19)	117.29(16)
C(1)-C(2)-H(2)	117.9	C(25)-C(18)-B(1)	121.71(17)
C(2)-C(3)-C(4)	120.13(17)	C(19)-C(18)-B(1)	120.91(17)
C(2)-C(3)-H(3)	119.9	C(21)-C(19)-C(18)	120.51(18)
C(4)-C(3)-H(3)	119.9	C(21)-C(19)-C(20)	117.08(18)
N(1)-C(4)-C(5)	121.34(17)	C(18)-C(19)-C(20)	122.41(17)
N(1)-C(4)-C(3)	121.58(17)	C(19)-C(20)-H(20A)	109.5
C(5)-C(4)-C(3)	117.07(17)	C(19)-C(20)-H(20B)	109.5
C(6)-C(5)-C(4)	122.63(17)	H(20A)-C(20)-H(20B)	109.5
C(6)-C(5)-H(5)	118.7	C(19)-C(20)-H(20C)	109.5
C(4)-C(5)-H(5)	118.7	H(20A)-C(20)-H(20C)	109.5
C(5)-C(6)-C(1)	120.56(16)	H(20B)-C(20)-H(20C)	109.5
C(5)-C(6)-C(7)	118.75(16)	C(22)-C(21)-C(19)	121.88(19)
C(1)-C(6)-C(7)	120.63(16)	C(22)-C(21)-H(21)	119.1
C(8)-C(7)-C(6)	125.93(17)	C(19)-C(21)-H(21)	119.1
C(8)-C(7)-H(7)	117.0	C(24)-C(22)-C(21)	117.73(17)
C(6)-C(7)-H(7)	117.0	C(24)-C(22)-C(23)	121.3(2)
C(7)-C(8)-C(9)	125.09(18)	C(21)-C(22)-C(23)	120.9(2)
C(7)-C(8)-H(8)	117.5	C(22)-C(23)-H(23A)	109.5
C(9)-C(8)-H(8)	117.5	C(22)-C(23)-H(23B)	109.5
C(10)-C(9)-C(14)	117.87(18)	H(23A)-C(23)-H(23B)	109.5
C(10)-C(9)-C(8)	122.59(17)	C(22)-C(23)-H(23C)	109.5
C(14)-C(9)-C(8)	119.53(17)	H(23A)-C(23)-H(23C)	109.5
C(11)-C(10)-C(9)	121.44(19)	H(23B)-C(23)-H(23C)	109.5
C(11)-C(10)-H(10)	119.3	C(22)-C(24)-C(25)	122.31(19)
C(9)-C(10)-H(10)	119.3	C(22)-C(24)-H(24)	118.8
C(12)-C(11)-C(10)	119.6(2)	C(25)-C(24)-H(24)	118.8
C(12)-C(11)-H(11)	120.2	C(24)-C(25)-C(18)	120.19(18)
C(10)-C(11)-H(11)	120.2	C(24)-C(25)-C(26)	117.53(17)
C(13)-C(12)-C(11)	120.4(2)	C(18)-C(25)-C(26)	122.28(17)
C(13)-C(12)-H(12)	119.8	C(25)-C(26)-H(26A)	109.5
C(11)-C(12)-H(12)	119.8	C(25)-C(26)-H(26B)	109.5
C(12)-C(13)-C(14)	120.12(19)	H(26A)-C(26)-H(26B)	109.5
C(12)-C(13)-H(13)	119.9	C(25)-C(26)-H(26C)	109.5
C(14)-C(13)-H(13)	119.9	H(26A)-C(26)-H(26C)	109.5
O(1)-C(14)-C(13)	124.26(18)	H(26B)-C(26)-H(26C)	109.5
O(1)-C(14)-C(9)	115.24(17)	C(34)-C(27)-C(28)	117.90(17)
C(13)-C(14)-C(9)	120.49(19)	C(34)-C(27)-B(1)	120.47(17)
O(1)-C(15)-H(15A)	109.5	C(28)-C(27)-B(1)	121.63(17)
O(1)-C(15)-H(15B)	109.5	C(30)-C(28)-C(27)	120.25(19)

C(30)-C(28)-C(29)	118.24(19)	H(32A)-C(32)-H(32B)	109.5
C(27)-C(28)-C(29)	121.42(17)	C(31)-C(32)-H(32C)	109.5
C(28)-C(29)-H(29A)	109.5	H(32A)-C(32)-H(32C)	109.5
C(28)-C(29)-H(29B)	109.5	H(32B)-C(32)-H(32C)	109.5
H(29A)-C(29)-H(29B)	109.5	C(31)-C(33)-C(34)	122.3(2)
C(28)-C(29)-H(29C)	109.5	C(31)-C(33)-H(33)	118.9
H(29A)-C(29)-H(29C)	109.5	C(34)-C(33)-H(33)	118.9
H(29B)-C(29)-H(29C)	109.5	C(33)-C(34)-C(27)	119.81(19)
C(31)-C(30)-C(28)	121.9(2)	C(33)-C(34)-C(35)	118.16(19)
C(31)-C(30)-H(30)	119.1	C(27)-C(34)-C(35)	122.03(18)
C(28)-C(30)-H(30)	119.1	C(34)-C(35)-H(35A)	109.5
C(30)-C(31)-C(33)	117.81(19)	C(34)-C(35)-H(35B)	109.5
C(30)-C(31)-C(32)	121.0(2)	H(35A)-C(35)-H(35B)	109.5
C(33)-C(31)-C(32)	121.1(2)	C(34)-C(35)-H(35C)	109.5
C(31)-C(32)-H(32A)	109.5	H(35A)-C(35)-H(35C)	109.5
C(31)-C(32)-H(32B)	109.5	H(35B)-C(35)-H(35C)	109.5

Table S75. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for **3a**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + ... \quad + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
B(1)	26(1)	22(1)	24(1)	1(1)	5(1)	-3(1)
O(1)	47(1)	21(1)	38(1)	-2(1)	5(1)	-7(1)
N(1)	47(1)	26(1)	22(1)	-3(1)	5(1)	-2(1)
C(1)	29(1)	19(1)	21(1)	1(1)	2(1)	-2(1)
C(2)	32(1)	18(1)	24(1)	4(1)	0(1)	-3(1)
C(3)	29(1)	26(1)	18(1)	5(1)	4(1)	-2(1)
C(4)	24(1)	23(1)	21(1)	-1(1)	0(1)	1(1)
C(5)	28(1)	18(1)	25(1)	1(1)	1(1)	-2(1)
C(6)	24(1)	20(1)	21(1)	2(1)	1(1)	0(1)
C(7)	28(1)	22(1)	22(1)	0(1)	3(1)	-4(1)
C(8)	32(1)	24(1)	22(1)	1(1)	2(1)	-3(1)
C(9)	27(1)	25(1)	26(1)	5(1)	2(1)	-3(1)
C(10)	45(1)	27(1)	29(1)	2(1)	3(1)	-6(1)
C(11)	57(2)	44(1)	26(1)	3(1)	9(1)	1(1)
C(12)	45(1)	45(1)	32(1)	16(1)	11(1)	4(1)
C(13)	30(1)	28(1)	42(1)	15(1)	6(1)	0(1)
C(14)	24(1)	25(1)	31(1)	4(1)	0(1)	0(1)
C(15)	38(1)	23(1)	67(2)	-4(1)	5(1)	-5(1)
C(16)	46(1)	40(1)	23(1)	-5(1)	7(1)	-3(1)
C(17)	47(1)	24(1)	32(1)	-8(1)	-1(1)	0(1)
C(18)	35(1)	20(1)	18(1)	-1(1)	5(1)	-2(1)
C(19)	37(1)	24(1)	23(1)	0(1)	4(1)	-2(1)
C(20)	38(1)	30(1)	42(1)	-1(1)	-5(1)	0(1)
C(21)	40(1)	26(1)	30(1)	4(1)	4(1)	5(1)
C(22)	49(1)	20(1)	26(1)	2(1)	13(1)	0(1)
C(23)	59(2)	22(1)	55(2)	3(1)	14(1)	1(1)
C(24)	43(1)	22(1)	23(1)	-2(1)	8(1)	-8(1)
C(25)	37(1)	24(1)	18(1)	-2(1)	5(1)	-3(1)
C(26)	40(1)	29(1)	45(1)	-4(1)	-4(1)	-7(1)
C(27)	34(1)	17(1)	22(1)	-1(1)	1(1)	-5(1)
C(28)	41(1)	21(1)	23(1)	-4(1)	0(1)	-7(1)
C(29)	43(1)	42(1)	31(1)	-5(1)	8(1)	4(1)

C(30)	52(1)	24(1)	24(1)	-5(1)	5(1)	-7(1)
C(31)	61(2)	24(1)	24(1)	-1(1)	-6(1)	-4(1)
C(32)	94(2)	55(2)	29(1)	5(1)	-10(1)	11(2)
C(33)	44(1)	21(1)	35(1)	0(1)	-10(1)	0(1)
C(34)	36(1)	19(1)	30(1)	0(1)	1(1)	-4(1)
C(35)	37(1)	30(1)	40(1)	2(1)	5(1)	4(1)

Table S76. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^{2}x 10^3) for **3a**.

	x	y	z	U(eq)
H(2)	5757	2626	5731	30
H(3)	5649	3245	6745	29
H(5)	7286	4626	5470	29
H(7)	8024	3829	3845	29
H(8)	7072	4954	4351	31
H(10)	7784	4156	2670	41
H(11)	8711	4554	1549	50
H(12)	9568	5557	1487	49
H(13)	9424	6168	2527	40
H(15A)	10095	6526	3726	64
H(15B)	8597	6650	4330	64
H(15C)	8018	6670	3462	64
H(16A)	4755	3992	7536	54
H(16B)	6027	4506	7905	54
H(16C)	6894	3871	7708	54
H(17A)	8158	5059	6679	52
H(17B)	6540	5227	7213	52
H(17C)	6143	5196	6331	52
H(20A)	10760	2029	5157	56
H(20B)	9309	2392	5623	56
H(20C)	9737	2600	4797	56
H(21)	9458	1093	5110	39
H(23A)	6246	-49	4522	67
H(23B)	7694	62	5203	67
H(23C)	8366	55	4369	67
H(24)	4476	785	4146	35
H(26A)	3549	1966	3301	57
H(26B)	2849	2208	4076	57
H(26C)	2452	1531	3831	57
H(29A)	9146	2518	2504	58
H(29B)	8318	2130	3157	58
H(29C)	9342	2747	3347	58
H(30)	6985	2987	1765	40
H(32A)	3659	3257	939	89
H(32B)	5114	3790	1032	89
H(32C)	3052	3885	1276	89
H(33)	2393	3703	2533	41
H(35A)	1650	3667	3747	53
H(35B)	3414	3810	4280	53
H(35C)	2543	3153	4265	53

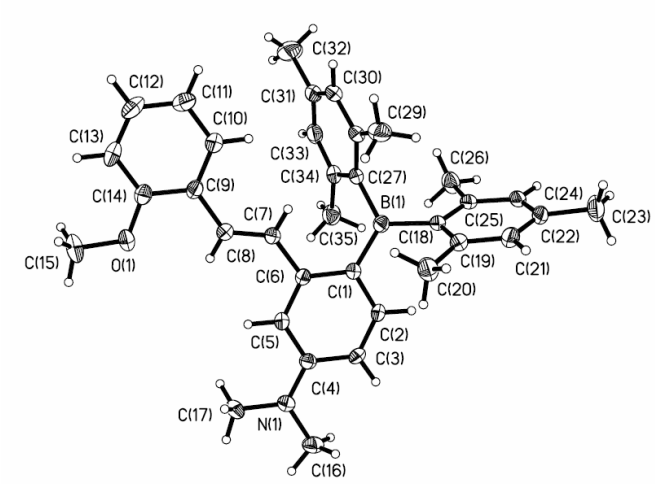


Figure S152. Structure of **3a**.

Table S77. Crystal data and structure refinement for **4a**.

Identification code	**4a**	
Empirical formula	C34 H38 B N	
Formula weight	471.46	
Temperature	180(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 7.868(2) Å	α= 69.575(8)°.
	b = 12.043(4) Å	β= 77.359(8)°.
	c = 16.695(5) Å	γ = 76.219(9)°.
Volume	1423.6(7) Å^3	
Z	2	
Density (calculated)	1.100 Mg/m^3	
Absorption coefficient	0.062 mm^{-1}	
F(000)	508	
Crystal size	0.150 x 0.100 x 0.100 mm^3	
Theta range for data collection	2.818 to 27.245°.	
Index ranges	-10<=h<=10, -15<=k<=15, -21<=l<=21	
Reflections collected	15953	
Independent reflections	6179 [R(int) = 0.1175]	
Completeness to theta = 25.242°	98.7 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.994 and 0.991	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	6179 / 0 / 326	
Goodness-of-fit on F^2	1.032	
Final R indices [I>2sigma(I)]	R1 = 0.0900, wR2 = 0.1975	
R indices (all data)	R1 = 0.2064, wR2 = 0.2380	
Extinction coefficient	0.020(4)	
Largest diff. peak and hole	0.311 and -0.284 e.Å^{-3}	

Table S78. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^{2}x 10^3) for **4a**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)

B(1)	2672(5)	3675(3)	2494(3)	30(1)
N(1)	4113(4)	3599(3)	5767(2)	45(1)
C(1)	3223(4)	3644(3)	3335(2)	29(1)
C(2)	2269(4)	4485(3)	3757(2)	33(1)
C(3)	2500(4)	4486(3)	4546(2)	34(1)
C(4)	3824(4)	3620(3)	4984(2)	31(1)
C(5)	4859(4)	2800(3)	4572(2)	32(1)
C(6)	4579(4)	2782(3)	3785(2)	29(1)
C(7)	5756(4)	1878(3)	3399(2)	32(1)
C(8)	6519(4)	784(3)	3830(2)	35(1)
C(9)	7634(4)	-130(3)	3453(2)	33(1)
C(10)	8481(5)	-1189(3)	3986(2)	40(1)
C(11)	9506(5)	-2087(3)	3651(3)	47(1)
C(12)	9686(5)	-1941(3)	2796(3)	53(1)
C(13)	8870(6)	-905(4)	2258(3)	57(1)
C(14)	7841(5)	-1(3)	2578(2)	51(1)
C(15)	5296(6)	2608(4)	6266(3)	65(1)
C(16)	3077(5)	4448(4)	6201(2)	52(1)
C(17)	1701(4)	4904(3)	1899(2)	30(1)
C(18)	2474(4)	5946(3)	1576(2)	30(1)
C(19)	1701(5)	6975(3)	975(2)	38(1)
C(20)	161(5)	7035(4)	683(2)	48(1)
C(21)	-622(5)	6027(4)	1021(3)	56(1)
C(22)	97(5)	4971(3)	1616(3)	43(1)
C(23)	-889(5)	3923(4)	1950(3)	72(2)
C(24)	4189(5)	5997(3)	1808(2)	43(1)
C(25)	-619(7)	8160(4)	20(3)	88(2)
C(26)	3034(4)	2515(3)	2202(2)	28(1)
C(27)	4026(5)	2509(3)	1384(2)	32(1)
C(28)	4347(5)	1487(3)	1130(2)	38(1)
C(29)	3688(5)	462(3)	1640(2)	41(1)
C(30)	2697(5)	472(3)	2430(2)	41(1)
C(31)	2390(5)	1459(3)	2727(2)	35(1)
C(32)	1335(6)	1349(4)	3612(2)	53(1)
C(33)	4019(7)	-635(3)	1345(3)	68(1)
C(34)	4811(6)	3589(3)	785(2)	53(1)

Table S79. Bond lengths [Å] and angles [°] for **4a**.

B(1)-C(1)	1.543(5)	C(6)-C(7)	1.484(4)
B(1)-C(26)	1.580(5)	C(7)-C(8)	1.329(4)
B(1)-C(17)	1.590(5)	C(7)-H(7A)	0.9500
N(1)-C(4)	1.366(4)	C(8)-C(9)	1.469(4)
N(1)-C(16)	1.447(4)	C(8)-H(8A)	0.9500
N(1)-C(15)	1.450(4)	C(9)-C(10)	1.387(4)
C(1)-C(2)	1.410(4)	C(9)-C(14)	1.392(5)
C(1)-C(6)	1.435(4)	C(10)-C(11)	1.393(5)
C(2)-C(3)	1.369(4)	C(10)-H(10A)	0.9500
C(2)-H(2A)	0.9500	C(11)-C(12)	1.355(5)
C(3)-C(4)	1.411(4)	C(11)-H(11A)	0.9500
C(3)-H(3A)	0.9500	C(12)-C(13)	1.365(5)
C(4)-C(5)	1.399(4)	C(12)-H(12A)	0.9500
C(5)-C(6)	1.388(4)	C(13)-C(14)	1.386(5)
C(5)-H(5A)	0.9500	C(13)-H(13A)	0.9500

C(14)-H(14A)	0.9500	C(3)-C(2)-C(1)	125.2(3)
C(15)-H(15A)	0.9800	C(3)-C(2)-H(2A)	117.4
C(15)-H(15B)	0.9800	C(1)-C(2)-H(2A)	117.4
C(15)-H(15C)	0.9800	C(2)-C(3)-C(4)	119.7(3)
C(16)-H(16A)	0.9800	C(2)-C(3)-H(3A)	120.2
C(16)-H(16B)	0.9800	C(4)-C(3)-H(3A)	120.2
C(16)-H(16C)	0.9800	N(1)-C(4)-C(5)	121.3(3)
C(17)-C(18)	1.408(5)	N(1)-C(4)-C(3)	121.5(3)
C(17)-C(22)	1.416(5)	C(5)-C(4)-C(3)	117.1(3)
C(18)-C(19)	1.398(4)	C(6)-C(5)-C(4)	122.8(3)
C(18)-C(24)	1.503(5)	C(6)-C(5)-H(5A)	118.6
C(19)-C(20)	1.380(5)	C(4)-C(5)-H(5A)	118.6
C(19)-H(19A)	0.9500	C(5)-C(6)-C(1)	120.9(3)
C(20)-C(21)	1.378(6)	C(5)-C(6)-C(7)	118.6(3)
C(20)-C(25)	1.513(5)	C(1)-C(6)-C(7)	120.4(3)
C(21)-C(22)	1.394(5)	C(8)-C(7)-C(6)	126.2(3)
C(21)-H(21A)	0.9500	C(8)-C(7)-H(7A)	116.9
C(22)-C(23)	1.514(6)	C(6)-C(7)-H(7A)	116.9
C(23)-H(23A)	0.9800	C(7)-C(8)-C(9)	126.4(3)
C(23)-H(23B)	0.9800	C(7)-C(8)-H(8A)	116.8
C(23)-H(23C)	0.9800	C(9)-C(8)-H(8A)	116.8
C(24)-H(24A)	0.9800	C(10)-C(9)-C(14)	117.6(3)
C(24)-H(24B)	0.9800	C(10)-C(9)-C(8)	119.6(3)
C(24)-H(24C)	0.9800	C(14)-C(9)-C(8)	122.8(3)
C(25)-H(25A)	0.9800	C(9)-C(10)-C(11)	120.9(4)
C(25)-H(25B)	0.9800	C(9)-C(10)-H(10A)	119.5
C(25)-H(25C)	0.9800	C(11)-C(10)-H(10A)	119.5
C(26)-C(31)	1.406(5)	C(12)-C(11)-C(10)	120.4(3)
C(26)-C(27)	1.418(5)	C(12)-C(11)-H(11A)	119.8
C(27)-C(28)	1.389(5)	C(10)-C(11)-H(11A)	119.8
C(27)-C(34)	1.509(5)	C(11)-C(12)-C(13)	119.9(3)
C(28)-C(29)	1.377(5)	C(11)-C(12)-H(12A)	120.1
C(28)-H(28A)	0.9500	C(13)-C(12)-H(12A)	120.1
C(29)-C(30)	1.379(5)	C(12)-C(13)-C(14)	120.8(4)
C(29)-C(33)	1.513(5)	C(12)-C(13)-H(13A)	119.6
C(30)-C(31)	1.393(5)	C(14)-C(13)-H(13A)	119.6
C(30)-H(30A)	0.9500	C(13)-C(14)-C(9)	120.5(3)
C(31)-C(32)	1.506(5)	C(13)-C(14)-H(14A)	119.8
C(32)-H(32A)	0.9800	C(9)-C(14)-H(14A)	119.8
C(32)-H(32B)	0.9800	N(1)-C(15)-H(15A)	109.5
C(32)-H(32C)	0.9800	N(1)-C(15)-H(15B)	109.5
C(33)-H(33A)	0.9800	H(15A)-C(15)-H(15B)	109.5
C(33)-H(33B)	0.9800	N(1)-C(15)-H(15C)	109.5
C(33)-H(33C)	0.9800	H(15A)-C(15)-H(15C)	109.5
C(34)-H(34A)	0.9800	H(15B)-C(15)-H(15C)	109.5
C(34)-H(34B)	0.9800	N(1)-C(16)-H(16A)	109.5
C(34)-H(34C)	0.9800	N(1)-C(16)-H(16B)	109.5
C(1)-B(1)-C(26)	122.0(3)	H(16A)-C(16)-H(16B)	109.5
C(1)-B(1)-C(17)	119.6(3)	N(1)-C(16)-H(16C)	109.5
C(26)-B(1)-C(17)	118.4(3)	H(16A)-C(16)-H(16C)	109.5
C(4)-N(1)-C(16)	122.4(3)	H(16B)-C(16)-H(16C)	109.5
C(4)-N(1)-C(15)	120.8(3)	C(18)-C(17)-C(22)	117.2(3)
C(16)-N(1)-C(15)	116.1(3)	C(18)-C(17)-B(1)	121.1(3)
C(2)-C(1)-C(6)	114.2(3)	C(22)-C(17)-B(1)	121.4(3)
C(2)-C(1)-B(1)	119.2(3)	C(19)-C(18)-C(17)	120.2(3)
C(6)-C(1)-B(1)	126.5(3)	C(19)-C(18)-C(24)	116.7(3)

C(17)-C(18)-C(24)	123.0(3)	C(28)-C(27)-C(26)	120.4(3)
C(20)-C(19)-C(18)	122.7(4)	C(28)-C(27)-C(34)	118.5(3)
C(20)-C(19)-H(19A)	118.6	C(26)-C(27)-C(34)	121.1(3)
C(18)-C(19)-H(19A)	118.6	C(29)-C(28)-C(27)	122.1(4)
C(21)-C(20)-C(19)	116.9(3)	C(29)-C(28)-H(28A)	119.0
C(21)-C(20)-C(25)	122.0(4)	C(27)-C(28)-H(28A)	119.0
C(19)-C(20)-C(25)	121.1(4)	C(28)-C(29)-C(30)	117.7(3)
C(20)-C(21)-C(22)	122.9(4)	C(28)-C(29)-C(33)	121.4(4)
C(20)-C(21)-H(21A)	118.5	C(30)-C(29)-C(33)	120.9(4)
C(22)-C(21)-H(21A)	118.5	C(29)-C(30)-C(31)	122.4(3)
C(21)-C(22)-C(17)	120.0(4)	C(29)-C(30)-H(30A)	118.8
C(21)-C(22)-C(23)	118.2(4)	C(31)-C(30)-H(30A)	118.8
C(17)-C(22)-C(23)	121.8(3)	C(30)-C(31)-C(26)	120.1(3)
C(22)-C(23)-H(23A)	109.5	C(30)-C(31)-C(32)	117.6(3)
C(22)-C(23)-H(23B)	109.5	C(26)-C(31)-C(32)	122.3(3)
H(23A)-C(23)-H(23B)	109.5	C(31)-C(32)-H(32A)	109.5
C(22)-C(23)-H(23C)	109.5	C(31)-C(32)-H(32B)	109.5
H(23A)-C(23)-H(23C)	109.5	H(32A)-C(32)-H(32B)	109.5
H(23B)-C(23)-H(23C)	109.5	C(31)-C(32)-H(32C)	109.5
C(18)-C(24)-H(24A)	109.5	H(32A)-C(32)-H(32C)	109.5
C(18)-C(24)-H(24B)	109.5	H(32B)-C(32)-H(32C)	109.5
H(24A)-C(24)-H(24B)	109.5	C(29)-C(33)-H(33A)	109.5
C(18)-C(24)-H(24C)	109.5	C(29)-C(33)-H(33B)	109.5
H(24A)-C(24)-H(24C)	109.5	H(33A)-C(33)-H(33B)	109.5
H(24B)-C(24)-H(24C)	109.5	C(29)-C(33)-H(33C)	109.5
C(20)-C(25)-H(25A)	109.5	H(33A)-C(33)-H(33C)	109.5
C(20)-C(25)-H(25B)	109.5	H(33B)-C(33)-H(33C)	109.5
H(25A)-C(25)-H(25B)	109.5	C(27)-C(34)-H(34A)	109.5
C(20)-C(25)-H(25C)	109.5	C(27)-C(34)-H(34B)	109.5
H(25A)-C(25)-H(25C)	109.5	H(34A)-C(34)-H(34B)	109.5
H(25B)-C(25)-H(25C)	109.5	C(27)-C(34)-H(34C)	109.5
C(31)-C(26)-C(27)	117.3(3)	H(34A)-C(34)-H(34C)	109.5
C(31)-C(26)-B(1)	122.2(3)	H(34B)-C(34)-H(34C)	109.5
C(27)-C(26)-B(1)	120.5(3)		

