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Electronic Supporting Information

Efficient Synthesis of an Unsupported Aryl Substituted Iminoborane Chain $(HNArBH)_2NAr$ (Ar = [1,1'-biphenyl]-2-yl)

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I. Experimental Details

General

All reactions were carried out under an inert atmosphere using argon as protective gas. 2-Aminobiphenyl was purchased from TCI Chemicals and triethylamine borane from Alfa Aesar. Acetonitrile was bought in HPLC grade from Sigma Aldrich. All chemicals were used without further purification. The NMR spectra were recorded on Bruker Avance II 400 in CD_2Cl_2 (bought from Sigma Aldrich, dried over molecular sieve).

Synthesis

Oligo iminoborane 1. 2-Aminobiphenyl (152 mmol) and triethylamine borane (151 mmol) were slowly heated to 165 °C over a period of two hours and held at this temperature for further 5.5 hours. The triethylamine released in this reaction was then distilled of *in vacuo*, and the remaining solid matter was recrystallized from acetonitrile giving pure product as colorless crystals (57 %).

^{1}H (400,16 MHz, CD_2Cl_2): 4.32–5.26 (m, 2H), 5.38-5.60 (m, 2H), 6.63-6.70 (m, 2H), 6.76-6.80 (m, 1H), 6.89-6.95 (m, 2H), 6.95-7.00 (m, 2H), 7.00-7.28(m, 19H), 7.38-7.43 (m, 2H).

$^{13}C\{^{1}H\}$ (100.62 MHz, CD_2Cl_2): 116.5, 121.5, 127.1, 127.2, 127.4, 128.0, 128.8, 129.0, 129.1, 129.2, 129.3, 130.5, 131.2, 131.8, 139.1, 139.5, 139.6, 141.3.

$^{11}B\{^{1}H\}$ (128.39 MHz, CD_2Cl_2): 31.3.

HR-APCI-MS: m/z: calc. 528.27888, found 528.27844.

