Electronic Supplementary Material (ESI) for Dalton Transactions.

Divergent reactivity of nucleophilic 1-bora-7a-azaindenide anions.

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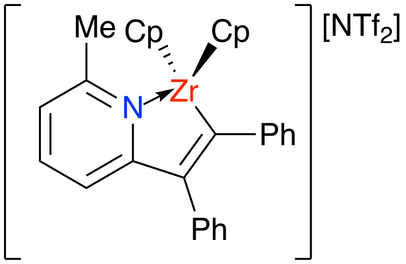
General Considerations: Storage and manipulation of all compounds were performed under an argon atmosphere either in a VAC glove box or using a double manifold high vacuum line using standard techniques. Passage of argon through an OxisorBW scrubber (Matheson Gas Products) removed any residual oxygen and moisture. Toluene and tetrahydrofuran were dried and purified using a Grubbs/Dow solvent purification system and stored in 500 mL thick-walled glass pressure flasks over sodium/benzophenone ketal. *n*-Pentane was purified using a M-Braun solvent purification system, dried over sodium/benzophenone ketal and stored in a 100 mL thick-walled glass pressure flask. Benzene-*d*6 was dried over sodium/benzophenone ketal and stored in a 100 mL thick-walled glass pressure flask. Dichloromethane and chlorobenzene were stored in the same manner except dried over calcium dihydride instead of sodium/benzophenone ketal. Dichloromethane-d_2 was dried over CaH_2 and stored in a 50 mL thick-walled glass pressure flask. All dried solvents were degassed and vacuum distilled prior to use. ^{1}H and ^{13}C NMR chemical shifts were referenced to residual solvent protons and naturally abundant ^{13}C resonances for all deuterated solvents. Chemical shift assignments are based on ^{1}H, ^{11}B, $^{13}C\{^{1}H\}$, ^{1}H-^{1}H-COSY, ^{1}H-^{13}C-HSQC and ^{1}H-^{13}C-HMBC NMR experiments performed on Avance III 400, Ascend-500, or Avance-600 MHz spectrometers. X-ray crystallographic analyses were performed on a Bruker system equipped with a Bruker Apex-II CCD using samples coated in Paratone 8277 oil (Exxon) and mounted on a glass fibre. All other commercially available starting materials were used without further purification. Compounds **1a** and **2a** were prepared as previously reported (see reference 34, main text) and 1-bromo-1,2-dideuterio-3,3-dimethylbutane was prepared using the procedure reported in reference 46. Elemental analyses were performed by staff at the Instrumentation Facility in the Department of Chemistry, University of Calgary

Synthesis of Zirconocyclic precursor to 2b



A two neck 100 mL round-bottom flask attached to a swivel frit apparatus was charged with $HNTf_2$ (1.0 g, 3.56 mmol), and a Teflon stirbar. To this, 50 mL of chlorobenzene was vacuum transferred, and a solution of 2-methylpyridine (0.35 mL, 3.56 mmol) in chlorobenzene (5mL). This was allowed to stir for 1 hour at room temperature, after which a solution of Cp_2ZrMe_2 (895 mg, 3.56 mmol) was added dropwise yielding effervescence of methane and a colour change from clear to pale yellow. After stirring at room temperature for 16 hours a solution of diphenylacetylene (700 mg, 3.92 mmol) in chlorobenzene (5 mL) was added to the reaction and heated to 80 for 16 hours under a flow of argon producing a dark orange solution. The solvent was condensed to approximately 25 mL and pentane (25 mL) was then vacuum-transferred into the flask with stirring, producing an orange precipitate which was filtered through the swivel frit. The solid was then washed with pentane again (2 × 15 mL), after which it was dried in vacuo, yielding the product **Pic*NTf$_2$** as an orange solid (2.20 g, 2.85 mmol, 80%). ^{1}H NMR (500 MHz, THF-d_8) δ 7.88 (t, J = 7.9 Hz, 1H), 7.27 (d, *J* = 7.7 Hz, 1H), 7.19 (dd, *J* = 8.3, 6.9 Hz, 2H), 7.16 – 7.09 (m, 5H), 7.01 – 6.92 (m, 3H), 6.92 – 6.85 (m, 1H), 6.81 (s, 10H), 1.99 (s, 3H). 13C NMR (126 MHz, THF) δ 211.80, 159.68, 157.45, 145.67, 141.75, 138.42, 137.46, 129.70, 127.34, 127.20, 126.12, 124.87, 123.92, 122.39, 121.03, 119.47 (q 124 Hz, -CF3), 116.39, 20.63. Elemental analysis calculated C 49.79, H 3.40, N 3.63, Found C 49.81, H 3.35, N 3.53.

Synthesis of 1b: A 50ml round bottom flask was charged with **Pic*NTf$_2$** (1.0 g, 1.30 mmol), $[nBu_4N][PhBCl_3]$ (982 mg, 1.30 mmol), dichloromethane (30ml), and a Teflon stirbar, producing an orange solution. The mixture was refluxed under argon for 16h producing a pale-yellow solution. The mixture was then run through a silica/dichloromethane plug under atmospheric conditions, where a faint yellow band passed through and was collected. The solvent of the collected solution was then removed *in vacuo*, yielding the product as a bright yellow powder (220 mg, 0.56mmol, 43%). ^{1}H NMR (500 MHz, Methylene Chloride-d_2) δ 7.86 (t, *J* = 7.9 Hz, 1H, Py**H**), 7.50 (d, *J* = 7.1 Hz, 2H), 7.44 (d, *J* = 7.2 Hz, 2H), 7.34 (d, *J* = 7.4 Hz, 2H), 7.25 (dd, *J* = 14.0, 8.0 Hz, 4H), 7.10 (d, *J* = 7.8 Hz, 2H), 7.06 (m, 5H), 2.53 (s, 3H, PyMe**H**).^{13}C NMR (126 MHz, CD_2Cl2) δ 167.36 (br), 160.76, 156.30, 141.66, 137.34, 134.50, 134.31, 131.34, 129.32, 128.53, 128.32, 127.18, 126.98, 126.80, 126.38, 125.99, 122.55, 116.07, 20.20 *Note: one carbon attached to boron is not observed*. ^{11}B NMR (161 MHz, CD_2Cl2) δ 7.17. Elemental analysis calculated C 79.32, H 5.38, N 3.56, Found C 79.19, H 5.40, N 3.53.

