Supporting Information

Simple Silver(I)-Salt Catalyzed Selective Hydroboration of Isocyanates, Pyridines, and Quinolines

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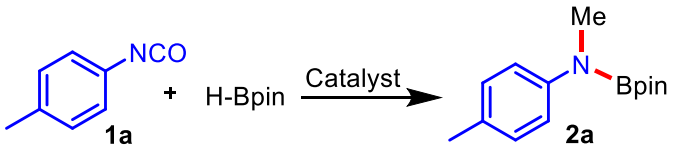
General experimental information:

Reactions were performed under an argon atmosphere using a glove box and/or standard Schlenk techniques unless stated otherwise. NMR spectra were recorded on the Bruker 400 and 500 MHz FT-NMR spectrometers at ambient temperature. All the ^{1}H and $^{13}C\{^{1}H\}$ NMR spectra were referenced internally to the residual solvent signals. ^{19}F NMR spectra were referenced externally to α,α,α-trifluorotoluene (0.05% in $CDCl_3$; δ = –63.73 ppm), ^{11}B NMR spectra were referenced externally to $BF_3{\cdot}Et_2O$ in $CDCl_3$ (δ = 0 ppm). H-Bpin was purchased from Alfa Aesar and all other chemicals including isocyanates[1b,c] were purchased from the commercial sources and used directly without further purification. The starting materials **5i-m**,[1a] were synthesized according to the literature procedures.

Table S1. Optimization of the reaction conditions for the hydroboration of isocyanate[a]

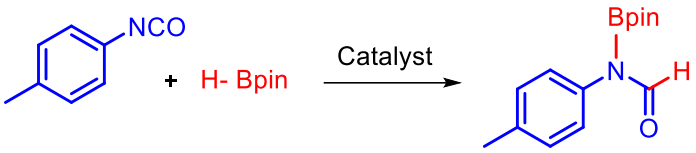


1a **2a**

Entry	Catalyst (mol%)	Temp	Solvent	Time (h)	Yield (%)[b]
1[c]	$AgSbF_6$ (2)	RT	neat	24	30[d]
2[c]	$AgSbF_6$ (2)	60 °C	neat	12	>99
3[c]	$AgSbF_6$ (1)	60 °C	neat	6	>99
4	$AgSbF_6$ (1)	60 °C	neat	6	>99
5	$AgSbF_6$ (1)	60 °C	thf	6	80
6	$AgSbF_6$ (1)	60 °C	toluene	6	82
7	$AgBF_4$ (1)	60 °C	neat	6	56
8	$AgPF_6$ (1)	60 °C	neat	6	90
9	AgOTf (1)	60 °C	neat	6	73
10	Ag_2CO_3 (1)	60 °C	neat	6	64
11[e]	$AgSbF_6$ (1)	60 °C	neat	6	ND[f]

[a]Reaction condition: *p*-tolyl isocyanate (0.5 mmol), H-Bpin (1.55 mmol). [b]Yields were calculated by ^{1}H NMR spectroscopy using hexamethyl benzene as an internal standard. [c]1.65 mmol of H-Bpin. [d]20% mono-borylated product was obtained. [e]B_2Pin_2 as boronic agent instead of HBpin. [f]No product formation was observed; ND: Not detected.

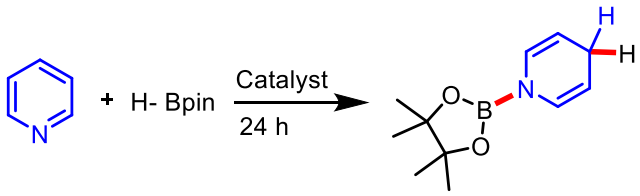
Table S2. Optimization of the monohydroboration reaction of isocyanate[a]



Entry	Catalyst	Mol%	Temp	Time	Yield(%)[b]
1[c]	$AgSbF_6$	1	RT	6	ND[d]
2	$AgSbF_6$	2	RT	12	84
3	$AgSbF_6$	2	RT	24	75
4	$AgSbF_6$	2	60 °C	6	15 (50)[e]

[a]Reaction condition: Isocyanate (0.5 mmol), Pinacolborane (0.75 mmol). [b]Conversion are based on ^{1}H NMR analysis. [c]1.1 equiv. of H-Bpin. [d]No borylated product was observed; ND: not detected. [e]Deoxygenative hydroborated product.

Table S3. Optimization of hydroboration reaction of pyridine[a]



Entry	Catalyst	Mol%	Temp	Solvent	Yield(%)[b]
1[c]	$AgSbF_6$	3	RT	neat	20
2[c]	$AgSbF_6$	2	60 °C	neat	82
3	$AgSbF_6$	2	60 °C	neat	>95
4	$AgSbF_6$	1	60 °C	neat	89
5	-	2	60 °C	neat	ND[d]
6	$AgBF_4$	2	60 °C	neat	16
7	$AgPF_6$	2	60 °C	neat	25
8	Ag_2CO_3	2	60 °C	neat	10
9	$AgSbF_6$	2	60 °C	Toluene	ND
10	$AgSbF_6$	2	60 °C	THF	ND

[a]Reaction condition: Pyridine (0.5 mmol), pinacolborane (0.60 mmol). [b]Conversions are based on ^{1}H NMR analysis. [c]1.1 equiv. H-Bpin was used. [d]No borylated product was observed; ND: not detected.

General procedure for the deoxygenative hydroboration of isocyanates: $AgSbF_6$ (1.7 mg, 0.005 mmol, 1.0 mol%) and pinacolborane (225 μL, 1.55 mmol) were taken in a Schlenk tube. Then isocyanate (0.5 mmol) was added to the reaction mixture. The reaction tube was then closed and heated to 60 ºC for 6-12 hours. The progress of the reaction was monitored by ^1H NMR and yields were calculated based on ^1H NMR analysis using hexamethylbenzene as an internal standard.

General procedure for the monohydroboration of isocyanates: $AgSbF_6$ (3.4 mg, 0.01 mmol, 2.0 mol%) and pinacolborane (109 μL, 0.75 mmol) were taken in a Schlenk tube. Then isocyanate (0.5 mmol) was added to the reaction mixture. The reaction tube was closed and allowed to stir at room temperature for 12-24 hours. The progress of the reaction was monitored by ^1H NMR spectroscopy.

General procedure for the synthesis of secondary amines *via* tri-hydroboration of isocyanates: $AgSbF_6$ (1.7 mg, 0.005 mmol, 1.0 mol%) and pinacolborane (225 μL, 1.55 mmol) were taken in a Schlenk tube. Then isocyanate (0.5 mmol) was added to the reaction mixture. The reaction tube was then closed and heated to 60 ºC for 6-12 hours. After completion of the reaction, the resulted boronate ester residue was hydrolysed with methanol at 60 ºC for 12 hours. The obtained residue after evaporation of all the volatiles was subjected to silica gel column chromatography and the products were isolated by using ethyl acetate-hexane as eluent.

General procedure for the pyridine hydroboration: $AgSbF_6$ (3.4 mg, 0.01 mmol, 2.0 mol%) and pinacolborane (94-109 μL, 0.60-0.75 mmol) was taken in a Schlenk tube. After the addition of pyridine (0.5 mmol), the reaction tube was closed and heated to 60 ºC for 24 hours. The progress of the reaction was monitored by ^1H NMR spectroscopy.

General procedure for the hydrogenation of quinoline derivatives: $AgSbF_6$ (3.4 mg, 0.01 mmol, 2.0 mol%) and pinacolborane (218 μL, 1.15 mmol) was taken in a Schlenk tube. After the addition of quinoline (0.5 mmol), the reaction tube was closed and heated to 60 ºC for 24-48 hours. After completion of the reaction, the resulted boronate ester residue was hydrolysed with methanol at 60 ºC for 12 hours. The obtained residue after evaporation of all the volatiles was subjected to silica gel column chromatography and the products were isolated by using ethyl acetate-hexane as eluent.

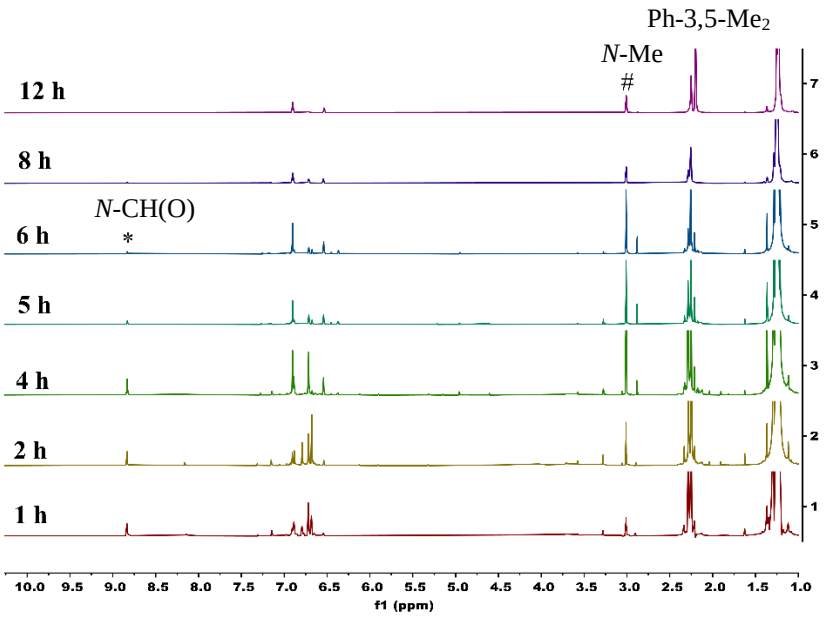


Figure S1. Stacked ^{1}H NMR spectra for the hydroboration of 3,5-dimethylphenyl isocyanate at different time interval. * = 3,5-Me_2-Ph-N(BPin)HC(O), # = 3,5-Me_2-Ph-N(BPin)CH_3.

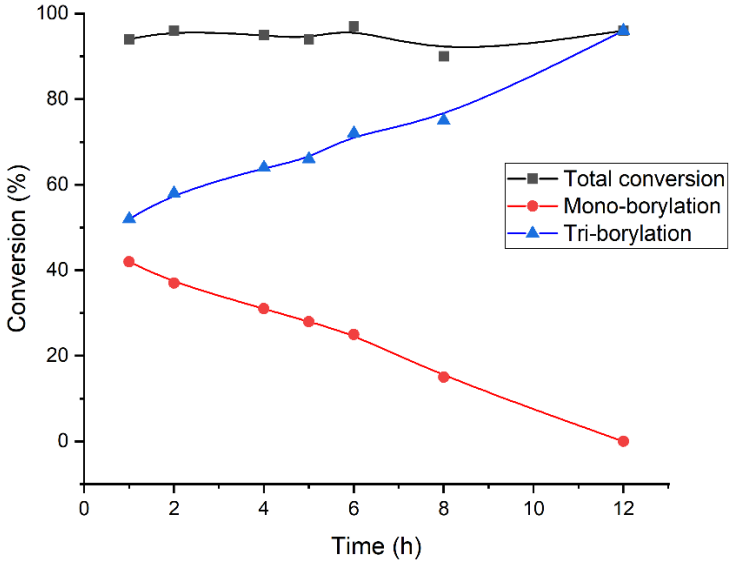
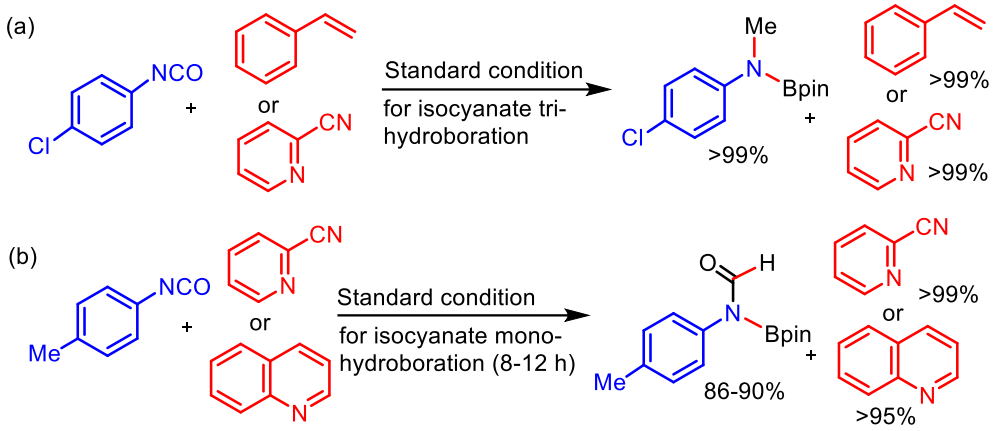
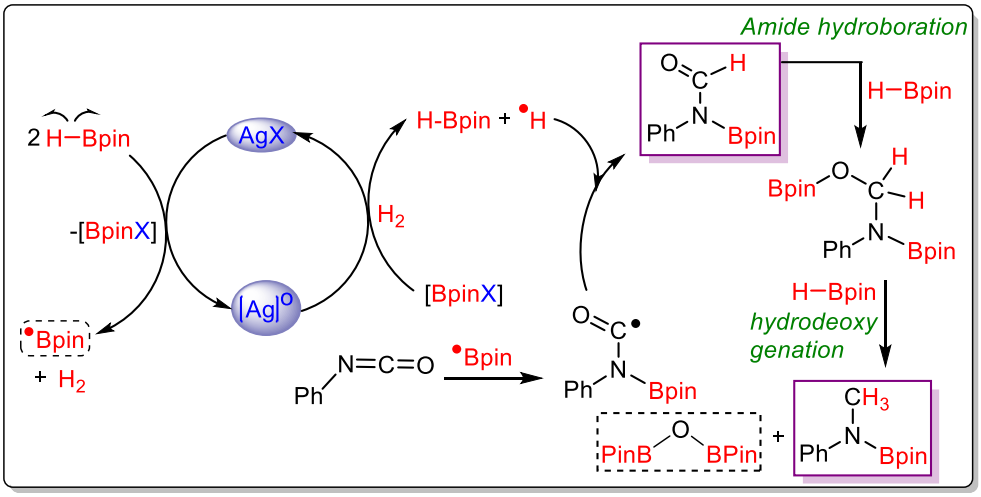


Figure S2. Time profile for the reaction progress of 3,5-dimethylphenyl isocyanate hydroboration.



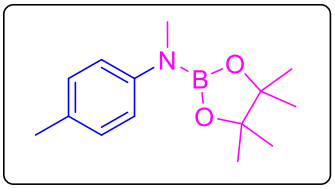
Scheme S1. Chemoselective hydroboration.



Scheme S2. A plausible mechanism.

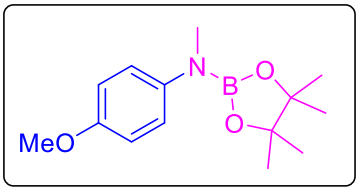
Analytical data for the isocyanate hydroborated products:

*N,4,4,5,5-pentamethyl-N-(p-tolyl)-1,3,2-dioxaborolan-2-amine (Compound-**2a**):*[2] Compound



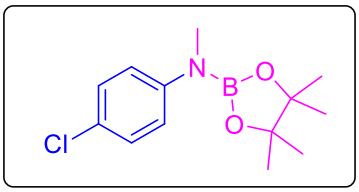
2a was synthesized following the general procedure by reacting 4-methylphenyl isocyanate (66.5 mg, 0.5 mmol) and pinacolborane (225 µL, 1.5 mmol) for 6 h at 60 ºC (yield: >99%).^{1}H NMR (400 MHz, $CDCl_3$) δ 7.07 (d, J = 8.5 Hz, 2H), 6.93 (d, J = 8.5 Hz, 2H), 2.92 (s, 3H), 2.16 (s, 3H), 1.17 (s, 12H), 1.15 (s, 24H) ppm. ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 144.9, 129.6, 128.9, 118.9, 82.4, 34.3, 24.5, 20.3 ppm. ^{11}B NMR (160 MHz, $CDCl_3$) δ 24.45 ppm.

*N-(4-methoxyphenyl)-N,4,4,5,5-pentamethyl-1,3,2-dioxaborolan-2-amine (Compound-**2b**):* [2]



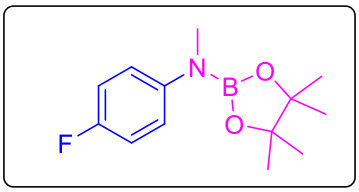
Compound **2b** was synthesized following the general procedure by reacting 4-methoxyphenyl isocyanate (74.5 mg, 0.5 mmol) and pinacolborane (225 µL, 1.5 mmol) for 6 h at 60 ºC (yield: >99%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25 (d, J = 8.8 Hz, 2H), 6.86 (d, J = 8.8 Hz, 2H), 3.80 (s, 3H), 3.09 (s, 3H), 1.34 (s, 12H), 1.33 (s, 24H) ppm. ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 154.1, 140.9, 120.5, 113.7, 82.4, 55.2, 34.8, 24.5 ppm. ^{11}B NMR (160 MHz, $CDCl_3$) δ 24.29 ppm.

*N-(4-chlorophenyl)-N,4,4,5,5-pentamethyl-1,3,2-dioxaborolan-2-amine (Compound-**2c**):* [2]



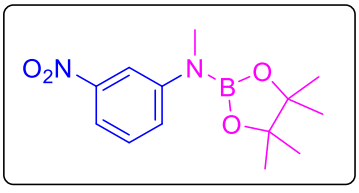
Compound **2c** was synthesized following the general procedure by reacting 4-chlorophenyl isocyanate (76.7 mg, 0.5 mmol) and pinacolborane (225 µL, 1.5 mmol) for 6 h at 60 ºC (yield: >99%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28 (d, J = 9.0 Hz, 2H), 7.21 (d, J = 9.0 Hz, 2H), 3.07 (s, 3H), 1.34 (s, 12H), 1.32 (s, 24H) ppm. ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 146.1, 128.3, 125.4, 119.9, 82.8, 34.2, 24.6 ppm. ^{11}B NMR (160 MHz, $CDCl_3$) δ 24.43 ppm.

*N-(4-fluorophenyl)-N,4,4,5,5-pentamethyl-1,3,2-dioxaborolan-2-amine (Compound-**2d**):* [2]



Compound **2d** was synthesized following the general procedure by reacting 4-fluorophenyl isocyanate (68.5 mg, 0.5 mmol) and pinacolborane (225 µL, 1.5 mmol) for 12 h at 60 ºC (yield: >99%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 (m, 2H), 6.99 (m, 2H), 3.09 (s, 3H), 1.34 (s, 36H) ppm. ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 165.1, 158.7, 156.3, 143.5, 120.1 (d, J = 7.5 Hz), 114.7 (d, J = 21.9 Hz), 82.7, 34.6, 24.5 ppm.^{11}B NMR (160 MHz, $CDCl_3$) δ 24.37 ppm. ^{19}F NMR (471 MHz, $CDCl_3$) δ -128.51 ppm.

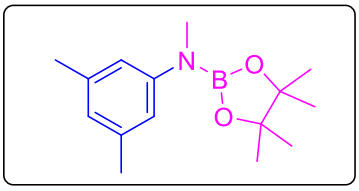
*N,4,4,5,5-pentamethyl-N-(3-nitrophenyl)-1,3,2-dioxaborolan-2-amine (Compound-**2e**):*[2]



Compound **2e** was synthesized following the general procedure by reacting 3-nitrophenyl isocyanate (82.1 mg, 0.5 mmol) and pinacolborane (225 µL, 1.5 mmol) for 6 h at 60 ºC (yield: >99%).^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (s, 1H), 7.58 (t, J = 7.2 Hz, 2H), 7.23 (t, J = 8.0 Hz, 1H), 2.97 (s, 3H), 1.20 (s, 12H), 1.14 (s, 24H) ppm. ^{13}C{^{1}H}

NMR (101 MHz, $CDCl_3$) δ 148.6, 148.5, 128.9, 124.1, 114.7, 112.2, 83.2, 33.9, 24.5 ppm. ^{11}B NMR (160 MHz, $CDCl_3$) δ 24.56 ppm.

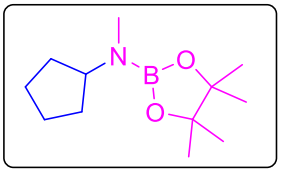
*N-(3,5-dimethylphenyl)-N,4,4,5,5-pentamethyl-1,3,2-dioxaborolan-2-amine (Compound-**2f**):* [2]



Compound **2f** was synthesized following the general procedure by reacting 3,5-dimethylphenyl isocyanate (73.6 mg, 0.5 mmol) and pinacolborane (225 µL, 1.5 mmol) for 12 h at 60 ºC (yield: >99%).^{1}H NMR (400 MHz, $CDCl_3$) δ 6.90 (s, 2H), 6.54 (s, 1H), 3.01 (s, 3H), 2.25 (s, 6H), 1.25 (s, 12H), 1.23 (s, 24H) ppm. $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 147.4, 137.6, 122.6, 117.1, 82.4, 34.4, 24.5, 21.5 ppm. ^{11}B NMR (160 MHz, $CDCl_3$) δ 24.64 ppm.

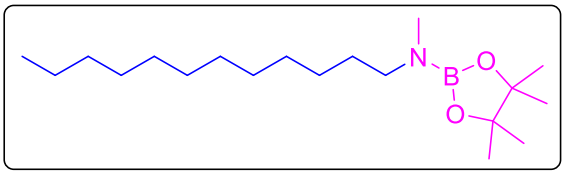
*N-(3,5-bis(trifluoromethyl)phenyl)-N,4,4,5,5-pentamethyl-1,3,2-dioxaborolan-2-amine (Compound-**2g**):* [2] Compound **2g** was synthesized following the general procedure by reacting 3,5-bis(trifluoromethyl)phenyl isocyanate (127.5 mg, 0.5 mmol) and pinacolborane (225 µL, 1.5 mmol) for 12 h at 60 ºC (yield: >99%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (s, 2H), 7.37 (s, 1H), 3.09 (s, 3H), 1.31 (s, 12H), 1.26 (s, 24H) ppm. $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 148.9, 132.1, 131.5, 131.2, 127.8, 125.1, 122.4, 117.8 (d, J = 3.5 Hz), 113.3 (q, J = 3.8 Hz), 83.6, 34.0, 24.6 ppm. ^{11}B NMR (160 MHz, $CDCl_3$) δ 24.77 ppm. ^{19}F NMR (471 MHz, $CDCl_3$) δ -63.10 ppm.

*N-cyclopentyl-N,4,4,5,5-pentamethyl-1,3,2-dioxaborolan-2-amine (Compound-**2h**):* [2]



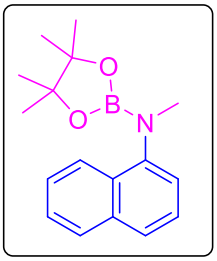
Compound **2h** was synthesized following the general procedure by reacting cyclopentyl isocyanate (55.5 mg, 0.5 mmol) and pinacolborane (225 µL, 1.5 mmol) for 24 h at 60 ºC (yield: >99%).^{1}H NMR (500 MHz, $CDCl_3$) δ 3.76-3.73 (m, 1H), 2.48 (s, 3H), 1.61-1.48 (m, 8H), 1.25 (s, 36H) ppm. $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$) δ 81.5, 57.3, 33.6, 28.6, 27.7, 24.8, 24.5, 24.2 ppm. ^{11}B NMR (160 MHz, $CDCl_3$) δ 24.06 ppm.

*N-dodecyl-N,4,4,5,5-pentamethyl-1,3,2-dioxaborolan-2-amine (Compound-**2i**):* [2] Compound



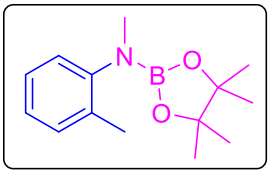
2i was synthesized following the general procedure by reacting dodecyl isocyanate (105.6 mg, 0.5 mmol) and pinacolborane (225 μL, 1.5 mmol) for 24 h at 60 ºC (yield: 95%).^{1}H NMR (400 MHz, $CDCl_3$) δ 2.89-2.85 (m, 2H), 2.55 (s, 3H), 1.44-1.37 (m, 4H), 1.26 (s, 36H), 1.23-1.20 (m, 16H), 0.89 (t, J = 6.6 Hz, 3H) ppm. ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 81.7, 48.3, 33.1, 31.9, 29.7, 29.7, 29.6, 29.6, 29.4, 29.3, 28.1, 26.4, 24.5, 22.6, 14.0 ppm. ^{11}B NMR (160 MHz, $CDCl_3$) δ 24.11 ppm.

*N,4,4,5,5-pentamethyl-N-(naphthalen-1-yl)-1,3,2-dioxaborolan-2-amine (Compound-**2j**):* [2]



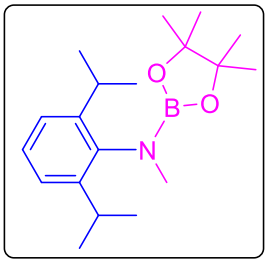
Compound **2j** was synthesized following the general procedure by reacting 1-naphthyl isocyanate (84.6 mg, 0.5 mmol) and pinacolborane (225 μL, 1.5 mmol) for 6 h at 60 ºC (yield: >99%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (d, J = 8.1 Hz, 1H), 7.77 (d, J = 7.8 Hz, 1H), 7.60 (d, J = 8.2 Hz, 1H), 7.42-7.35 (m, 3H), 7.26 (d, J = 7.2 Hz, 1H), 3.09 (s, 3H), 1.22 (s, 36H) ppm. ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 144.1, 134.7, 130.8, 128.2, 125.9, 125.6, 125.6, 125.4, 124.3, 123.5, 82.4, 38.5, 24.7 ppm. ^{11}B NMR (160 MHz, $CDCl_3$) δ 24.26 ppm.

*N,4,4,5,5-pentamethyl-N-(o-tolyl)-1,3,2-dioxaborolan-2-amine (Compound-**2k**):* [2] Compound



2k was synthesized following the general procedure by reacting *o*-tolyl isocyanate (66.5 mg, 0.5 mmol) and pinacolborane (225 μL, 1.5 mmol) for 24 h at 60 ºC (yield: 95%).^{1}H NMR (400 MHz, $CDCl_3$) δ 7.23 (d, J = 7.5 Hz, 1H), 7.19-7.16 (m, 2H), 7.13-7.09 (m, 1H), 3.01 (s, 3H), 2.33 (s, 3H), 1.33 (s, 36H) ppm. ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 146.1, 134.8, 130.6, 127.5, 126.5, 125.1, 82.2, 37.4, 24.8, 17.8, ppm.^{11}B NMR (160 MHz, $CDCl_3$) δ 23.95 ppm.

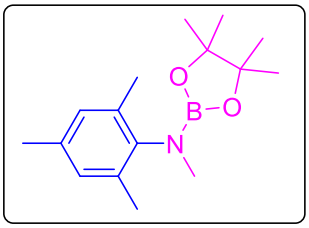
*N-(2,6-diisopropylphenyl)-N,4,4,5,5-pentamethyl-1,3,2-dioxaborolan-2-amine (Compound-**2l**):* [2]



Compound **2l** was synthesized following the general procedure by reacting 2,6-diisopropylphenyl isocyanate (101.6 mg, 0.5 mmol) and pinacolborane (225 μL, 1.5 mmol) for 24 h at 60 ºC (yield: 60%).^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24-7.19 (m, 2H), 7.17 (s, 2H), 7.16 (s, 1H), 3.32-3.25 (m, 3H), 2.87 (s, 2H), 1.31 (s, 36H), 1.26 (d, J = 6.8 Hz, 6H), 1.19 (m, 4H) ppm.^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 146.6, 142.9, 141.1, 128.6, 126.6,

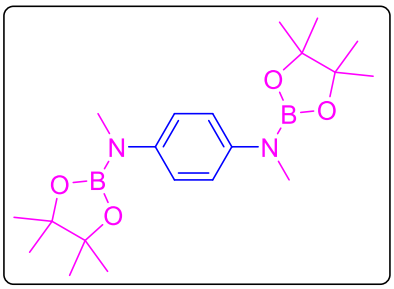
126.1, 123.5, 123.3, 83.1, 38.0, 29.5, 27.8, 24.5, 22.8 ppm. ^{11}B NMR (160 MHz, $CDCl_3$) δ 24.03 ppm.

*N-mesityl-N,4,4,5,5-pentamethyl-1,3,2-dioxaborolan-2-amine (Compound-**2m**):* [2] Compound



2m was synthesized following the general procedure by reacting trimethylphenyl isocyanate (80.6 mg, 0.5 mmol) and pinacolborane (225 µL, 1.5 mmol) for 24 h at 60 ºC (yield: 56%).^{1}H NMR (400 MHz, $CDCl_3$) δ 6.88 (s, 1H), 6.86 (s, 2H), 2.83 (s, 2H), 2.30 (s, 5H), 2.28 (s, 9H), 1.30 (s, 36H) ppm. ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 141.5, 135.5, 134.9, 134.8, 132.4, 128.9, 128.7, 83.1, 35.4, 24.7, 20.8, 20.6, 18.4, 17.6 ppm.^{11}B NMR (160 MHz, $CDCl_3$) δ 23.90 ppm.