II. Spectra

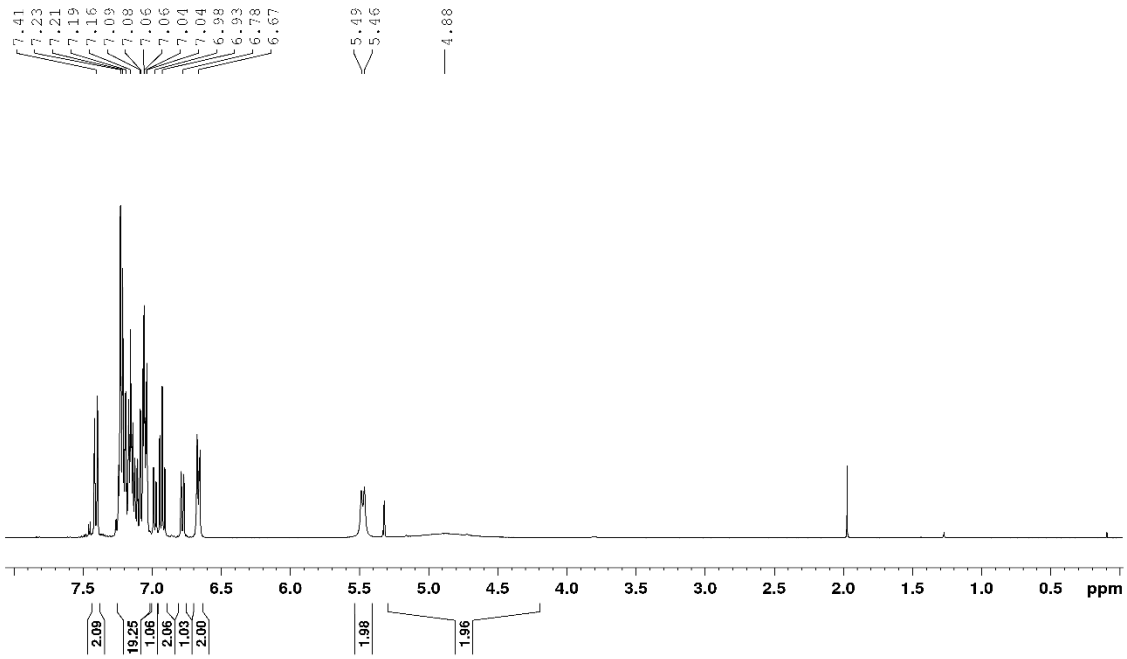

Figure S1. ^{1}H NMR (400,16 MHz, CD_2Cl_2) of **1**

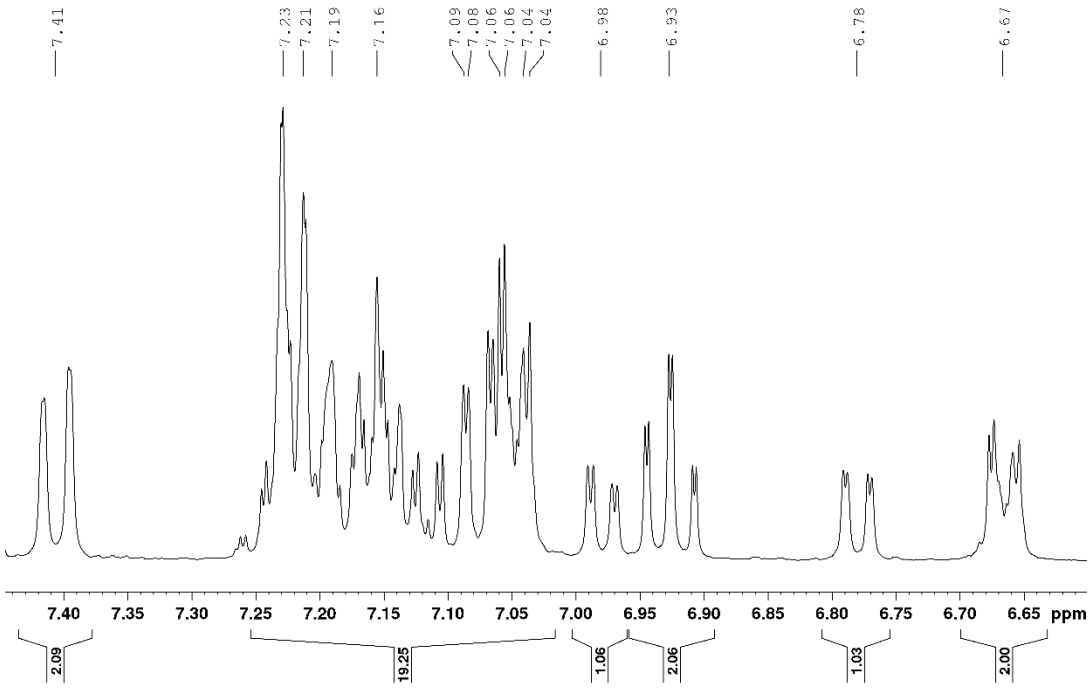

Figure S2. ^{1}H NMR (400.16 MHz, CD_2Cl_2) of **1**, detail aromatic region