Table S80. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for **4a**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + ...\ + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
B(1)	21(2)	31(2)	35(2)	-12(2)	4(2)	-7(2)
N(1)	54(2)	44(2)	42(2)	-23(2)	-17(2)	6(2)
C(1)	26(2)	28(2)	36(2)	-15(2)	-3(2)	-4(2)
C(2)	31(2)	30(2)	34(2)	-16(2)	-5(2)	8(2)
C(3)	31(2)	30(2)	40(2)	-21(2)	-2(2)	4(2)
C(4)	31(2)	26(2)	39(2)	-12(2)	-3(2)	-7(2)
C(5)	29(2)	27(2)	41(2)	-14(2)	-8(2)	1(2)
C(6)	27(2)	25(2)	35(2)	-14(2)	-3(2)	-3(2)
C(7)	27(2)	32(2)	36(2)	-16(2)	-3(2)	1(2)
C(8)	37(2)	33(2)	35(2)	-15(2)	-4(2)	0(2)
C(9)	29(2)	26(2)	43(2)	-14(2)	-7(2)	3(2)
C(10)	45(2)	31(2)	40(2)	-12(2)	-2(2)	0(2)
C(11)	44(2)	26(2)	59(3)	-9(2)	-1(2)	7(2)
C(12)	51(3)	33(2)	70(3)	-29(2)	10(2)	3(2)

C(13)	73(3)	47(3)	44(2)	-26(2)	-2(2)	11(2)
C(14)	59(3)	43(2)	44(2)	-18(2)	-14(2)	18(2)
C(15)	85(3)	62(3)	52(3)	-24(2)	-34(3)	9(3)
C(16)	57(3)	59(3)	52(3)	-34(2)	-9(2)	-5(2)
C(17)	27(2)	34(2)	31(2)	-19(2)	-4(2)	1(2)
C(18)	30(2)	29(2)	35(2)	-20(2)	-5(2)	1(2)
C(19)	46(2)	30(2)	34(2)	-14(2)	-3(2)	3(2)
C(20)	49(3)	45(2)	43(2)	-11(2)	-20(2)	10(2)
C(21)	35(2)	65(3)	70(3)	-24(2)	-24(2)	3(2)
C(22)	28(2)	48(2)	56(3)	-20(2)	-11(2)	0(2)
C(23)	35(2)	70(3)	121(4)	-29(3)	-22(3)	-15(2)
C(24)	44(2)	34(2)	55(2)	-18(2)	-14(2)	-6(2)
C(25)	93(4)	67(3)	88(4)	-4(3)	-51(3)	17(3)
C(26)	32(2)	24(2)	29(2)	-7(1)	-7(2)	-5(2)
C(27)	37(2)	27(2)	33(2)	-11(2)	-7(2)	-4(2)
C(28)	49(2)	35(2)	32(2)	-16(2)	-6(2)	-3(2)
C(29)	54(3)	30(2)	43(2)	-17(2)	-14(2)	-1(2)
C(30)	55(3)	25(2)	44(2)	-5(2)	-15(2)	-12(2)
C(31)	40(2)	33(2)	34(2)	-10(2)	-11(2)	-7(2)
C(32)	68(3)	53(3)	42(2)	-14(2)	6(2)	-29(2)
C(33)	108(4)	38(2)	66(3)	-27(2)	-16(3)	-9(3)
C(34)	70(3)	41(2)	44(2)	-20(2)	19(2)	-17(2)

Table S81. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for **4a**.

	x	y	z	U(eq)
H(2A)	1397	5101	3470	39
H(3A)	1773	5067	4797	40
H(5A)	5792	2231	4843	39
H(7A)	5984	2104	2786	38
H(8A)	6325	571	4443	42
H(10A)	8361	-1304	4587	48
H(11A)	10081	-2806	4024	57
H(12A)	10378	-2559	2571	64
H(13A)	9009	-802	1658	68
H(14A)	7272	711	2196	61
H(15A)	5340	2745	6805	97
H(15B)	4864	1855	6399	97
H(15C)	6485	2553	5930	97
H(16A)	3495	4279	6750	78
H(16B)	3208	5268	5834	78
H(16C)	1828	4371	6312	78
H(19A)	2259	7662	758	45
H(21A)	-1699	6051	841	67
H(23A)	-238	3247	2360	109
H(23B)	-2072	4168	2241	109
H(23C)	-996	3677	1464	109
H(24A)	4603	5231	2231	64
H(24B)	5076	6144	1287	64
H(24C)	4005	6651	2056	64
H(25A)	129	8771	-138	131
H(25B)	-678	7967	-496	131
H(25C)	-1813	8471	265	131

H(28A)	5043	1495	586	46
H(30A)	2207	-220	2784	49
H(32A)	1214	2099	3742	80
H(32B)	159	1196	3625	80
H(32C)	1947	681	4043	80
H(33A)	3449	-1269	1793	102
H(33B)	3527	-420	809	102
H(33C)	5296	-927	1243	102
H(34A)	4477	4238	1047	80
H(34B)	6103	3367	687	80
H(34C)	4362	3864	232	80

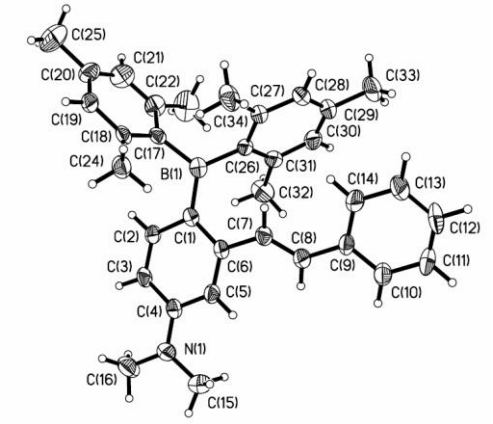


Figure S153. Structure of **4a**.

Table S82. Crystal data and structure refinement for **5a**.

Identification code	**5a**	
Empirical formula	C31H32B1N1	
Formula weight	429.39	
Temperature	230(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	$P2_1/c$	
Unit cell dimensions	a = 11.8634(7) Å	α= 90°.
	b = 11.8780(8) Å	β= 92.179(2)°.
	c = 18.2134(11) Å	γ = 90°.
Volume	2564.7(3) $Å^3$	
Z	4	
Density (calculated)	1.112 Mg/m^3	
Absorption coefficient	0.063 mm^{-1}	
F(000)	920	
Crystal size	0.548 x 0.423 x 0.358 mm^3	
Theta range for data collection	2.645 to 27.173°.	
Index ranges	-15<=h<=15, -15<=k<=15, -23<=l<=23	
Reflections collected	47866	
Independent reflections	5664 [R(int) = 0.0592]	
Completeness to theta = 25.242°	99.7 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.978 and 0.966	
Refinement method	Full-matrix least-squares on F^2	

Data / restraints / parameters	5664 / 0 / 304
Goodness-of-fit on F^2	1.063
Final R indices [I>2sigma(I)]	R1 = 0.0581, wR2 = 0.1450
R indices (all data)	R1 = 0.0841, wR2 = 0.1595
Extinction coefficient	n/a
Largest diff. peak and hole	0.225 and -0.225 e.Å^{-3}

Table S83. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^{2}x 10^3) for **5a**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
B(1)	6216(1)	7232(1)	9239(1)	32(1)
N(1)	10924(1)	8561(2)	11013(1)	72(1)
C(1)	6063(1)	7478(1)	10080(1)	32(1)
C(2)	4991(1)	7271(1)	10350(1)	37(1)
C(3)	4778(2)	7332(2)	11090(1)	44(1)
C(4)	5630(2)	7648(2)	11581(1)	47(1)
C(5)	6683(2)	7906(2)	11335(1)	44(1)
C(6)	6930(1)	7808(1)	10591(1)	35(1)
C(7)	8062(1)	8072(2)	10350(1)	41(1)
C(8)	8996(2)	8130(2)	10755(1)	55(1)
C(9)	10125(2)	8359(2)	10494(1)	52(1)
C(10)	10369(2)	8360(3)	9767(1)	103(1)
C(11)	11454(2)	8580(3)	9560(2)	112(1)
C(12)	12267(2)	8778(2)	10084(2)	71(1)
C(13)	11965(2)	8768(2)	10788(2)	74(1)
C(14)	5150(1)	7491(1)	8718(1)	31(1)
C(15)	4731(1)	8598(1)	8648(1)	37(1)
C(16)	5334(2)	9590(2)	8996(1)	50(1)
C(17)	3753(1)	8810(2)	8230(1)	44(1)
C(18)	3138(1)	7960(2)	7886(1)	45(1)
C(19)	2060(2)	8223(2)	7449(1)	72(1)
C(20)	3542(1)	6873(2)	7958(1)	42(1)
C(21)	4538(1)	6624(1)	8355(1)	35(1)
C(22)	4909(2)	5417(2)	8406(1)	52(1)
C(23)	7338(1)	6688(1)	8959(1)	37(1)
C(24)	7942(1)	7199(2)	8390(1)	42(1)
C(25)	7598(2)	8318(2)	8070(1)	52(1)
C(26)	8932(2)	6712(2)	8156(1)	56(1)
C(27)	9361(2)	5733(2)	8460(1)	65(1)
C(28)	10443(2)	5211(3)	8194(2)	104(1)
C(29)	8785(2)	5238(2)	9021(1)	61(1)
C(30)	7789(1)	5696(2)	9278(1)	45(1)
C(31)	7229(2)	5084(2)	9894(1)	60(1)

Table S84. Bond lengths [Å] and angles [°] for **5a**.

B(1)-C(1)	1.577(2)	C(1)-C(2)	1.403(2)
B(1)-C(23)	1.581(2)	C(1)-C(6)	1.416(2)
B(1)-C(14)	1.582(2)	C(2)-C(3)	1.382(2)
N(1)-C(9)	1.334(2)	C(3)-C(4)	1.376(3)
N(1)-C(13)	1.339(3)	C(4)-C(5)	1.377(3)

C(5)-C(6)	1.402(2)	C(1)-C(6)-C(7)	120.93(14)
C(6)-C(7)	1.463(2)	C(8)-C(7)-C(6)	127.51(16)
C(7)-C(8)	1.310(2)	C(7)-C(8)-C(9)	126.33(17)
C(8)-C(9)	1.462(3)	N(1)-C(9)-C(10)	120.98(19)
C(9)-C(10)	1.367(3)	N(1)-C(9)-C(8)	115.98(18)
C(10)-C(11)	1.379(3)	C(10)-C(9)-C(8)	123.04(18)
C(11)-C(12)	1.351(3)	C(9)-C(10)-C(11)	119.9(2)
C(12)-C(13)	1.345(3)	C(12)-C(11)-C(10)	119.3(2)
C(14)-C(15)	1.409(2)	C(13)-C(12)-C(11)	117.6(2)
C(14)-C(21)	1.410(2)	N(1)-C(13)-C(12)	125.1(2)
C(15)-C(17)	1.387(2)	C(15)-C(14)-C(21)	117.73(14)
C(15)-C(16)	1.506(2)	C(15)-C(14)-B(1)	120.45(13)
C(17)-C(18)	1.381(3)	C(21)-C(14)-B(1)	121.65(14)
C(18)-C(20)	1.382(3)	C(17)-C(15)-C(14)	120.26(15)
C(18)-C(19)	1.514(2)	C(17)-C(15)-C(16)	117.59(15)
C(20)-C(21)	1.393(2)	C(14)-C(15)-C(16)	122.12(14)
C(21)-C(22)	1.501(2)	C(18)-C(17)-C(15)	122.16(17)
C(23)-C(30)	1.411(2)	C(17)-C(18)-C(20)	117.70(15)
C(23)-C(24)	1.418(2)	C(17)-C(18)-C(19)	120.54(18)
C(24)-C(26)	1.390(3)	C(20)-C(18)-C(19)	121.76(18)
C(24)-C(25)	1.502(3)	C(18)-C(20)-C(21)	122.14(16)
C(26)-C(27)	1.377(3)	C(20)-C(21)-C(14)	119.98(15)
C(27)-C(29)	1.382(3)	C(20)-C(21)-C(22)	118.40(15)
C(27)-C(28)	1.522(3)	C(14)-C(21)-C(22)	121.58(15)
C(29)-C(30)	1.397(3)	C(30)-C(23)-C(24)	117.68(15)
C(30)-C(31)	1.511(3)	C(30)-C(23)-B(1)	121.26(15)
C(1)-B(1)-C(23)	121.25(14)	C(24)-C(23)-B(1)	121.03(15)
C(1)-B(1)-C(14)	115.32(13)	C(26)-C(24)-C(23)	120.11(18)
C(23)-B(1)-C(14)	123.30(13)	C(26)-C(24)-C(25)	117.99(17)
C(9)-N(1)-C(13)	117.1(2)	C(23)-C(24)-C(25)	121.70(15)
C(2)-C(1)-C(6)	117.66(14)	C(27)-C(26)-C(24)	122.17(19)
C(2)-C(1)-B(1)	116.57(14)	C(26)-C(27)-C(29)	118.06(18)
C(6)-C(1)-B(1)	125.60(13)	C(26)-C(27)-C(28)	121.3(2)
C(3)-C(2)-C(1)	122.24(16)	C(29)-C(27)-C(28)	120.6(3)
C(4)-C(3)-C(2)	119.45(16)	C(27)-C(29)-C(30)	122.0(2)
C(3)-C(4)-C(5)	120.12(15)	C(29)-C(30)-C(23)	119.93(18)
C(4)-C(5)-C(6)	121.47(16)	C(29)-C(30)-C(31)	117.61(18)
C(5)-C(6)-C(1)	118.96(15)	C(23)-C(30)-C(31)	122.46(16)
C(5)-C(6)-C(7)	120.10(15)		

Table S85. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for **5a**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + ... \ + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
B(1)	31(1)	32(1)	33(1)	1(1)	5(1)	-7(1)
N(1)	44(1)	105(2)	64(1)	3(1)	-17(1)	-9(1)
C(1)	31(1)	35(1)	31(1)	3(1)	4(1)	2(1)
C(2)	33(1)	40(1)	38(1)	4(1)	7(1)	2(1)
C(3)	40(1)	48(1)	44(1)	11(1)	18(1)	8(1)
C(4)	58(1)	55(1)	30(1)	5(1)	14(1)	17(1)
C(5)	47(1)	53(1)	31(1)	-2(1)	-2(1)	10(1)
C(6)	36(1)	39(1)	31(1)	1(1)	2(1)	4(1)
C(7)	37(1)	53(1)	33(1)	-4(1)	0(1)	-3(1)

C(8)	42(1)	84(2)	39(1)	2(1)	-4(1)	-5(1)
C(9)	36(1)	71(1)	50(1)	-5(1)	-7(1)	-5(1)
C(10)	43(1)	211(4)	55(1)	-31(2)	2(1)	-32(2)
C(11)	51(1)	218(4)	70(2)	-32(2)	14(1)	-32(2)
C(12)	37(1)	82(2)	94(2)	-4(1)	3(1)	-8(1)
C(13)	39(1)	92(2)	90(2)	1(1)	-20(1)	-11(1)
C(14)	29(1)	39(1)	26(1)	2(1)	6(1)	-4(1)
C(15)	36(1)	42(1)	33(1)	2(1)	4(1)	-2(1)
C(16)	56(1)	39(1)	56(1)	-2(1)	-6(1)	-2(1)
C(17)	43(1)	49(1)	42(1)	6(1)	1(1)	7(1)
C(18)	35(1)	66(1)	34(1)	3(1)	-1(1)	2(1)
C(19)	50(1)	103(2)	62(1)	-2(1)	-19(1)	12(1)
C(20)	35(1)	58(1)	34(1)	-5(1)	2(1)	-12(1)
C(21)	36(1)	43(1)	28(1)	1(1)	6(1)	-7(1)
C(22)	55(1)	42(1)	59(1)	-6(1)	-6(1)	-7(1)
C(23)	30(1)	46(1)	34(1)	-9(1)	1(1)	-3(1)
C(24)	32(1)	62(1)	33(1)	-15(1)	6(1)	-11(1)
C(25)	50(1)	66(1)	40(1)	0(1)	13(1)	-16(1)
C(26)	39(1)	79(2)	51(1)	-20(1)	14(1)	-11(1)
C(27)	36(1)	85(2)	74(1)	-31(1)	12(1)	1(1)
C(28)	52(1)	131(3)	131(3)	-34(2)	28(2)	23(2)
C(29)	45(1)	58(1)	79(1)	-19(1)	-6(1)	13(1)
C(30)	35(1)	50(1)	49(1)	-10(1)	-2(1)	1(1)
C(31)	58(1)	50(1)	70(1)	11(1)	-1(1)	7(1)

Table S86. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for **5a**.

	x	y	z	U(eq)
H(2A)	4396	7084	10016	44
H(3A)	4058	7158	11256	52
H(4A)	5493	7688	12085	57
H(5A)	7247	8152	11673	52
H(7A)	8126	8216	9845	49
H(8A)	8936	8014	11262	66
H(10A)	9798	8211	9408	123
H(11A)	11625	8592	9061	135
H(12A)	13016	8918	9960	85
H(13A)	12530	8917	11151	89
H(16A)	4799	10048	9253	76
H(16B)	5674	10037	8618	76
H(16C)	5917	9324	9341	76
H(17A)	3500	9557	8178	53
H(19A)	1562	8660	7749	108
H(19B)	1690	7526	7302	108
H(19C)	2236	8653	7015	108
H(20A)	3132	6282	7731	51
H(22A)	4427	4959	8084	79
H(22B)	4856	5157	8908	79
H(22C)	5684	5356	8258	79
H(25A)	7980	8438	7615	78
H(25B)	7803	8912	8415	78
H(25C)	6788	8326	7972	78

H(26A)	9321	7063	7779	67
H(28A)	10503	5356	7672	156
H(28B)	10431	4405	8278	156
H(28C)	11086	5538	8460	156
H(29A)	9071	4572	9236	73
H(31D)	7513	4319	9926	89
H(31A)	6419	5068	9796	89
H(31B)	7393	5471	10354	89

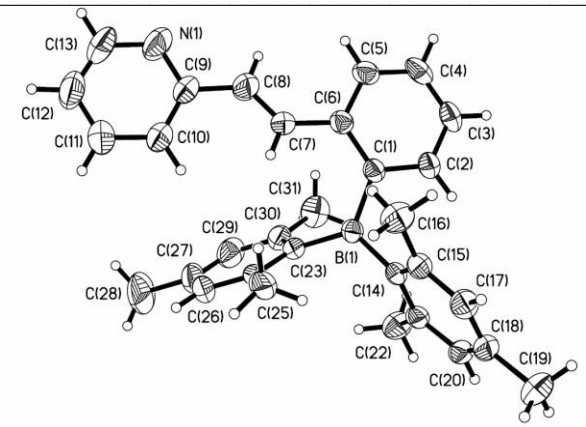


Figure S154. Crystal structure of **5a**

Table S87. Crystal data and structure refinement for **6a**.

Identification code	**6a**	
Empirical formula	C32H36B1N1S1	
Formula weight	477.49	
Temperature	220(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	$P2_1/c$	
Unit cell dimensions	a = 7.9250(4) Å	α= 90°.
	b = 21.8524(8) Å	β= 98.766(2)°.
	c = 16.0075(6) Å	γ = 90°.
Volume	2739.8(2) $Å^3$	
Z	4	
Density (calculated)	1.158 Mg/m^3	
Absorption coefficient	0.139 mm^{-1}	
F(000)	1024	
Crystal size	0.200 x 0.180 x 0.060 mm^3	
Theta range for data collection	2.265 to 27.130°.	
Index ranges	-10<=h<=10, -28<=k<=27, -20<=l<=20	
Reflections collected	60597	
Independent reflections	6043 [R(int) = 0.0960]	
Completeness to theta = 25.242°	99.8 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.992 and 0.973	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	6043 / 0 / 324	
Goodness-of-fit on F^2	1.150	
Final R indices [I>2sigma(I)]	R1 = 0.0861, wR2 = 0.2213	
R indices (all data)	R1 = 0.1264, wR2 = 0.2442	

Extinction coefficient	n/a
Largest diff. peak and hole	0.854 and -1.096 e.Å^{-3}

Table S88. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^{2}x 10^3) for **6a**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
B(1)	4588(4)	7327(2)	5382(2)	29(1)
S(1)	6085(2)	5562(1)	7585(1)	79(1)
N(1)	-57(4)	5744(1)	3224(2)	43(1)
C(1)	3375(4)	6864(1)	4854(2)	30(1)
C(2)	3097(4)	6240(1)	5051(2)	28(1)
C(3)	1962(4)	5879(1)	4507(2)	33(1)
C(4)	1091(4)	6104(1)	3736(2)	32(1)
C(5)	1400(4)	6714(1)	3529(2)	37(1)
C(6)	2473(4)	7069(1)	4078(2)	36(1)
C(7)	3955(4)	5968(1)	5844(2)	32(1)
C(8)	4257(4)	5378(1)	5996(2)	34(1)
C(9)	5125(4)	5122(1)	6784(2)	33(1)
C(10)	5214(4)	4453(1)	7015(2)	32(1)
C(11)	6254(5)	4423(2)	7832(3)	57(1)
C(12)	6749(6)	4960(2)	8187(2)	62(1)
C(13)	-159(6)	5097(2)	3379(3)	57(1)
C(14)	-919(5)	5975(2)	2425(3)	59(1)
C(15)	6277(4)	7129(1)	5981(2)	30(1)
C(16)	6629(4)	7322(1)	6837(2)	34(1)
C(17)	5391(5)	7716(2)	7227(2)	56(1)
C(18)	8102(4)	7125(1)	7352(2)	38(1)
C(19)	9287(4)	6744(1)	7060(2)	39(1)
C(20)	10881(5)	6537(2)	7630(3)	62(1)
C(21)	8955(4)	6567(1)	6218(2)	35(1)
C(22)	7503(4)	6744(1)	5682(2)	31(1)
C(23)	7316(5)	6526(2)	4780(2)	49(1)
C(24)	4038(4)	8027(1)	5238(2)	30(1)
C(25)	2413(4)	8226(1)	5378(2)	33(1)
C(26)	1251(5)	7819(2)	5811(3)	50(1)
C(27)	1821(4)	8808(1)	5123(2)	38(1)
C(28)	2786(5)	9203(1)	4717(2)	40(1)
C(29)	2085(6)	9814(2)	4375(3)	62(1)
C(30)	4393(5)	9014(2)	4603(2)	43(1)
C(31)	5048(4)	8439(2)	4858(2)	38(1)
C(32)	6805(5)	8275(2)	4685(3)	70(1)

Table S89. Bond lengths [Å] and angles [°] for **6a**.

