Supporting Information

Catalytic Dehydrocoupling of Amines and Boranes by an Incipient Tin(II) Hydride

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General experimental procedures.

All manipulations were performed under strictly anhydrous and anaerobic conditions by use of modified Schlenk techniques. All solvents were initially dried using a Grubbs-style solvent purification system and further dried over NaK. Pinacolborane was purchased from Synquest or Oakwood and distilled prior to use. All amines were dried over calcium hydride and distilled prior to use. All NMR spectroscopy was carried out on a Bruker 400 MHz spectrometer. ^{119}Sn NMR spectra were referenced to $SnBu_4$ (-11.7 ppm).[1] Infrared spectroscopy was collected as a Nujol mull using a Bruker Tensor 27 IR spectrometer. Melting points were measured using a Mel-Temp II apparatus using capillary tubes sealed under a nitrogen atmosphere and **1** was synthesized as below and its properties were identical to those reported earlier for **1** prepared with the reaction of **Sn{Ar^{Me_6}}$_2$** with methanol.[2]

{Ar^{Me_6}SnOMe}$_2$ (1). {Ar^{Me_6}SnCl}$_2$ (1.545 g, 3.30 mmol) in Et_2O (*ca.* 50 mL) was cooled to 0 °C and NaOMe (0.1785 g, 3.30 mmol) as a slurry in Et_2O (*ca.* 30 mL) was added dropwise over 30 minutes. The mixture was allowed to warm to room temperature overnight. The resultant yellow solution was filtered and the Et_2O removed under reduced pressure. The remaining yellow powder was washed with cold hexanes (*ca.* 5 mL) to afford **1** as a fine yellow powder. Yield: 1.33 g, 87%.

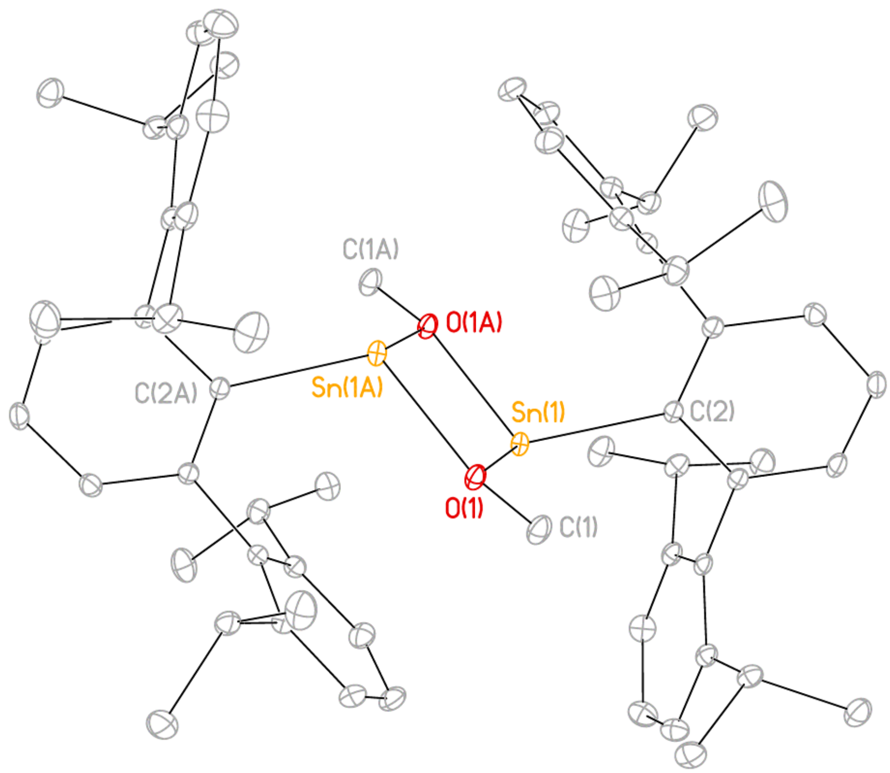
{Ar^{iPr_4}SnOMe}$_2$ (2). {Ar^{iPr_4}SnCl}$_2$ (0.5155 g, 0.4672 mmol) in Et_2O (*ca.* 60 mL) was cooled to 0 °C and NaOMe (0.0505 g, 0.9343 mmol) as a slurry in Et_2O (*ca.* 25 mL) was added dropwise over 30 minutes. The mixture was allowed to warm to room temperature overnight. The Et_2O was removed under reduced pressure and hexane (*ca.* 50 mL) was added. The mixture was filtered via cannula, its volume reduced to *ca.* 20 mL, and stored at *ca.* -28 °C overnight to afford orange/yellow crystals. Yield: 0.355 g, 70%. M.p.: 159-166 °C. ^{1}H NMR (400 MHz, benzene-d_6, 25 ºC, ppm): 1.13 (m, 24H, CH(C**H**$_3$)$_2$), 2.11 (s, 6H, OMe), 2.91 (sept, 4H, C**H**(CH$_3$)$_2$), 7.05 (m, 2H), 7.12 (m, 4H), 7.19 (d, 8H, *m*-C$_6$H$_3$), 7.31 (t, 4H, *p*-C$_6$H$_3$). ^{13}C{^{1}H} NMR (126MHz, benzene-d_6, 25° C, ppm): 24.37, 24.48, 30.79, 122.90, 129.34, 131.47, 139.73, 141.11, 146.90. IR: 2920 (br), 2850 (s), 1590 (w), 1560 (w), 1450 (m), 1370 (m), 1250 (w), 1050 (br), 800 (w), 750 (w), 710 (w).

{Ar^{Me_6}Sn(μ-NEt$_2$)}$_2$ (3). {Ar^{Me_6}SnCl}$_2$ (0.7902 g, 0.8450 mmol) in Et_2O (*ca.* 35 mL) was cooled to 0 °C and $LiNEt_2$ (0.1236 g, 0.9343 mmol) in Et_2O (*ca.* 30 mL) was added dropwise over 30 minutes. The mixture was allowed to warm to room temperature overnight. The Et_2O was removed under reduced pressure and toluene (*ca.* 50 mL) was added. The mixture was filtered via cannula to afford a copper-colored solution which was reduced in volume to *ca.* 10 mL. Storage at -28 °C for three days afforded copper-colored powder of **3**. Yield:0.176 g, 22.2%. M.p.: 139-144 °C, ^{1}H NMR (400 MHz, benzene-d_6, 25 ºC, ppm): 0.81 (t, J_{HH} = 7.0 Hz, 12H, NCH$_2$C**H**$_3$), 2.12 (s, 12H, *p*-Me), 2.27 (s, 24H, *o*-Me), 3.47 (m, 8H, NC**H**$_2$CH$_3$), 6.84 (s, 8H,

$C_6\mathbf{H}_2$), 7.12 (d, J_{HH} = 7.5 Hz, 4H, *m*-C_6H_3), 7.31 (t, J_{HH} = 7.5 Hz, 2H, *p*-C_6H_3). $^{13}C\{^1H\}$ NMR (126MHz, benzene-*d₆*, 25° C, ppm): 20.63, 20.72, 20.89, 21.12, 21.56, 21.71, 128.71, 128.87, 135.24, 135.96, 136.23, 136.65, 138.71, 146.82, 148.60, 175.52. $^{119}Sn\{^1H\}$ NMR (186.36 MHz, benzene-d_6, 25 °C): −155.23 ppm. IR: 2950(s), 2900(s), 2850(s), 2650 (br), 1450(m), 1375(m), 1260(s), 1100(m), 1000(m), 800(s), 700(s).

$Ar^{Me_6}Sn(\mu\text{-}NEt_2)(\mu\text{-}H)SnAr^{Me_6}$ (4). $\{Ar^{Me_6}SnCl\}_2$ (0.255 g, 0.253 mmol) in Et_2O (*ca.* 20 mL) was cooled to -78 °C and HBPin (36.4 µl, 0.253 mmol) in Et_2O (*ca.* 40 mL) was added dropwise over 30 minutes. The mixture was stirred for 30 min and Et_2O was removed under reduced pressure and toluene (*ca.* 70 mL) was added. The resulting mixture was filtered via cannula to afford a copper-colored solution. The toluene was removed under reduced pressure and pentane (*ca.* 30 mL) was added. The mixture was sonicated briefly (ca. 5 minutes) and then allowed to sit until all solid settled. The standing liquor was decanted and the remaining solid dried under reduced pressure to afford **4** as a yellow powder. Yield: 20%. M.p.: 139-144 ºC. ^1H NMR (400 MHz, benzene-d_6, 25 ºC, ppm): 0.63 (t, J_{HH} = 7.0 Hz, 6H, $NCH_2C\mathbf{H}_3$), 2.04 (s, 12H, *p*-Me), 2.18 (s, 12H, *o*-Me), 2.26 (s, 12H, *o*-Me), 2.34 (dq, J_{HH} = 13.5/6.7 Hz, 1H, $NC\mathbf{H}_2CH_3$), 2.86 (dq, J_{HH} = 13.5/6.7 Hz, 1H, $NC\mathbf{H}_2CH_3$), 4.10 (s, 1H, Sn**H**Sn, ^{119}Sn satellites $J_{H^{119}Sn}$ = 64 Hz), 6.85 (s, 4H, *m*-C_6H_2), 6.87 (s, 4H, *m*-C_6H_2), 6.92 (d, J_{HH} = 7.5 Hz, 4H, *m*-C_6H_3), 7.12 (t, J_{HH} = 7.5 Hz, 2H, *p*-C_6H_3). $^{13}C\{^1H\}$ NMR (126MHz, benzene-d_6, 25° C, ppm): 16.73 ($NCH_2C\mathbf{H}_3$), 21.28 (*p*-Me), 21.95 (*o*-Me), 22.10 (*o*-Me), 45.50 ($NC\mathbf{H}_2CH_3$), 128.58, 129.09, 129.59, 135.62, 136.35, 136.62, 148.99, 169.37 $^{119}Sn\{^1H\}$ NMR (186.36 MHz, benzene-d_6, 25 °C): −150.33 ppm. IR: 2920 (br), 2720 (s), 1450 (s), 1370 (s), 1300 (m), 1255 (s), 1090 (br), 1015 (s), 950 (w), 800 (s), 720 (s), 390 (w).

Figure S1. Crystal Structure of {Ar^{iPr_4}SnOMe}$_2$ (**2**).



Thermal ellipsoid (30%) plot of **2**. Hydrogen atoms are not shown for clarity. Selected bond lengths (Å) and angles (°): Sn(1)-O(1) 2.1379(11), Sn(1)-O(1A) 2.2080(10), O(1)-C(1) 1.4268(17), Sn(1)-C(2) 2.2720(14), Sn(1)-O(1)-Sn(1A) 108.33(4), O(1)-Sn(1)-O(1A) 71.68(4), O(1)-Sn(1)-C(2) 94.11(4).

Table S1. Crystal Data and Refinement Summary for **2** and **4**.

Identifier	**2**	**4**
Formula	$C_{62}H_{80}O_2Sn_2$	$C_{52}H_{60}NSn_2$, $2(C_{3.5}H_4)$
fw (g mol^{-1})	1094.64	1029.53
Crystal system	monoclinic	monoclinic
Space group	$P2_1/n$	C 2/c
a (Å)	13.542(3)	25.5341(12)
b (Å)	13.931(3)	22.0810(11)
c (Å)	14.562(3)	21.1566(16)
α (°)	90	90
β (°)	97.201(3)	122.3359(11)
γ (°)	90	90
V ($Å^3$)	2725.6(10)	10078.7(10)
Z	2	8
Radiation	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)
T (K)	90.15	100
cryst. size (mm)	0.311 x 0.310 x 0.128	0.460 x 0.312 x 0.184
F(000)	1136.0	4240.0
ρ_{calc} (g cm^{-3})	1.334	1.357
μ (mm^{-1})	0.957	1.029
$2\theta_{max}$ (°)	3.872 to 55.09	4.336 to 55.13
reflns. collected	36195	168181
unique reflns.	6271	11633
R_{int}	0.0235	0.0549
reflns. [I>2σ(I)]	5780	10305
R_1 [I>2σ(I)]	0.0179	0.0426
wR_2 (all data)	0.0487	0.1123
GoF (F^2)	1.042	1.052

Figure S2. ^{1}H NMR Spectrum of **1** (400 MHz, benzene-d_6, 25 ºC, ppm).

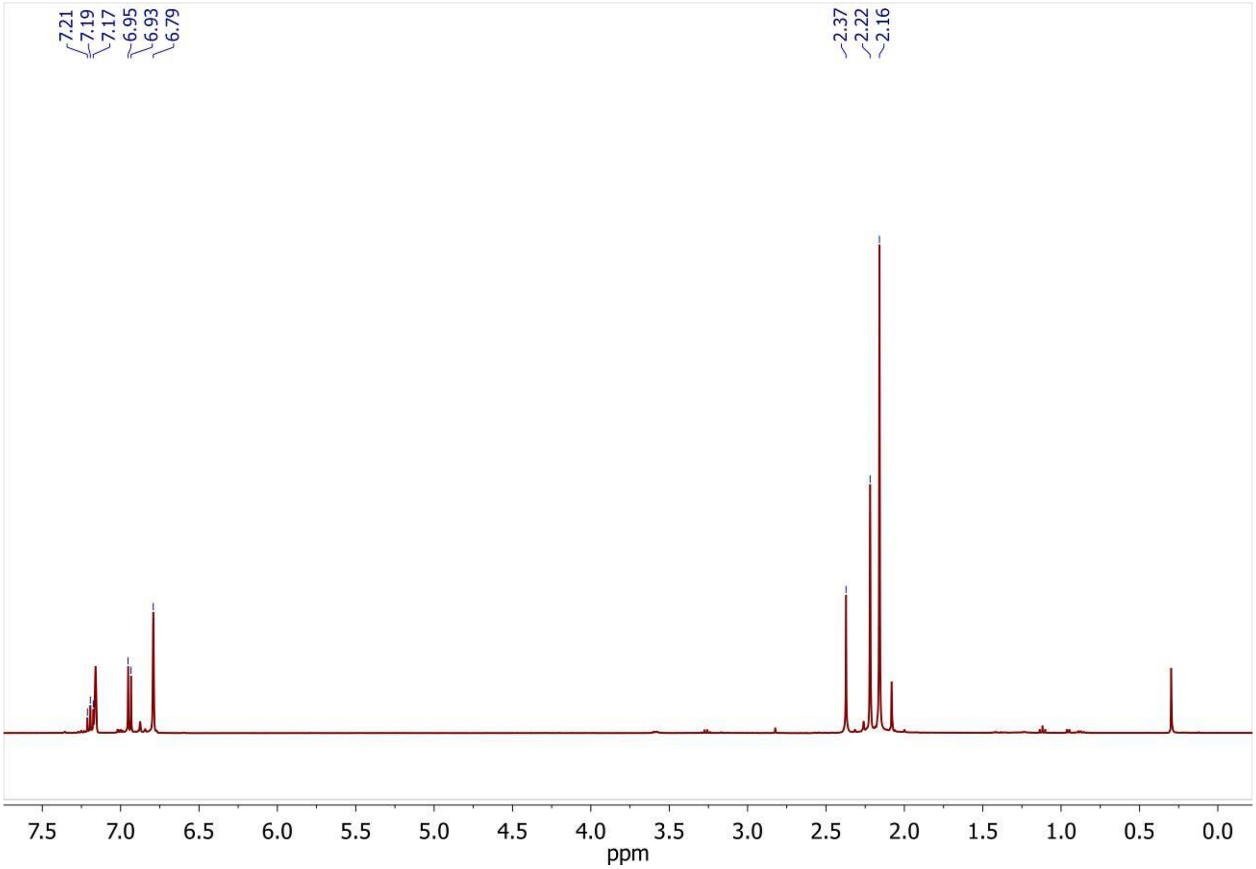
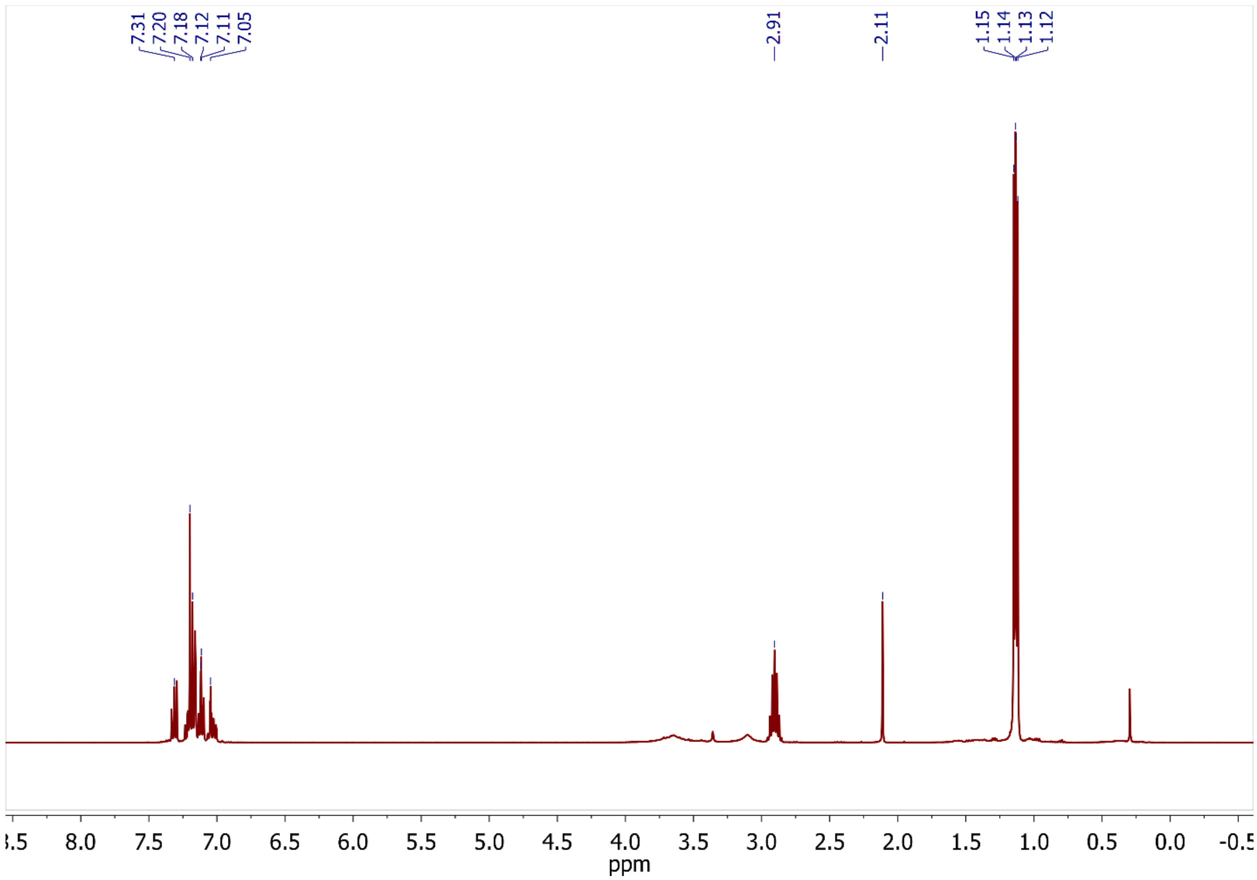
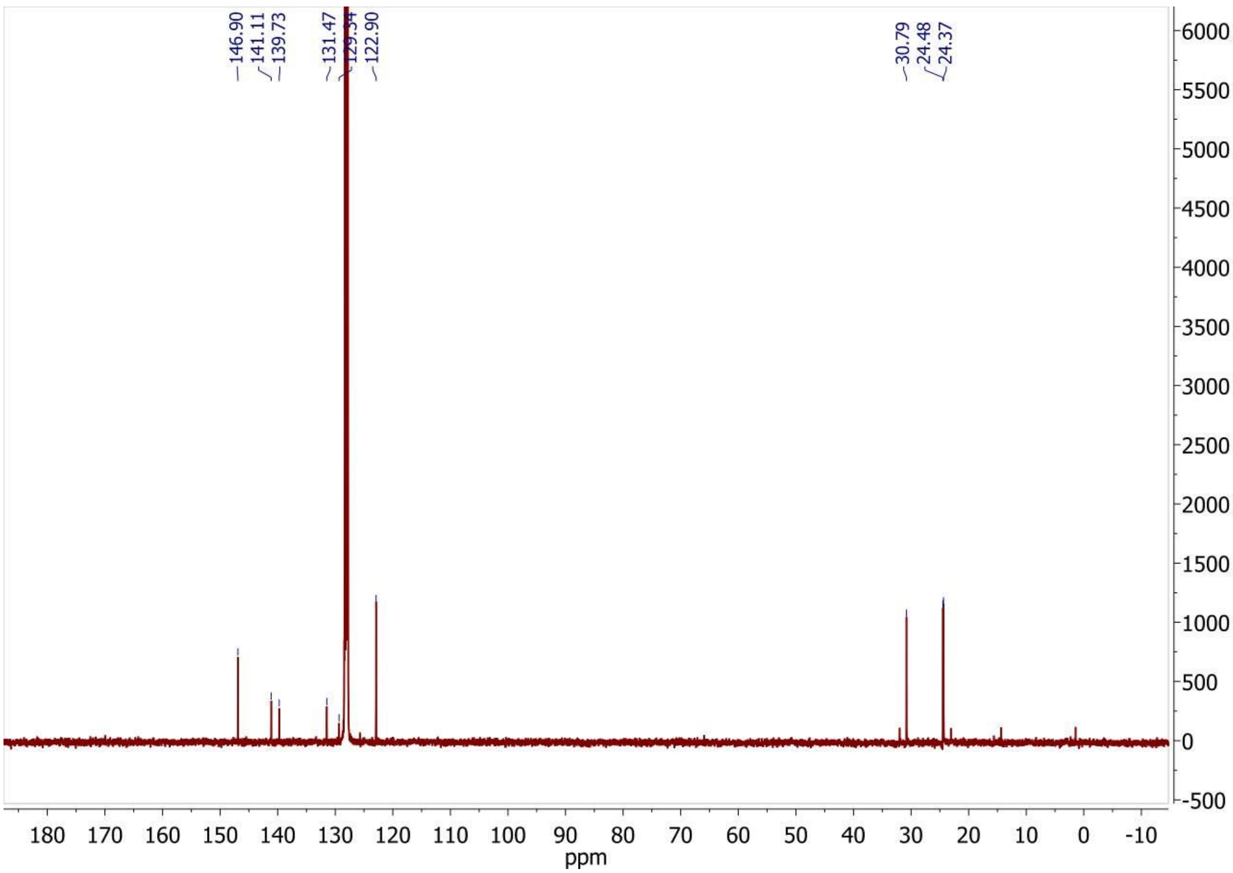


Figure S3. ^{1}H NMR Spectrum of **2** (400 MHz, benzene-d_6, 25 ºC, ppm).



^{1}H NMR (400 MHz, benzene-d_6, 25 ºC, ppm): 1.13 (m, 24H, CH(C**H**$_3$)$_2$), 2.11 (s, 6H, OMe), 2.91 (sept, 4H, C**H**(CH$_3$)$_2$), 7.05 (m, 2H), 7.12 (m, 4H), 7.19 (d, 8H, *m*-C_6H_3), 7.31 (t, 4H, *p*-C_6H_3).

Figure S4. $^{13}C\{^1H\}$ NMR Spectrum of **2** (Small hexane impurity). (126MHz, benzene-d_6, 25° C, ppm)



$^{13}C\{^1H\}$ NMR (126MHz, benzene-d_6, 25° C, ppm): 24.37, 24.48, 30.79, 122.90, 129.34, 131.47, 139.73, 141.11, 146.90.

Figure S5. IR Spectrum of **2** as Nujol Mull.