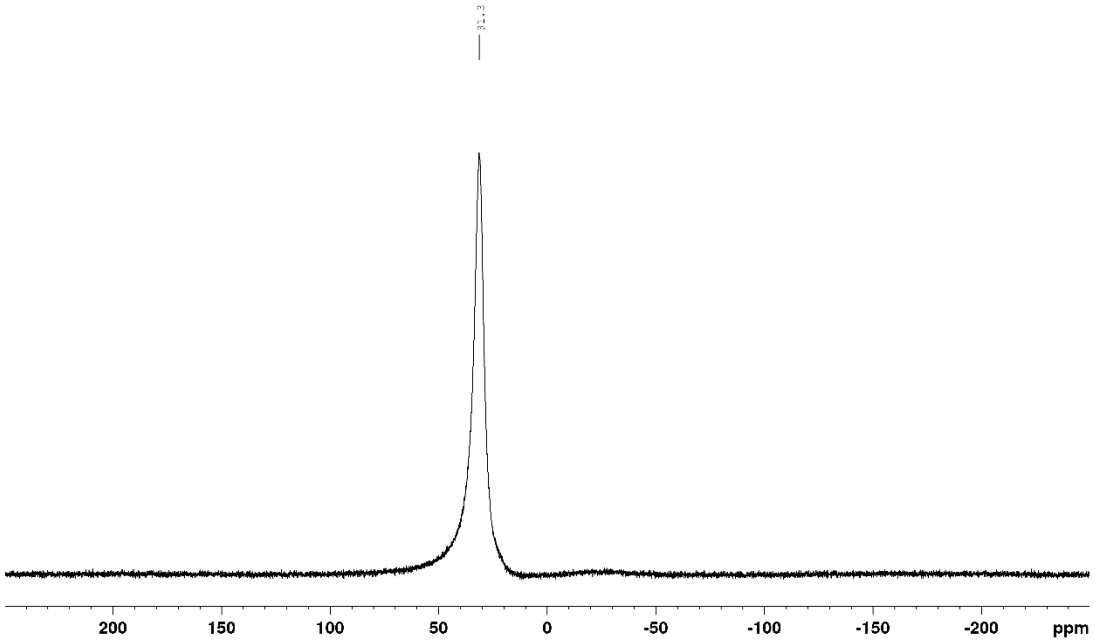

Figure S3. $^{11}B\{^{1}H\}$ NMR (128.39 MHz, CD_2Cl_2)

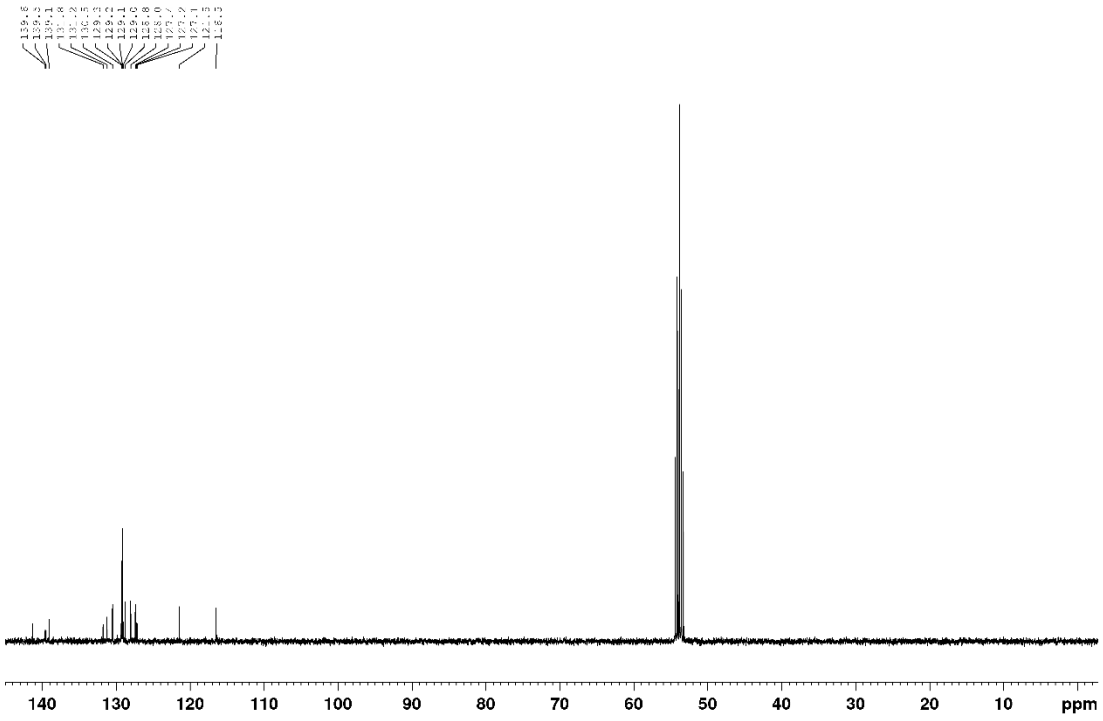

Figure S4. ^{13}C NMR (100.62 MHz, CD_2Cl_2)