Synthesis of 2b: To a solution of chloroborane **1b** (200 mg, 0.508 mmol) in THF (10 mL), solid KC_8 (144 mg, 1.067 mmol) was added, causing the pale yellow solution to turn a dark orange colour with the simultaneous formation of black graphite precipitate. This solution was stirred for 5 minutes then filtered through a swivel frit apparatus. After filtration a solution of 2,2,2-cryptand (192 mg, 0.508 mmol) in THF (2 mL) was added and the solution allowed to sit at room temperature for two hours. During this time the product crystalized into bright orange crystals that were then collected by filtration to give **2b** (350 mg, 0.453 mmol, 89%) ^{1}H NMR (500 MHz, THF-d_8) δ 7.60 – 7.52 (m, 2H, Ar**H**), 7.23 (dd, *J* = 8.1, 1.4 Hz, 2H, Ar**H**), 7.05 (t, *J* = 7.7 Hz, 2H, Ar**H**), 7.03 – 6.92 (m, 4H, Ar/Py**H**), 6.78 (dd, *J* = 8.3, 1.4 Hz, 2H, Ar**H**), 6.55 (dd, *J* = 8.3, 7.1 Hz, 2H, Ar**H**), 6.34 – 6.27 (m, 1H, Py**H**), 5.49 (dd, *J* = 8.8, 5.9 Hz, 1H, Py**H**), 5.28 (dt, *J* = 5.9, 1.2 Hz, 1H, Py**H**), 3.45 (s, 12H, Crypt**H**), 3.43 – 3.38 (m, 12H, Crypt**H**), 2.46 – 2.40 (m, 12H, Crypt**H**), 1.87 (s, 3H, Me**H**). ^{13}C NMR (126 MHz, THF-d_8) δ 146.92, 142.77, 136.08, 134.67, 130.47, 129.24, 127.68, 125.72, 124.83, 123.87, 122.27, 120.38, 116.57, 116.47, 115.84, 105.06, 104.65, 69.67, 66.85, 53.17, 24.81.^{11}B NMR (161 MHz, THF-d8) δ 26.5. Elemental analysis calculated C 68.20, H 7.54, N 5.42, Found C 68.55, H 7.75, N 5.19.

Equilibrium Experiment with CO_2: In a J young NMR tube **2a** (5mg) and **6b** (5.2mg) were taken up in THF-d_8. This was allowed to stir at room temperature and monitored via ^{1}H NMR periodically for 16 hours. Throughout the experiment there seemed to be no change in the ratio of products observed over time. A representative ^{1}H NMR spectra is shown in Figure S11. The same equilibrium was obtained when **2b** (5mg) and **6a** (5.1 mg) were mixed together. In each case the equilibrium constant was found by integrating the diagnostic signals shown in Figure S11 to give an approximate equilibrium constant of 54(5) favoring **2a** and **6b**.

Computational Details

Geometries of minimum structures and transition states were optimized with Gaussian 09 program package [S1] using PBE0 hybrid density functional [S2] and Ahlrichs' small triple-ζ valence quality def-TVZP basis sets.[S3] Solvent contributions (toluene, dichloromethane) to energies were included using polarizable continuum model as implemented in Gaussian 09.[S4] Dispersion forces were treated in calculations using the empirical D3BJ model of Grimme et al.[S5] Frequency calculations were performed to ascertain the nature of stationary points, estimate thermal contributions to Gibb's free energies and to confirm that all reported transition states have single negative eigenfrequency along the intended reaction coordinate. Nucleus independent chemical shifts (NICS) were calculated to estimate the aromatic/nonaromatic character of the calculated structures.[S6]

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S1 M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, M. J. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Ö.; Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski and D. J. Fox, *GAUSSIAN 09* (*Revision D.01*), Gaussian, Inc., Wallingford CT, 2013.

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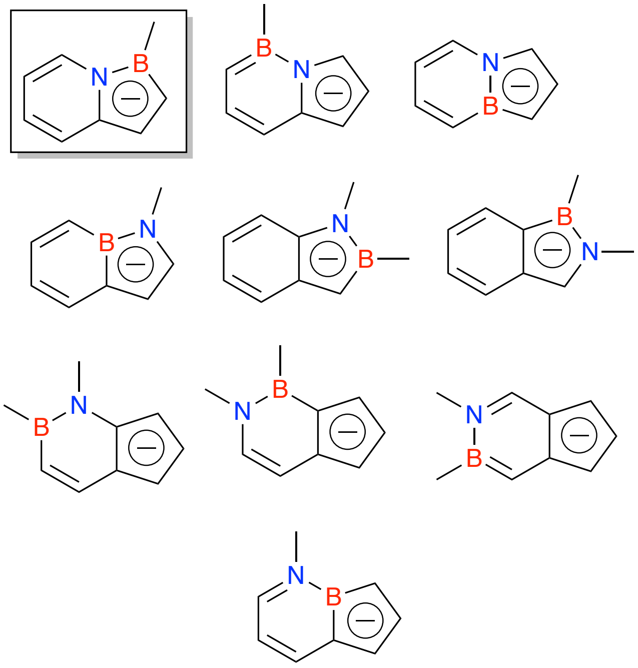
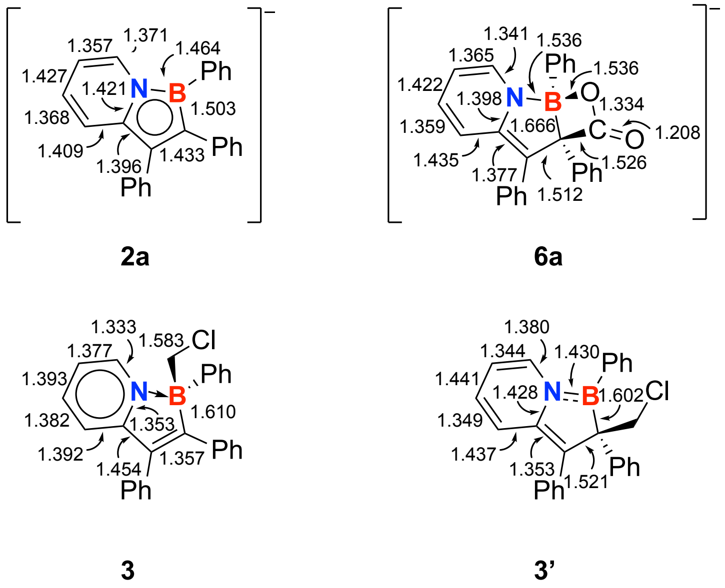


Scheme S1. All 10 possible 1,2-BN isomers of the indenide anion.



2a **6a**

3 **3’**

Scheme S2. Bond lengths of ring bonds in optimized structures of **2a**, **6a**, **3**, and **3’**.

Table S1. Nucleus independent chemical shifts (at PBE0/def-TZVP level of theory) for five-membered (A) and six-membered (B) rings of indenide, **2a**, **6a**, **3**, and **3'**.

