

***CI*-BODIPYs: a BODIPY class enabling facile *B*-substitution**

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1.1 General Experimental

All ¹H NMR (500 MHz), ¹³C NMR (125 MHz) and ¹¹B NMR (160 MHz) spectra were recorded using a Bruker Avance AV-500 spectrometer. ¹⁵N NMR (125 MHz) spectra were recorded using a Bruker Avance AV-300 spectrometer. Chemical shifts are expressed in parts per million (ppm) using the solvent signal [CDCl₃ (¹H 7.26 ppm; ¹³C 71.16 ppm); THF-*d*₈ (¹H 1.73, 3.58 ppm; ¹³C 67.57, 25.37 ppm); MeOD-*d*₄ (¹H 3.31 ppm, ¹³C 49.00 ppm); Acetone-*d*₆ (¹H 2.05 ppm, ¹³C 29.84 ppm)] as an internal reference for ¹H and ¹³C and BF₃•OEt₂ as an external reference for ¹¹B. Splitting patterns are indicated as follows: br, broad; s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet. All coupling constants (*J*) are reported in Hertz (Hz). Mass spectra were obtained using ion trap (ESI) instruments operating in positive mode. Melting points are reported uncorrected. Column chromatography was performed using 230-400 mesh ultra pure silica or 150 mesh Brockmann III activated, basic alumina oxide, as indicated. Compounds **5a**^[1] and **6**^[1] have been previously reported in the literature.

1.2 General Procedure for Absorption and Emission Measurements

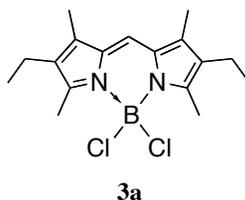
The absorbance measurements were performed using a CARY 100 Bio UV/Visible spectrophotometer. The fluorescence measurements were performed using a Shimadzu RF-5301PC Spectrofluorimeter. A 10 mm quartz cuvette was used in all measurements. For the fluorescence experiments, the slit width was 3 nm for both excitation and emission. Relative quantum efficiencies of derivatives were obtained by comparing the areas under the emission spectra of the samples with that of a solution of rhodamine 6G in ethanol ($\Phi_F = 0.94$)^{S[2]} excited at the same wavelength. The excitation wavelength was 510 nm for **2a** and **2b** and 520 nm for **3a** and **3b**. Quantum yields were determined using Equation 1.^{S[3]}

$$\phi_X = \phi_{st} \left(\frac{I_X}{I_{st}} \right) \left(\frac{A_{st}}{A_X} \right) \left(\frac{\eta_X^2}{\eta_{st}^2} \right) \quad \dots \text{Equation 1}$$

Where ϕ_{st} is the reported quantum yield of the standard, I is the area from the integrated emission spectra, A is the absorbance at the excitation wavelength and η is the refractive index of the solvent used. The X subscript denotes the unknown, and “st” denotes the standard.

1.3 Characterization Data

1,3,5,7-Tetramethyl-2,6-diethyl-8-phenyl-4,4'-dichloro-bora-3a,4a-diaza-s-indacene (**3a**)



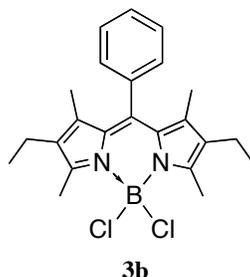
Boron trichloride (0.20 mL of a 1.0 M solution in hexanes, 0.20 mmol) was slowly added to a solution of **1a** (50 mg, 0.20 mmol) in anhydrous toluene (20 mL) under an N₂ atmosphere in a glovebox. The reaction mixture was stirred at room temperature for 1 h. The reaction mixture was then filtered over Celite, washed with anhydrous toluene and the filtrate was concentrated *in vacuo* to give **3a** as a red powder (64 mg, 98%). UV/Vis (CH₂Cl₂) λ_{max} (nm): 540, ϵ 35 000

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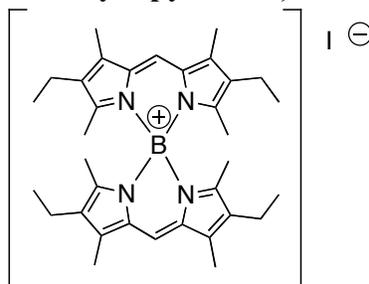
$\text{mol L}^{-1}\text{cm}^{-1}$; δ_{H} (500 MHz, THF- d_8) 7.34 (1H, s), 2.69 (6H, s), 2.43 (4H, q, $J = 7.6$), 2.21 (6H, s),
1.07 (6H, t, $J = 7.6$); δ_{C} (125 MHz, THF- d_8) 157.0, 138.3, 133.7, 132.3, 120.3, 18.0, 14.6, 14.4,
9.1; δ_{B} (160 MHz, THF- d_8) 2.39 (s); δ_{N} (30 MHz, THF- d_8) 197.8 (s).

1,3,5,7-Tetramethyl-2,6-diethyl-8-phenyl-4,4'-dichloro-bora-3a,4a-diaza-s-indacene (3b)



Boron trichloride (0.15 mL of a 1.0 M solution in hexanes, 0.15 mmol) was slowly added to a solution of **1b** (50 mg, 0.15 mmol) in anhydrous toluene (20 mL) under an N_2 atmosphere in a glovebox. The reaction mixture was stirred at room temperature for 1 h. The reaction mixture was then filtered over Celite, washed with anhydrous toluene and the filtrate was concentrated *in vacuo* to give **3b** as a red powder (60 mg, 97%). UV/Vis (CH_2Cl_2) λ_{max} (nm): 533, ϵ 30 000 $\text{mol L}^{-1}\text{cm}^{-1}$; δ_{H} (500 MHz, THF- d_8) 7.55-7.51 (3H, m), 7.37-7.36 (2H, m), 2.74 (6H, s), 2.35 (4H, q, $J = 7.5$), 1.32 (6H, s), 0.98 (6H, t, $J = 7.6$); δ_{C} (125 MHz, THF- d_8) 156.4, 141.4, 139.6, 136.4, 135.1, 130.5, 130.1, 129.9, 129.3, 17.8, 14.8, 14.7, 12.0; δ_{B} (160 MHz, THF- d_8) 2.39 (s); δ_{N} (30 MHz, THF- d_8) 199.5 (s).

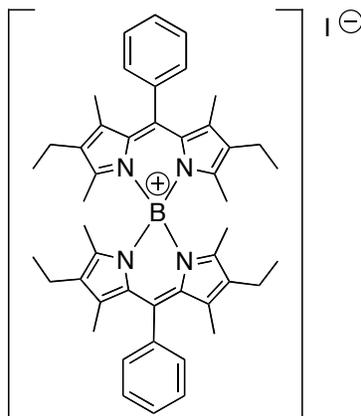
κ^2 -(4,4'-Diethyl-3,3',5,5'-tetramethyldipyrinato) boronium iodide (4aI)



To a solution of 4,4'-diethyl-3,3',5,5'-tetramethyldipyrrin hydrochloride^[4] (100 mg, 0.30 mmol) in anhydrous dichloromethane (15 mL) under nitrogen was added triethylamine (0.25 mL, 1.80 mmol) and the solution was stirred for 10 min. Solid BI₃ (1.04 g, 2.70 mmol) was added in parts, slowly, and the resulting solution was stirred for 18 h at room temperature. The reaction mixture was cooled to 0 °C and methanol (4 mL) was added dropwise. The reaction mixture was diluted with dichloromethane (25 mL) and distilled water (25 mL) and the layers were separated. The aqueous layer was extracted with dichloromethane (2 x 25 mL) and the combined organic fractions were dried over sodium sulfate and concentrated *in vacuo* to give a red solid. Purification over neutral alumina eluting with a gradient of dichloromethane:methanol (100:0 to 95:5) and removal of the solvent *in vacuo* gave **4aI** as a red solid (55 mg, 0.08 mmol, 56%). m.p. = > 300 °C; δ_H (500 MHz, CD₃OD) 7.80 (2H, s), 2.40 (8H, q, *J*=7), 2.35 (12H, s), 1.75 (12H, s), 1.01 (12H, t, *J*=7); δ_C (125 MHz, CD₃OD) 157.5, 141.2, 136.5, 135.2, 122.4, 17.9, 14.9, 11.6, 9.6. δ_B (160 MHz, CD₃OD) -2.79. UV/Vis (CH₃CN) λ (nm), ε (mol L⁻¹ cm⁻¹): 386 (15 600), 531 (57 000). *m/z* ESI⁺ found 521.3784 [M]⁺ calculated for C₃₄H₄₆N₄B 521.3810. A crystal suitable for x-ray crystallography was obtained from a slow evaporation of a solution of compound **4aI** in a 1:1 solution of pentane to dichloromethane.