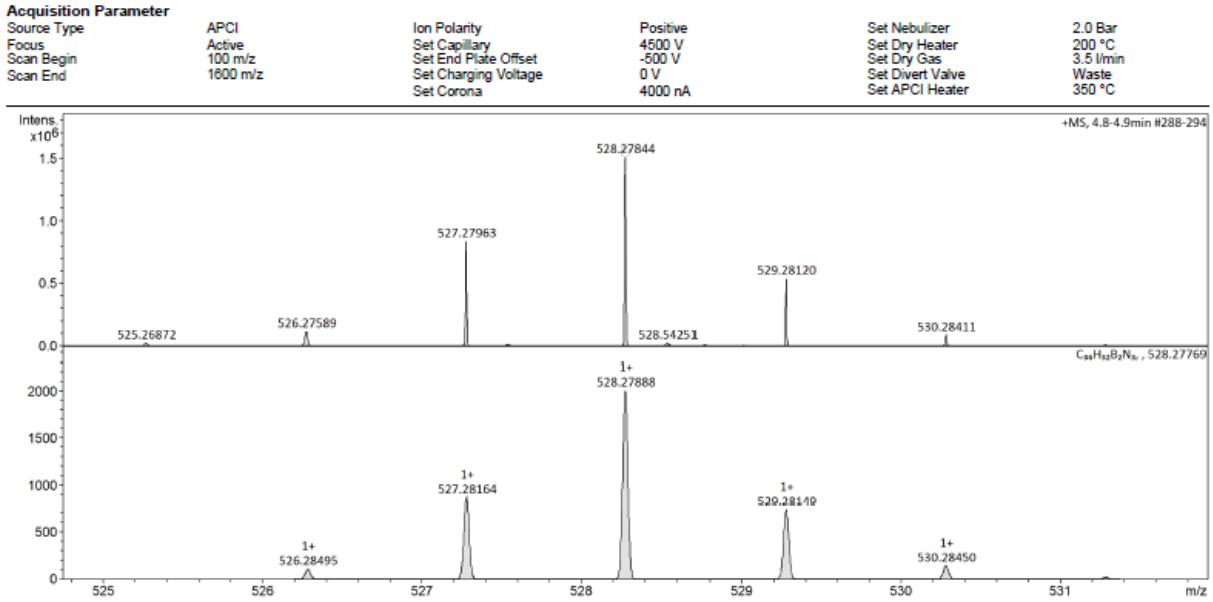

Figure S5. HR-APCI-MS calculated (bottom), found (top)