		NICS(1)	NICS(0)	$\text{NICS}_{zz}(1)$
indenide	A	–13.6	–15.8	–40.0
	B	–9.3	–9.1	–27.1
2a	A	–11.4	–12.5	–29.5
	B	–1.8	0.0	–3.6
6a	A	–1.0	–1.7	–2.3
	B	0.2	3.5	–0.4
3	A	–1.9	0.7	0.2
	B	–8.2	–5.9	–2.4
3′	A	0.3	0.2	–2.8
	B	2.5	5.9	–1.7

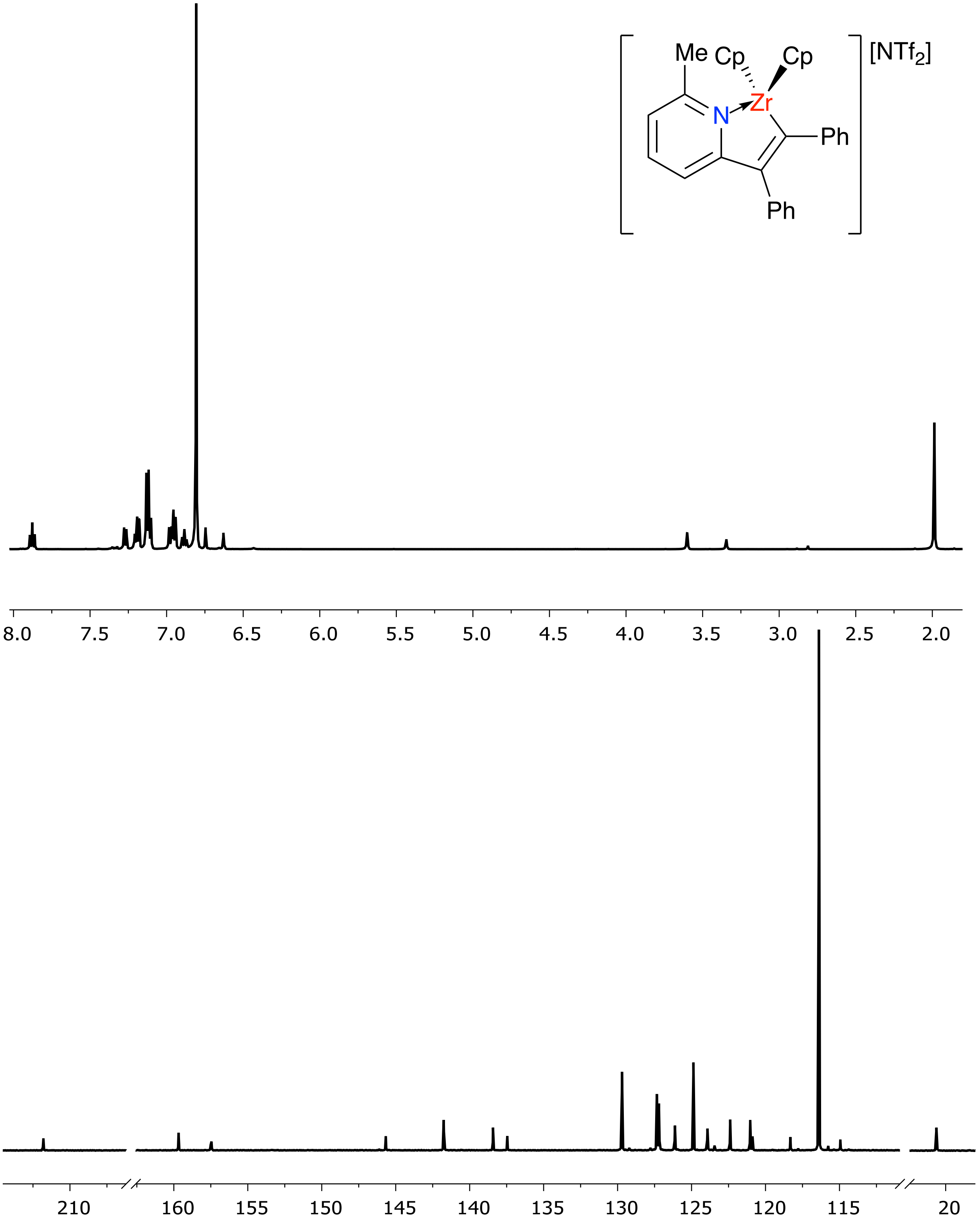


Figure S1: ^{1}H (top) and ^{13}C NMR (bottom) spectra of **Pic*NTf2**.

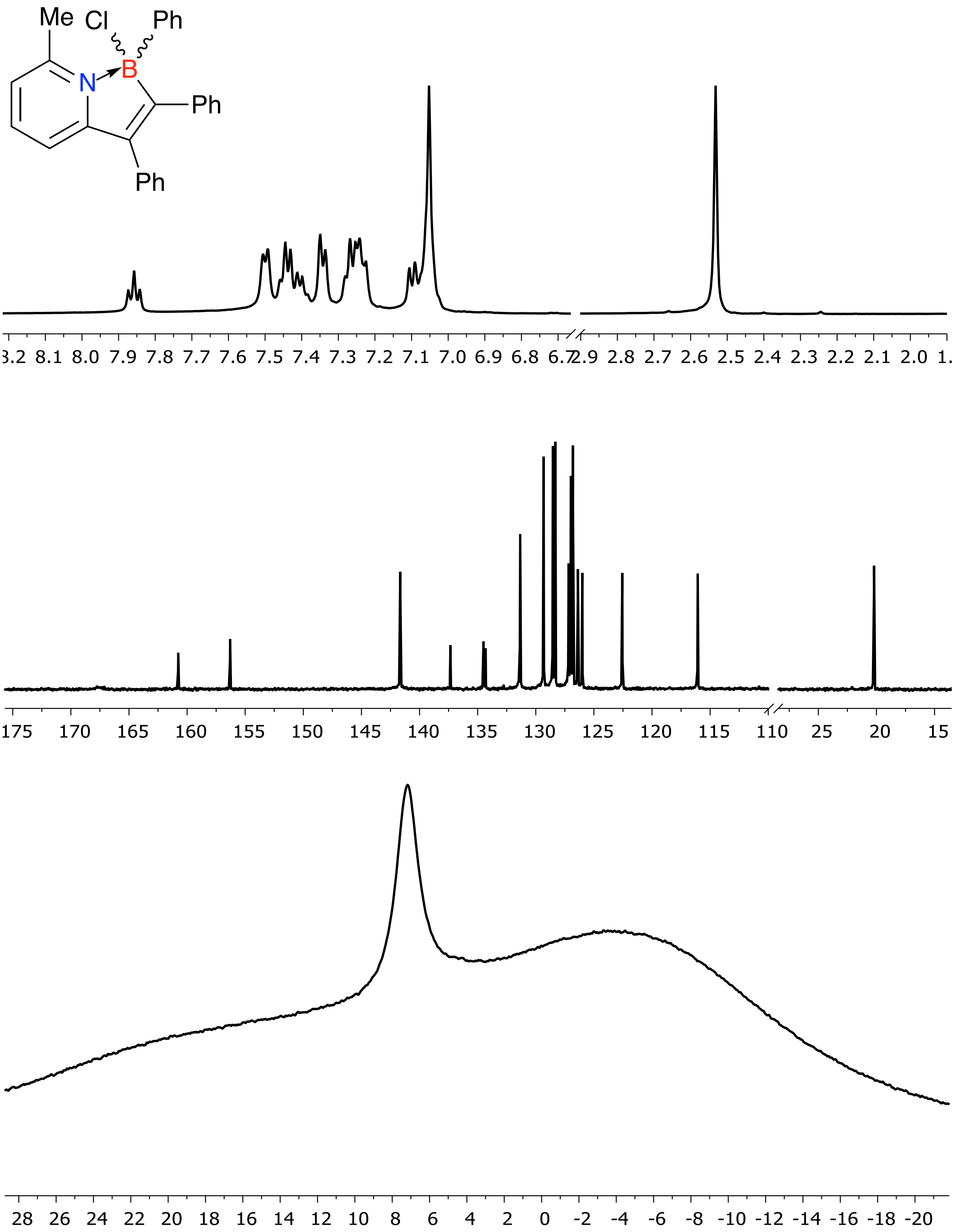


Figure S2: ^{1}H (top), ^{13}C (middle), and ^{11}B (bottom) NMR spectra of **1b** in CD_2Cl_2.