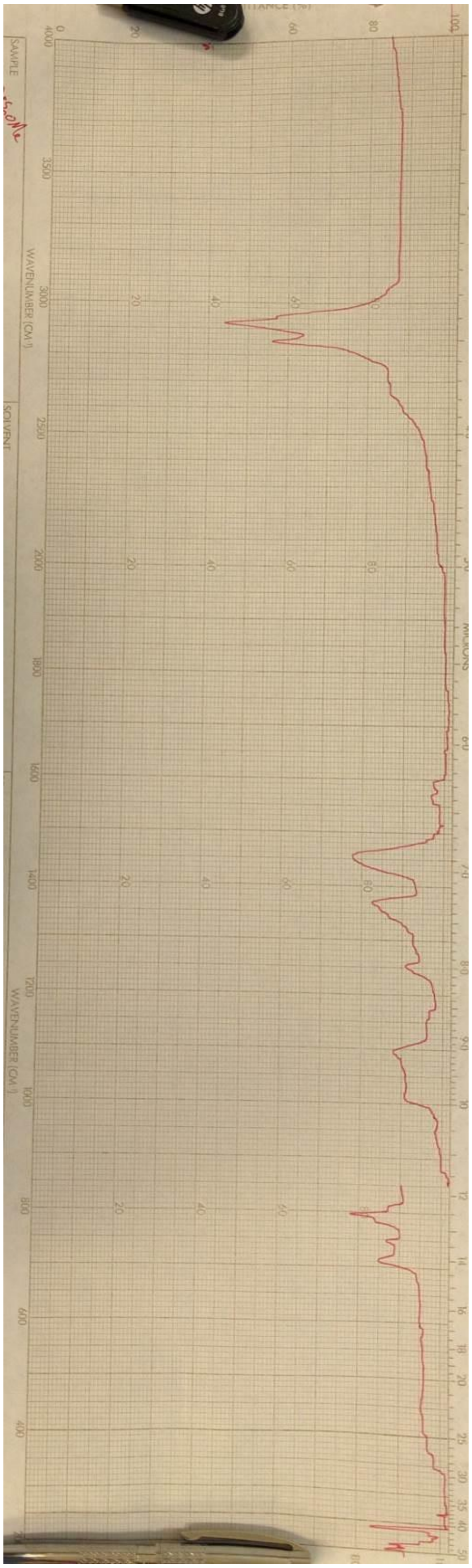
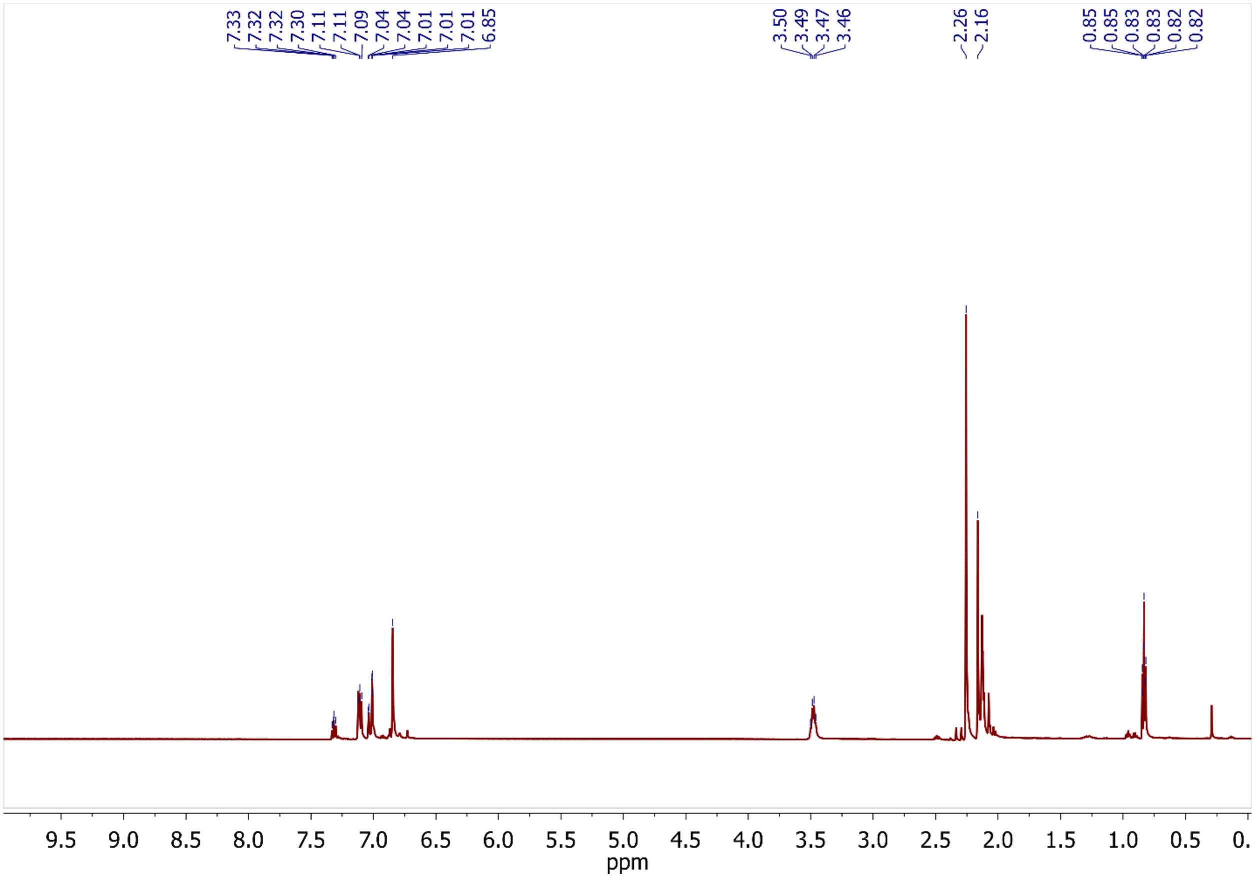
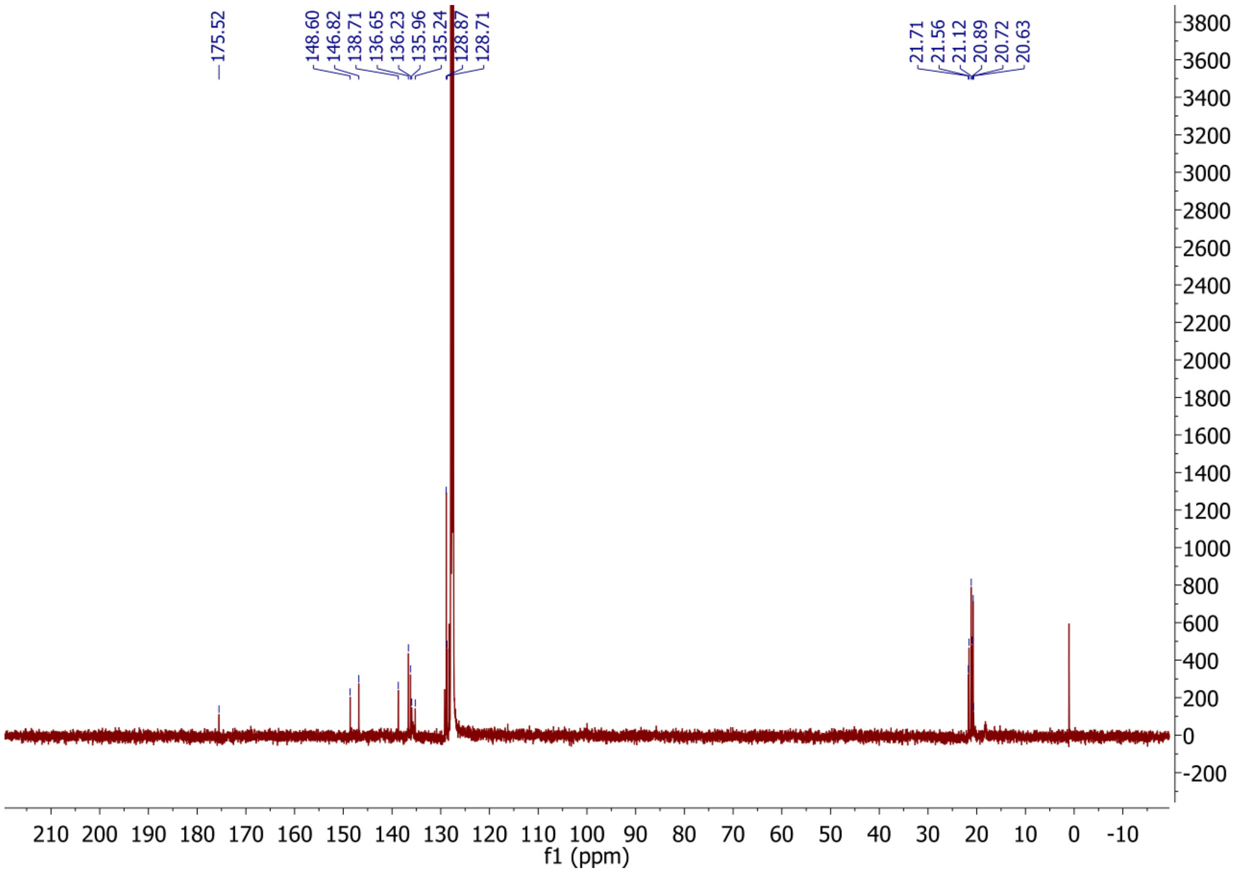


Figure S6. ^{1}H NMR Spectrum of **3** (Some residual toluene). (400 MHz, benzene-d_6, 25 ºC, ppm)



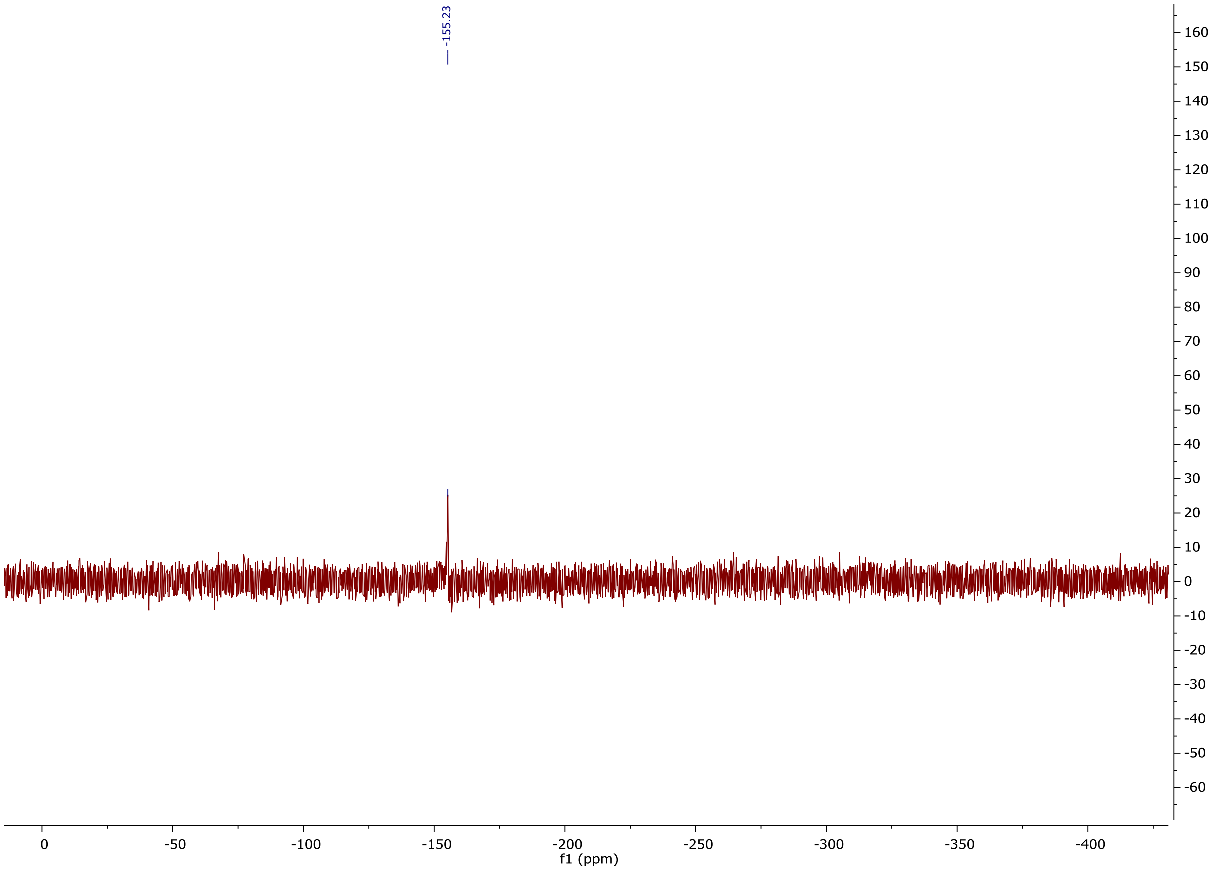
^{1}H NMR (400 MHz, benzene-d_6, 25 ºC, ppm): 0.81 (t, J_{HH} = 7.0 Hz, 12H, $NCH_2C\mathbf{H}_3$), 2.12 (s, 12H, *p*-Me), 2.27 (s, 24H, *o*-Me), 3.47 (m, 8H, $NC\mathbf{H}_2CH_3$), 6.84 (s, 8H, $C_6\mathbf{H}_2$), 7.12 (d, J_{HH} = 7.5 Hz, 4H, *m*-C_6H_3), 7.31 (t, J_{HH} = 7.5 Hz, 2H, *p*-C_6H_3)

Figure S7. $^{13}C\{^1H\}$ NMR Spectrum of **3**. (126MHz, benzene-d_6, 25° C, ppm)



$^{13}C\{^1H\}$ NMR (126MHz, benzene-d_6, 25° C, ppm): 20.63, 20.72, 20.89, 21.12, 21.56, 21.71, 128.71, 128.87, 135.24, 135.96, 136.23, 136.65, 138.71, 146.82, 148.60, 175.52.

Figure S8. ^{119}Sn NMR Spectrum of **3** (186.36 MHz, benzene-d_6, 25 °C, ppm):



^{119}Sn{^{1}H} NMR (186.36 MHz, benzene-d_6, 25 °C): −155.23 ppm.

Figure S9. IR Spectrum of **3** as Nujol Mull

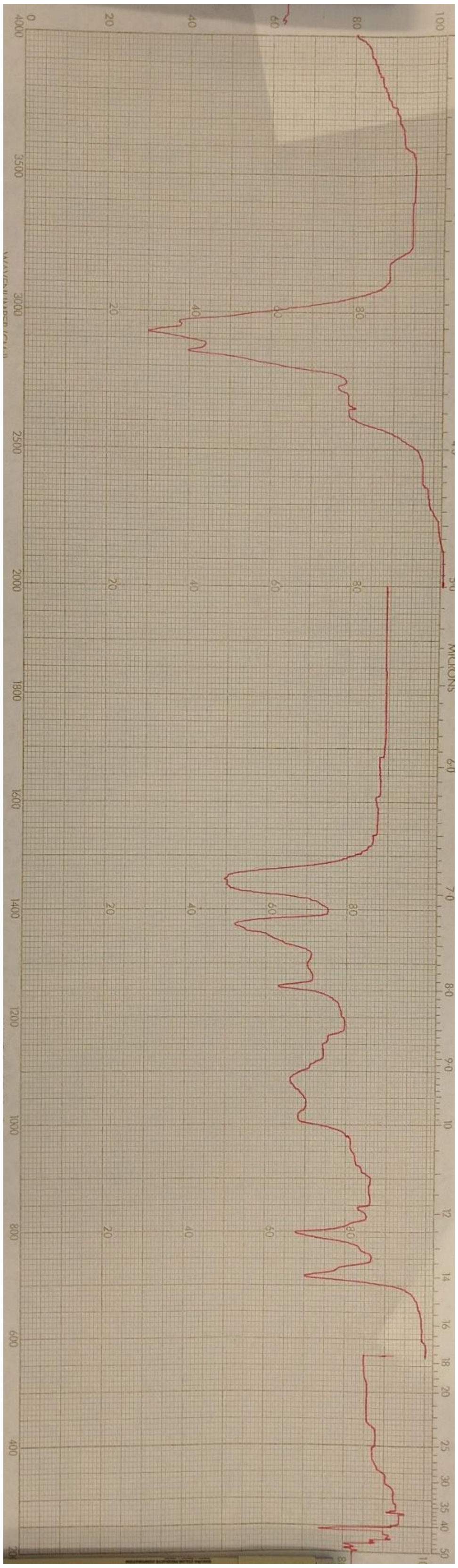
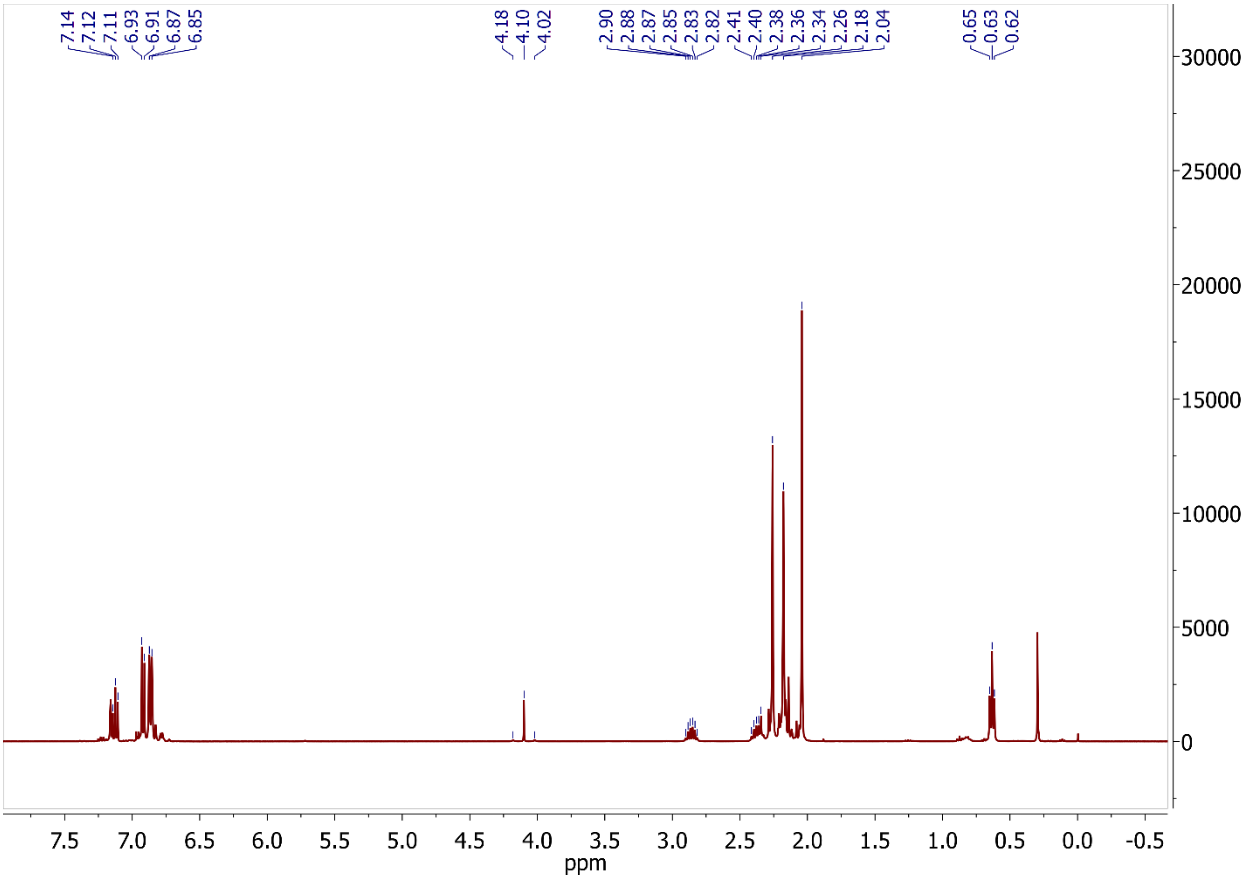
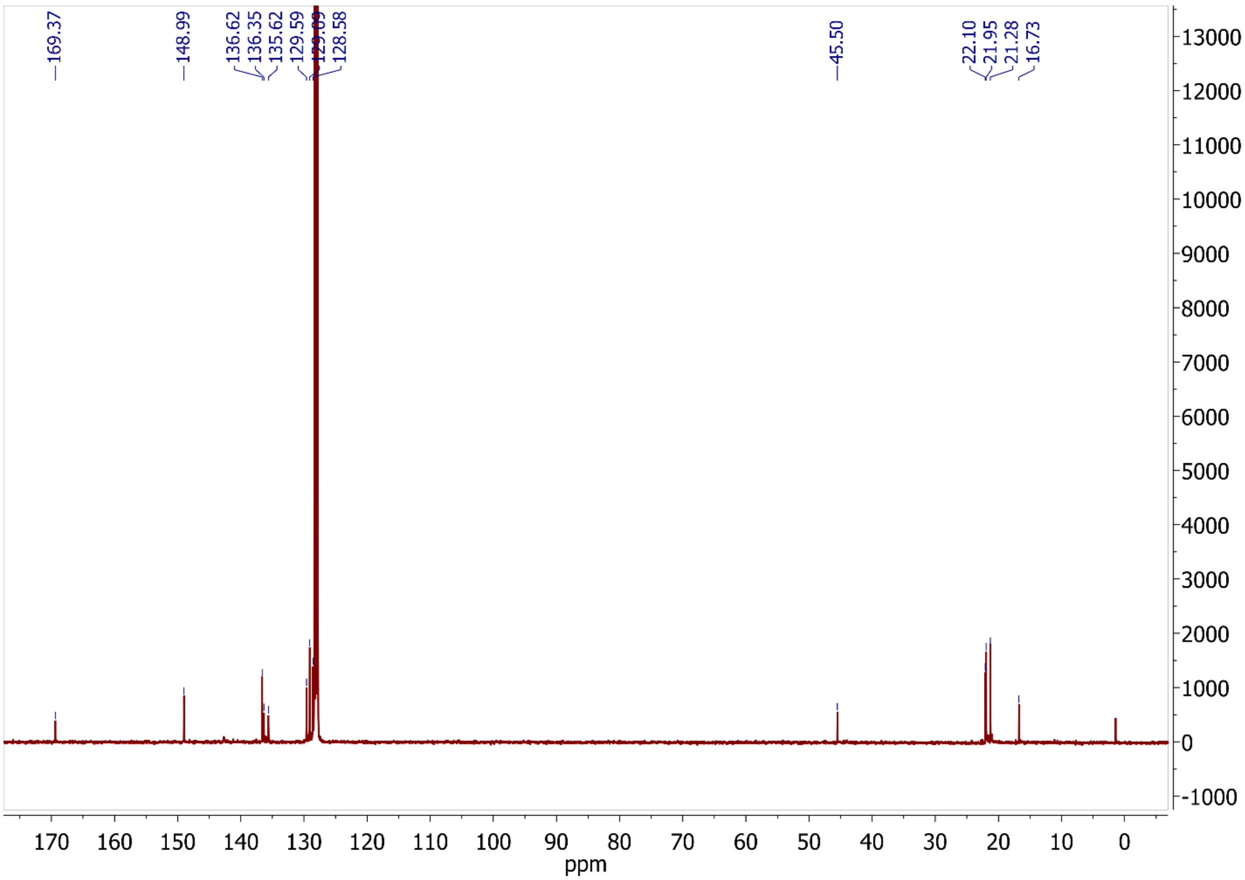


Figure S10. ^{1}H Spectrum of **4**. (400 MHz, benzene-d_6, 25 ºC, ppm)



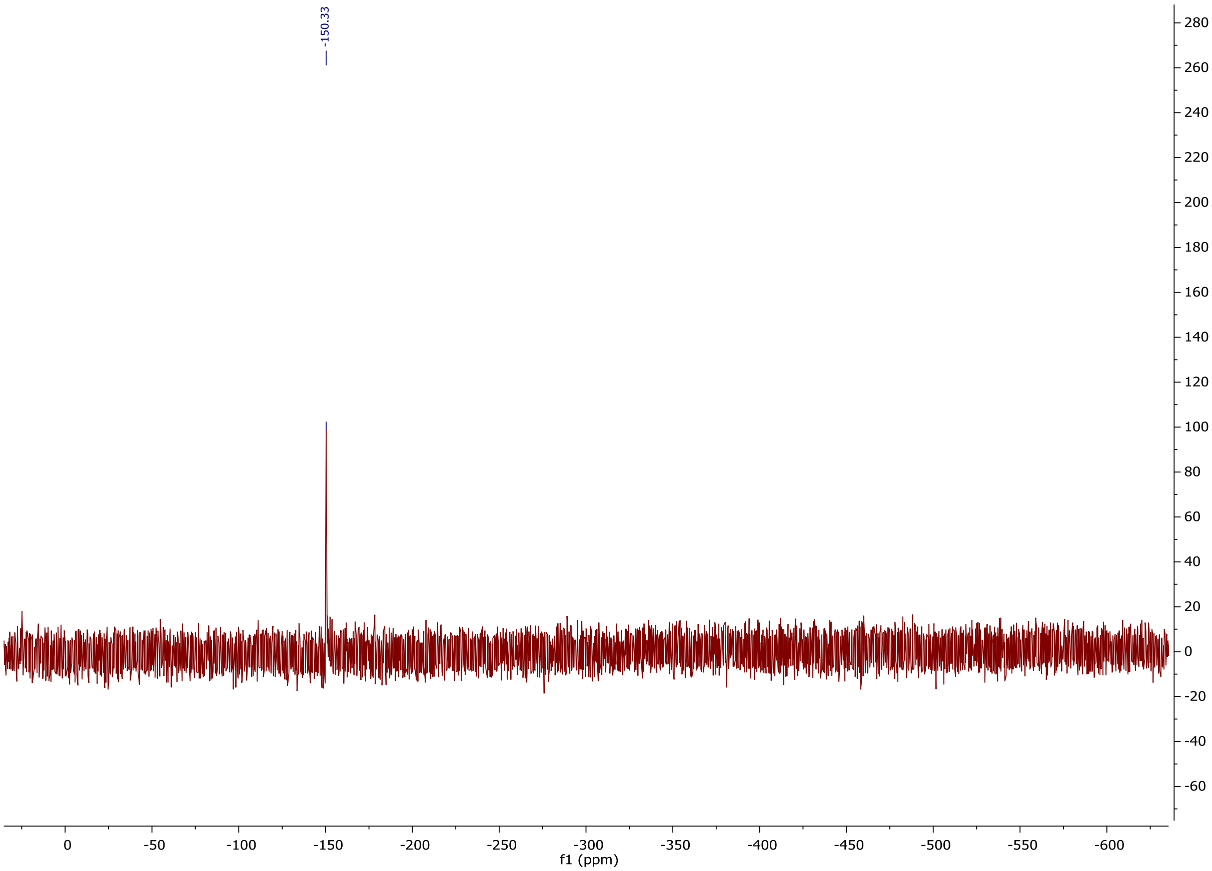
^{1}H NMR (400 MHz, benzene-d_6, 25 ºC, ppm): 0.63 (t, J_{HH} = 7.0 Hz, 6H, $NCH_2C\mathbf{H}_3$), 2.04 (s, 12H, *p*-Me), 2.18 (s, 12H, *o*-Me), 2.26 (s, 12H, *o*-Me), 2.34 (dq, J_{HH} = 13.5/6.7 Hz, 1H, $NC\mathbf{H}_2CH_3$), 2.86 (dq, J_{HH} = 13.5/6.7 Hz, 1H, $NC\mathbf{H}_2CH_3$), 4.10 (s, 1H, Sn**H**Sn, ^{119}Sn satellites $J_{H^{119}Sn}$ = 64 Hz), 6.85 (s, 4H, *m*-C_6H_2), 6.87 (s, 4H, *m*-C_6H_2), 6.92 (d, J_{HH} = 7.5 Hz, 4H, *m*-C_6H_3), 7.12 (t, J_{HH} = 7.5 Hz, 2H, *p*-C_6H_3).