Crystallographic data for **4aI** (CCDC 842813): C₃₄H₄₆N₄BI, M = 648.48 g, deep-red plate, 0.41 x 0.22 x 0.09 mm³, primitive monoclinic, *P*2₁/*c*, *Z* = 4, *a* = 10.9061(4) Å, *b* = 14.5040(5) Å, *c* = 21.1718(7) Å, β = 100.216(2)°, *V* = 3295.91(20) Å³, *T* = 173(1) K, 25370 reflections (9298 unique, *R*_{int} = 0.042), *R* = 0.0361(3σ), *R*_w = 0.0414(3σ, 6538 reflections). These data may be accessed free-of-charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

κ^2 -(4,4'-Diethyl-3,3',5,5'-tetramethyl-meso-phenyl-dipyrrinato) boronium iodide
(4bI)



4bI

To a solution of 4,4'-diethyl-3,3',5,5'-tetramethyl-8-phenyl-dipyrrin (100 mg, 0.30 mmol) in anhydrous dichloromethane (15 mL) under nitrogen was added triethylamine (0.25 mL, 1.80 mmol) and the solution was then stirred for 10 min. Solid BI_3 (1.04 g, 2.70 mmol) was added in parts, slowly, and the resulting solution was stirred for 18 h at room temperature. The reaction mixture was cooled to 0 °C and methanol (4 mL) was added dropwise. The reaction mixture was diluted with dichloromethane (25 mL) and distilled water (25 mL) and the layers were separated. The aqueous layer was extracted with dichloromethane (2 x 25 mL) and the combined organic fractions were dried over sodium sulfate and concentrated *in vacuo* to give a brown solid. The solid was suspended in methanol, stirred 30 min at room temperature and isolated using suction filtration to give **4bI** as a brown solid (72 mg, 0.09 mmol, 60%). m.p. = 256-257 °C; δ_{H} (500 MHz, acetone- d_6) 7.70-7.68 (6H, m), 7.50-7.48 (4H, m), 2.36 (8H, q, $J=7$), 2.06 (12H, s), 1.46 (12H, s), 0.93 (12H, t, $J=7$). δ_{C} (125 MHz, acetone- d_6) 156.9, 142.8, 141.6, 136.1, 135.4, 134.8, 130.61, 130.58, 128.9, 17.5, 14.9, 12.3, 11.8. δ_{B} (160 MHz, acetone- d_6) 2.41.

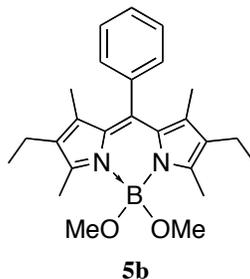
UV/Vis (CH₃CN) λ (nm), ϵ (mol L⁻¹ cm⁻¹): 356 (15 200), 514 (63 400). m/z ESI⁺ found 673.4411 [M]⁺ calculated for C₄₆H₅₄BN₄ 673.4436.

1,3,5,7-Tetramethyl-2,6-diethyl-8-*H*-4,4'-dimethoxy-bora-3a,4a-diaza-*s*-indacene (5a)^[1]



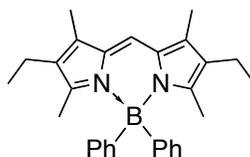
To a solution of **3a** (50 mg, 0.15 mmol) in anhydrous methanol (10 mL) was added solid sodium methoxide (52 mg, 0.95 mmol) and the reaction mixture was stirred at room temperature for 3 h in a glovebox. The reaction mixture was then removed from the glovebox, poured into water (20 mL) and extracted with ethyl acetate (20 mL). The organic layer was washed with water (2 x 20 mL) and the combined organic layers were dried over Na₂SO₄ and concentrated *in vacuo* to give **5a** as an orange crystalline solid (48 mg, 98%). δ_{H} (500 MHz, CDCl₃) 6.90 (1H, s), 2.84 (6H, s), 2.47 (6H, s), 2.38 (4H, q, $J=7.5$), 2.17 (6H, s), 1.06 (6H, t, $J=7.5$); δ_{C} (125 MHz, CDCl₃) 154.9, 134.6, 133.8, 131.2, 118.4, 49.3, 17.5, 14.9, 12.3, 9.5; δ_{B} (160 MHz, CDCl₃) 2.66 (s); m/z ESI⁺ found 351.2214 [M+Na]⁺ calculated for C₁₉H₂₉BN₂O₂Na 351.2220.

1,3,5,7-Tetramethyl-2,6-diethyl-8-phenyl-4,4'-dimethoxy-bora-3a,4a-diaza-*s*-indacene (5b)



To a solution of **3b** (50 mg, 0.12 mmol) in anhydrous methanol (10 mL) was added solid sodium methoxide (46 mg, 0.81 mmol) and the reaction mixture was stirred at room temperature for 3 h in a glovebox. The reaction mixture was then removed from the glovebox, poured into water (20 mL) and extracted with ethyl acetate (20 mL). The organic layer was washed with water (2 x 20 mL) and the combined organic layers were dried over Na₂SO₄ and concentrated *in vacuo* to give **5b** as a red crystalline solid (48 mg, 99%). δ_{H} (500 MHz, CDCl₃) 7.48-7.45 (3H, m), 7.32-7.28 (2H, m), 2.94 (6H, s), 2.53 (6H, s), 2.32 (4H, q, $J=7.5$), 1.29 (6H, s), 1.00 (6H, t, $J=7.5$); δ_{C} (125 MHz, CDCl₃) 154.0, 140.1, 136.6, 136.3, 132.3, 128.9 (2C), 128.6, 128.5, 49.2, 17.2, 14.8, 12.3, 11.8; δ_{B} (160 MHz, CDCl₃) 2.46 (s); m/z ESI⁺ found 427.2527 [M+Na]⁺ calculated for C₂₅H₃₃BN₂O₂Na 427.2533.

1,3,5,7-Tetramethyl-2,6-diethyl-8-*H*-4,4'-diphenyl-bora-3a,4a-diaza-s-indacene (6a)^[1]

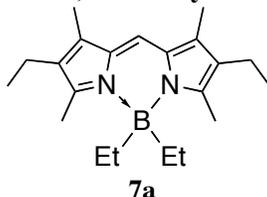


6a

Phenyl lithium (0.20 mL of a 1.8 M solution in di-*n*-butyl ether, 0.36 mmol) was slowly added to a round-bottom flask containing a solution of **3a** (61 mg, 0.18 mmol) in anhydrous THF (15 mL) at room temperature in a glovebox. The solution was allowed to stir for 1 h. The reaction mixture was then filtered through Celite and concentrated *in vacuo* to give a dark red-brown powder. The crude solid was purified over silica gel eluting with 4 % EtOAc in hexanes to give **6a** as a bright orange solid (38 mg, 50 %). δ_{H} (500 MHz, CDCl₃) 7.29-7.16 (10H, m), 2.32 (4H, q, $J=7.5$), 2.21 (6H, s), 1.75 (6H, s),

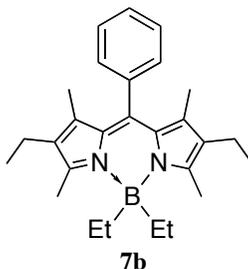
0.98 (6H, t, $J=7.5$); δ_C (125 MHz, $CDCl_3$) 154.0, 134.1, 133.9, 133.8, 132.3, 131.6, 127.3, 125.7, 119.5, 17.7, 14.9, 14.4, 9.5; δ_B (160 MHz, $CDCl_3$) 0.19 (s).