B(1)-C(1)	1.554(4)	C(1)-C(6)	1.409(4)
B(1)-C(15)	1.583(4)	C(1)-C(2)	1.423(4)
B(1)-C(24)	1.598(4)	C(2)-C(3)	1.397(4)
S(1)-C(12)	1.668(4)	C(2)-C(7)	1.471(4)
S(1)-C(9)	1.689(3)	C(3)-C(4)	1.408(4)
N(1)-C(4)	1.375(4)	C(3)-H(3)	0.9400
N(1)-C(13)	1.439(5)	C(4)-C(5)	1.404(4)
N(1)-C(14)	1.446(5)	C(5)-C(6)	1.368(4)

C(5)-H(5)	0.9400	C(32)-H(32B)	0.9700
C(6)-H(6)	0.9400	C(32)-H(32C)	0.9700
C(7)-C(8)	1.327(4)	C(1)-B(1)-C(15)	123.2(3)
C(7)-H(7)	0.9400	C(1)-B(1)-C(24)	114.4(3)
C(8)-C(9)	1.454(4)	C(15)-B(1)-C(24)	122.4(3)
C(8)-H(8)	0.9400	C(12)-S(1)-C(9)	93.17(19)
C(9)-C(10)	1.507(4)	C(4)-N(1)-C(13)	120.6(3)
C(10)-C(11)	1.437(5)	C(4)-N(1)-C(14)	120.5(3)
C(10)-H(10A)	0.9400	C(13)-N(1)-C(14)	117.6(3)
C(11)-C(12)	1.337(6)	C(6)-C(1)-C(2)	115.2(3)
C(11)-H(11)	0.9400	C(6)-C(1)-B(1)	117.4(3)
C(12)-H(12)	0.9400	C(2)-C(1)-B(1)	127.4(3)
C(13)-H(13A)	0.9700	C(3)-C(2)-C(1)	120.7(3)
C(13)-H(13B)	0.9700	C(3)-C(2)-C(7)	118.6(3)
C(13)-H(13C)	0.9700	C(1)-C(2)-C(7)	120.8(3)
C(14)-H(14A)	0.9700	C(2)-C(3)-C(4)	122.2(3)
C(14)-H(14B)	0.9700	C(2)-C(3)-H(3)	118.9
C(14)-H(14C)	0.9700	C(4)-C(3)-H(3)	118.9
C(15)-C(16)	1.420(4)	N(1)-C(4)-C(5)	121.8(3)
C(15)-C(22)	1.421(4)	N(1)-C(4)-C(3)	120.9(3)
C(16)-C(18)	1.391(5)	C(5)-C(4)-C(3)	117.3(3)
C(16)-C(17)	1.509(5)	C(6)-C(5)-C(4)	120.1(3)
C(17)-H(17A)	0.9700	C(6)-C(5)-H(5)	120.0
C(17)-H(17B)	0.9700	C(4)-C(5)-H(5)	120.0
C(17)-H(17C)	0.9700	C(5)-C(6)-C(1)	124.6(3)
C(18)-C(19)	1.388(5)	C(5)-C(6)-H(6)	117.7
C(18)-H(18)	0.9400	C(1)-C(6)-H(6)	117.7
C(19)-C(21)	1.389(5)	C(8)-C(7)-C(2)	126.8(3)
C(19)-C(20)	1.510(5)	C(8)-C(7)-H(7)	116.6
C(20)-H(20A)	0.9700	C(2)-C(7)-H(7)	116.6
C(20)-H(20B)	0.9700	C(7)-C(8)-C(9)	125.6(3)
C(20)-H(20C)	0.9700	C(7)-C(8)-H(8)	117.2
C(21)-C(22)	1.382(4)	C(9)-C(8)-H(8)	117.2
C(21)-H(21)	0.9400	C(8)-C(9)-C(10)	125.8(3)
C(22)-C(23)	1.507(4)	C(8)-C(9)-S(1)	122.6(2)
C(23)-H(23A)	0.9700	C(10)-C(9)-S(1)	111.6(2)
C(23)-H(23B)	0.9700	C(11)-C(10)-C(9)	105.5(3)
C(23)-H(23C)	0.9700	C(11)-C(10)-H(10A)	127.3
C(24)-C(31)	1.402(4)	C(9)-C(10)-H(10A)	127.3
C(24)-C(25)	1.410(4)	C(12)-C(11)-C(10)	116.0(3)
C(25)-C(27)	1.394(4)	C(12)-C(11)-H(11)	122.0
C(25)-C(26)	1.521(5)	C(10)-C(11)-H(11)	122.0
C(26)-H(26A)	0.9700	C(11)-C(12)-S(1)	113.6(3)
C(26)-H(26B)	0.9700	C(11)-C(12)-H(12)	123.2
C(26)-H(26C)	0.9700	S(1)-C(12)-H(12)	123.2
C(27)-C(28)	1.379(5)	N(1)-C(13)-H(13A)	109.5
C(27)-H(27)	0.9400	N(1)-C(13)-H(13B)	109.5
C(28)-C(30)	1.377(5)	H(13A)-C(13)-H(13B)	109.5
C(28)-C(29)	1.517(5)	N(1)-C(13)-H(13C)	109.5
C(29)-H(29A)	0.9700	H(13A)-C(13)-H(13C)	109.5
C(29)-H(29B)	0.9700	H(13B)-C(13)-H(13C)	109.5
C(29)-H(29C)	0.9700	N(1)-C(14)-H(14A)	109.5
C(30)-C(31)	1.397(5)	N(1)-C(14)-H(14B)	109.5
C(30)-H(30)	0.9400	H(14A)-C(14)-H(14B)	109.5
C(31)-C(32)	1.504(5)	N(1)-C(14)-H(14C)	109.5
C(32)-H(32A)	0.9700	H(14A)-C(14)-H(14C)	109.5

H(14B)-C(14)-H(14C)	109.5	C(31)-C(24)-C(25)	117.8(3)
C(16)-C(15)-C(22)	117.2(3)	C(31)-C(24)-B(1)	121.1(3)
C(16)-C(15)-B(1)	121.8(3)	C(25)-C(24)-B(1)	120.5(3)
C(22)-C(15)-B(1)	121.0(3)	C(27)-C(25)-C(24)	120.6(3)
C(18)-C(16)-C(15)	120.3(3)	C(27)-C(25)-C(26)	117.8(3)
C(18)-C(16)-C(17)	118.1(3)	C(24)-C(25)-C(26)	121.6(3)
C(15)-C(16)-C(17)	121.6(3)	C(25)-C(26)-H(26A)	109.5
C(16)-C(17)-H(17A)	109.5	C(25)-C(26)-H(26B)	109.5
C(16)-C(17)-H(17B)	109.5	H(26A)-C(26)-H(26B)	109.5
H(17A)-C(17)-H(17B)	109.5	C(25)-C(26)-H(26C)	109.5
C(16)-C(17)-H(17C)	109.5	H(26A)-C(26)-H(26C)	109.5
H(17A)-C(17)-H(17C)	109.5	H(26B)-C(26)-H(26C)	109.5
H(17B)-C(17)-H(17C)	109.5	C(28)-C(27)-C(25)	121.5(3)
C(19)-C(18)-C(16)	122.4(3)	C(28)-C(27)-H(27)	119.2
C(19)-C(18)-H(18)	118.8	C(25)-C(27)-H(27)	119.2
C(16)-C(18)-H(18)	118.8	C(30)-C(28)-C(27)	117.7(3)
C(18)-C(19)-C(21)	117.2(3)	C(30)-C(28)-C(29)	120.8(3)
C(18)-C(19)-C(20)	121.5(3)	C(27)-C(28)-C(29)	121.5(3)
C(21)-C(19)-C(20)	121.3(3)	C(28)-C(29)-H(29A)	109.5
C(19)-C(20)-H(20A)	109.5	C(28)-C(29)-H(29B)	109.5
C(19)-C(20)-H(20B)	109.5	H(29A)-C(29)-H(29B)	109.5
H(20A)-C(20)-H(20B)	109.5	C(28)-C(29)-H(29C)	109.5
C(19)-C(20)-H(20C)	109.5	H(29A)-C(29)-H(29C)	109.5
H(20A)-C(20)-H(20C)	109.5	H(29B)-C(29)-H(29C)	109.5
H(20B)-C(20)-H(20C)	109.5	C(28)-C(30)-C(31)	122.7(3)
C(22)-C(21)-C(19)	122.7(3)	C(28)-C(30)-H(30)	118.6
C(22)-C(21)-H(21)	118.6	C(31)-C(30)-H(30)	118.6
C(19)-C(21)-H(21)	118.6	C(30)-C(31)-C(24)	119.5(3)
C(21)-C(22)-C(15)	120.3(3)	C(30)-C(31)-C(32)	118.3(3)
C(21)-C(22)-C(23)	117.2(3)	C(24)-C(31)-C(32)	122.2(3)
C(15)-C(22)-C(23)	122.5(3)	C(31)-C(32)-H(32A)	109.5
C(22)-C(23)-H(23A)	109.5	C(31)-C(32)-H(32B)	109.5
C(22)-C(23)-H(23B)	109.5	H(32A)-C(32)-H(32B)	109.5
H(23A)-C(23)-H(23B)	109.5	C(31)-C(32)-H(32C)	109.5
C(22)-C(23)-H(23C)	109.5	H(32A)-C(32)-H(32C)	109.5
H(23A)-C(23)-H(23C)	109.5	H(32B)-C(32)-H(32C)	109.5
H(23B)-C(23)-H(23C)	109.5		

Table S90. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for **6a**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
B(1)	32(2)	30(2)	26(2)	2(1)	6(1)	-1(1)
S(1)	125(1)	51(1)	52(1)	1(1)	-14(1)	7(1)
N(1)	46(2)	39(2)	41(2)	-9(1)	-5(1)	-6(1)
C(1)	32(2)	29(2)	28(1)	0(1)	0(1)	1(1)
C(2)	29(2)	27(1)	29(1)	-2(1)	6(1)	0(1)
C(3)	37(2)	26(2)	36(2)	-1(1)	8(1)	-1(1)
C(4)	30(2)	34(2)	31(2)	-7(1)	2(1)	1(1)
C(5)	41(2)	34(2)	31(2)	0(1)	-7(1)	6(1)
C(6)	41(2)	29(2)	37(2)	4(1)	-3(1)	1(1)
C(7)	34(2)	30(2)	30(2)	0(1)	3(1)	-4(1)
C(8)	38(2)	31(2)	34(2)	2(1)	4(1)	1(1)

C(9)	37(2)	30(2)	34(2)	4(1)	6(1)	2(1)
C(10)	43(2)	21(1)	26(1)	-1(1)	-15(1)	19(1)
C(11)	59(2)	42(2)	68(3)	20(2)	3(2)	10(2)
C(12)	76(3)	69(3)	35(2)	1(2)	-8(2)	21(2)
C(13)	62(3)	43(2)	61(2)	-10(2)	-2(2)	-17(2)
C(14)	60(3)	57(2)	52(2)	-11(2)	-20(2)	-4(2)
C(15)	32(2)	28(1)	30(2)	-1(1)	3(1)	-4(1)
C(16)	40(2)	30(2)	31(2)	-4(1)	2(1)	-5(1)
C(17)	57(2)	70(3)	40(2)	-20(2)	3(2)	7(2)
C(18)	47(2)	36(2)	28(2)	0(1)	-6(1)	-9(1)
C(19)	40(2)	31(2)	43(2)	6(1)	-9(1)	-5(1)
C(20)	60(3)	50(2)	64(3)	2(2)	-26(2)	6(2)
C(21)	30(2)	28(2)	46(2)	0(1)	1(1)	-1(1)
C(22)	33(2)	29(2)	32(2)	0(1)	3(1)	-4(1)
C(23)	40(2)	64(2)	42(2)	-15(2)	5(2)	9(2)
C(24)	32(2)	27(1)	28(1)	-1(1)	-3(1)	-5(1)
C(25)	34(2)	28(2)	36(2)	-1(1)	-1(1)	-3(1)
C(26)	41(2)	42(2)	71(3)	8(2)	18(2)	0(2)
C(27)	38(2)	34(2)	38(2)	-6(1)	-5(1)	5(1)
C(28)	56(2)	27(2)	32(2)	0(1)	-9(2)	-2(1)
C(29)	87(3)	33(2)	59(2)	9(2)	-8(2)	7(2)
C(30)	52(2)	34(2)	42(2)	7(1)	2(2)	-12(2)
C(31)	37(2)	36(2)	40(2)	5(1)	0(1)	-7(1)
C(32)	51(2)	66(3)	101(4)	28(3)	31(2)	-2(2)

Table S91. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for 6a.

	x	y	z	U(eq)
H(3)	1773	5472	4661	40
H(5)	870	6878	3012	44
H(6)	2618	7480	3928	44
H(7)	4327	6240	6288	38
H(8)	3878	5102	5556	41
H(10A)	4697	4125	6692	38
H(11)	6567	4048	8099	69
H(12)	7408	4994	8726	74
H(13A)	-995	4913	2946	85
H(13B)	-499	5031	3929	85
H(13C)	948	4911	3367	85
H(14A)	-97	6031	2040	89
H(14B)	-1455	6363	2514	89
H(14C)	-1784	5684	2184	89
H(17A)	5092	8072	6873	84
H(17B)	5918	7847	7785	84
H(17C)	4369	7482	7272	84
H(18)	8302	7255	7919	45
H(20A)	11349	6181	7385	93
H(20B)	10601	6433	8181	93
H(20C)	11718	6865	7688	93
H(21)	9751	6315	6004	42
H(23A)	6538	6794	4423	73
H(23B)	6868	6112	4744	73

H(23C)	8423	6532	4591	73
H(26A)	436	7616	5388	76
H(26B)	645	8067	6171	76
H(26C)	1933	7515	6152	76
H(27)	741	8934	5230	46
H(29A)	3023	10094	4344	93
H(29B)	1346	9982	4749	93
H(29C)	1438	9758	3816	93
H(30)	5077	9283	4342	52
H(32A)	6741	7909	4339	105
H(32B)	7546	8200	5216	105
H(32C)	7259	8609	4389	105

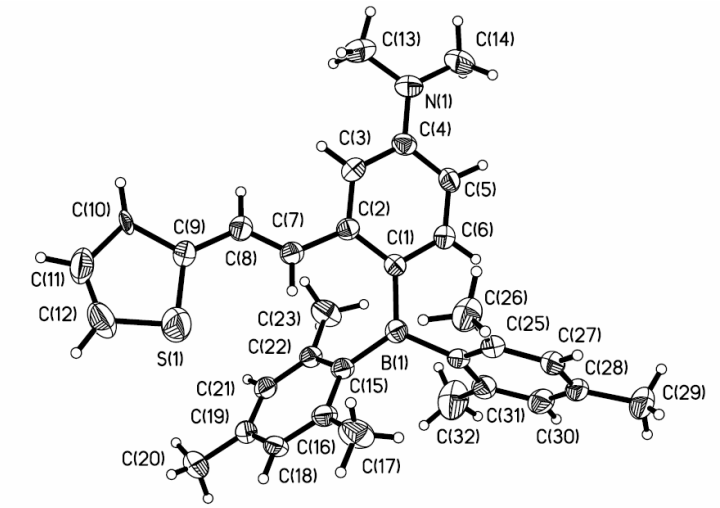


Figure S155. Structure of **6a**.

Table S92. Crystal data and structure refinement for **7a**.

Identification code	**7a**	
Empirical formula	C32 H36 B N S	
Formula weight	477.49	
Temperature	220(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	$P2_1/c$	
Unit cell dimensions	a = 7.9779(4) Å	α= 90°.
	b = 21.8456(11) Å	β= 98.411(2)°.
	c = 15.7662(8) Å	γ = 90°.
Volume	2718.2(2) $Å^3$	
Z	4	
Density (calculated)	1.167 Mg/m^3	
Absorption coefficient	0.140 mm^{-1}	
F(000)	1024	
Crystal size	0.300 x 0.220 x 0.100 mm^3	
Theta range for data collection	2.581 to 27.168°.	
Index ranges	-10<=h<=9, -28<=k<=28, -19<=l<=20	
Reflections collected	27885	
Independent reflections	6016 [R(int) = 0.1047]	
Completeness to theta = 25.242°	99.9 %	

Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.968 and 0.959
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	6016 / 0 / 348
Goodness-of-fit on F^2	1.019
Final R indices [I>2sigma(I)]	R1 = 0.0642, wR2 = 0.1418
R indices (all data)	R1 = 0.1222, wR2 = 0.1665
Extinction coefficient	n/a
Largest diff. peak and hole	0.228 and -0.277 e.$Å^{-3}$

Table S93. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for **7a**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
S(1)	2841(6)	5037(2)	1722(3)	43(1)
S(1A)	3667(3)	4340(1)	2096(1)	53(1)
C(1)	6644(3)	6869(1)	5120(1)	30(1)
N(1)	10068(3)	5747(1)	6749(1)	44(1)
B(1)	5447(3)	7334(1)	4591(2)	31(1)
C(2)	6904(3)	6243(1)	4920(1)	29(1)
C(6)	7560(3)	7074(1)	5901(2)	36(1)
C(5)	8629(3)	6716(1)	6449(2)	37(1)
C(4)	8924(3)	6106(1)	6235(1)	33(1)
C(3)	8033(3)	5886(1)	5464(2)	32(1)
C(7)	6034(3)	5973(1)	4121(2)	32(1)
C(9)	4779(3)	5131(1)	3184(1)	33(1)
C(8)	5680(3)	5385(1)	3979(2)	36(1)
C(10)	3815(4)	5463(1)	2533(2)	49(1)
C(11)	4726(4)	4511(1)	2978(2)	52(1)
C(12)	3670(30)	4381(12)	2083(14)	214(9)
C(12A)	3200(20)	5071(10)	1843(13)	64(6)
C(13)	10195(4)	5102(1)	6582(2)	54(1)
C(14)	10954(3)	5982(1)	7547(2)	55(1)
C(15)	5987(3)	8030(1)	4740(1)	31(1)
C(16)	4973(3)	8446(1)	5119(2)	38(1)
C(17)	3204(4)	8283(1)	5277(2)	69(1)
C(18)	5614(3)	9018(1)	5386(2)	43(1)
C(19)	7214(3)	9208(1)	5280(2)	38(1)
C(20)	7896(4)	9820(1)	5625(2)	58(1)
C(21)	8177(3)	8810(1)	4869(2)	38(1)
C(22)	8752(3)	7831(1)	4164(2)	50(1)
C(23)	7602(3)	8231(1)	4604(1)	33(1)
C(24)	3759(3)	7133(1)	3994(1)	30(1)
C(25)	2543(3)	6754(1)	4307(1)	33(1)
C(26)	2728(3)	6539(1)	5226(2)	49(1)
C(27)	1093(3)	6571(1)	3770(2)	36(1)
C(28)	768(3)	6744(1)	2920(2)	39(1)
C(29)	-807(4)	6535(1)	2350(2)	64(1)
C(30)	1945(3)	7120(1)	2612(2)	40(1)
C(31)	3413(3)	7316(1)	3129(2)	34(1)
C(32)	4638(3)	7707(1)	2724(2)	54(1)

Table S94. Bond lengths [Å] and angles [°] for **7a**.

S(1)-C(12)	1.64(3)	C(23)-C(22)	1.508(3)
S(1)-C(10)	1.676(5)	C(24)-C(31)	1.410(3)
S(1A)-C(11)	1.564(4)	C(24)-C(25)	1.418(3)
S(1A)-C(12A)	1.67(2)	C(25)-C(27)	1.388(3)
C(1)-C(6)	1.409(3)	C(25)-C(26)	1.509(3)
C(1)-C(2)	1.426(3)	C(26)-H(26A)	0.9700
C(1)-B(1)	1.552(3)	C(26)-H(26B)	0.9700
N(1)-C(4)	1.373(3)	C(26)-H(26C)	0.9700
N(1)-C(13)	1.440(3)	C(27)-C(28)	1.380(3)
N(1)-C(14)	1.443(3)	C(27)-H(27A)	0.9400
B(1)-C(24)	1.587(3)	C(28)-C(30)	1.388(3)
B(1)-C(15)	1.589(3)	C(28)-C(29)	1.506(3)
C(2)-C(3)	1.389(3)	C(29)-H(29A)	0.9700
C(2)-C(7)	1.470(3)	C(29)-H(29B)	0.9700
C(6)-C(5)	1.369(3)	C(29)-H(29C)	0.9700
C(6)-H(6A)	0.9400	C(30)-C(31)	1.393(3)
C(5)-C(4)	1.403(3)	C(30)-H(30A)	0.9400
C(5)-H(5A)	0.9400	C(31)-C(32)	1.508(3)
C(4)-C(3)	1.400(3)	C(32)-H(32A)	0.9700
C(3)-H(3A)	0.9400	C(32)-H(32B)	0.9700
C(7)-C(8)	1.328(3)	C(32)-H(32C)	0.9700
C(7)-H(7A)	0.9400	C(22)-H(22A)	0.9700
C(9)-C(11)	1.392(3)	C(22)-H(22B)	0.9700
C(9)-C(10)	1.393(3)	C(22)-H(22C)	0.9700
C(9)-C(8)	1.459(3)	C(12)-S(1)-C(10)	95.9(8)
C(8)-H(8A)	0.9400	C(11)-S(1A)-C(12A)	93.2(6)
C(10)-C(12A)	1.413(18)	C(6)-C(1)-C(2)	115.15(19)
C(10)-H(10A)	0.92(3)	C(6)-C(1)-B(1)	117.5(2)
C(11)-C(12)	1.56(2)	C(2)-C(1)-B(1)	127.3(2)
C(11)-H(11A)	0.91(3)	C(4)-N(1)-C(13)	120.5(2)
C(12)-H(12B)	0.9400	C(4)-N(1)-C(14)	120.7(2)
C(12A)-H(12A)	0.9400	C(13)-N(1)-C(14)	117.9(2)
C(13)-H(13A)	0.9700	C(1)-B(1)-C(24)	122.7(2)
C(13)-H(13B)	0.9700	C(1)-B(1)-C(15)	114.47(19)
C(13)-H(13C)	0.9700	C(24)-B(1)-C(15)	122.73(19)
C(14)-H(14A)	0.9700	C(3)-C(2)-C(1)	120.3(2)
C(14)-H(14B)	0.9700	C(3)-C(2)-C(7)	119.1(2)
C(14)-H(14C)	0.9700	C(1)-C(2)-C(7)	120.64(19)
C(15)-C(16)	1.406(3)	C(5)-C(6)-C(1)	124.4(2)
C(15)-C(23)	1.406(3)	C(5)-C(6)-H(6A)	117.8
C(16)-C(18)	1.393(3)	C(1)-C(6)-H(6A)	117.8
C(16)-C(17)	1.511(4)	C(6)-C(5)-C(4)	120.1(2)
C(17)-H(17A)	0.9700	C(6)-C(5)-H(5A)	119.9
C(17)-H(17B)	0.9700	C(4)-C(5)-H(5A)	119.9
C(17)-H(17C)	0.9700	N(1)-C(4)-C(3)	121.8(2)
C(18)-C(19)	1.376(3)	N(1)-C(4)-C(5)	121.3(2)
C(18)-H(18A)	0.9400	C(3)-C(4)-C(5)	116.9(2)
C(19)-C(21)	1.383(3)	C(2)-C(3)-C(4)	123.0(2)
C(19)-C(20)	1.514(3)	C(2)-C(3)-H(3A)	118.5
C(20)-H(20A)	0.9700	C(4)-C(3)-H(3A)	118.5
C(20)-H(20B)	0.9700	C(8)-C(7)-C(2)	126.5(2)
C(20)-H(20C)	0.9700	C(8)-C(7)-H(7A)	116.7
C(21)-C(23)	1.388(3)	C(2)-C(7)-H(7A)	116.7
C(21)-H(21A)	0.9400	C(11)-C(9)-C(10)	109.8(2)

C(11)-C(9)-C(8)	124.4(2)	H(20A)-C(20)-H(20B)	109.5
C(10)-C(9)-C(8)	125.8(2)	C(19)-C(20)-H(20C)	109.5
C(7)-C(8)-C(9)	125.3(2)	H(20A)-C(20)-H(20C)	109.5
C(7)-C(8)-H(8A)	117.3	H(20B)-C(20)-H(20C)	109.5
C(9)-C(8)-H(8A)	117.3	C(19)-C(21)-C(23)	122.1(2)
C(9)-C(10)-C(12A)	110.1(9)	C(19)-C(21)-H(21A)	118.9
C(9)-C(10)-S(1)	114.7(3)	C(23)-C(21)-H(21A)	118.9
C(9)-C(10)-H(10A)	127.4(16)	C(21)-C(23)-C(15)	120.6(2)
C(12A)-C(10)-H(10A)	122.5(19)	C(21)-C(23)-C(22)	118.0(2)
S(1)-C(10)-H(10A)	117.8(16)	C(15)-C(23)-C(22)	121.5(2)
C(9)-C(11)-C(12)	112.4(10)	C(31)-C(24)-C(25)	117.07(19)
C(9)-C(11)-S(1A)	115.7(2)	C(31)-C(24)-B(1)	121.6(2)
C(9)-C(11)-H(11A)	123.6(17)	C(25)-C(24)-B(1)	121.33(19)
C(12)-C(11)-H(11A)	123.9(19)	C(27)-C(25)-C(24)	120.5(2)
S(1A)-C(11)-H(11A)	120.6(17)	C(27)-C(25)-C(26)	116.9(2)
C(11)-C(12)-S(1)	106.9(14)	C(24)-C(25)-C(26)	122.6(2)
C(11)-C(12)-H(12B)	126.6	C(25)-C(26)-H(26A)	109.5
S(1)-C(12)-H(12B)	126.6	C(25)-C(26)-H(26B)	109.5
C(10)-C(12A)-S(1A)	110.8(13)	H(26A)-C(26)-H(26B)	109.5
C(10)-C(12A)-H(12A)	124.6	C(25)-C(26)-H(26C)	109.5
S(1A)-C(12A)-H(12A)	124.6	H(26A)-C(26)-H(26C)	109.5
N(1)-C(13)-H(13A)	109.5	H(26B)-C(26)-H(26C)	109.5
N(1)-C(13)-H(13B)	109.5	C(28)-C(27)-C(25)	122.4(2)
H(13A)-C(13)-H(13B)	109.5	C(28)-C(27)-H(27A)	118.8
N(1)-C(13)-H(13C)	109.5	C(25)-C(27)-H(27A)	118.8
H(13A)-C(13)-H(13C)	109.5	C(27)-C(28)-C(30)	117.5(2)
H(13B)-C(13)-H(13C)	109.5	C(27)-C(28)-C(29)	121.3(2)
N(1)-C(14)-H(14A)	109.5	C(30)-C(28)-C(29)	121.3(2)
N(1)-C(14)-H(14B)	109.5	C(28)-C(29)-H(29A)	109.5
H(14A)-C(14)-H(14B)	109.5	C(28)-C(29)-H(29B)	109.5
N(1)-C(14)-H(14C)	109.5	H(29A)-C(29)-H(29B)	109.5
H(14A)-C(14)-H(14C)	109.5	C(28)-C(29)-H(29C)	109.5
H(14B)-C(14)-H(14C)	109.5	H(29A)-C(29)-H(29C)	109.5
C(16)-C(15)-C(23)	117.4(2)	H(29B)-C(29)-H(29C)	109.5
C(16)-C(15)-B(1)	121.3(2)	C(28)-C(30)-C(31)	122.1(2)
C(23)-C(15)-B(1)	120.72(19)	C(28)-C(30)-H(30A)	119.0
C(18)-C(16)-C(15)	120.0(2)	C(31)-C(30)-H(30A)	119.0
C(18)-C(16)-C(17)	118.2(2)	C(30)-C(31)-C(24)	120.5(2)
C(15)-C(16)-C(17)	121.8(2)	C(30)-C(31)-C(32)	117.9(2)
C(16)-C(17)-H(17A)	109.5	C(24)-C(31)-C(32)	121.5(2)
C(16)-C(17)-H(17B)	109.5	C(31)-C(32)-H(32A)	109.5
H(17A)-C(17)-H(17B)	109.5	C(31)-C(32)-H(32B)	109.5
C(16)-C(17)-H(17C)	109.5	H(32A)-C(32)-H(32B)	109.5
H(17A)-C(17)-H(17C)	109.5	C(31)-C(32)-H(32C)	109.5
H(17B)-C(17)-H(17C)	109.5	H(32A)-C(32)-H(32C)	109.5
C(19)-C(18)-C(16)	122.7(2)	H(32B)-C(32)-H(32C)	109.5
C(19)-C(18)-H(18A)	118.7	C(23)-C(22)-H(22A)	109.5
C(16)-C(18)-H(18A)	118.7	C(23)-C(22)-H(22B)	109.5
C(18)-C(19)-C(21)	117.2(2)	H(22A)-C(22)-H(22B)	109.5
C(18)-C(19)-C(20)	120.9(2)	C(23)-C(22)-H(22C)	109.5
C(21)-C(19)-C(20)	121.9(2)	H(22A)-C(22)-H(22C)	109.5
C(19)-C(20)-H(20A)	109.5	H(22B)-C(22)-H(22C)	109.5
C(19)-C(20)-H(20B)	109.5		