Figure S11. $^{13}C\{^{1}H\}$ Spectrum of **4**. (126 MHz benzene-d_6, 25 ºC, ppm)



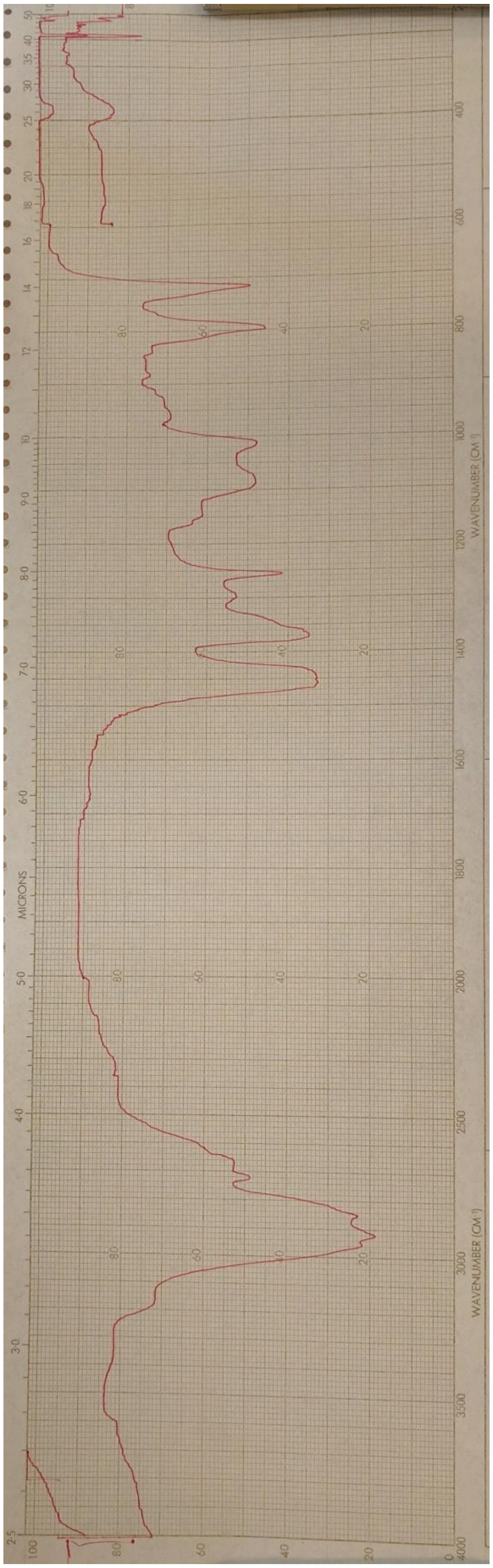
$^{13}C\{^{1}H\}$ NMR (126MHz, benzene-d_6, 25° C, ppm): 16.73 ($NCH_2C\mathbf{H}_3$), 21.28 (*p*-Me), 21.95 (*o*-Me), 22.10 (*o*-Me), 45.50 ($NC\mathbf{H}_2CH_3$), 128.58, 129.09, 129.59, 135.62, 136.35, 136.62, 148.99, 169.37.

Figure S12. ^{119}Sn NMR Spectrum of **4**. (186.36 MHz, benzene-d_6, 25 °C, ppm)



^{119}Sn{^{1}H} NMR (186.36 MHz, benzene-d_6, 25 °C): −150.33 ppm.

Figure S13. IR Spectrum of **4** as Nujol Mull



Initial Investigation into Catalytic Activity.

To test if $\{Ar^{Me_6}SnH\}_4$ could catalyze the dehydrocoupling of Et_2NH and HBPin, **1** (0.047 g, 0.0515 mmol) was first reacted with HBPin in an NMR scale experiment to synthesize $\{Ar^{Me_6}SnH\}_4$, which was confirmed by its ^1H NMR spectrum. An excess of Et_2NH and HBPin was then added, but no reaction was found at a rate greater than the background and the ^1H NMR resonances of $\{Ar^{Me_6}SnH\}_4$ were still readily visible. This same method was used in an initial testing of the catalytic activity of $\{Ar^{iPr_4}Sn(\mu\text{-}H)\}_2$ towards Et_2NH and HBPin, which also gave no advantage over the background reaction. The addition of HBPin to a mixture of aniline and $\{Ar^{iPr_4}Sn(\mu\text{-}H)\}_2$ resulted in the production of PhN(H)BPin at a rate greater than the background.

Catalytic NMR Experiments.

Standard solutions of **1** and **2** were made and used throughout all catalytic experiments. Pinacolborane and all amines were distilled prior to use. All substances were added directly to a Youngs tap NMR tube under an inert atmosphere, which were then inverted repeatedly to ensure a homogeneous solution. All liquids and the stock solutions of **1** and **2** were measured with Eppendorf pipettes. Aminoboranes presented in Table were identified by comparison to published data and their ^1H NMR spectra are shown below. Novel compounds were characterized by ^1H, ^{11}B and ^{13}C NMR and are also presented below.[3]

_s_BuNH$_2$:HBPin: ^1H NMR (400 MHz, benzene-d_6, 25 ºC, ppm): 0.85 (t, 3H, $CH_2C\mathbf{H}_3$), 0.96 (d, 3H, $CHC\mathbf{H}_3$), 1.14 (s, 12H, Pin)), 1.27 (m, 1H, C(**H**)HCH_3), 1.90 (s, 1H, NH), 3.23 (m, 1H, C(**H**)HCH_3). ^{11}B NMR (128.26 MHz, benzene-d_6, 25 ºC, ppm): 24.55 (sBuNH**B**Pin). $^{13}C\{^1H\}$ NMR (126MHz, benzene-d_6, 25° C, ppm): 10.56 ($CH_2\mathbf{C}H_3$), 23.97 ($CH\mathbf{C}H_3$), 24.38 (**Me**-Pin), 24.49 (**Me**-Pin), 32.76 ($\mathbf{C}H_2CH_3$), 47.90 (**C**H), 48.36 (**C**H), 81.32 (Pin).

4-fluoroaniline:HBPin: ^1H NMR (400 MHz, benzene-d_6, 25 ºC, ppm): 0.84 (s, 12H, Pin), 4.04 (s, 1H, NH), 6.53 (t, 2H, *o*-C_6H_4), 6.60 (t, 2H, *m*-C_6H_4). ^{11}B NMR (128.26 MHz, benzene-d_6, 25 ºC, ppm): 24.07 (4-fluoroaniline**B**Pin) $^{13}C\{^1H\}$ NMR (126MHz, benzene-d_6, 25° C, ppm): 24.52 (**Me**-Pin), 83.26 (Pin), 116.46, 120.38, 135.49, 146.12 (Ar).

4-chloroaniline:HBPin: ^1H NMR (400 MHz, benzene-d_6, 25 ºC, ppm): 1.05 (s, 12H, Pin), 4.27 (s, 1H, NH), 6.80 (d, 2H, *o*-C_6H_4), 7.05 (d, 2H, *m*-C_6H_4). ^{11}B NMR (128.26 MHz, benzene-d_6, 25 ºC, ppm): 24.05 (4-chloroaniline**B**Pin) $^{13}C\{^1H\}$ NMR (126MHz, benzene-d_6, 25° C, ppm): 24.66 (**Me**-Pin), 82.89 (Pin), 116.11, 119.28, 129.17, 129.30 (Ar).

4-bromoaniline:HBPin: ^1H NMR (400 MHz, benzene-d_6, 25 ºC, ppm): 1.05 (s, 12H, Pin), 4.26 (s, 1H, NH), 6.75 (d, 2H, *o*-C_6H_4), 7.19 (d, 2H, *m*-C_6H_4). ^{11}B NMR (128.26 MHz, benzene-d_6, 25 ºC, ppm): 24.03 (4-bromoaniline**B**Pin) $^{13}C\{^1H\}$ NMR (126MHz, benzene-d_6, 25° C, ppm): 24.66 (**Me**-Pin), 82.91 (Pin), 116.38, 119.29, 129.16, 128.32 (Ar).

4-ethylaniline:HBPin: ^1H NMR (400 MHz, benzene-d_6, 25 ºC, ppm): 1.04 (t, 3H, $CH_2C\mathbf{H}_3$), 1.10 (s, 12H, Pin) 2.42 (q, 2H, $C\mathbf{H}_2CH_3$), 6.98 (d, 2H, *o*-C_6H_4), 7.07 (d, 2H, *m*-C_6H_4). ^{11}B NMR (128.26 MHz, benzene-d_6, 25 ºC, ppm): 24.22 (4-ethylaniline**B**Pin) $^{13}C\{^1H\}$ NMR (126MHz, benzene-d_6, 25° C, ppm): 15.88 ($CH_2\mathbf{C}H_3$), 24.35 (**Me**-Pin), 28.13 ($\mathbf{C}H_2CH_3$), 82.24 (Pin), 114.97, 117.80, 128.24, 128.42 (Ar).

3,5-dichloroaniline:HBPin: ^{1}H NMR (400 MHz, benzene-d_6, 25 ºC, ppm): 0.99 (s, 12H, Pin), 4.26 (s, 1H, NH), 6.84 (s, 1H, *p*-C_6H_3), 6.85 (s, 2H, *o*-C_6H_3). ^{11}B NMR (128.26 MHz, benzene-d_6, 25 ºC, ppm): 23.88 (3,5-dichloroaniline**B**Pin) $^{13}C\{^{1}H\}$ NMR (126MHz, benzene-d_6, 25° C, ppm): 24.52 (**Me**-Pin), 83.26 (Pin), 116.46, 120.38, 135.49, 146.12 (Ar).

NH_2BPin: ^{1}H NMR (400 MHz, benzene-d_6, 25 ºC, ppm): 0.13 (NH_3), 1.07 (s, 12H, H_2NB**Pin**), 2.60 (s, 2H, **H_2**NBPin). ^{11}B NMR (128.26 MHz, benzene-d_6, 25 ºC, ppm) 25.05 (NH_2**B**Pin) $^{13}C\{^{1}H\}$ NMR (126MHz, benzene-d_6, 25° C, ppm): 24.58 (**Me**-Pin), 81.66 (Pin).

PinNH_2:HBPin. Excess HBPin: ^{1}H NMR (400 MHz, benzene-d_6, 25 ºC, ppm): 0.99 (HBPin), 1.05 (HN{B**Pin**}$_2$), 3.33 (**H**N{BPin}$_2$). ^{11}B NMR (128.26 MHz, benzene-d_6, 25 ºC, ppm) 25.60 (NH_2**B**Pin) $^{13}C\{^{1}H\}$ NMR (126MHz, benzene-d_6, 25° C, ppm): 24.76, 24.66 (**Me**-Pin), 82.93, 82.47 (Pin).

Figure S14. ^{1}H NMR spectrum from Table 1, Entry 1a: *n*BuNH$_2$:HBPin. 10% excess HBPin (400 MHz, benzene-d_6, 25 ºC, ppm)

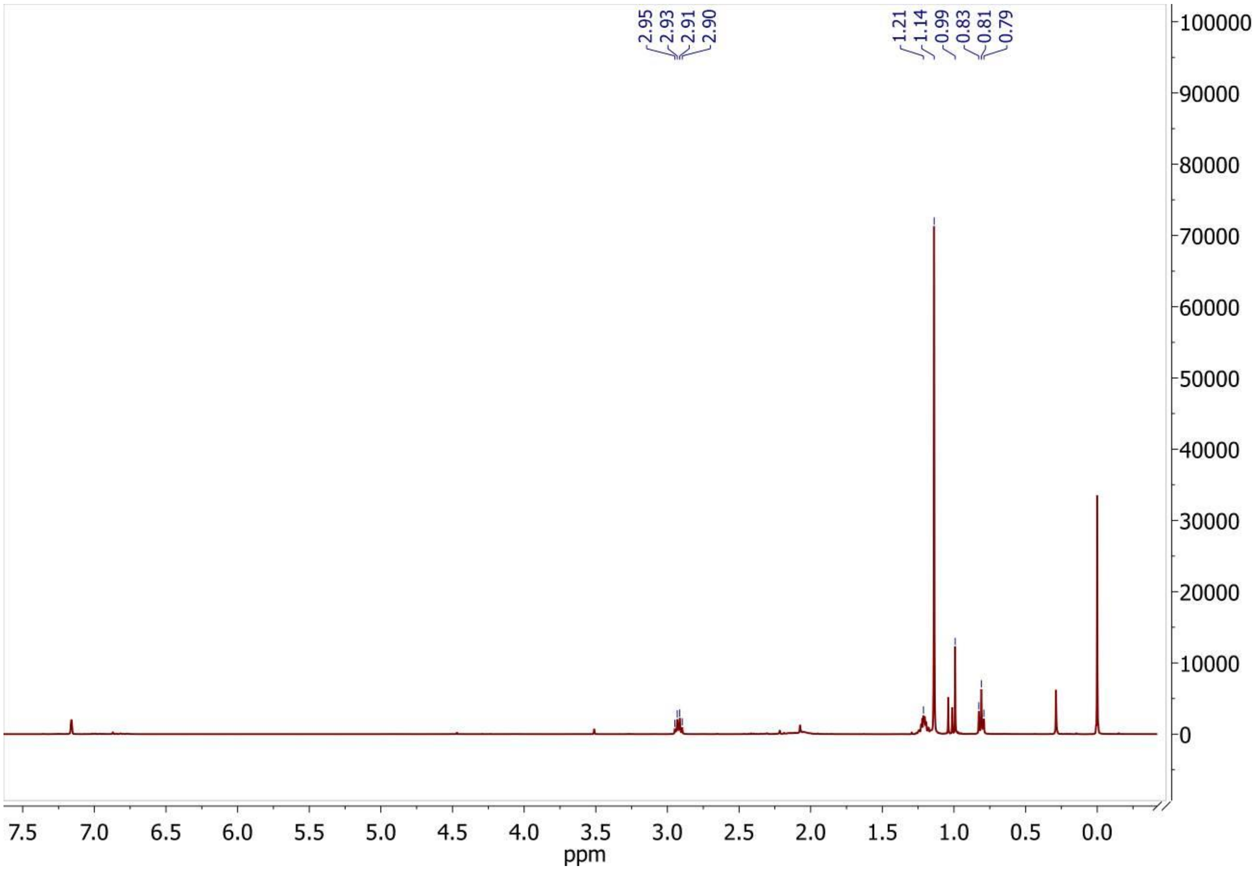
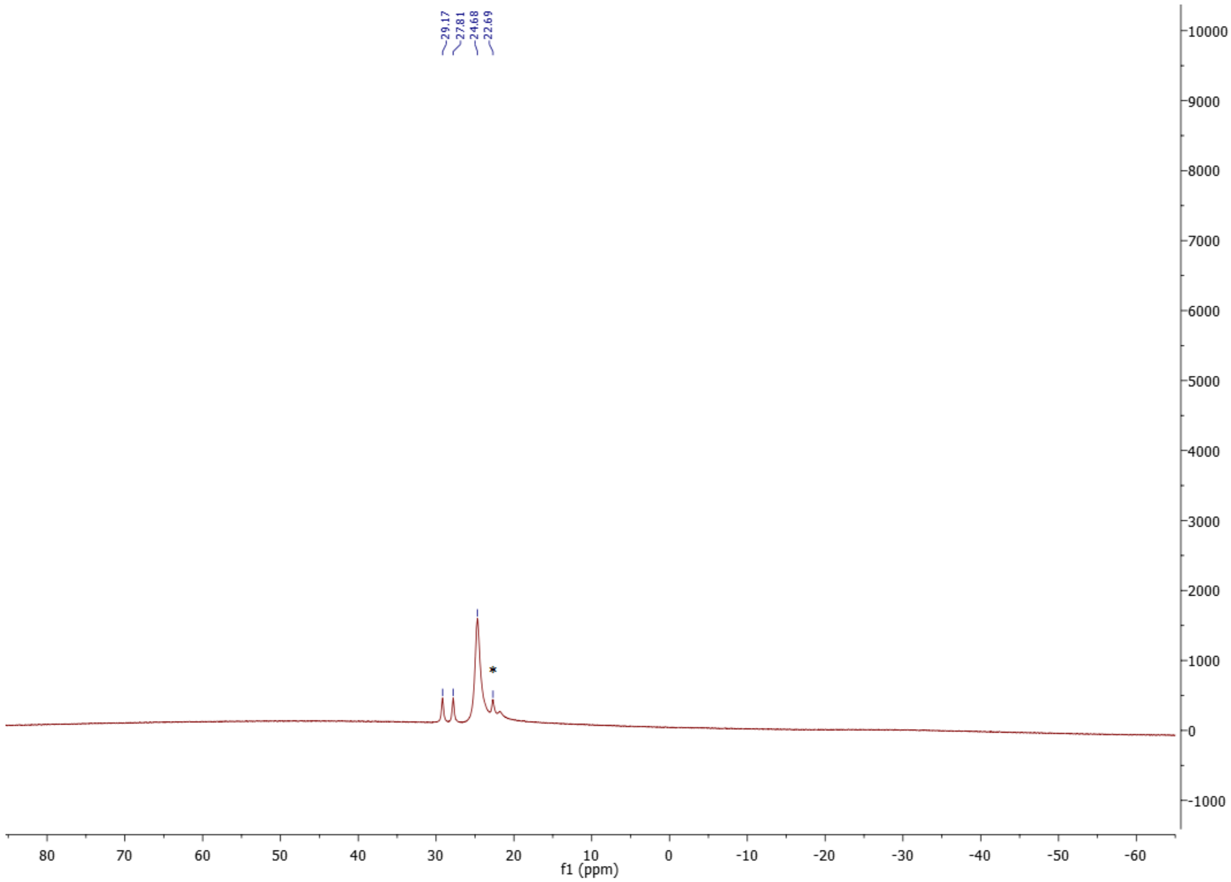


Figure S15. ^{11}B NMR spectrum from Table 1, Entry 1a: *n*$BuNH_2$:HBPin. 10% excess HBPin. (128.26 MHz, benzene-d_6, 25 ºC, ppm)



* PinBOBPin

Figure S16 ^{1}H NMR spectrum from Table 1, Entry 2a: *s*BuNH$_2$:HBPin. (400 MHz, benzene-*d*$_6$, 25 ºC, ppm)

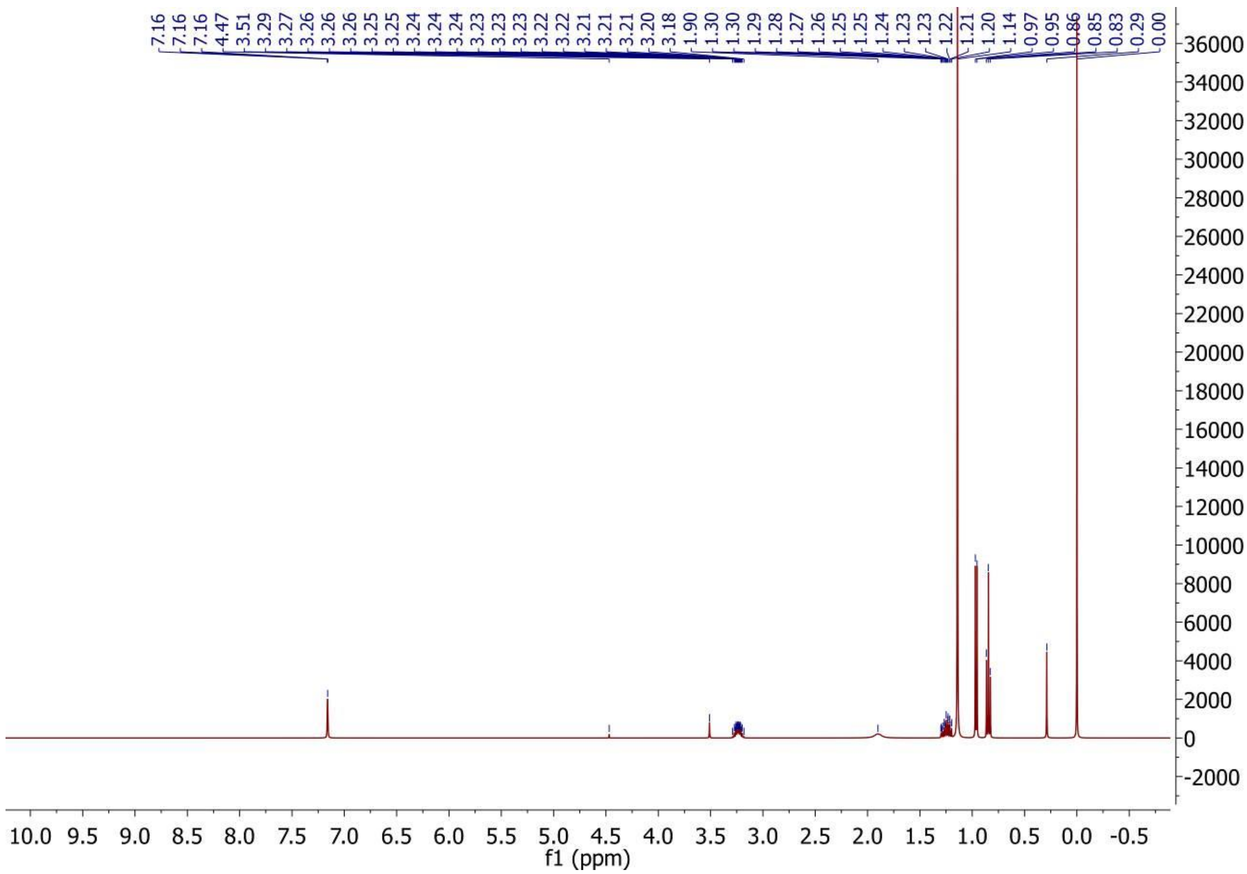
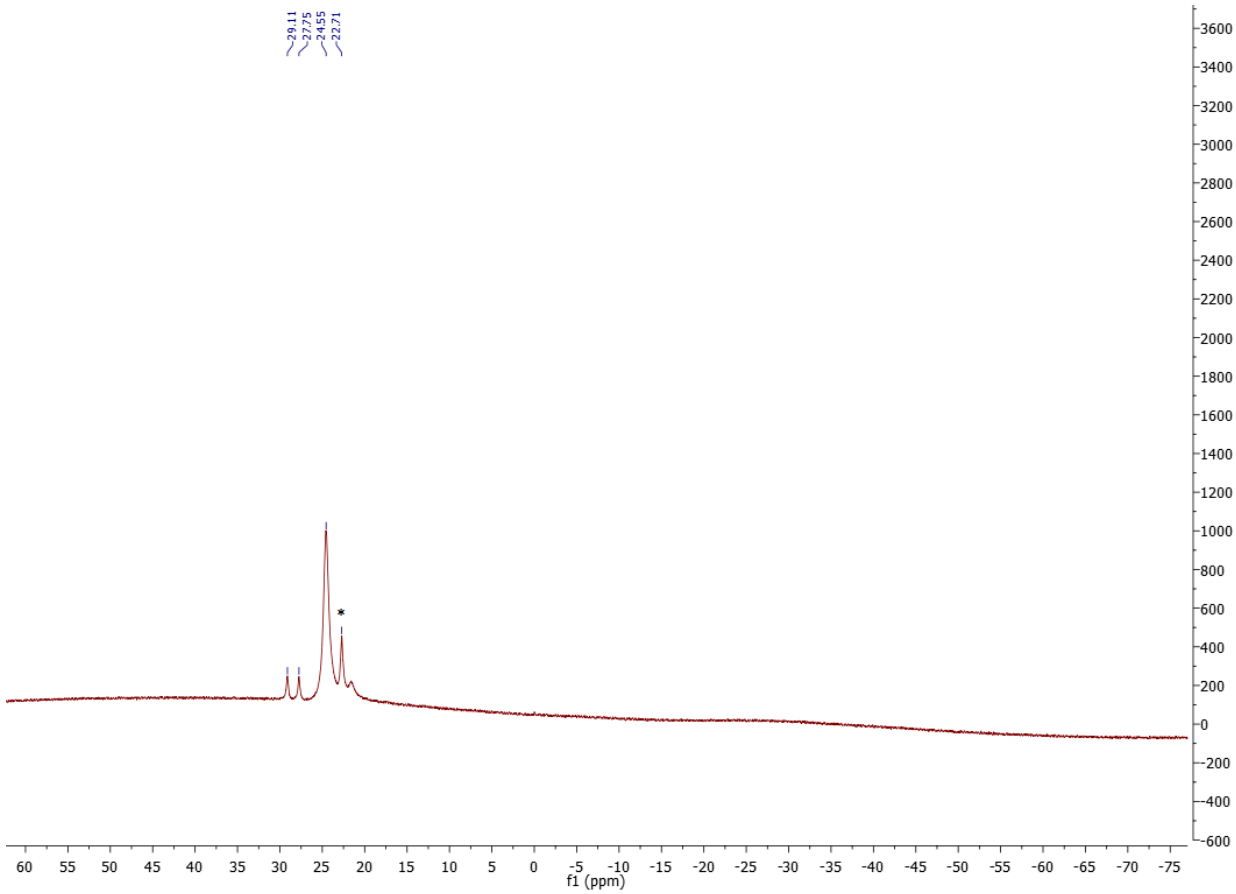