1,3,5,7-Tetramethyl-2,6-diethyl-8-*H*-4,4'-diethyl-bora-3a,4a-diaza-*s*-indacene (7a)



To a solution of **3a** (50 mg, 0.15 mmol) in anhydrous diethyl ether (15 mL) was added ethyl magnesium bromide (0.10 mL, 3.0 M, 0.30 mmol) and the reaction mixture was stirred at room temperature for 3 h in a glovebox. The reaction mixture was then removed from the glovebox, extracted with water (20 mL) and the layers were separated. The aqueous layer was extracted with diethyl ether (3 x 10 mL) and the combined organic layers were dried over Na_2SO_4 and concentrated *in vacuo*. Purification over silica gel eluting with 17 % EtOAc in hexanes gave **7a** as a red crystalline solid (47 mg, 98%). δ_H (500 MHz, $CDCl_3$) 6.99 (1H, s), 2.44-2.39 (10H, m, $2x(CH_3+CH_2)$), 2.18 (6H, s), 1.06 (6H, t, $J=7.6$), 0.82 (4H, q, $J=7.6$), 0.31 (6H, t, $J=7.6$); δ_C (125 MHz, $CDCl_3$) 151.1, 132.6, 131.8, 131.1, 119.4, 17.9, 15.0, 13.9, 9.43, 9.40 (one signal obscured); δ_B (160 MHz, $CDCl_3$) 2.50 (s).

1,3,5,7-Tetramethyl-2,6-diethyl-8-phenyl-4,4'-diethyl-bora-3a,4a-diaza-*s*-indacene (7b)



To a solution of **3b** (62 mg, 0.15 mmol) in anhydrous diethyl ether (15 mL) was added ethyl magnesium bromide (0.10 mL, 3.0 M, 0.30 mmol) and the reaction mixture was stirred at room temperature for 3 h in a glovebox. The reaction mixture was then removed from the glovebox, extracted with water (20 mL) and the layers were separated. The aqueous layer was extracted with diethyl ether (3 x 10 mL) and the combined organic layers were dried over Na₂SO₄ and concentrated *in vacuo*. Purification over silica gel eluting with 17 % EtOAc in hexanes gave **7b** as a red crystalline solid (59 mg, 98%). δ_{H} (500 MHz, CDCl₃) 7.44 (3H, br), 7.29-7.28 (2H, m), 2.44 (6H, s), 2.32 (4H, q, $J=7.1$), 1.25 (6H, s), 0.97 (6H, t, $J=7.1$), 0.87 (4H, q, $J=7.3$), 0.41 (6H, t, $J=7.0$); δ_{C} (125 MHz, CDCl₃) 150.2, 140.9, 137.7, 133.4, 132.4, 131.1, 129.0, 128.8, 128.3, 29.9, 17.6, 15.0, 14.1, 12.0, 9.6; δ_{B} (160 MHz, CDCl₃) 1.85 (s).

1.4 References

- [1] S. M. Crawford, A. Thompson, *Org. Lett.* **2010**, *12*, 1424.
- [2] K. Rurack, in *Standardization and Quality Assurance in Fluorescence Measurements I, Vol. 5* (Ed.: U. Resch-Genger), Springer Berlin Heidelberg, **2008**, pp. 101.
- [3] A. T. R. Williams, S. A. Winfield, J. N. Miller, *Analyst* **1983**, *108*, 1067.
- [4] B. Tu, C. Wang, J. Ma, *Org. Prep. Proced. Int.* **1999**, *31*, 349.

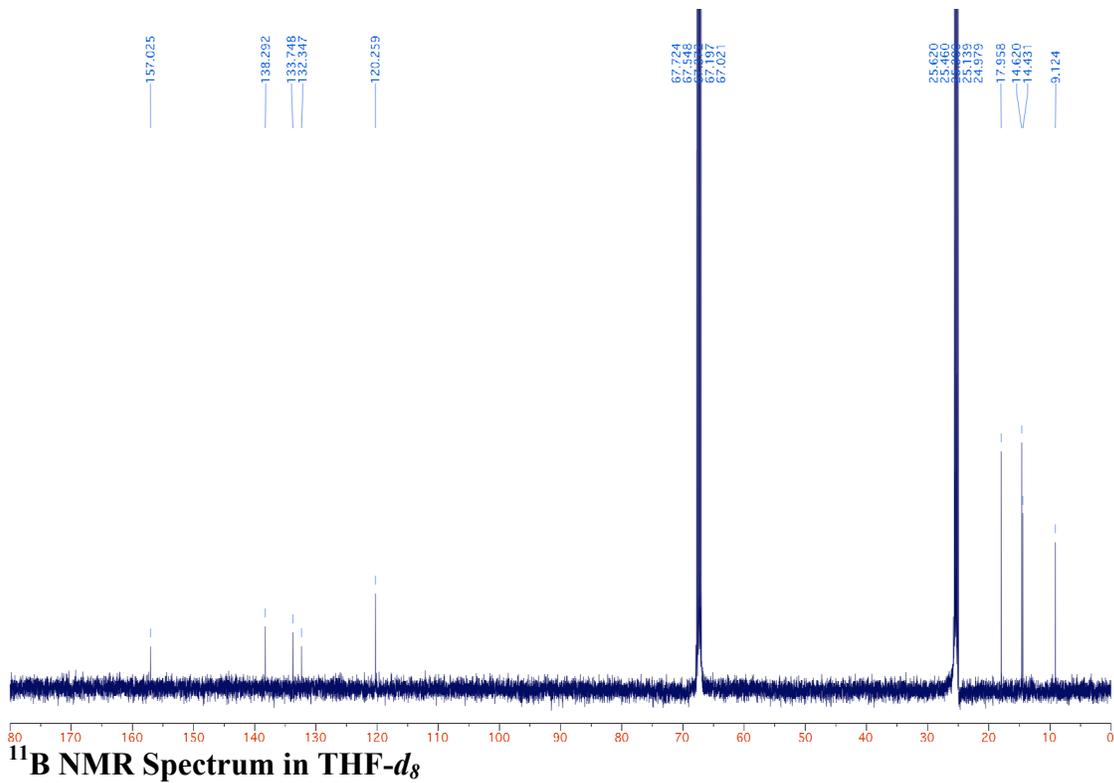
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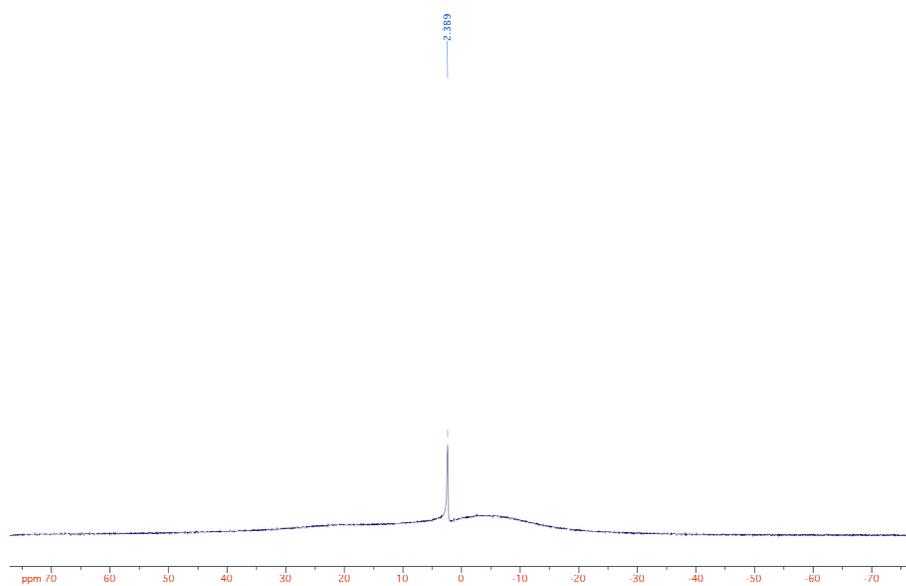
1.5 ^{11}B and ^{13}C NMR Spectra

1,3,5,7-Tetramethyl-2,6-diethyl-8-*H*-4,4'-dichloro-bora-3a,4a-diaza-*s*-indacene (3a)