Table S95. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for **7a**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + ... \quad + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
S(1)	50(1)	45(1)	31(1)	-4(1)	-6(1)	-6(1)
S(1A)	66(1)	40(1)	49(1)	-7(1)	-5(1)	-7(1)
C(1)	33(1)	30(1)	27(1)	0(1)	0(1)	-2(1)
N(1)	49(1)	39(1)	39(1)	7(1)	-6(1)	8(1)
B(1)	36(1)	32(1)	25(1)	-1(1)	8(1)	3(1)
C(2)	32(1)	29(1)	27(1)	1(1)	5(1)	-1(1)
C(6)	42(1)	29(1)	35(1)	-2(1)	-2(1)	-2(1)
C(5)	43(1)	34(1)	30(1)	1(1)	-6(1)	-4(1)
C(4)	32(1)	35(1)	31(1)	8(1)	3(1)	0(1)
C(3)	37(1)	28(1)	33(1)	0(1)	7(1)	3(1)
C(7)	37(1)	31(1)	30(1)	-1(1)	3(1)	4(1)
C(9)	36(1)	34(1)	30(1)	-3(1)	5(1)	-3(1)
C(8)	42(1)	33(1)	31(1)	1(1)	2(1)	0(1)
C(10)	63(2)	36(1)	42(2)	-2(1)	-9(1)	-1(1)
C(11)	66(2)	30(1)	54(2)	-2(1)	-10(2)	-1(1)
C(12)	190(20)	320(30)	140(19)	-6(18)	51(16)	-18(19)
C(12A)	74(11)	63(7)	48(8)	23(6)	-19(6)	-20(6)
C(13)	58(2)	47(2)	54(2)	9(1)	1(1)	17(1)
C(14)	54(2)	57(2)	48(2)	10(1)	-16(1)	5(1)
C(15)	33(1)	30(1)	28(1)	2(1)	-2(1)	5(1)
C(16)	38(1)	34(1)	43(2)	-2(1)	3(1)	6(1)
C(17)	50(2)	58(2)	106(3)	-22(2)	31(2)	1(1)
C(18)	52(2)	35(1)	41(2)	-6(1)	4(1)	13(1)
C(19)	49(2)	28(1)	34(1)	0(1)	-10(1)	4(1)
C(20)	75(2)	35(1)	58(2)	-7(1)	-11(2)	-2(1)
C(21)	38(1)	35(1)	38(1)	5(1)	-3(1)	-1(1)
C(23)	34(1)	30(1)	32(1)	2(1)	-2(1)	3(1)
C(24)	33(1)	27(1)	28(1)	0(1)	1(1)	4(1)
C(25)	34(1)	32(1)	31(1)	0(1)	1(1)	4(1)
C(26)	49(2)	61(2)	37(2)	10(1)	5(1)	-8(1)
C(27)	33(1)	30(1)	43(2)	1(1)	2(1)	1(1)
C(28)	40(1)	31(1)	41(2)	-5(1)	-8(1)	6(1)
C(29)	63(2)	56(2)	62(2)	-3(2)	-28(2)	-6(2)
C(30)	49(1)	38(1)	28(1)	1(1)	-6(1)	9(1)
C(31)	39(1)	32(1)	31(1)	4(1)	0(1)	6(1)
C(32)	58(2)	66(2)	37(2)	18(1)	3(1)	-7(1)
C(22)	40(1)	44(2)	68(2)	-6(1)	18(1)	-1(1)

Table S96. Hydrogen coordinates ($x\ 10^4$) and isotropic displacement parameters ($Å^2 x\ 10^3$) for **7a**.

	x	y	z	U(eq)
H(6A)	7427	7485	6055	43
H(5A)	9166	6878	6971	44
H(3A)	8207	5478	5307	39
H(7A)	5694	6244	3665	39
H(8A)	6039	5109	4427	43
H(10A)	3610(30)	5875(12)	2519(16)	50

H(11A)	5210(30)	4213(12)	3339(17)	50
H(12B)	3525	4001	1803	257
H(12A)	2617	5203	1314	77
H(13A)	10524	5043	6019	81
H(13B)	9107	4909	6601	81
H(13C)	11041	4920	7013	81
H(14A)	11412	6383	7452	83
H(14B)	11870	5706	7762	83
H(14C)	10173	6013	7962	83
H(17A)	2704	8630	5531	104
H(17B)	3255	7936	5664	104
H(17C)	2516	8177	4737	104
H(18A)	4925	9285	5651	52
H(20A)	7021	10037	5870	87
H(20B)	8240	10060	5163	87
H(20C)	8865	9754	6064	87
H(21A)	9256	8935	4765	45
H(26A)	1666	6599	5445	74
H(26B)	3614	6773	5569	74
H(26C)	3024	6109	5254	74
H(27A)	304	6321	3994	43
H(29A)	-614	6543	1756	96
H(29B)	-1740	6805	2421	96
H(29C)	-1082	6121	2503	96
H(30A)	1745	7246	2036	48
H(32A)	4098	7848	2167	81
H(32B)	5634	7468	2657	81
H(32C)	4969	8058	3089	81
H(22A)	9376	8083	3811	75
H(22B)	8079	7533	3806	75
H(22C)	9543	7620	4591	75

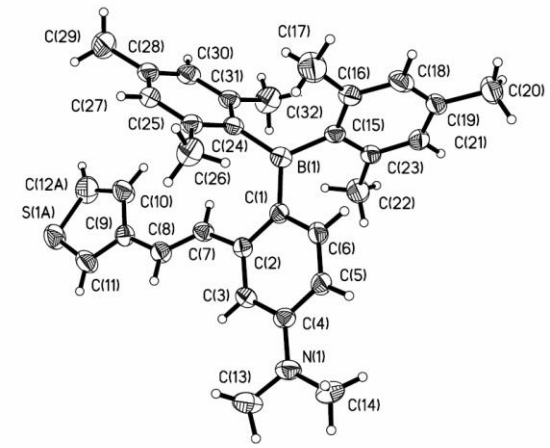


Figure S156. Structure of **7a**.

Table S97. Crystal data and structure refinement for **9a**.

Identification code	**9a**
Empirical formula	C34 H39 B N2
Formula weight	486.48
Temperature	180(2) K
Wavelength	0.71073 Å

Crystal system	Monoclinic	
Space group	$P2_1/n$	
Unit cell dimensions	a = 8.410(5) Å	α= 90°.
	b = 34.22(2) Å	β= 97.87(2)°.
	c = 10.140(7) Å	γ = 90°.
Volume	2891(3) $Å^3$	
Z	4	
Density (calculated)	1.118 Mg/m^3	
Absorption coefficient	0.064 mm^{-1}	
F(000)	1048	
Crystal size	0.260 x 0.210 x 0.177 mm^3	
Theta range for data collection	2.516 to 27.275°.	
Index ranges	-10<=h<=10, -44<=k<=43, -12<=l<=11	
Reflections collected	28859	
Independent reflections	6298 [R(int) = 0.1426]	
Completeness to theta = 25.242°	99.8 %	
Absorption correction	Multi-sca	
Max. and min. transmission	0.989 and 0.984	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	6298 / 0 / 344	
Goodness-of-fit on F^2	1.030	
Final R indices [I>2sigma(I)]	R1 = 0.0729, wR2 = 0.1755	
R indices (all data)	R1 = 0.1708, wR2 = 0.2124	
Extinction coefficient	0.010(2)	
Largest diff. peak and hole	0.213 and -0.209 $e.Å^{-3}$	

Table S98. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for **9a**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
B(1)	7298(3)	3936(1)	4501(3)	36(1)
N(1)	8197(3)	2630(1)	-114(2)	47(1)
N(2)	10796(3)	3348(1)	8339(3)	64(1)
C(1)	8293(3)	3568(1)	5070(3)	36(1)
C(2)	8960(3)	3588(1)	6413(3)	40(1)
C(3)	10072(3)	3310(1)	7030(3)	42(1)
C(4)	10395(3)	2994(1)	6239(3)	49(1)
C(5)	9688(3)	2960(1)	4932(3)	48(1)
C(6)	8650(3)	3243(1)	4291(3)	38(1)
C(7)	7965(3)	3203(1)	2896(3)	43(1)
C(8)	8330(3)	2945(1)	2001(3)	45(1)
C(9)	7671(3)	2930(1)	580(3)	42(1)
C(10)	6608(3)	3204(1)	-46(3)	55(1)
C(11)	6093(3)	3177(1)	-1396(3)	60(1)
C(12)	6620(3)	2870(1)	-2100(3)	55(1)
C(13)	7668(3)	2602(1)	-1434(3)	50(1)
C(14)	8259(4)	2260(1)	-2155(3)	74(1)
C(15)	11823(4)	3042(1)	8983(3)	76(1)
C(16)	10374(4)	3654(1)	9169(3)	73(1)
C(17)	6088(3)	4124(1)	5387(2)	34(1)
C(18)	4782(3)	3906(1)	5755(2)	37(1)
C(19)	4423(3)	3499(1)	5244(3)	50(1)

C(20)	3734(3)	4073(1)	6545(3)	44(1)
C(21)	3903(3)	4455(1)	6989(3)	48(1)
C(22)	2721(4)	4629(1)	7823(3)	74(1)
C(23)	5174(3)	4665(1)	6621(3)	48(1)
C(24)	6268(3)	4510(1)	5849(3)	40(1)
C(25)	7671(3)	4759(1)	5580(3)	54(1)
C(26)	7578(3)	4118(1)	3110(2)	35(1)
C(27)	6286(3)	4199(1)	2079(3)	42(1)
C(28)	4553(3)	4110(1)	2250(3)	64(1)
C(29)	6592(3)	4348(1)	874(3)	48(1)
C(30)	8137(3)	4441(1)	613(3)	48(1)
C(31)	8414(4)	4619(1)	-701(3)	72(1)
C(32)	9388(3)	4367(1)	1624(3)	46(1)
C(33)	9155(3)	4204(1)	2839(3)	40(1)
C(34)	10629(3)	4134(1)	3857(3)	56(1)

Table S99. Bond lengths [Å] and angles [°] for **9a**.

B(1)-C(1)	1.576(4)	C(16)-H(16B)	0.9800
B(1)-C(17)	1.584(4)	C(16)-H(16C)	0.9800
B(1)-C(26)	1.589(4)	C(17)-C(24)	1.403(3)
N(1)-C(9)	1.353(3)	C(17)-C(18)	1.418(3)
N(1)-C(13)	1.355(4)	C(18)-C(20)	1.393(3)
N(2)-C(3)	1.388(4)	C(18)-C(19)	1.501(4)
N(2)-C(16)	1.421(4)	C(19)-H(19A)	0.9800
N(2)-C(15)	1.453(4)	C(19)-H(19B)	0.9800
C(1)-C(2)	1.402(4)	C(19)-H(19C)	0.9800
C(1)-C(6)	1.419(3)	C(20)-C(21)	1.383(4)
C(2)-C(3)	1.418(3)	C(20)-H(20)	0.9500
C(2)-H(2)	0.9500	C(21)-C(23)	1.380(4)
C(3)-C(4)	1.394(4)	C(21)-C(22)	1.512(4)
C(4)-C(5)	1.381(4)	C(22)-H(22A)	0.9800
C(4)-H(4)	0.9500	C(22)-H(22B)	0.9800
C(5)-C(6)	1.402(3)	C(22)-H(22C)	0.9800
C(5)-H(5)	0.9500	C(23)-C(24)	1.392(3)
C(6)-C(7)	1.459(4)	C(23)-H(23)	0.9500
C(7)-C(8)	1.332(3)	C(24)-C(25)	1.512(3)
C(7)-H(7)	0.9500	C(25)-H(25A)	0.9800
C(8)-C(9)	1.472(4)	C(25)-H(25B)	0.9800
C(8)-H(8)	0.9500	C(25)-H(25C)	0.9800
C(9)-C(10)	1.387(4)	C(26)-C(33)	1.421(3)
C(10)-C(11)	1.381(4)	C(26)-C(27)	1.428(4)
C(10)-H(10)	0.9500	C(27)-C(29)	1.380(4)
C(11)-C(12)	1.377(4)	C(27)-C(28)	1.522(3)
C(11)-H(11)	0.9500	C(28)-H(28A)	0.9800
C(12)-C(13)	1.382(4)	C(28)-H(28B)	0.9800
C(12)-H(12)	0.9500	C(28)-H(28C)	0.9800
C(13)-C(14)	1.501(4)	C(29)-C(30)	1.398(4)
C(14)-H(14A)	0.9800	C(29)-H(29)	0.9500
C(14)-H(14B)	0.9800	C(30)-C(32)	1.388(4)
C(14)-H(14C)	0.9800	C(30)-C(31)	1.513(4)
C(15)-H(15A)	0.9800	C(31)-H(31A)	0.9800
C(15)-H(15B)	0.9800	C(31)-H(31B)	0.9800
C(15)-H(15C)	0.9800	C(31)-H(31C)	0.9800
C(16)-H(16A)	0.9800	C(32)-C(33)	1.391(4)

C(32)-H(32)	0.9500	H(14B)-C(14)-H(14C)	109.5
C(33)-C(34)	1.520(4)	N(2)-C(15)-H(15A)	109.5
C(34)-H(34A)	0.9800	N(2)-C(15)-H(15B)	109.5
C(34)-H(34B)	0.9800	H(15A)-C(15)-H(15B)	109.5
C(34)-H(34C)	0.9800	N(2)-C(15)-H(15C)	109.5
C(1)-B(1)-C(17)	117.8(2)	H(15A)-C(15)-H(15C)	109.5
C(1)-B(1)-C(26)	120.2(2)	H(15B)-C(15)-H(15C)	109.5
C(17)-B(1)-C(26)	121.9(2)	N(2)-C(16)-H(16A)	109.5
C(9)-N(1)-C(13)	118.8(2)	N(2)-C(16)-H(16B)	109.5
C(3)-N(2)-C(16)	121.5(2)	H(16A)-C(16)-H(16B)	109.5
C(3)-N(2)-C(15)	121.2(3)	N(2)-C(16)-H(16C)	109.5
C(16)-N(2)-C(15)	116.5(3)	H(16A)-C(16)-H(16C)	109.5
C(2)-C(1)-C(6)	119.4(2)	H(16B)-C(16)-H(16C)	109.5
C(2)-C(1)-B(1)	116.0(2)	C(24)-C(17)-C(18)	117.3(2)
C(6)-C(1)-B(1)	124.3(2)	C(24)-C(17)-B(1)	121.6(2)
C(1)-C(2)-C(3)	123.2(2)	C(18)-C(17)-B(1)	121.1(2)
C(1)-C(2)-H(2)	118.4	C(20)-C(18)-C(17)	120.6(2)
C(3)-C(2)-H(2)	118.4	C(20)-C(18)-C(19)	117.8(2)
N(2)-C(3)-C(4)	121.8(2)	C(17)-C(18)-C(19)	121.5(2)
N(2)-C(3)-C(2)	122.4(2)	C(18)-C(19)-H(19A)	109.5
C(4)-C(3)-C(2)	115.8(3)	C(18)-C(19)-H(19B)	109.5
C(5)-C(4)-C(3)	121.7(2)	H(19A)-C(19)-H(19B)	109.5
C(5)-C(4)-H(4)	119.2	C(18)-C(19)-H(19C)	109.5
C(3)-C(4)-H(4)	119.2	H(19A)-C(19)-H(19C)	109.5
C(4)-C(5)-C(6)	123.1(3)	H(19B)-C(19)-H(19C)	109.5
C(4)-C(5)-H(5)	118.5	C(21)-C(20)-C(18)	122.1(2)
C(6)-C(5)-H(5)	118.5	C(21)-C(20)-H(20)	119.0
C(5)-C(6)-C(1)	116.6(2)	C(18)-C(20)-H(20)	119.0
C(5)-C(6)-C(7)	121.5(2)	C(23)-C(21)-C(20)	116.9(2)
C(1)-C(6)-C(7)	121.8(2)	C(23)-C(21)-C(22)	122.7(3)
C(8)-C(7)-C(6)	128.7(2)	C(20)-C(21)-C(22)	120.5(3)
C(8)-C(7)-H(7)	115.6	C(21)-C(22)-H(22A)	109.5
C(6)-C(7)-H(7)	115.6	C(21)-C(22)-H(22B)	109.5
C(7)-C(8)-C(9)	126.7(2)	H(22A)-C(22)-H(22B)	109.5
C(7)-C(8)-H(8)	116.6	C(21)-C(22)-H(22C)	109.5
C(9)-C(8)-H(8)	116.6	H(22A)-C(22)-H(22C)	109.5
N(1)-C(9)-C(10)	120.7(3)	H(22B)-C(22)-H(22C)	109.5
N(1)-C(9)-C(8)	115.4(2)	C(21)-C(23)-C(24)	123.3(2)
C(10)-C(9)-C(8)	123.9(3)	C(21)-C(23)-H(23)	118.3
C(11)-C(10)-C(9)	120.2(3)	C(24)-C(23)-H(23)	118.3
C(11)-C(10)-H(10)	119.9	C(23)-C(24)-C(17)	119.8(2)
C(9)-C(10)-H(10)	119.9	C(23)-C(24)-C(25)	118.6(2)
C(12)-C(11)-C(10)	119.1(3)	C(17)-C(24)-C(25)	121.6(2)
C(12)-C(11)-H(11)	120.5	C(24)-C(25)-H(25A)	109.5
C(10)-C(11)-H(11)	120.5	C(24)-C(25)-H(25B)	109.5
C(11)-C(12)-C(13)	118.8(3)	H(25A)-C(25)-H(25B)	109.5
C(11)-C(12)-H(12)	120.6	C(24)-C(25)-H(25C)	109.5
C(13)-C(12)-H(12)	120.6	H(25A)-C(25)-H(25C)	109.5
N(1)-C(13)-C(12)	122.4(3)	H(25B)-C(25)-H(25C)	109.5
N(1)-C(13)-C(14)	116.8(3)	C(33)-C(26)-C(27)	117.1(2)
C(12)-C(13)-C(14)	120.7(3)	C(33)-C(26)-B(1)	120.5(2)
C(13)-C(14)-H(14A)	109.5	C(27)-C(26)-B(1)	122.4(2)
C(13)-C(14)-H(14B)	109.5	C(29)-C(27)-C(26)	120.3(2)
H(14A)-C(14)-H(14B)	109.5	C(29)-C(27)-C(28)	118.2(2)
C(13)-C(14)-H(14C)	109.5	C(26)-C(27)-C(28)	121.5(2)
H(14A)-C(14)-H(14C)	109.5	C(27)-C(28)-H(28A)	109.5

C(27)-C(28)-H(28B)	109.5	H(31A)-C(31)-H(31C)	109.5
H(28A)-C(28)-H(28B)	109.5	H(31B)-C(31)-H(31C)	109.5
C(27)-C(28)-H(28C)	109.5	C(30)-C(32)-C(33)	122.9(2)
H(28A)-C(28)-H(28C)	109.5	C(30)-C(32)-H(32)	118.6
H(28B)-C(28)-H(28C)	109.5	C(33)-C(32)-H(32)	118.6
C(27)-C(29)-C(30)	122.9(3)	C(32)-C(33)-C(26)	120.2(2)
C(27)-C(29)-H(29)	118.6	C(32)-C(33)-C(34)	117.7(2)
C(30)-C(29)-H(29)	118.6	C(26)-C(33)-C(34)	122.1(2)
C(32)-C(30)-C(29)	116.6(3)	C(33)-C(34)-H(34A)	109.5
C(32)-C(30)-C(31)	122.1(2)	C(33)-C(34)-H(34B)	109.5
C(29)-C(30)-C(31)	121.2(3)	H(34A)-C(34)-H(34B)	109.5
C(30)-C(31)-H(31A)	109.5	C(33)-C(34)-H(34C)	109.5
C(30)-C(31)-H(31B)	109.5	H(34A)-C(34)-H(34C)	109.5
H(31A)-C(31)-H(31B)	109.5	H(34B)-C(34)-H(34C)	109.5
C(30)-C(31)-H(31C)	109.5		

Table S100. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for **9a**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + ... \ + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
B(1)	30(1)	42(2)	35(2)	-2(1)	-3(1)	-2(1)
N(1)	59(1)	41(1)	41(2)	-3(1)	8(1)	-4(1)
N(2)	79(2)	64(2)	43(2)	4(1)	-12(1)	18(1)
C(1)	34(1)	41(1)	34(2)	4(1)	7(1)	4(1)
C(2)	41(1)	42(2)	37(2)	3(1)	8(1)	3(1)
C(3)	41(1)	49(2)	36(2)	7(1)	3(1)	1(1)
C(4)	46(2)	50(2)	51(2)	11(2)	7(1)	15(1)
C(5)	52(2)	45(2)	45(2)	-1(1)	7(2)	13(1)
C(6)	35(1)	41(2)	39(2)	6(1)	7(1)	4(1)
C(7)	39(1)	42(2)	46(2)	3(1)	6(1)	3(1)
C(8)	50(2)	40(2)	44(2)	0(1)	3(1)	7(1)
C(9)	42(1)	39(2)	43(2)	1(1)	7(1)	-5(1)
C(10)	66(2)	51(2)	49(2)	0(2)	6(2)	8(2)
C(11)	67(2)	62(2)	48(2)	8(2)	-4(2)	9(2)
C(12)	66(2)	55(2)	42(2)	3(2)	4(2)	-14(2)
C(13)	61(2)	45(2)	44(2)	2(1)	10(2)	-11(1)
C(14)	120(3)	56(2)	47(2)	-9(2)	16(2)	2(2)
C(15)	74(2)	88(2)	61(2)	22(2)	-13(2)	12(2)
C(16)	89(2)	78(2)	45(2)	3(2)	-9(2)	-1(2)
C(17)	34(1)	37(1)	31(2)	5(1)	1(1)	7(1)
C(18)	34(1)	41(1)	36(2)	7(1)	3(1)	5(1)
C(19)	51(2)	46(2)	55(2)	2(1)	10(1)	-3(1)
C(20)	37(1)	54(2)	42(2)	8(1)	10(1)	4(1)
C(21)	45(2)	56(2)	44(2)	2(1)	12(1)	14(1)
C(22)	70(2)	80(2)	78(3)	-8(2)	34(2)	18(2)
C(23)	53(2)	41(2)	49(2)	-4(1)	4(1)	9(1)
C(24)	39(1)	43(2)	36(2)	4(1)	3(1)	5(1)
C(25)	60(2)	47(2)	55(2)	-1(1)	11(2)	-5(1)
C(26)	31(1)	39(1)	36(2)	1(1)	6(1)	7(1)
C(27)	36(1)	49(2)	41(2)	4(1)	5(1)	6(1)
C(28)	37(2)	96(2)	57(2)	20(2)	-4(1)	0(2)
C(29)	48(2)	58(2)	37(2)	7(1)	0(1)	9(1)
C(30)	57(2)	54(2)	37(2)	2(1)	17(1)	6(1)

C(31)	82(2)	94(2)	45(2)	17(2)	19(2)	5(2)
C(32)	41(1)	54(2)	47(2)	5(1)	16(1)	4(1)
C(33)	40(1)	42(2)	40(2)	5(1)	9(1)	5(1)
C(34)	35(1)	74(2)	59(2)	18(2)	5(1)	-1(1)

Table S101. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for **9a**.

	x	y	z	U(eq)
H(2)	8653	3798	6936	48
H(4)	11120	2798	6609	59
H(5)	9917	2735	4445	57
H(7)	7149	3386	2583	51
H(8)	9095	2750	2312	54
H(10)	6234	3411	455	66
H(11)	5384	3367	-1833	72
H(12)	6270	2843	-3026	66
H(14A)	7593	2030	-2039	111
H(14B)	9376	2204	-1792	111
H(14C)	8193	2321	-3105	111
H(15A)	12623	2969	8411	115
H(15B)	11170	2814	9136	115
H(15C)	12369	3138	9837	115
H(16A)	10640	3907	8797	109
H(16B)	10972	3625	10063	109
H(16C)	9220	3644	9221	109
H(19A)	3817	3512	4348	76
H(19B)	3786	3362	5839	76
H(19C)	5432	3358	5211	76
H(20)	2877	3920	6787	53
H(22A)	1632	4606	7343	110
H(22B)	2980	4905	7998	110
H(22C)	2787	4487	8669	110
H(23)	5309	4928	6909	58
H(25A)	7704	4772	4619	80
H(25B)	8672	4645	6022	80
H(25C)	7547	5024	5924	80
H(28A)	3837	4208	1478	97
H(28B)	4293	4236	3060	97
H(28C)	4414	3826	2321	97
H(29)	5715	4388	192	58
H(31A)	7912	4455	-1433	109
H(31B)	9570	4637	-739	109
H(31C)	7941	4881	-783	109
H(32)	10450	4431	1480	56
H(34A)	10869	3853	3908	84
H(34B)	10423	4227	4731	84
H(34C)	11547	4275	3589	84

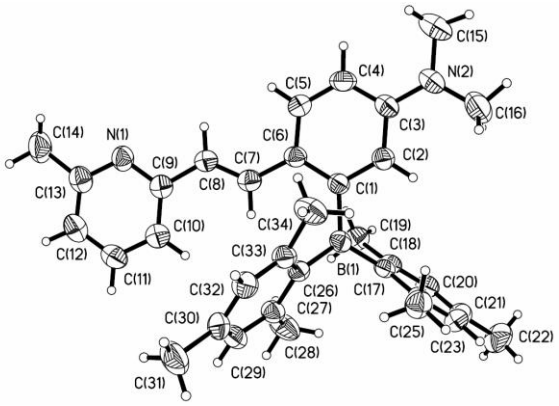


Figure S157. Structure of **9a**.