Figure S17. ^{11}B NMR spectrum from Table 1, Entry 2a: *s*BuNH$_2$:HBPin. (128.26 MHz, benzene-d_6, 25 ºC, ppm)



* PinBOBPin

Figure S18. $^{13}C\{^{1}H\}$ NMR spectrum from Table 1, Entry 2a: *s*$BuNH_2$:HBPin. (126MHz, benzene-d_6, 25° C, ppm)

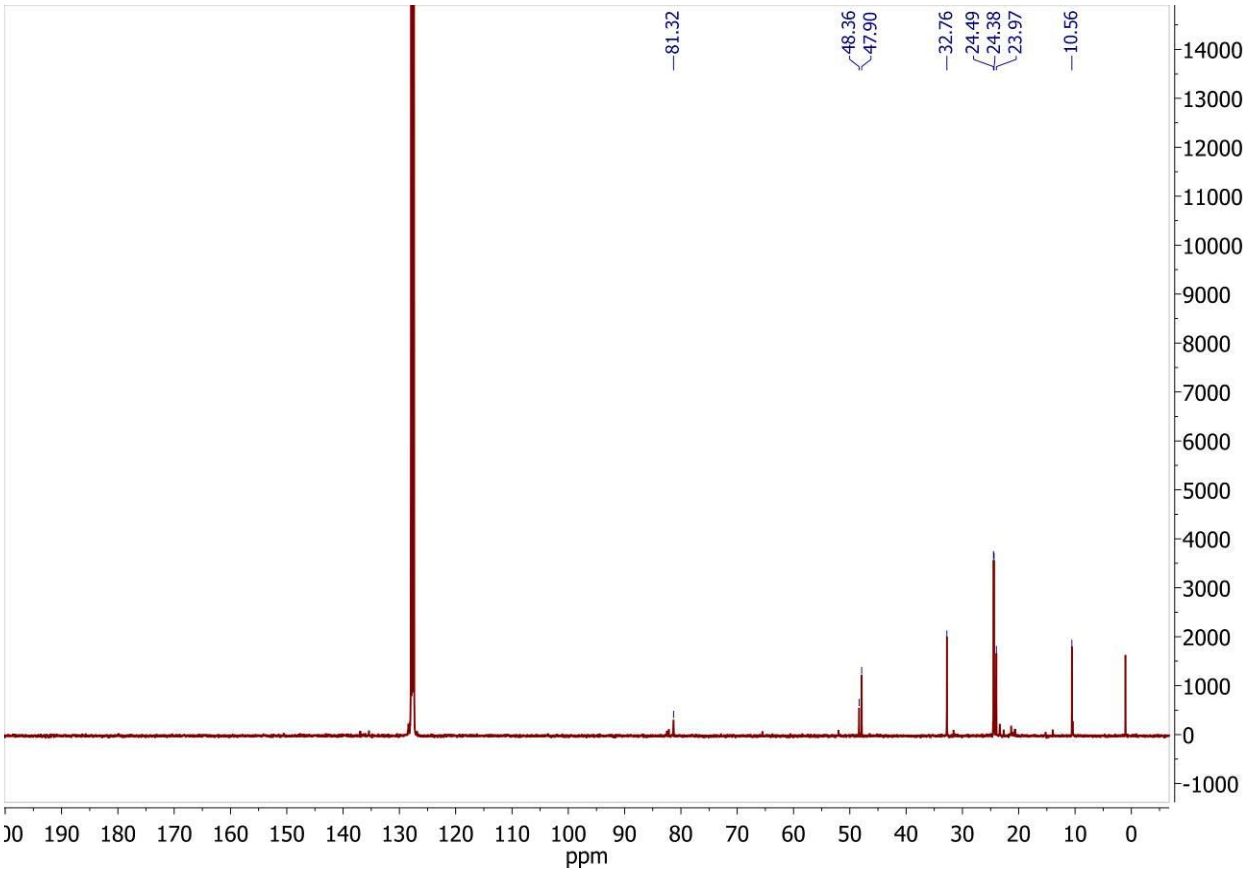


Figure S19.[1]H NMR spectrum from Table 1, Entry 3a: $PhNH_2$:HBPin. (400MHz, benzene-d_6, 25° C, ppm)

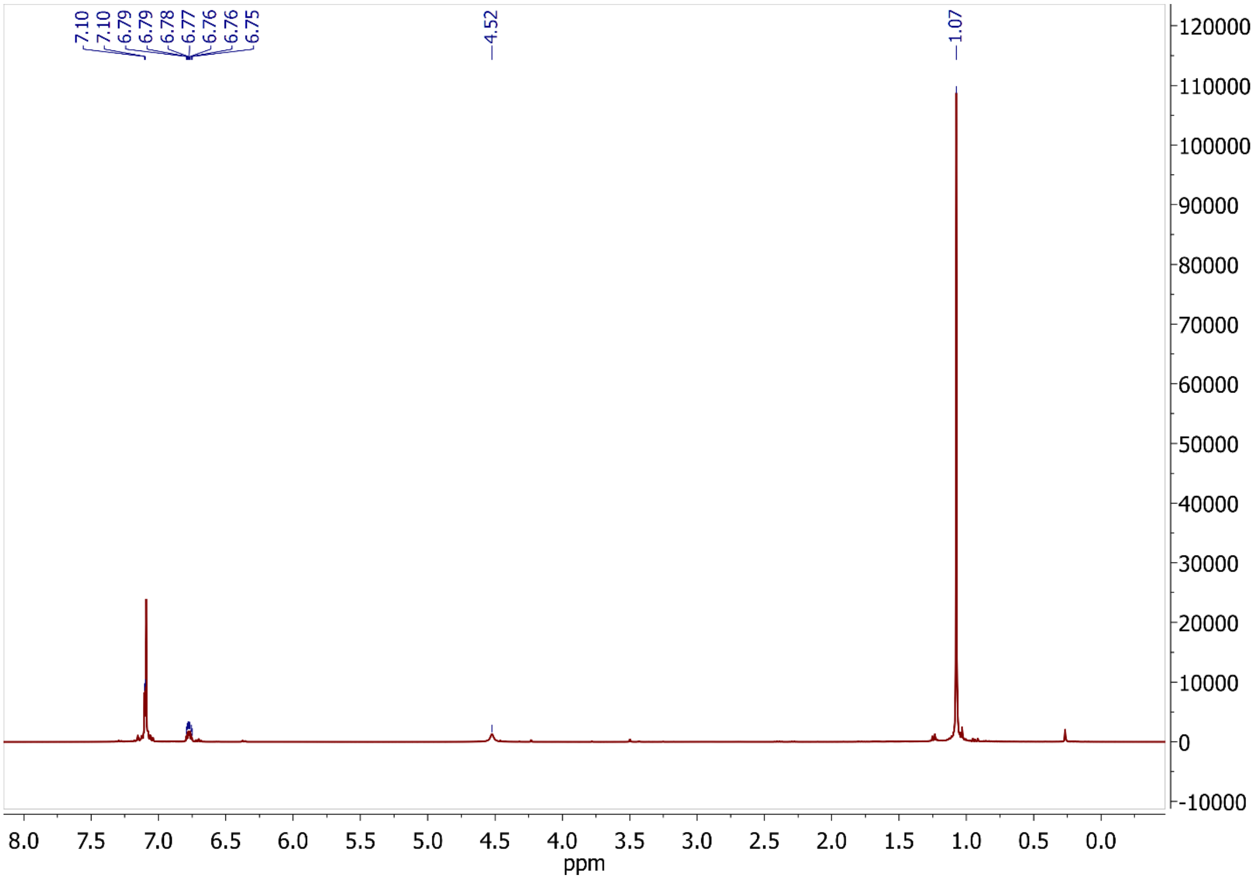
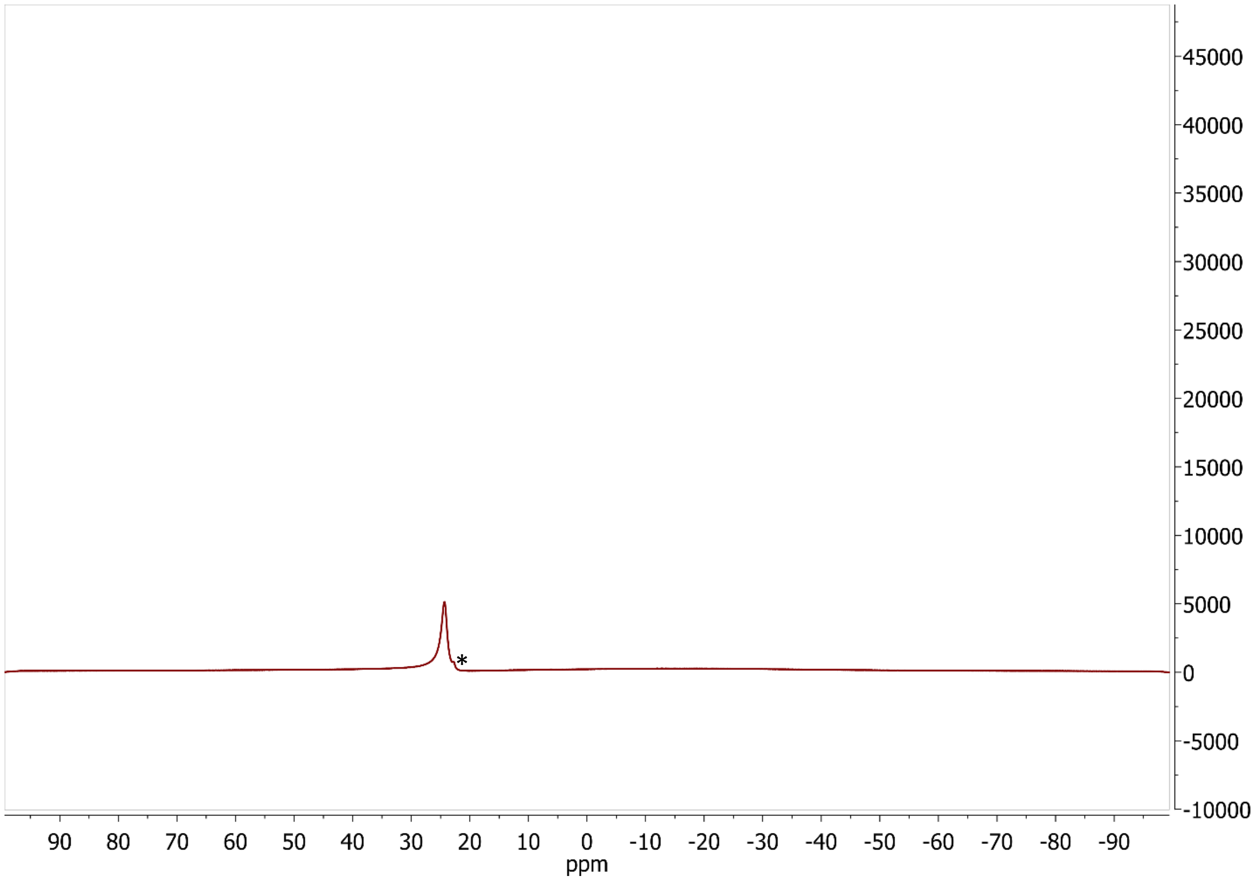


Figure S20.[11]B NMR spectrum from Table 1a, Entry 3: $PhNH_2$:HBPin. (128.26MHz, benzene-d_6, 25° C, ppm)



* PinBOBPin

Figure S21.[1]H NMR spectrum from Table 1b, Entry 4: 4-fluoroaniline:HBPin. (400MHz, benzene-d_6, 25° C, ppm)

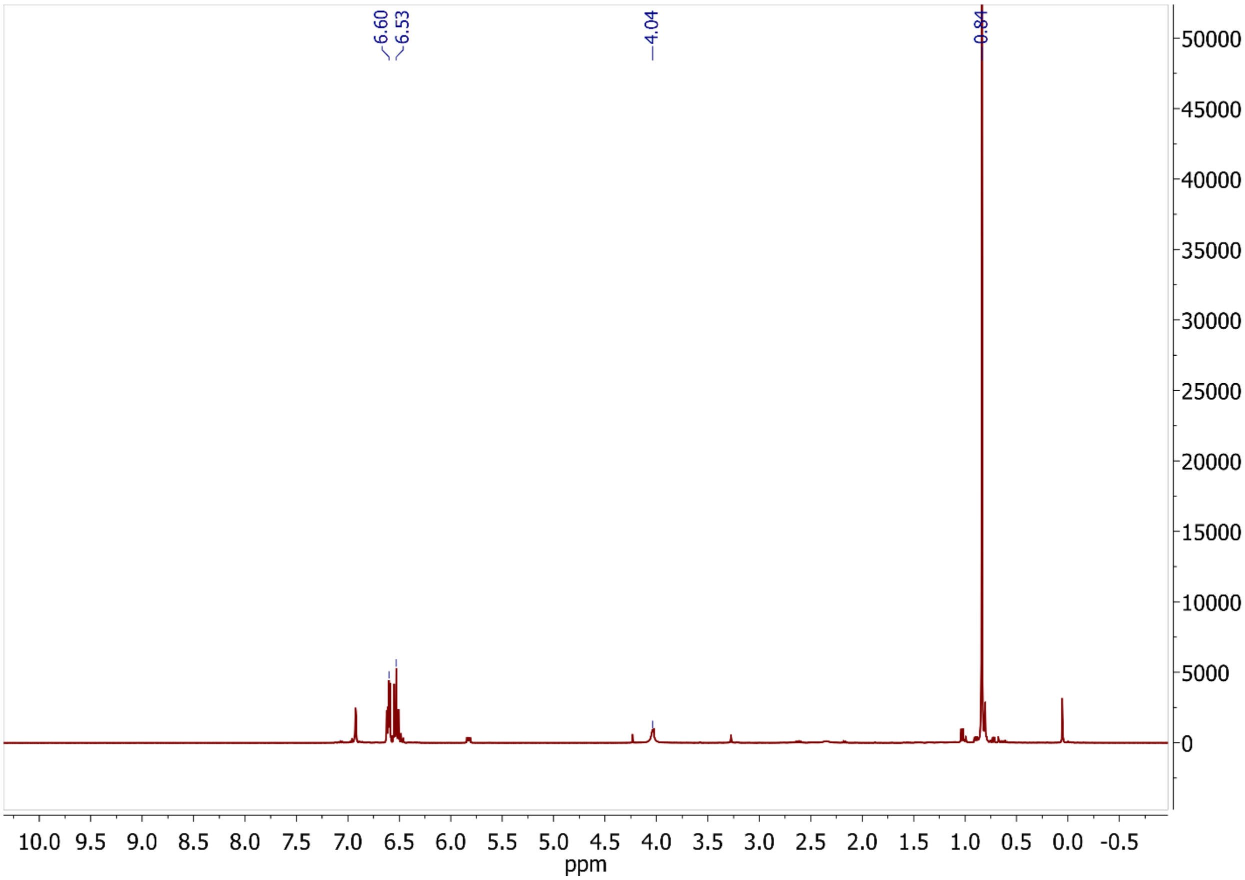
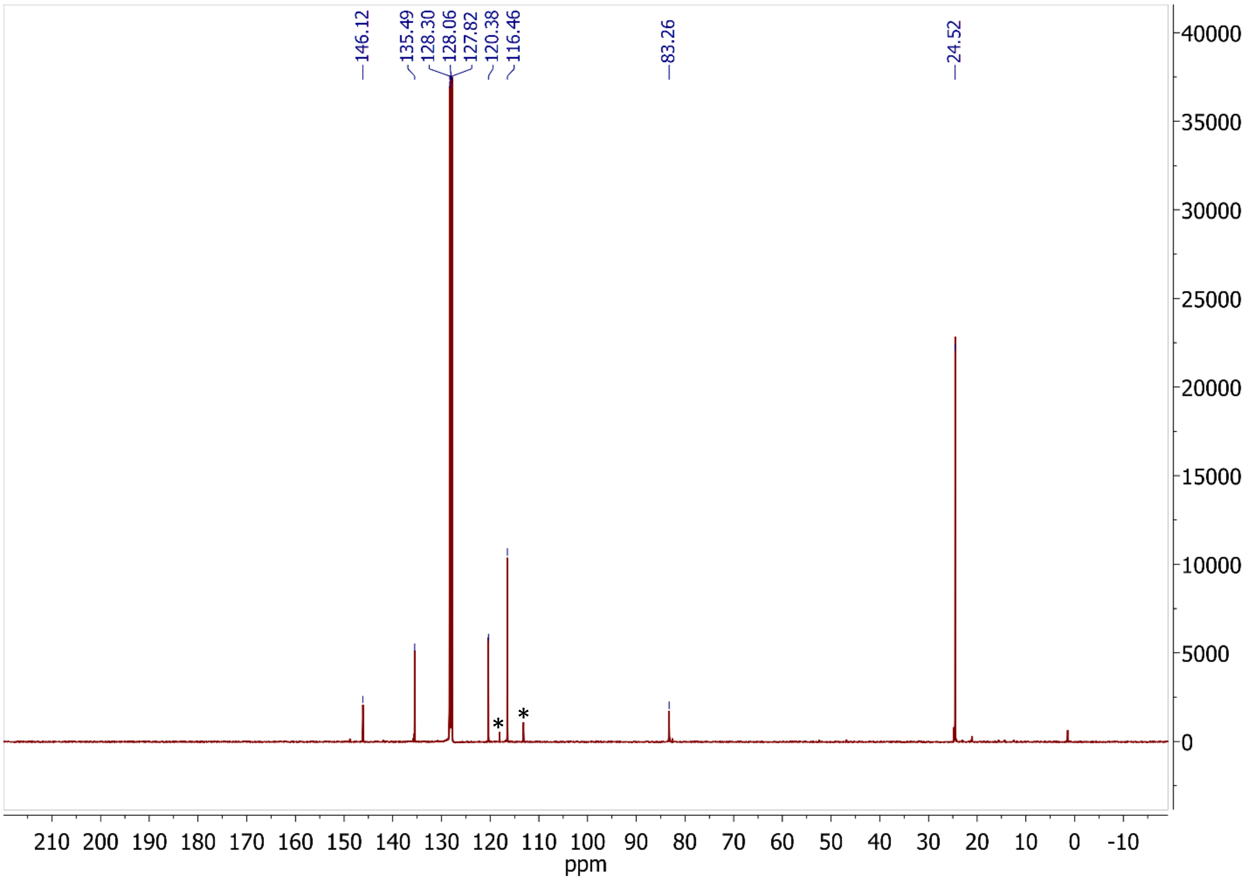


Figure S22. $^{13}C\{^{1}H\}$ NMR spectrum from Table 1b, Entry 4: 4-fluoroaniline:HBPin. (126MHz, benzene-*d*$_6$, 25° C, ppm)



* slight excess of 4-fluoroaniline

Figure S23. ^{11}B NMR spectrum from Table 1b, Entry 4: 4-fluoroaniline:HBPin. (128.26MHz, benzene-d_6, 25° C, ppm)

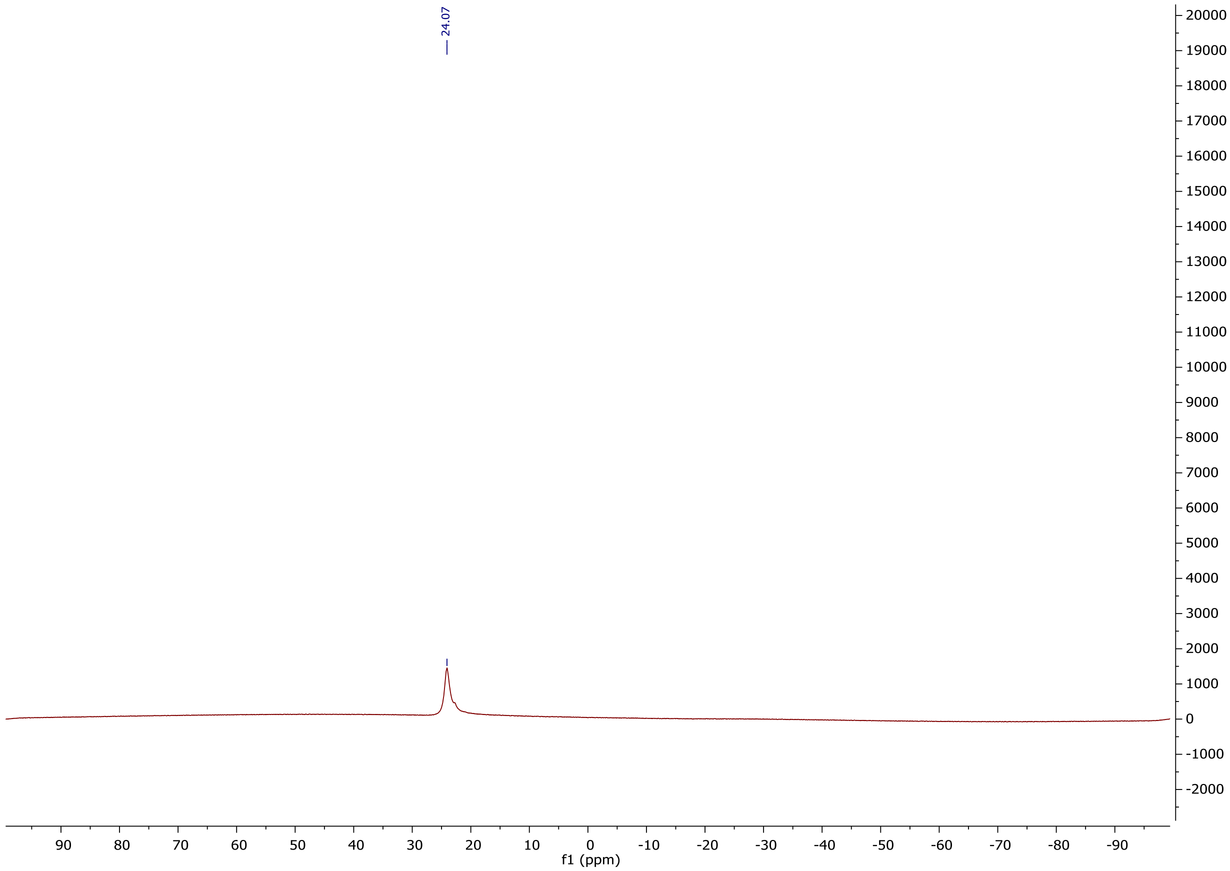


Figure S24. ^{1}H NMR spectrum from Table 1b, Entry 5: 4-chloroaniline:HBPin. (400MHz, benzene-d_6, 25° C, ppm)

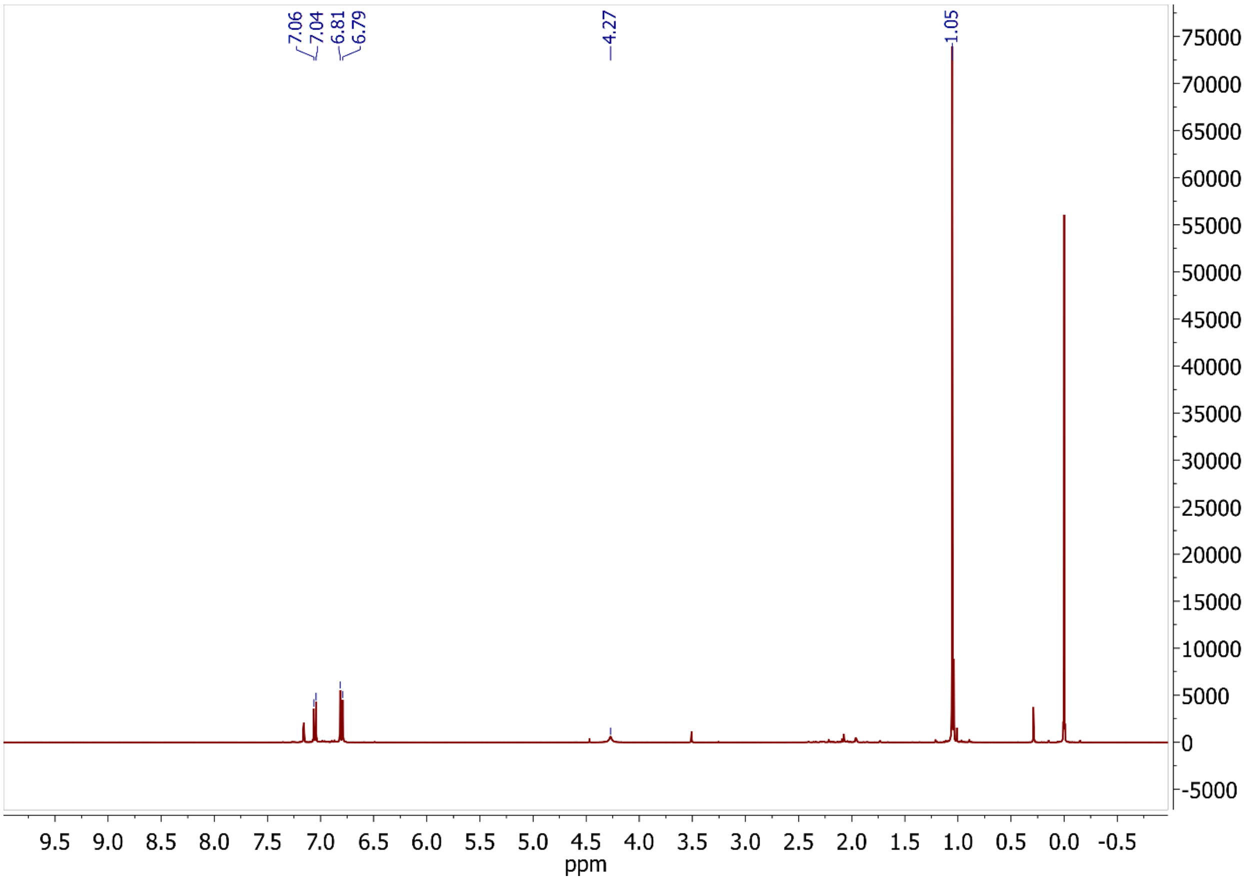


Figure S25. $^{13}C\{^{1}H\}$ NMR spectrum from Table 1, Entry 5b: 4-chloroaniline:HBPin. (126MHz, benzene-d_6, 25° C, ppm)