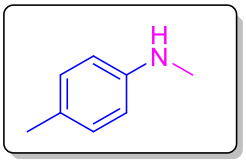
N^1,N^4-dimethyl-N^1,N^4-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzene-1,4-diamine



*(Compound-**2n**):* [2] Compound **2n** was synthesized following the general procedure by reacting 1,4-phenylene diisocyanate (80.0 mg, 0.5 mmol) and pinacolborane (225 µL, 1.5 mmol) for 12 h at 60 ºC (yield: >99%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.23 (s, 4H), 3.08 (s, 6H), 1.33 (s, 72H) ppm. ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 141.1, 119.5, 82.8, 34.5, 24.4, ppm. ^{11}B NMR (160 MHz, $CDCl_3$) δ 24.51 ppm.

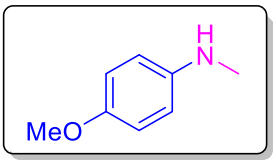
Analytical data for the secondary amine products:

N,4-dimethylaniline: Compound was synthesized following general procedure by reacting **2a**



and methanol for 12 h at 60 ºC (yield: 54 mg (0.445 mmol), 89%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.04 (d, J = 7.5 Hz, 2H), 6.58 (d, J = 7.5 Hz, 2H), 3.22 (s, 1H), 2.84 (s, 3H), 2.28 (s, 3H) ppm. ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 147.2, 129.8, 126.7, 112.8, 31.2, 20.5 ppm. HRMS (ESI) m/z: $[M + H]^+$: Calcd for $C_8H_{11}N$ 122.0970; Found 122.0959.

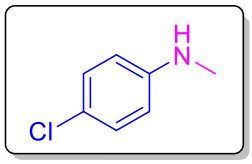
4-methoxy-N-methylaniline:[3] Compound was synthesized following general procedure by



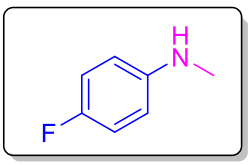
reacting **2b** and methanol for 12 h at 60 ºC (yield: 58.5 mg (0.426 mmol), 85%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.82-6.77 (m, 2H), 6.61-6.57 (m, 2H), 3.73 (s, 3H), 3.09 (s, 1H), 2.78 (s, 3H) ppm. ^{13}C{^{1}H}

NMR (101 MHz, $CDCl_3$) δ 152.3, 143.7, 115.0, 113.8, 56.0, 31.8 ppm. HRMS (ESI) *m/z*: [M + H]$^+$: Calcd for $C_8H_{11}NO$ 138.0919; Found 138.0913.

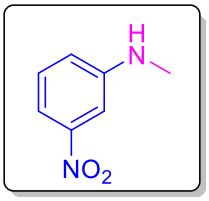
4-chloro-N-methylaniline:[3] Compound was synthesized following general procedure by reacting **2c** and methanol for 12 h at 60 ºC (yield: 58 mg (0.409 mmol), 82%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.18 (d, J = 7.7 Hz, 2H), 6.53 (d, J = 7.7 Hz, 2H), 3.52 (s, 1H), 2.81 (s, 3H) ppm. ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 148.0, 129.1, 121.9, 113.5, 30.9 ppm. HRMS (ESI) *m/z*: [M + H]$^+$: Calcd for C_7H_8ClN 142.0424; Found 142.0411.



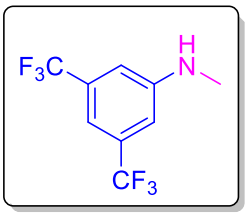
4-fluoro-N-methylaniline: Compound was synthesized following general procedure by reacting **2d** and methanol for 12 h at 60 ºC (yield: 54 mg (0.431 mmol), 86%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.93-6.89 (m, 2H), 6.57-6.54 (m, 2H), 3.37 (s, 1H), 2.81 (s, 3H) ppm. ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 157.1, 154.8, 145.7, 115.8, 115.6, 113.4, 113.3, 31.5 ppm. HRMS (ESI) *m/z*: [M + H]$^+$: Calcd for C_7H_8FN 126.0719; Found 126.0716. ^{19}F NMR (471 MHz, $CDCl_3$) δ -123.84 ppm.



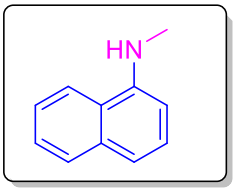
N-methyl-3-nitroaniline: Compound was synthesized following general procedure by reacting **2e** and methanol for 12 h at 60 ºC (yield: 64 mg (0.420 mmol), 84%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 (d, J = 8.1 Hz, 1H), 7.29 (s, 1H), 7.20-7.16 (m, 1H), 6.78 (d, J = 8.1 Hz, 1H), 4.04 (s, 1H), 2.81 (s, 3H) ppm. ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 150.1, 149.6, 129.7, 118.6, 111.8, 105.8, 30.6 ppm. HRMS (ESI) *m/z*: [M + H]$^+$: Calcd for $C_7H_8N_2O_2$ 153.0664; Found 153.0652.



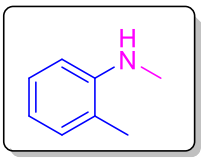
N-methyl-3,5-bis(trifluoromethyl)aniline: Compound was synthesized following general procedure by reacting **2g** and methanol for 12 h at 60 ºC (yield: 101 mg (0.415 mmol), 83%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.15 (s, 1H), 6.92 (s, 2H), 4.16 (s, 1H), 2.90 (s, 3H) ppm. ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 149.9, 132.5 (q, J = 32.1 Hz), 123.8 (q, J = 271.5 Hz), 111.6, 110.1 (q, J = 3.8 Hz), 30.4 ppm. HRMS (ESI) *m/z*: [M + H]$^+$: Calcd for $C_9H_7F_6N$ 244.0561; Found 244.0546. ^{19}F NMR (471 MHz, $CDCl_3$) δ -63.25 ppm.



N-methylnaphthalen-1-amine: Compound was synthesized following general procedure by reacting **2j** and methanol for 12 h at 60 ºC (yield: 66 mg (0.419 mmol), 84%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70-7.64 (m, 2H), 7.36-7.28 (m, 3H), 7.15 (d, J = 8.2 Hz, 1H), 6.49 (d, J = 7.5 Hz, 1H), 4.13 (s, 1H), 2.88 (s, 3H) ppm. ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 144.6, 134.4, 128.8, 126.8, 125.8, 124.8, 123.6, 119.9, 117.5, 104.0, 31.1 ppm. HRMS (ESI) *m*/*z*: $[M + H]^+$: Calcd for $C_{11}H_{11}N$ 158.0970; Found 158.0957.



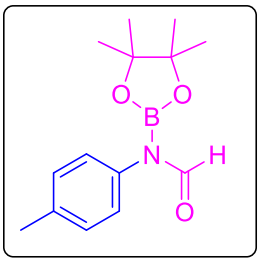
N,2-dimethylaniline: Compound was synthesized following general procedure by reacting **2k** and methanol for 12 h at 60 ºC (yield: 48.5 mg (0.400 mmol), 80%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.22-7.18 (m, 1H), 7.10 (d, *J* = 8.2 Hz, 1H), 6.73-6.70 (m, 1H), 6.66 (d, *J* = 8.2 Hz, 1H), 3.49 (s, 1H), 2.93 (s, 3H), 2.17 (s, 3H) ppm. ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 147.3, 130.0, 127.3, 122.0, 117.0, 109.3, 30.9, 17.5 ppm. HRMS (ESI) *m*/*z*: $[M + H]^+$: Calcd for $C_8H_{11}N$ 122.0970; Found 122.0966.



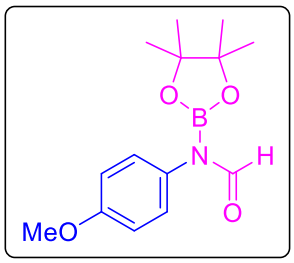
Analytical data for the monohydroboration of isocyanate compounds:

*N-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-N-(p-tolyl)formamide (compound-**3a**):*[2]

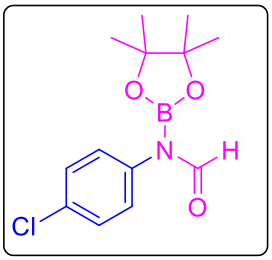
Compound **3a** was synthesized following the general procedure by reacting 4-methylphenyl isocyanate (66.5 mg, 0.5 mmol) and pinacolborane (109 µL, 0.75 mmol) for 12 h at room temperature (yield: 84%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.86 (s, 1H), 7.17 (d, *J* = 7.8 Hz, 2H), 7.02 (d, *J* = 7.8 Hz, 2H), 2.33 (s, 3H), 1.30 (s, 12H) ppm. ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 165.6, 136.8, 129.5, 127.1, 119.9, 84.5, 24.4, 21.0 ppm.



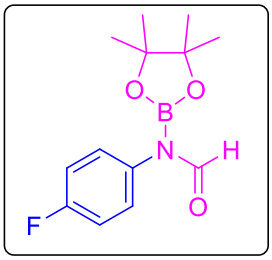
*N-(4-methoxyphenyl)-N-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)formamide (compound-**3b**):* [2] Compound **3b** was synthesized following the general procedure by reacting 4-methoxyphenyl isocyanate (74.5 mg, 0.5 mmol) and pinacolborane (109 µL, 0.75 mmol) for 12 h at room temperature (yield: 90%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.83 (s, 1H), 7.03 (d, *J* = 8.4 Hz, 2H), 6.86 (d, *J* = 8.4 Hz, 2H), 3.74 (s, 3H), 1.28 (s, 12H) ppm. ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 165.6, 158.2, 128.2, 121.4, 114.0, 84.4, 55.2, 24.4 ppm.



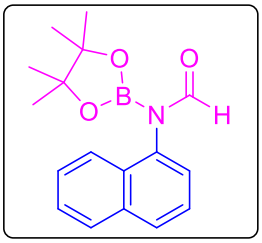
*N-(4-chlorophenyl)-N-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)formamide (compound-**3c**):* [2] Compound **3c** was synthesized following the general procedure by reacting 4-chlorophenyl isocyanate (76.7 mg, 0.5 mmol) and pinacolborane (109 µL, 0.75 mmol) for 3 h at 60 ºC (yield: 70%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.84 (s, 1H), 7.32 (d, J = 8.5 Hz, 2H), 7.09 (d, J = 8.5 Hz, 2H), 1.31 (s, 12H) ppm. $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 165.1, 129.7, 128.9, 128.7, 125.9, 84.8, 24.5 ppm.



*N-(4-fluorophenyl)-N-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)formamide (compound-**3d**):* [2] Compound **3d** was synthesized following the general procedure by reacting 4-fluorophenyl isocyanate (68.5 mg, 0.5 mmol) and pinacolborane (109 µL, 0.75 mmol) for 24 h at room temperature (yield: >95%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.84 (s, 1H), 7.09 (d, J = 8.4 Hz, 2H), 7.04 (d, J = 8.4 Hz, 2H), 1.30 (s, 12H) ppm. $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$) δ 165.3, 162.3, 160.4, 129.0 (d, J = 8.5 Hz), 115.6 (d, J = 22.7 Hz), 84.7, 24.4 ppm.

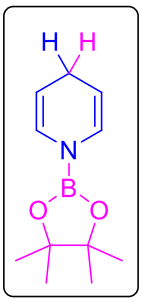


N-(naphthalen-1-yl)-N-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)formamide*(compound-**3j**):* [2] Compound **3j** was synthesized following the general procedure by reacting 1-naphthyl isocyanate (84.6 mg, 0.5 mmol) and pinacolborane (109 µL, 0.75 mmol) for 12 h at room temperature (yield: 54%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.16 (s, 1H), 8.09 (d, J = 8.3 Hz, 1H), 7.88-7.82 (m, 3H), 7.76 (d, J = 7.9 Hz, 1H), 7.69 (d, J = 8.3 Hz, 1H), 7.39-7.35 (m, 1H), 1.30 (s, 12H) ppm. $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 165.5, 134.3, 128.4, 128.2, 126.7, 126.5, 126.0, 125.6, 125.4, 122.5, 121.9, 83.2, 24.8 ppm.



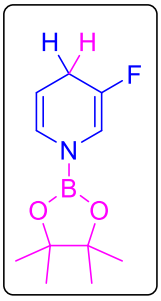
Analytical data for the pyridine hydroboration and hydrogenation of heteroaromatic compounds:

*1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1,4-dihydropyridine (compound-**5a**):*[4]

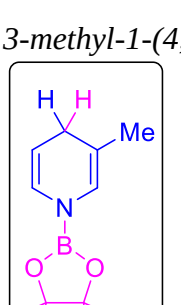


Compound **5a** was synthesized following the general procedure by reacting pyridine (39.5 mg, 0.5 mmol) and pinacolborane (87 μL, 0.6 mmol) for 24 h at 60 ºC (yield: >95%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.18 (d, J = 8.2 Hz, 2H), 4.61-4.59 (m, 2H), 2.86 (m, 2H), 1.23 (s, 12H) ppm. ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 127.1, 102.3, 83.4, 24.6, 22.3 ppm. ^{11}B NMR (160 MHz, $CDCl_3$) δ 23.41 ppm.

*3-fluoro-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1,4-dihydropyridine (compound-**5b**):* [6] Compound **5b** was synthesized following the general procedure by reacting 3-fluoropyridine (48.5 mg, 0.5 mmol) and pinacolborane (109 μL, 0.75 mmol) for 24 h at 60 ºC (yield: >95%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.27 (d, J = 10.5 Hz, 1H), 6.17 (d, J = 7.9 Hz, 1H), 4.75-4.69 (m, 1H), 3.13 (m, 2H), 1.27 (s, 12H) ppm. ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 146.5 (d, J = 241.8 Hz), 126.5 (d, J = 2.1 Hz), 110.2 (d, J = 38.1 Hz), 101.3 (d, J = 15.0 Hz), 83.2, 24.6, 22.8 ppm. ^{11}B NMR (160 MHz, $CDCl_3$) δ 23.64 ppm.

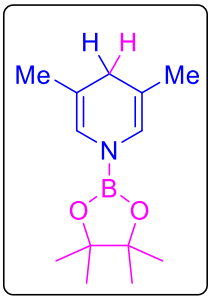


*3-methyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1,4-dihydropyridine (compound-**5c**):* [4] Compound **5c** was synthesized following the general procedure by reacting 3-methylpyridine (46.5 mg, 0.5 mmol) and pinacolborane (109 μL, 0.75 mmol) for 48 h at 60 ºC (yield: >50%).^{1}H NMR (400 MHz, $CDCl_3$) δ 6.27 (d, J = 8.2 Hz, 1H), 6.17 (d, J = 8.0 Hz, 1H), 4.74-4.69 (m, 1H), 3.13 (s, 2H), 1.37 (s, 3H), 1.27 (s, 12 H) ppm. ^{11}B NMR (160 MHz, $CDCl_3$) δ 23.46 ppm.



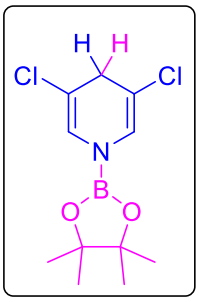
*3-phenyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1,4-dihydropyridine (compound-**5d**):*[7] Compound **5d** was synthesized following the general procedure by reacting 3-phenylpyridine (77.6 mg, 0.5 mmol) and pinacolborane (109 μL, 0.75 mmol) for 24 h at 60 ºC (yield: >99%).^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36-7.33 (m, 2H), 7.29-7.25 (m, 2H), 7.18-7.13 (m, 1H), 6.83 (s, 1H), 6.31 (d, J = 7.0 Hz, 1H), 4.88–4.84 (m, 1H), 3.22 (s, 2H), 1.25 (s, 12H) ppm. ^{11}B NMR (160 MHz, $CDCl_3$) δ 24.16 ppm.

3,5-dimethyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1,4-dihydropyridine

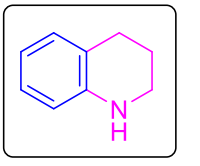


*(compound-**5e**):*[4] Compound **5e** was synthesized following the general procedure by reacting 3,5-dimethylpyridine (53.5 mg, 0.5 mmol) and pinacolborane (109 µL, 0.75 mmol) for 24 h at 60 ºC (yield: 65%).^{1}H NMR (500 MHz, $CDCl_3$) δ 5.99 (s, 2H), 2.54 (s, 2H), 1.47 (s, 6H), 1.17 (s, 12H) ppm. ^{11}B NMR (160 MHz, $CDCl_3$) δ 23.80 ppm.

*3,5-dichloro-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1,4-dihydropyridine compound-**5f**):*[5] Compound **5f** was synthesized following the general procedure by reacting 3,5-dichloropyridine (74.0 mg, 0.5 mmol) and pinacolborane (109 µL, 0.75 mmol) for 24 h at 60 ºC (yield: >99%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.45 (s, 2H), 3.31 (s, 2H), 1.25 (s, 12H) ppm. ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 123.9, 110.1, 84.4, 37.7, 24.6 ppm. ^{11}B NMR (160 MHz, $CDCl_3$) δ 23.46 ppm.

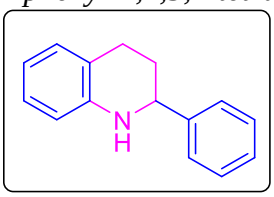


*1,2,3,4-tetrahydroquinoline (Compound-**5g**):* Compound **5g** was synthesized following the general procedure by reacting quinoline (64.6 mg, 0.5 mmol) and pinacolborane (218 µL, 1.5 mmol) for 24 h at 60 ºC (yield: 40 mg (0.300 mmol), 60%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.99-6.95 (m, 2H), 6.61 (t, J = 7.3 Hz, 1H), 6.48 (d, J = 7.8 Hz, 1H), 3.81 (s, 1H), 3.31 (t, J = 5.5 Hz, 2H), 2.78 (t, J = 6.4 Hz, 2H), 1.98–1.92 (m, 2H) ppm. ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 144.9, 129.6, 126.8, 121.6, 117.1, 114.3, 42.1, 27.1, 22.3 ppm. HRMS (ESI) *m*/*z*: $[M + H]^+$: Calcd for $C_9H_{11}NH$ 134.0970; Found 134.0961.



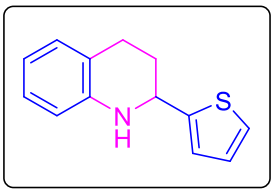
*2-methyl-1,2,3,4-tetrahydroquinoline (Compound-**5h**):* Compound **5h** was synthesized following the general procedure by reacting 2-methyl quinoline (71.6 mg, 0.5 mmol) and pinacolborane (218 µL, 1.5 mmol) for 24 h at 60 ºC (yield: 45 mg (0.305 mmol), 61%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.99-6.97 (m, 2H), 6.63 (t, J = 7.3 Hz, 1H), 6.49 (d, J = 7.9 Hz, 1H), 3.65 (s, 1H), 3.44-3.39 (m, 1H), 2.90-2.73 (m, 2H), 1.97-1.56 (m, 2H), 1.23 (d, J = 6.2 Hz, 3H) ppm. ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 144.9, 129.4, 126.8, 121.2, 117.1, 114.1, 47.3, 30.3, 26.7, 22.7 ppm. HRMS (ESI) *m*/*z*: $[M + H]^+$: Calcd for $C_{10}H_{13}NH$ 148.1126; Found 148.1116.

*2-phenyl-1,2,3,4-tetrahydroquinoline (Compound-**5i**):* Compound **5i** was synthesized



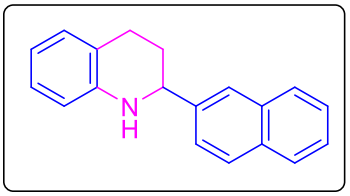
following the general procedure by reacting 2-phenyl quinoline (102.6 mg, 0.5 mmol) and pinacolborane (167 μL, 1.15 mmol) for 24 h at 60 ºC (yield: 58 mg (0.277 mmol), 55%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40-7.28 (m, 5H), 7.03-6.99 (m, 2H), 6.65 (t, J = 7.2 Hz, 1H), 6.54 (d, J = 7.5 Hz, 1H), 4.45-4.43 (m, 1H), 4.04 (s, 1H), 2.95-2.72 (m, 2H), 2.11–1.99 (m, 2H) ppm. ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 148.6, 147.7, 145.8, 135.4, 126.8, 124.8, 124.0, 121.3, 109.0, 108.3, 100.9, 69.4, 41.0, 31.8 ppm. HRMS (ESI) *m*/*z*: $[M + H]^+$: Calcd for $C_{15}H_{15}NH$ 210.1283; Found 210.1273.

*2-(thiophen-2-yl)-1,2,3,4-tetrahydroquinoline (Compound-**5j**):* Compound **5j** was synthesized



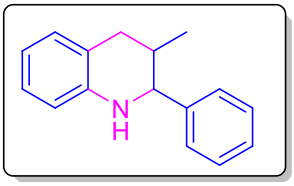
following the general procedure by reacting 2-(thiophen-2-yl) quinoline (105.6 mg, 0.5 mmol) and pinacolborane (167 μL, 1.15 mmol) for 24 h at 60 ºC (yield: 65 mg (0.301 mmol), 60%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (s, 1H), 7.42-7.38 (m, 1H), 7.19-7.16 (m, 1H), 6.99-6.92 (m, 2H), 6.61-6.57 (m, 1H), 6.41 (d, J = 8.3 Hz, 1H), 5.26 (s, 1H), 4.67 (s, 2H), 1.27-1.22 (m, 3H) ppm. ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 158.2, 148.0, 142.7, 137.6, 126.8, 125.2, 124.6, 113.4, 107.2, 41.3, 24.9, 24.6 ppm. HRMS (ESI) *m*/*z*: $[M + NH_4]^+$: Calcd for $C_{13}H_{13}NSNH_4$ 233.1112; Found 233.1090.

*2-(naphthalen-2-yl)-1,2,3,4-tetrahydroquinoline (compound-**5k**):* Compound **5k** was



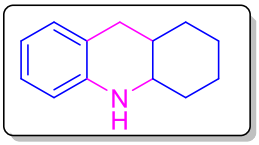
synthesized following the general procedure by reacting 2-(naphthalen-2-yl) quinoline (127.6 mg, 0.5 mmol) and pinacolborane (218 μL, 1.5 mmol) for 24 h at 60 ºC (yield: 83 mg (0.320 mmol), 64%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85-7.82 (m, 4H), 7.54-7.47 (m, 3H), 7.04-7.03 (m, 2H), 6.70 (t, J = 7.3 Hz, 1H), 6.60 (d, J = 8.1 Hz, 1H), 4.63-4.60 (m, 1H), 4.10 (s, 1H), 3.01-2.75 (m, 2H), 2.23-2.06 (m, 2H) ppm. ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 142.2, 133.6, 133.1, 129.5, 128.5, 128.0, 127.8, 127.1, 126.3, 125.9, 125.3, 125.0, 121.3, 117.6, 114.4, 56.5, 31.0, 26.5 ppm. HRMS (ESI) *m*/*z*: $[M + H]^+$: Calcd for $C_{19}H_{17}NH$ 260.1439; Found 260.1422.

*3-methyl-2-phenyl-1,2,3,4-tetrahydroquinoline (compound-**5l**):* Compound **5l** was synthesized following the general procedure by reacting 3-methyl-2-phenylquinoline (109.6 mg, 0.5 mmol) and pinacolborane (218 μL, 1.5 mmol) for 24 h at 60 ºC (yield: 65 mg (0.291 mmol), 58%).



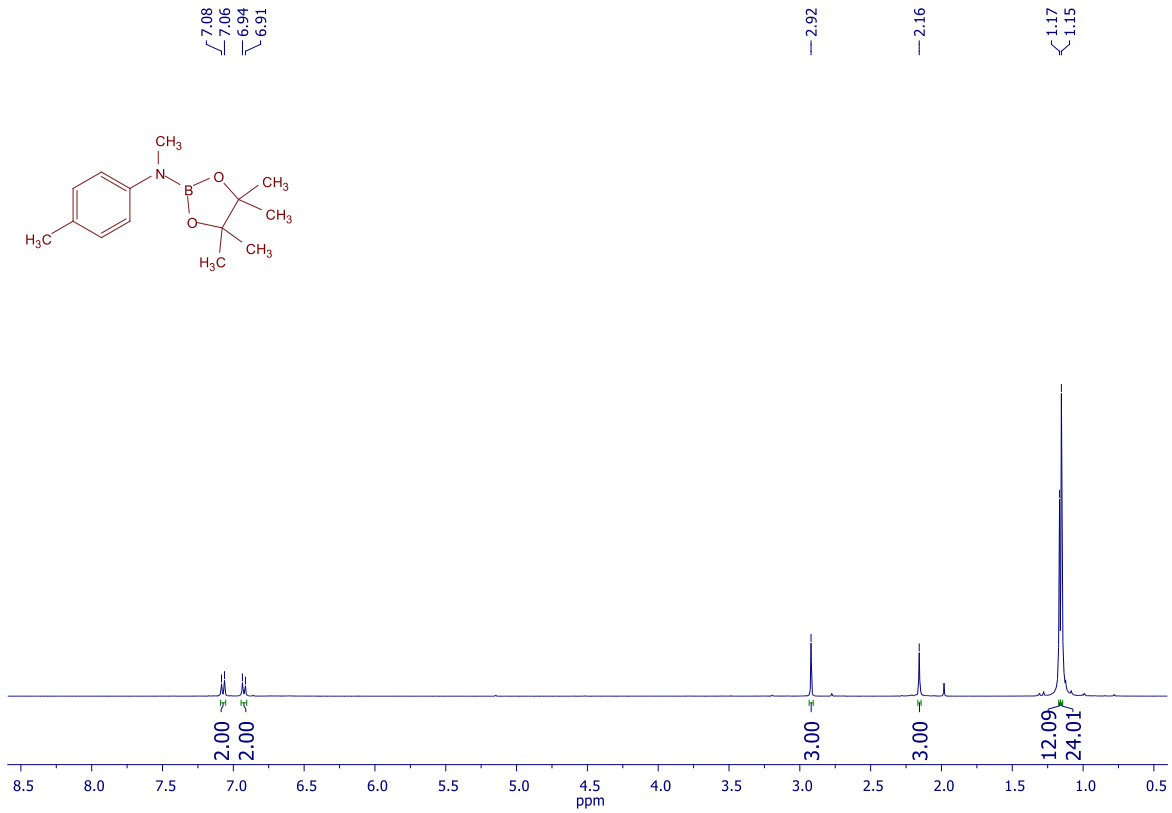
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24-7.17 (m, 5H), 6.96-6.90 (m, 2H), 6.57 (t, J = 7.3 Hz, 1H), 6.48 (d, J = 7.9 Hz, 1H), 4.43 (d, J = 3.1 Hz, 1H), 2.92-2.86 (m, 1H), 2.45-2.39 (m, 1H), 2.25-2.20 (m, 1H), 0.74 (d, J = 6.8 Hz, 3H) ppm. ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 144.3, 143.1, 129.9, 128.3, 127.3, 127.3, 127.0, 120.2, 117.2, 113.8, 59.5, 33.5, 32.1, 15.3 ppm. HRMS (ESI) *m*/*z*: $[M + H]^+$: Calcd for $C_{16}H_{17}NH$ 224.1439; Found 224.1431.

*1,2,3,4,4^a,9,9^a,10-octahydroacridine (compound-**5m**):* Compound **5m** was synthesized following the general procedure by reacting 1,2,3,4-tetrahydroacridine (91.6 mg, 0.5 mmol) and pinacolborane (218 μL, 1.5 mmol) for 24 h at 60 ºC (yield: 47 mg (0.251 mmol), 50%).