Table S102. Crystal data and structure refinement for **1c**.

Identification code	**1c**	
Empirical formula	C45 H49 B N2	
Formula weight	628.67	
Temperature	180(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 11.4473(10) Å	α= 94.282(4)°.
	b = 11.8684(11) Å	β= 106.166(3)°.
	c = 15.9919(15) Å	γ = 114.679(3)°.
Volume	1850.2(3) $Å^3$	
Z	2	
Density (calculated)	1.128 Mg/m^3	
Absorption coefficient	0.064 mm^{-1}	
F(000)	676	
Crystal size	0.348 x 0.233 x 0.110 mm^3	
Theta range for data collection	2.718 to 27.174°.	
Index ranges	-14<=h<=14, -15<=k<=15, -20<=l<=20	
Reflections collected	21084	
Independent reflections	8129 [R(int) = 0.1347]	
Completeness to theta = 25.242°	99.1 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.993 and 0.978	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	8129 / 0 / 441	
Goodness-of-fit on F^2	0.972	
Final R indices [I>2sigma(I)]	R1 = 0.0746, wR2 = 0.1766	
R indices (all data)	R1 = 0.1533, wR2 = 0.2135	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.251 and -0.266 e.$Å^{-3}$	

Table S103. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for **1c**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
N(1)	6609(3)	2150(2)	5668(2)	45(1)
C(1)	3324(2)	1802(2)	6861(2)	23(1)

B(1)	3334(3)	3090(2)	6814(2)	24(1)
C(2)	3623(2)	1489(2)	7670(2)	27(1)
N(2)	3490(2)	-1654(2)	7226(1)	33(1)
C(3)	3555(3)	296(2)	7808(2)	30(1)
C(4)	3544(2)	-504(2)	7146(2)	28(1)
C(5)	3665(2)	-46(2)	6306(2)	26(1)
C(8)	4199(3)	1480(2)	5069(2)	35(1)
C(7)	3040(3)	1168(2)	5229(2)	30(1)
C(6)	2881(2)	730(2)	6071(2)	24(1)
C(9)	5363(3)	1447(2)	5712(2)	34(1)
C(10)	5147(3)	738(2)	6371(2)	29(1)
C(11)	6267(3)	794(2)	7005(2)	38(1)
C(12)	7559(3)	1534(3)	6974(2)	49(1)
C(13)	7669(3)	2178(3)	6301(2)	52(1)
C(14)	3755(3)	-2409(2)	6615(2)	46(1)
C(15)	3437(4)	-2065(3)	8055(2)	51(1)
C(16)	2484(2)	3361(2)	5958(2)	25(1)
C(17)	3113(2)	4405(2)	5589(2)	26(1)
C(18)	4634(3)	5242(2)	5955(2)	34(1)
C(19)	2338(3)	4651(2)	4859(2)	34(1)
C(20)	936(3)	3921(3)	4476(2)	38(1)
C(21)	115(3)	4227(3)	3695(2)	64(1)
C(22)	326(3)	2909(2)	4842(2)	36(1)
C(23)	1052(2)	2607(2)	5561(2)	29(1)
C(24)	276(3)	1478(2)	5907(2)	37(1)
C(25)	4226(3)	4184(2)	7694(2)	27(1)
C(26)	5650(3)	4667(2)	8048(2)	32(1)
C(27)	6442(3)	4225(3)	7609(2)	44(1)
C(28)	6399(3)	5633(2)	8817(2)	40(1)
C(29)	5796(3)	6133(2)	9260(2)	40(1)
C(30)	6627(4)	7182(3)	10092(2)	63(1)
C(31)	4386(3)	5636(2)	8924(2)	37(1)
C(32)	3599(3)	4697(2)	8147(2)	31(1)
C(33)	2073(3)	4196(3)	7834(2)	43(1)
C(34)	7653(3)	8141(3)	7679(2)	61(1)
C(35)	8192(3)	9130(3)	8386(2)	59(1)
C(36)	9466(3)	10124(3)	8557(2)	56(1)
C(37)	10195(3)	10110(3)	8020(2)	58(1)
C(38)	9663(4)	9118(3)	7302(2)	61(1)
C(39)	8383(4)	8126(3)	7131(2)	64(1)
C(40)	10672(4)	7486(5)	9177(3)	80(1)
C(41)	11769(5)	8596(5)	9670(3)	85(1)
C(42)	12844(5)	8560(5)	10270(3)	91(1)
C(43)	12858(5)	7450(6)	10381(3)	87(1)
C(44)	11784(5)	6335(5)	9893(3)	81(1)
C(45)	10683(4)	6348(5)	9283(3)	84(1)

Table S104. Bond lengths [Å] and angles [°] for **1c**.

N(1)-C(13)	1.333(4)	B(1)-C(25)	1.590(3)
N(1)-C(9)	1.344(3)	C(2)-C(3)	1.423(3)
C(1)-C(2)	1.364(3)	C(2)-H(2)	0.9500
C(1)-C(6)	1.528(3)	N(2)-C(4)	1.357(3)
C(1)-B(1)	1.531(4)	N(2)-C(14)	1.452(3)
B(1)-C(16)	1.584(4)	N(2)-C(15)	1.456(3)

C(3)-C(4)	1.362(3)	C(30)-H(30A)	0.9800
C(3)-H(3)	0.9500	C(30)-H(30B)	0.9800
C(4)-C(5)	1.506(3)	C(30)-H(30C)	0.9800
C(5)-C(10)	1.525(3)	C(31)-C(32)	1.388(3)
C(5)-C(6)	1.532(3)	C(31)-H(31)	0.9500
C(5)-H(5)	1.0000	C(32)-C(33)	1.502(4)
C(8)-C(7)	1.325(3)	C(33)-H(33A)	0.9800
C(8)-C(9)	1.456(4)	C(33)-H(33B)	0.9800
C(8)-H(8)	0.9500	C(33)-H(33C)	0.9800
C(7)-C(6)	1.510(3)	C(34)-C(35)	1.358(4)
C(7)-H(7)	0.9500	C(34)-C(39)	1.373(5)
C(6)-H(6)	1.0000	C(34)-H(34)	0.9500
C(9)-C(10)	1.408(4)	C(35)-C(36)	1.373(4)
C(10)-C(11)	1.368(4)	C(35)-H(35)	0.9500
C(11)-C(12)	1.387(4)	C(36)-C(37)	1.359(4)
C(11)-H(11)	0.9500	C(36)-H(36)	0.9500
C(12)-C(13)	1.370(4)	C(37)-C(38)	1.373(5)
C(12)-H(12)	0.9500	C(37)-H(37)	0.9500
C(13)-H(13)	0.9500	C(38)-C(39)	1.377(5)
C(14)-H(14A)	0.9800	C(38)-H(38)	0.9500
C(14)-H(14B)	0.9800	C(39)-H(39)	0.9500
C(14)-H(14C)	0.9800	C(40)-C(41)	1.359(6)
C(15)-H(15A)	0.9800	C(40)-C(45)	1.378(6)
C(15)-H(15B)	0.9800	C(40)-H(40)	0.9500
C(15)-H(15C)	0.9800	C(41)-C(42)	1.352(6)
C(16)-C(23)	1.415(3)	C(41)-H(41)	0.9500
C(16)-C(17)	1.416(3)	C(42)-C(43)	1.349(6)
C(17)-C(19)	1.387(4)	C(42)-H(42)	0.9500
C(17)-C(18)	1.504(3)	C(43)-C(44)	1.351(6)
C(18)-H(18A)	0.9800	C(43)-H(43)	0.9500
C(18)-H(18B)	0.9800	C(44)-C(45)	1.370(6)
C(18)-H(18C)	0.9800	C(44)-H(44)	0.9500
C(19)-C(20)	1.383(4)	C(45)-H(45)	0.9500
C(19)-H(19)	0.9500	C(13)-N(1)-C(9)	116.7(3)
C(20)-C(22)	1.381(4)	C(2)-C(1)-C(6)	113.8(2)
C(20)-C(21)	1.508(4)	C(2)-C(1)-B(1)	119.4(2)
C(21)-H(21A)	0.9800	C(6)-C(1)-B(1)	126.6(2)
C(21)-H(21B)	0.9800	C(1)-B(1)-C(16)	123.7(2)
C(21)-H(21C)	0.9800	C(1)-B(1)-C(25)	116.8(2)
C(22)-C(23)	1.385(4)	C(16)-B(1)-C(25)	119.5(2)
C(22)-H(22)	0.9500	C(1)-C(2)-C(3)	125.4(2)
C(23)-C(24)	1.509(3)	C(1)-C(2)-H(2)	117.3
C(24)-H(24A)	0.9800	C(3)-C(2)-H(2)	117.3
C(24)-H(24B)	0.9800	C(4)-N(2)-C(14)	124.3(2)
C(24)-H(24C)	0.9800	C(4)-N(2)-C(15)	119.0(2)
C(25)-C(26)	1.401(3)	C(14)-N(2)-C(15)	115.6(2)
C(25)-C(32)	1.415(3)	C(4)-C(3)-C(2)	119.6(2)
C(26)-C(28)	1.394(3)	C(4)-C(3)-H(3)	120.2
C(26)-C(27)	1.514(4)	C(2)-C(3)-H(3)	120.2
C(27)-H(27A)	0.9800	N(2)-C(4)-C(3)	123.2(2)
C(27)-H(27B)	0.9800	N(2)-C(4)-C(5)	119.3(2)
C(27)-H(27C)	0.9800	C(3)-C(4)-C(5)	117.4(2)
C(28)-C(29)	1.373(4)	C(4)-C(5)-C(10)	112.6(2)
C(28)-H(28)	0.9500	C(4)-C(5)-C(6)	110.79(19)
C(29)-C(31)	1.384(4)	C(10)-C(5)-C(6)	109.68(19)
C(29)-C(30)	1.510(4)	C(4)-C(5)-H(5)	107.9

C(10)-C(5)-H(5)	107.9	C(22)-C(20)-C(19)	117.1(2)
C(6)-C(5)-H(5)	107.9	C(22)-C(20)-C(21)	121.7(3)
C(7)-C(8)-C(9)	121.0(2)	C(19)-C(20)-C(21)	121.2(3)
C(7)-C(8)-H(8)	119.5	C(20)-C(21)-H(21A)	109.5
C(9)-C(8)-H(8)	119.5	C(20)-C(21)-H(21B)	109.5
C(8)-C(7)-C(6)	120.6(2)	H(21A)-C(21)-H(21B)	109.5
C(8)-C(7)-H(7)	119.7	C(20)-C(21)-H(21C)	109.5
C(6)-C(7)-H(7)	119.7	H(21A)-C(21)-H(21C)	109.5
C(7)-C(6)-C(1)	114.29(18)	H(21B)-C(21)-H(21C)	109.5
C(7)-C(6)-C(5)	108.54(19)	C(20)-C(22)-C(23)	123.0(2)
C(1)-C(6)-C(5)	111.07(19)	C(20)-C(22)-H(22)	118.5
C(7)-C(6)-H(6)	107.6	C(23)-C(22)-H(22)	118.5
C(1)-C(6)-H(6)	107.6	C(22)-C(23)-C(16)	119.9(2)
C(5)-C(6)-H(6)	107.6	C(22)-C(23)-C(24)	118.4(2)
N(1)-C(9)-C(10)	123.2(3)	C(16)-C(23)-C(24)	121.7(2)
N(1)-C(9)-C(8)	117.6(2)	C(23)-C(24)-H(24A)	109.5
C(10)-C(9)-C(8)	119.1(2)	C(23)-C(24)-H(24B)	109.5
C(11)-C(10)-C(9)	118.0(2)	H(24A)-C(24)-H(24B)	109.5
C(11)-C(10)-C(5)	125.5(2)	C(23)-C(24)-H(24C)	109.5
C(9)-C(10)-C(5)	116.5(2)	H(24A)-C(24)-H(24C)	109.5
C(10)-C(11)-C(12)	119.3(3)	H(24B)-C(24)-H(24C)	109.5
C(10)-C(11)-H(11)	120.3	C(26)-C(25)-C(32)	117.8(2)
C(12)-C(11)-H(11)	120.3	C(26)-C(25)-B(1)	121.5(2)
C(13)-C(12)-C(11)	118.6(3)	C(32)-C(25)-B(1)	120.8(2)
C(13)-C(12)-H(12)	120.7	C(28)-C(26)-C(25)	119.9(2)
C(11)-C(12)-H(12)	120.7	C(28)-C(26)-C(27)	117.3(2)
N(1)-C(13)-C(12)	124.3(3)	C(25)-C(26)-C(27)	122.7(2)
N(1)-C(13)-H(13)	117.9	C(26)-C(27)-H(27A)	109.5
C(12)-C(13)-H(13)	117.9	C(26)-C(27)-H(27B)	109.5
N(2)-C(14)-H(14A)	109.5	H(27A)-C(27)-H(27B)	109.5
N(2)-C(14)-H(14B)	109.5	C(26)-C(27)-H(27C)	109.5
H(14A)-C(14)-H(14B)	109.5	H(27A)-C(27)-H(27C)	109.5
N(2)-C(14)-H(14C)	109.5	H(27B)-C(27)-H(27C)	109.5
H(14A)-C(14)-H(14C)	109.5	C(29)-C(28)-C(26)	122.5(3)
H(14B)-C(14)-H(14C)	109.5	C(29)-C(28)-H(28)	118.7
N(2)-C(15)-H(15A)	109.5	C(26)-C(28)-H(28)	118.7
N(2)-C(15)-H(15B)	109.5	C(28)-C(29)-C(31)	117.7(2)
H(15A)-C(15)-H(15B)	109.5	C(28)-C(29)-C(30)	121.7(3)
N(2)-C(15)-H(15C)	109.5	C(31)-C(29)-C(30)	120.6(3)
H(15A)-C(15)-H(15C)	109.5	C(29)-C(30)-H(30A)	109.5
H(15B)-C(15)-H(15C)	109.5	C(29)-C(30)-H(30B)	109.5
C(23)-C(16)-C(17)	117.3(2)	H(30A)-C(30)-H(30B)	109.5
C(23)-C(16)-B(1)	121.2(2)	C(29)-C(30)-H(30C)	109.5
C(17)-C(16)-B(1)	121.4(2)	H(30A)-C(30)-H(30C)	109.5
C(19)-C(17)-C(16)	120.3(2)	H(30B)-C(30)-H(30C)	109.5
C(19)-C(17)-C(18)	118.6(2)	C(29)-C(31)-C(32)	121.9(3)
C(16)-C(17)-C(18)	121.1(2)	C(29)-C(31)-H(31)	119.1
C(17)-C(18)-H(18A)	109.5	C(32)-C(31)-H(31)	119.1
C(17)-C(18)-H(18B)	109.5	C(31)-C(32)-C(25)	120.2(2)
H(18A)-C(18)-H(18B)	109.5	C(31)-C(32)-C(33)	118.5(2)
C(17)-C(18)-H(18C)	109.5	C(25)-C(32)-C(33)	121.2(2)
H(18A)-C(18)-H(18C)	109.5	C(32)-C(33)-H(33A)	109.5
H(18B)-C(18)-H(18C)	109.5	C(32)-C(33)-H(33B)	109.5
C(20)-C(19)-C(17)	122.3(2)	H(33A)-C(33)-H(33B)	109.5
C(20)-C(19)-H(19)	118.8	C(32)-C(33)-H(33C)	109.5
C(17)-C(19)-H(19)	118.8	H(33A)-C(33)-H(33C)	109.5

H(33B)-C(33)-H(33C)	109.5	C(41)-C(40)-C(45)	119.7(4)
C(35)-C(34)-C(39)	120.1(3)	C(41)-C(40)-H(40)	120.2
C(35)-C(34)-H(34)	120.0	C(45)-C(40)-H(40)	120.2
C(39)-C(34)-H(34)	120.0	C(42)-C(41)-C(40)	119.1(5)
C(34)-C(35)-C(36)	120.5(3)	C(42)-C(41)-H(41)	120.4
C(34)-C(35)-H(35)	119.7	C(40)-C(41)-H(41)	120.4
C(36)-C(35)-H(35)	119.7	C(43)-C(42)-C(41)	121.5(5)
C(37)-C(36)-C(35)	119.6(3)	C(43)-C(42)-H(42)	119.2
C(37)-C(36)-H(36)	120.2	C(41)-C(42)-H(42)	119.2
C(35)-C(36)-H(36)	120.2	C(42)-C(43)-C(44)	120.5(4)
C(36)-C(37)-C(38)	120.6(3)	C(42)-C(43)-H(43)	119.8
C(36)-C(37)-H(37)	119.7	C(44)-C(43)-H(43)	119.8
C(38)-C(37)-H(37)	119.7	C(43)-C(44)-C(45)	119.0(4)
C(37)-C(38)-C(39)	119.5(3)	C(43)-C(44)-H(44)	120.5
C(37)-C(38)-H(38)	120.2	C(45)-C(44)-H(44)	120.5
C(39)-C(38)-H(38)	120.2	C(44)-C(45)-C(40)	120.2(4)
C(34)-C(39)-C(38)	119.7(3)	C(44)-C(45)-H(45)	119.9
C(34)-C(39)-H(39)	120.2	C(40)-C(45)-H(45)	119.9
C(38)-C(39)-H(39)	120.2		

Table S105. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for **1c**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
N(1)	50(2)	34(1)	68(2)	20(1)	38(2)	22(1)
C(1)	25(1)	21(1)	25(1)	6(1)	8(1)	12(1)
B(1)	23(1)	21(1)	29(2)	6(1)	11(1)	8(1)
C(2)	31(1)	26(1)	27(1)	6(1)	11(1)	15(1)
N(2)	47(1)	26(1)	39(1)	18(1)	20(1)	22(1)
C(3)	41(2)	29(1)	28(1)	14(1)	16(1)	21(1)
C(4)	28(1)	24(1)	35(1)	12(1)	14(1)	14(1)
C(5)	30(1)	20(1)	28(1)	6(1)	11(1)	12(1)
C(8)	53(2)	28(1)	34(2)	14(1)	25(1)	21(1)
C(7)	42(2)	22(1)	25(1)	4(1)	7(1)	16(1)
C(6)	28(1)	19(1)	26(1)	6(1)	9(1)	12(1)
C(9)	43(2)	24(1)	46(2)	11(1)	27(1)	18(1)
C(10)	35(1)	23(1)	37(2)	9(1)	20(1)	16(1)
C(11)	38(2)	35(2)	51(2)	17(1)	20(2)	22(1)
C(12)	36(2)	44(2)	75(2)	18(2)	21(2)	24(1)
C(13)	44(2)	40(2)	87(3)	20(2)	39(2)	20(2)
C(14)	64(2)	28(1)	67(2)	21(1)	36(2)	30(2)
C(15)	84(2)	33(2)	47(2)	22(1)	25(2)	32(2)
C(16)	29(1)	20(1)	30(1)	5(1)	9(1)	16(1)
C(17)	32(1)	18(1)	30(1)	5(1)	12(1)	12(1)
C(18)	36(2)	26(1)	35(1)	11(1)	12(1)	10(1)
C(19)	44(2)	26(1)	35(2)	12(1)	14(1)	18(1)
C(20)	43(2)	34(1)	38(2)	12(1)	5(1)	22(1)
C(21)	56(2)	64(2)	58(2)	25(2)	-1(2)	26(2)
C(22)	26(1)	30(1)	44(2)	7(1)	2(1)	12(1)
C(23)	28(1)	20(1)	39(2)	8(1)	11(1)	12(1)
C(24)	27(1)	30(1)	53(2)	14(1)	13(1)	10(1)
C(25)	39(2)	19(1)	28(1)	9(1)	11(1)	16(1)
C(26)	35(2)	24(1)	31(1)	8(1)	5(1)	13(1)

C(27)	36(2)	42(2)	50(2)	6(1)	10(2)	19(1)
C(28)	41(2)	29(1)	32(2)	6(1)	0(1)	9(1)
C(29)	63(2)	22(1)	26(1)	7(1)	8(2)	14(1)
C(30)	95(3)	37(2)	35(2)	1(1)	11(2)	17(2)
C(31)	66(2)	26(1)	30(1)	12(1)	21(2)	27(1)
C(32)	47(2)	22(1)	31(1)	11(1)	15(1)	21(1)
C(33)	53(2)	44(2)	43(2)	8(1)	20(2)	31(2)
C(34)	45(2)	46(2)	67(2)	16(2)	5(2)	7(2)
C(35)	53(2)	65(2)	63(2)	20(2)	25(2)	27(2)
C(36)	61(2)	47(2)	54(2)	7(2)	13(2)	23(2)
C(37)	49(2)	46(2)	71(2)	25(2)	18(2)	14(2)
C(38)	78(3)	68(2)	58(2)	32(2)	36(2)	40(2)
C(39)	89(3)	45(2)	46(2)	9(2)	7(2)	31(2)
C(40)	66(3)	141(4)	70(3)	58(3)	31(2)	69(3)
C(41)	106(4)	96(3)	73(3)	20(3)	32(3)	63(3)
C(42)	92(3)	101(4)	62(3)	-4(3)	13(3)	38(3)
C(43)	71(3)	147(5)	60(3)	36(3)	14(2)	69(3)
C(44)	86(3)	100(3)	98(3)	56(3)	50(3)	63(3)
C(45)	56(2)	93(3)	87(3)	23(3)	27(2)	18(2)

Table S106. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^{2}x 10^3) for **1c**.

	x	y	z	U(eq)
H(2)	3900	2120	8184	33
H(3)	3518	59	8358	35
H(5)	3239	-809	5808	31
H(8)	4272	1728	4527	42
H(7)	2301	1220	4809	36
H(6)	1889	147	5938	29
H(11)	6161	332	7461	46
H(12)	8352	1592	7411	59
H(13)	8558	2677	6284	63
H(14A)	3495	-2240	6019	69
H(14B)	3218	-3313	6591	69
H(14C)	4731	-2185	6825	69
H(15A)	2687	-2002	8202	77
H(15B)	4305	-1521	8537	77
H(15C)	3284	-2948	7986	77
H(18A)	5106	4737	5880	51
H(18B)	4911	5606	6590	51
H(18C)	4877	5929	5632	51
H(19)	2785	5345	4614	40
H(21A)	717	4729	3388	96
H(21B)	-294	4716	3910	96
H(21C)	-610	3436	3280	96
H(22)	-636	2396	4590	43
H(24A)	-682	1309	5740	56
H(24B)	683	1662	6558	56
H(24C)	325	732	5646	56
H(27A)	5824	3650	7030	65
H(27B)	6840	3777	7991	65
H(27C)	7174	4962	7520	65

H(28)	7365	5957	9043	48
H(30A)	7599	7538	10161	95
H(30B)	6483	6837	10613	95
H(30C)	6338	7851	10040	95
H(31)	3944	5946	9233	44
H(33A)	1750	4282	7218	64
H(33B)	1833	4681	8220	64
H(33C)	1641	3298	7860	64
H(34)	6770	7458	7564	73
H(35)	7684	9134	8764	70
H(36)	9835	10817	9049	68
H(37)	11080	10792	8141	70
H(38)	10175	9115	6926	74
H(39)	8006	7435	6636	77
H(40)	9902	7494	8761	96
H(41)	11781	9387	9595	102
H(42)	13606	9335	10622	110
H(43)	13627	7452	10806	105
H(44)	11793	5552	9971	97
H(45)	9924	5571	8932	101

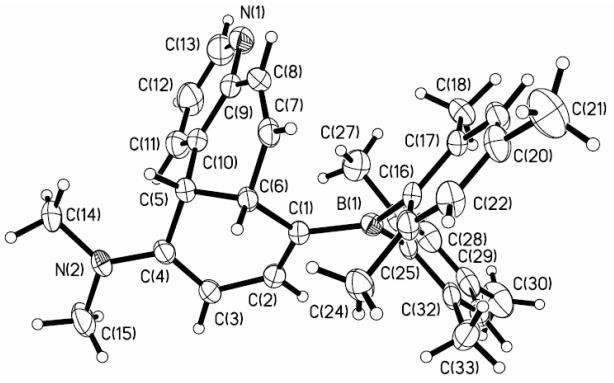


Figure S158. Structure of **1c**.

Table S107. Crystal data and structure refinement for **2c**.

Identification code	**2c**	
Empirical formula	C2.43 H2.79 B0.07 N0.14	
Formula weight	34.75	
Temperature	180(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 10.294(3) Å	α= 66.239(11)°.
	b = 11.896(4) Å	β= 88.621(11)°.
	c = 13.128(5) Å	γ = 75.243(12)°.
Volume	1417.2(8) $Å^3$	
Z	28	
Density (calculated)	1.140 Mg/m^3	
Absorption coefficient	0.065 mm^{-1}	
F(000)	524	
Crystal size	0.180 x 0.174 x 0.095 mm^3	
Theta range for data collection	2.419 to 27.261°.	