^{13}C NMR Spectrum in $\text{THF-}d_8$



^{11}B NMR Spectrum in $\text{THF-}d_8$

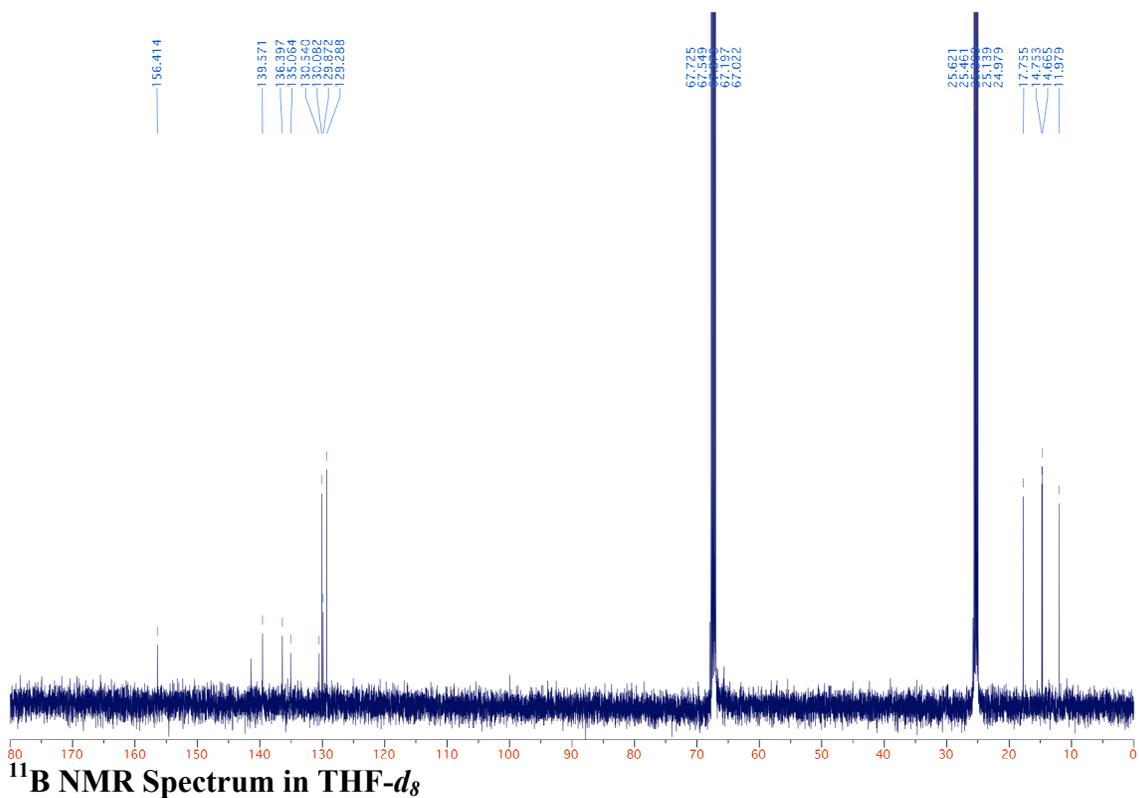


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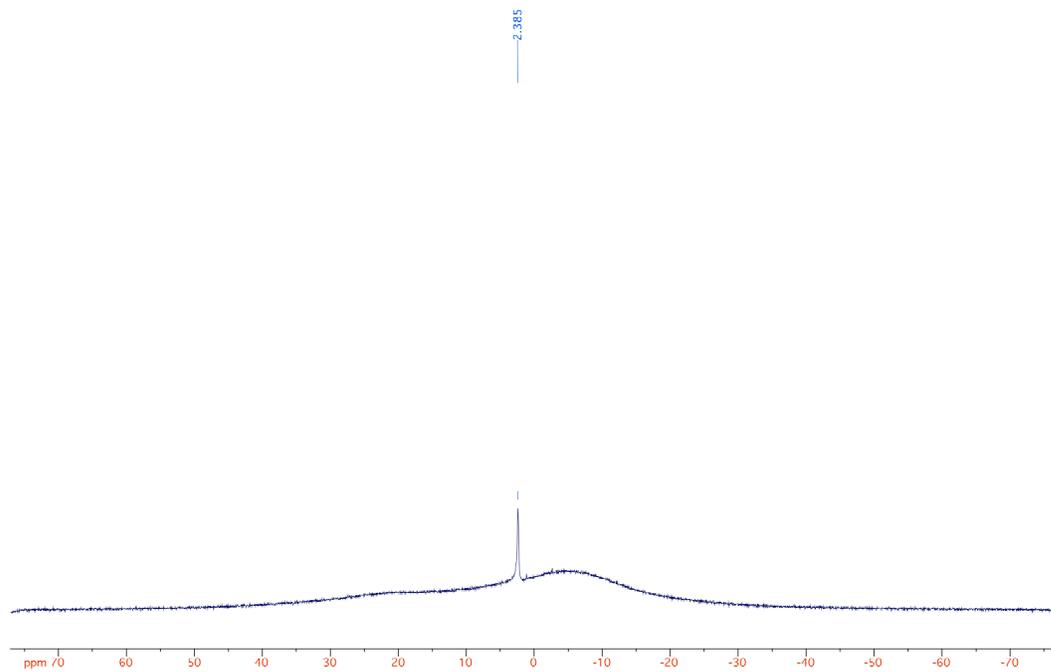
Supporting Information

1,3,5,7-Tetramethyl-2,6-diethyl-8-phenyl-4,4'-dichloro-bora-3a,4a-diaza-s-indacene
(3b)