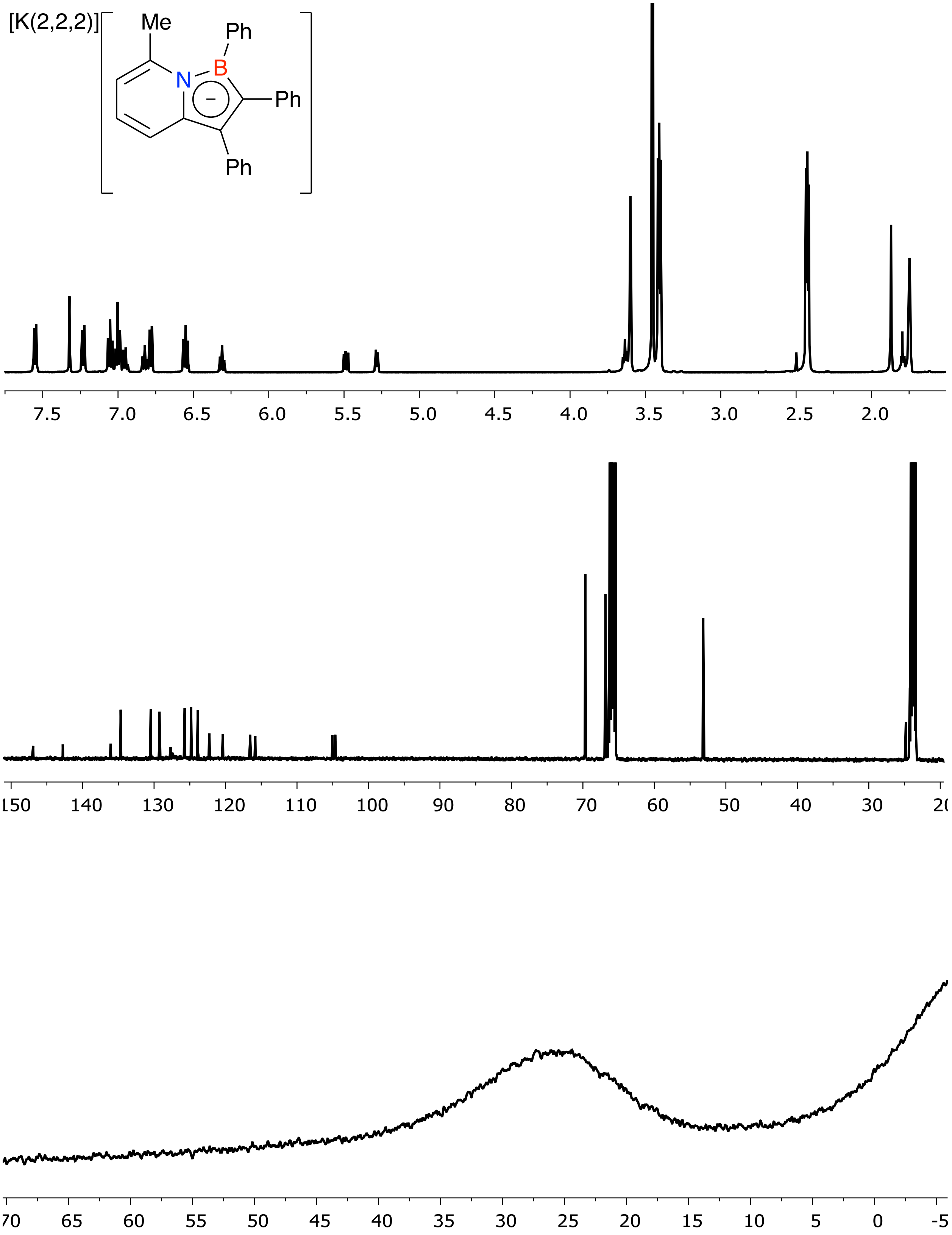


Figure S3: ^{1}H (top), ^{13}C (middle), and ^{11}B (bottom) NMR spectra of **2b** in THF-d$_8$.