Index ranges	-13<=h<=13, -15<=k<=15, -16<=l<=16
Reflections collected	19796
Independent reflections	6268 [R(int) = 0.0885]
Completeness to theta = 25.242°	99.9 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.994 and 0.988
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	6268 / 0 / 344
Goodness-of-fit on F^2	1.036
Final R indices [I>2sigma(I)]	R1 = 0.0671, wR2 = 0.1647
R indices (all data)	R1 = 0.1333, wR2 = 0.2045
Extinction coefficient	0.089(7)
Largest diff. peak and hole	0.484 and -0.433 e.Å^{-3}

Table S108. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for **2c**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
N(1)	949(2)	6561(2)	4156(2)	43(1)
N(2)	3366(2)	1705(2)	7652(2)	52(1)
C(1)	2795(2)	5377(2)	7667(2)	33(1)
C(2)	4034(2)	4541(2)	7810(2)	36(1)
C(3)	4254(2)	3263(2)	7915(2)	40(1)
C(4)	3242(2)	2905(2)	7575(2)	38(1)
C(5)	1941(2)	3926(2)	7038(2)	35(1)
C(6)	1600(2)	4853(2)	7617(2)	36(1)
C(7)	320(2)	5870(2)	7020(2)	42(1)
C(8)	62(2)	6305(2)	5926(2)	44(1)
C(9)	1025(2)	5826(2)	5256(2)	37(1)
C(10)	2001(2)	4675(2)	5793(2)	35(1)
C(11)	2950(2)	4274(2)	5159(2)	43(1)
C(12)	2888(3)	5031(2)	4030(2)	48(1)
C(13)	1891(3)	6157(2)	3554(2)	47(1)
C(14)	1798(3)	7027(3)	2340(2)	68(1)
C(15)	2427(3)	1346(2)	7125(2)	55(1)
C(16)	4616(3)	730(3)	8192(3)	78(1)
C(17)	3928(2)	7257(2)	7342(2)	34(1)
C(18)	4268(2)	7617(2)	6229(2)	36(1)
C(19)	3495(3)	7435(2)	5361(2)	46(1)
C(20)	5327(2)	8176(2)	5890(2)	41(1)
C(21)	6137(2)	8328(2)	6627(2)	44(1)
C(22)	7283(3)	8930(3)	6246(3)	59(1)
C(23)	5843(2)	7922(2)	7732(2)	43(1)
C(24)	4748(2)	7432(2)	8092(2)	38(1)
C(25)	4462(3)	7075(3)	9305(2)	55(1)
C(26)	1480(2)	7319(2)	8241(2)	35(1)
C(27)	719(2)	8593(2)	7640(2)	37(1)
C(28)	920(3)	9329(2)	6435(2)	46(1)
C(29)	-282(2)	9191(2)	8124(2)	46(1)
C(30)	-598(3)	8562(3)	9206(2)	52(1)
C(31)	-1671(3)	9227(3)	9728(3)	83(1)
C(32)	129(3)	7308(3)	9781(2)	50(1)
C(33)	1144(2)	6672(2)	9337(2)	42(1)
C(34)	1883(3)	5313(2)	10084(2)	56(1)
B(1)	2706(3)	6646(2)	7740(2)	34(1)

Table S109. Bond lengths [Å] and angles [°] for **2c**.

N(1)-C(9)	1.345(3)		
N(1)-C(13)	1.352(3)	C(2)-H(2)	0.9500
N(2)-C(4)	1.362(3)	C(3)-C(4)	1.366(3)
N(2)-C(15)	1.442(3)	C(3)-H(3)	0.9500
N(2)-C(16)	1.458(3)	C(4)-C(5)	1.514(3)
C(1)-C(2)	1.366(3)	C(5)-C(10)	1.524(3)
C(1)-C(6)	1.528(3)	C(5)-C(6)	1.543(3)
C(1)-B(1)	1.530(3)	C(5)-H(5)	1.0000
C(2)-C(3)	1.427(3)	C(6)-C(7)	1.513(3)

C(6)-H(6)	1.0000	C(31)-H(31C)	0.9800
C(7)-C(8)	1.322(3)	C(32)-C(33)	1.389(3)
C(7)-H(7)	0.9500	C(32)-H(32)	0.9500
C(8)-C(9)	1.468(3)	C(33)-C(34)	1.512(3)
C(8)-H(8)	0.9500	C(34)-H(34A)	0.9800
C(9)-C(10)	1.391(3)	C(34)-H(34B)	0.9800
C(10)-C(11)	1.385(3)	C(34)-H(34C)	0.9800
C(11)-C(12)	1.382(3)	C(9)-N(1)-C(13)	117.5(2)
C(11)-H(11)	0.9500	C(4)-N(2)-C(15)	125.2(2)
C(12)-C(13)	1.376(3)	C(4)-N(2)-C(16)	118.1(2)
C(12)-H(12)	0.9500	C(15)-N(2)-C(16)	116.3(2)
C(13)-C(14)	1.499(3)	C(2)-C(1)-C(6)	114.91(18)
C(14)-H(14A)	0.9800	C(2)-C(1)-B(1)	118.90(19)
C(14)-H(14B)	0.9800	C(6)-C(1)-B(1)	125.55(19)
C(14)-H(14C)	0.9800	C(1)-C(2)-C(3)	124.7(2)
C(15)-H(15A)	0.9800	C(1)-C(2)-H(2)	117.6
C(15)-H(15B)	0.9800	C(3)-C(2)-H(2)	117.6
C(15)-H(15C)	0.9800	C(4)-C(3)-C(2)	119.9(2)
C(16)-H(16A)	0.9800	C(4)-C(3)-H(3)	120.0
C(16)-H(16B)	0.9800	C(2)-C(3)-H(3)	120.0
C(16)-H(16C)	0.9800	N(2)-C(4)-C(3)	123.6(2)
C(17)-C(18)	1.410(3)	N(2)-C(4)-C(5)	119.0(2)
C(17)-C(24)	1.422(3)	C(3)-C(4)-C(5)	117.32(19)
C(17)-B(1)	1.585(3)	C(4)-C(5)-C(10)	112.05(17)
C(18)-C(20)	1.392(3)	C(4)-C(5)-C(6)	110.80(18)
C(18)-C(19)	1.520(3)	C(10)-C(5)-C(6)	109.41(17)
C(19)-H(19A)	0.9800	C(4)-C(5)-H(5)	108.2
C(19)-H(19B)	0.9800	C(10)-C(5)-H(5)	108.2
C(19)-H(19C)	0.9800	C(6)-C(5)-H(5)	108.2
C(20)-C(21)	1.386(3)	C(7)-C(6)-C(1)	113.94(17)
C(20)-H(20)	0.9500	C(7)-C(6)-C(5)	108.21(18)
C(21)-C(23)	1.385(3)	C(1)-C(6)-C(5)	110.82(17)
C(21)-C(22)	1.506(3)	C(7)-C(6)-H(6)	107.9
C(22)-H(22A)	0.9800	C(1)-C(6)-H(6)	107.9
C(22)-H(22B)	0.9800	C(5)-C(6)-H(6)	107.9
C(22)-H(22C)	0.9800	C(8)-C(7)-C(6)	121.1(2)
C(23)-C(24)	1.386(3)	C(8)-C(7)-H(7)	119.5
C(23)-H(23)	0.9500	C(6)-C(7)-H(7)	119.5
C(24)-C(25)	1.516(3)	C(7)-C(8)-C(9)	120.7(2)
C(25)-H(25A)	0.9800	C(7)-C(8)-H(8)	119.6
C(25)-H(25B)	0.9800	C(9)-C(8)-H(8)	119.6
C(25)-H(25C)	0.9800	N(1)-C(9)-C(10)	123.5(2)
C(26)-C(27)	1.412(3)	N(1)-C(9)-C(8)	117.6(2)
C(26)-C(33)	1.414(3)	C(10)-C(9)-C(8)	118.8(2)
C(26)-B(1)	1.592(3)	C(11)-C(10)-C(9)	118.0(2)
C(27)-C(29)	1.390(3)	C(11)-C(10)-C(5)	124.2(2)
C(27)-C(28)	1.507(3)	C(9)-C(10)-C(5)	117.78(19)
C(28)-H(28A)	0.9800	C(12)-C(11)-C(10)	118.8(2)
C(28)-H(28B)	0.9800	C(12)-C(11)-H(11)	120.6
C(28)-H(28C)	0.9800	C(10)-C(11)-H(11)	120.6
C(29)-C(30)	1.388(3)	C(13)-C(12)-C(11)	120.1(2)
C(29)-H(29)	0.9500	C(13)-C(12)-H(12)	120.0
C(30)-C(32)	1.381(4)	C(11)-C(12)-H(12)	120.0
C(30)-C(31)	1.507(4)	N(1)-C(13)-C(12)	122.1(2)
C(31)-H(31A)	0.9800	N(1)-C(13)-C(14)	115.8(2)
C(31)-H(31B)	0.9800	C(12)-C(13)-C(14)	122.2(2)

C(13)-C(14)-H(14A)	109.5	C(17)-C(24)-C(25)	121.1(2)
C(13)-C(14)-H(14B)	109.5	C(24)-C(25)-H(25A)	109.5
H(14A)-C(14)-H(14B)	109.5	C(24)-C(25)-H(25B)	109.5
C(13)-C(14)-H(14C)	109.5	H(25A)-C(25)-H(25B)	109.5
H(14A)-C(14)-H(14C)	109.5	C(24)-C(25)-H(25C)	109.5
H(14B)-C(14)-H(14C)	109.5	H(25A)-C(25)-H(25C)	109.5
N(2)-C(15)-H(15A)	109.5	H(25B)-C(25)-H(25C)	109.5
N(2)-C(15)-H(15B)	109.5	C(27)-C(26)-C(33)	117.1(2)
H(15A)-C(15)-H(15B)	109.5	C(27)-C(26)-B(1)	122.04(18)
N(2)-C(15)-H(15C)	109.5	C(33)-C(26)-B(1)	120.9(2)
H(15A)-C(15)-H(15C)	109.5	C(29)-C(27)-C(26)	121.1(2)
H(15B)-C(15)-H(15C)	109.5	C(29)-C(27)-C(28)	117.7(2)
N(2)-C(16)-H(16A)	109.5	C(26)-C(27)-C(28)	121.2(2)
N(2)-C(16)-H(16B)	109.5	C(27)-C(28)-H(28A)	109.5
H(16A)-C(16)-H(16B)	109.5	C(27)-C(28)-H(28B)	109.5
N(2)-C(16)-H(16C)	109.5	H(28A)-C(28)-H(28B)	109.5
H(16A)-C(16)-H(16C)	109.5	C(27)-C(28)-H(28C)	109.5
H(16B)-C(16)-H(16C)	109.5	H(28A)-C(28)-H(28C)	109.5
C(18)-C(17)-C(24)	117.23(19)	H(28B)-C(28)-H(28C)	109.5
C(18)-C(17)-B(1)	120.98(19)	C(30)-C(29)-C(27)	121.9(2)
C(24)-C(17)-B(1)	121.77(19)	C(30)-C(29)-H(29)	119.1
C(20)-C(18)-C(17)	120.1(2)	C(27)-C(29)-H(29)	119.1
C(20)-C(18)-C(19)	117.8(2)	C(32)-C(30)-C(29)	116.8(2)
C(17)-C(18)-C(19)	122.07(19)	C(32)-C(30)-C(31)	121.8(2)
C(18)-C(19)-H(19A)	109.5	C(29)-C(30)-C(31)	121.4(3)
C(18)-C(19)-H(19B)	109.5	C(30)-C(31)-H(31A)	109.5
H(19A)-C(19)-H(19B)	109.5	C(30)-C(31)-H(31B)	109.5
C(18)-C(19)-H(19C)	109.5	H(31A)-C(31)-H(31B)	109.5
H(19A)-C(19)-H(19C)	109.5	C(30)-C(31)-H(31C)	109.5
H(19B)-C(19)-H(19C)	109.5	H(31A)-C(31)-H(31C)	109.5
C(21)-C(20)-C(18)	122.4(2)	H(31B)-C(31)-H(31C)	109.5
C(21)-C(20)-H(20)	118.8	C(30)-C(32)-C(33)	123.5(2)
C(18)-C(20)-H(20)	118.8	C(30)-C(32)-H(32)	118.3
C(23)-C(21)-C(20)	117.5(2)	C(33)-C(32)-H(32)	118.3
C(23)-C(21)-C(22)	120.8(2)	C(32)-C(33)-C(26)	119.7(2)
C(20)-C(21)-C(22)	121.7(2)	C(32)-C(33)-C(34)	117.3(2)
C(21)-C(22)-H(22A)	109.5	C(26)-C(33)-C(34)	122.9(2)
C(21)-C(22)-H(22B)	109.5	C(33)-C(34)-H(34A)	109.5
H(22A)-C(22)-H(22B)	109.5	C(33)-C(34)-H(34B)	109.5
C(21)-C(22)-H(22C)	109.5	H(34A)-C(34)-H(34B)	109.5
H(22A)-C(22)-H(22C)	109.5	C(33)-C(34)-H(34C)	109.5
H(22B)-C(22)-H(22C)	109.5	H(34A)-C(34)-H(34C)	109.5
C(21)-C(23)-C(24)	122.0(2)	H(34B)-C(34)-H(34C)	109.5
C(21)-C(23)-H(23)	119.0	C(1)-B(1)-C(17)	117.3(2)
C(24)-C(23)-H(23)	119.0	C(1)-B(1)-C(26)	122.5(2)
C(23)-C(24)-C(17)	120.6(2)	C(17)-B(1)-C(26)	120.12(19)
C(23)-C(24)-C(25)	118.3(2)		

Table S110. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for **2c**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
N(1)	44(1)	44(1)	42(1)	-19(1)	-4(1)	-11(1)

N(2)	63(1)	33(1)	63(1)	-23(1)	-5(1)	-9(1)
C(1)	41(1)	35(1)	27(1)	-13(1)	6(1)	-16(1)
C(2)	41(1)	36(1)	34(1)	-14(1)	3(1)	-14(1)
C(3)	40(1)	36(1)	44(1)	-18(1)	-2(1)	-7(1)
C(4)	48(1)	31(1)	36(1)	-15(1)	6(1)	-11(1)
C(5)	38(1)	37(1)	38(1)	-18(1)	6(1)	-16(1)
C(6)	40(1)	36(1)	35(1)	-17(1)	8(1)	-14(1)
C(7)	36(1)	46(1)	54(2)	-29(1)	10(1)	-13(1)
C(8)	34(1)	46(1)	54(2)	-25(1)	-2(1)	-6(1)
C(9)	35(1)	39(1)	42(1)	-22(1)	-3(1)	-10(1)
C(10)	36(1)	37(1)	40(1)	-21(1)	0(1)	-12(1)
C(11)	45(1)	42(1)	44(1)	-22(1)	4(1)	-10(1)
C(12)	49(2)	54(2)	44(1)	-25(1)	10(1)	-11(1)
C(13)	51(2)	54(2)	41(1)	-22(1)	1(1)	-19(1)
C(14)	75(2)	73(2)	42(2)	-13(1)	0(1)	-12(2)
C(15)	73(2)	46(2)	60(2)	-30(1)	4(1)	-24(1)
C(16)	80(2)	37(2)	109(3)	-31(2)	-15(2)	1(2)
C(17)	39(1)	28(1)	35(1)	-15(1)	2(1)	-8(1)
C(18)	42(1)	33(1)	39(1)	-19(1)	6(1)	-12(1)
C(19)	60(2)	54(2)	38(1)	-23(1)	9(1)	-27(1)
C(20)	45(1)	37(1)	45(1)	-20(1)	11(1)	-15(1)
C(21)	38(1)	34(1)	65(2)	-25(1)	6(1)	-9(1)
C(22)	44(2)	54(2)	86(2)	-31(1)	9(1)	-21(1)
C(23)	40(1)	34(1)	56(2)	-22(1)	-9(1)	-7(1)
C(24)	45(1)	31(1)	41(1)	-17(1)	-4(1)	-7(1)
C(25)	70(2)	61(2)	37(1)	-19(1)	-7(1)	-25(1)
C(26)	43(1)	37(1)	32(1)	-17(1)	4(1)	-16(1)
C(27)	41(1)	42(1)	35(1)	-19(1)	3(1)	-19(1)
C(28)	56(2)	41(1)	36(1)	-12(1)	0(1)	-10(1)
C(29)	44(1)	48(1)	49(1)	-24(1)	4(1)	-9(1)
C(30)	46(2)	66(2)	52(2)	-31(1)	12(1)	-16(1)
C(31)	71(2)	99(3)	76(2)	-44(2)	28(2)	-4(2)
C(32)	60(2)	61(2)	37(1)	-22(1)	15(1)	-27(1)
C(33)	53(2)	45(1)	35(1)	-20(1)	8(1)	-21(1)
C(34)	84(2)	48(2)	33(1)	-12(1)	11(1)	-20(1)
B(1)	46(2)	32(1)	23(1)	-9(1)	-3(1)	-9(1)

Table S111. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^{2}x 10^3) for **2c**.

	x	y	z	U(eq)
H(2)	4805	4830	7842	44
H(3)	5102	2663	8221	48
H(5)	1198	3499	7133	42
H(6)	1414	4365	8401	43
H(7)	-309	6202	7437	50
H(8)	-754	6935	5570	53
H(11)	3632	3493	5493	52
H(12)	3535	4774	3583	58
H(14A)	2191	6527	1916	103
H(14B)	2293	7660	2246	103
H(14C)	850	7462	2065	103
H(15A)	1672	2091	6724	83

H(15B)	2086	681	7695	83
H(15C)	2884	1020	6597	83
H(16A)	5349	904	7711	117
H(16B)	4507	-109	8317	117
H(16C)	4834	741	8910	117
H(19A)	3667	7986	4611	70
H(19B)	2528	7659	5448	70
H(19C)	3793	6543	5462	70
H(20)	5501	8465	5125	49
H(22A)	7348	9146	5447	89
H(22B)	8129	8330	6666	89
H(22C)	7118	9707	6379	89
H(23)	6408	7982	8259	51
H(25A)	3586	7616	9346	82
H(25B)	5170	7197	9704	82
H(25C)	4445	6179	9650	82
H(28A)	629	8950	5973	69
H(28B)	1877	9300	6363	69
H(28C)	386	10218	6187	69
H(29)	-765	10054	7703	56
H(31A)	-2362	9880	9145	125
H(31B)	-1264	9629	10109	125
H(31C)	-2087	8603	10270	125
H(32)	-77	6856	10520	60
H(34A)	2582	4978	9682	84
H(34B)	1244	4788	10299	84
H(34C)	2303	5292	10756	84

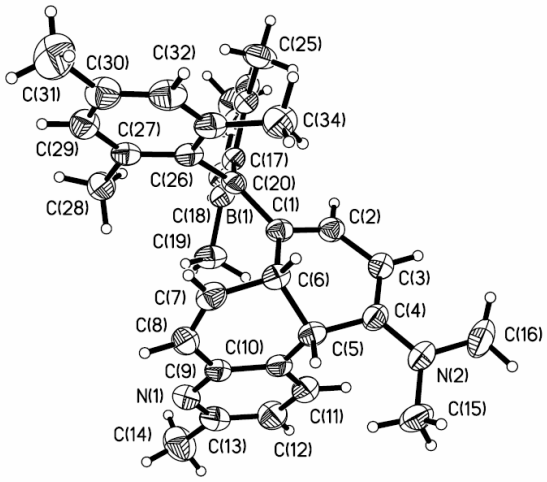


Figure S159. Structure of **2c**.

Table S112. Crystal data and structure refinement for **1d**.

Identification code	**1d**	
Empirical formula	C33 H35 B N2	
Formula weight	470.44	
Temperature	180(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	$P2_1/c$	
Unit cell dimensions	a = 22.112(6) Å	α= 90°.
	b = 8.318(2) Å	β= 110.321(8)°.

	c = 15.429(4) Å γ = 90°.
Volume	2661.1(13) $Å^3$
Z	4
Density (calculated)	1.174 Mg/m^3
Absorption coefficient	0.067 mm^{-1}
F(000)	1008
Crystal size	0.220 x 0.210 x 0.160 mm^3
Theta range for data collection	2.638 to 27.202°.
Index ranges	-28<=h<=28, -10<=k<=10, -19<=l<=19
Reflections collected	30375
Independent reflections	5916 [R(int) = 0.1436]
Completeness to theta = 25.242°	99.9 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.989 and 0.985
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	5916 / 0 / 334
Goodness-of-fit on F^2	1.059
Final R indices [I>2sigma(I)]	R1 = 0.0973, wR2 = 0.2120
R indices (all data)	R1 = 0.1778, wR2 = 0.2474
Extinction coefficient	0.0055(13)
Largest diff. peak and hole	0.453 and -0.222 $e.Å^{-3}$

Table S113. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for **1d**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
N(1)	400(2)	-377(5)	1158(3)	69(1)
C(1)	2429(2)	2103(4)	4173(3)	42(1)
B(1)	3019(2)	2968(5)	4043(3)	40(1)
N(2)	936(2)	-329(4)	4798(2)	51(1)
C(2)	2404(2)	1990(5)	5068(3)	45(1)
C(3)	1914(2)	1257(5)	5264(3)	47(1)
C(4)	1404(2)	532(5)	4570(3)	43(1)
C(5)	1367(2)	654(4)	3629(2)	34(1)
C(7)	1907(2)	1427(4)	2526(3)	42(1)
C(6)	1896(2)	1431(4)	3464(3)	40(1)
C(9)	875(2)	147(5)	1947(3)	54(1)
C(8)	1429(2)	777(5)	1830(3)	51(1)
C(10)	830(2)	118(4)	2823(3)	42(1)
C(11)	211(2)	-341(5)	2841(3)	55(1)
C(12)	-259(2)	-824(6)	2068(4)	68(1)
C(13)	-143(3)	-852(7)	1225(4)	76(2)
C(14)	894(2)	-9(7)	5717(3)	70(2)
C(15)	934(2)	-2075(5)	4649(4)	65(1)
C(16)	3688(2)	2538(4)	4773(3)	38(1)
C(17)	3872(2)	892(4)	4980(3)	45(1)
C(18)	3452(3)	-463(5)	4415(3)	67(1)
C(19)	4443(2)	504(5)	5661(3)	51(1)
C(20)	4854(2)	1649(5)	6199(3)	51(1)
C(21)	5453(2)	1200(7)	6986(4)	80(2)
C(22)	4694(2)	3252(5)	5991(3)	45(1)
C(23)	4133(2)	3695(4)	5291(3)	41(1)

C(24)	4013(2)	5480(4)	5098(3)	51(1)
C(25)	2946(2)	4291(4)	3278(2)	36(1)
C(26)	3333(2)	4258(4)	2713(3)	40(1)
C(27)	3792(2)	2877(5)	2758(3)	61(1)
C(28)	3286(2)	5473(5)	2083(3)	46(1)
C(29)	2875(2)	6776(5)	1985(3)	45(1)
C(30)	2846(3)	8112(6)	1319(3)	73(2)
C(31)	2496(2)	6814(5)	2529(3)	44(1)
C(32)	2516(2)	5593(4)	3153(3)	39(1)
C(33)	2080(2)	5793(5)	3717(3)	56(1)

Table S114. Bond lengths [Å] and angles [°] for **1d**.