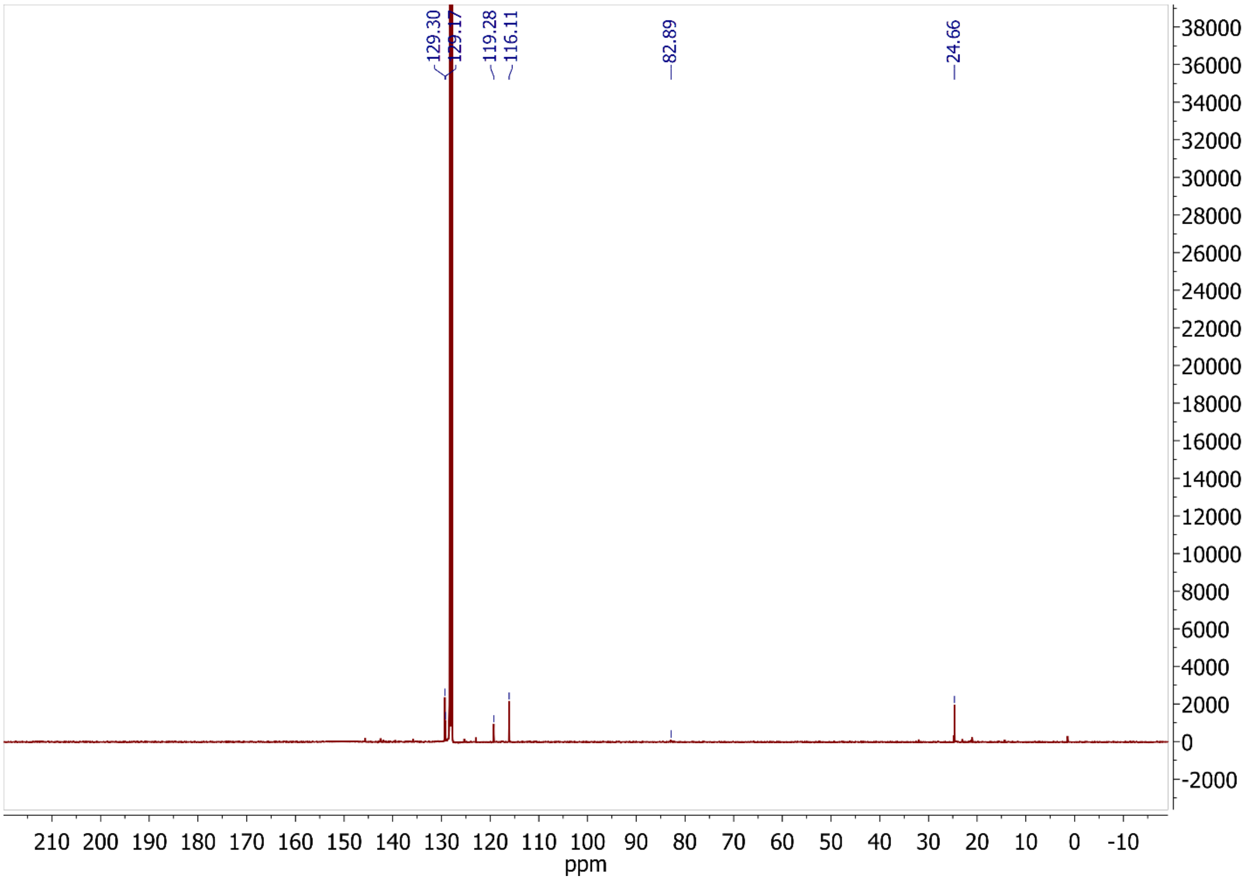
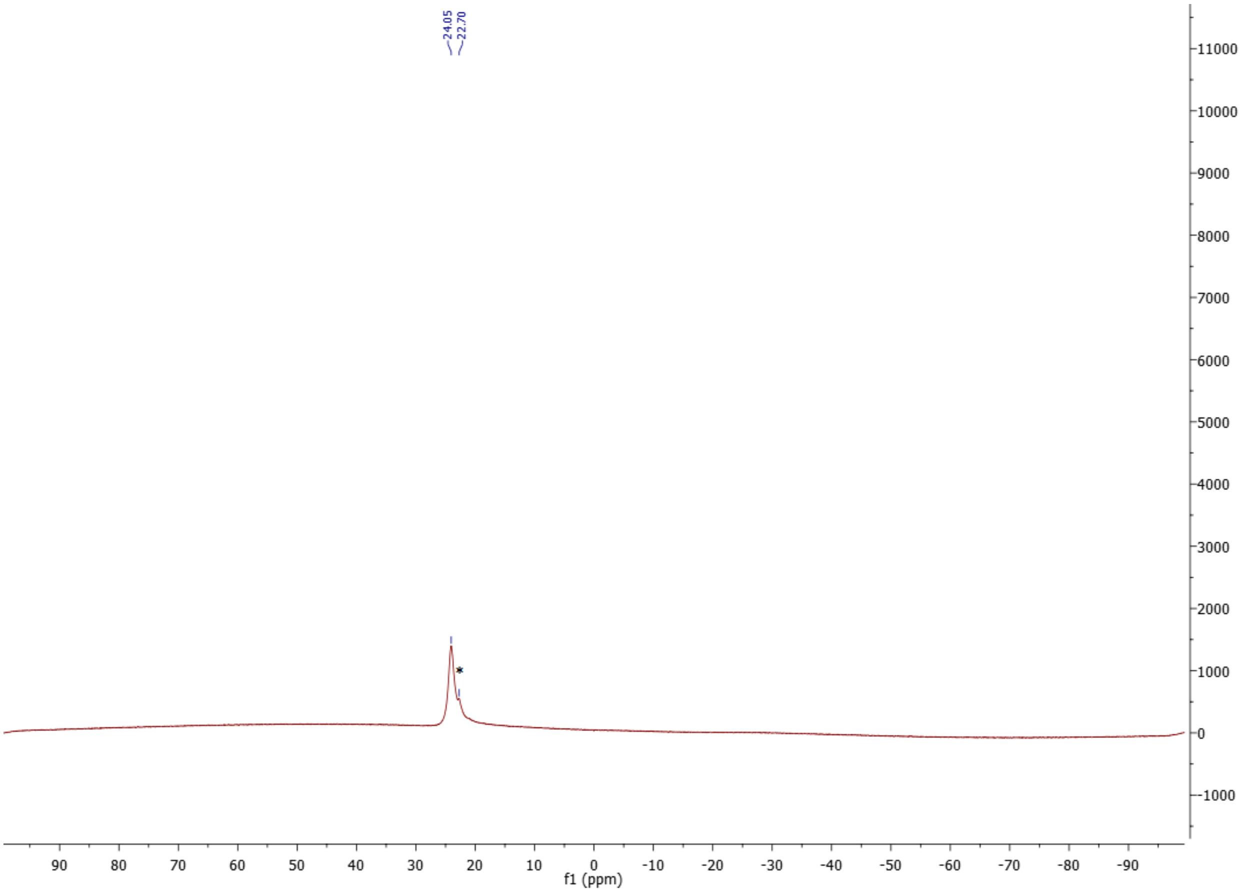


Figure S26. ^{11}B NMR spectrum from Table 1, Entry 5b: 4-chloroaniline:HBPin. (126MHz, benzene-d_6, 25° C, ppm)



* PinBOBPin

Figure S27. ^{1}H NMR spectrum from Table 1, Entry 6b: 4-bromoaniline:HBPin. (400MHz, benzene-d_6, 25° C, ppm)

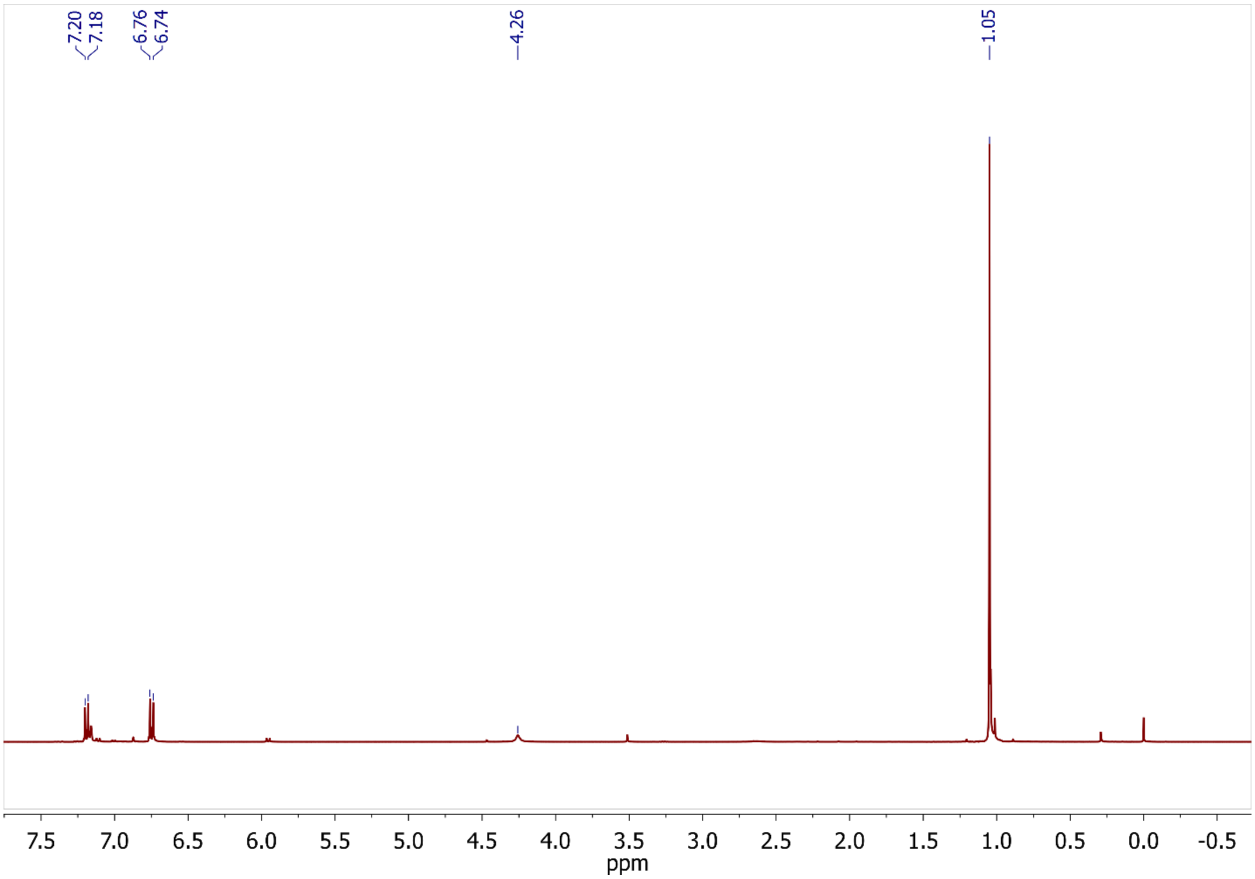
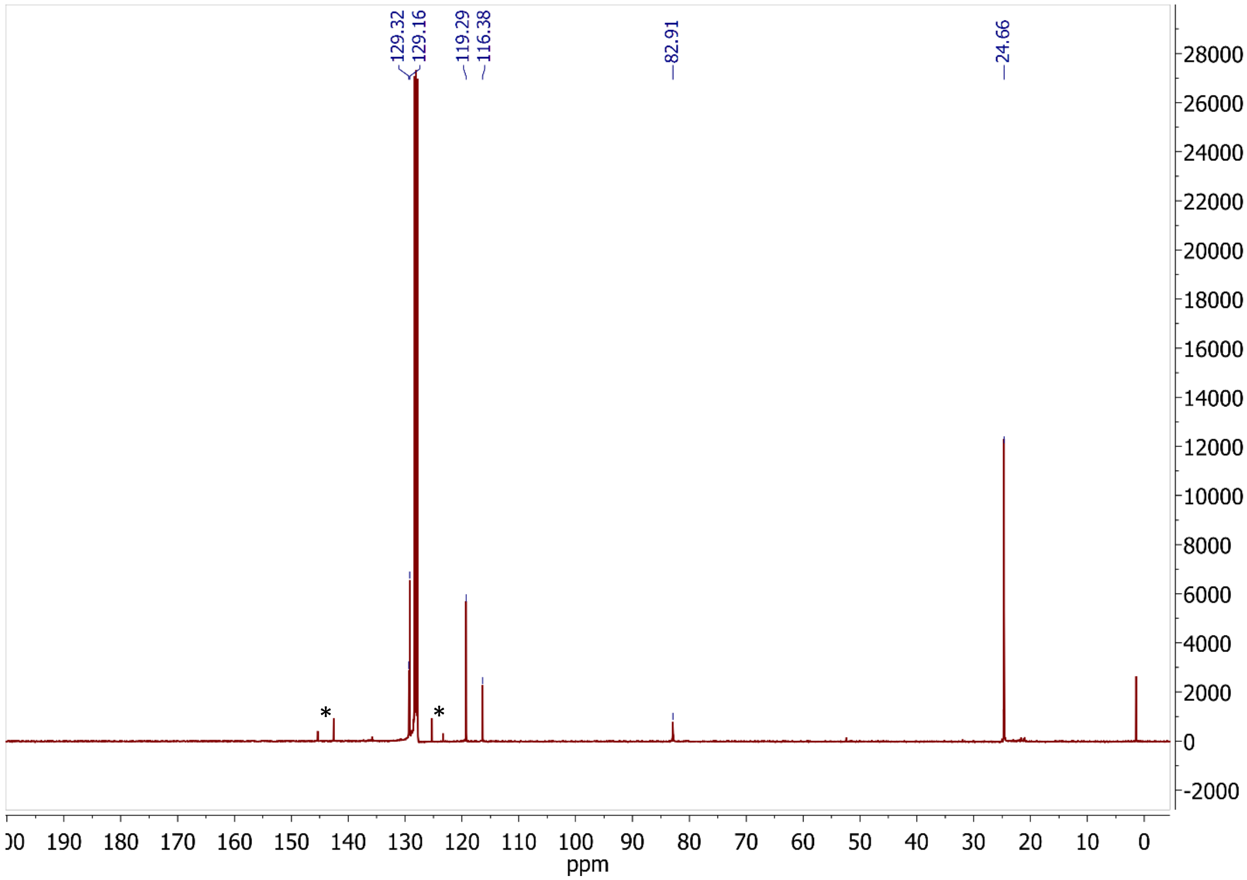
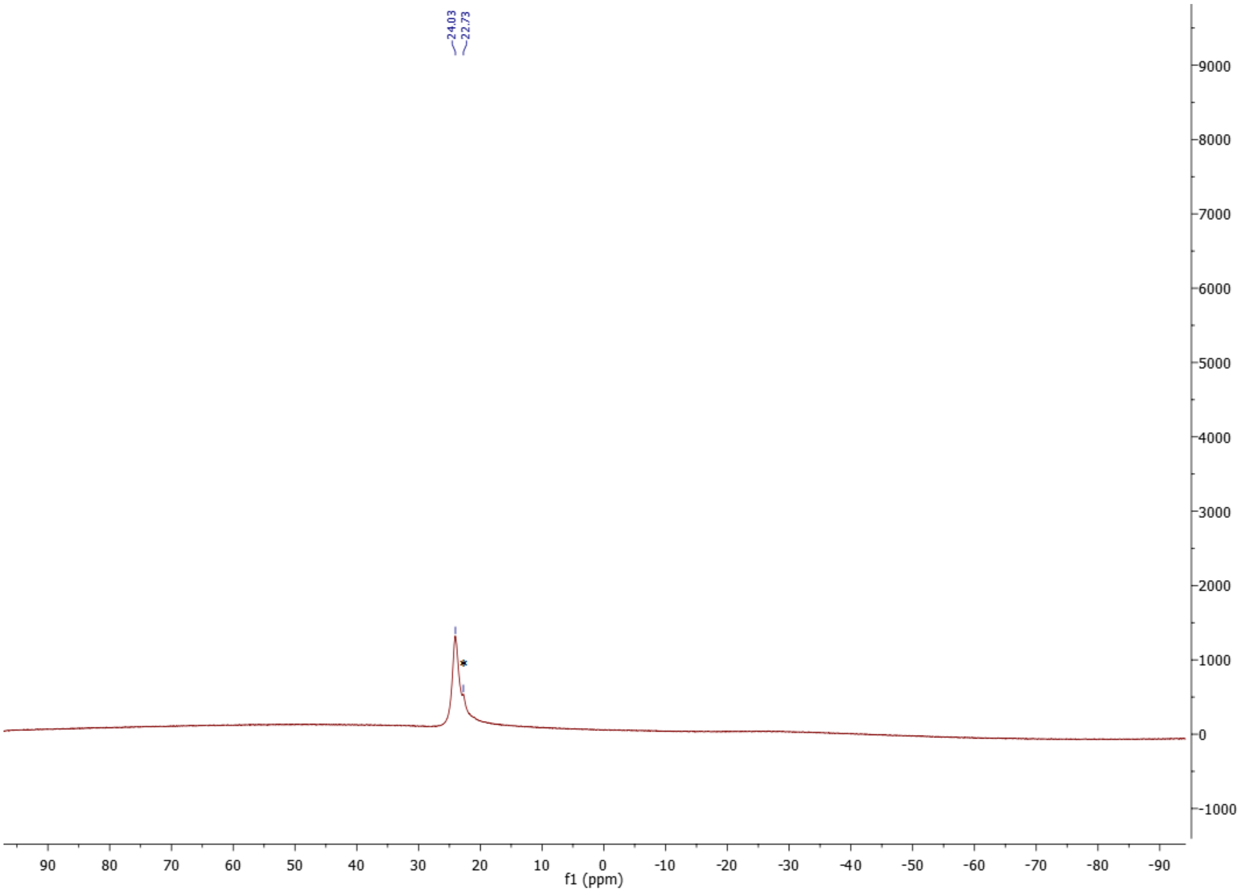


Figure S28. $^{13}C\{^1H\}$ NMR spectrum Table 1, Entry 6b: 4-bromoaniline:HBPin. (126MHz, benzene-d_6, 25° C, ppm)



* Excess 4-bromoaniline

Figure S29. ^{11}B NMR spectrum from Table 1, Entry 6b: 4-bromoaniline:HBPin. (128.26MHz, benzene-*d*$_6$, 25 ° C, ppm)



* PinBOBPin

Figure S30. ^{1}H NMR spectrum from Table 1, Entry 7b: 4-ethylaniline:HBPin. (400MHz, benzene-d_6, 25° C, ppm)

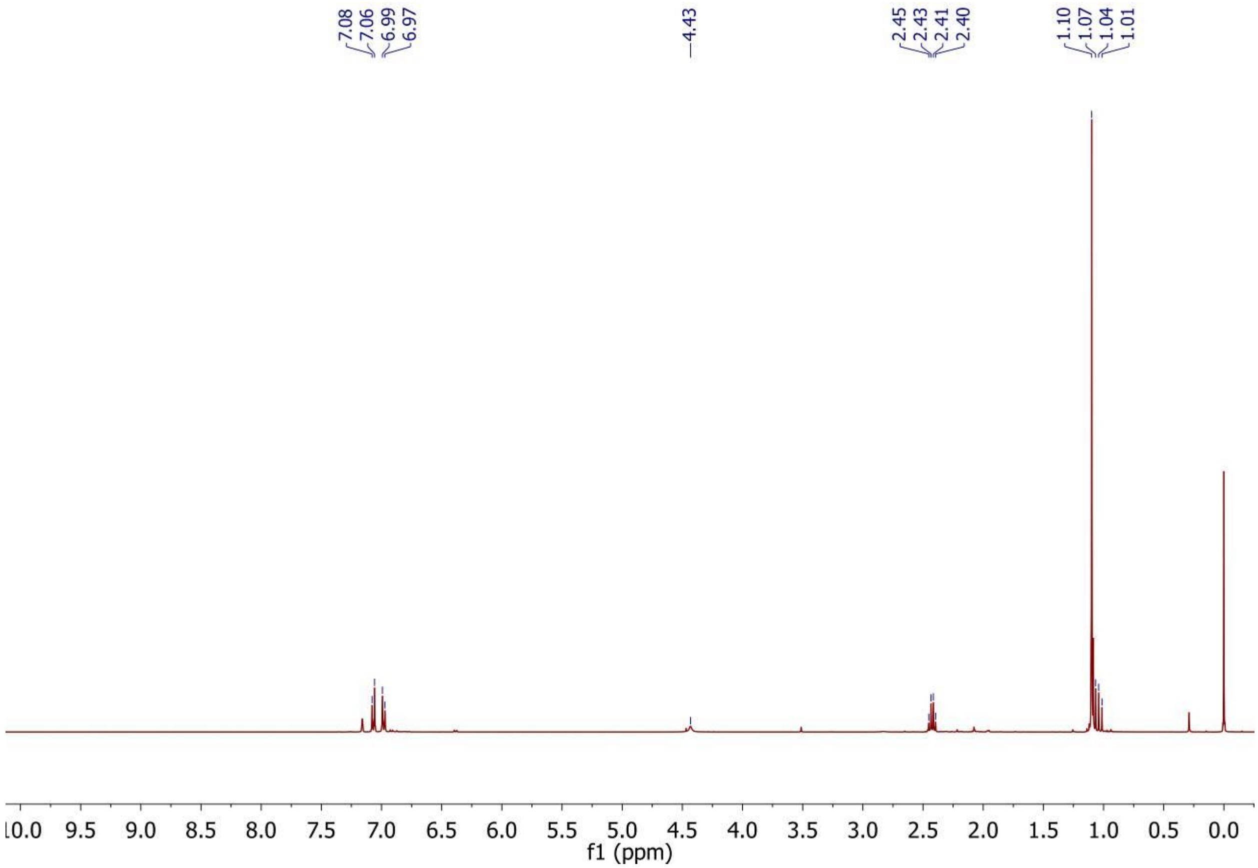
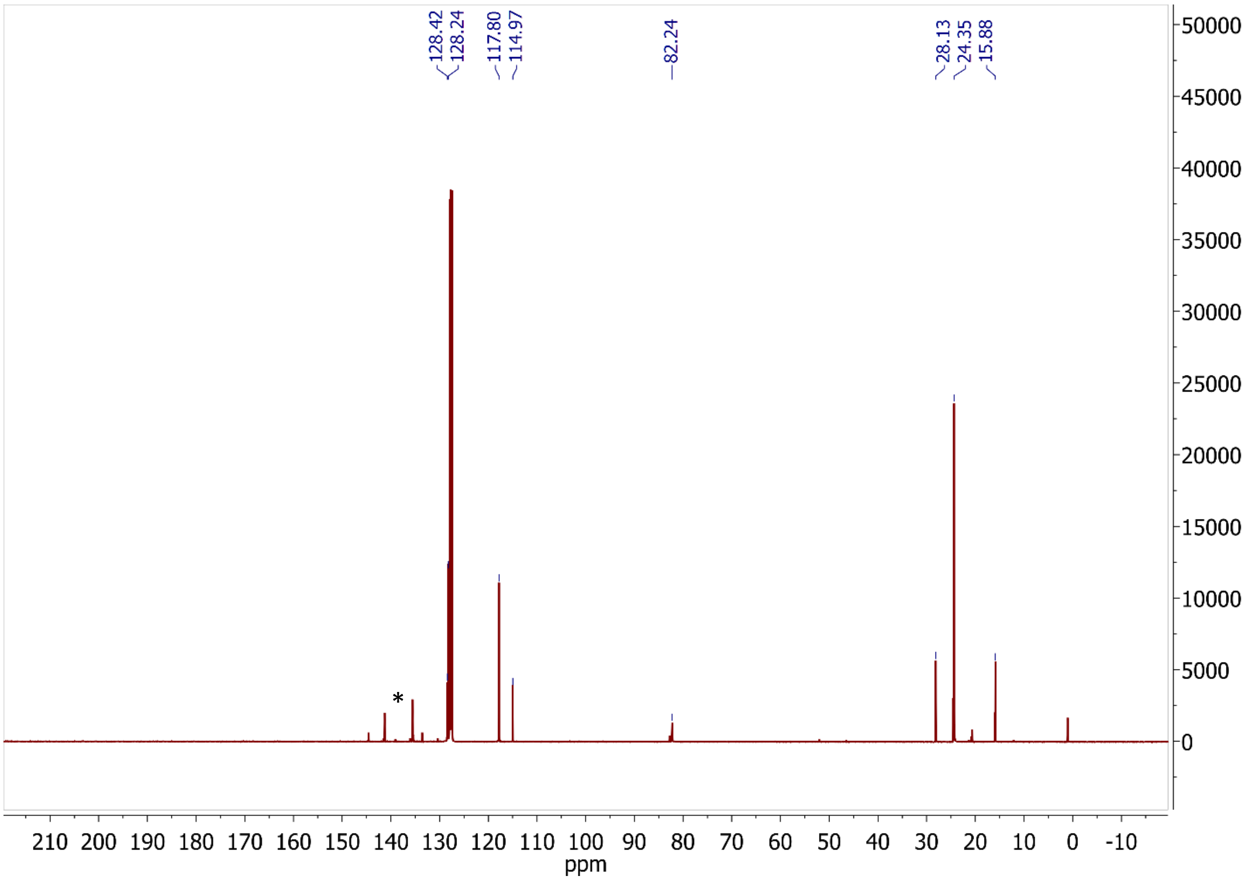
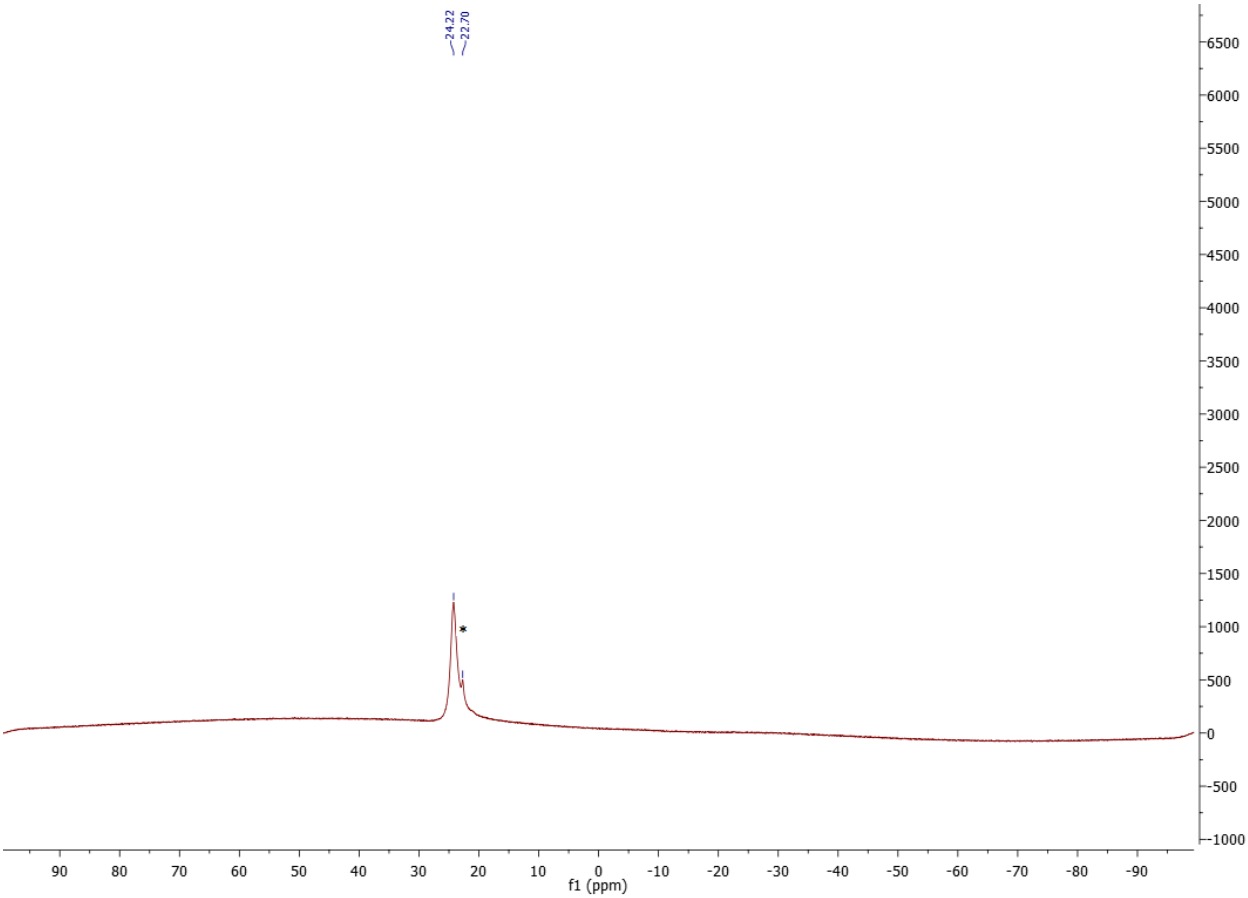