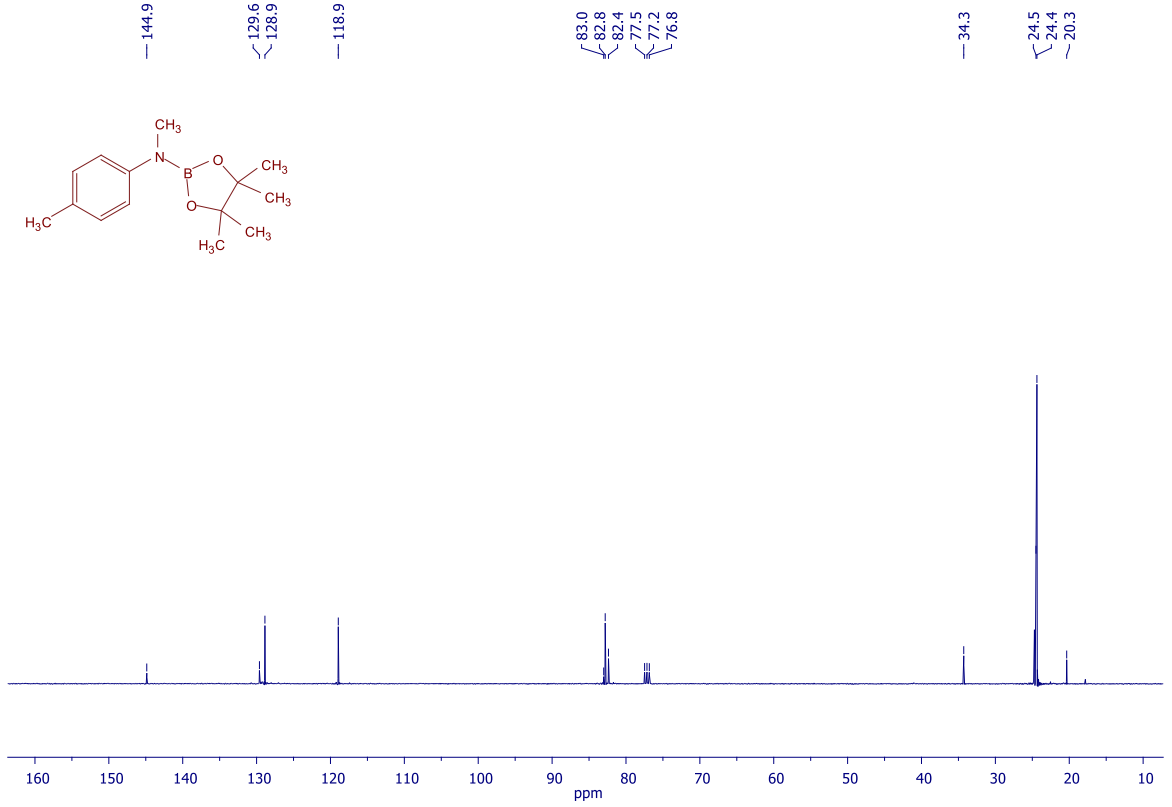


^{1}H NMR (500 MHz, $CDCl_3$) δ 6.97-6.93 (m, 2H), 6.59-6.56 (m, 1H), 6.46 (d, J = 7.9 Hz, 1H), 3.52-3.50 (m, 1H), 2.92-2.88 (m, 1H), 2.54-2.50 (m, 1H), 2.00-1.94 (m, 1H), 1.70-1.59 (m, 6H), 1.45-1.37 (m, 3H) ppm. ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 143.9, 129.9, 126.7, 119.6, 116.7, 113.5, 50.2, 33.1, 31.8, 29.8, 27.4, 24.8, 20.9 ppm. HRMS (ESI) *m*/*z*: $[M + H]^+$: Calcd for $C_{13}H_{17}NH$ 188.1439; Found 188.1433.

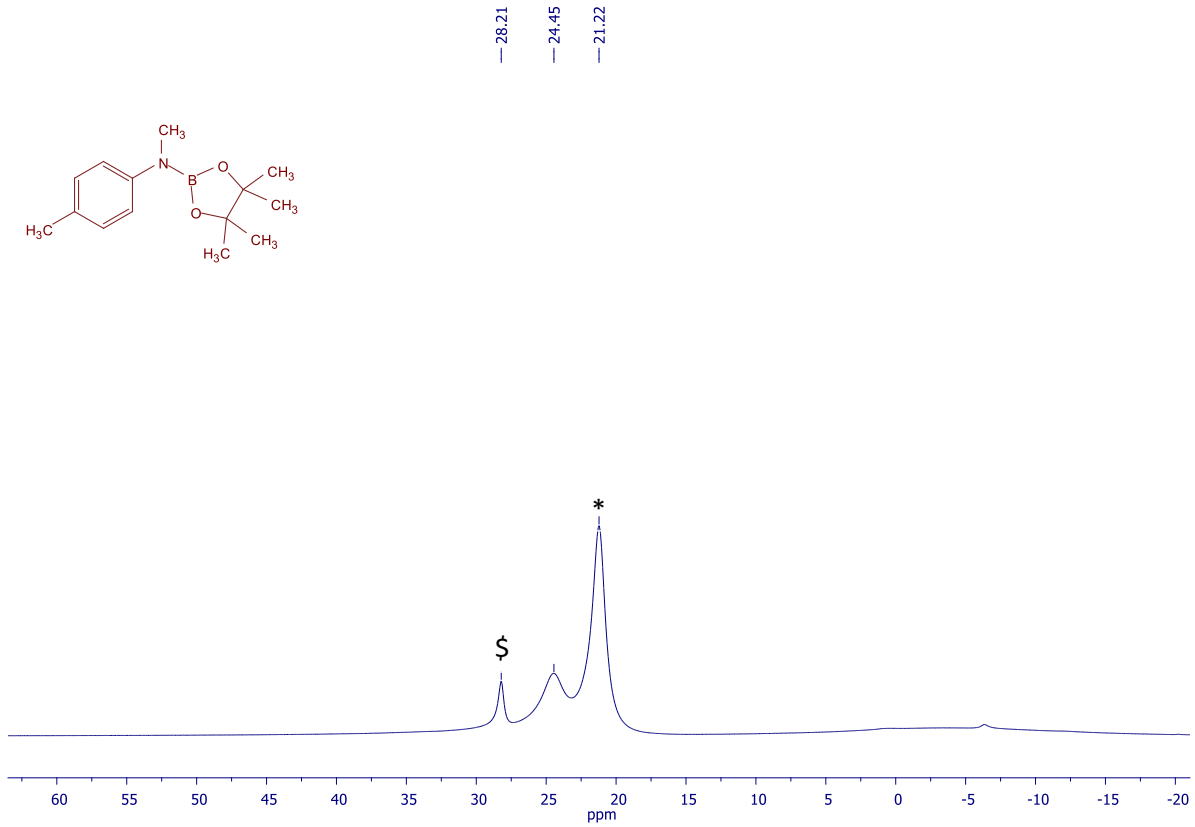
^{1}H, ^{13}C{^{1}H} and ^{11}B NMR spectra of isocyanate hydroborated products in $CDCl_3$ using hexamethylbenzene as an internal standard (#):



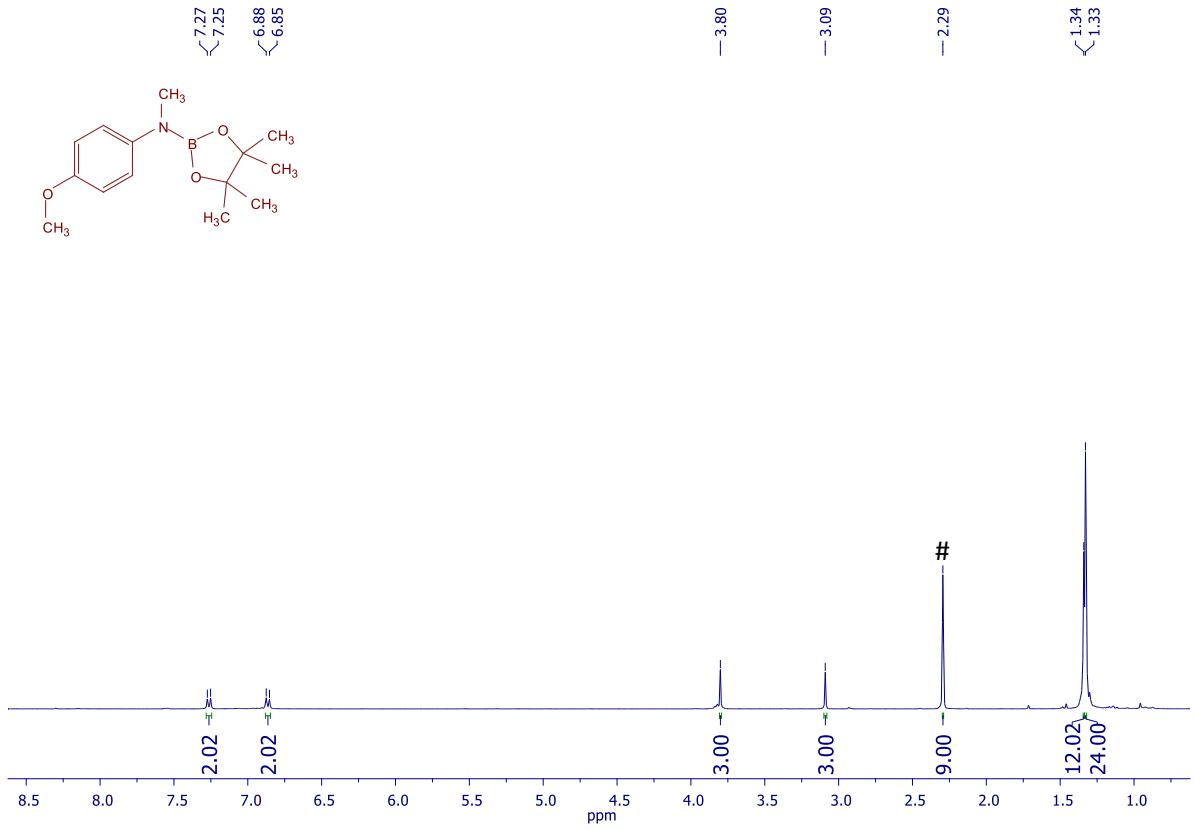
*^{1}H NMR spectrum of N,4,4,5,5-pentamethyl-N-(p-tolyl)-1,3,2-dioxaborolan-2-amine (Compound-**2a**)*



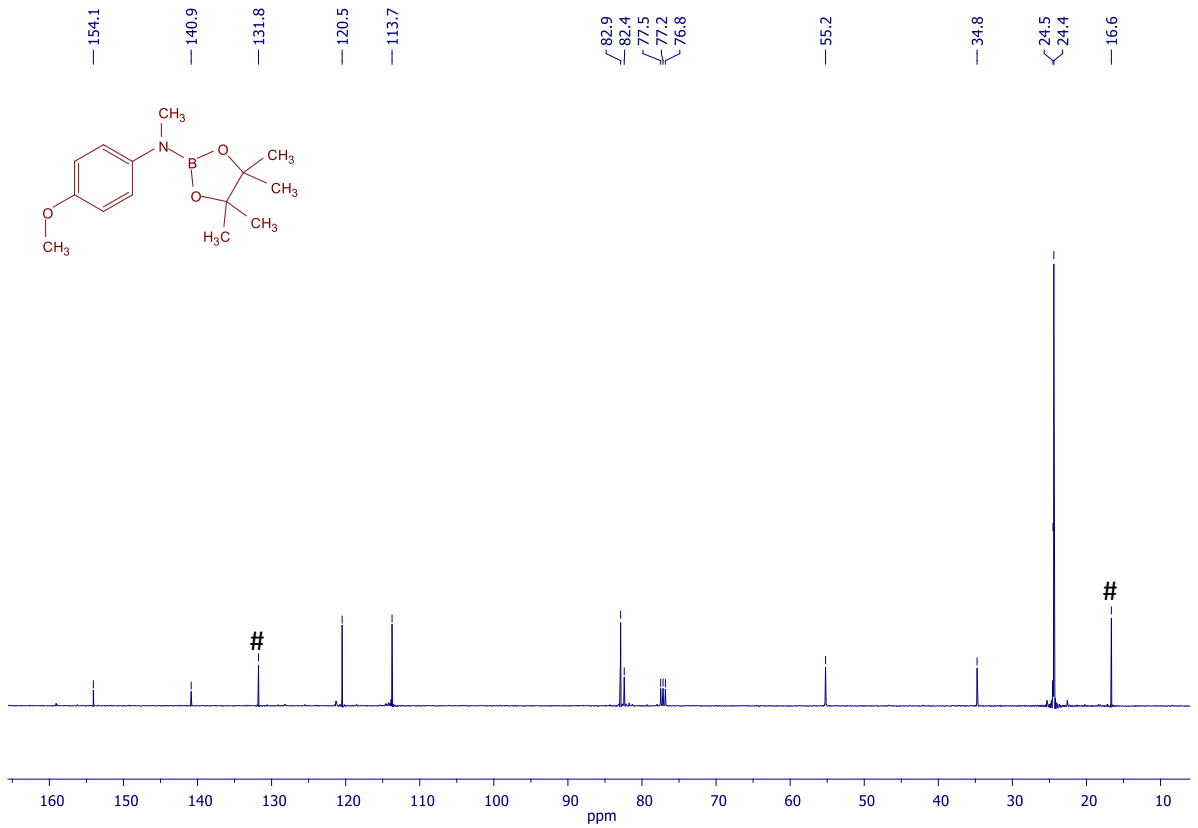
*^{13}C {^{1}H} NMR spectrum of N,4,4,5,5-pentamethyl-N-(p-tolyl)-1,3,2-dioxaborolan-2-amine (Compound-**2a**)*



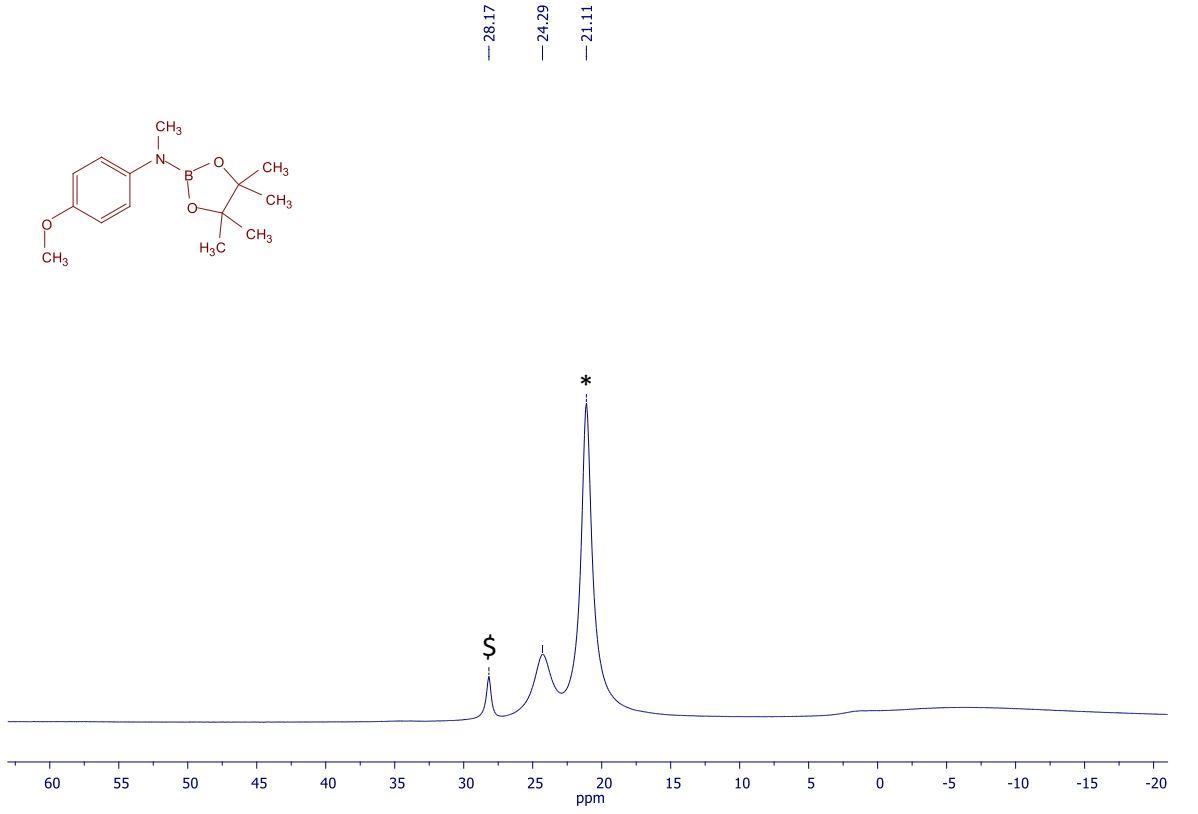
*^{11}B NMR spectrum of N,4,4,5,5-pentamethyl-N-(p-tolyl)-1,3,2-dioxaborolan-2-amine (Compound-**2a**), $ indicates the excess HBpin and * indicates the byproduct $(Bpin)_2O$.*



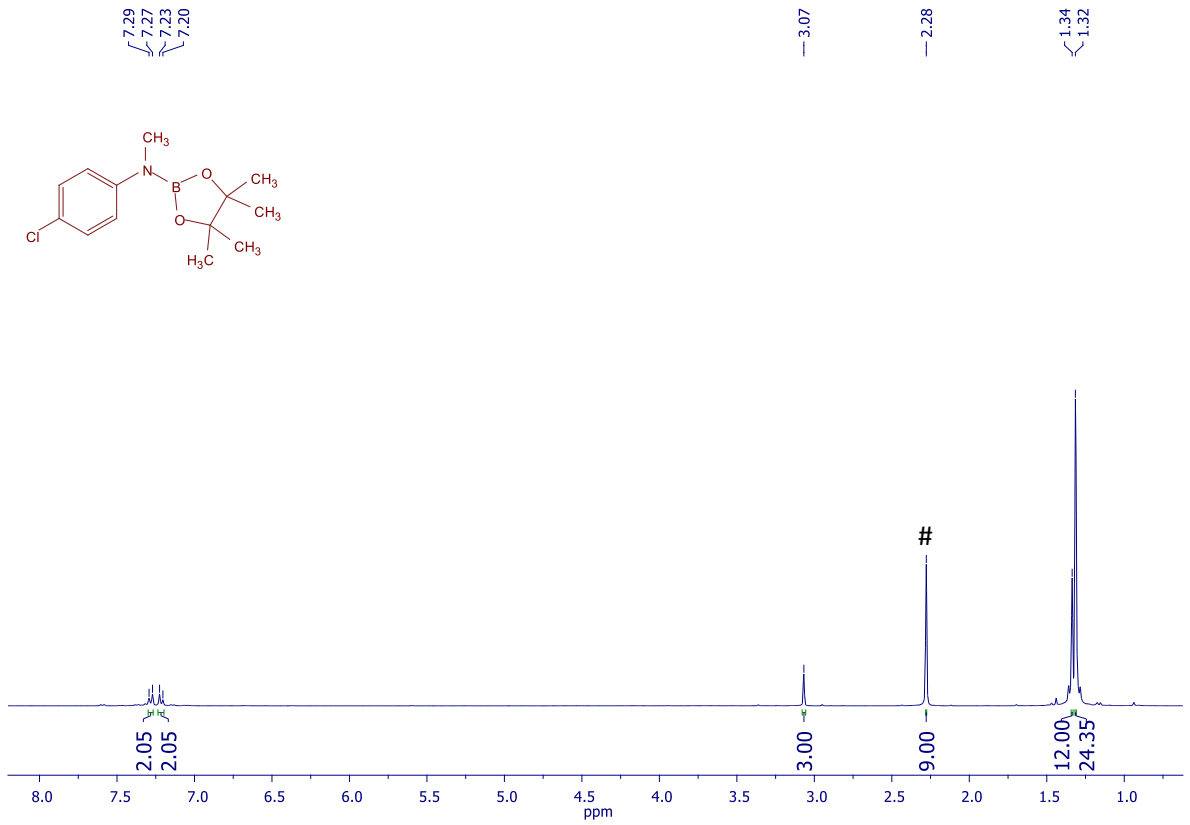
*^{1}H NMR spectrum of N-(4-methoxyphenyl)-N,4,4,5,5-pentamethyl-1,3,2-dioxaborolan-2-amine (Compound-**2b**)*



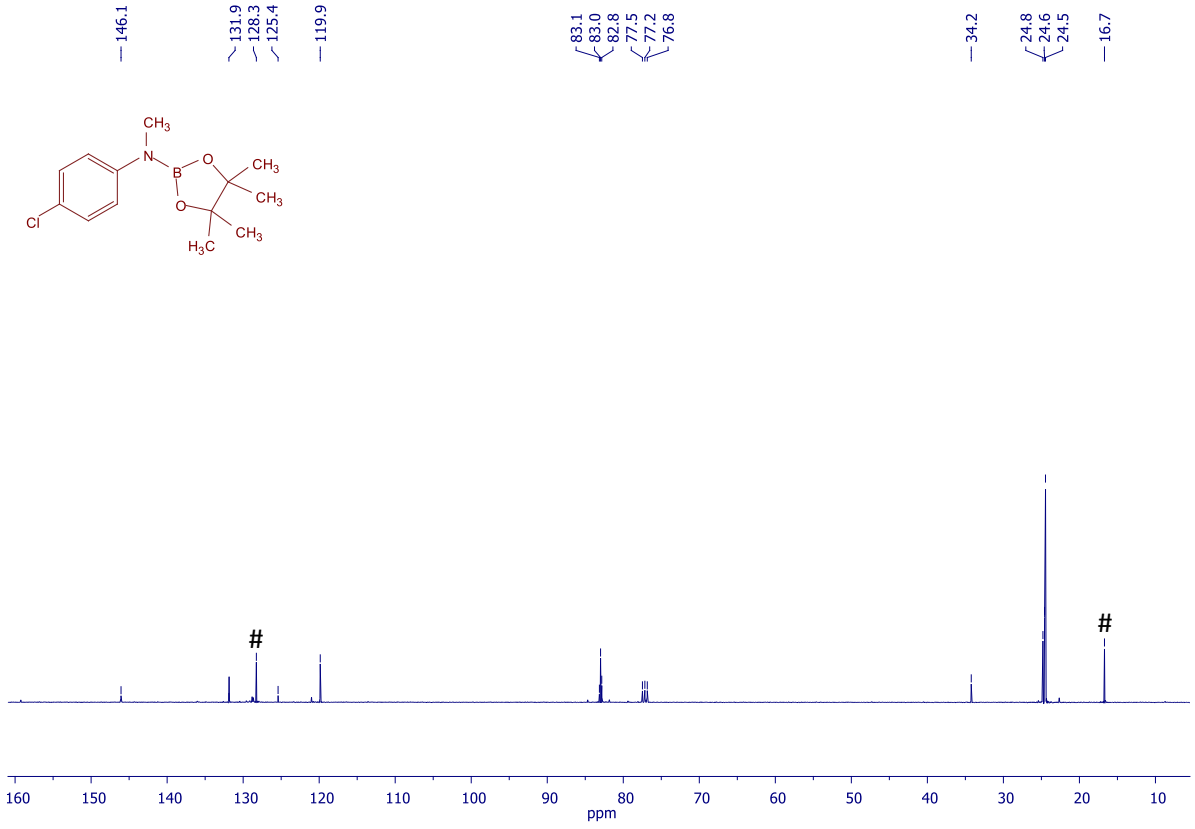
*^{13}C {^{1}H} NMR spectrum of N-(4-methoxyphenyl)-N,4,4,5,5-pentamethyl-1,3,2-dioxaborolan-2-amine (Compound-**2b**)*



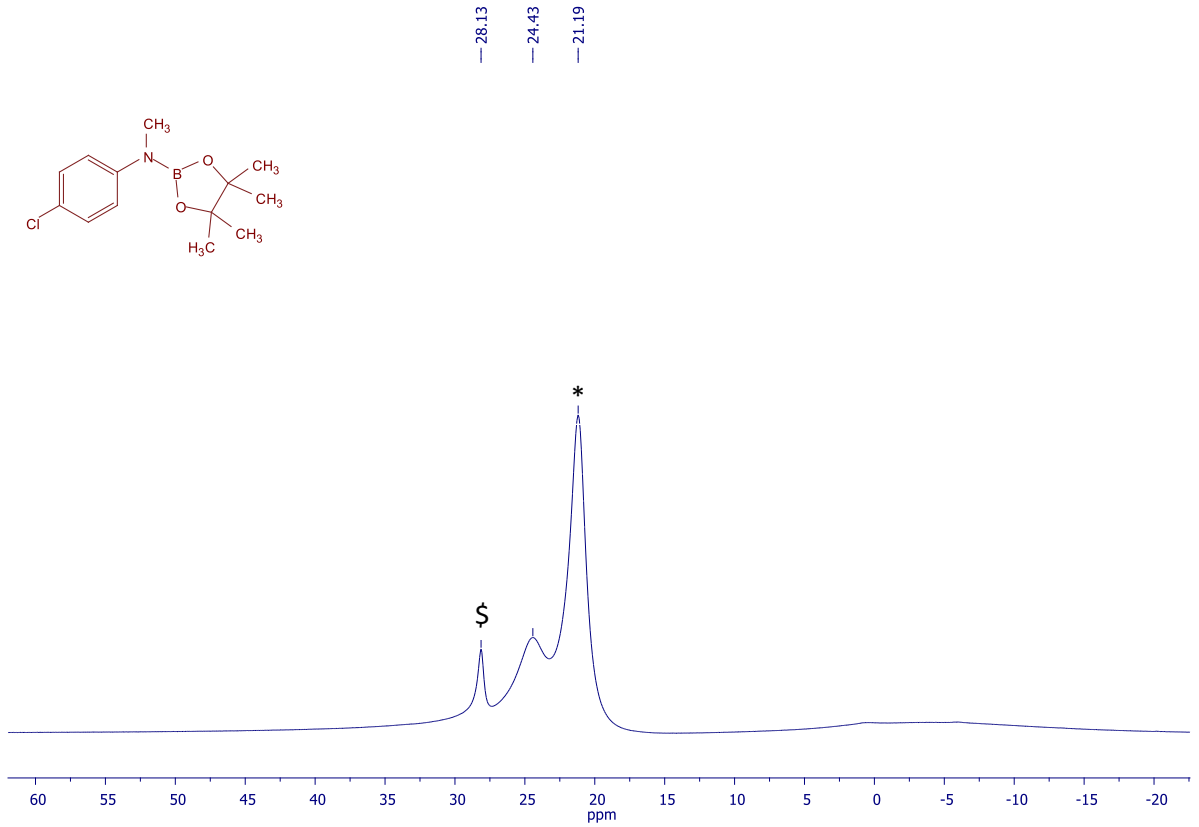
*^{11}B NMR spectrum of N-(4-methoxyphenyl)-N,4,4,5,5-pentamethyl-1,3,2-dioxaborolan-2-amine (Compound-**2b**), $ indicates the excess of HBpin and * indicates the byproduct $(Bpin)_2O$.*



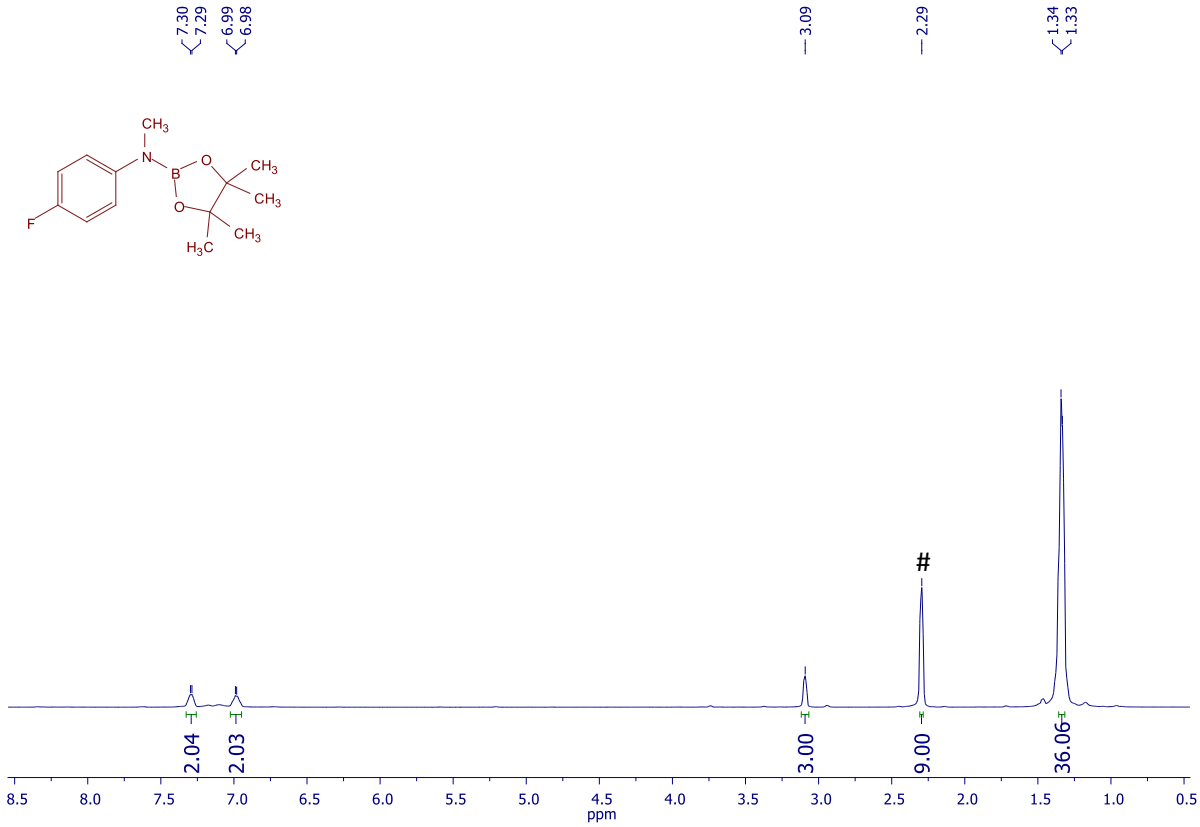
*^{1}H NMR spectrum of N-(4-chlorophenyl)-N,4,4,5,5-pentamethyl-1,3,2-dioxaborolan-2-amine (Compound-**2c**)*