N(1)-C(13)	1.302(7)	C(19)-C(20)	1.377(6)
N(1)-C(9)	1.374(5)	C(19)-H(19)	0.9500
C(1)-C(2)	1.403(5)	C(20)-C(22)	1.389(6)
C(1)-C(6)	1.416(5)	C(20)-C(21)	1.501(6)
C(1)-B(1)	1.563(6)	C(21)-H(21A)	0.9800
B(1)-C(16)	1.559(6)	C(21)-H(21B)	0.9800
B(1)-C(25)	1.581(6)	C(21)-H(21C)	0.9800
N(2)-C(4)	1.401(5)	C(22)-C(23)	1.382(6)
N(2)-C(15)	1.471(5)	C(22)-H(22)	0.9500
N(2)-C(14)	1.476(5)	C(23)-C(24)	1.520(5)
C(2)-C(3)	1.366(5)	C(24)-H(24A)	0.9800
C(2)-H(2)	0.9500	C(24)-H(24B)	0.9800
C(3)-C(4)	1.393(5)	C(24)-H(24C)	0.9800
C(3)-H(3)	0.9500	C(25)-C(32)	1.410(5)
C(4)-C(5)	1.430(5)	C(25)-C(26)	1.417(5)
C(5)-C(6)	1.434(5)	C(26)-C(28)	1.382(5)
C(5)-C(10)	1.459(5)	C(26)-C(27)	1.518(5)
C(7)-C(8)	1.333(5)	C(27)-H(27A)	0.9800
C(7)-C(6)	1.456(5)	C(27)-H(27B)	0.9800
C(7)-H(7)	0.9500	C(27)-H(27C)	0.9800
C(9)-C(10)	1.391(6)	C(28)-C(29)	1.388(6)
C(9)-C(8)	1.401(6)	C(28)-H(28)	0.9500
C(8)-H(8)	0.9500	C(29)-C(31)	1.377(6)
C(10)-C(11)	1.430(6)	C(29)-C(30)	1.500(6)
C(11)-C(12)	1.343(6)	C(30)-H(30A)	0.9800
C(11)-H(11)	0.9500	C(30)-H(30B)	0.9800
C(12)-C(13)	1.409(7)	C(30)-H(30C)	0.9800
C(12)-H(12)	0.9500	C(31)-C(32)	1.389(5)
C(13)-H(13)	0.9500	C(31)-H(31)	0.9500
C(14)-H(14A)	0.9800	C(32)-C(33)	1.515(5)
C(14)-H(14B)	0.9800	C(33)-H(33A)	0.9800
C(14)-H(14C)	0.9800	C(33)-H(33B)	0.9800
C(15)-H(15A)	0.9800	C(33)-H(33C)	0.9800
C(15)-H(15B)	0.9800	C(13)-N(1)-C(9)	117.9(4)
C(15)-H(15C)	0.9800	C(2)-C(1)-C(6)	115.3(4)
C(16)-C(23)	1.409(5)	C(2)-C(1)-B(1)	118.5(4)
C(16)-C(17)	1.432(5)	C(6)-C(1)-B(1)	126.2(4)
C(17)-C(19)	1.372(6)	C(16)-B(1)-C(1)	115.3(3)
C(17)-C(18)	1.526(6)	C(16)-B(1)-C(25)	121.6(3)
C(18)-H(18A)	0.9800	C(1)-B(1)-C(25)	122.9(4)
C(18)-H(18B)	0.9800	C(4)-N(2)-C(15)	115.2(3)
C(18)-H(18C)	0.9800	C(4)-N(2)-C(14)	116.6(3)

C(15)-N(2)-C(14)	109.3(4)	C(17)-C(18)-H(18B)	109.5
C(3)-C(2)-C(1)	123.6(4)	H(18A)-C(18)-H(18B)	109.5
C(3)-C(2)-H(2)	118.2	C(17)-C(18)-H(18C)	109.5
C(1)-C(2)-H(2)	118.2	H(18A)-C(18)-H(18C)	109.5
C(2)-C(3)-C(4)	121.0(4)	H(18B)-C(18)-H(18C)	109.5
C(2)-C(3)-H(3)	119.5	C(17)-C(19)-C(20)	122.6(4)
C(4)-C(3)-H(3)	119.5	C(17)-C(19)-H(19)	118.7
C(3)-C(4)-N(2)	120.0(4)	C(20)-C(19)-H(19)	118.7
C(3)-C(4)-C(5)	119.7(4)	C(19)-C(20)-C(22)	117.6(4)
N(2)-C(4)-C(5)	120.3(4)	C(19)-C(20)-C(21)	121.9(4)
C(4)-C(5)-C(6)	116.7(3)	C(22)-C(20)-C(21)	120.6(4)
C(4)-C(5)-C(10)	125.9(3)	C(20)-C(21)-H(21A)	109.5
C(6)-C(5)-C(10)	117.4(3)	C(20)-C(21)-H(21B)	109.5
C(8)-C(7)-C(6)	121.3(4)	H(21A)-C(21)-H(21B)	109.5
C(8)-C(7)-H(7)	119.4	C(20)-C(21)-H(21C)	109.5
C(6)-C(7)-H(7)	119.4	H(21A)-C(21)-H(21C)	109.5
C(1)-C(6)-C(5)	123.5(3)	H(21B)-C(21)-H(21C)	109.5
C(1)-C(6)-C(7)	118.2(4)	C(23)-C(22)-C(20)	121.6(4)
C(5)-C(6)-C(7)	118.2(3)	C(23)-C(22)-H(22)	119.2
N(1)-C(9)-C(10)	124.4(4)	C(20)-C(22)-H(22)	119.2
N(1)-C(9)-C(8)	116.0(4)	C(22)-C(23)-C(16)	121.4(3)
C(10)-C(9)-C(8)	119.6(4)	C(22)-C(23)-C(24)	117.5(4)
C(7)-C(8)-C(9)	122.2(4)	C(16)-C(23)-C(24)	121.1(4)
C(7)-C(8)-H(8)	118.9	C(23)-C(24)-H(24A)	109.5
C(9)-C(8)-H(8)	118.9	C(23)-C(24)-H(24B)	109.5
C(9)-C(10)-C(11)	114.6(4)	H(24A)-C(24)-H(24B)	109.5
C(9)-C(10)-C(5)	120.7(4)	C(23)-C(24)-H(24C)	109.5
C(11)-C(10)-C(5)	124.5(4)	H(24A)-C(24)-H(24C)	109.5
C(12)-C(11)-C(10)	120.8(5)	H(24B)-C(24)-H(24C)	109.5
C(12)-C(11)-H(11)	119.6	C(32)-C(25)-C(26)	117.0(3)
C(10)-C(11)-H(11)	119.6	C(32)-C(25)-B(1)	121.7(3)
C(11)-C(12)-C(13)	119.5(5)	C(26)-C(25)-B(1)	121.2(3)
C(11)-C(12)-H(12)	120.2	C(28)-C(26)-C(25)	120.3(4)
C(13)-C(12)-H(12)	120.2	C(28)-C(26)-C(27)	118.1(4)
N(1)-C(13)-C(12)	122.4(5)	C(25)-C(26)-C(27)	121.5(3)
N(1)-C(13)-H(13)	118.8	C(26)-C(27)-H(27A)	109.5
C(12)-C(13)-H(13)	118.8	C(26)-C(27)-H(27B)	109.5
N(2)-C(14)-H(14A)	109.5	H(27A)-C(27)-H(27B)	109.5
N(2)-C(14)-H(14B)	109.5	C(26)-C(27)-H(27C)	109.5
H(14A)-C(14)-H(14B)	109.5	H(27A)-C(27)-H(27C)	109.5
N(2)-C(14)-H(14C)	109.5	H(27B)-C(27)-H(27C)	109.5
H(14A)-C(14)-H(14C)	109.5	C(26)-C(28)-C(29)	122.2(4)
H(14B)-C(14)-H(14C)	109.5	C(26)-C(28)-H(28)	118.9
N(2)-C(15)-H(15A)	109.5	C(29)-C(28)-H(28)	118.9
N(2)-C(15)-H(15B)	109.5	C(31)-C(29)-C(28)	117.8(4)
H(15A)-C(15)-H(15B)	109.5	C(31)-C(29)-C(30)	120.7(4)
N(2)-C(15)-H(15C)	109.5	C(28)-C(29)-C(30)	121.5(4)
H(15A)-C(15)-H(15C)	109.5	C(29)-C(30)-H(30A)	109.5
H(15B)-C(15)-H(15C)	109.5	C(29)-C(30)-H(30B)	109.5
C(23)-C(16)-C(17)	116.0(4)	H(30A)-C(30)-H(30B)	109.5
C(23)-C(16)-B(1)	123.6(3)	C(29)-C(30)-H(30C)	109.5
C(17)-C(16)-B(1)	120.3(4)	H(30A)-C(30)-H(30C)	109.5
C(19)-C(17)-C(16)	120.6(4)	H(30B)-C(30)-H(30C)	109.5
C(19)-C(17)-C(18)	118.6(4)	C(29)-C(31)-C(32)	121.7(4)
C(16)-C(17)-C(18)	120.7(4)	C(29)-C(31)-H(31)	119.1
C(17)-C(18)-H(18A)	109.5	C(32)-C(31)-H(31)	119.1

C(31)-C(32)-C(25)	120.9(4)	H(33A)-C(33)-H(33B)	109.5
C(31)-C(32)-C(33)	116.4(3)	C(32)-C(33)-H(33C)	109.5
C(25)-C(32)-C(33)	122.6(3)	H(33A)-C(33)-H(33C)	109.5
C(32)-C(33)-H(33A)	109.5	H(33B)-C(33)-H(33C)	109.5
C(32)-C(33)-H(33B)	109.5		

Table S115. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for **1d**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
N(1)	72(3)	70(3)	51(2)	-13(2)	4(2)	-7(2)
C(1)	48(2)	34(2)	45(2)	2(2)	18(2)	0(2)
B(1)	55(3)	26(2)	48(3)	-10(2)	29(2)	-5(2)
N(2)	50(2)	51(2)	58(2)	0(2)	27(2)	-3(2)
C(2)	56(3)	49(2)	31(2)	-2(2)	16(2)	-7(2)
C(3)	43(2)	53(3)	44(2)	-1(2)	14(2)	-4(2)
C(4)	42(2)	45(2)	50(2)	3(2)	25(2)	4(2)
C(5)	38(2)	31(2)	34(2)	-2(2)	16(2)	4(2)
C(7)	53(3)	38(2)	38(2)	4(2)	21(2)	-2(2)
C(6)	44(2)	32(2)	42(2)	2(2)	11(2)	6(2)
C(9)	60(3)	40(2)	51(3)	-3(2)	6(2)	4(2)
C(8)	65(3)	45(2)	42(2)	-1(2)	16(2)	-4(2)
C(10)	49(2)	28(2)	43(2)	1(2)	7(2)	3(2)
C(11)	52(3)	45(2)	64(3)	-7(2)	15(2)	-7(2)
C(12)	47(3)	64(3)	83(4)	-1(3)	7(3)	-5(2)
C(13)	71(4)	77(4)	65(3)	-14(3)	3(3)	-11(3)
C(14)	74(3)	93(4)	61(3)	-14(3)	47(3)	-19(3)
C(15)	75(3)	46(3)	88(4)	-4(3)	46(3)	-7(2)
C(16)	49(2)	25(2)	50(2)	7(2)	28(2)	3(2)
C(17)	65(3)	25(2)	57(3)	6(2)	36(2)	0(2)
C(18)	97(4)	24(2)	83(3)	5(2)	36(3)	3(2)
C(19)	65(3)	32(2)	66(3)	18(2)	33(2)	16(2)
C(20)	54(3)	43(2)	65(3)	14(2)	32(2)	9(2)
C(21)	66(3)	75(4)	92(4)	23(3)	18(3)	18(3)
C(22)	50(3)	39(2)	52(2)	3(2)	24(2)	0(2)
C(23)	49(2)	28(2)	56(3)	1(2)	32(2)	0(2)
C(24)	68(3)	25(2)	64(3)	-2(2)	26(2)	-3(2)
C(25)	41(2)	31(2)	40(2)	-5(2)	19(2)	-1(2)
C(26)	47(2)	31(2)	49(2)	-2(2)	23(2)	-1(2)
C(27)	75(3)	48(3)	78(3)	6(2)	50(3)	15(2)
C(28)	59(3)	51(2)	36(2)	-1(2)	25(2)	-6(2)
C(29)	54(3)	42(2)	36(2)	7(2)	12(2)	-2(2)
C(30)	86(4)	78(4)	58(3)	30(3)	28(3)	11(3)
C(31)	46(2)	33(2)	47(2)	0(2)	10(2)	2(2)
C(32)	44(2)	32(2)	41(2)	-6(2)	14(2)	-2(2)
C(33)	62(3)	50(3)	69(3)	-2(2)	37(2)	13(2)

Table S116. Hydrogen coordinates ($x\ 10^4$) and isotropic displacement parameters ($Å^2 x\ 10^3$) for **1d**.

	x	y	z	U(eq)

H(2)	2747	2449	5564	54
H(3)	1921	1240	5883	56
H(7)	2262	1898	2409	50
H(8)	1465	739	1234	62
H(11)	131	-303	3407	66
H(12)	-666	-1144	2088	82
H(13)	-474	-1232	686	92
H(14A)	855	1151	5795	105
H(14B)	1284	-409	6198	105
H(14C)	515	-556	5768	105
H(15A)	901	-2290	4009	98
H(15B)	566	-2559	4766	98
H(15C)	1335	-2540	5072	98
H(18A)	3238	-102	3776	100
H(18B)	3127	-759	4684	100
H(18C)	3723	-1399	4421	100
H(19)	4560	-597	5766	62
H(21A)	5772	753	6741	120
H(21B)	5347	395	7375	120
H(21C)	5633	2158	7356	120
H(22)	4977	4065	6338	55
H(24A)	4168	5800	4601	77
H(24B)	4243	6092	5659	77
H(24C)	3550	5699	4911	77
H(27A)	3558	1856	2685	91
H(27B)	4144	2891	3357	91
H(27C)	3970	2992	2262	91
H(28)	3544	5416	1703	56
H(30A)	2838	7657	729	110
H(30B)	3227	8800	1572	110
H(30C)	2456	8750	1220	110
H(31)	2214	7699	2476	52
H(33A)	1929	6908	3674	84
H(33B)	2320	5528	4365	84
H(33C)	1709	5071	3478	84

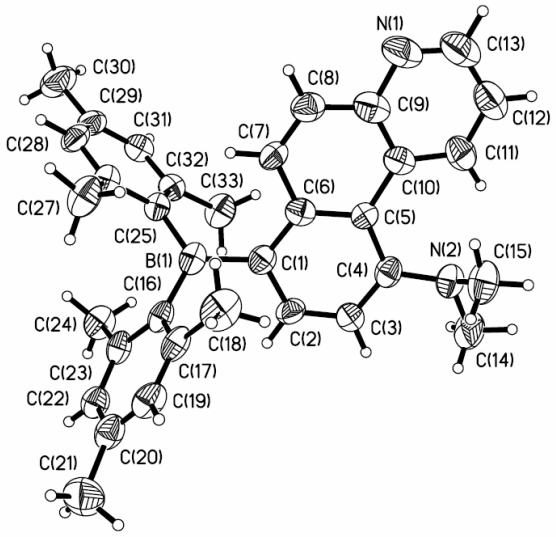


Figure S160. Structure of **1d**.

Table S117. Crystal data and structure refinement for **2d**.

Identification code	**2d**	
Empirical formula	C34 H37 B N2	
Formula weight	484.46	
Temperature	180(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	$P2_1/c$	
Unit cell dimensions	a = 22.653(2) Å	α= 90°.
	b = 8.3251(7) Å	β= 107.682(3)°.
	c = 15.2916(13) Å	γ = 90°.
Volume	2747.6(4) $Å^3$	
Z	4	
Density (calculated)	1.171 Mg/m^3	
Absorption coefficient	0.067 mm^{-1}	
F(000)	1040	
Crystal size	0.120 x 0.081 x 0.075 mm^3	
Theta range for data collection	2.622 to 27.122°.	
Index ranges	-29<=h<=29, -10<=k<=10, -19<=l<=19	
Reflections collected	25922	
Independent reflections	6057 [R(int) = 0.1291]	
Completeness to theta = 25.242°	99.8 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.995 and 0.992	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	6057 / 0 / 344	
Goodness-of-fit on F^2	1.014	
Final R indices [I>2sigma(I)]	R1 = 0.0642, wR2 = 0.1199	
R indices (all data)	R1 = 0.1462, wR2 = 0.1471	
Extinction coefficient	0.0055(7)	
Largest diff. peak and hole	0.247 and -0.214 $e.Å^{-3}$	

Table S118. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for **2d**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
N(1)	4499(1)	-321(2)	8573(1)	31(1)
N(2)	3922(1)	-516(2)	4915(1)	30(1)
C(1)	2507(1)	2008(3)	5672(2)	27(1)
C(2)	2511(1)	1852(3)	4773(2)	33(1)
C(3)	2979(1)	1070(3)	4533(2)	32(1)
C(4)	3471(1)	363(3)	5187(2)	26(1)
C(5)	3520(1)	534(3)	6143(2)	25(1)
C(6)	3022(1)	1328(2)	6362(2)	25(1)
C(7)	3028(1)	1387(3)	7303(2)	29(1)
C(8)	3494(1)	799(3)	7990(2)	30(1)
C(9)	4028(1)	141(3)	7817(2)	26(1)
C(10)	4054(1)	30(3)	6905(2)	26(1)
C(11)	4630(1)	-482(3)	6828(2)	33(1)
C(12)	5104(1)	-896(3)	7588(2)	38(1)
C(13)	5023(1)	-848(3)	8461(2)	32(1)
C(14)	5518(1)	-1381(3)	9305(2)	38(1)

C(15)	3977(1)	-175(3)	4004(2)	43(1)
C(16)	3916(1)	-2251(3)	5067(2)	48(1)
C(17)	1288(1)	2472(3)	5160(2)	26(1)
C(18)	865(1)	3653(3)	4678(2)	28(1)
C(19)	984(1)	5434(3)	4852(2)	39(1)
C(20)	321(1)	3207(3)	4018(2)	35(1)
C(21)	158(1)	1616(3)	3814(2)	38(1)
C(22)	-426(1)	1166(4)	3073(2)	62(1)
C(23)	556(1)	454(3)	4321(2)	39(1)
C(24)	1112(1)	836(3)	4975(2)	33(1)
C(25)	1506(1)	-523(3)	5495(2)	48(1)
C(26)	2012(1)	4232(3)	6604(2)	25(1)
C(27)	2429(1)	5528(3)	6690(2)	29(1)
C(28)	2874(1)	5652(3)	6128(2)	47(1)
C(29)	2437(1)	6787(3)	7294(2)	31(1)
C(30)	2057(1)	6806(3)	7845(2)	33(1)
C(31)	2073(1)	8175(3)	8499(2)	55(1)
C(32)	1660(1)	5510(3)	7790(2)	35(1)
C(33)	1627(1)	4248(3)	7180(2)	30(1)
C(34)	1187(1)	2880(3)	7178(2)	45(1)
B(1)	1942(1)	2898(3)	5846(2)	27(1)

Table S119. Bond lengths [Å] and angles [°] for **2d**.

N(1)-C(13)	1.326(3)	C(15)-H(15B)	0.9800
N(1)-C(9)	1.368(3)	C(15)-H(15C)	0.9800
N(2)-C(4)	1.419(3)	C(16)-H(16A)	0.9800
N(2)-C(15)	1.462(3)	C(16)-H(16B)	0.9800
N(2)-C(16)	1.464(3)	C(16)-H(16C)	0.9800
C(1)-C(2)	1.383(3)	C(17)-C(18)	1.414(3)
C(1)-C(6)	1.431(3)	C(17)-C(24)	1.424(3)
C(1)-B(1)	1.569(4)	C(17)-B(1)	1.574(3)
C(2)-C(3)	1.386(3)	C(18)-C(20)	1.385(3)
C(2)-H(2)	0.9500	C(18)-C(19)	1.517(3)
C(3)-C(4)	1.383(3)	C(19)-H(19A)	0.9800
C(3)-H(3)	0.9500	C(19)-H(19B)	0.9800
C(4)-C(5)	1.439(3)	C(19)-H(19C)	0.9800
C(5)-C(6)	1.432(3)	C(20)-C(21)	1.385(3)
C(5)-C(10)	1.463(3)	C(20)-H(20)	0.9500
C(6)-C(7)	1.436(3)	C(21)-C(23)	1.387(3)
C(7)-C(8)	1.337(3)	C(21)-C(22)	1.505(3)
C(7)-H(7)	0.9500	C(22)-H(22A)	0.9800
C(8)-C(9)	1.423(3)	C(22)-H(22B)	0.9800
C(8)-H(8)	0.9500	C(22)-H(22C)	0.9800
C(9)-C(10)	1.417(3)	C(23)-C(24)	1.387(3)
C(10)-C(11)	1.412(3)	C(23)-H(23)	0.9500
C(11)-C(12)	1.365(3)	C(24)-C(25)	1.508(3)
C(11)-H(11)	0.9500	C(25)-H(25A)	0.9800
C(12)-C(13)	1.401(3)	C(25)-H(25B)	0.9800
C(12)-H(12)	0.9500	C(25)-H(25C)	0.9800
C(13)-C(14)	1.496(3)	C(26)-C(27)	1.414(3)
C(14)-H(14A)	0.9800	C(26)-C(33)	1.416(3)
C(14)-H(14B)	0.9800	C(26)-B(1)	1.578(3)
C(14)-H(14C)	0.9800	C(27)-C(29)	1.394(3)
C(15)-H(15A)	0.9800	C(27)-C(28)	1.513(3)

C(28)-H(28A)	0.9800	N(1)-C(13)-C(12)	120.9(2)
C(28)-H(28B)	0.9800	N(1)-C(13)-C(14)	116.9(2)
C(28)-H(28C)	0.9800	C(12)-C(13)-C(14)	122.2(2)
C(29)-C(30)	1.376(3)	C(13)-C(14)-H(14A)	109.5
C(29)-H(29)	0.9500	C(13)-C(14)-H(14B)	109.5
C(30)-C(32)	1.390(3)	H(14A)-C(14)-H(14B)	109.5
C(30)-C(31)	1.509(3)	C(13)-C(14)-H(14C)	109.5
C(31)-H(31A)	0.9800	H(14A)-C(14)-H(14C)	109.5
C(31)-H(31B)	0.9800	H(14B)-C(14)-H(14C)	109.5
C(31)-H(31C)	0.9800	N(2)-C(15)-H(15A)	109.5
C(32)-C(33)	1.392(3)	N(2)-C(15)-H(15B)	109.5
C(32)-H(32)	0.9500	H(15A)-C(15)-H(15B)	109.5
C(33)-C(34)	1.514(3)	N(2)-C(15)-H(15C)	109.5
C(34)-H(34A)	0.9800	H(15A)-C(15)-H(15C)	109.5
C(34)-H(34B)	0.9800	H(15B)-C(15)-H(15C)	109.5
C(34)-H(34C)	0.9800	N(2)-C(16)-H(16A)	109.5
C(13)-N(1)-C(9)	118.9(2)	N(2)-C(16)-H(16B)	109.5
C(4)-N(2)-C(15)	117.18(19)	H(16A)-C(16)-H(16B)	109.5
C(4)-N(2)-C(16)	114.80(19)	N(2)-C(16)-H(16C)	109.5
C(15)-N(2)-C(16)	110.5(2)	H(16A)-C(16)-H(16C)	109.5
C(2)-C(1)-C(6)	116.5(2)	H(16B)-C(16)-H(16C)	109.5
C(2)-C(1)-B(1)	117.7(2)	C(18)-C(17)-C(24)	117.2(2)
C(6)-C(1)-B(1)	125.8(2)	C(18)-C(17)-B(1)	122.90(19)
C(1)-C(2)-C(3)	122.9(2)	C(24)-C(17)-B(1)	119.9(2)
C(1)-C(2)-H(2)	118.5	C(20)-C(18)-C(17)	120.4(2)
C(3)-C(2)-H(2)	118.5	C(20)-C(18)-C(19)	117.5(2)
C(4)-C(3)-C(2)	121.4(2)	C(17)-C(18)-C(19)	122.1(2)
C(4)-C(3)-H(3)	119.3	C(18)-C(19)-H(19A)	109.5
C(2)-C(3)-H(3)	119.3	C(18)-C(19)-H(19B)	109.5
C(3)-C(4)-N(2)	120.1(2)	H(19A)-C(19)-H(19B)	109.5
C(3)-C(4)-C(5)	119.3(2)	C(18)-C(19)-H(19C)	109.5
N(2)-C(4)-C(5)	120.6(2)	H(19A)-C(19)-H(19C)	109.5
C(6)-C(5)-C(4)	117.4(2)	H(19B)-C(19)-H(19C)	109.5
C(6)-C(5)-C(10)	117.8(2)	C(18)-C(20)-C(21)	122.5(2)
C(4)-C(5)-C(10)	124.7(2)	C(18)-C(20)-H(20)	118.8
C(1)-C(6)-C(5)	122.2(2)	C(21)-C(20)-H(20)	118.8
C(1)-C(6)-C(7)	118.9(2)	C(20)-C(21)-C(23)	117.3(2)
C(5)-C(6)-C(7)	118.8(2)	C(20)-C(21)-C(22)	121.4(2)
C(8)-C(7)-C(6)	122.6(2)	C(23)-C(21)-C(22)	121.4(2)
C(8)-C(7)-H(7)	118.7	C(21)-C(22)-H(22A)	109.5
C(6)-C(7)-H(7)	118.7	C(21)-C(22)-H(22B)	109.5
C(7)-C(8)-C(9)	120.6(2)	H(22A)-C(22)-H(22B)	109.5
C(7)-C(8)-H(8)	119.7	C(21)-C(22)-H(22C)	109.5
C(9)-C(8)-H(8)	119.7	H(22A)-C(22)-H(22C)	109.5
N(1)-C(9)-C(10)	124.0(2)	H(22B)-C(22)-H(22C)	109.5
N(1)-C(9)-C(8)	116.1(2)	C(21)-C(23)-C(24)	122.5(2)
C(10)-C(9)-C(8)	119.9(2)	C(21)-C(23)-H(23)	118.8
C(11)-C(10)-C(9)	114.6(2)	C(24)-C(23)-H(23)	118.8
C(11)-C(10)-C(5)	125.6(2)	C(23)-C(24)-C(17)	120.0(2)
C(9)-C(10)-C(5)	119.6(2)	C(23)-C(24)-C(25)	118.1(2)
C(12)-C(11)-C(10)	120.9(2)	C(17)-C(24)-C(25)	121.8(2)
C(12)-C(11)-H(11)	119.6	C(24)-C(25)-H(25A)	109.5
C(10)-C(11)-H(11)	119.6	C(24)-C(25)-H(25B)	109.5
C(11)-C(12)-C(13)	120.5(2)	H(25A)-C(25)-H(25B)	109.5
C(11)-C(12)-H(12)	119.7	C(24)-C(25)-H(25C)	109.5
C(13)-C(12)-H(12)	119.7	H(25A)-C(25)-H(25C)	109.5