^{13}C NMR Spectrum in $\text{THF-}d_8$



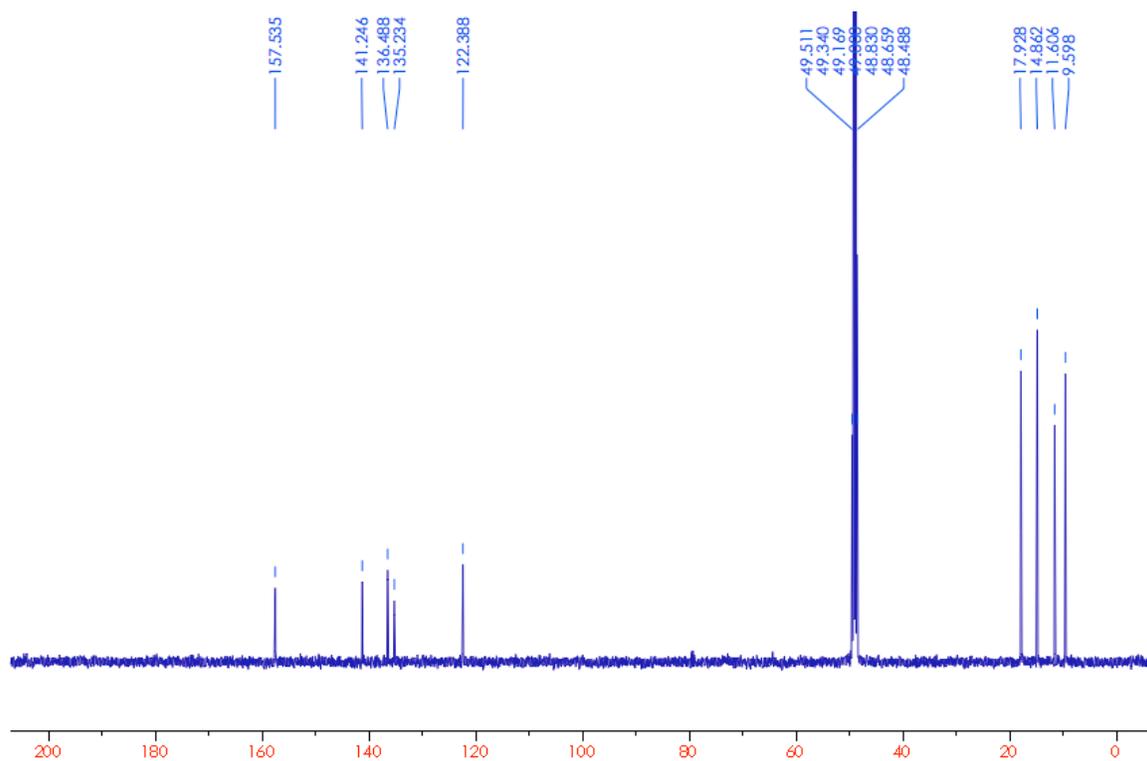
^{11}B NMR Spectrum in $\text{THF-}d_8$



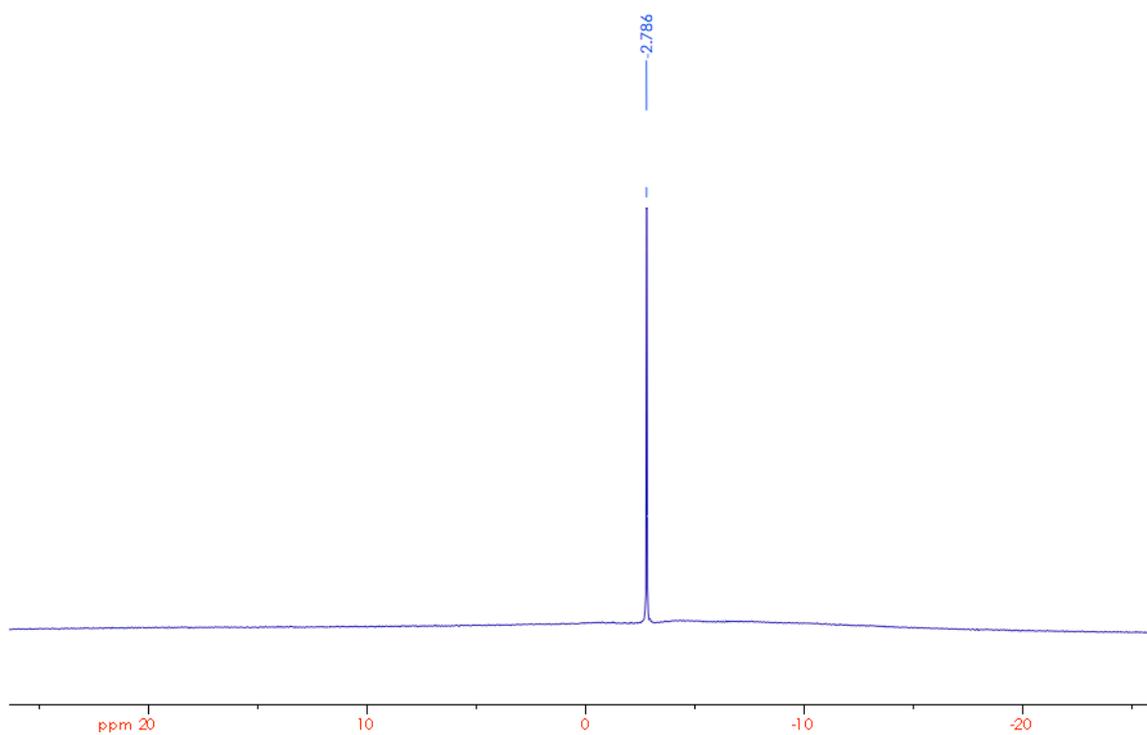
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κ^2 -(4,4'-Diethyl-3,3',5,5'-tetramethyldipyrrinato) boronium iodide (4aI)
 ^{13}C NMR Spectrum in methanol- d_4



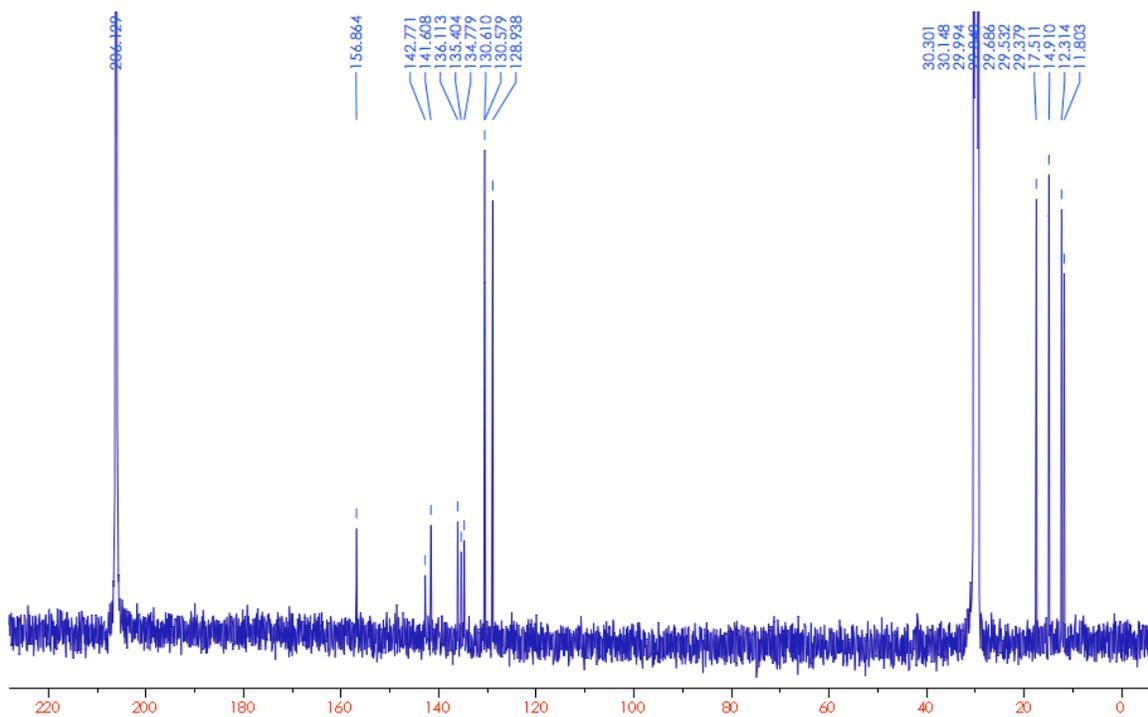
^{11}B NMR Spectrum in methanol- d_4



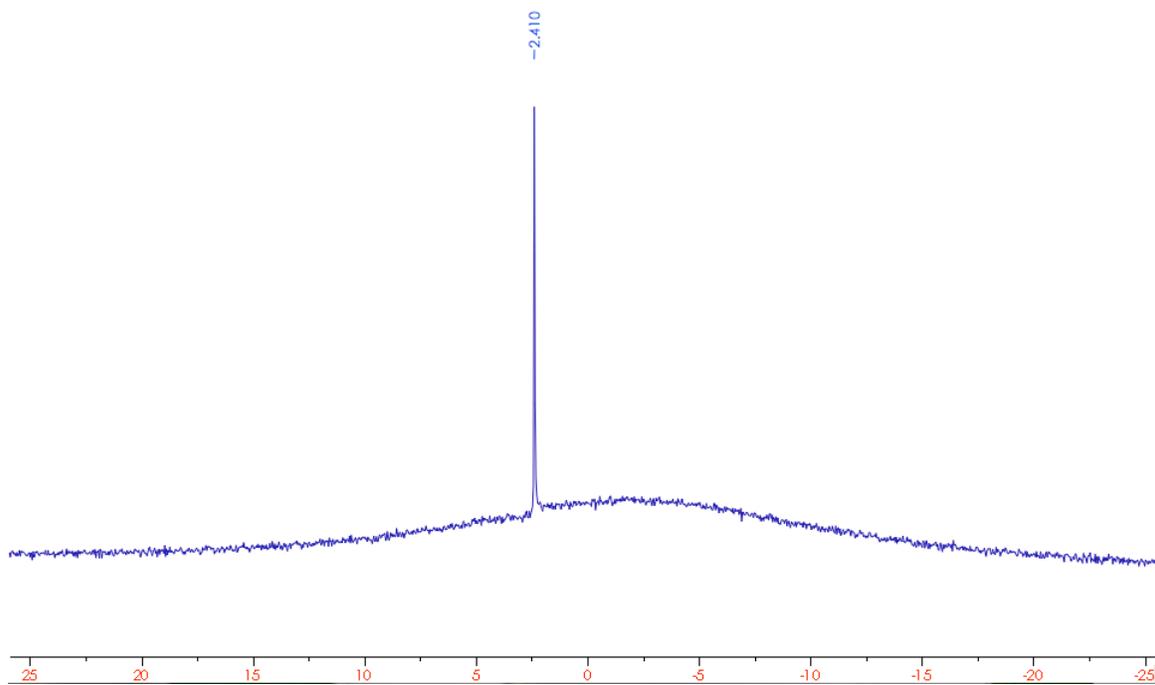
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κ^2 -(4,4'-Diethyl-3,3',5,5'-tetramethyl-8-phenyl-dipyrinato) boronium iodide (4bI)
 ^{13}C NMR Spectrum in acetone- d_6