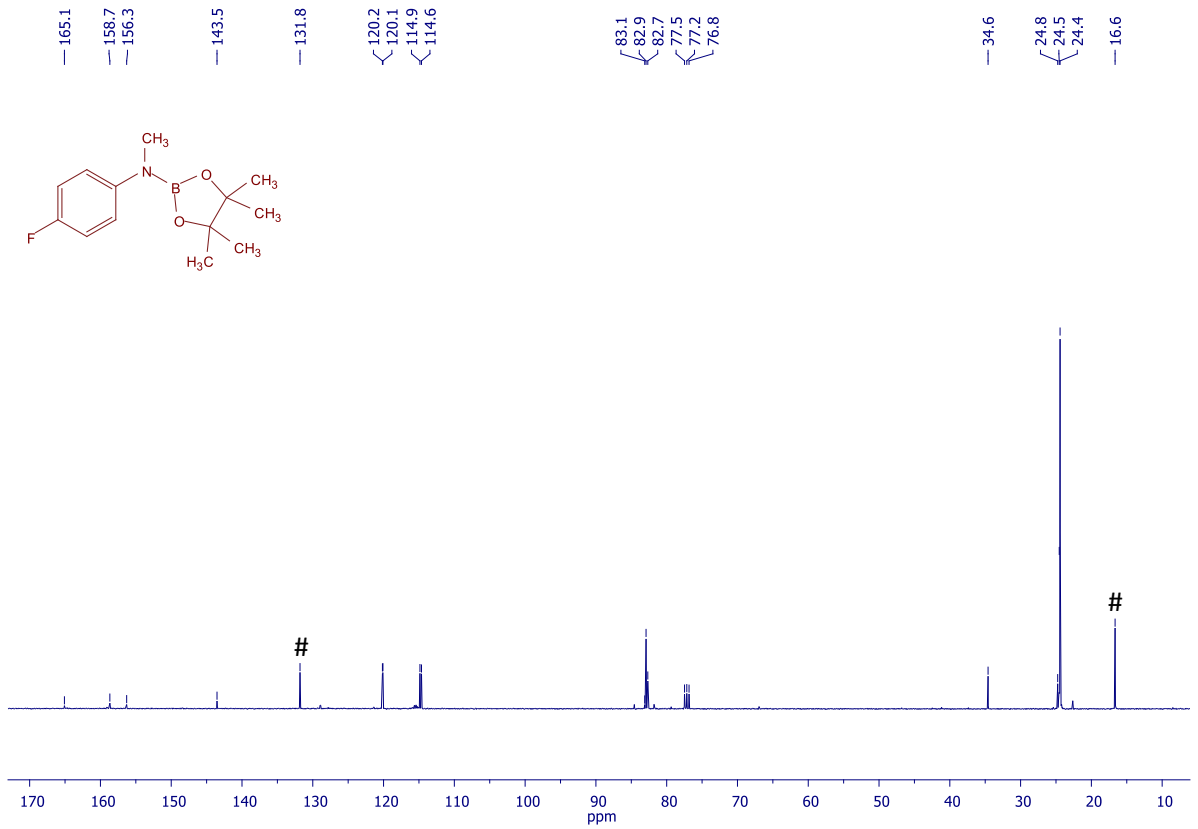
*^{13}C {^{1}H} NMR spectrum of N-(4-chlorophenyl)-N,4,4,5,5-pentamethyl-1,3,2-dioxaborolan-2-amine (Compound-**2c**)*



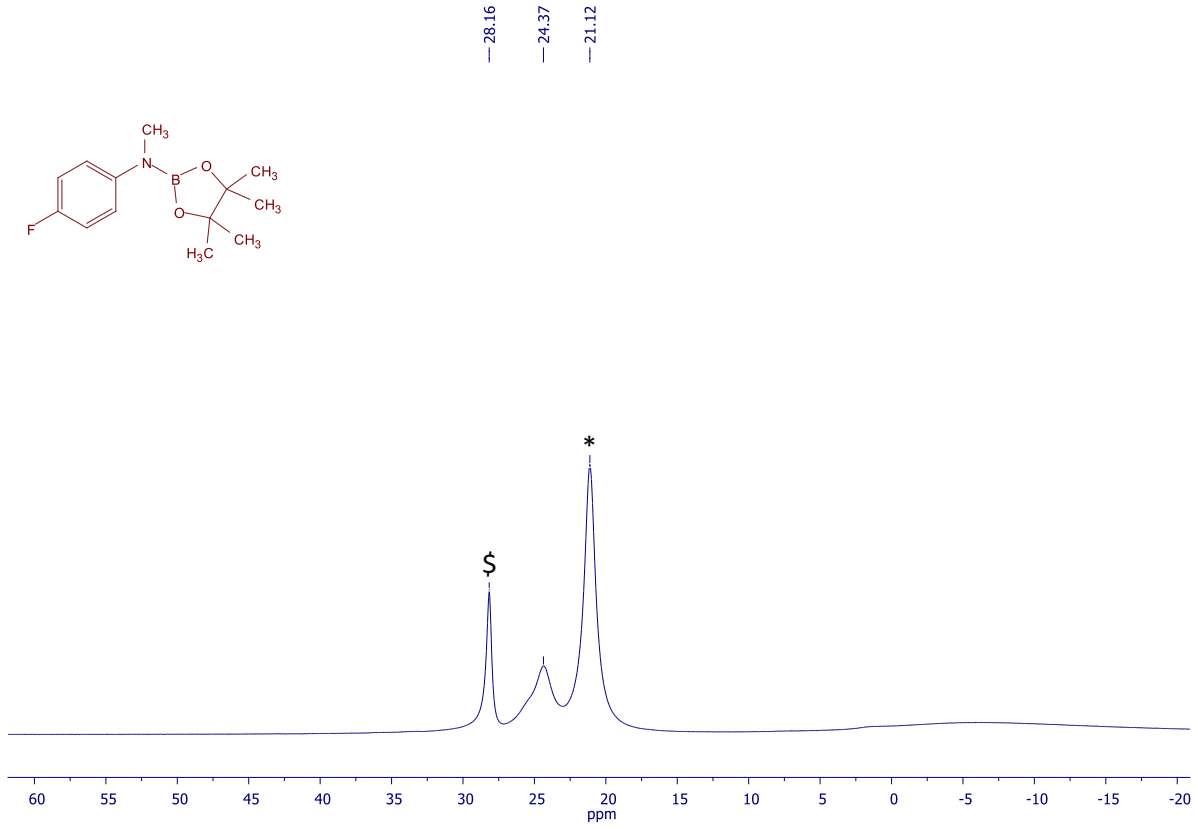
*^{11}B NMR spectrum of N-(4-chlorophenyl)-N,4,4,5,5-pentamethyl-1,3,2-dioxaborolan-2-amine (Compound-**2c**), $ indicates the excess of HBpin and * indicates the byproduct $(Bpin)_2O$.*



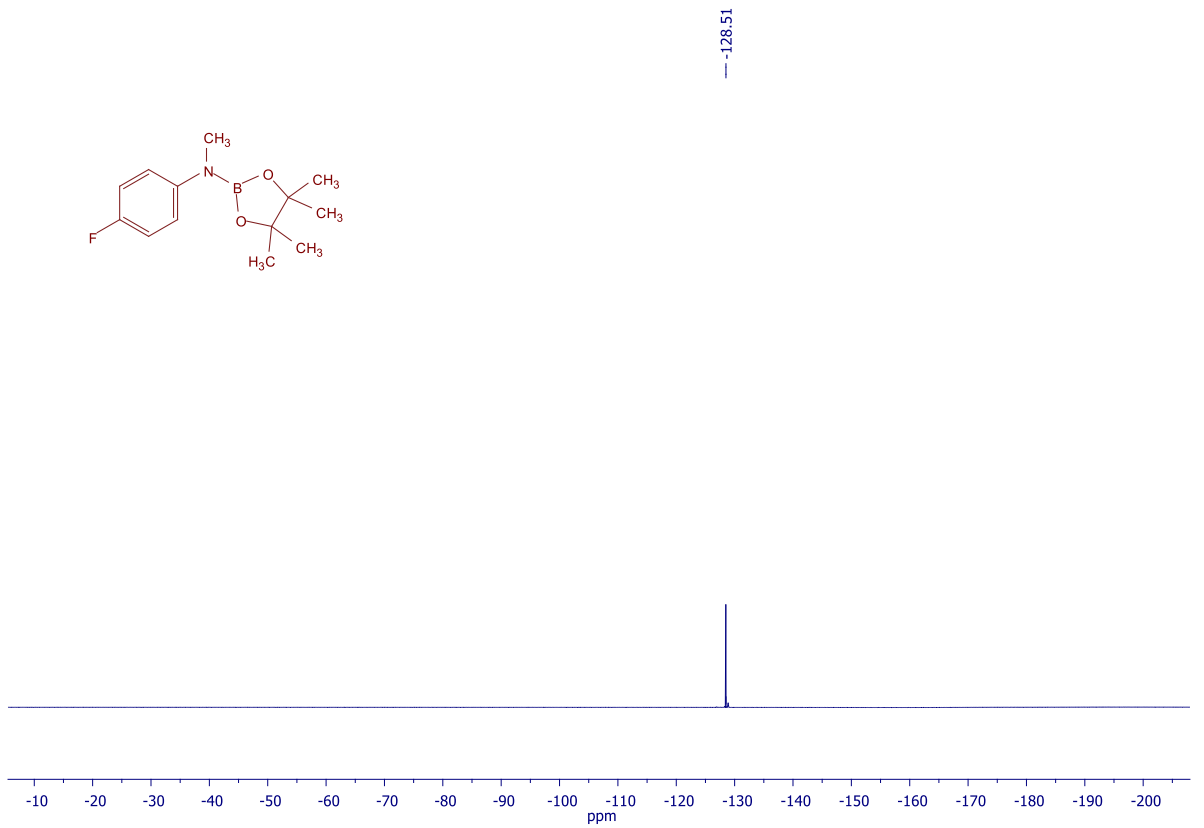
*^{1}H NMR spectrum of N-(4-fluorophenyl)-N,4,4,5,5-pentamethyl-1,3,2-dioxaborolan-2-amine (Compound-**2d**)*



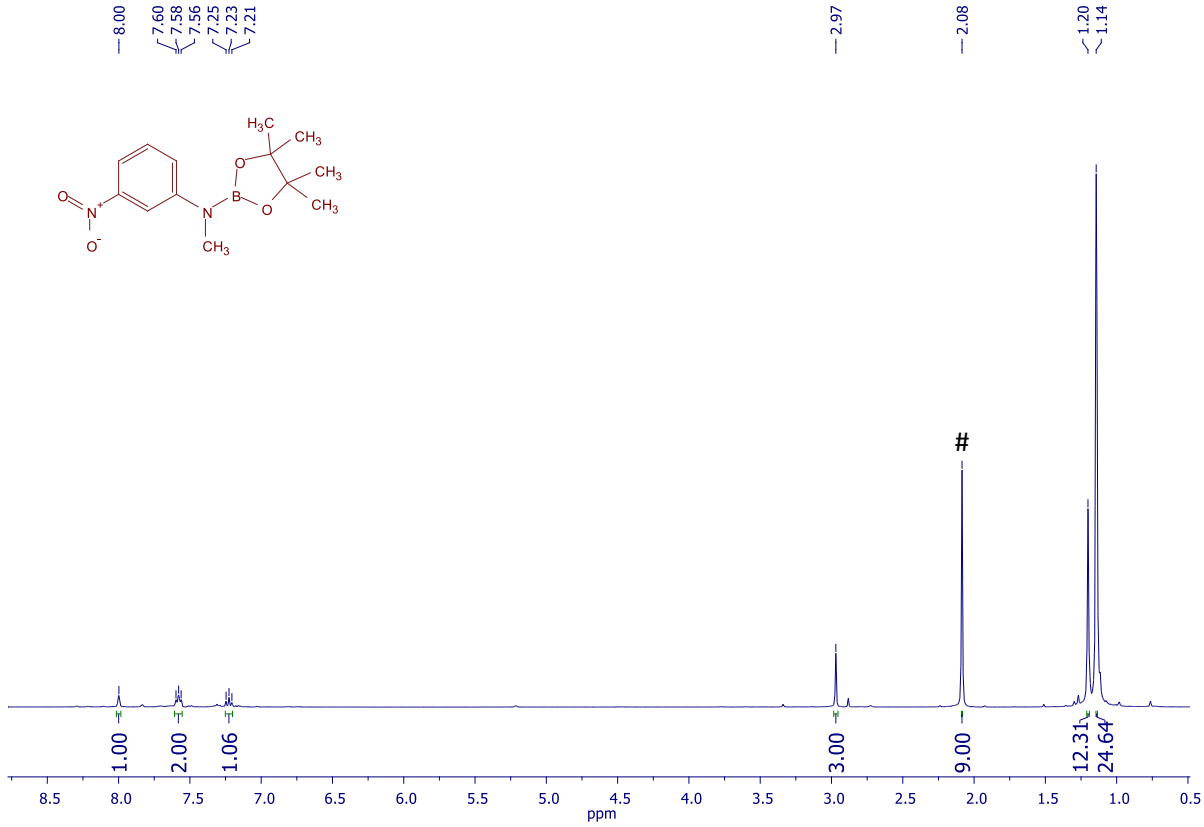
*^{13}C {^{1}H} NMR spectrum of N-(4-fluorophenyl)-N,4,4,5,5-pentamethyl-1,3,2-dioxaborolan-2-amine (Compound-**2d**)*



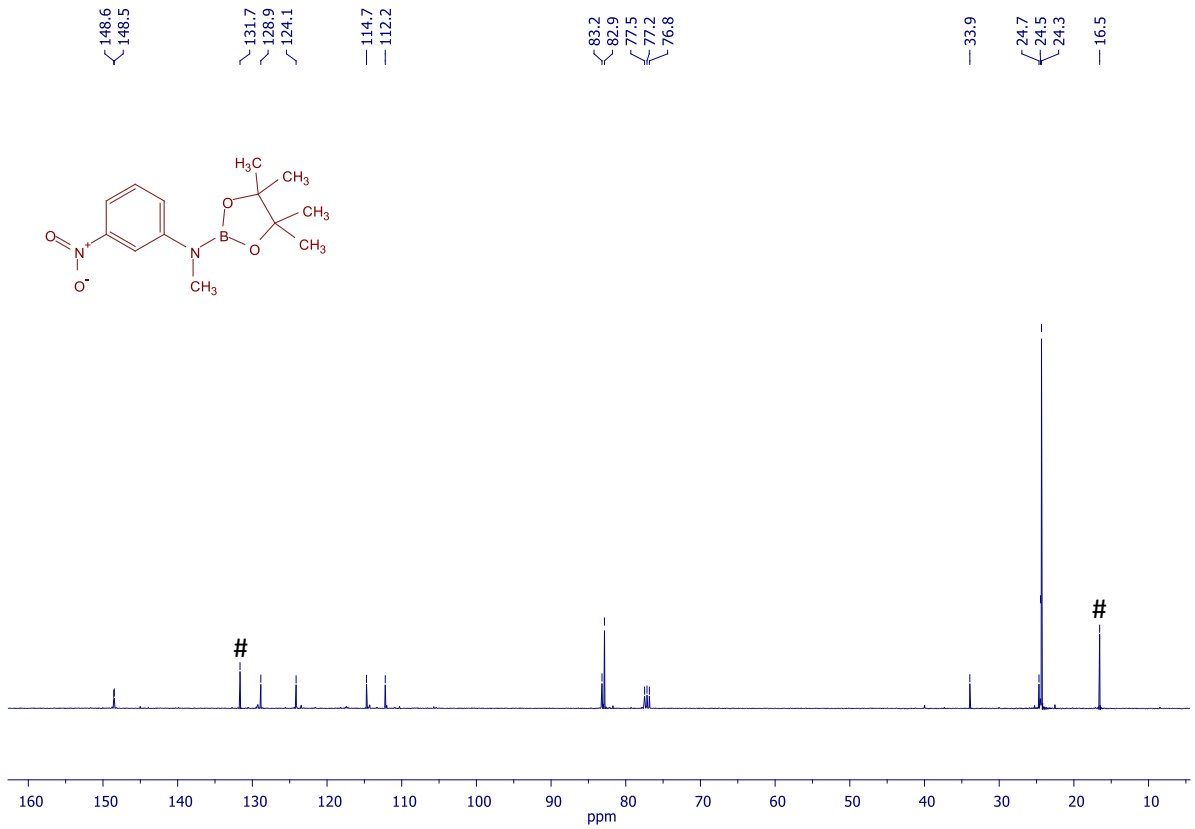
*^{11}B NMR spectrum of N-(4-fluorophenyl)-N,4,4,5,5-pentamethyl-1,3,2-dioxaborolan-2-amine (Compound-**2d**), $ indicates the excess of HBpin and * indicates the byproduct $(Bpin)_2O$.*



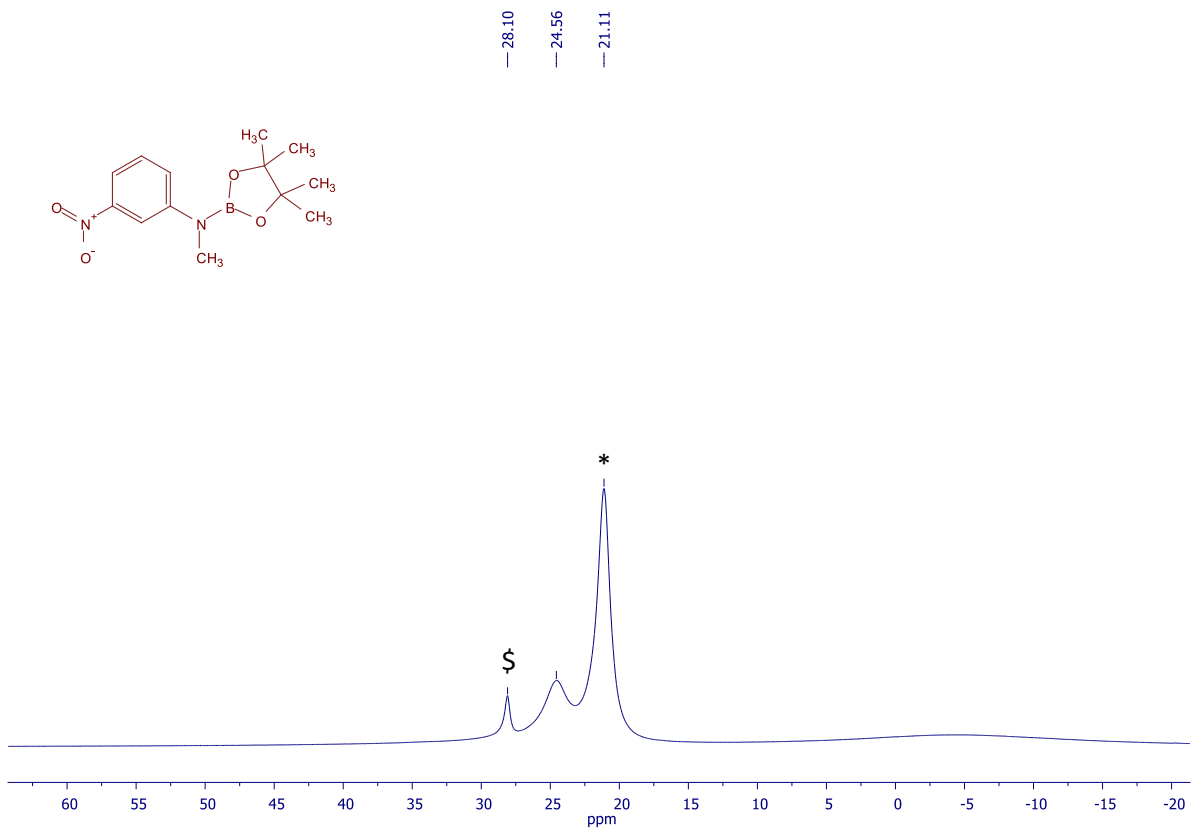
*^{19}F NMR spectrum of N-(4-fluorophenyl)-N,4,4,5,5-pentamethyl-1,3,2-dioxaborolan-2-amine (Compound-**2d**)*



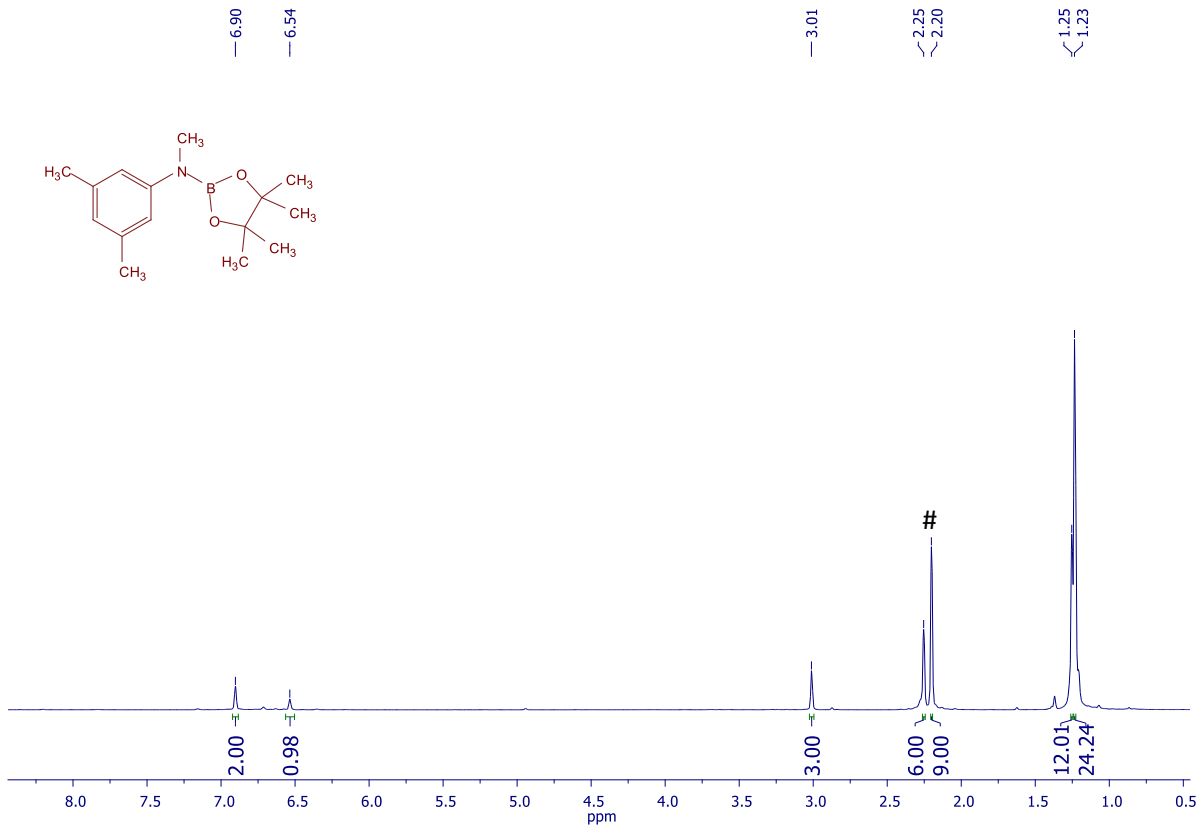
*^{1}H NMR spectrum of N,4,4,5,5-pentamethyl-N-(3-nitrophenyl)-1,3,2-dioxaborolan-2-amine (Compound-**2e**)*



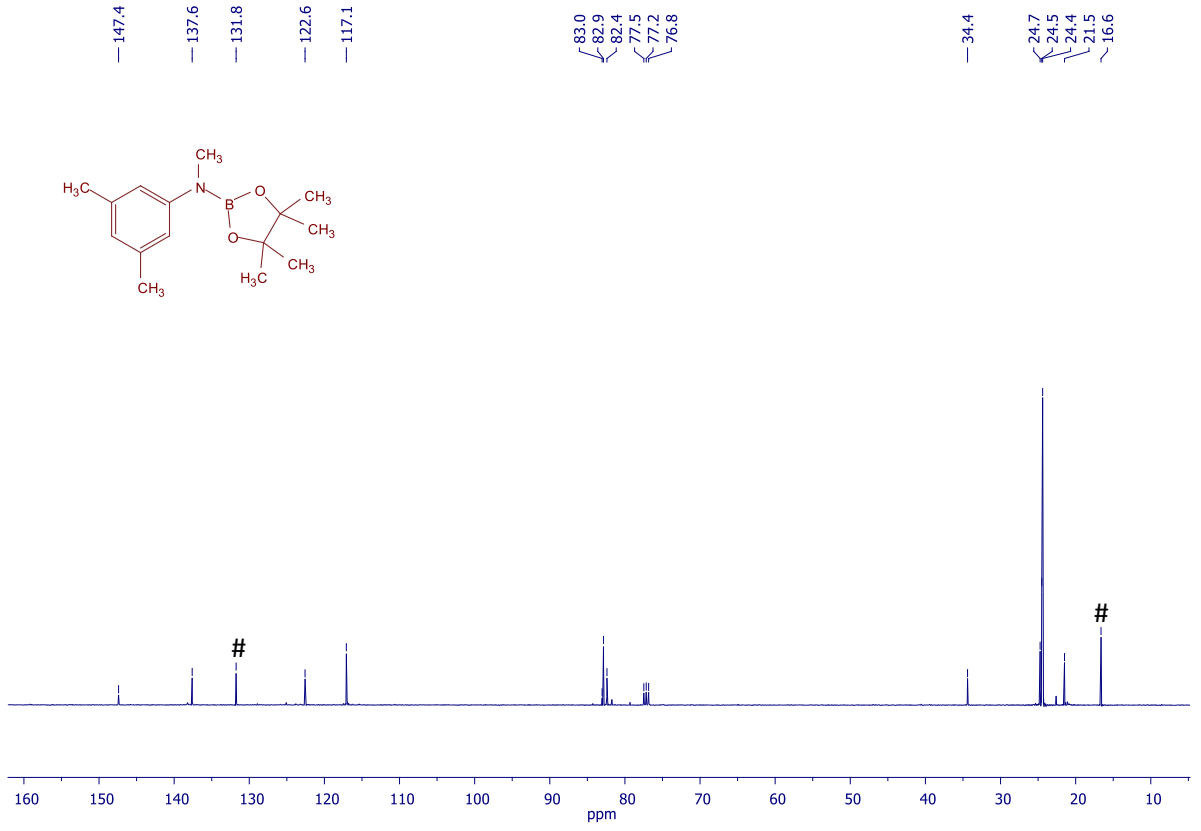
*^{13}C {^{1}H} NMR spectrum of N,4,4,5,5-pentamethyl-N-(3-nitrophenyl)-1,3,2-dioxaborolan-2-amine (Compound-**2e**)*