H(25B)-C(25)-H(25C)	109.5	C(30)-C(31)-H(31B)	109.5
C(27)-C(26)-C(33)	117.1(2)	H(31A)-C(31)-H(31B)	109.5
C(27)-C(26)-B(1)	121.4(2)	C(30)-C(31)-H(31C)	109.5
C(33)-C(26)-B(1)	121.4(2)	H(31A)-C(31)-H(31C)	109.5
C(29)-C(27)-C(26)	120.6(2)	H(31B)-C(31)-H(31C)	109.5
C(29)-C(27)-C(28)	116.6(2)	C(30)-C(32)-C(33)	121.9(2)
C(26)-C(27)-C(28)	122.7(2)	C(30)-C(32)-H(32)	119.0
C(27)-C(28)-H(28A)	109.5	C(33)-C(32)-H(32)	119.0
C(27)-C(28)-H(28B)	109.5	C(32)-C(33)-C(26)	120.5(2)
H(28A)-C(28)-H(28B)	109.5	C(32)-C(33)-C(34)	118.1(2)
C(27)-C(28)-H(28C)	109.5	C(26)-C(33)-C(34)	121.5(2)
H(28A)-C(28)-H(28C)	109.5	C(33)-C(34)-H(34A)	109.5
H(28B)-C(28)-H(28C)	109.5	C(33)-C(34)-H(34B)	109.5
C(30)-C(29)-C(27)	122.1(2)	H(34A)-C(34)-H(34B)	109.5
C(30)-C(29)-H(29)	119.0	C(33)-C(34)-H(34C)	109.5
C(27)-C(29)-H(29)	119.0	H(34A)-C(34)-H(34C)	109.5
C(29)-C(30)-C(32)	117.8(2)	H(34B)-C(34)-H(34C)	109.5
C(29)-C(30)-C(31)	121.4(2)	C(1)-B(1)-C(17)	115.6(2)
C(32)-C(30)-C(31)	120.8(2)	C(1)-B(1)-C(26)	123.5(2)
C(30)-C(31)-H(31A)	109.5	C(17)-B(1)-C(26)	120.8(2)

Table S120. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for **2d**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + ... \quad + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
N(1)	32(1)	32(1)	30(1)	1(1)	10(1)	5(1)
N(2)	32(1)	34(1)	29(1)	-2(1)	17(1)	1(1)
C(1)	29(1)	28(1)	25(1)	-5(1)	8(1)	-1(1)
C(2)	27(1)	39(1)	29(1)	-2(1)	3(1)	7(1)
C(3)	34(1)	41(1)	22(1)	-4(1)	9(1)	0(1)
C(4)	24(1)	28(1)	28(1)	-5(1)	12(1)	-4(1)
C(5)	25(1)	23(1)	28(1)	-2(1)	11(1)	-1(1)
C(6)	26(1)	22(1)	27(1)	-3(1)	10(1)	0(1)
C(7)	30(1)	33(1)	27(1)	-1(1)	12(1)	4(1)
C(8)	34(1)	33(1)	25(1)	-1(1)	14(1)	6(1)
C(9)	28(1)	24(1)	27(1)	2(1)	10(1)	1(1)
C(10)	26(1)	24(1)	29(1)	1(1)	11(1)	-1(1)
C(11)	33(1)	42(1)	29(1)	4(1)	16(1)	7(1)
C(12)	31(1)	50(2)	37(2)	4(1)	15(1)	12(1)
C(13)	32(1)	31(1)	32(1)	3(1)	9(1)	5(1)
C(14)	35(2)	44(2)	34(1)	2(1)	9(1)	11(1)
C(15)	39(2)	66(2)	30(1)	-2(1)	20(1)	2(1)
C(16)	56(2)	35(2)	65(2)	-8(1)	38(2)	1(1)
C(17)	29(1)	23(1)	28(1)	-2(1)	14(1)	0(1)
C(18)	26(1)	27(1)	33(1)	-1(1)	13(1)	-1(1)
C(19)	42(2)	25(1)	46(2)	6(1)	9(1)	3(1)
C(20)	28(1)	40(2)	37(1)	1(1)	9(1)	3(1)
C(21)	29(1)	45(2)	40(2)	-11(1)	13(1)	-7(1)
C(22)	40(2)	71(2)	64(2)	-18(2)	0(2)	-12(2)
C(23)	39(2)	31(1)	51(2)	-13(1)	20(1)	-11(1)
C(24)	36(2)	28(1)	38(1)	-5(1)	16(1)	0(1)
C(25)	58(2)	23(1)	61(2)	2(1)	14(2)	2(1)
C(26)	23(1)	26(1)	25(1)	2(1)	6(1)	2(1)

C(27)	26(1)	31(1)	30(1)	2(1)	8(1)	1(1)
C(28)	51(2)	44(2)	56(2)	-6(1)	31(2)	-14(1)
C(29)	29(1)	28(1)	33(1)	2(1)	4(1)	0(1)
C(30)	34(2)	31(1)	31(1)	-2(1)	6(1)	4(1)
C(31)	59(2)	55(2)	51(2)	-23(2)	16(2)	-1(2)
C(32)	34(1)	44(2)	30(1)	0(1)	15(1)	7(1)
C(33)	28(1)	32(1)	30(1)	3(1)	11(1)	2(1)
C(34)	48(2)	45(2)	51(2)	-2(1)	30(1)	-11(1)
B(1)	32(2)	23(1)	28(2)	7(1)	11(1)	1(1)

Table S121. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^{2}x 10^3) for **2d**.

	x	y	z	U(eq)
H(2)	2178	2301	4299	39
H(3)	2961	1018	3905	39
H(7)	2686	1863	7443	35
H(8)	3470	820	8599	35
H(11)	4689	-538	6240	40
H(12)	5491	-1220	7525	46
H(14A)	5474	-2534	9397	57
H(14B)	5478	-789	9837	57
H(14C)	5926	-1169	9231	57
H(15A)	3614	-600	3534	65
H(15B)	4352	-686	3943	65
H(15C)	4002	989	3925	65
H(16A)	3550	-2724	4623	71
H(16B)	3902	-2459	5691	71
H(16C)	4291	-2733	4988	71
H(19A)	1421	5666	4933	58
H(19B)	883	5743	5409	58
H(19C)	724	6045	4328	58
H(20)	50	4024	3692	42
H(22A)	-759	1908	3087	93
H(22B)	-545	67	3176	93
H(22C)	-354	1230	2474	93
H(23)	443	-644	4217	46
H(25A)	1241	-1444	5515	72
H(25B)	1724	-172	6122	72
H(25C)	1809	-835	5185	72
H(28A)	2672	5254	5506	71
H(28B)	3244	5006	6416	71
H(28C)	2994	6777	6099	71
H(29)	2713	7659	7326	38
H(31A)	2395	8944	8471	83
H(31B)	2166	7756	9125	83
H(31C)	1670	8715	8326	83
H(32)	1404	5484	8180	42
H(34A)	829	2943	6625	67
H(34B)	1046	2957	7723	67
H(34C)	1400	1854	7186	67

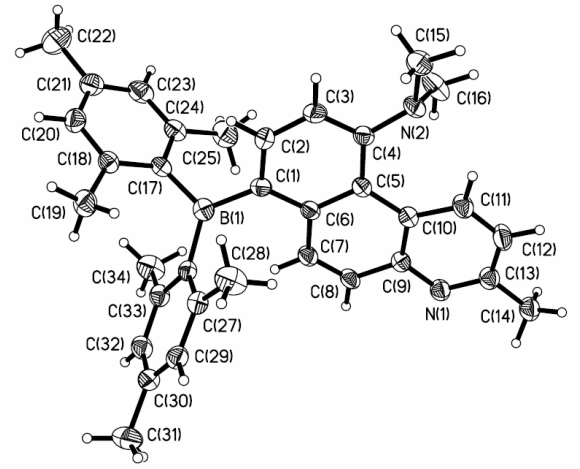


Figure S161. Structure of **2d**.

Table S122. Crystal data and structure refinement for **6d**.

Identification code	**6d**	
Empirical formula	C32 H34 B N S	
Formula weight	475.47	
Temperature	180(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	$Pna2_1$	
Unit cell dimensions	a = 32.54(4) Å	α= 90°.
	b = 9.129(10) Å	β= 90°.
	c = 9.286(12) Å	γ = 90°.
Volume	2759(6) $Å^3$	
Z	4	
Density (calculated)	1.145 Mg/m^3	
Absorption coefficient	0.137 mm^{-1}	
F(000)	1016	
Crystal size	0.200 x 0.120 x 0.110 mm^3	
Theta range for data collection	2.317 to 28.695°.	
Index ranges	-41<=h<=42, -11<=k<=11, -11<=l<=11	
Reflections collected	21468	
Independent reflections	5909 [R(int) = 0.2018]	
Completeness to theta = 25.242°	99.5 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.985 and 0.973	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	5909 / 1 / 324	
Goodness-of-fit on F^2	1.004	
Final R indices [I>2sigma(I)]	R1 = 0.0801, wR2 = 0.1818	
R indices (all data)	R1 = 0.1957, wR2 = 0.2266	
Absolute structure parameter	0.03(11)	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.260 and -0.320 e.$Å^{-3}$	

Table S123. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for **6d**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
S(1)	7299(1)	2214(2)	9515(2)	50(1)
N(1)	7464(2)	5166(8)	8998(7)	45(2)
B(1)	6141(2)	6118(10)	4778(9)	34(2)
C(1)	6493(2)	5754(8)	5891(8)	31(2)
C(2)	6736(2)	6907(9)	6369(8)	35(2)
C(3)	7066(2)	6729(8)	7354(8)	36(2)
C(4)	7146(2)	5387(9)	7940(7)	34(2)
C(5)	6902(2)	4110(8)	7547(7)	31(2)
C(6)	6581(2)	4336(9)	6471(7)	34(2)
C(7)	6332(2)	3086(9)	6116(8)	37(2)
C(8)	6387(2)	1754(10)	6740(8)	43(2)
C(9)	6696(2)	1521(9)	7833(8)	38(2)
C(10)	6947(2)	2735(9)	8196(7)	35(2)
C(11)	7109(3)	454(10)	9542(10)	61(2)
C(12)	6786(2)	205(9)	8632(8)	45(2)
C(13)	5906(2)	7612(8)	5045(8)	33(2)
C(14)	5714(2)	7921(9)	6415(8)	38(2)
C(15)	5748(2)	6836(10)	7682(9)	51(2)
C(16)	5475(2)	9156(9)	6600(9)	46(2)
C(17)	5424(2)	10200(10)	5506(10)	48(2)
C(18)	5164(3)	11570(12)	5737(13)	75(3)
C(19)	5620(2)	9927(10)	4188(9)	47(2)
C(20)	5856(2)	8701(9)	3960(8)	40(2)
C(21)	6060(2)	8523(11)	2483(9)	56(2)
C(22)	6023(2)	5087(9)	3473(7)	36(2)
C(23)	5604(2)	4750(9)	3153(8)	39(2)
C(24)	5251(2)	5398(11)	4042(10)	60(3)
C(25)	5509(2)	3803(9)	2063(8)	42(2)
C(26)	5807(2)	3179(10)	1158(9)	47(2)
C(27)	5691(3)	2138(13)	-48(10)	74(3)
C(28)	6213(2)	3541(9)	1450(8)	44(2)
C(29)	6329(2)	4433(9)	2574(8)	38(2)
C(30)	6786(2)	4741(11)	2791(10)	60(3)
C(31)	7867(2)	4816(12)	8368(10)	70(3)
C(32)	7495(3)	6317(12)	10058(10)	67(3)

Table S124. Bond lengths [Å] and angles [°] for **6d**.

S(1)-C(11)	1.722(10)	C(5)-C(10)	1.401(10)
S(1)-C(10)	1.743(7)	C(5)-C(6)	1.460(9)
N(1)-C(32)	1.444(11)	C(6)-C(7)	1.439(10)
N(1)-C(4)	1.441(8)	C(7)-C(8)	1.358(11)
N(1)-C(31)	1.471(9)	C(7)-H(7)	0.9500
B(1)-C(1)	1.580(10)	C(8)-C(9)	1.445(10)
B(1)-C(22)	1.582(12)	C(8)-H(8)	0.9500
B(1)-C(13)	1.583(11)	C(9)-C(10)	1.418(11)
C(1)-C(2)	1.389(10)	C(9)-C(12)	1.443(11)
C(1)-C(6)	1.431(10)	C(11)-C(12)	1.367(11)
C(2)-C(3)	1.420(10)	C(11)-H(11)	0.9500
C(2)-H(2)	0.9500	C(12)-H(12)	0.9500
C(3)-C(4)	1.366(10)	C(13)-C(20)	1.425(10)
C(3)-H(3)	0.9500	C(13)-C(14)	1.444(10)
C(4)-C(5)	1.457(10)	C(14)-C(16)	1.381(11)

C(14)-C(15)	1.542(11)	C(4)-C(3)-C(2)	120.3(6)
C(15)-H(15A)	0.9800	C(4)-C(3)-H(3)	119.9
C(15)-H(15B)	0.9800	C(2)-C(3)-H(3)	119.9
C(15)-H(15C)	0.9800	C(3)-C(4)-N(1)	122.3(6)
C(16)-C(17)	1.404(11)	C(3)-C(4)-C(5)	120.9(6)
C(16)-H(16)	0.9500	N(1)-C(4)-C(5)	116.8(7)
C(17)-C(19)	1.403(12)	C(10)-C(5)-C(4)	123.5(6)
C(17)-C(18)	1.525(12)	C(10)-C(5)-C(6)	119.7(6)
C(18)-H(18A)	0.9800	C(4)-C(5)-C(6)	116.7(7)
C(18)-H(18B)	0.9800	C(1)-C(6)-C(7)	121.3(6)
C(18)-H(18C)	0.9800	C(1)-C(6)-C(5)	121.9(6)
C(19)-C(20)	1.374(11)	C(7)-C(6)-C(5)	116.6(7)
C(19)-H(19)	0.9500	C(8)-C(7)-C(6)	122.6(7)
C(20)-C(21)	1.532(11)	C(8)-C(7)-H(7)	118.7
C(21)-H(21A)	0.9800	C(6)-C(7)-H(7)	118.7
C(21)-H(21B)	0.9800	C(7)-C(8)-C(9)	121.5(7)
C(21)-H(21C)	0.9800	C(7)-C(8)-H(8)	119.2
C(22)-C(23)	1.429(9)	C(9)-C(8)-H(8)	119.2
C(22)-C(29)	1.430(10)	C(10)-C(9)-C(12)	114.2(7)
C(23)-C(25)	1.366(11)	C(10)-C(9)-C(8)	117.0(7)
C(23)-C(24)	1.533(10)	C(12)-C(9)-C(8)	128.8(7)
C(24)-H(24A)	0.9800	C(5)-C(10)-C(9)	122.5(6)
C(24)-H(24B)	0.9800	C(5)-C(10)-S(1)	128.0(6)
C(24)-H(24C)	0.9800	C(9)-C(10)-S(1)	109.5(6)
C(25)-C(26)	1.405(11)	C(12)-C(11)-S(1)	115.0(7)
C(25)-H(25)	0.9500	C(12)-C(11)-H(11)	122.5
C(26)-C(28)	1.387(10)	S(1)-C(11)-H(11)	122.5
C(26)-C(27)	1.517(12)	C(11)-C(12)-C(9)	109.7(8)
C(27)-H(27A)	0.9800	C(11)-C(12)-H(12)	125.2
C(27)-H(27B)	0.9800	C(9)-C(12)-H(12)	125.2
C(27)-H(27C)	0.9800	C(20)-C(13)-C(14)	116.0(7)
C(28)-C(29)	1.377(10)	C(20)-C(13)-B(1)	123.0(7)
C(28)-H(28)	0.9500	C(14)-C(13)-B(1)	121.0(6)
C(29)-C(30)	1.527(9)	C(16)-C(14)-C(13)	120.8(7)
C(30)-H(30A)	0.9800	C(16)-C(14)-C(15)	118.0(7)
C(30)-H(30B)	0.9800	C(13)-C(14)-C(15)	121.1(7)
C(30)-H(30C)	0.9800	C(14)-C(15)-H(15A)	109.5
C(31)-H(00D)	0.9800	C(14)-C(15)-H(15B)	109.5
C(31)-H(00E)	0.9800	H(15A)-C(15)-H(15B)	109.5
C(31)-H(00F)	0.9800	C(14)-C(15)-H(15C)	109.5
C(32)-H(00A)	0.9800	H(15A)-C(15)-H(15C)	109.5
C(32)-H(00B)	0.9800	H(15B)-C(15)-H(15C)	109.5
C(32)-H(00C)	0.9800	C(14)-C(16)-C(17)	122.1(7)
C(11)-S(1)-C(10)	91.6(4)	C(14)-C(16)-H(16)	118.9
C(32)-N(1)-C(4)	114.4(7)	C(17)-C(16)-H(16)	118.9
C(32)-N(1)-C(31)	111.5(7)	C(19)-C(17)-C(16)	117.1(7)
C(4)-N(1)-C(31)	113.5(6)	C(19)-C(17)-C(18)	121.4(8)
C(1)-B(1)-C(22)	123.6(7)	C(16)-C(17)-C(18)	121.4(8)
C(1)-B(1)-C(13)	115.4(7)	C(17)-C(18)-H(18A)	109.5
C(22)-B(1)-C(13)	121.0(6)	C(17)-C(18)-H(18B)	109.5
C(2)-C(1)-C(6)	116.9(6)	H(18A)-C(18)-H(18B)	109.5
C(2)-C(1)-B(1)	117.6(7)	C(17)-C(18)-H(18C)	109.5
C(6)-C(1)-B(1)	125.5(6)	H(18A)-C(18)-H(18C)	109.5
C(1)-C(2)-C(3)	123.3(7)	H(18B)-C(18)-H(18C)	109.5
C(1)-C(2)-H(2)	118.3	C(20)-C(19)-C(17)	122.3(7)
C(3)-C(2)-H(2)	118.3	C(20)-C(19)-H(19)	118.9

C(17)-C(19)-H(19)	118.9	H(00A)-C(32)-H(00C)	109.5
C(19)-C(20)-C(13)	121.5(7)	H(00B)-C(32)-H(00C)	109.5
C(19)-C(20)-C(21)	117.8(7)		
C(13)-C(20)-C(21)	120.7(7)		
C(20)-C(21)-H(21A)	109.5		
C(20)-C(21)-H(21B)	109.5		
H(21A)-C(21)-H(21B)	109.5		
C(20)-C(21)-H(21C)	109.5		
H(21A)-C(21)-H(21C)	109.5		
H(21B)-C(21)-H(21C)	109.5		
C(23)-C(22)-C(29)	117.0(7)		
C(23)-C(22)-B(1)	121.3(6)		
C(29)-C(22)-B(1)	121.7(5)		
C(25)-C(23)-C(22)	120.4(6)		
C(25)-C(23)-C(24)	118.3(6)		
C(22)-C(23)-C(24)	121.3(7)		
C(23)-C(24)-H(24A)	109.5		
C(23)-C(24)-H(24B)	109.5		
H(24A)-C(24)-H(24B)	109.5		
C(23)-C(24)-H(24C)	109.5		
H(24A)-C(24)-H(24C)	109.5		
H(24B)-C(24)-H(24C)	109.5		
C(23)-C(25)-C(26)	123.0(6)		
C(23)-C(25)-H(25)	118.5		
C(26)-C(25)-H(25)	118.5		
C(28)-C(26)-C(25)	116.3(7)		
C(28)-C(26)-C(27)	122.0(7)		
C(25)-C(26)-C(27)	121.6(7)		
C(26)-C(27)-H(27A)	109.5		
C(26)-C(27)-H(27B)	109.5		
H(27A)-C(27)-H(27B)	109.5		
C(26)-C(27)-H(27C)	109.5		
H(27A)-C(27)-H(27C)	109.5		
H(27B)-C(27)-H(27C)	109.5		
C(29)-C(28)-C(26)	123.4(7)		
C(29)-C(28)-H(28)	118.3		
C(26)-C(28)-H(28)	118.3		
C(28)-C(29)-C(22)	119.9(6)		
C(28)-C(29)-C(30)	118.4(6)		
C(22)-C(29)-C(30)	121.6(7)		
C(29)-C(30)-H(30A)	109.5		
C(29)-C(30)-H(30B)	109.5		
H(30A)-C(30)-H(30B)	109.5		
C(29)-C(30)-H(30C)	109.5		
H(30A)-C(30)-H(30C)	109.5		
H(30B)-C(30)-H(30C)	109.5		
N(1)-C(31)-H(00D)	109.5		
N(1)-C(31)-H(00E)	109.5		
H(00D)-C(31)-H(00E)	109.5		
N(1)-C(31)-H(00F)	109.5		
H(00D)-C(31)-H(00F)	109.5		
H(00E)-C(31)-H(00F)	109.5		
N(1)-C(32)-H(00A)	109.5		
N(1)-C(32)-H(00B)	109.5		
H(00A)-C(32)-H(00B)	109.5		
N(1)-C(32)-H(00C)	109.5		

Table S125. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for **6d**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + ...\ + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
S(1)	60(1)	56(2)	34(1)	-1(1)	-10(1)	14(1)
N(1)	35(3)	72(6)	30(3)	4(4)	-8(3)	-4(3)
B(1)	22(3)	46(6)	34(5)	10(4)	-1(3)	-3(3)
C(1)	31(3)	34(5)	28(4)	5(4)	-2(3)	3(3)
C(2)	37(4)	36(5)	31(4)	0(4)	3(3)	-3(3)
C(3)	33(3)	36(5)	39(4)	1(4)	-5(3)	-8(3)
C(4)	30(3)	51(6)	21(4)	-3(4)	-1(3)	-1(3)
C(5)	28(3)	42(5)	23(4)	-3(4)	3(3)	5(3)
C(6)	31(3)	51(6)	20(4)	-7(4)	4(3)	-1(3)
C(7)	33(4)	40(5)	38(5)	2(4)	-9(3)	0(3)
C(8)	43(4)	59(6)	26(4)	-8(4)	0(3)	-9(4)
C(9)	43(4)	50(6)	21(4)	-3(4)	4(3)	4(4)
C(10)	36(3)	48(5)	20(4)	5(4)	1(3)	10(3)
C(11)	88(6)	58(7)	37(5)	2(5)	-1(5)	17(5)
C(12)	63(5)	34(6)	39(5)	-5(4)	0(4)	7(4)
C(13)	28(3)	38(5)	32(4)	6(3)	-5(3)	-2(3)
C(14)	35(4)	43(5)	36(4)	3(4)	0(3)	-2(3)
C(15)	54(4)	60(6)	38(5)	11(4)	15(4)	5(4)
C(16)	34(4)	54(6)	50(5)	-13(5)	2(3)	4(4)
C(17)	40(4)	46(6)	58(6)	1(5)	-15(4)	5(4)
C(18)	64(5)	70(8)	90(8)	-23(6)	-17(5)	20(5)
C(19)	43(4)	55(6)	43(5)	18(4)	-13(3)	2(4)
C(20)	36(4)	43(5)	43(5)	10(4)	-6(3)	-7(3)
C(21)	68(5)	67(7)	35(5)	12(4)	2(4)	2(4)
C(22)	32(3)	51(6)	26(4)	5(4)	3(3)	7(3)
C(23)	35(3)	50(6)	31(4)	-2(4)	0(3)	8(3)
C(24)	29(3)	87(8)	64(6)	-24(5)	5(3)	3(4)
C(25)	37(4)	50(6)	40(5)	-4(4)	-5(3)	-1(3)
C(26)	51(4)	60(7)	30(4)	-4(4)	-3(3)	13(4)
C(27)	62(5)	117(10)	43(6)	-26(6)	-1(4)	13(5)
C(28)	44(4)	55(6)	33(4)	-8(4)	5(3)	9(4)
C(29)	32(3)	53(6)	30(4)	0(4)	1(3)	4(3)
C(30)	33(4)	99(8)	49(6)	-21(5)	9(4)	2(4)

C(31)	36(4)	128(10)	46(6)	24(6)	-9(4)	9(5)
C(32)	80(6)	73(8)	48(5)	-2(5)	-24(4)	-13(5)

Table S126. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^{2}x 10^3) for **6d**.

	x	y	z	U(eq)
H(2)	6679	7863	6018	42
H(3)	7231	7547	7607	43
H(7)	6121	3196	5418	45
H(8)	6218	958	6451	51
H(11)	7220	-288	10145	74
H(12)	6644	-698	8539	54
H(15A)	5702	5837	7332	76
H(15B)	5541	7078	8411	76
H(15C)	6023	6904	8110	76
H(16)	5341	9304	7497	55
H(18A)	5079	11966	4802	112
H(18B)	5326	12306	6255	112
H(18C)	4920	11319	6302	112
H(19)	5589	10614	3427	56
H(21A)	5888	7898	1872	85
H(21B)	6331	8071	2601	85
H(21C)	6091	9487	2031	85
H(24A)	5232	6453	3859	90
H(24B)	5303	5230	5068	90
H(24C)	4992	4926	3767	90
H(25)	5229	3556	1911	51
H(27A)	5675	2679	-958	111
H(27B)	5423	1693	162	111
H(27C)	5899	1367	-129	111
H(28)	6421	3153	843	53
H(30A)	6943	4301	2000	91
H(30B)	6876	4317	3708	91
H(30C)	6832	5801	2804	91
H(00D)	7838	3989	7703	105
H(00E)	8060	4556	9137	105
H(00F)	7971	5671	7844	105
H(00A)	7630	7173	9628	100
H(00B)	7658	5972	10879	100
H(00C)	7220	6590	10388	100

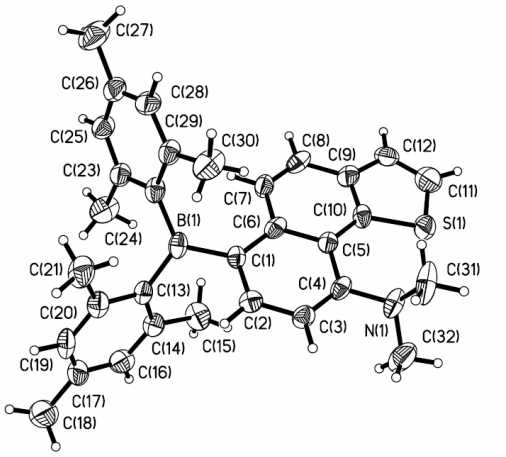


Figure S162. Structure of **6d**.

S10: References

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