^{11}B NMR Spectrum in acetone- d_6

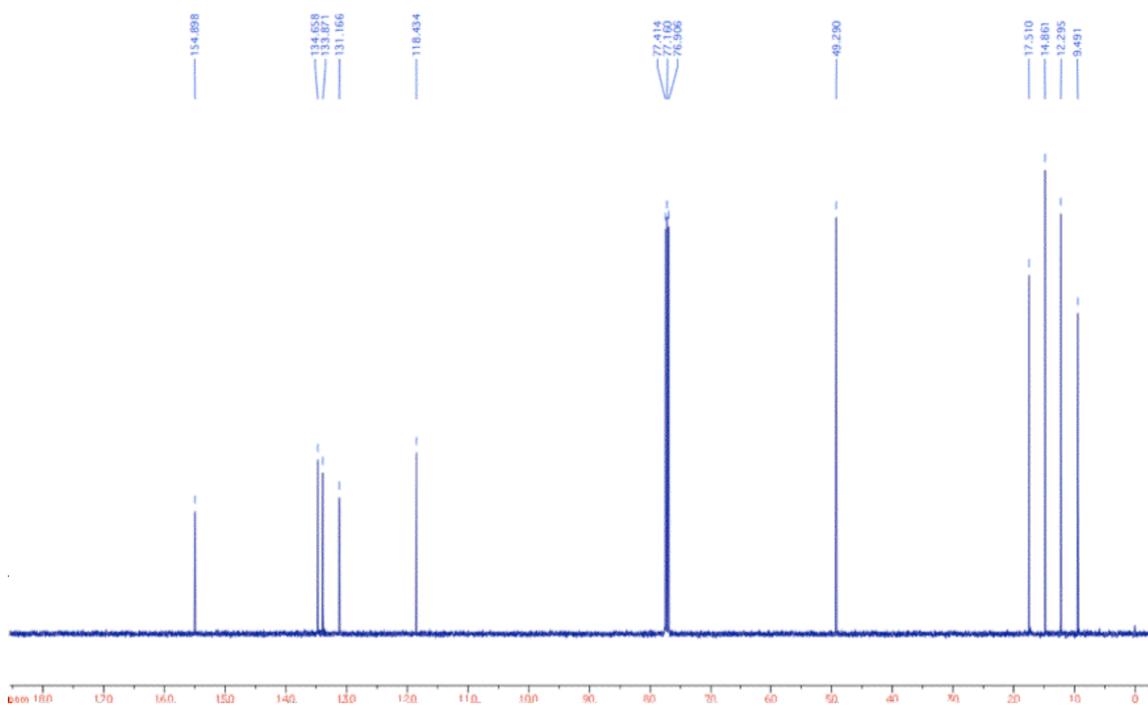


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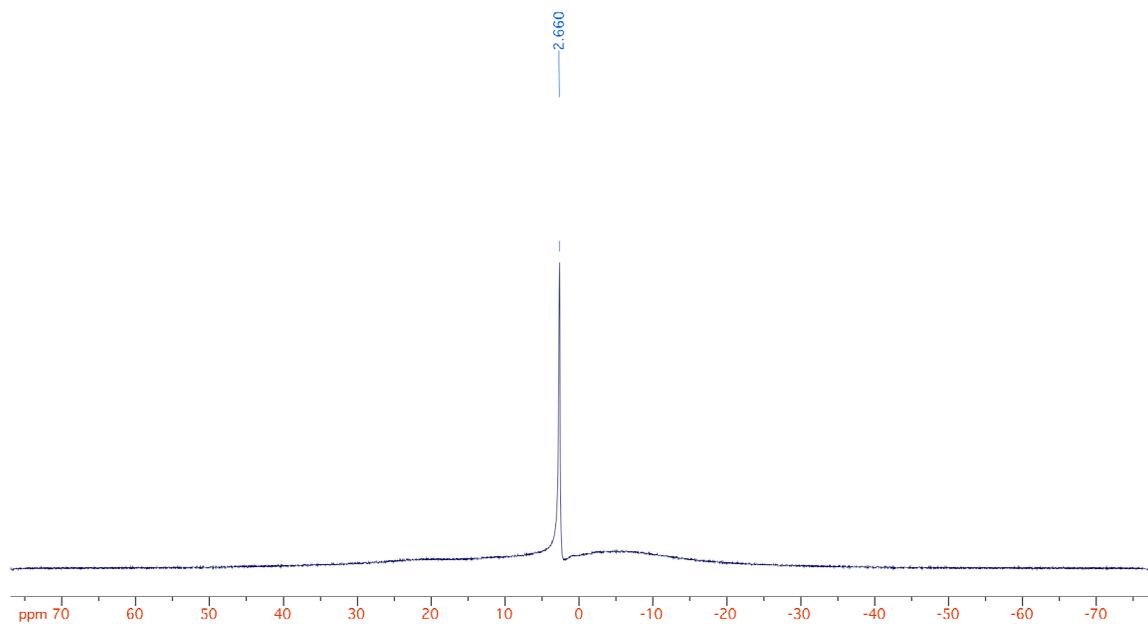
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1,3,5,7-Tetramethyl-2,6-diethyl-8-H-4,4'-dimethoxy-bora-3a,4a-diaza-s-indacene
(5a)^[11]