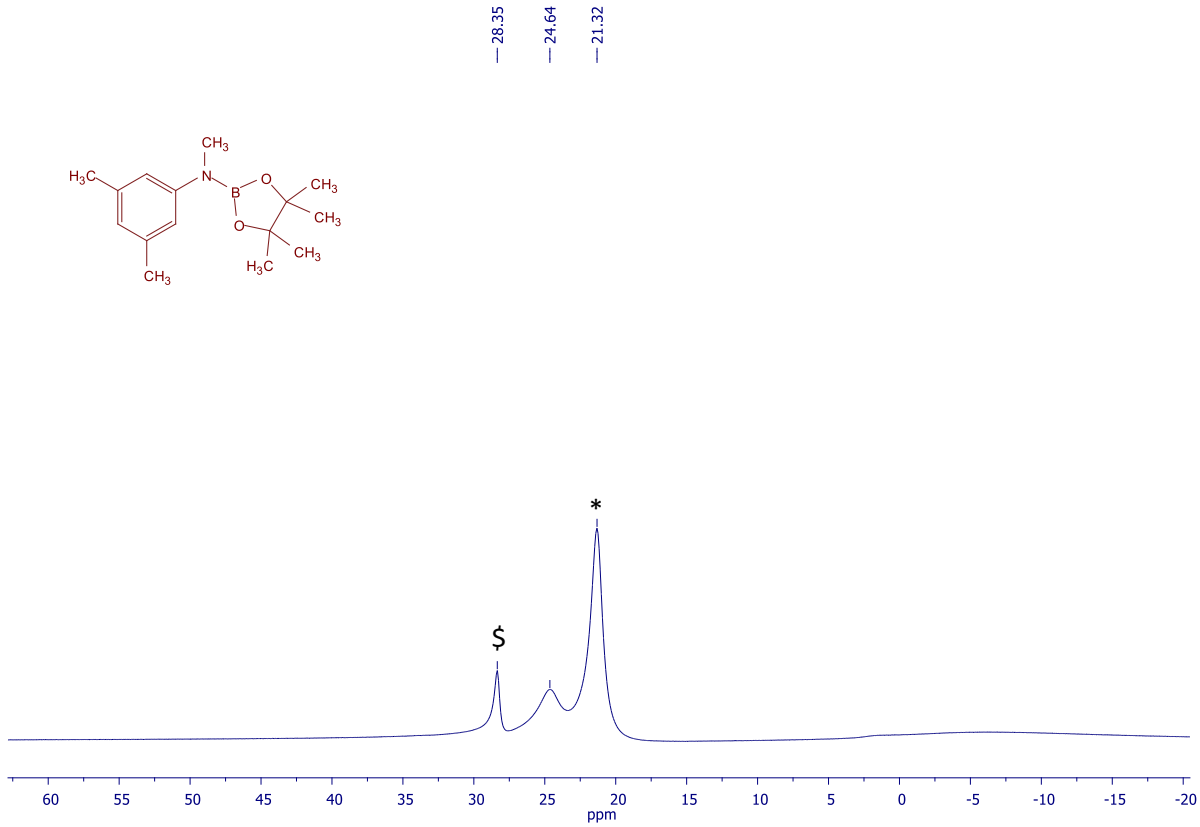
*^{11}B NMR spectrum of N,4,4,5,5-pentamethyl-N-(3-nitrophenyl)-1,3,2-dioxaborolan-2-amine (Compound-**2e**), $ indicates the excess of HBpin and * indicates the byproduct $(Bpin)_2O$.*



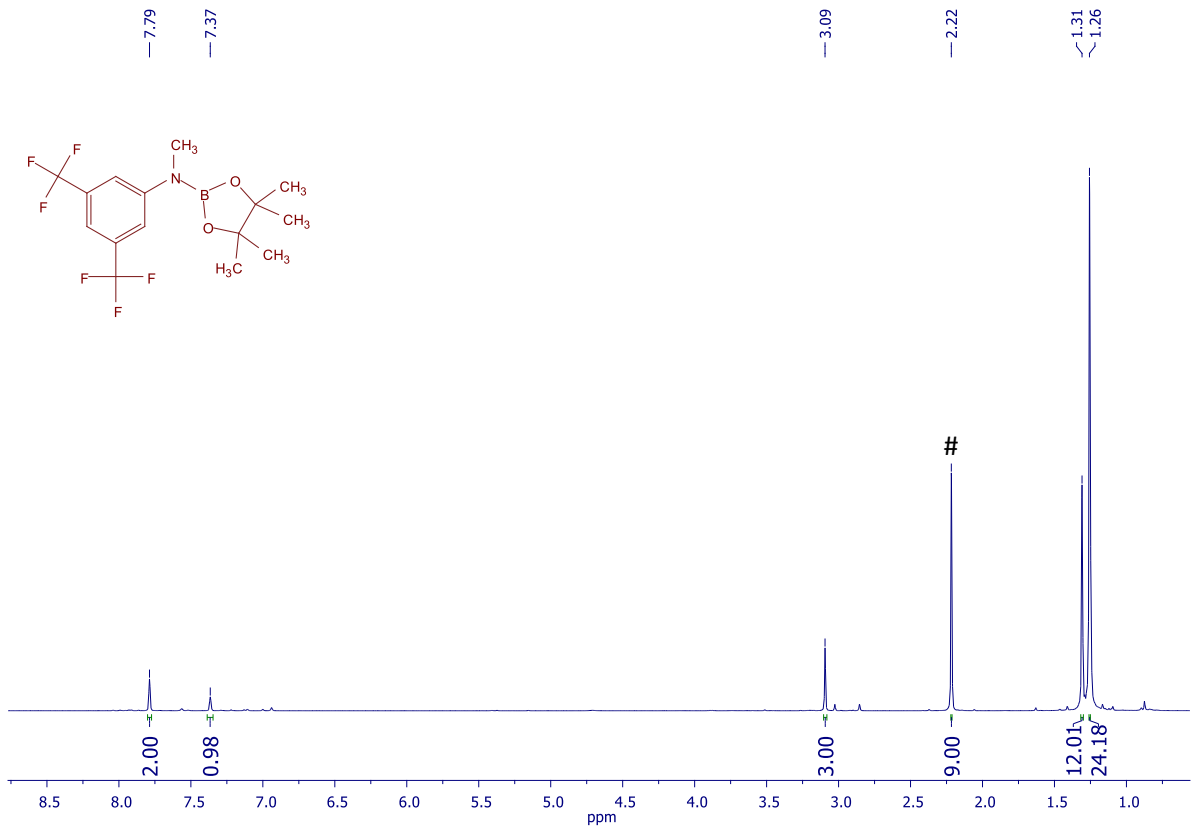
*^{1}H NMR spectrum of N-(3,5-dimethylphenyl)-N,4,4,5,5-pentamethyl-1,3,2-dioxaborolan-2-amine (Compound-**2f**)*



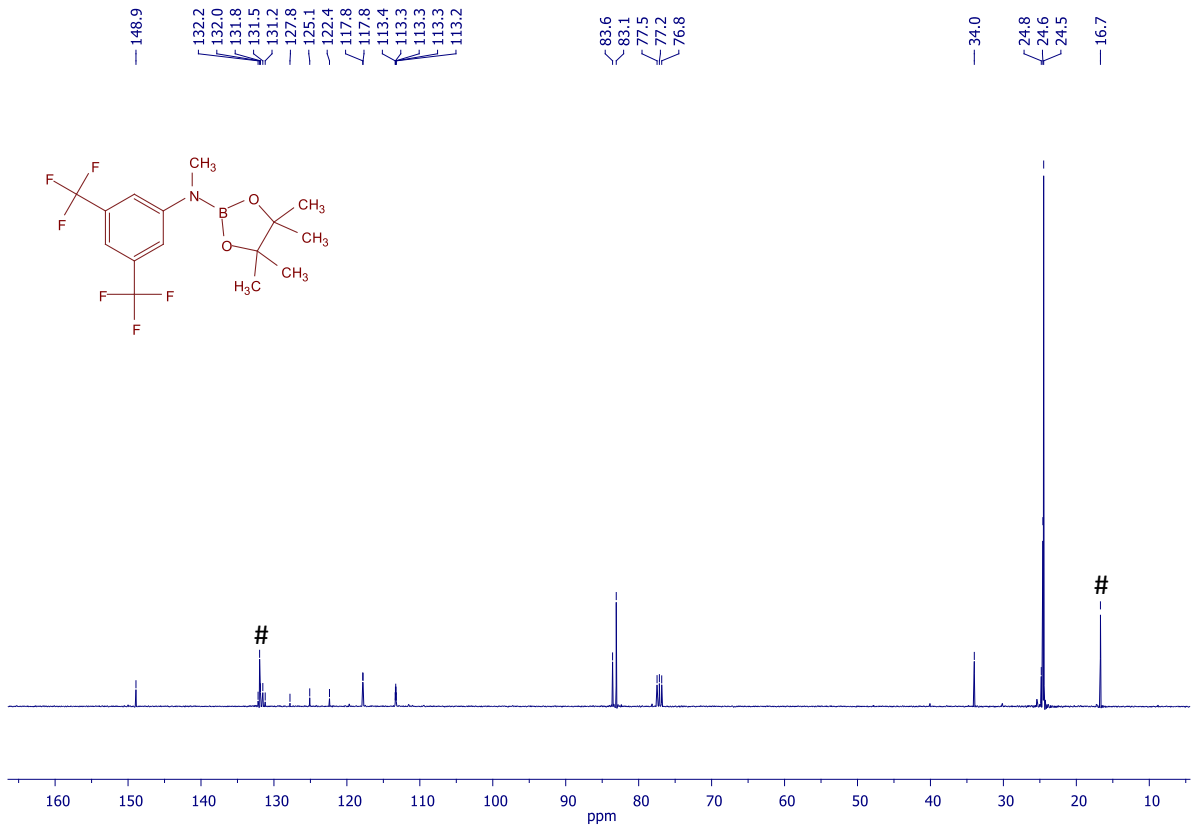
*^{13}C {^{1}H} NMR spectrum of N-(3,5-dimethylphenyl)-N,4,4,5,5-pentamethyl-1,3,2-dioxaborolan-2-amine (Compound-**2f**)*



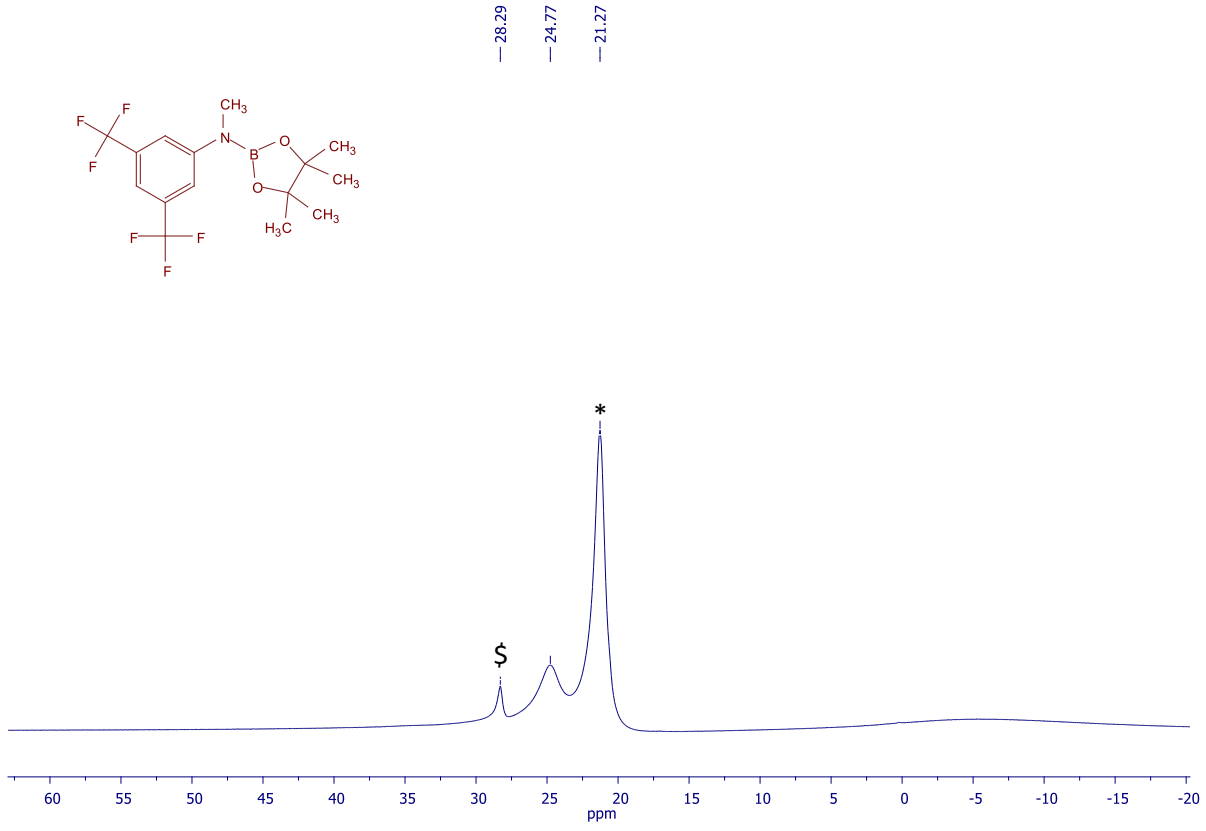
*^{11}B NMR spectrum of N-(3,5-dimethylphenyl)-N,4,4,5,5-pentamethyl-1,3,2-dioxaborolan-2-amine (Compound-**2f**), $ indicates the excess of HBpin and * indicates the byproduct $(Bpin)_2O$.*



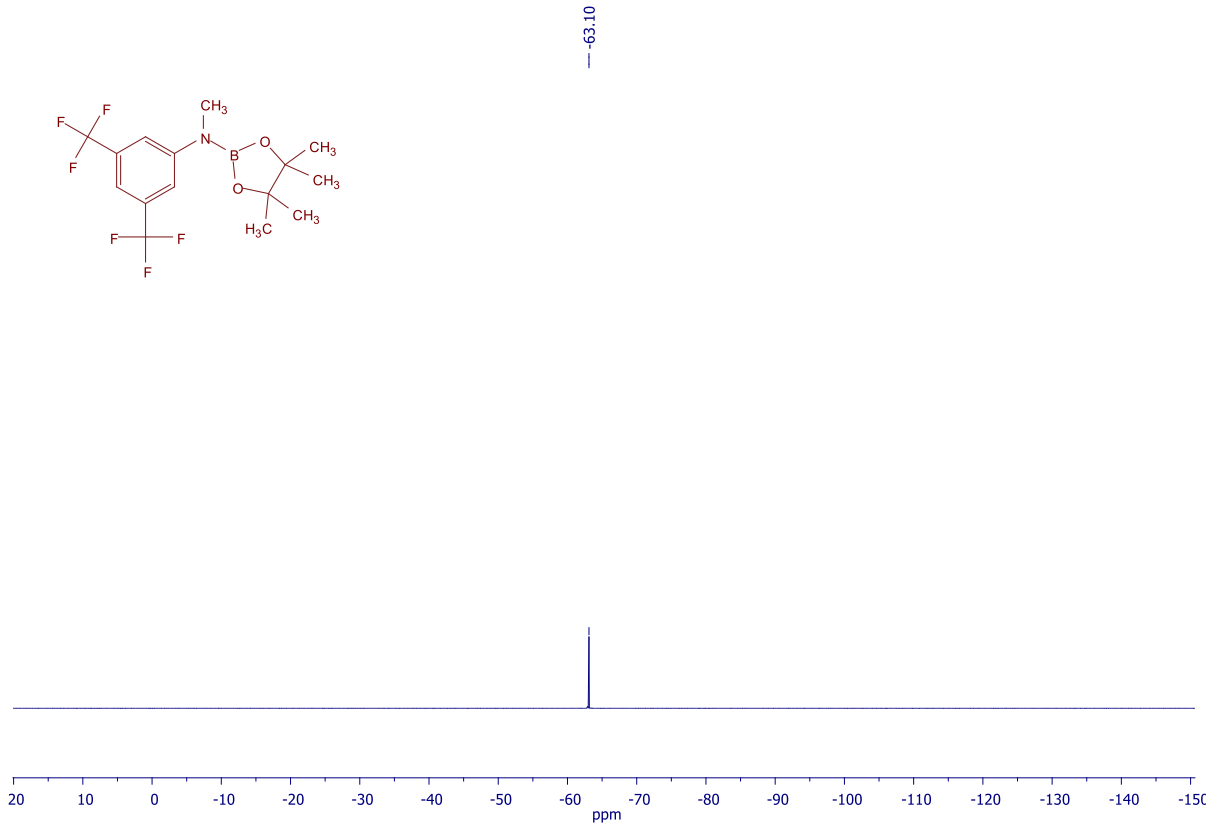
*^{1}H NMR spectrum of N-(3,5-bis(trifluoromethyl)phenyl)-N,4,4,5,5-pentamethyl-1,3,2-dioxaborolan-2-amine (Compound-**2g**)*



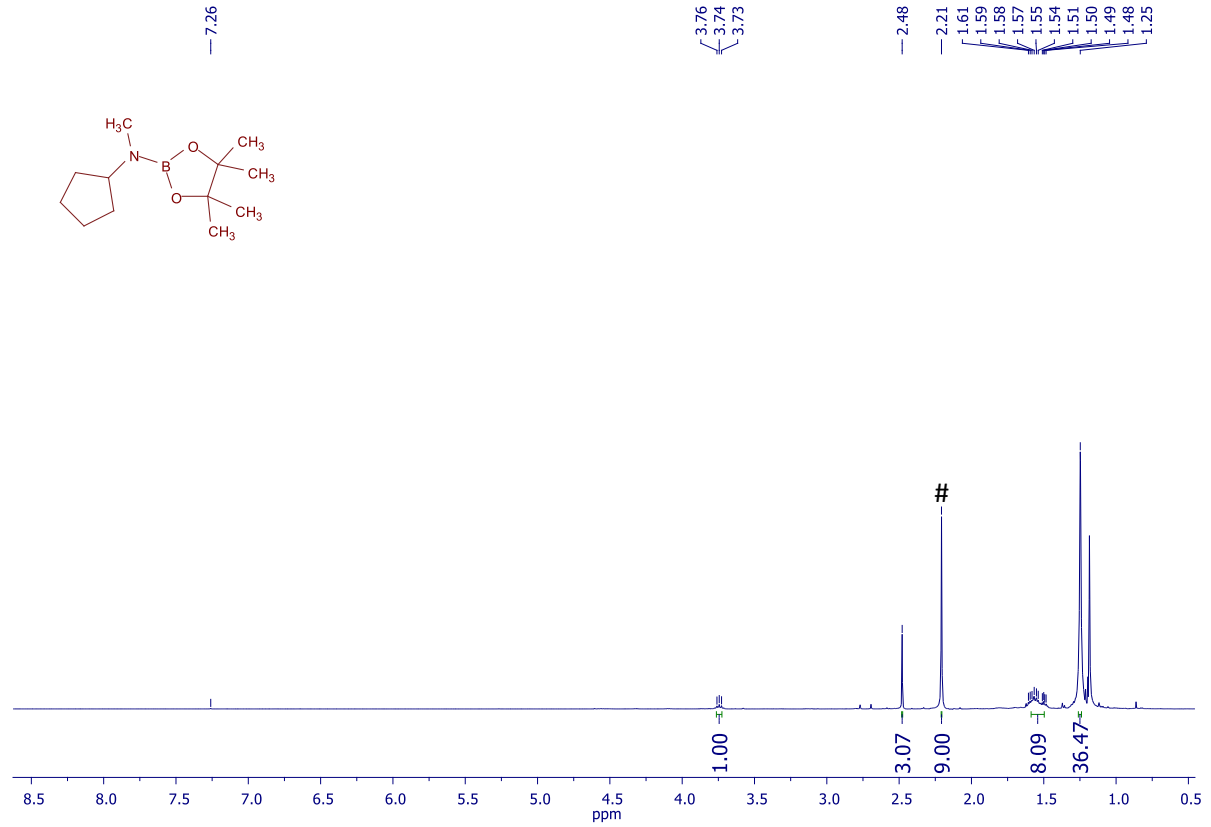
*^{13}C {^{1}H} NMR spectrum of N-(3,5-bis(trifluoromethyl)phenyl)-N,4,4,5,5-pentamethyl-1,3,2-dioxaborolan-2-amine (Compound-**2g**)*



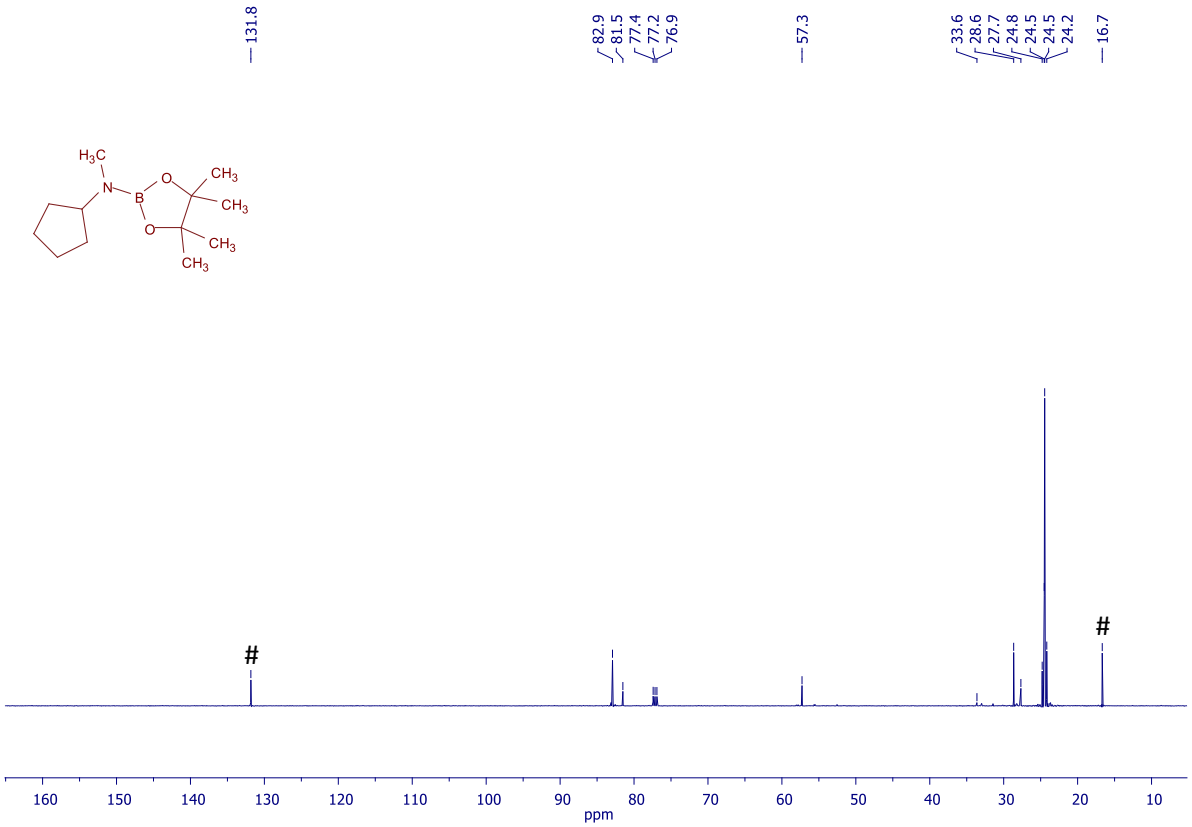
*^{11}B NMR spectrum of N-(3,5-bis(trifluoromethyl)phenyl)-N,4,4,5,5-pentamethyl-1,3,2-dioxaborolan-2-amine (Compound-**2g**), $ indicates the excess of HBpin and * indicates the byproduct $(Bpin)_2O$.*



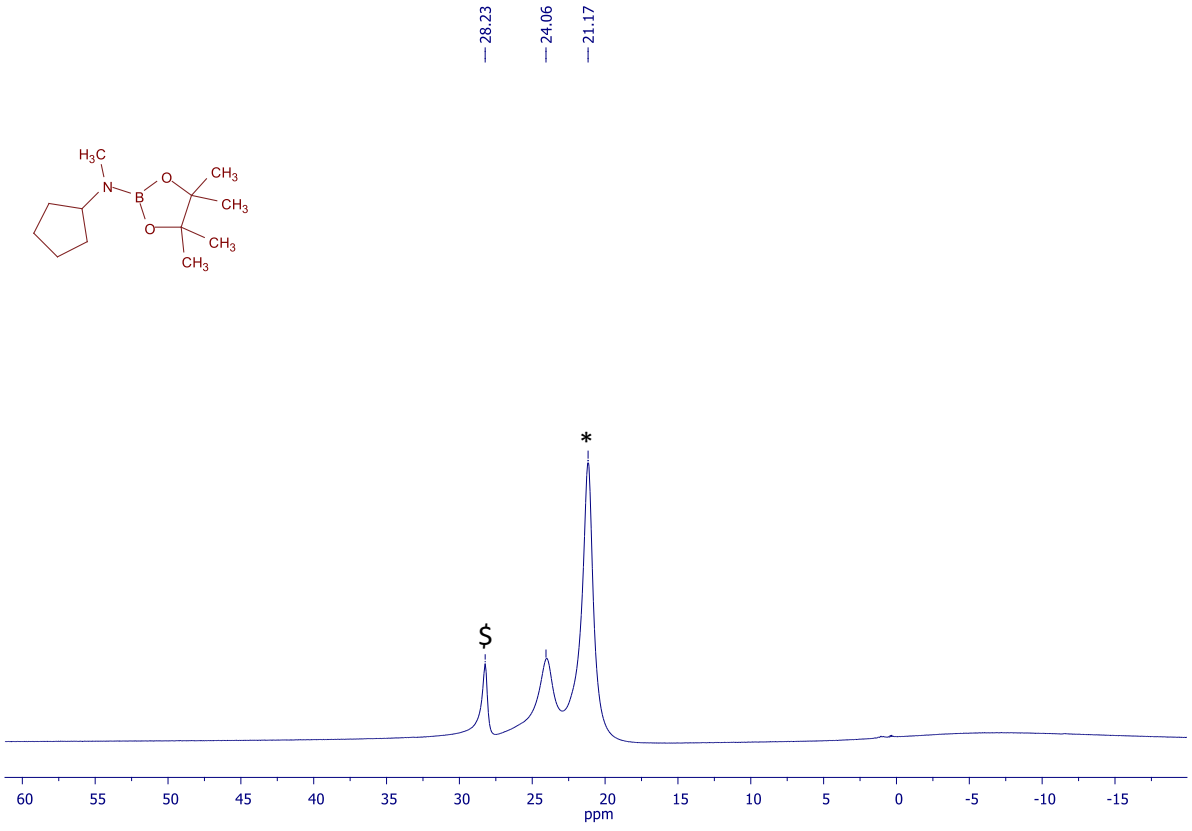
*^{19}F NMR spectrum of N-(3,5-bis(trifluoromethyl)phenyl)-N,4,4,5,5-pentamethyl-1,3,2-dioxaborolan-2-amine (Compound-**2g**)*



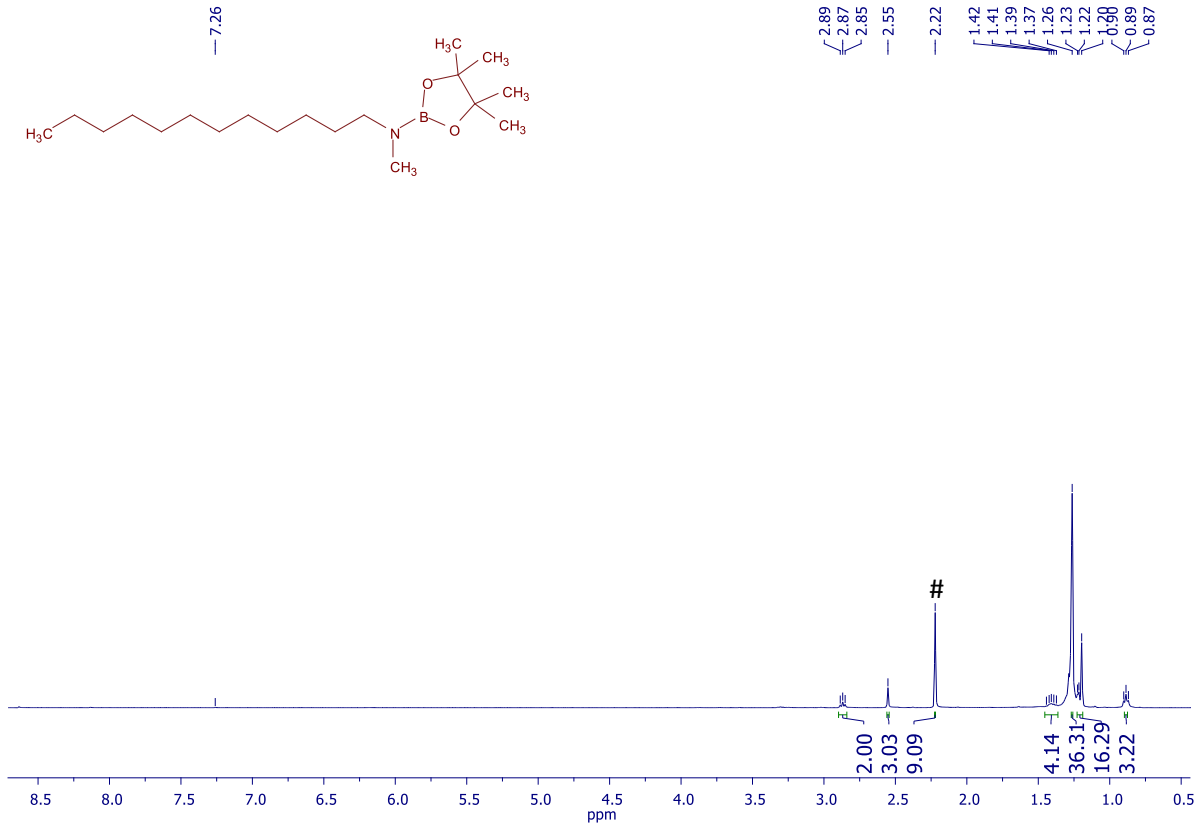
*^{1}H NMR spectrum of N-cyclopentyl-N,4,4,5,5-pentamethyl-1,3,2-dioxaborolan-2-amine (Compound-**2h**)*