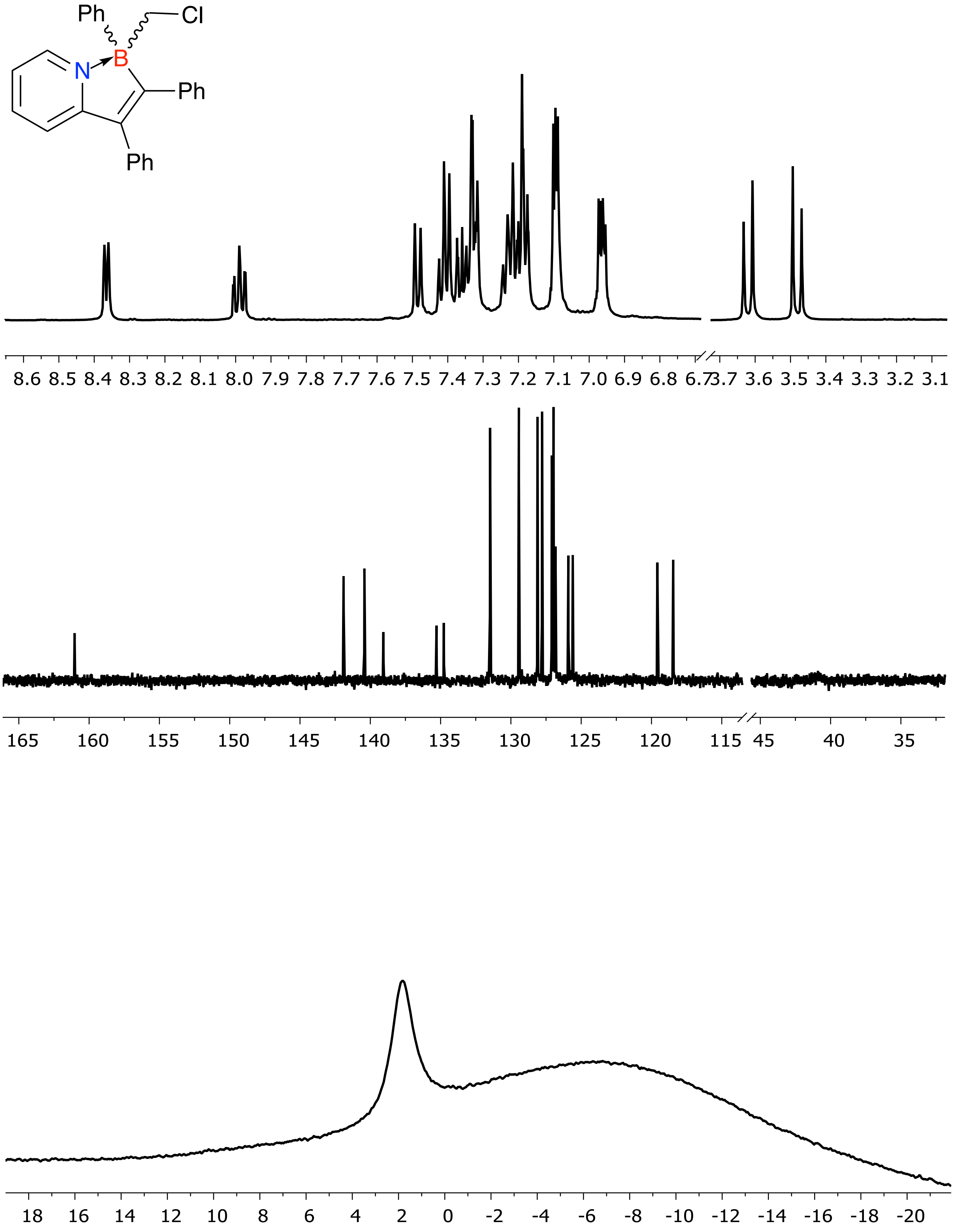


Figure S4: ^{1}H (top), ^{13}C (middle), and ^{11}B (bottom) NMR spectra of **3** in CD_2Cl_2.

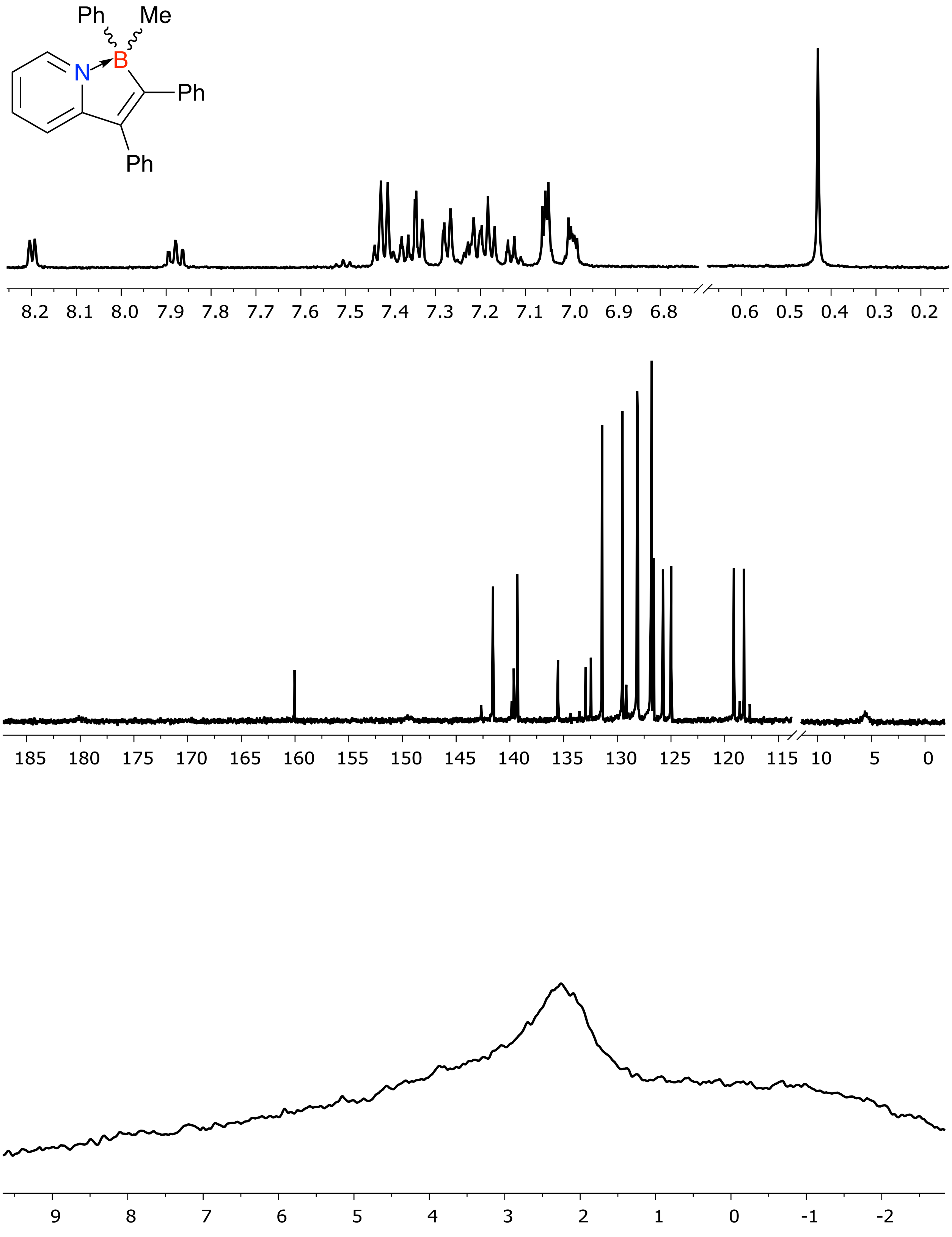


Figure S5: ^{1}H (top), ^{13}C (middle), and ^{11}B (bottom) NMR spectra of **4a** in CD_2Cl_2.