¹³C NMR Spectrum in CDCl₃



¹¹B NMR Spectrum in CDCl₃

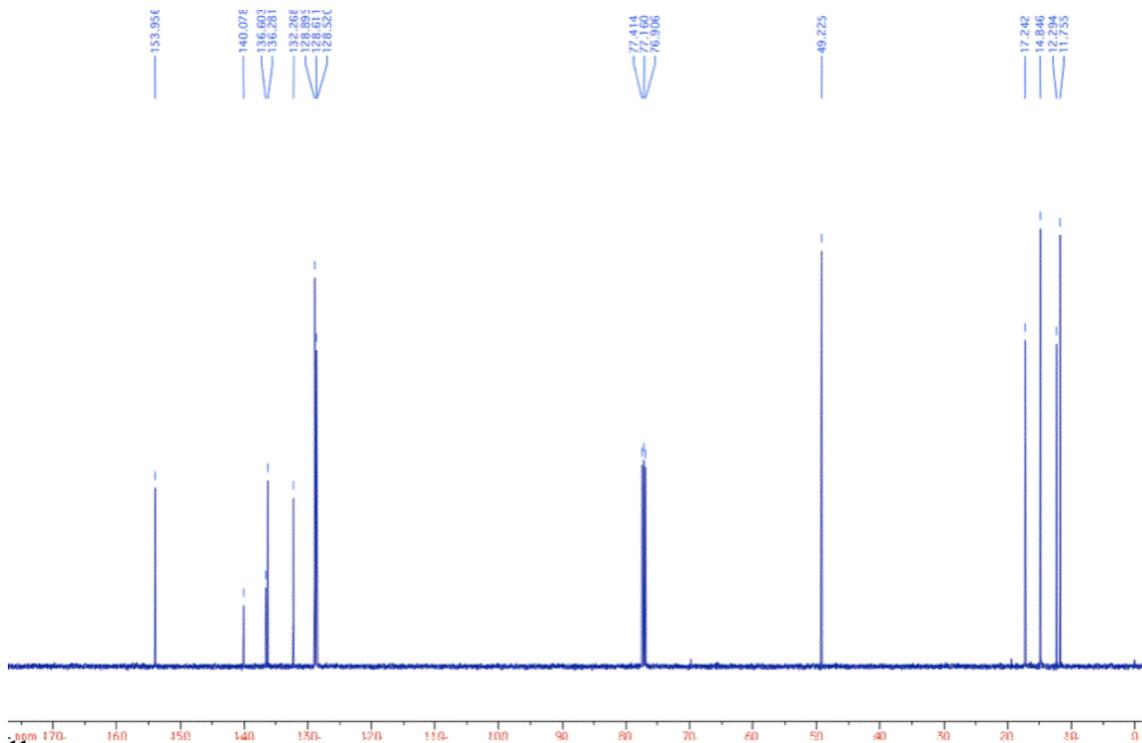


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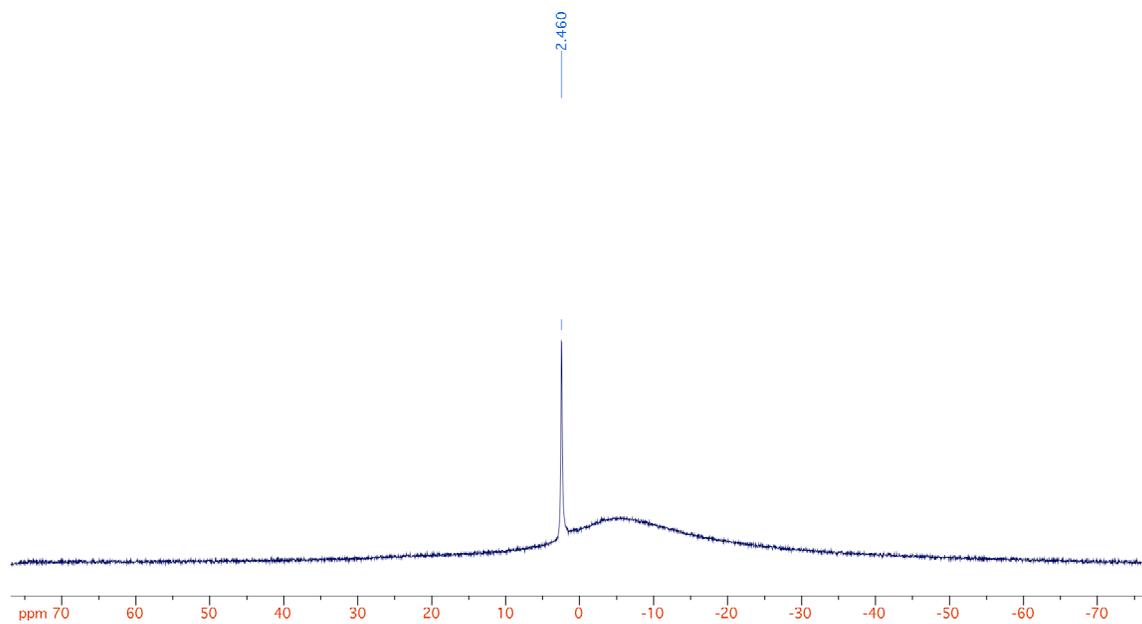
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1,3,5,7-Tetramethyl-2,6-diethyl-8-phenyl-4,4'-dimethoxy-bora-3a,4a-diaza-*s*-indacene (5b)

¹³C NMR Spectrum in CDCl₃



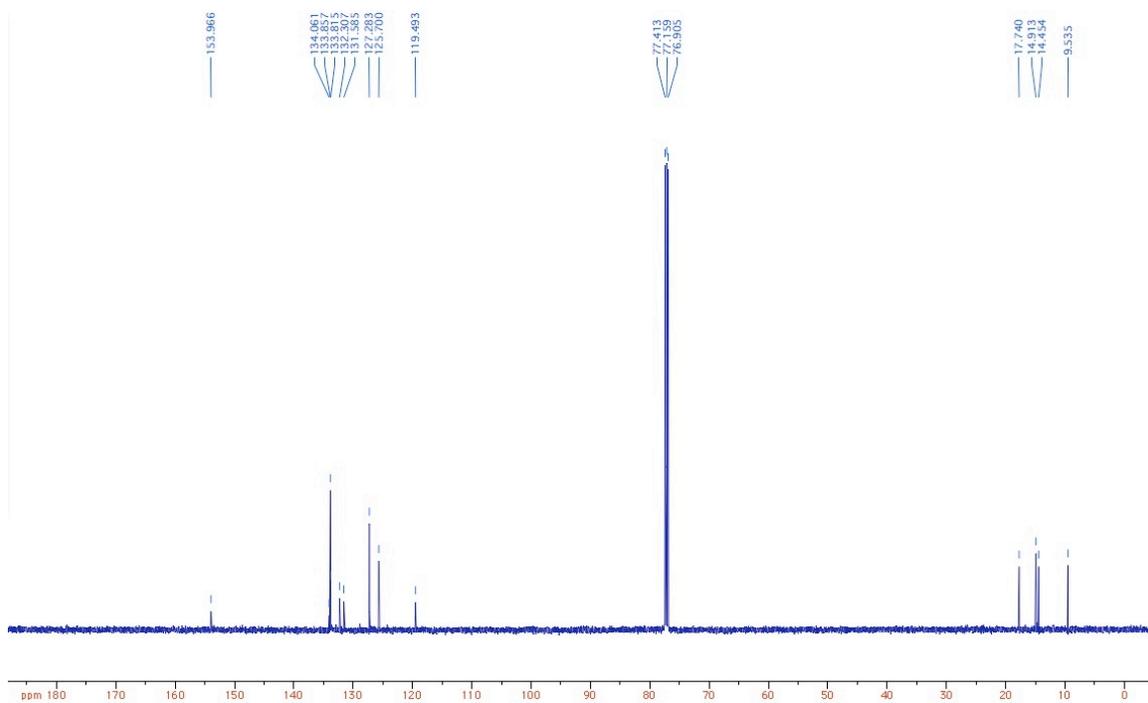
¹¹B NMR Spectrum in CDCl₃



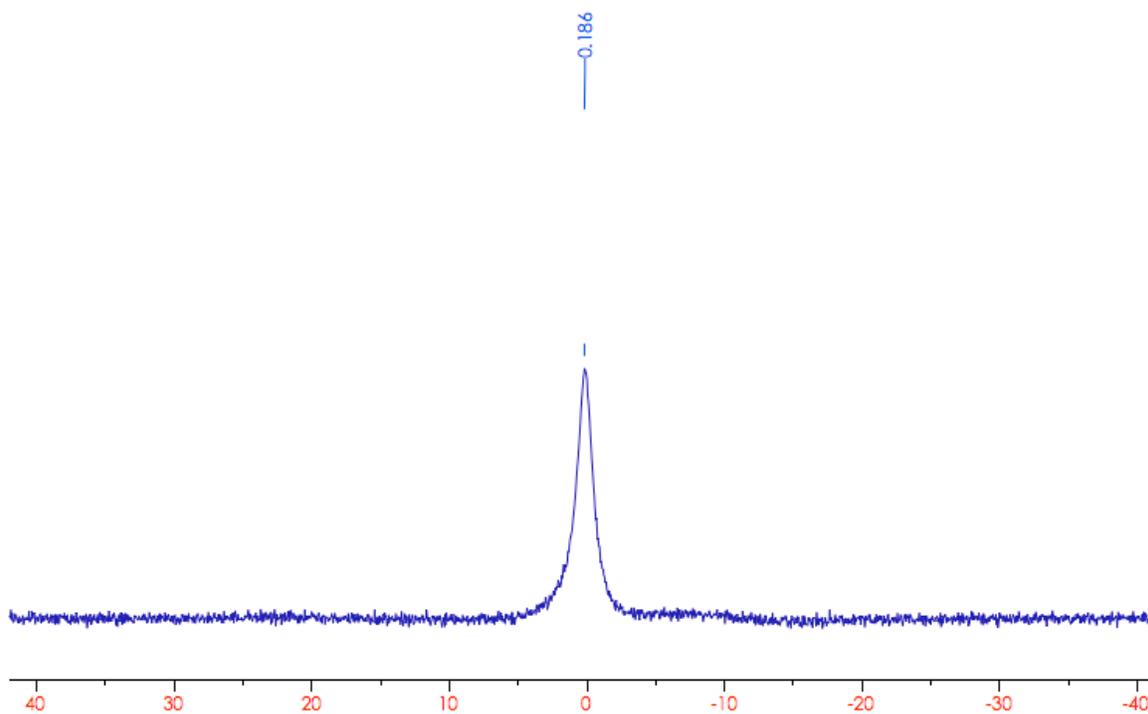
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1,3,5,7-Tetramethyl-2,6-diethyl-8-H-4,4'-diphenyl-bora-3a,4a-diaza-s-indacene
(6a)^[11]
¹³C NMR Spectrum in CDCl₃