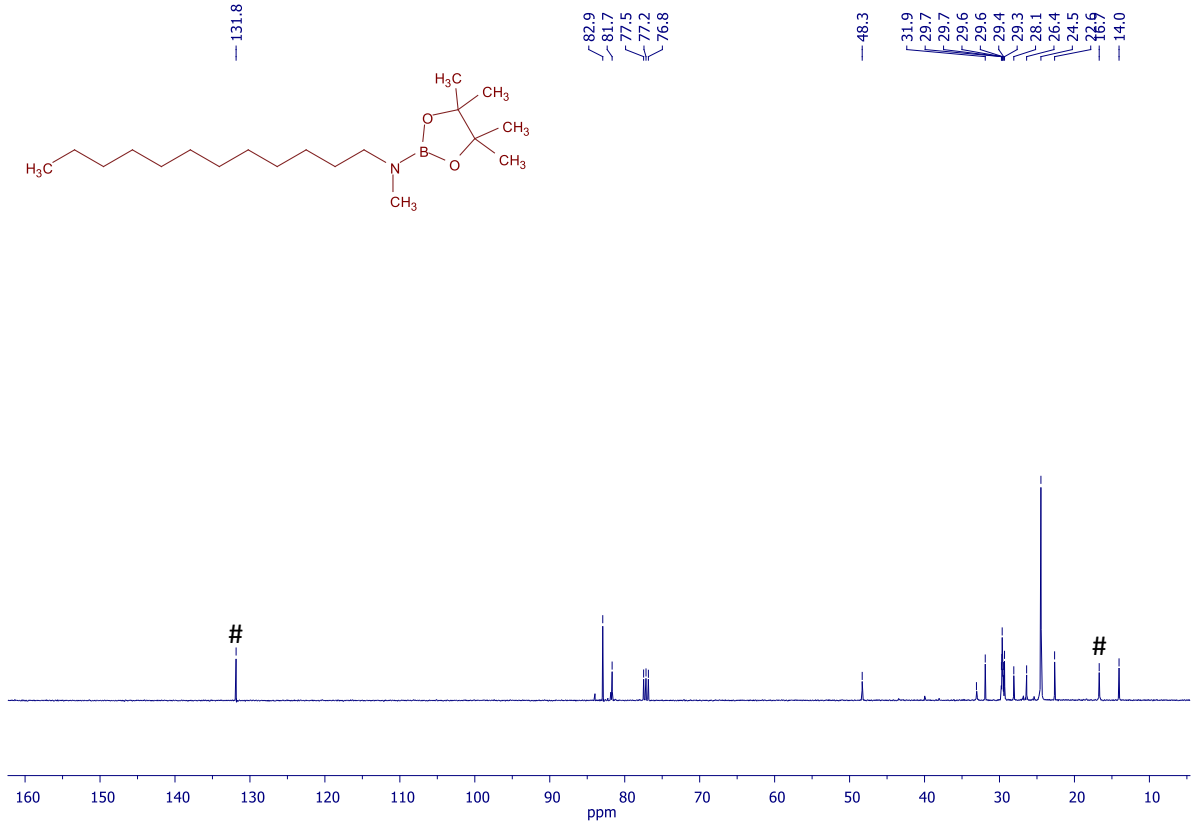
*^{13}C {^{1}H} NMR spectrum of N-cyclopentyl-N,4,4,5,5-pentamethyl-1,3,2-dioxaborolan-2-amine (Compound-**2h**)*



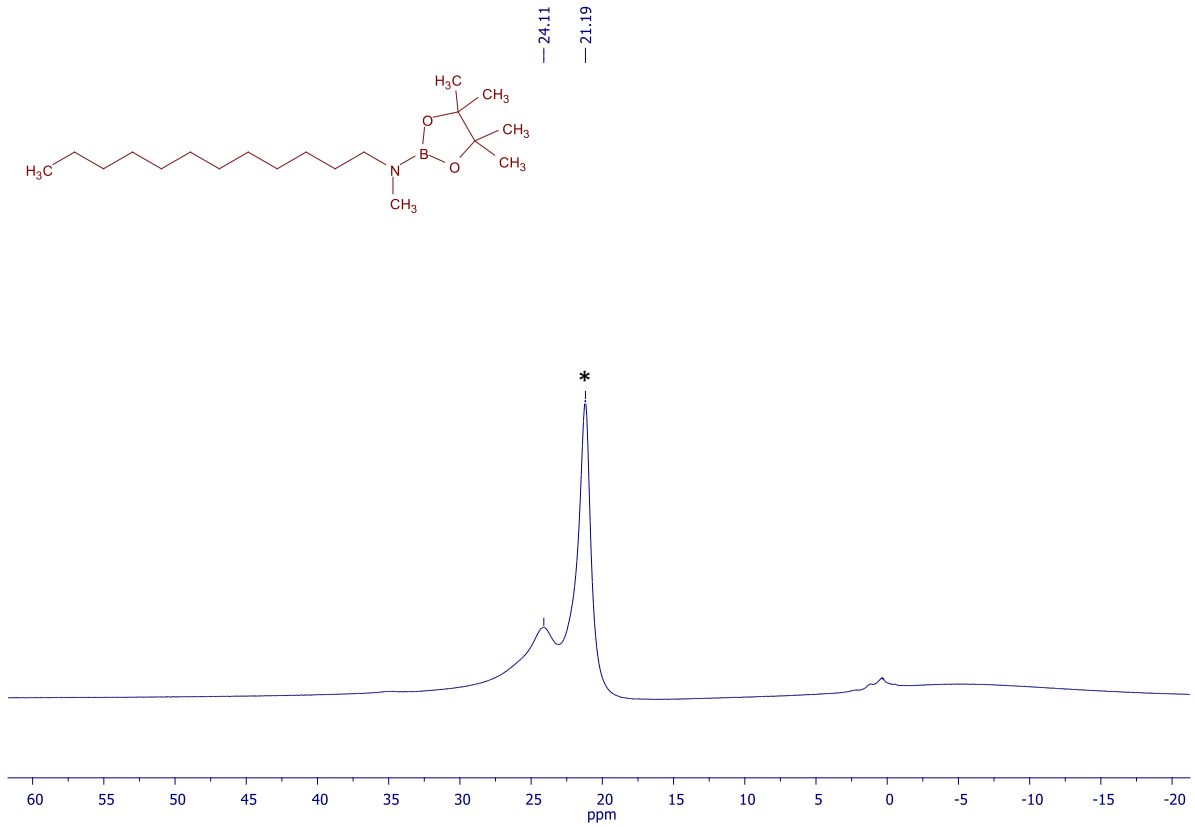
*^{11}B NMR spectrum of N-cyclopentyl-N,4,4,5,5-pentamethyl-1,3,2-dioxaborolan-2-amine (Compound-**2h**), $ indicates the excess of HBpin and * indicates the byproduct $(Bpin)_2O$.*



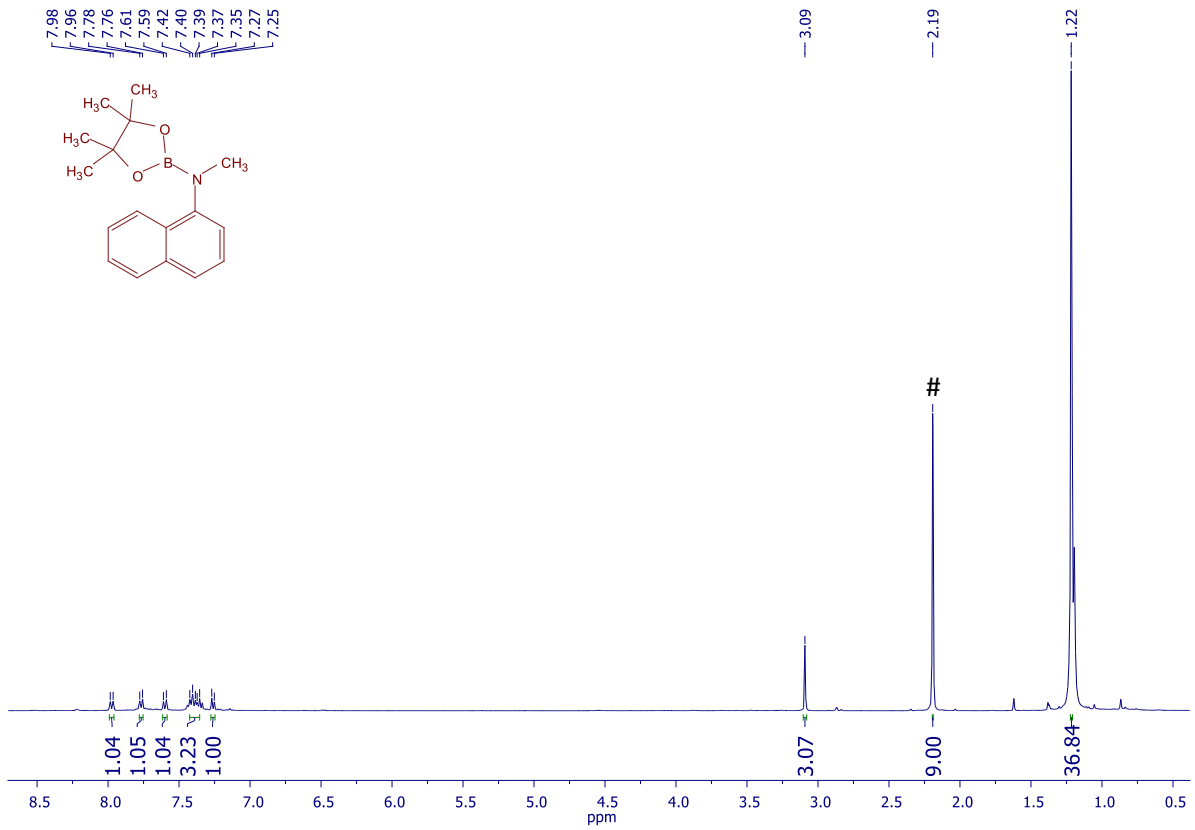
*[1]H NMR spectrum of N-dodecyl-N,4,4,5,5-pentamethyl-1,3,2-dioxaborolan-2-amine (Compound-**2i**)*



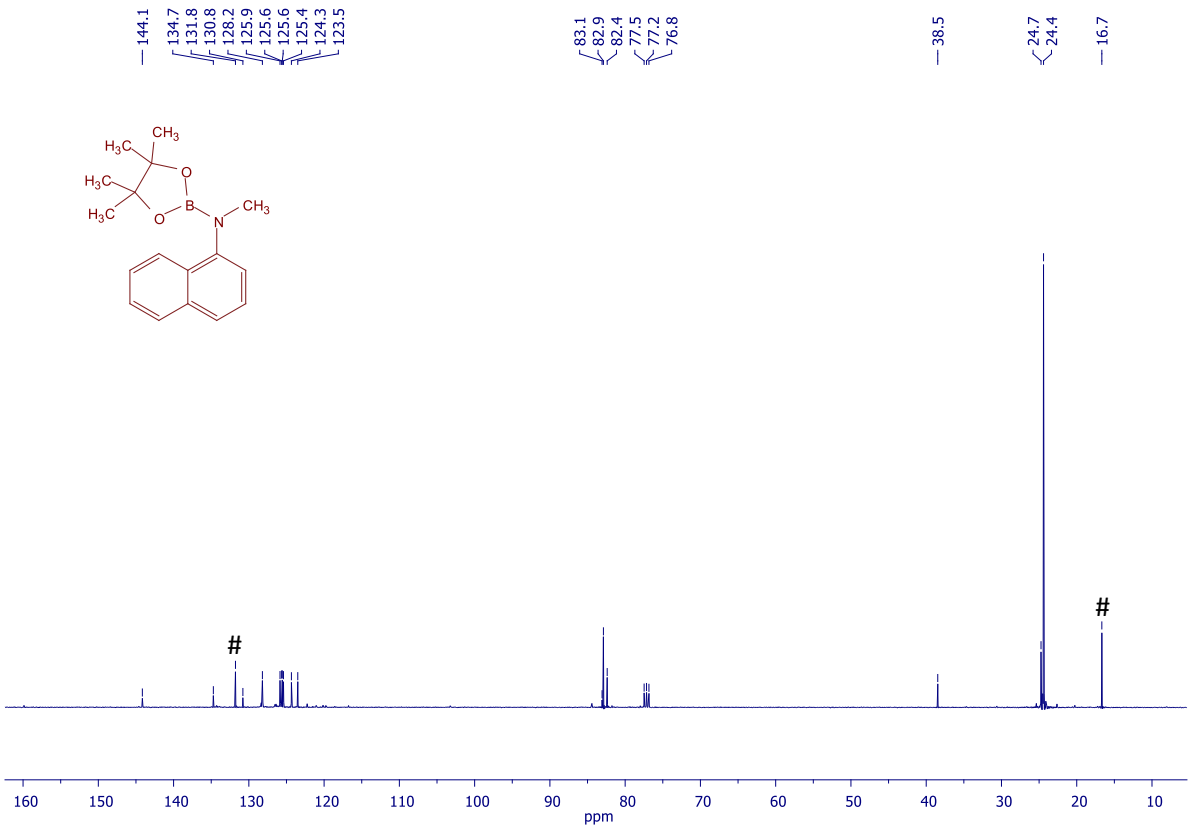
*[13]C {[1]H} NMR spectrum of N-dodecyl-N,4,4,5,5-pentamethyl-1,3,2-dioxaborolan-2-amine (Compound-**2i**)*



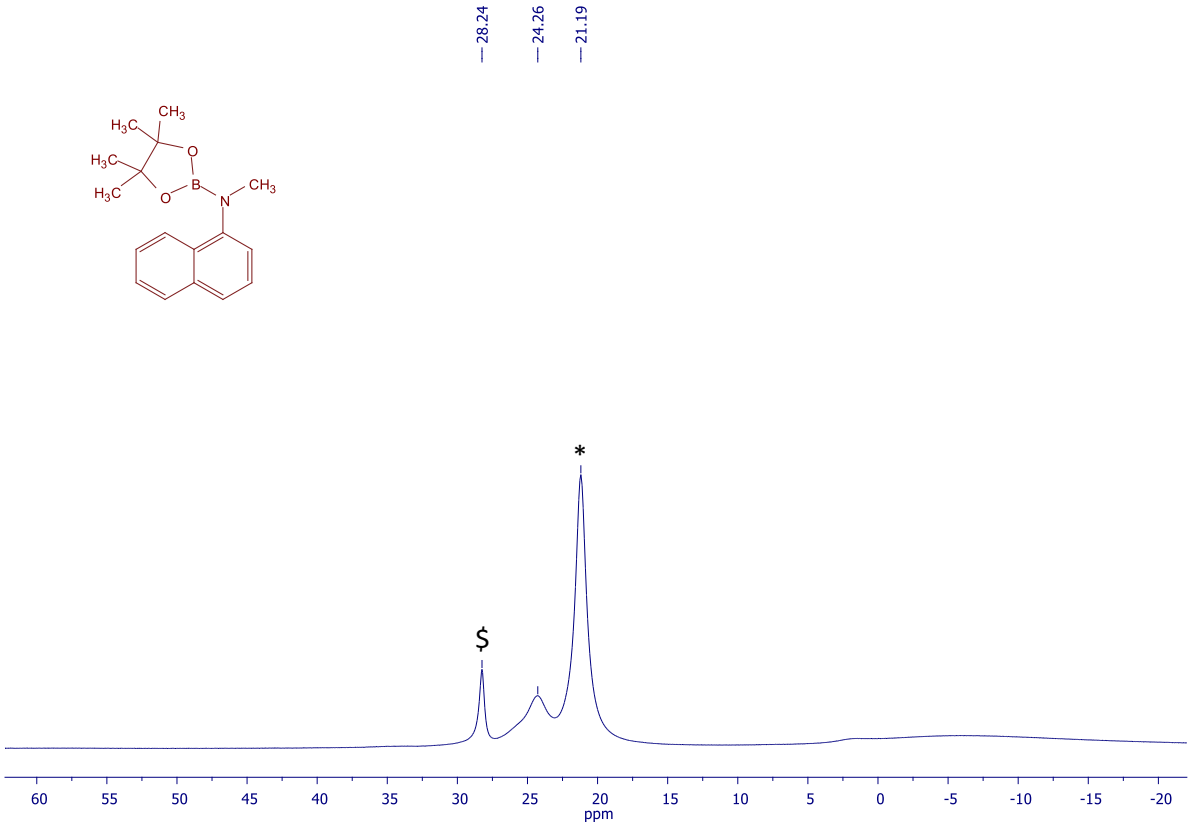
*^{11}B NMR spectrum of N-dodecyl-N,4,4,5,5-pentamethyl-1,3,2-dioxaborolan-2-amine (Compound-**2i**), * indicates the byproduct $(Bpin)_2O$.*



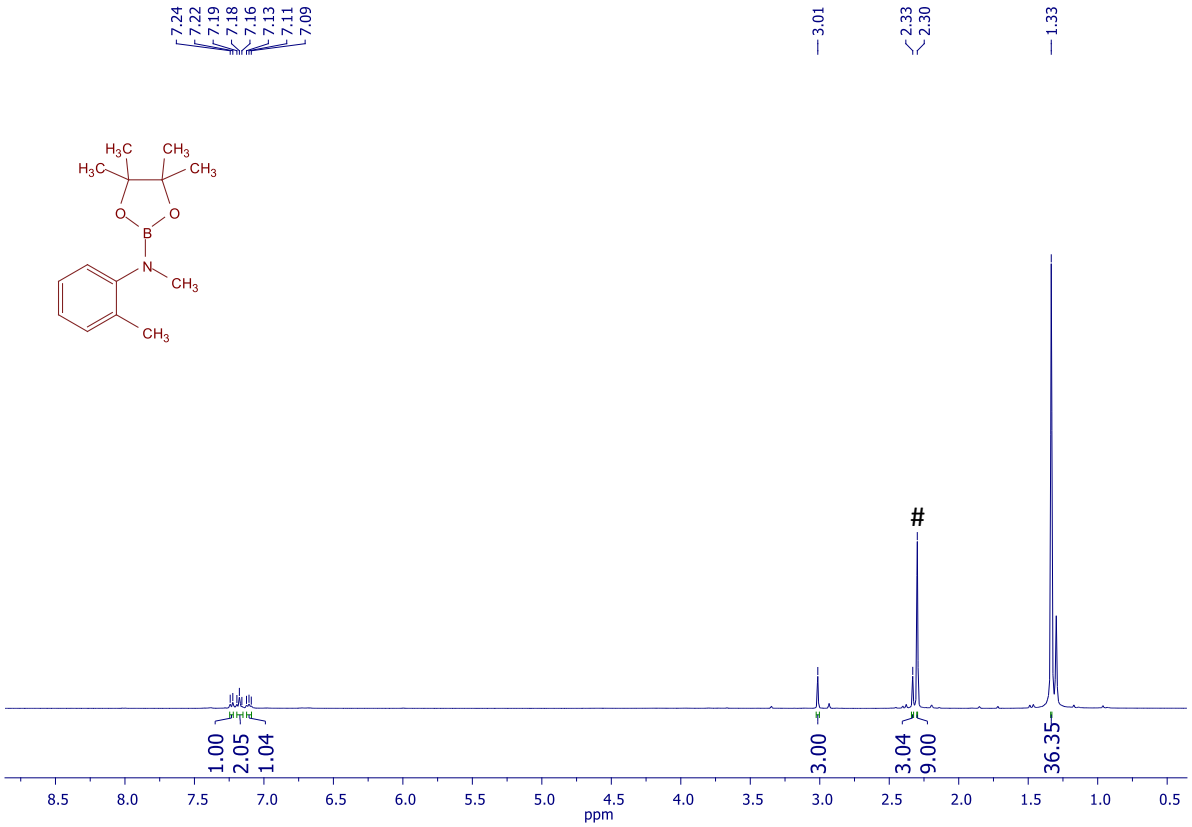
*^{1}H NMR spectrum of N,4,4,5,5-pentamethyl-N-(naphthalen-1-yl)-1,3,2-dioxaborolan-2-amine (Compound-**2j**)*



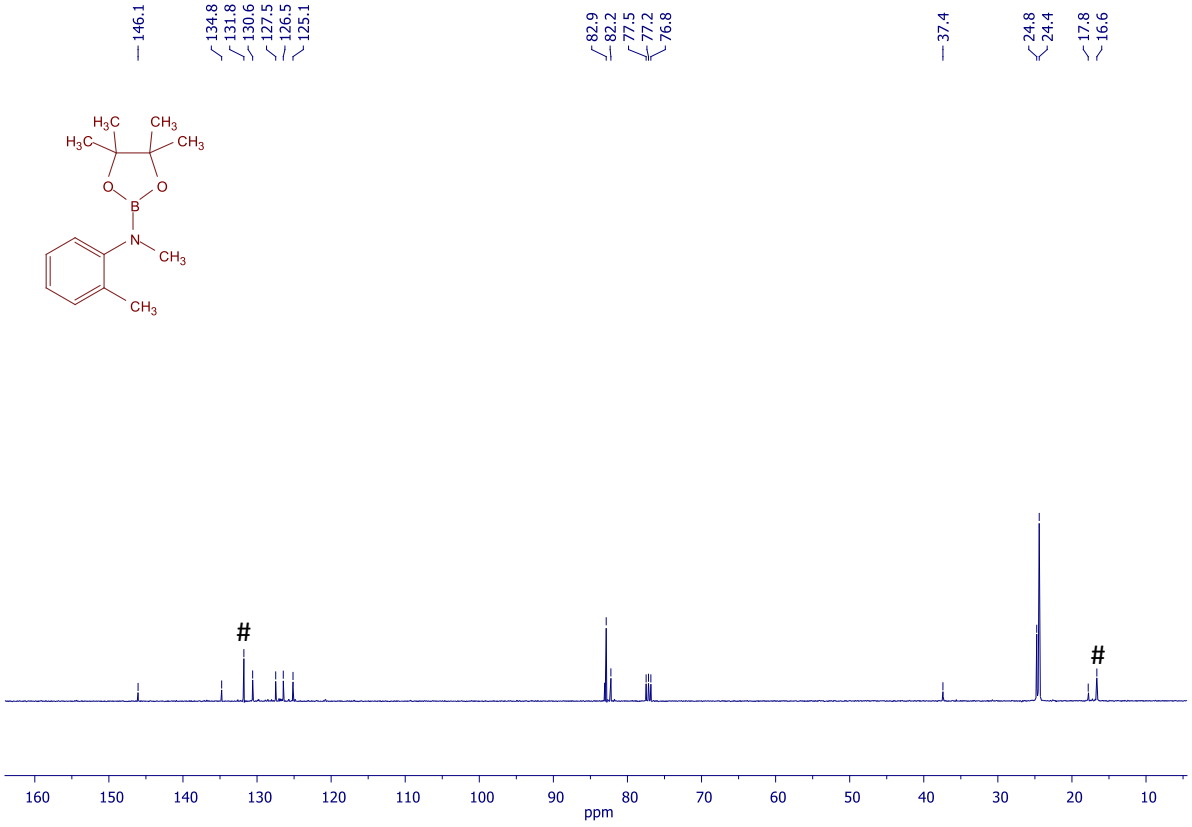
*^{13}C {^{1}H} NMR spectrum of N,4,4,5,5-pentamethyl-N-(naphthalen-1-yl)-1,3,2-dioxaborolan-2-amine (Compound-**2j**)*



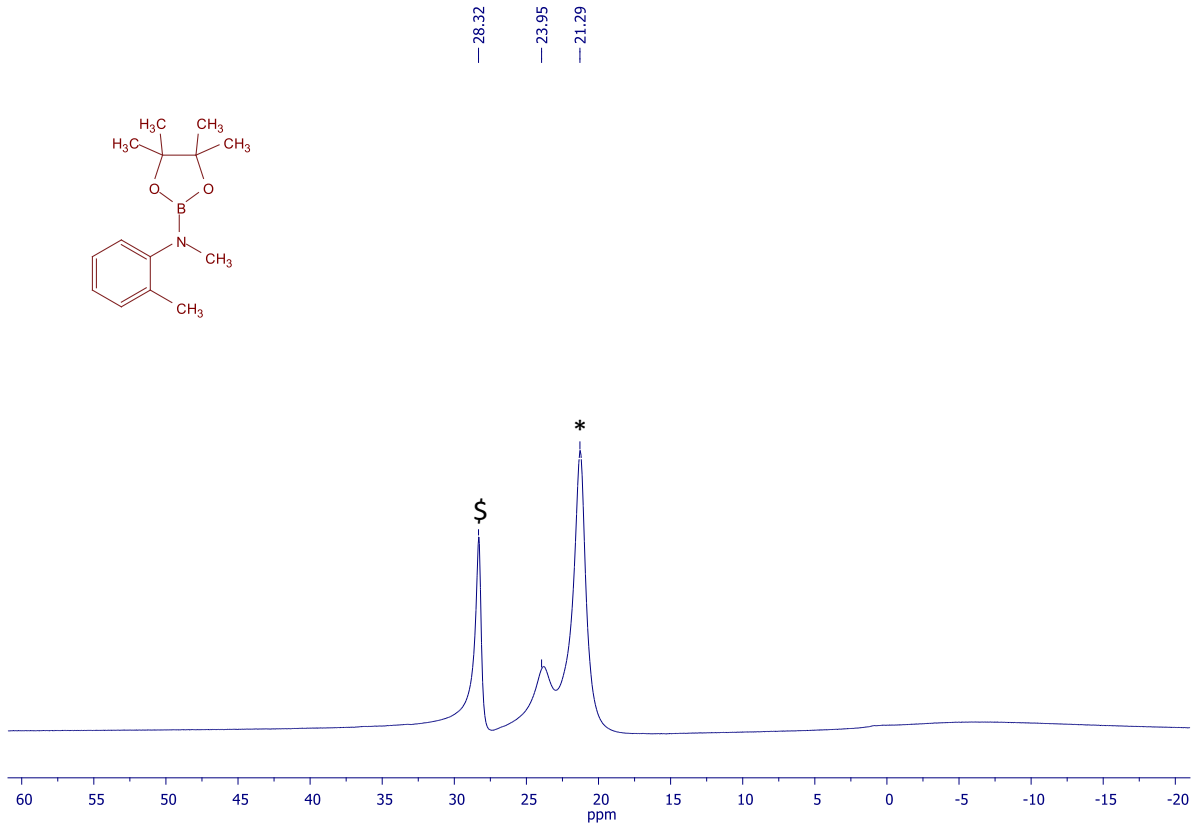
*^{11}B NMR spectrum of N,4,4,5,5-pentamethyl-N-(naphthalen-1-yl)-1,3,2-dioxaborolan-2-amine (Compound-**2j**), $ indicates the excess of HBpin and * indicates the byproduct $(Bpin)_2O$.*