Figure S31. $^{13}C\{^1H\}$ NMR spectrum from Table 1, Entry 7b: 4-ethylaniline:HBPin. (126MHz, benzene-d_6, 25° C, ppm)



* Excess 4-ethylaniline

Figure S32. ^{11}B NMR spectrum from Table 1, Entry 7b: 4-ethylaniline:HBPin. (128.26MHz, benzene-d_6, 25° C, ppm)



* PinBOBPin

Figure S33. ^{1}H NMR spectrum from Table 1, Entry 8a: 2,6-diisopropylaniline:HBPin. (400MHz, benzene-d_6, 25° C, ppm)

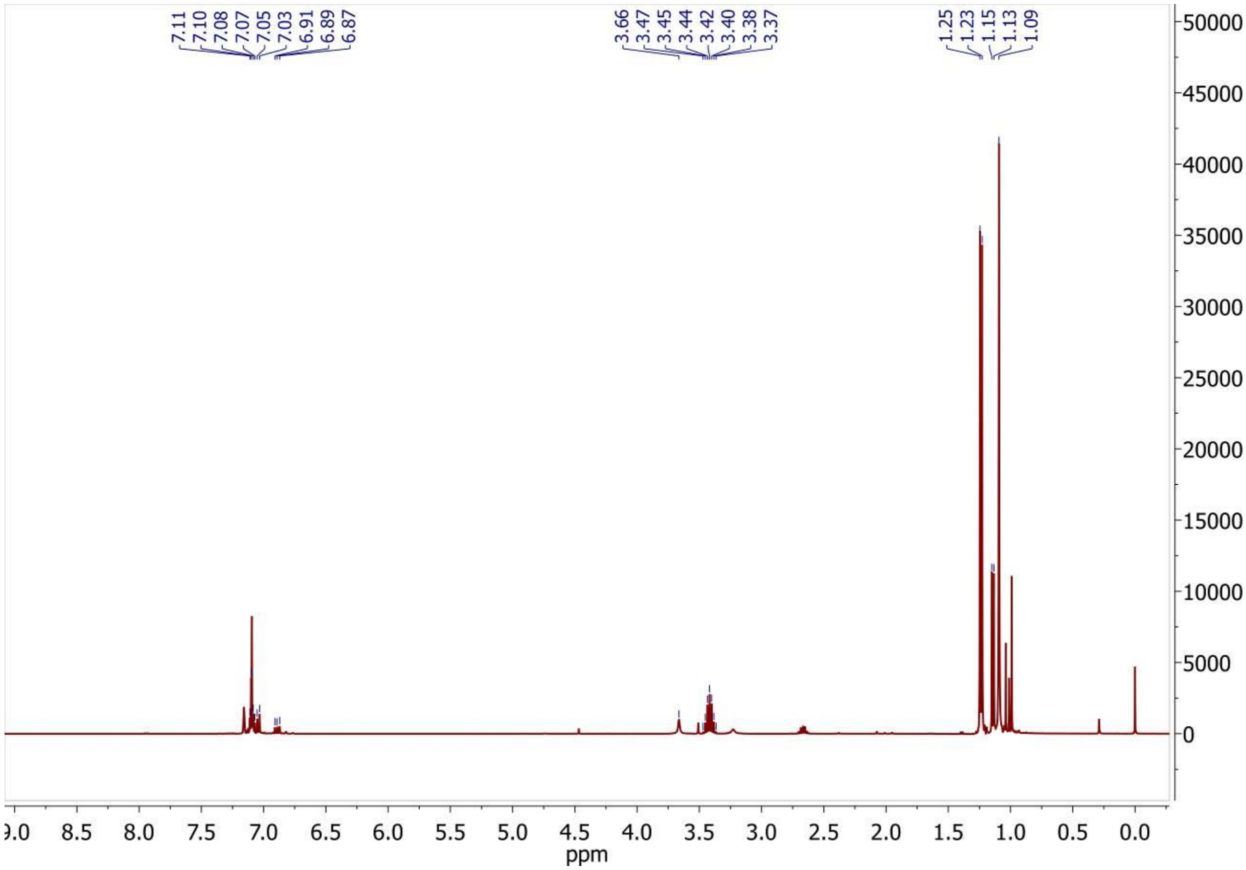
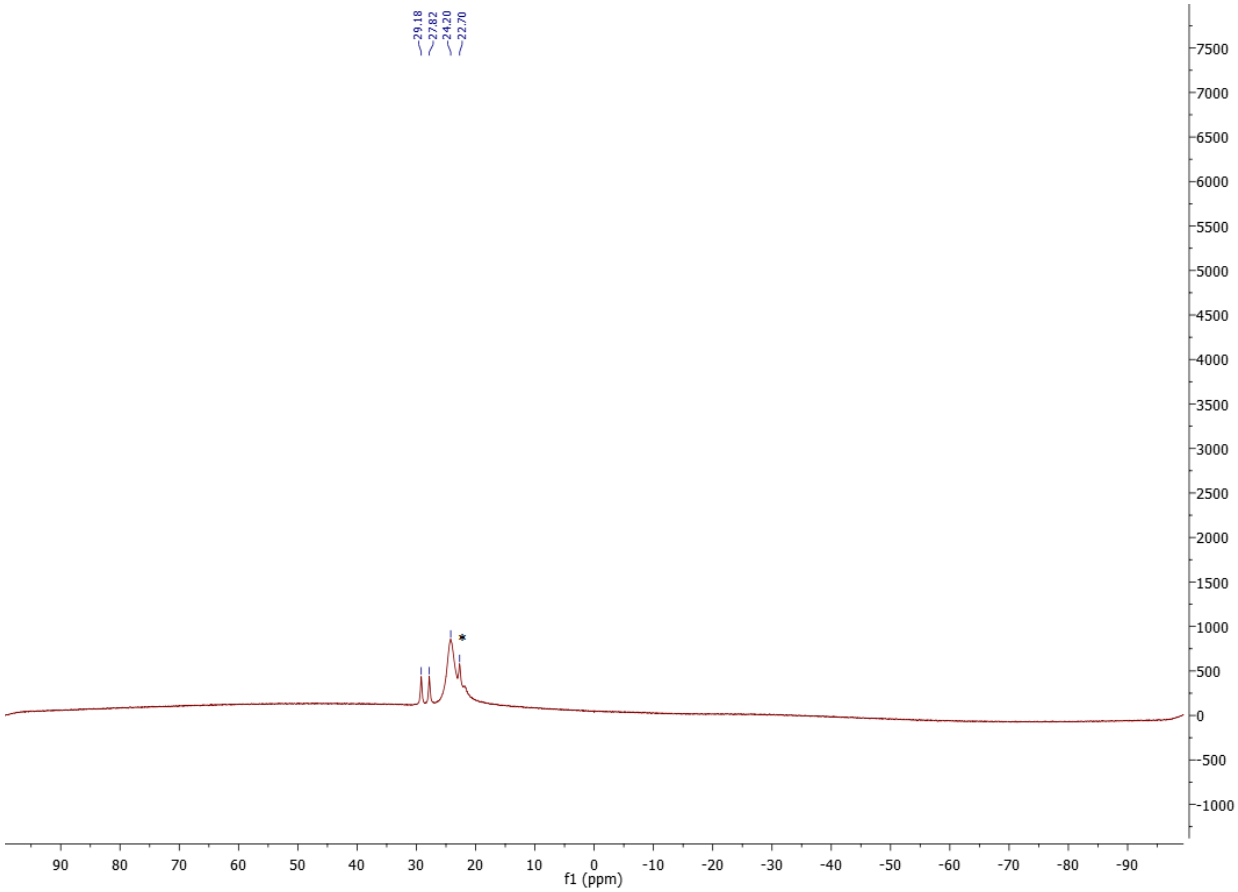


Figure S34. ^{11}B NMR spectrum from Table 1, Entry 8a: 2,6-diisopropylaniline:HBPin. (128.26MHz, benzene-d_6, 25° C, ppm)



* PinBOBPin

Figure S35. ^{1}H NMR spectrum from Table 1, Entry 9b: 3,5-dichloroaniline:HBPin. (400MHz, benzene-d_6, 25° C, ppm)

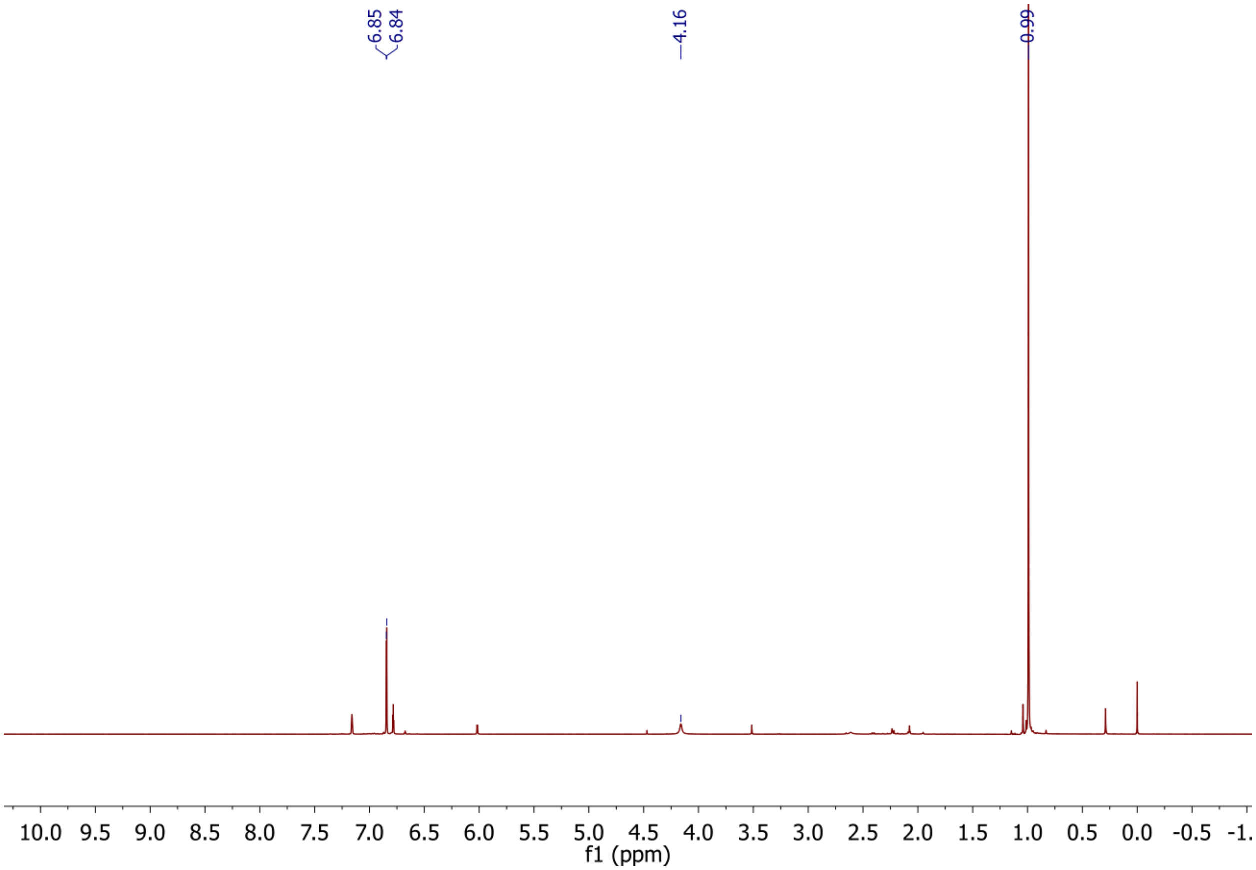
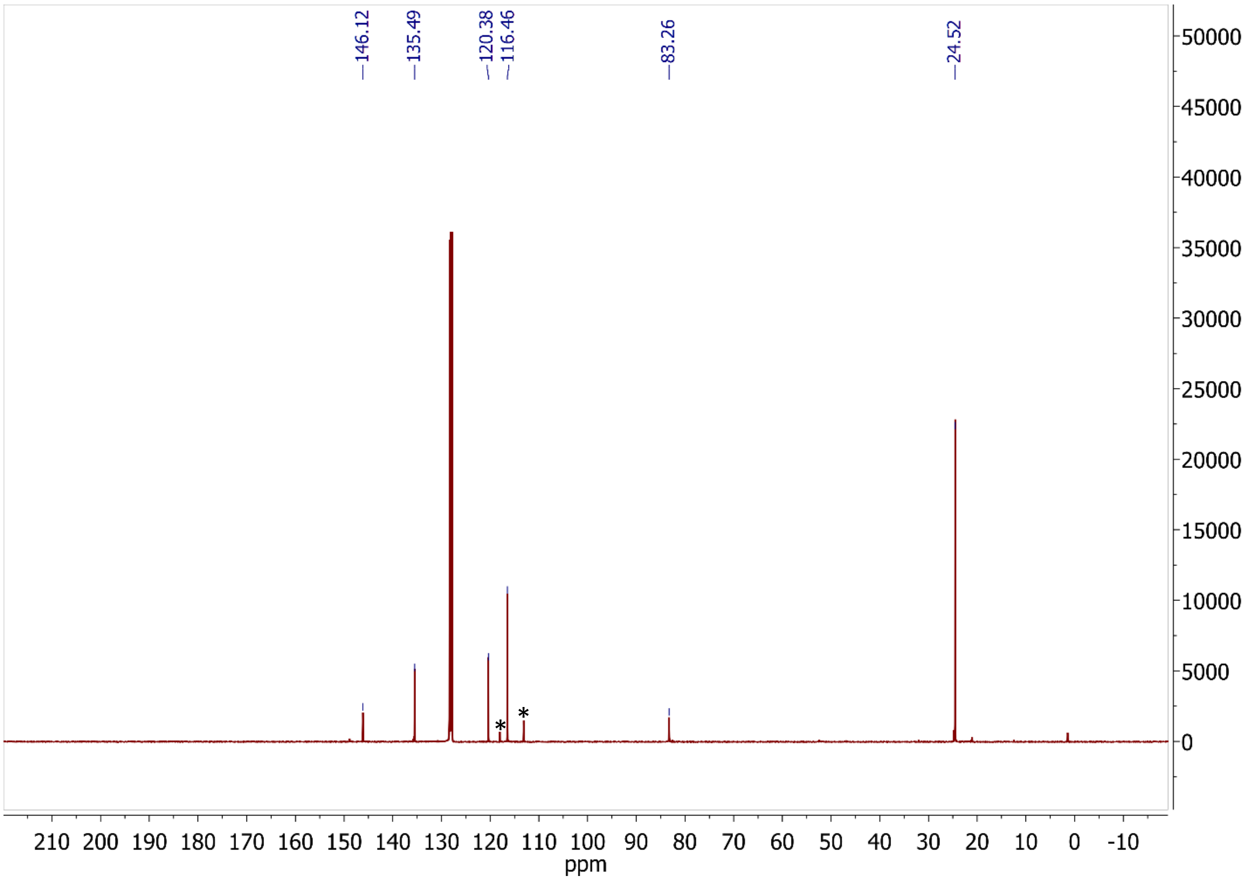
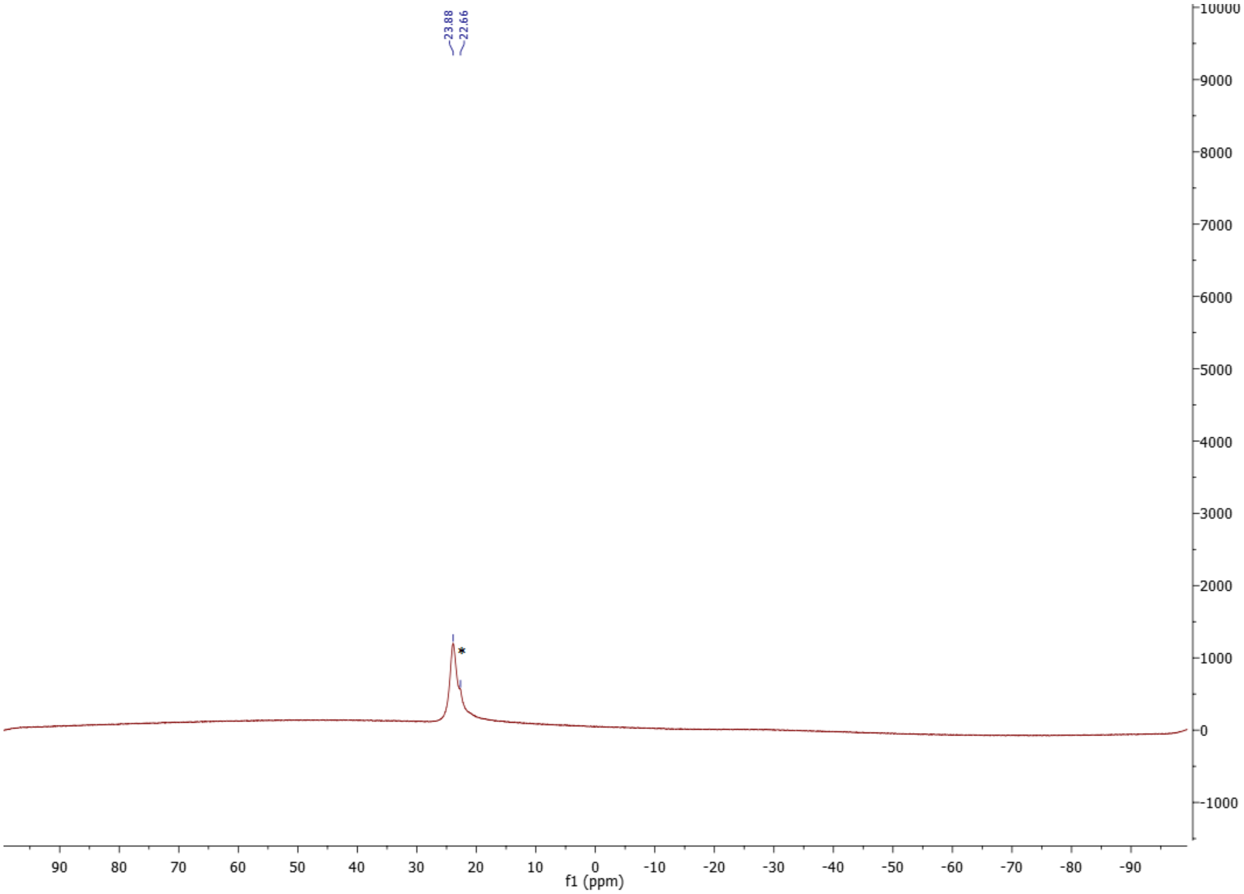


Figure S36. $^{13}C\{^1H\}$ NMR spectrum from Table 1, Entry 9b: 3,5-dichloroaniline:HBPin. (126MHz, benzene-d_6, 25° C, ppm)



* Excess 3,5-dichloroaniline

Figure S37. ^{11}B NMR spectrum from Table 1, Entry 9b: 3,5-dichloroaniline:HBPin. (128.26MHz, benzene-d_6, 25° C, ppm)



* PinBOBPin

Figure S38. ^{1}H NMR spectrum from Table 1, Entry 10a: Et_2NH:HBPin. (400MHz, benzene-d_6, 25° C, ppm)