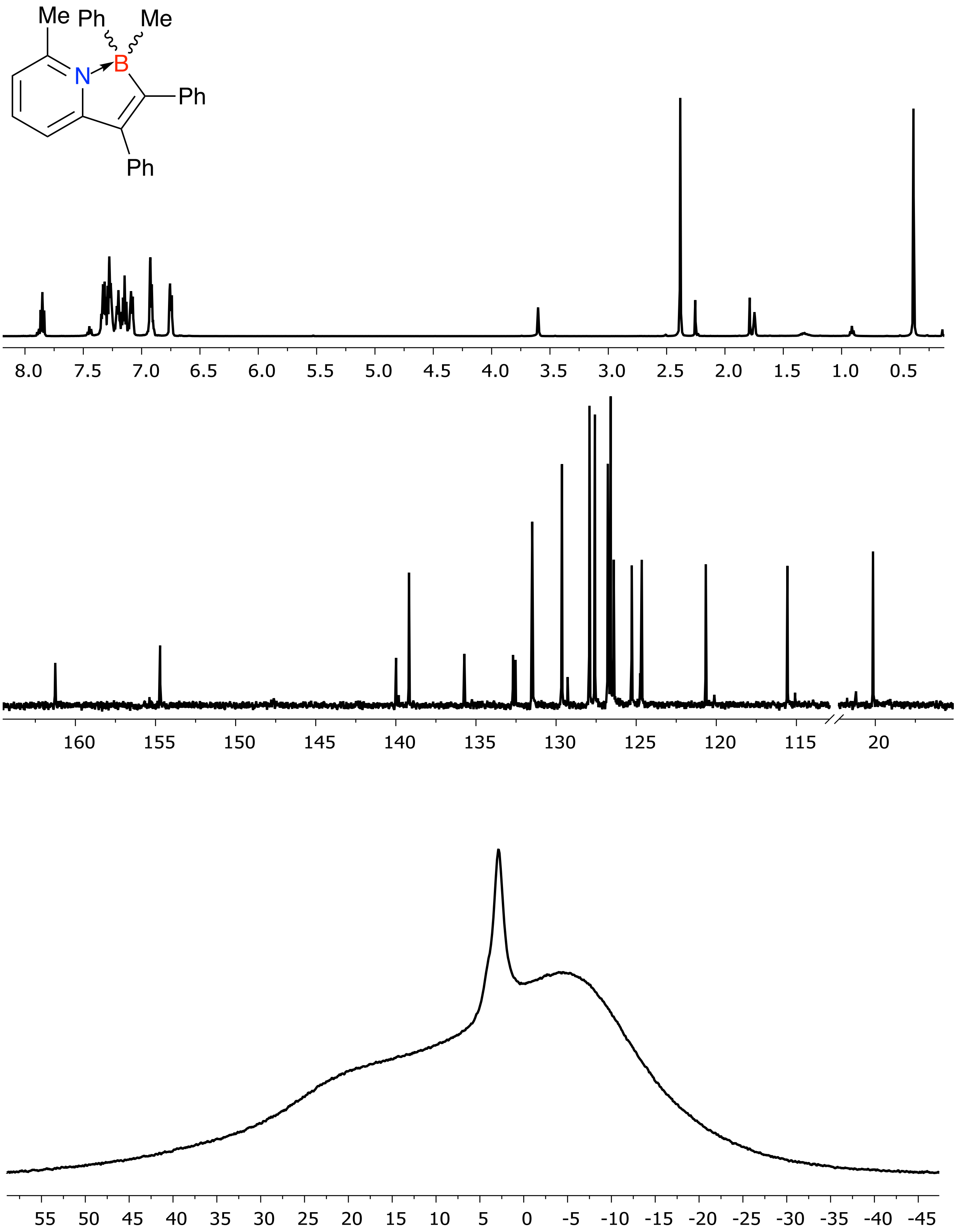


Figure S6: ^{1}H (top), ^{13}C (middle), and ^{11}B (bottom) NMR spectra of **4b** in CD_2Cl_2.

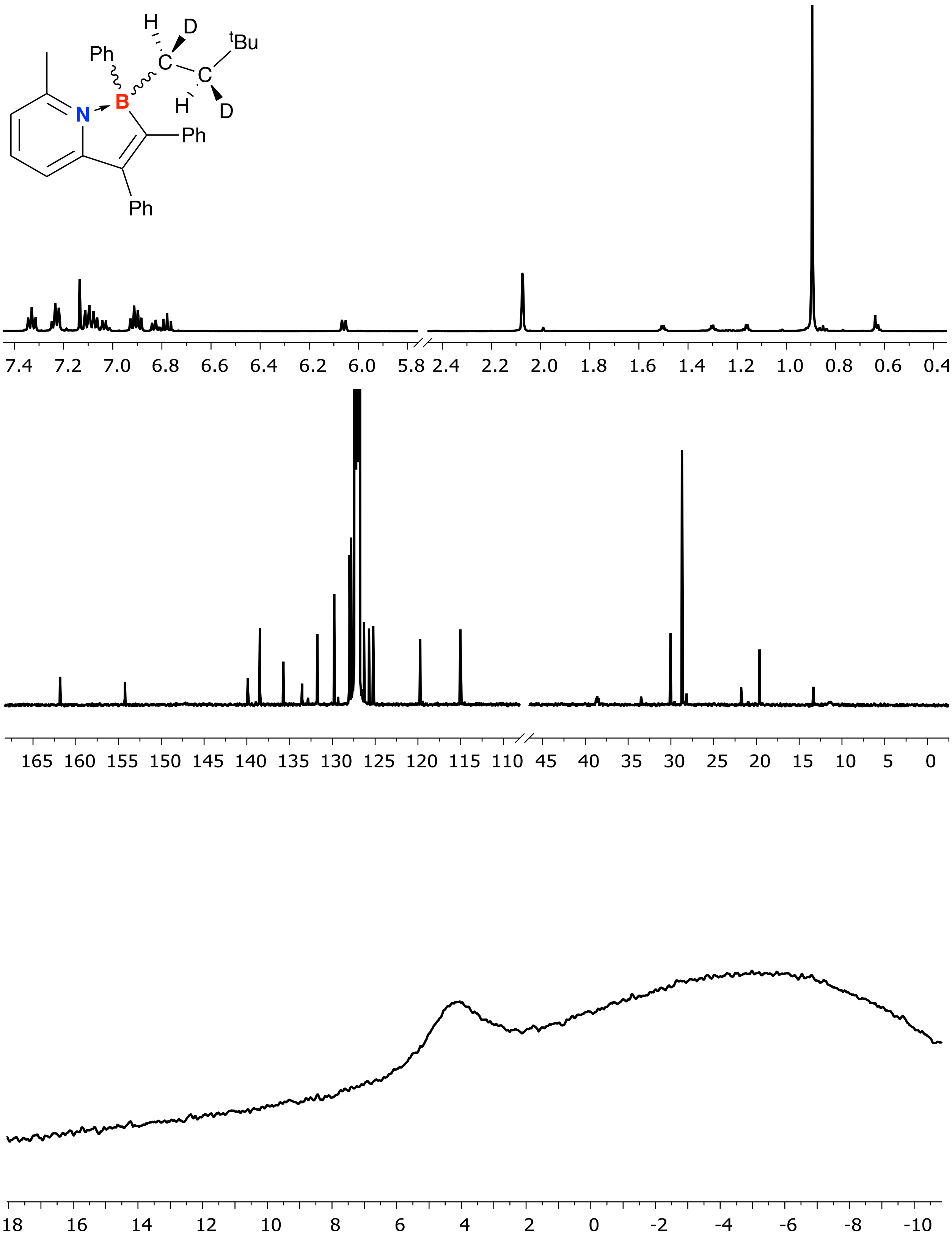


Figure S7: ^{1}H (top), ^{13}C (middle), and ^{11}B (bottom) NMR spectra of **5** in C_6D_6.