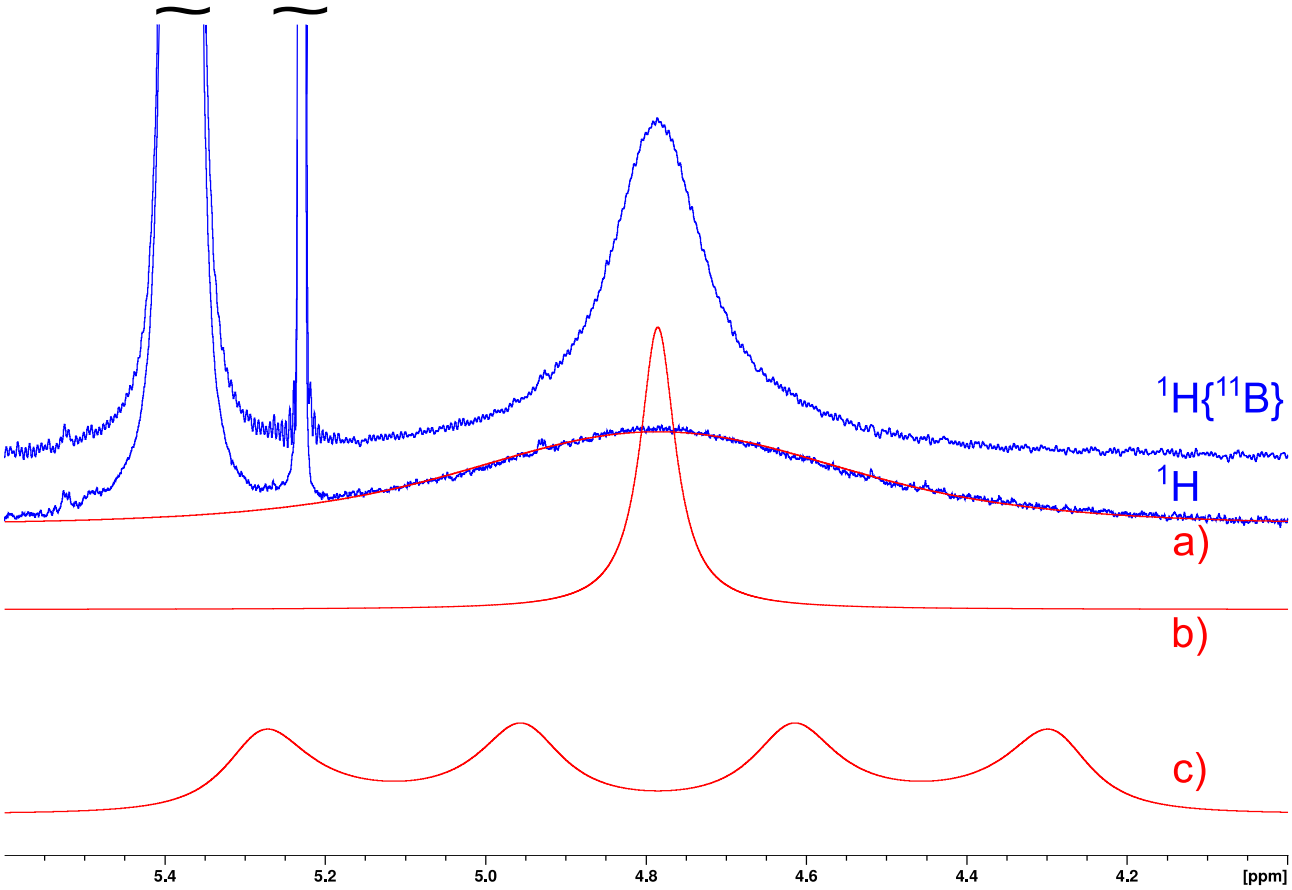

Figure S6. Experimental (blue) and calculated (red) 300.13 MHz ^{1}H NMR spectra of the proton directly bonded to the boron atom. The experimental ^{1}H spectrum exhibits partial narrowing upon ^{11}B decoupling. For the calculations, a $^1J(^{11}B,^1H)$ of 100 Hz has been used, in combination with ^{11}B spin-lattice relaxation times T_{1Q} of (a) 0.88 ms, deduced from the line width in the $^{11}B\{^1H\}$ NMR spectrum, 361 Hz; (b) 0.09 ms; (c) 8.8 ms.

III. X-ray crystallography

Crystals were grown by standard techniques from saturated solution using acetonitrile. A suitable crystal with dimensions 0.17×0.11×0.05 mm^3 was selected and mounted on a XtaLAB Synergy, Dualflex, HyPix diffractometer. Data were measured using ω scans with Cu K_α radiation. The structure was solved with the ShelXT solution program using dual methods and by using Olex2 1.5-ac5-024 as the graphical interface. The model was refined with olex2.refine 1.5-ac5-024 using full matrix least squares minimisation on F^2.

Table 1. Crystal data and structure refinements

Empirical formula	$C_{36}H_{31}B_2N_3$
CCDC	2307985
Formula weight	527.316
Temperature	100.00(11) K
Crystal system	monoclinic
Space group	$P2_1/n$
Unit cell dimensions	a = 23.5173(12) Å b = 9.9015(4) Å c = 26.2782(13) Å α = 90° β = 109.964(6)° γ = 90°
Volume	5751.3(5) $Å^3$
Z	8
Density (calculated)	1.218 g cm^{-3}
Crystal size	0.17×0.11×0.05 mm^3
Θ range for data collection	4.00° to 75.70°
Reflections collected	42123
Independent reflections	11296
Completeness to Θ = 75.70	99.40%
Goodness to fit on F^2	1.0298
Final R indices [I>2sigma(I)]	R_1 = 0.0309 wR_2 = 0.0747
R indices (all data)	R_1 = 0.0482 wR_2 = 0.0812