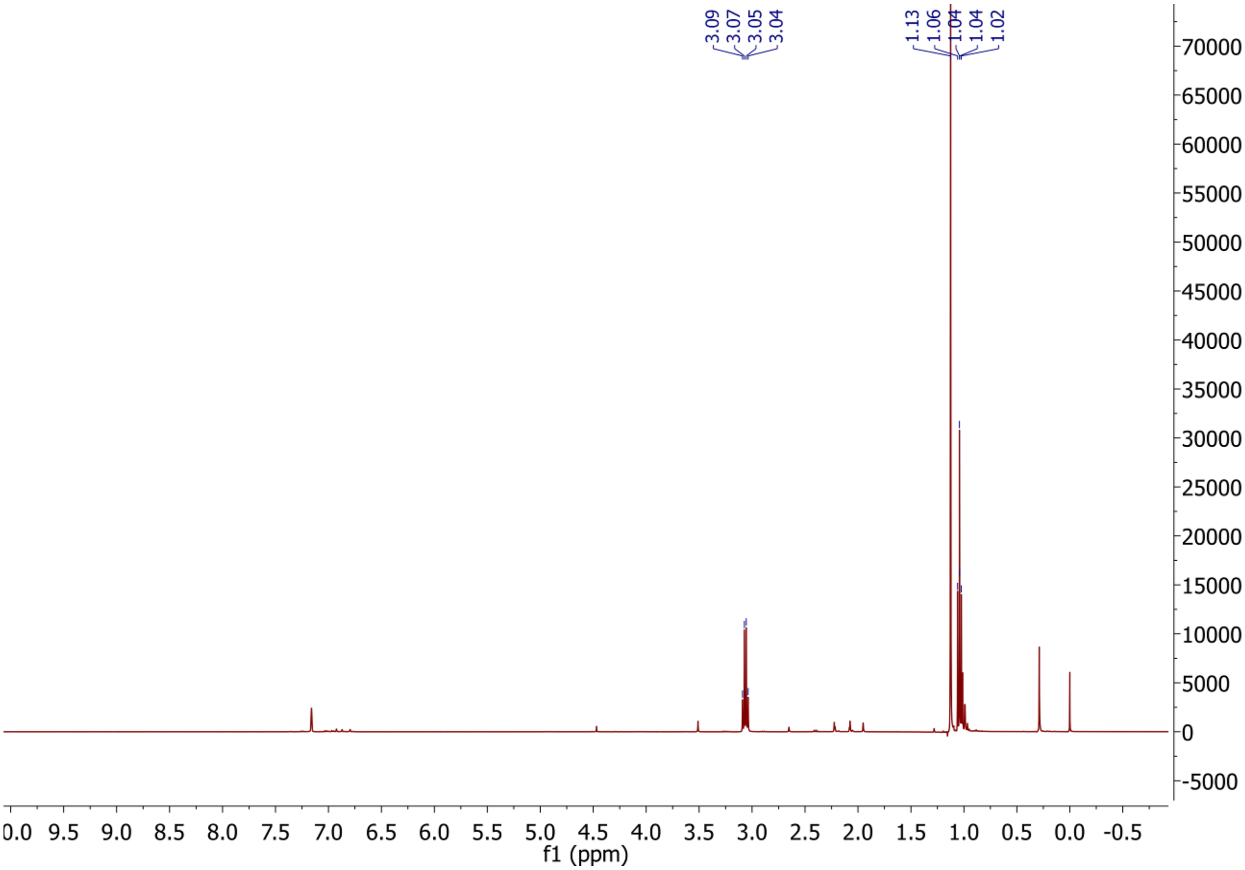
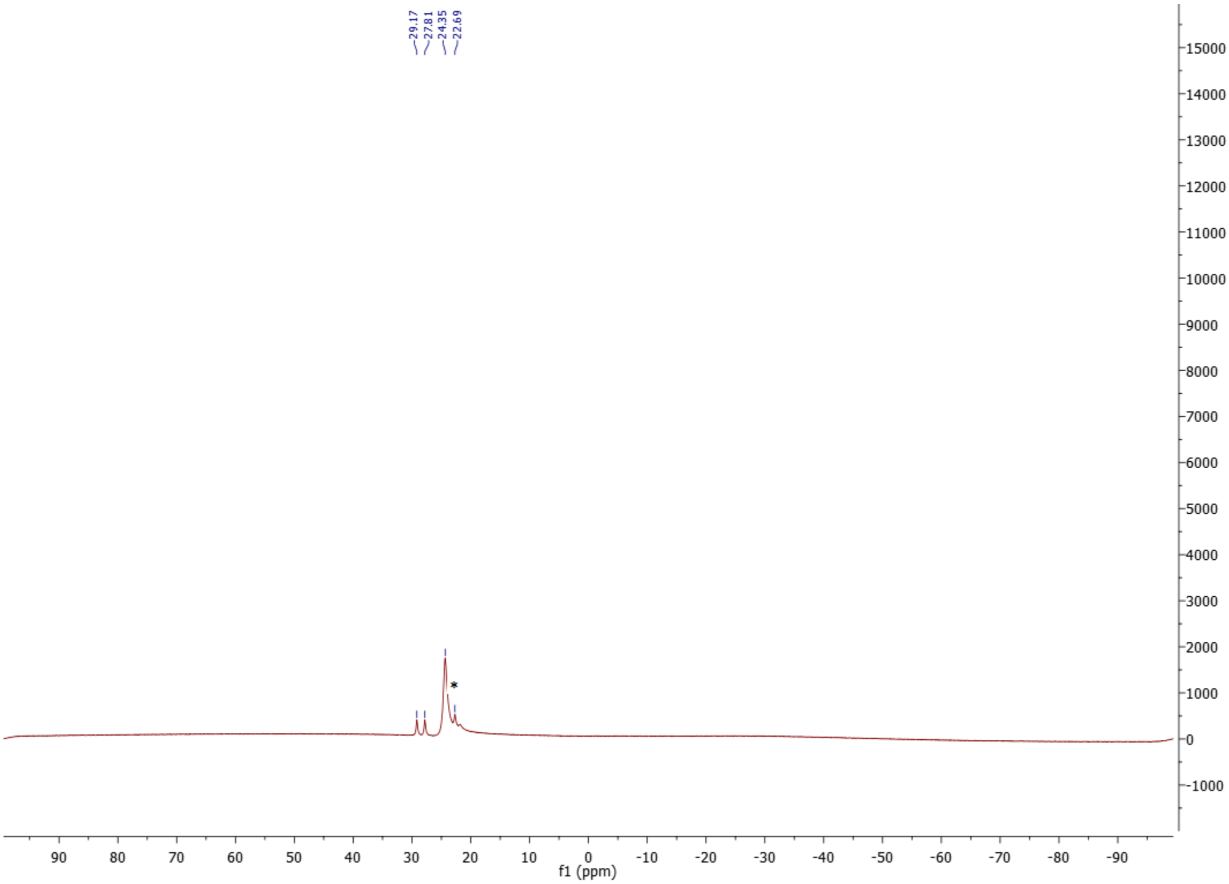


Figure S39. ^{11}B NMR spectrum from Table 1, Entry 10a: Et_2NH:HBPin. (128.26MHz, benzene-d_6, 25° C, ppm)



* PinBOBPin

Figure S40. ^{1}H NMR spectrum from Table 1, Entry 11a: *i*Pr_2NH:HBPin. (400MHz, benzene-d_6, 25° C, ppm)

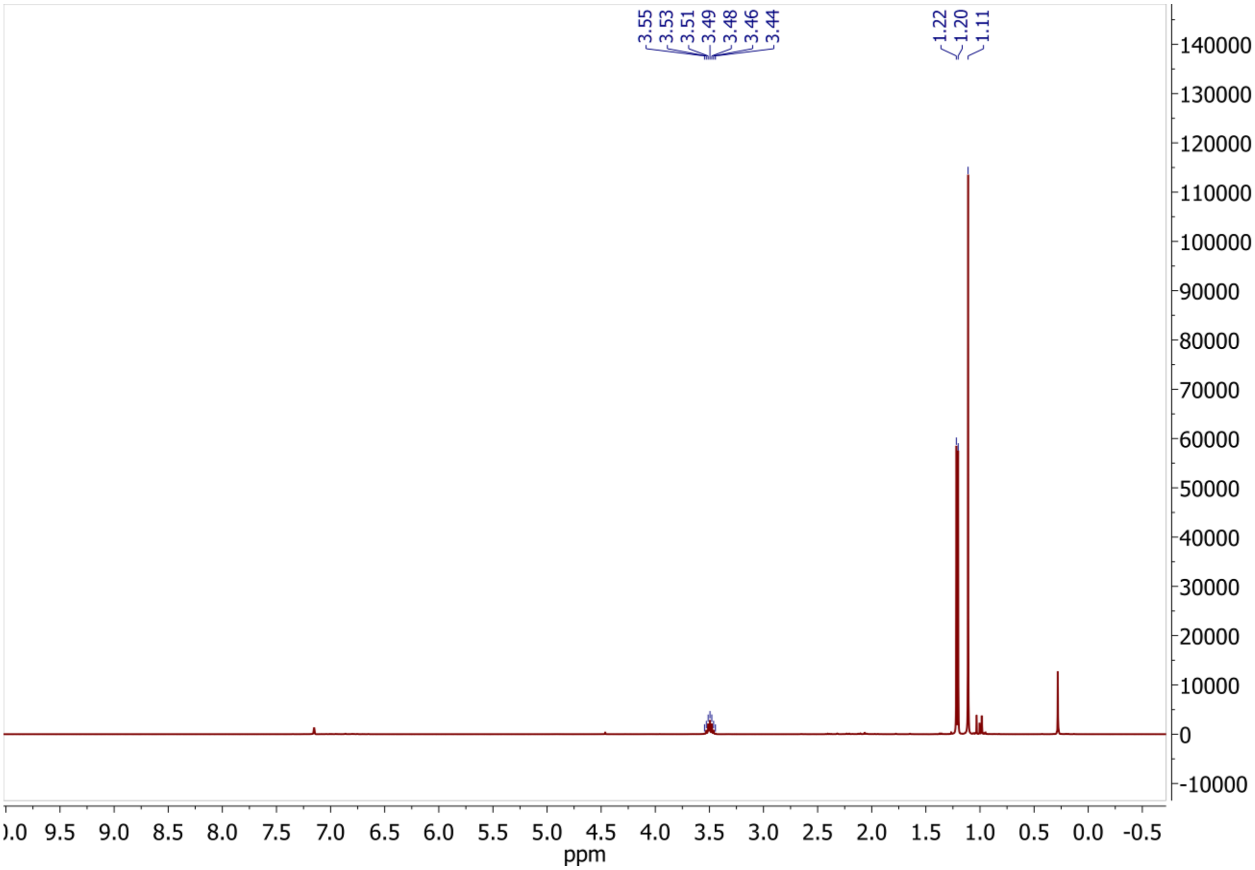
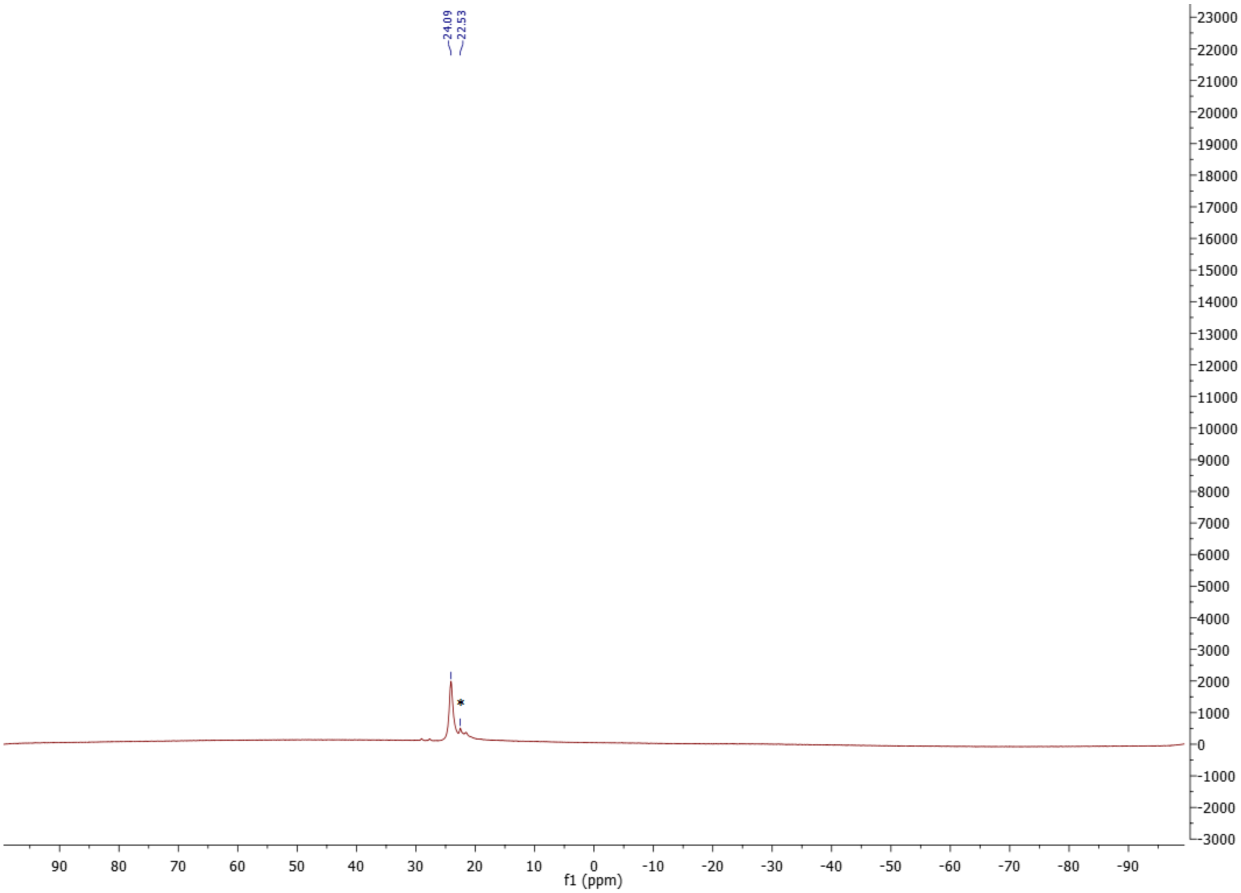


Figure S41. [11]B NMR spectrum from Table 1, Entry 11a: *i*Pr_2NH:HBPin. (128.26MHz, benzene-d_6, 25° C, ppm)



* PinBOBPin

Figure S42. ^{1}H NMR spectrum from Table 1, Entry 12a: Cy_2NH:HBPin. (400MHz, benzene-d_6, 25° C, ppm)

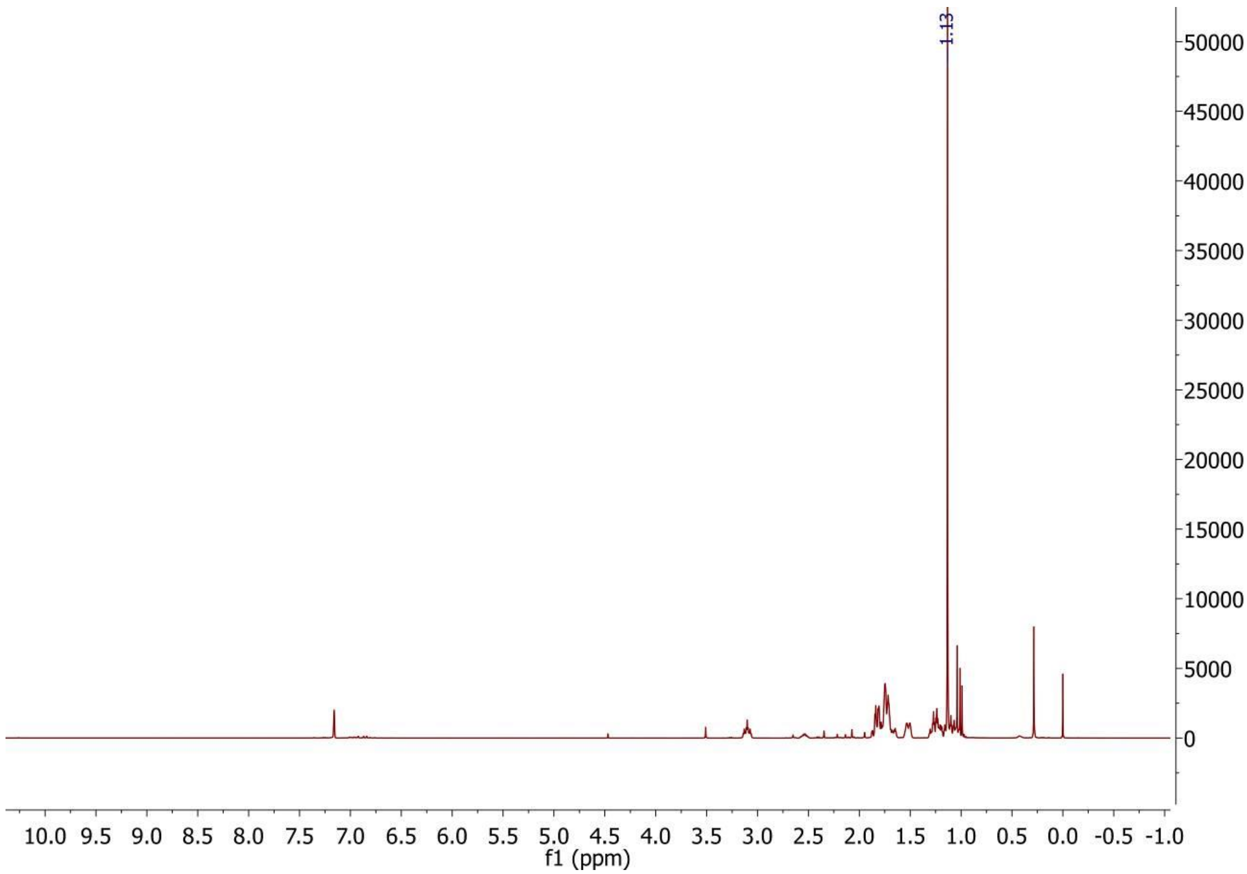
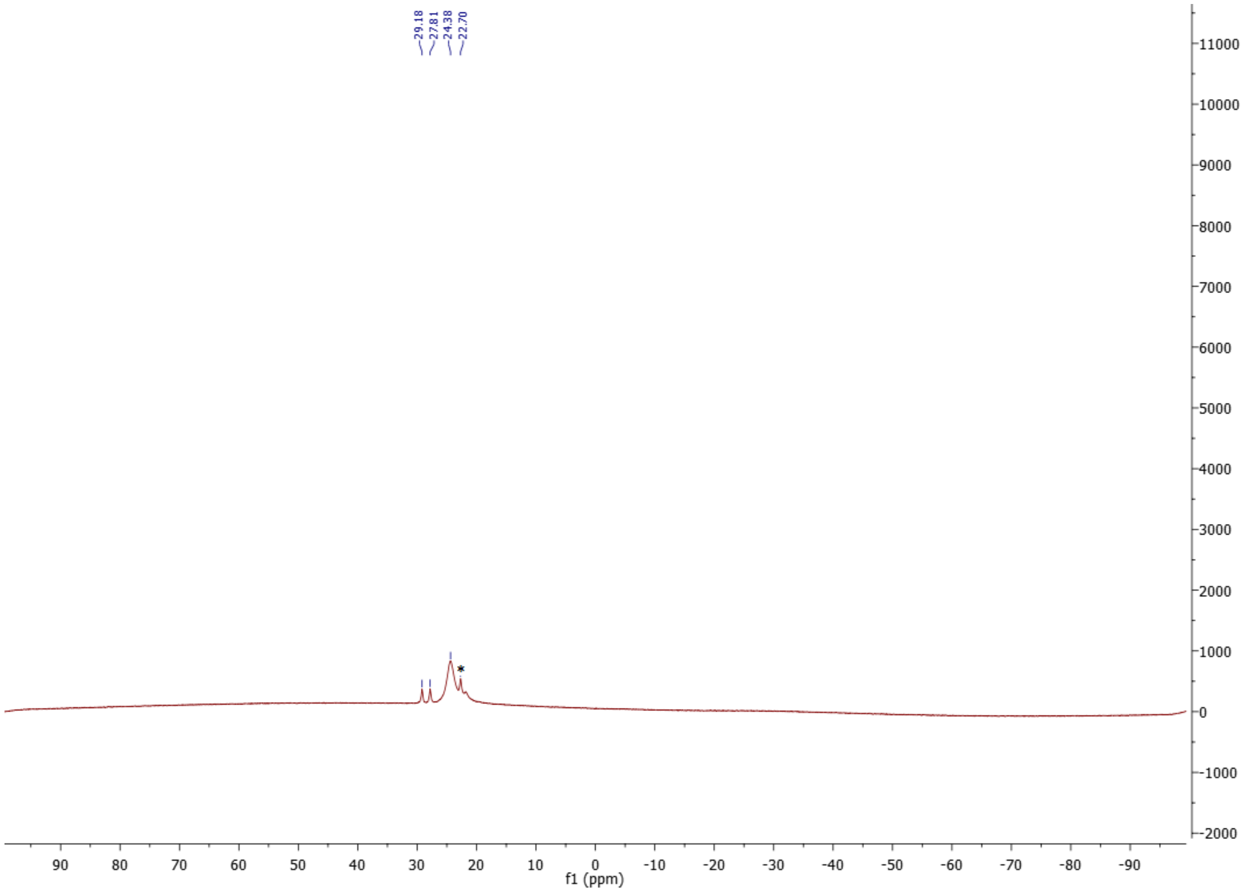


Figure S43 ^{11}B NMR spectrum from Table 1, Entry 12a: Cy_2NH:HBPin. (128.26MHz, benzene-d_6, 25° C, ppm)



* PinBOBPin

Figure S44. ^{1}H NMR spectrum from Table 1, Entry 13a: Ph_2NH:HBPin. (400MHz, benzene-d_6, 25° C, ppm)