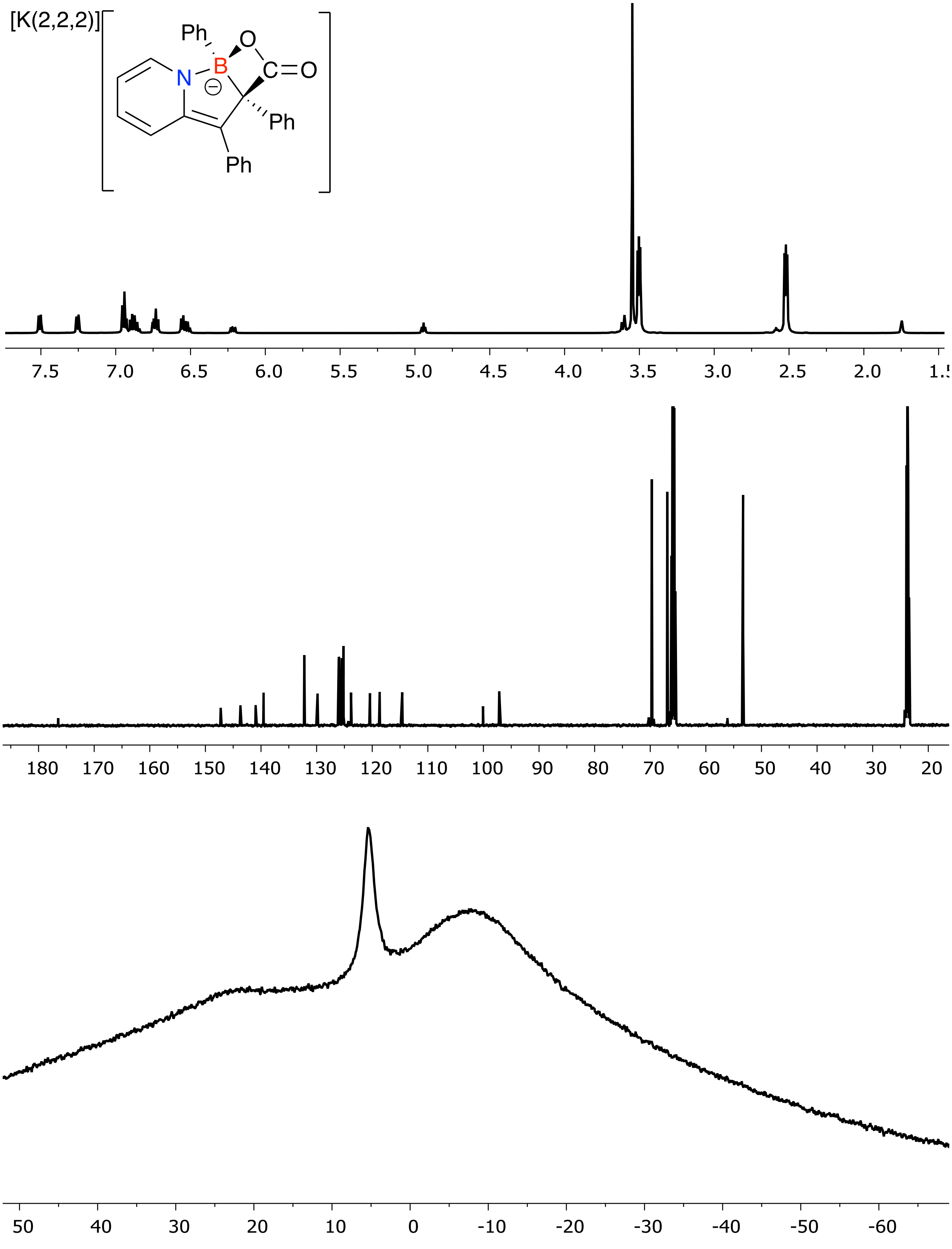


Figure S8: ^{1}H (top), ^{13}C (middle), and ^{11}B (bottom) NMR spectra of **6a** in THF-d$_8$.

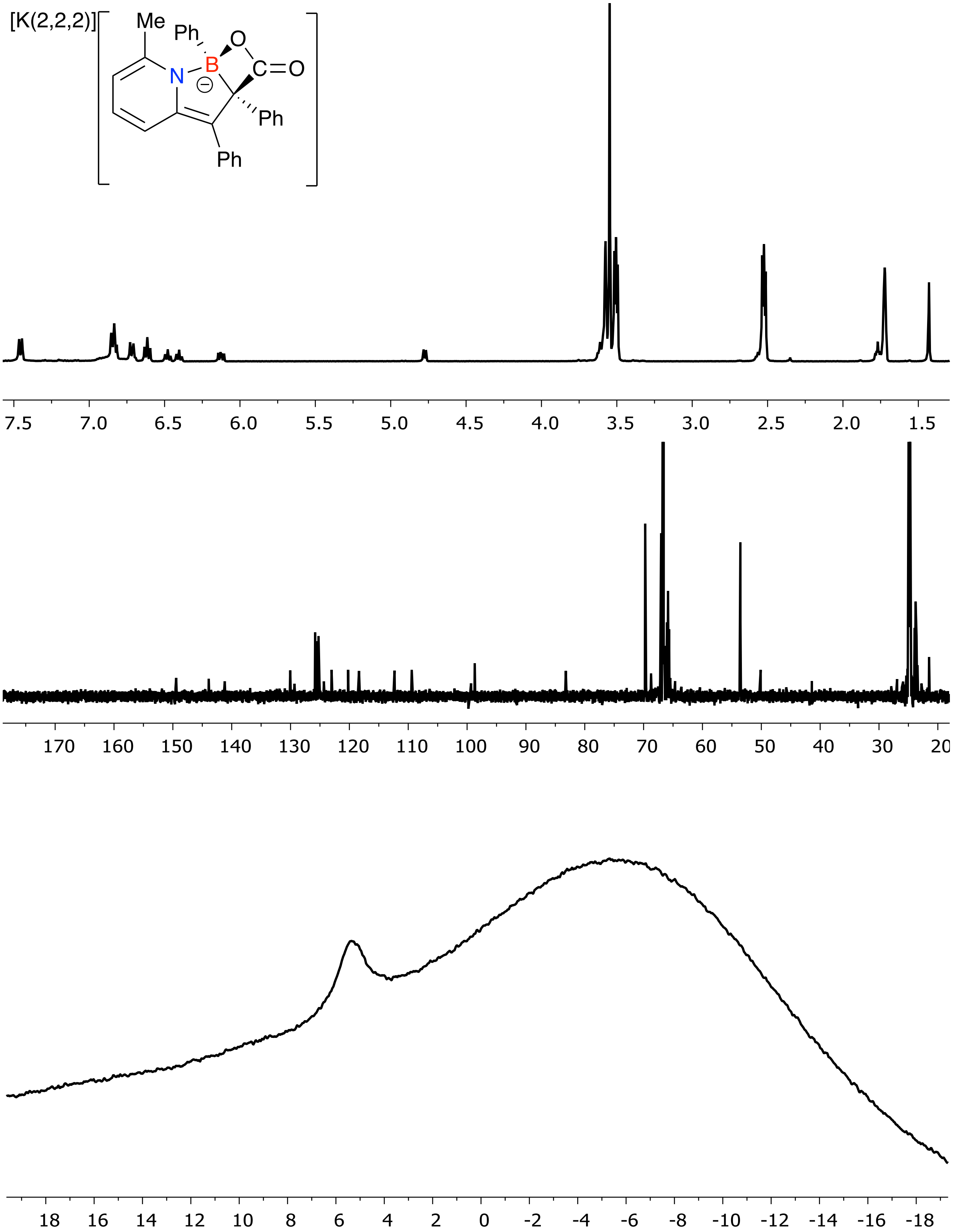


Figure S9: ^{1}H (top), ^{13}C (middle), and ^{11}B (bottom) NMR spectra of **6b** in THF-d_8.