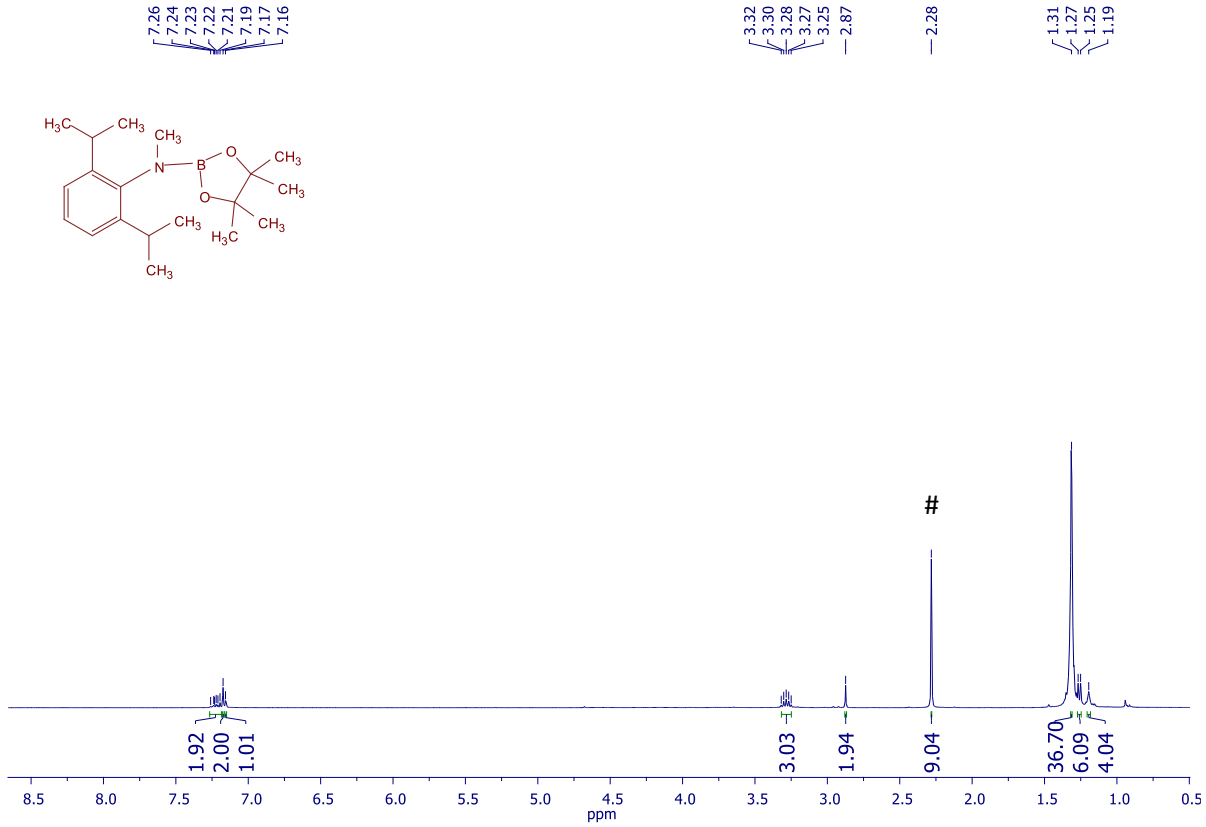
*[1]H NMR spectrum of N,4,4,5,5-pentamethyl-N-(o-tolyl)-1,3,2-dioxaborolan-2-amine (Compound-**2k**)*



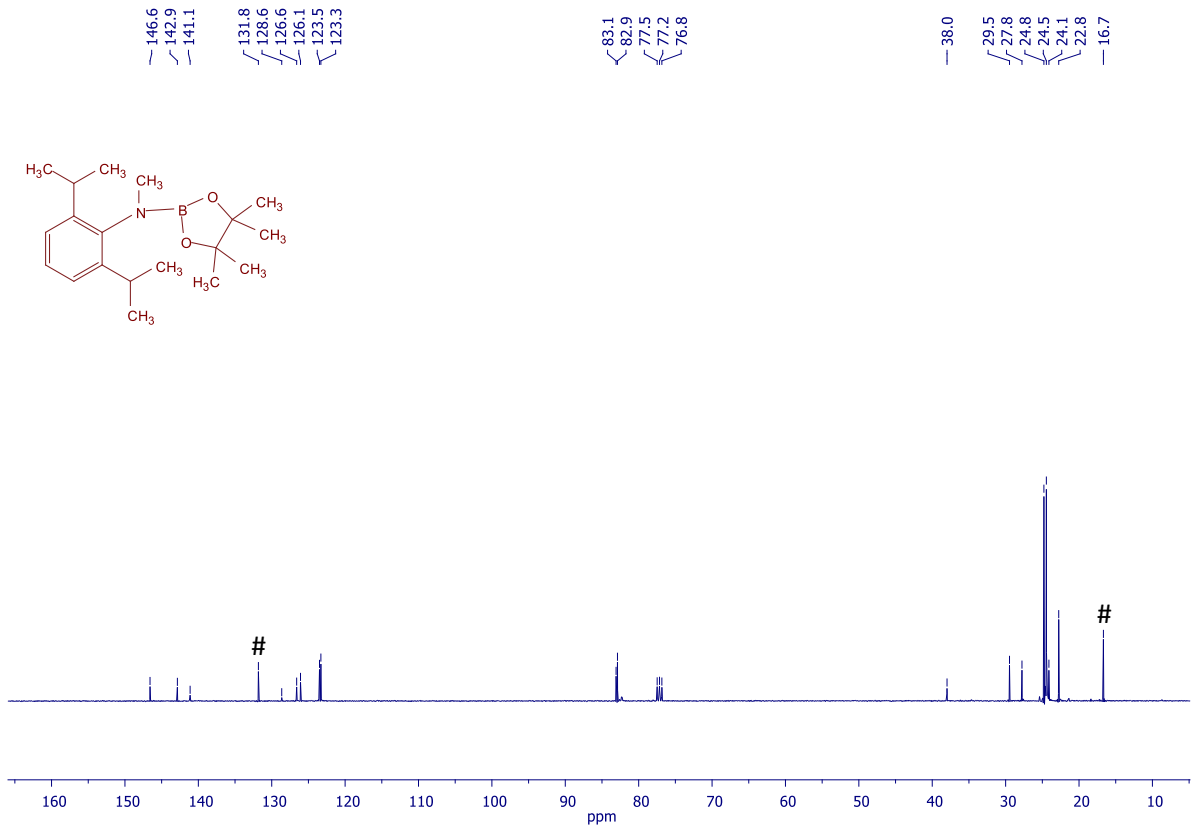
*[13]C{[1]H} NMR spectrum of N,4,4,5,5-pentamethyl-N-(o-tolyl)-1,3,2-dioxaborolan-2-amine (Compound-**2k**)*



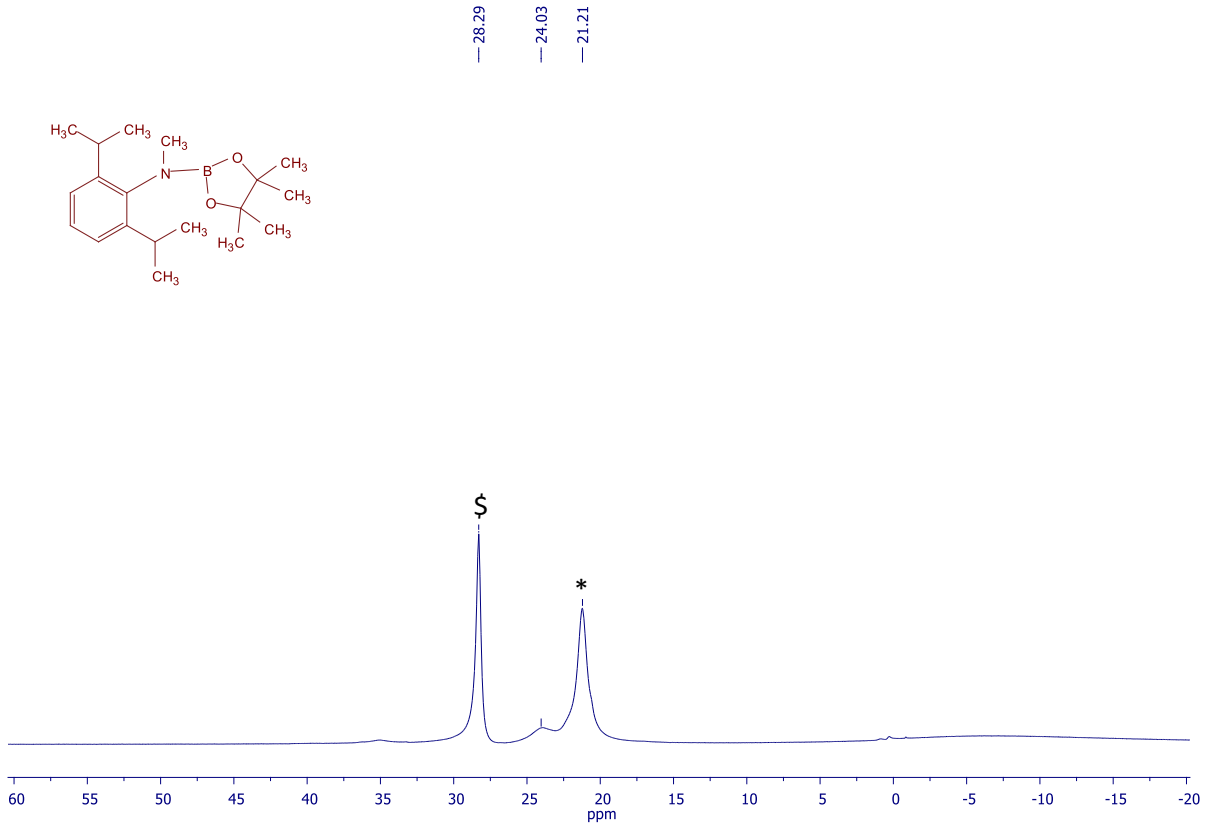
*^{11}B NMR spectrum of N,4,4,5,5-pentamethyl-N-(o-tolyl)-1,3,2-dioxaborolan-2-amine (Compound-**2k**), $ indicates the excess of HBpin and * indicates the byproduct $(Bpin)_2O$.*



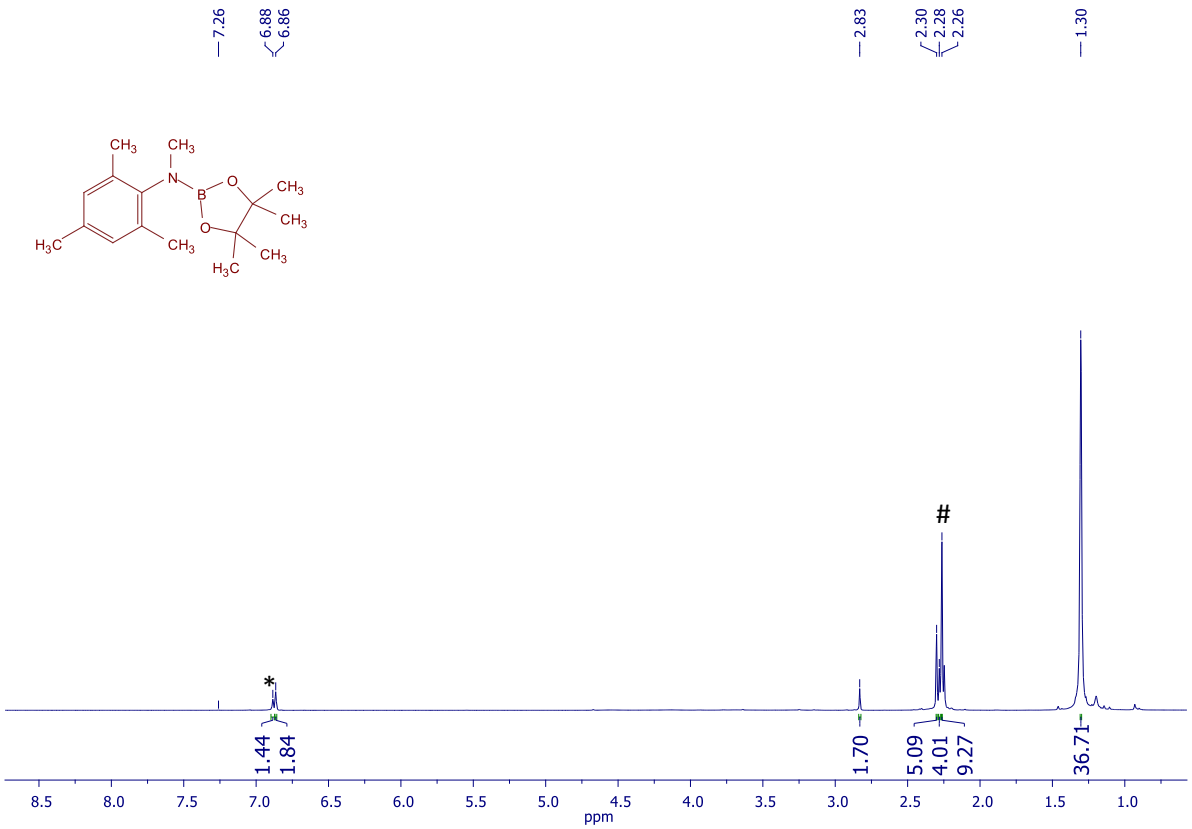
*^{1}H NMR spectrum of N-(2,6-diisopropylphenyl)-N,4,4,5,5-pentamethyl-1,3,2-dioxaborolan-2-amine (Compound-**2l**), (* represents starting material in the reaction mixture)*



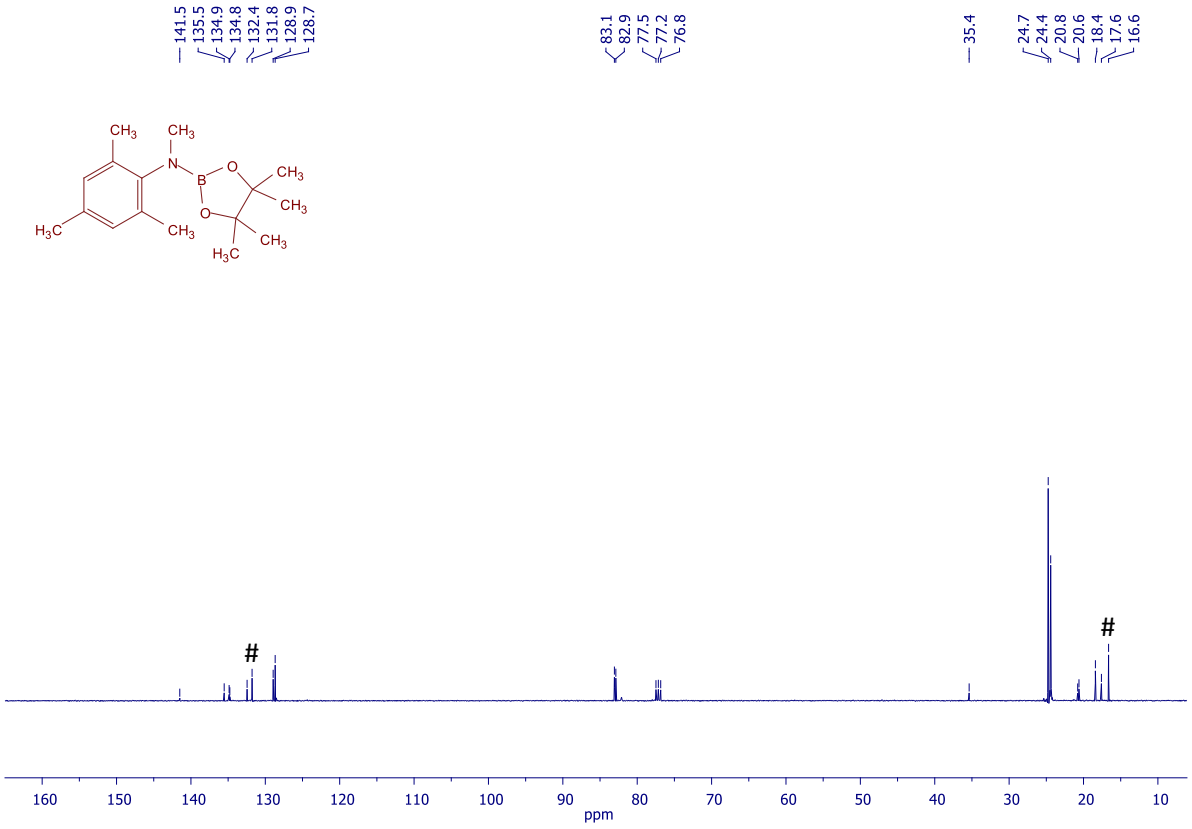
*^{13}C {^{1}H} NMR spectrum of N-(2,6-diisopropylphenyl)-N,4,4,5,5-pentamethyl-1,3,2-dioxaborolan-2-amine (Compound-**2l**)*



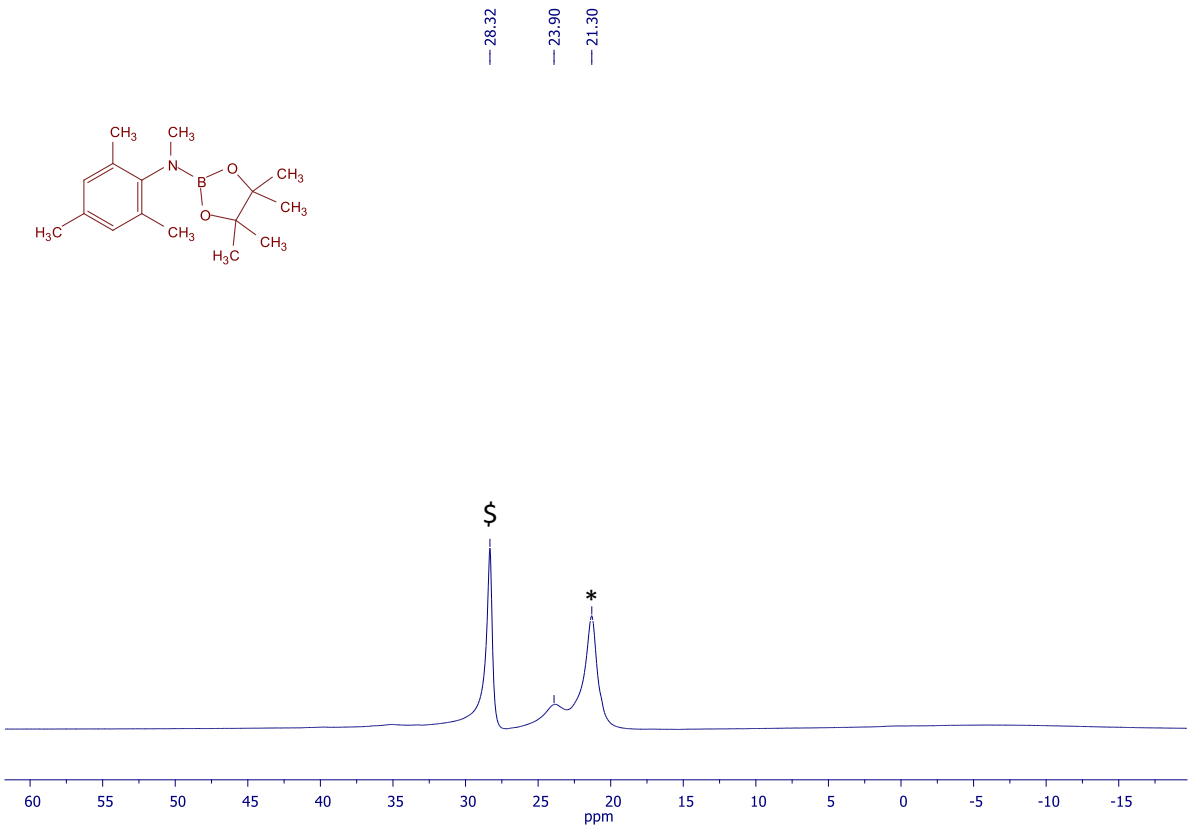
*^{11}B NMR spectrum of N-(2,6-diisopropylphenyl)-N,4,4,5,5-pentamethyl-1,3,2-dioxaborolan-2-amine (Compound-**2l**), $ indicates the excess of HBpin and * indicates the byproduct $(Bpin)_2O$.*



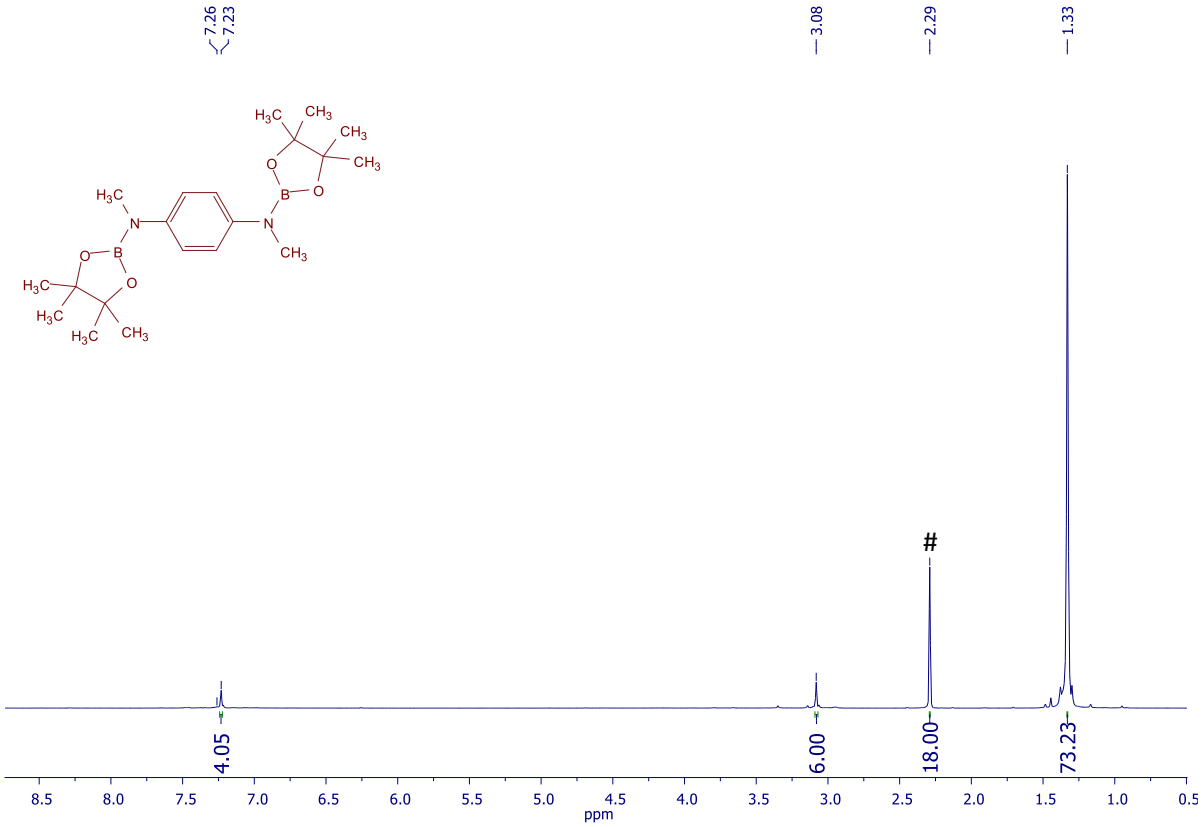
*^{1}H NMR spectrum of N-mesityl-N,4,4,5,5-pentamethyl-1,3,2-dioxaborolan-2-amine (Compound-**2m**), (* represents starting material in the reaction mixture)*



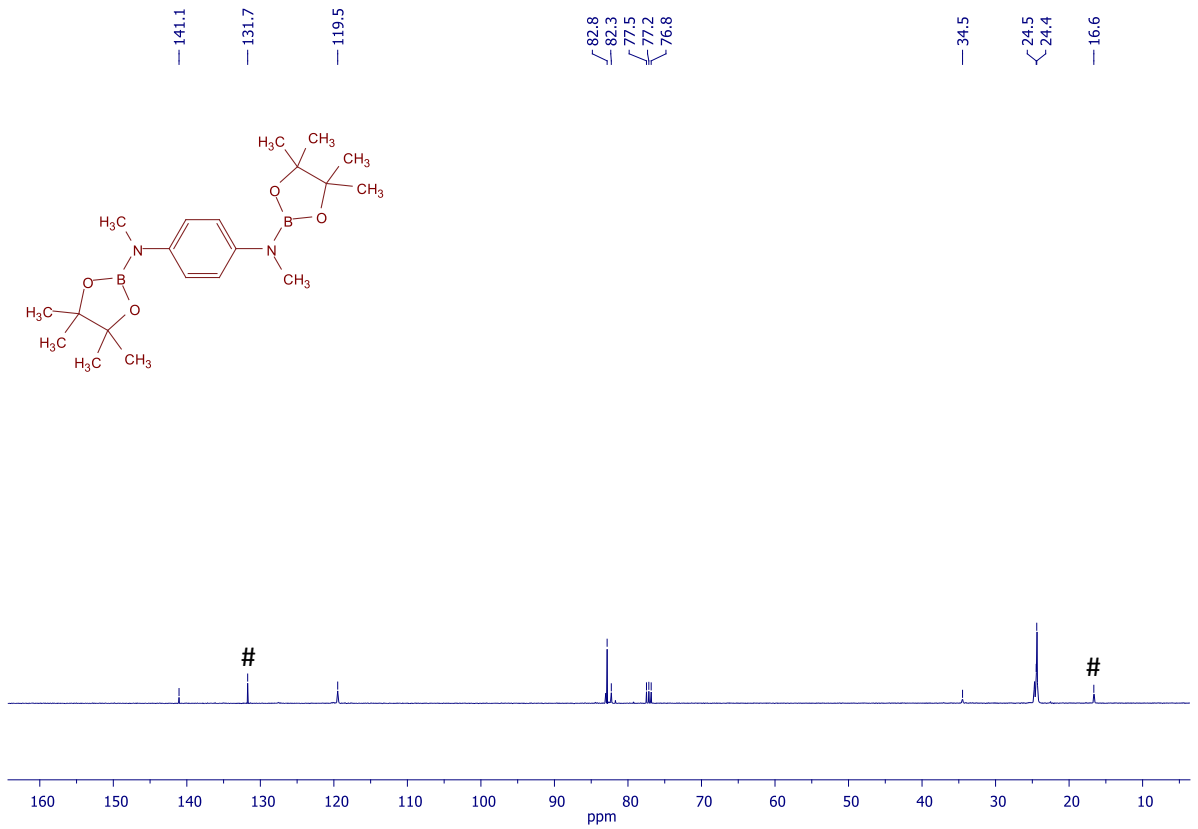
*^{13}C {^{1}H} NMR spectrum of N-mesityl-N,4,4,5,5-pentamethyl-1,3,2-dioxaborolan-2-amine (Compound-**2m**)*



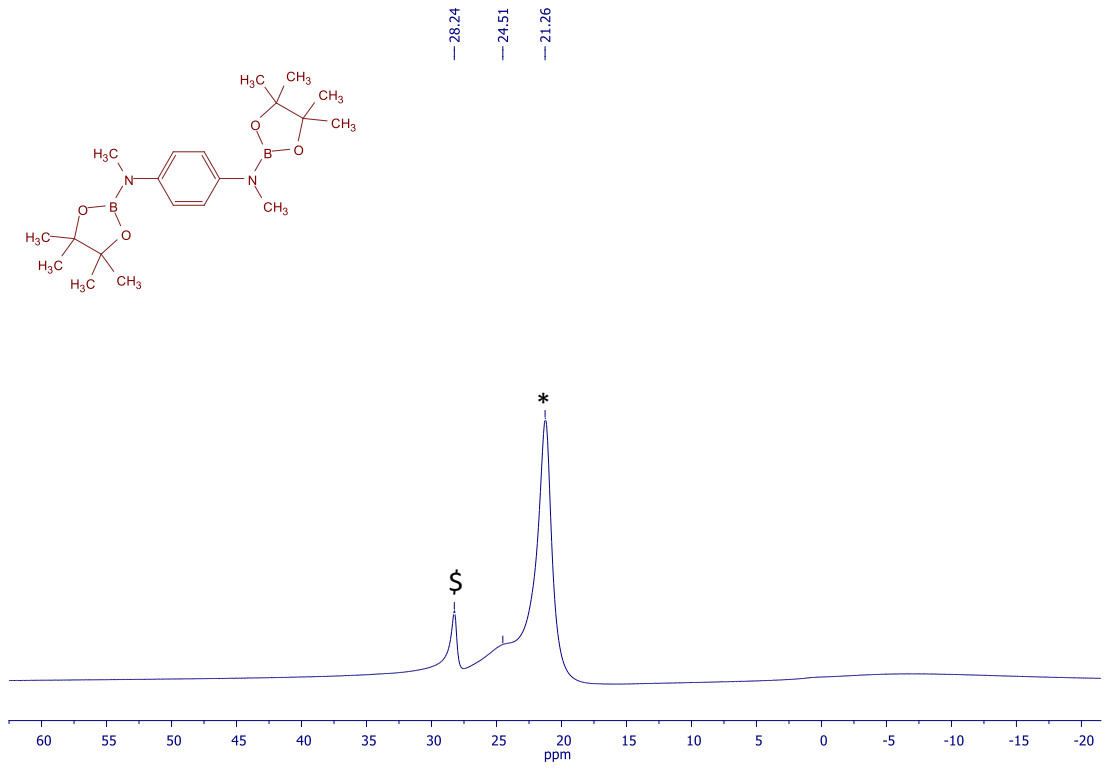
*^{11}B NMR spectrum of N-mesityl-N,4,4,5,5-pentamethyl-1,3,2-dioxaborolan-2-amine (Compound-**2m**), $ indicates the excess of HBpin and * indicates the byproduct $(Bpin)_2O$.*



*^{1}H NMR spectrum of N^1, N^4-dimethyl-N^1,N^4-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzene-1,4-diamine (Compound-**2n**)*