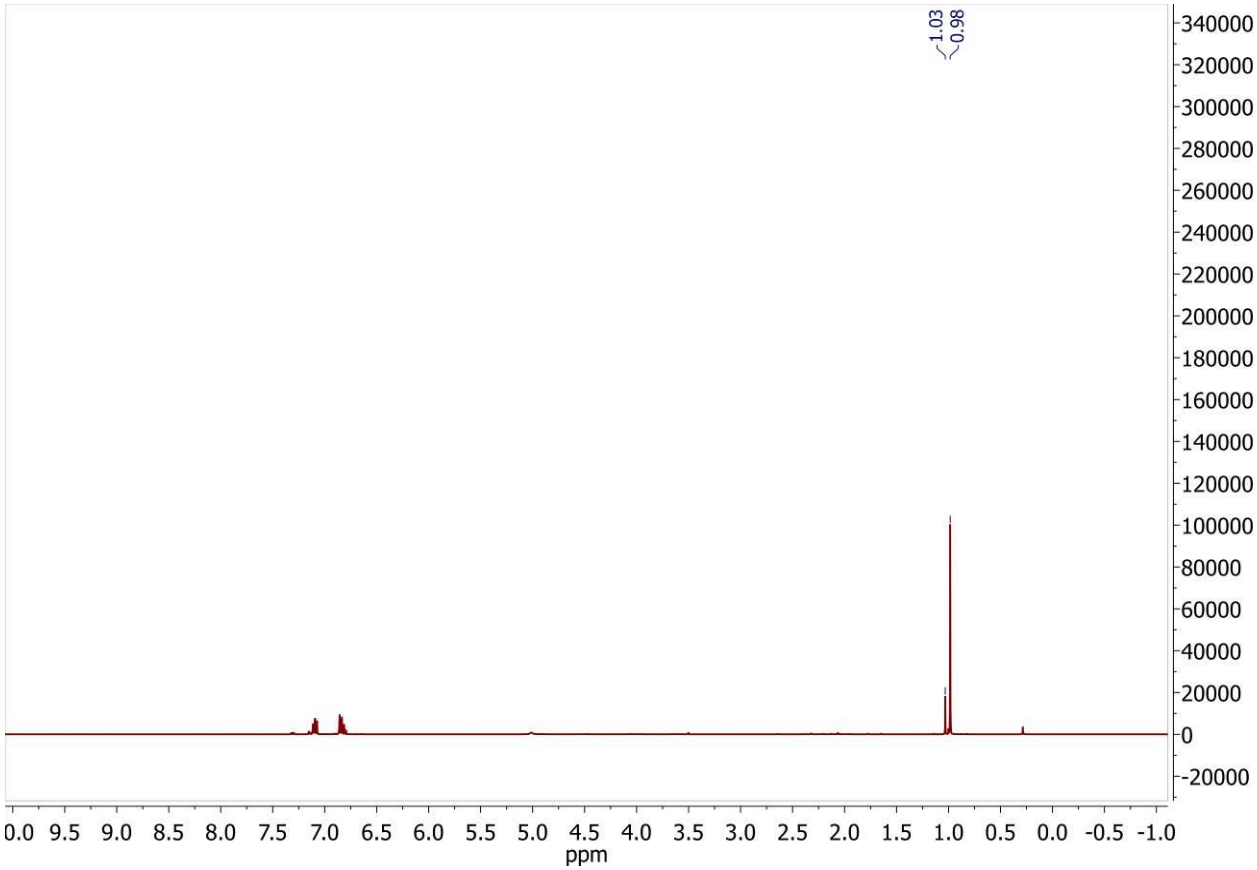
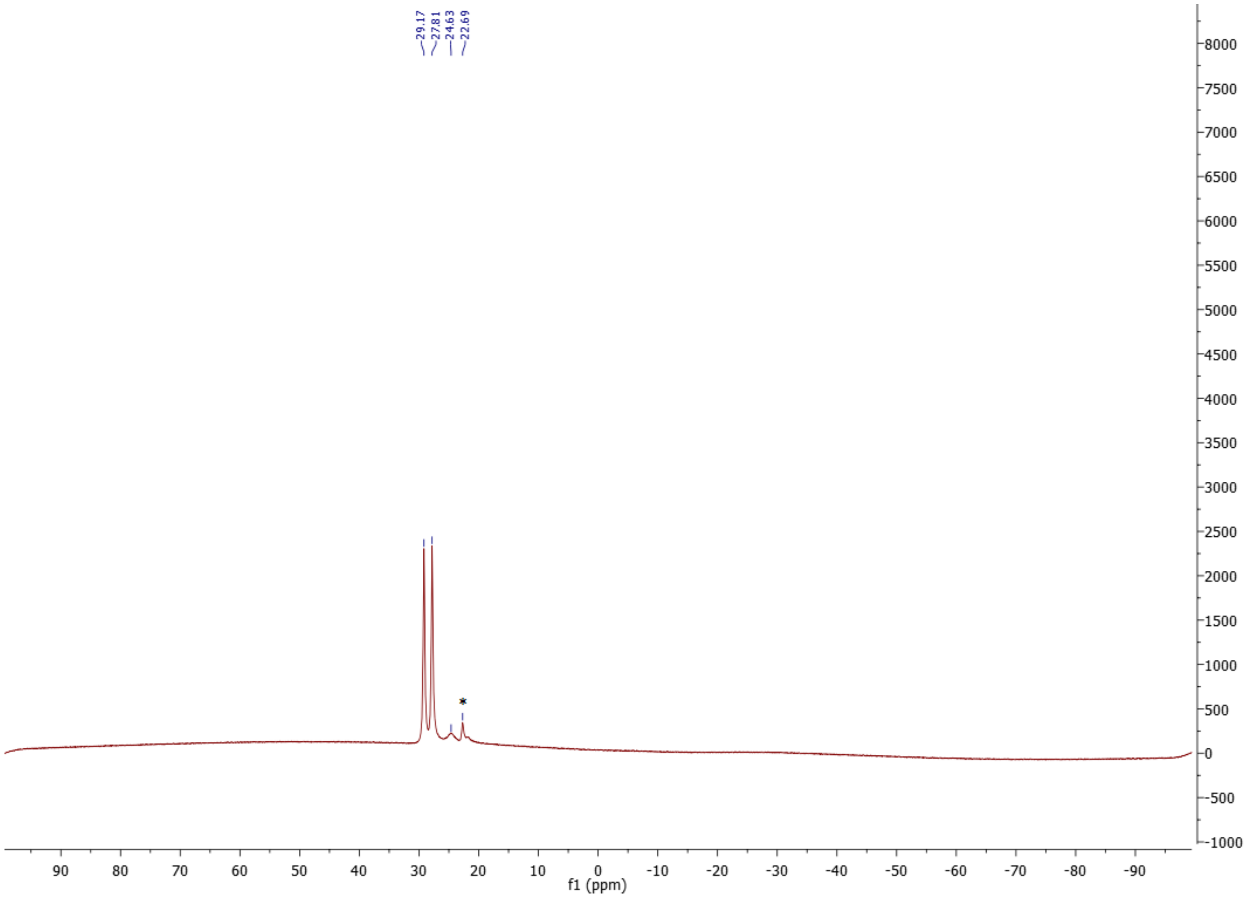
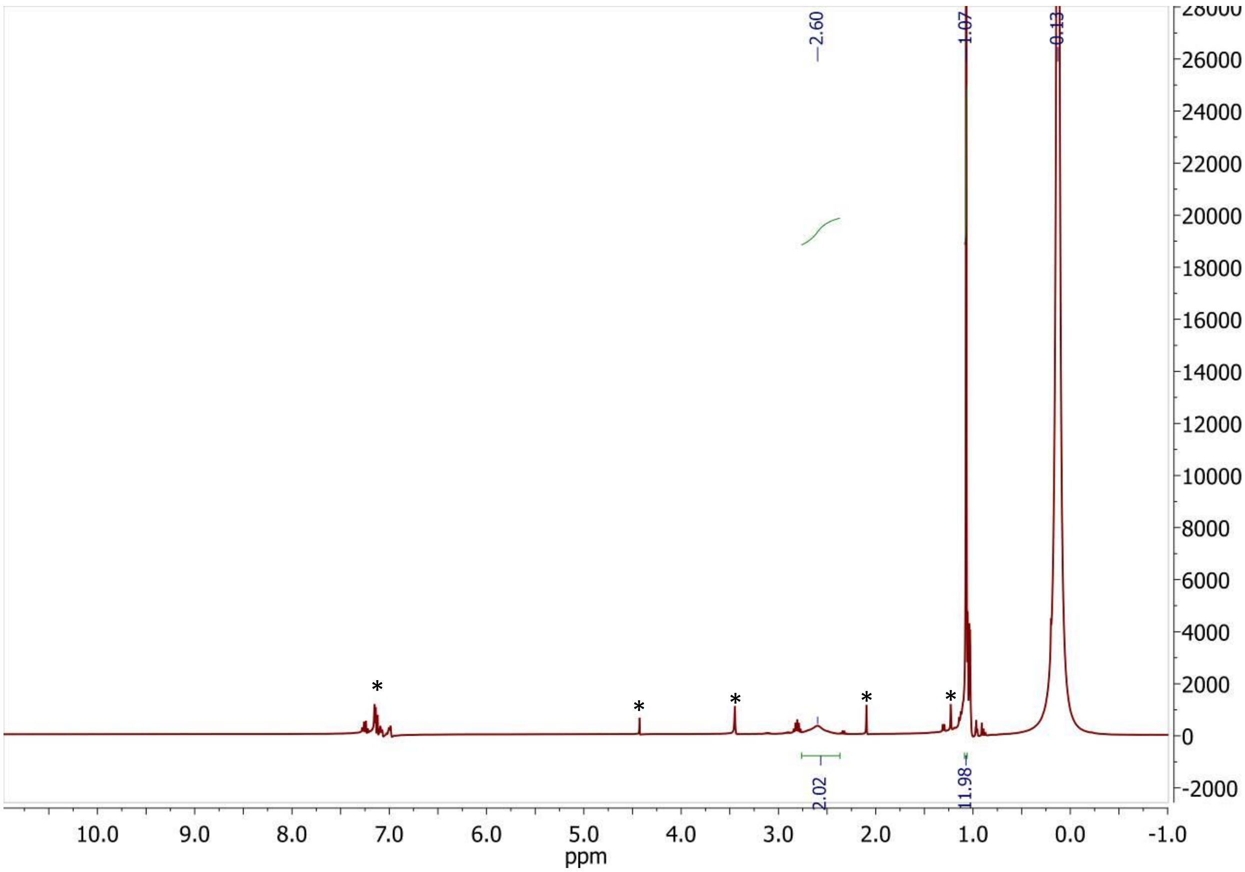


Figure S45. ^{11}B NMR spectrum from Table 1, Entry 13a: Ph_2NH:HBPin. (128.26MHz, benzene-d_6, 25° C, ppm)



* PinBOBPin

Figure S46. ^{1}H NMR spectrum Table 1, Entry 15b: NH_3:HBPin. Excess NH_3. (400MHz, benzene-d_6, 25° C, ppm)



* {JSnH}$_4$

Figure S47. $^{13}C\{^1H\}$ NMR spectrum from Table 1, Entry 15b: NH_3:HBPin. (126MHz, benzene-d_6, 25° C, ppm)

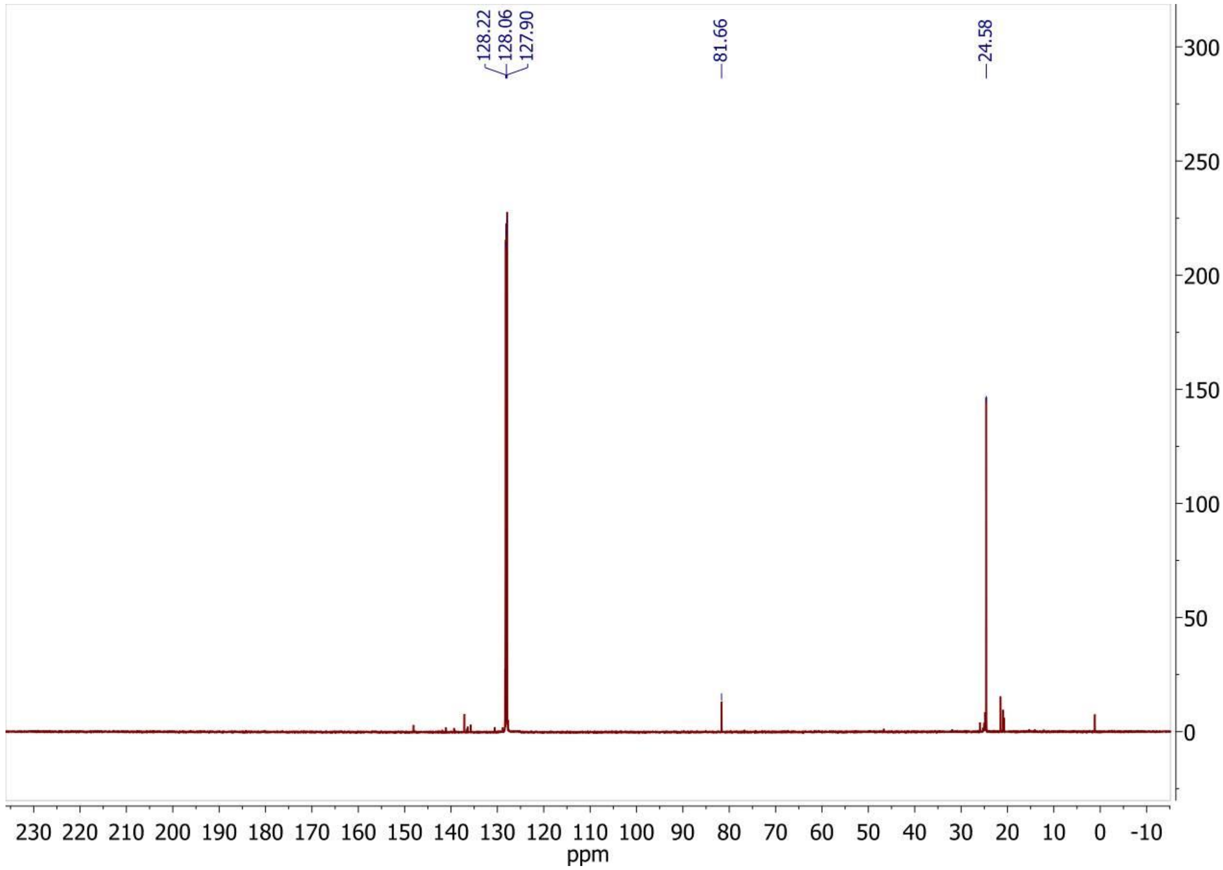
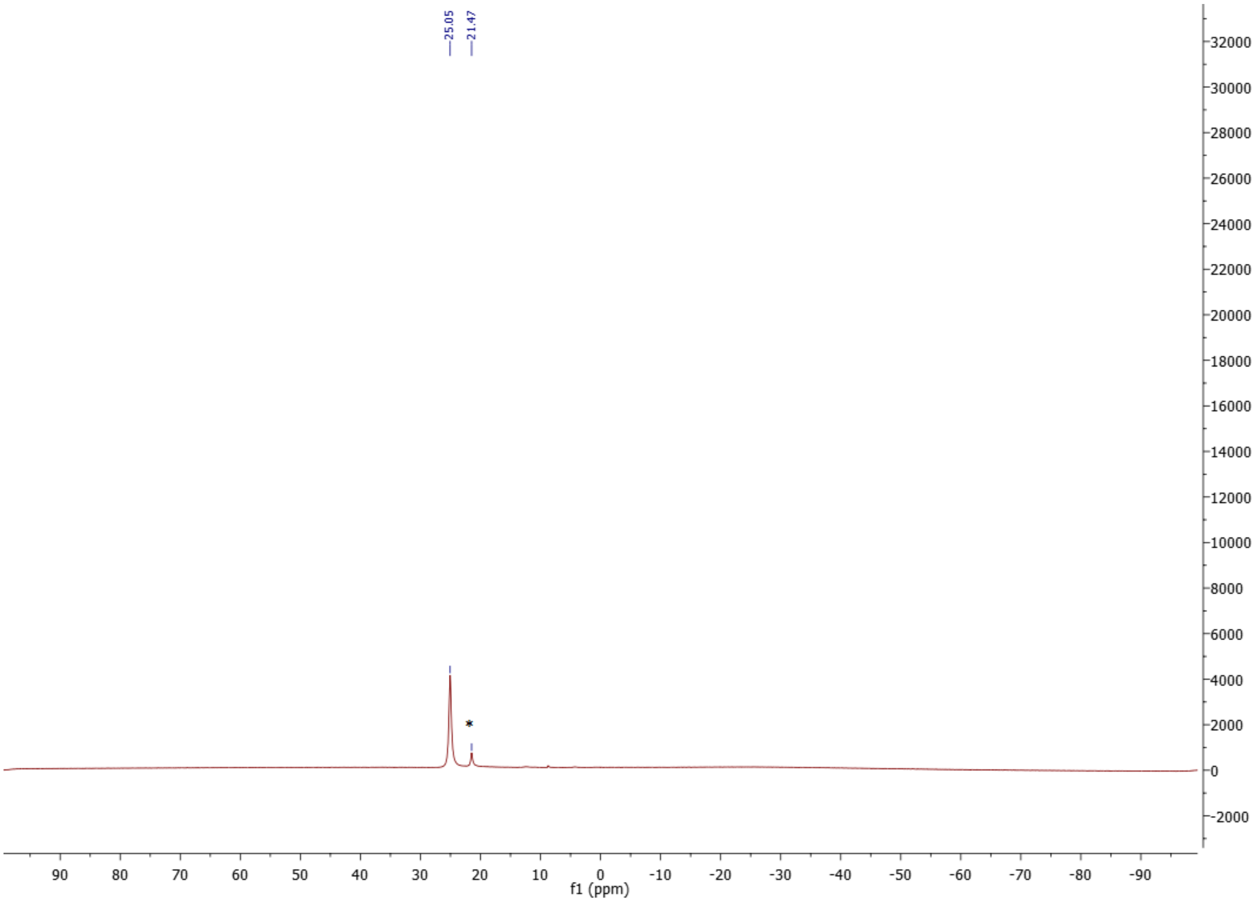


Figure S48. ^{11}B NMR spectrum from Table 1, Entry 15b: NH_3:HBPin. (128.26MHz, benzene-d_6, 25° C, ppm)



* PinBOBPin

Figure S49. ^{1}H NMR spectrum from Table 1, Entry 16b: $PinNH_2$:HBPin. Excess HBPin. (400MHz, benzene-d_6, 25° C, ppm)

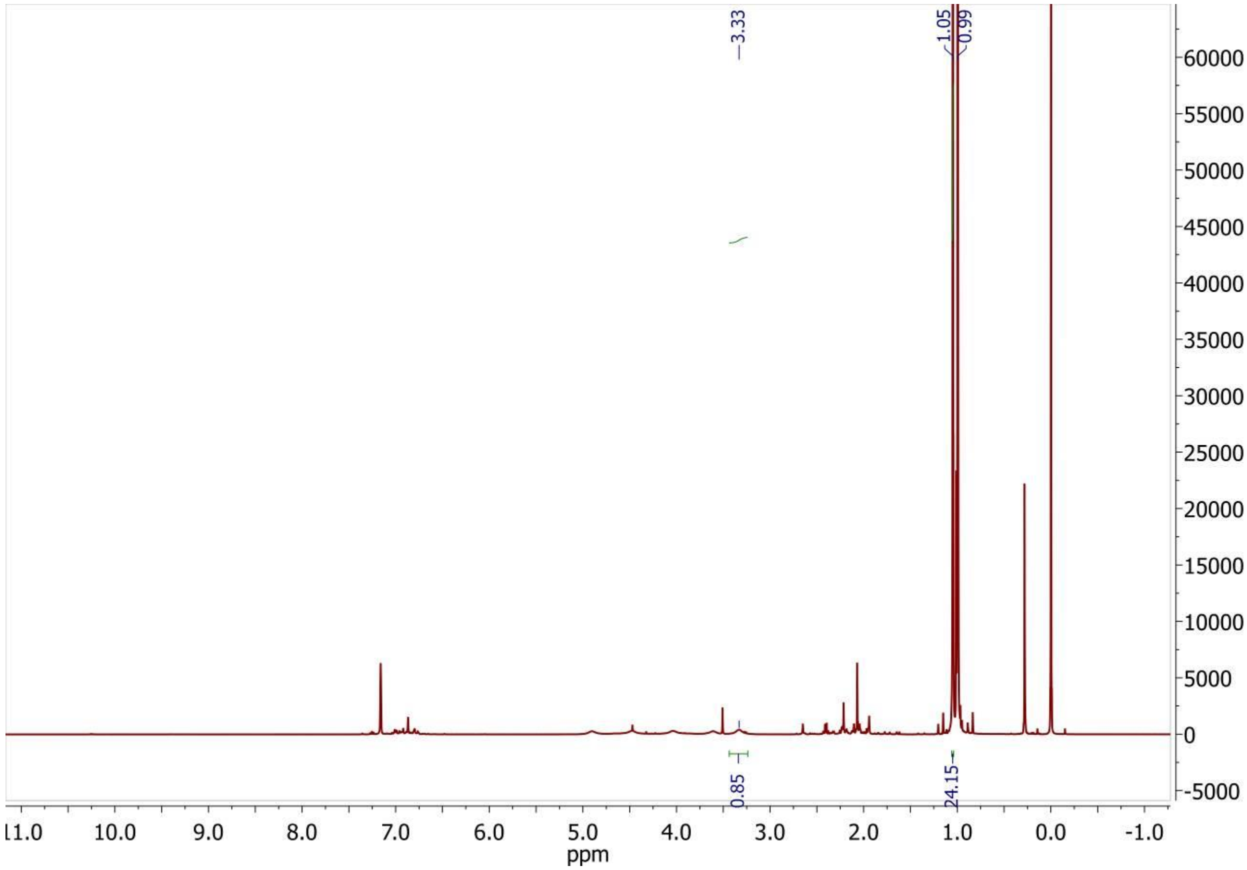
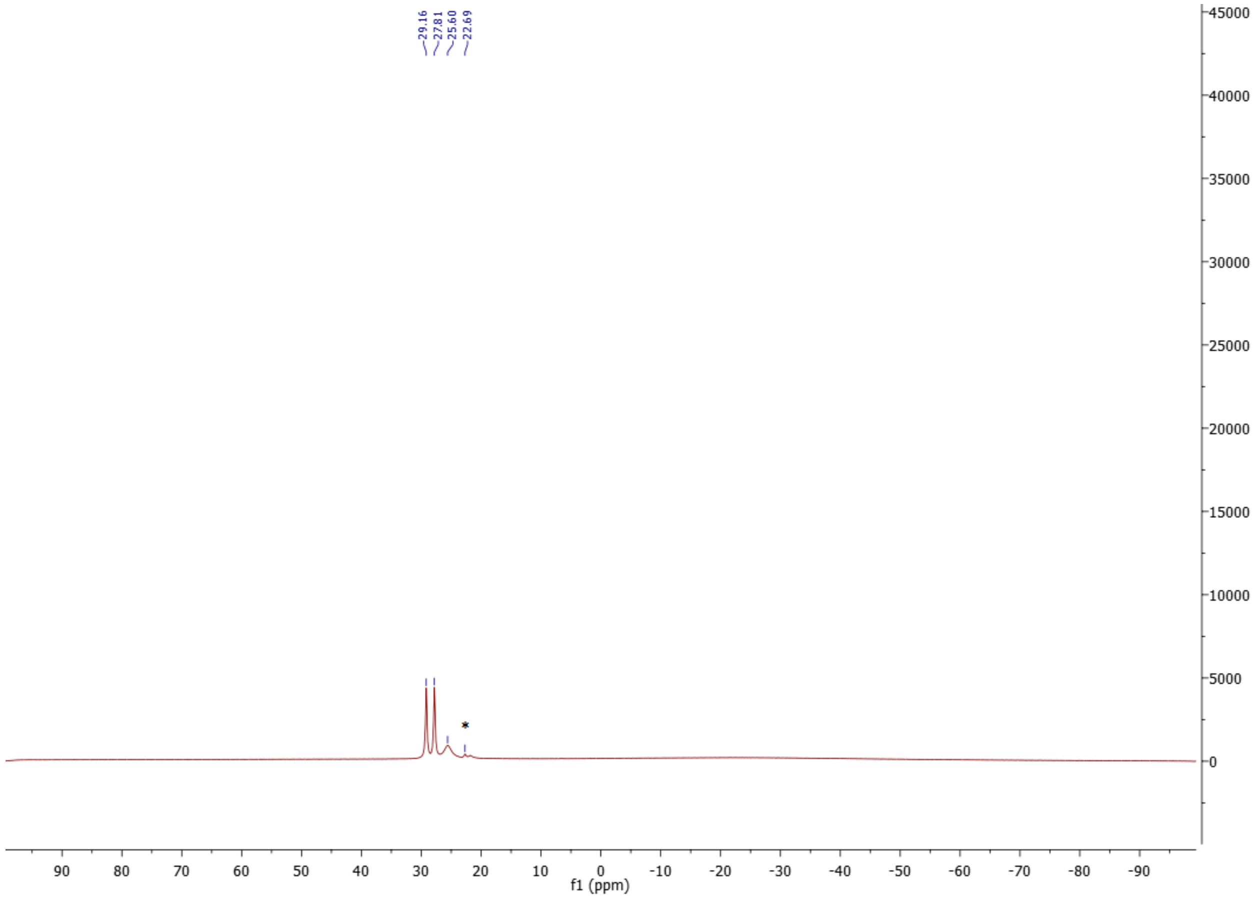
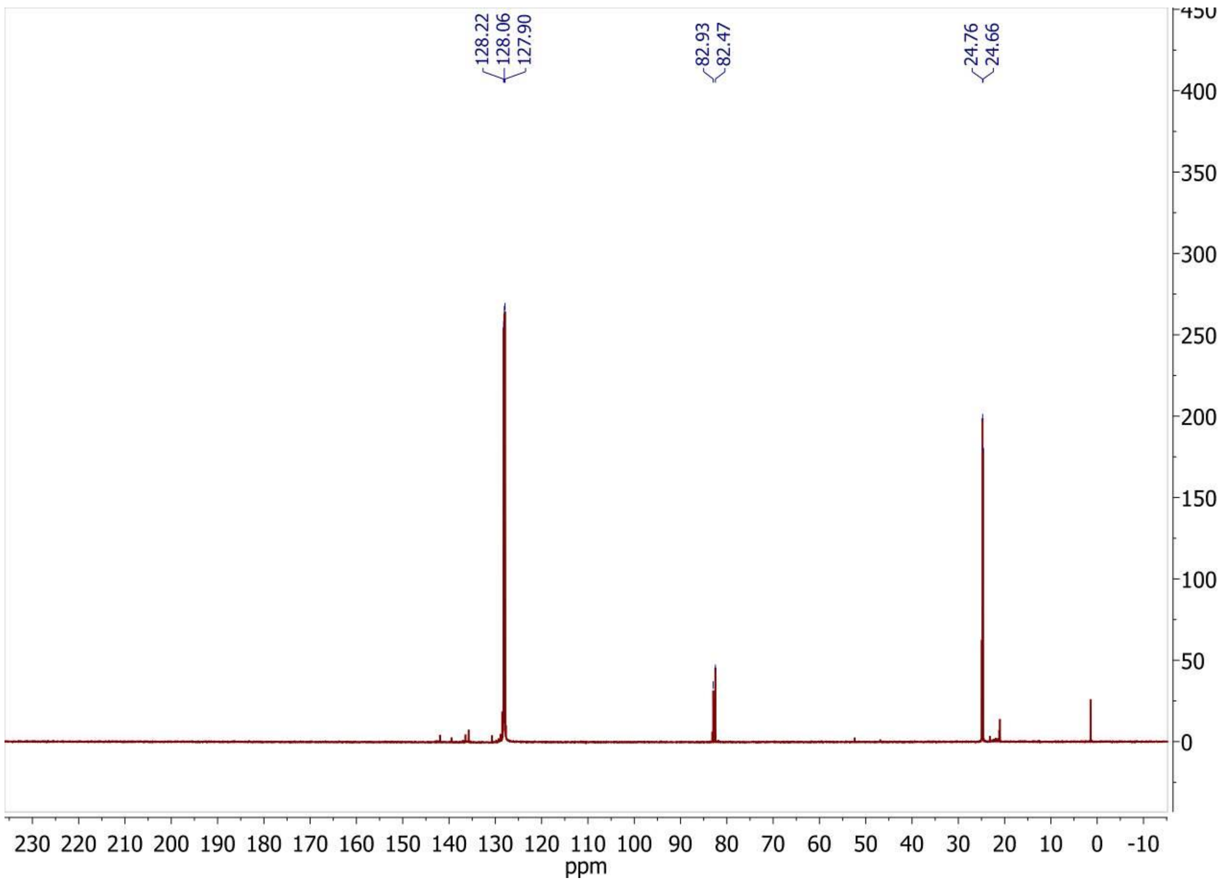


Figure S50. ^{11}B NMR spectrum from Table 1, Entry 16a: $PinNH_2$:HBPin. Excess HBPin. (128.26MHz, benzene-d_6, 25° C, ppm)



* PinBOBPin

Figure S51. $^{13}C\{^{1}H\}$ NMR spectrum from Table 1, Entry 16a: $PinNH_2$:HBPin. (126MHz, benzene-d_6, 25° C, ppm)



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2. J. D. Erickson, P. Vasko, R. D. Riparetti, J. C. Fettinger, H. M. Tuononen and P. P. Power, *Organometallics*, 2015, **34**, 5785-5791.
3. See D. J. Liptrot, M. S. Hill, M. F. Mahon and A. S. S. Wilson, *Angew. Chem., Int. Ed.*, 2015, **54**, 13362-13365; Z. Yang, M. Zhong, X. Ma, K. Nijesh, S. De, P. Parameswaran and H. W. Roesky, *J. Am. Chem. Soc.*, 2016, **138**, 2548-2551; E. A. Romero, J. L. Peltier, R. Jazzar and G. Bertrand, *Chem. Commun.*, 2016, **52**, 10563-10565 and references therein.