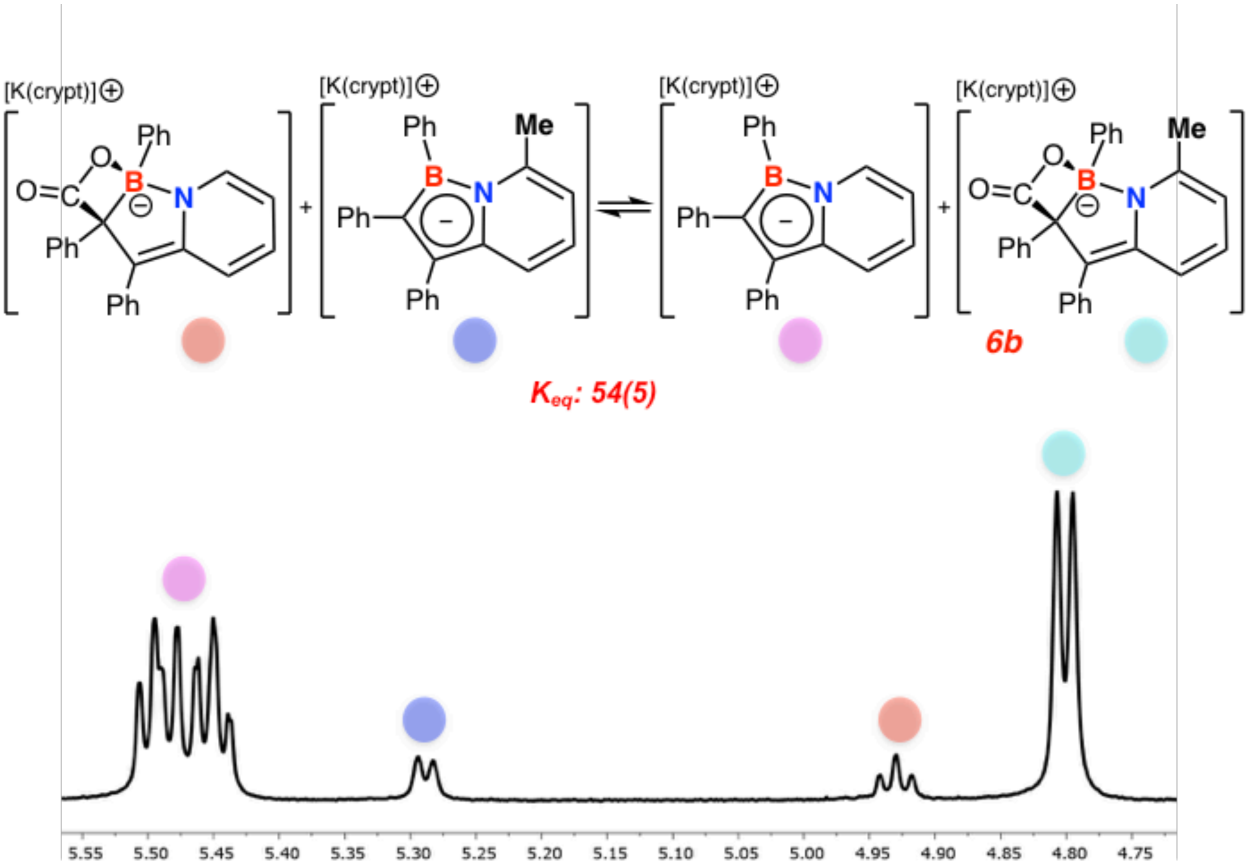


Figure S10: ^{1}H NMR (THF-d_8) spectra of equilibrium reaction mixture.

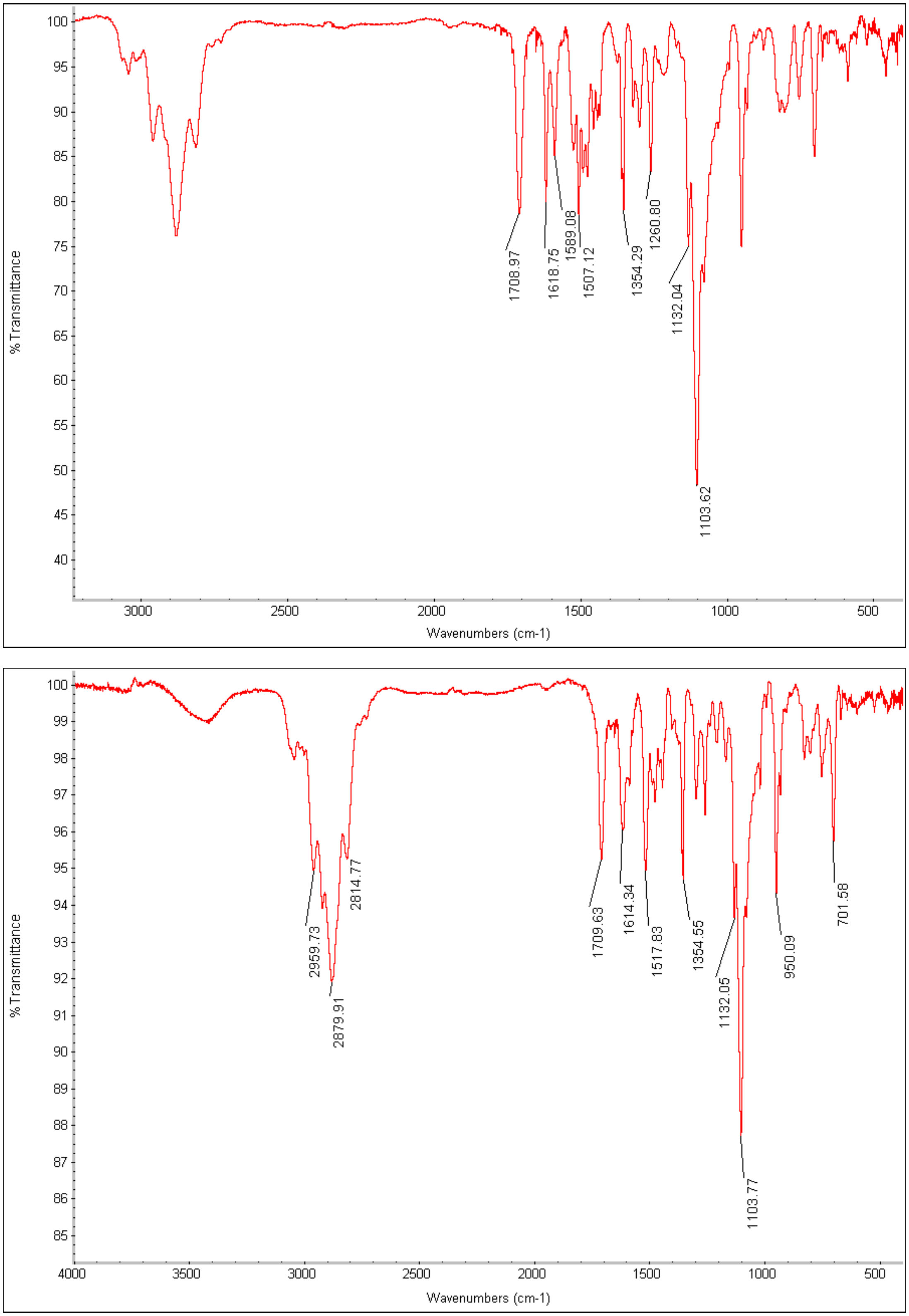


Figure S11: IR Spectra (KBr pellet) of **6a** (top) and **6b** (bottom).