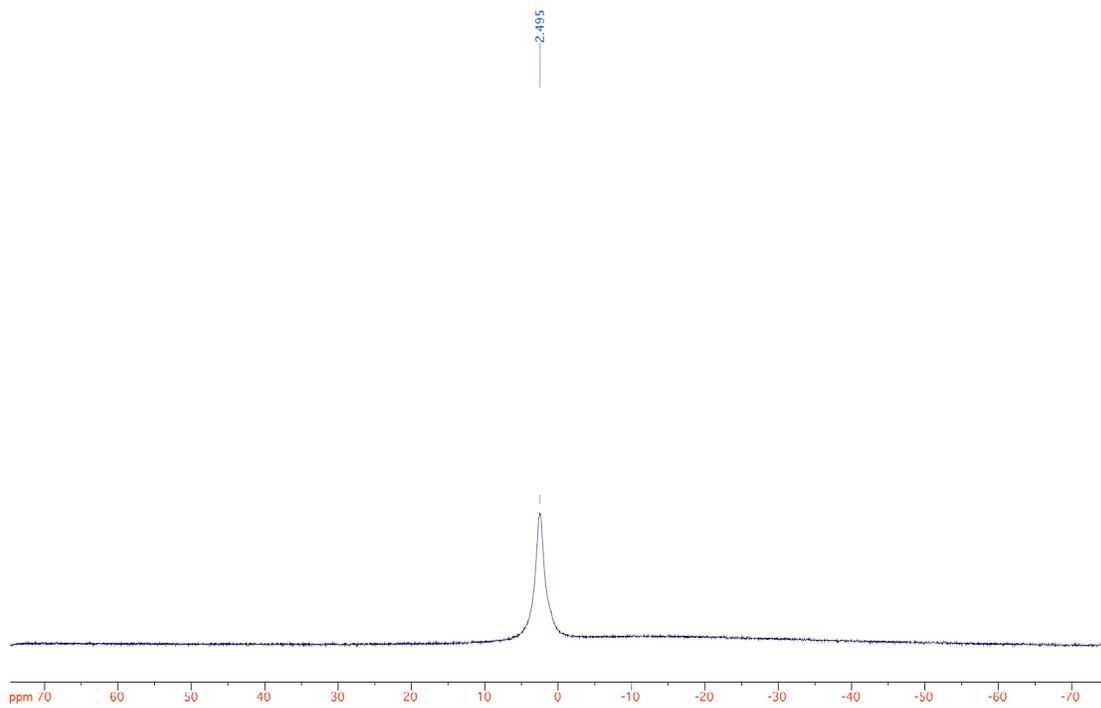
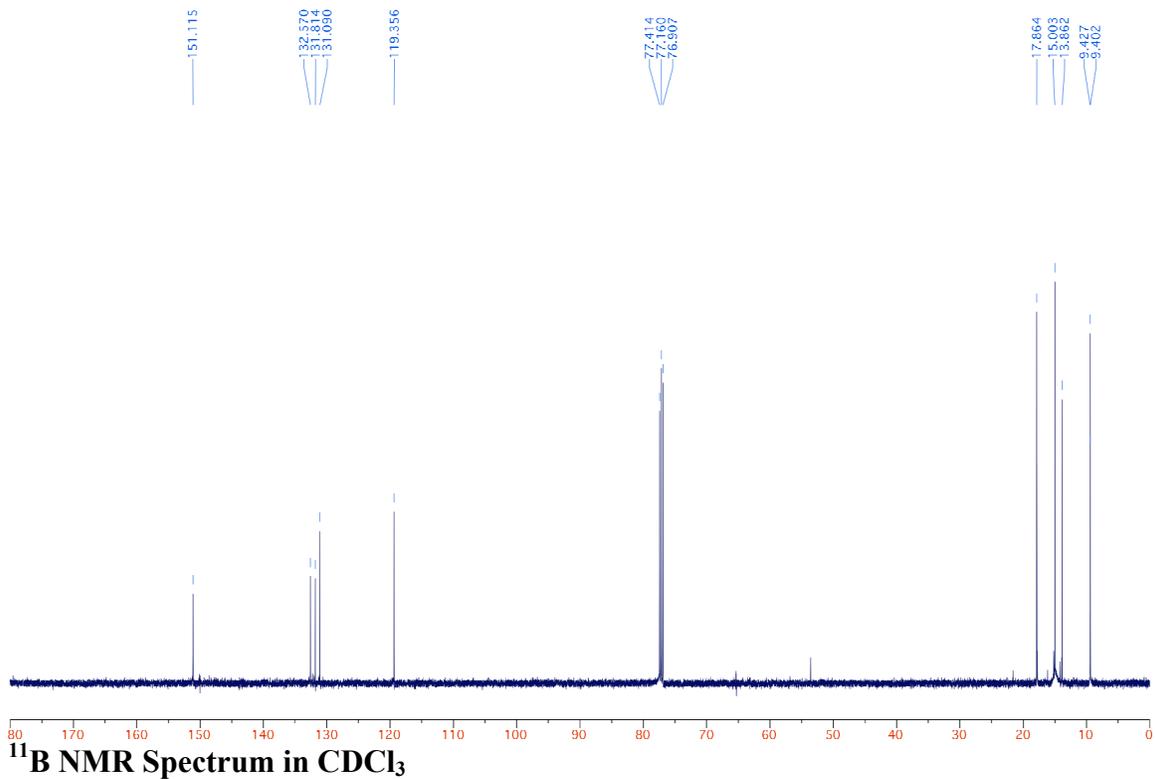
¹¹B NMR Spectrum in CDCl₃



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1,3,5,7-Tetramethyl-2,6-diethyl-8-H-4,4'-diethyl-bora-3a,4a-diaza-s-indacene (7a)
¹³C NMR Spectrum in CDCl₃

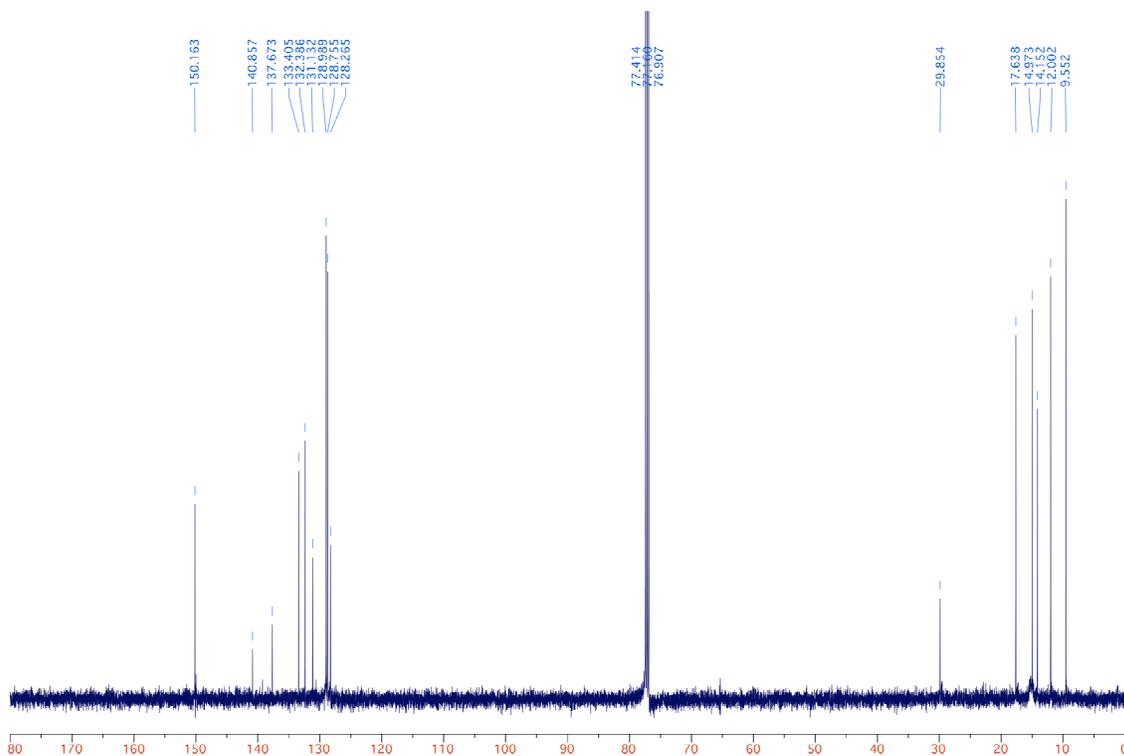


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Supporting Information

**1,3,5,7-Tetramethyl-2,6-diethyl-8-phenyl-4,4'-diethyl-bora-3a,4a-diaza-s-indacene
(7b)**

¹³C NMR Spectrum in CDCl₃



¹¹B NMR Spectrum in CDCl₃