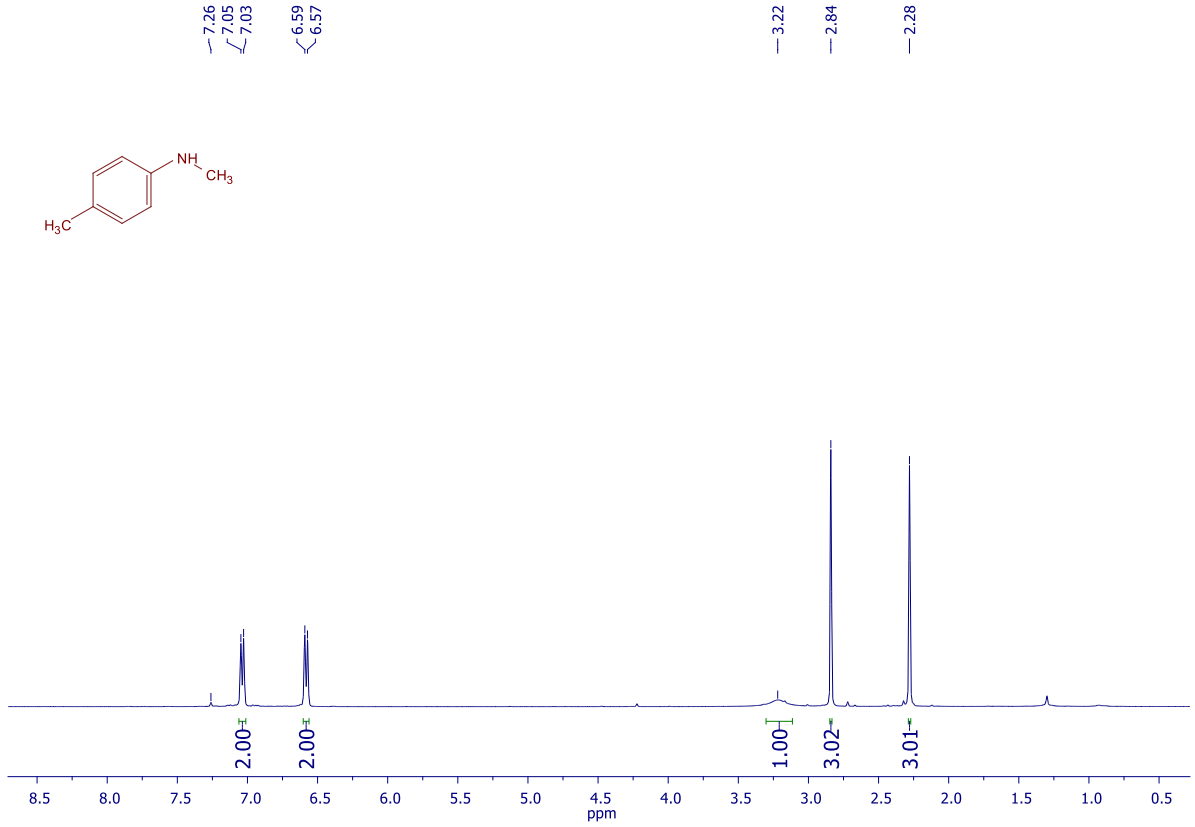


*^{13}C {^{1}H} NMR spectrum of N^1, N^4-dimethyl-N^1, N^4-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzene-1,4-diamine (Compound-**2n**)*

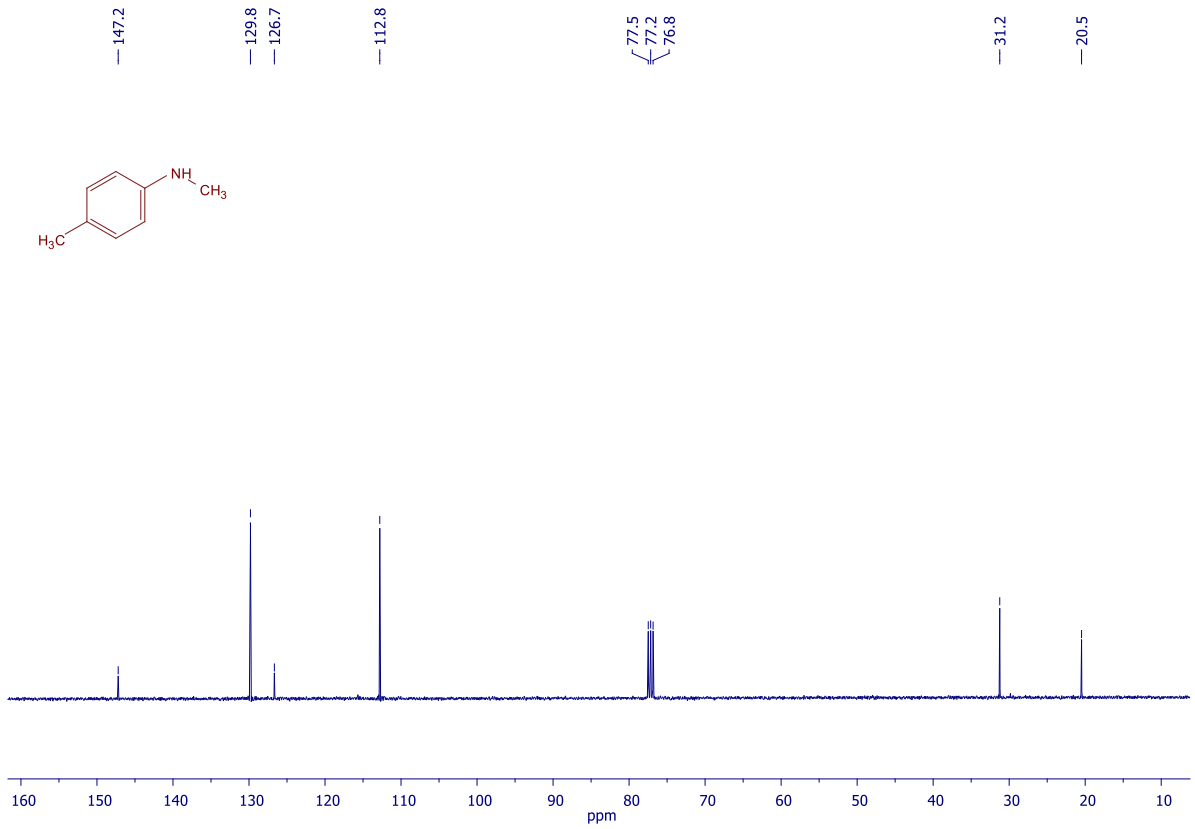


*^{11}B NMR spectrum of N^1, N^4-dimethyl-N^1, N^4-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzene-1,4-diamine (Compound-**2n**), $ indicates the excess of HBpin and * indicates the byproduct $(Bpin)_2O$.*

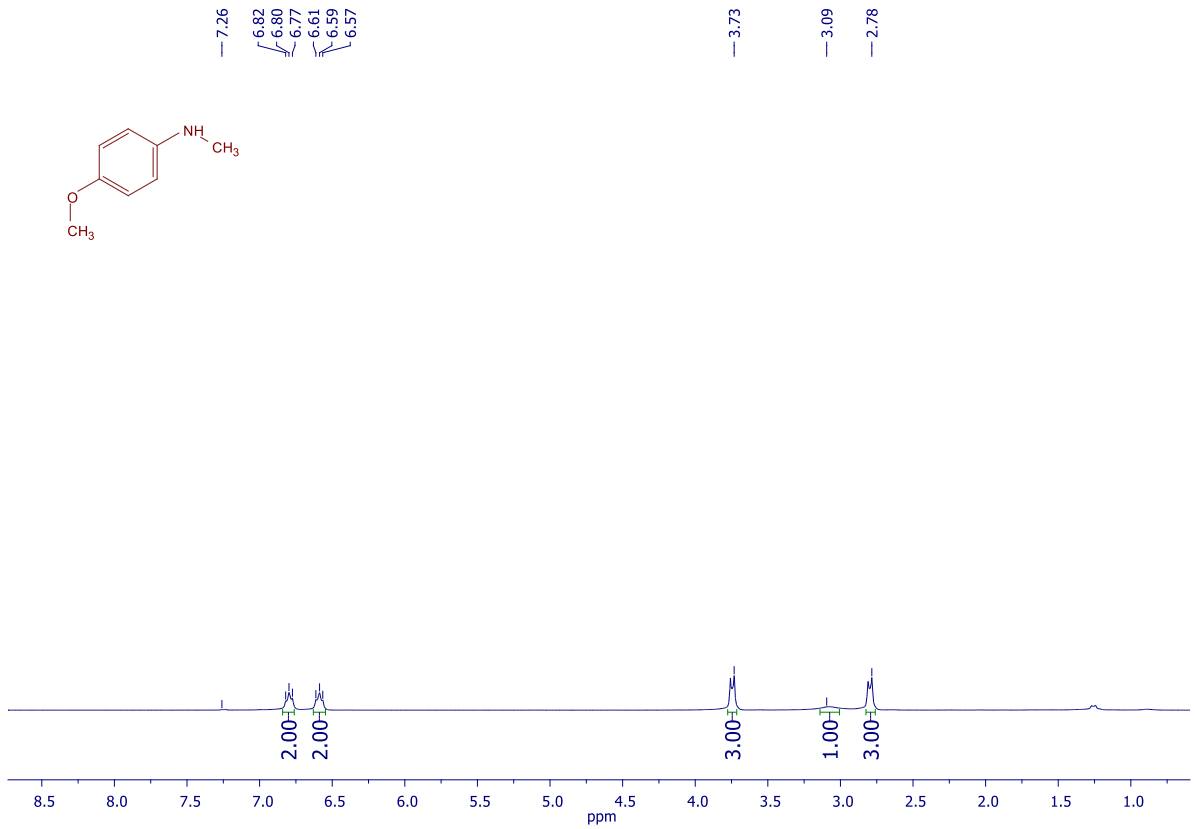
NMR spectra for the synthesis of secondary amines in $CDCl_3$:



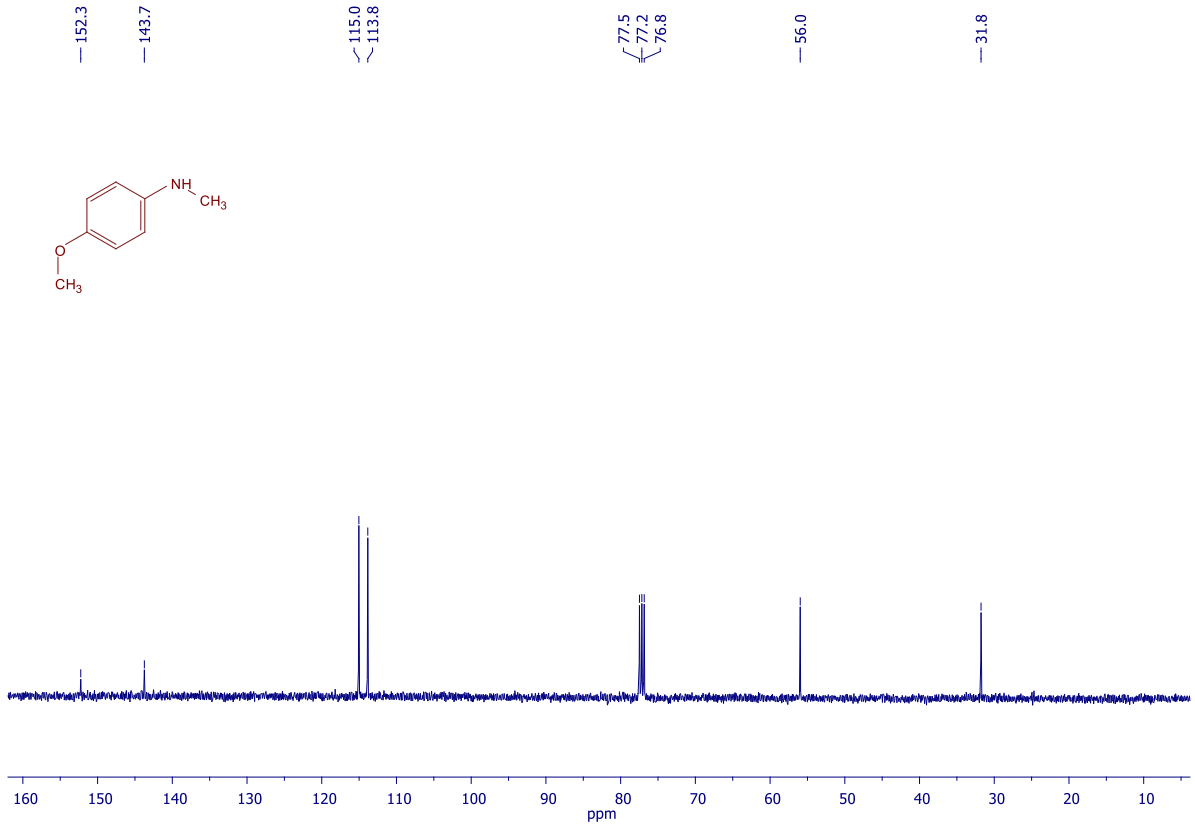
^{1}H NMR spectrum of N,4-dimethylaniline



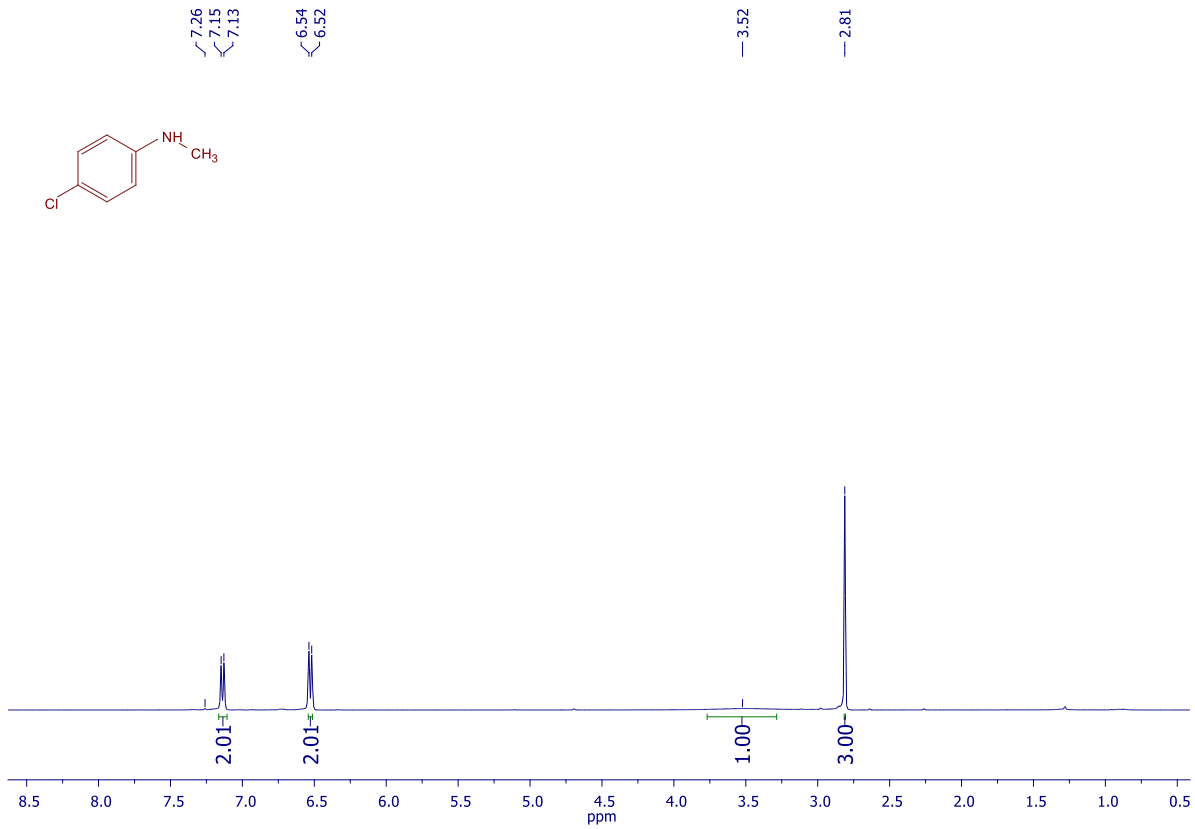
^{13}C {^{1}H} NMR spectrum of N,4-dimethylaniline



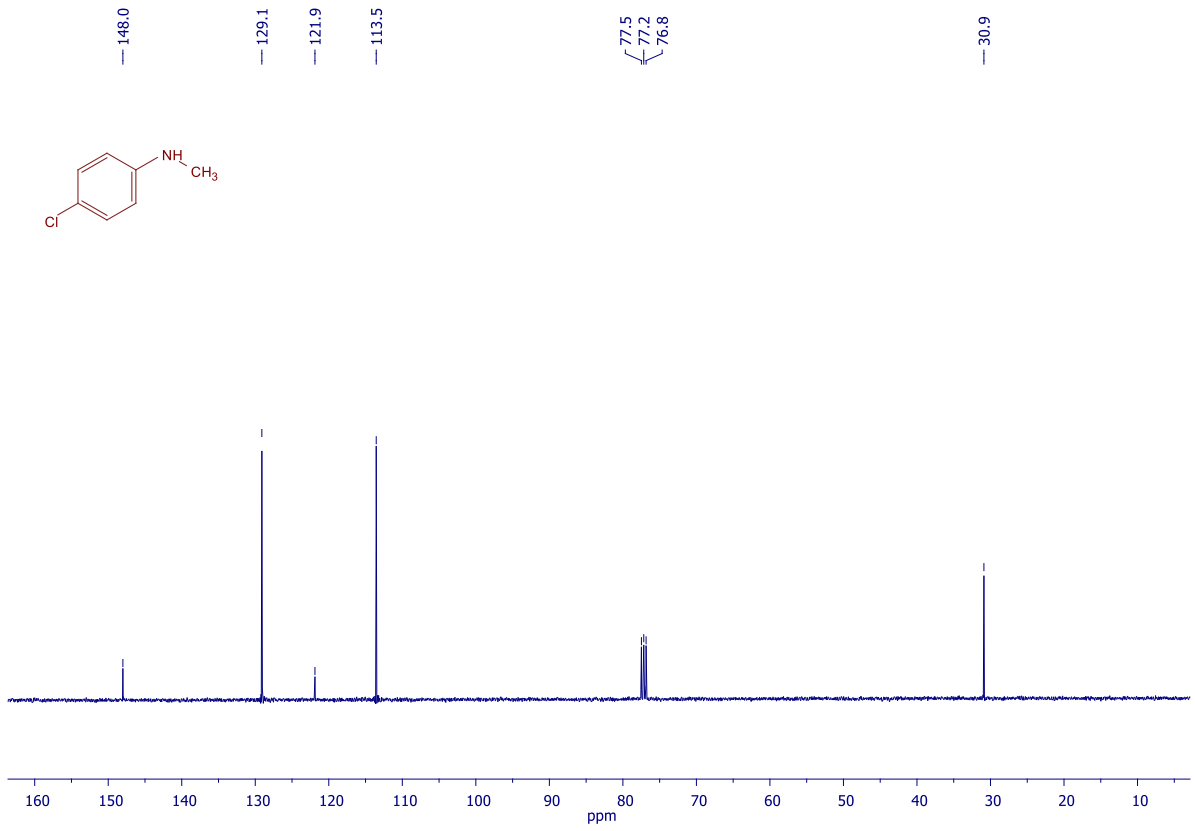
[1]H NMR spectrum of 4-methoxy-N-methylaniline



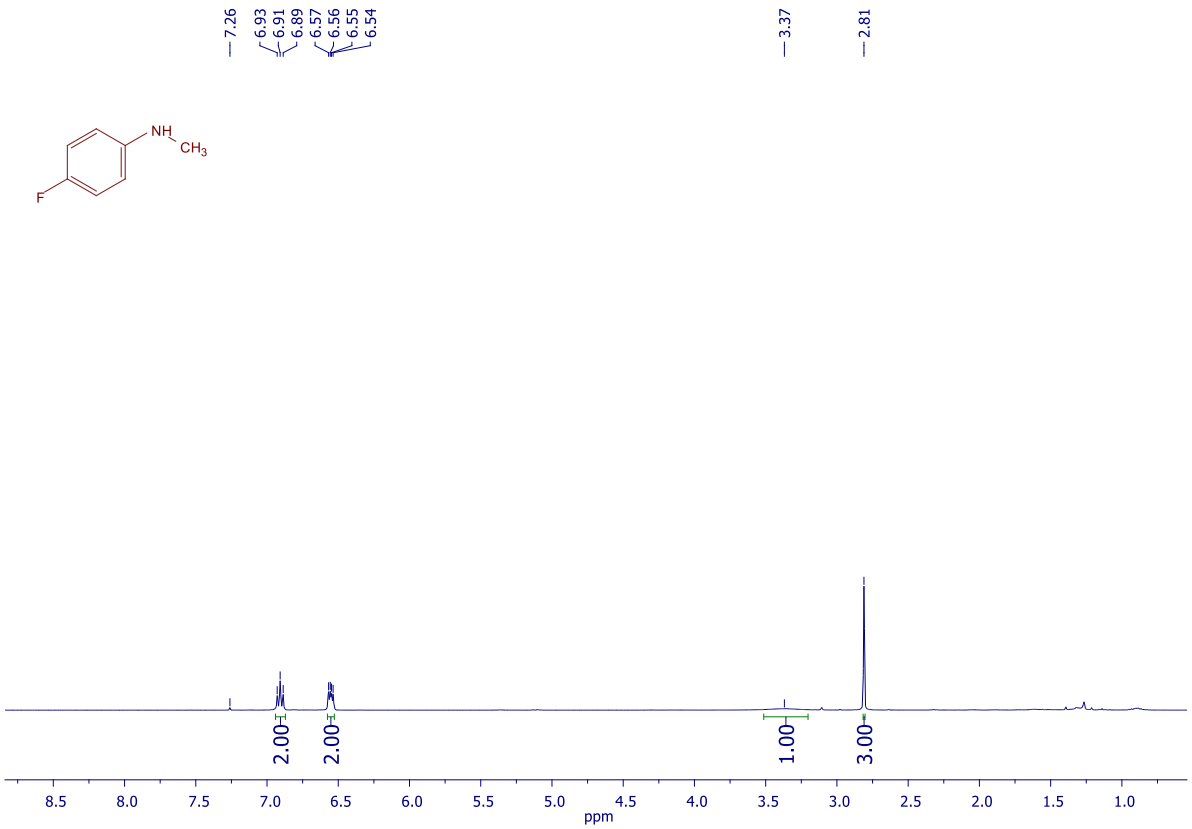
[13]C {[1]H} NMR spectrum of 4-methoxy-N-methylaniline



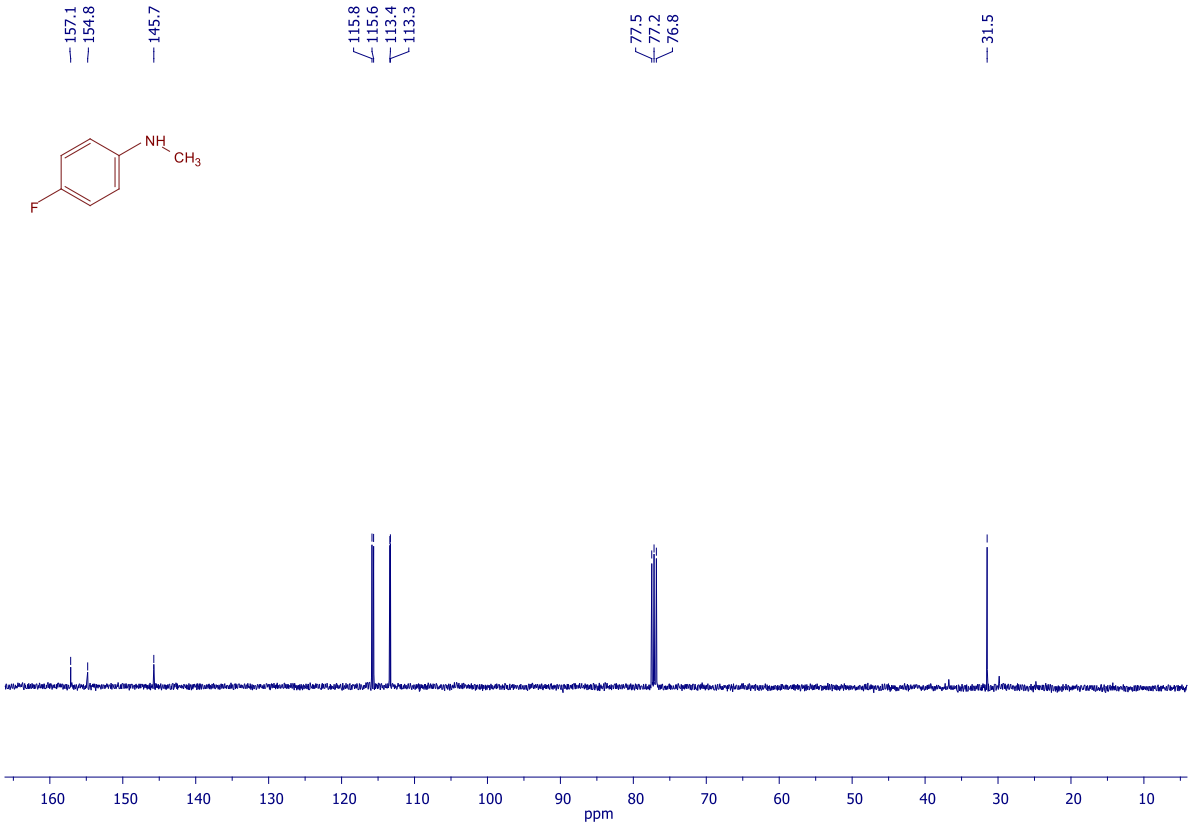
^{1}H NMR spectrum of 4-chloro-N-methylaniline



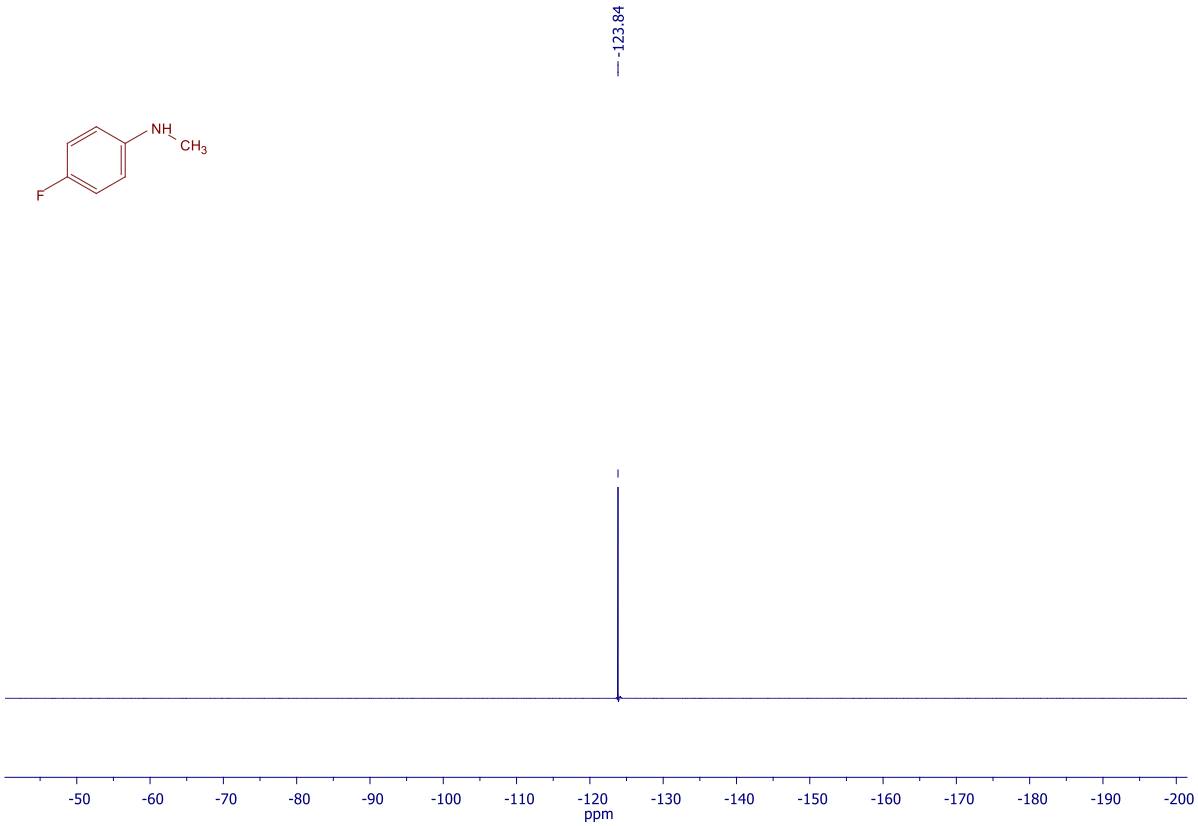
^{13}C {^{1}H} NMR spectrum of 4-chloro-N-methylaniline



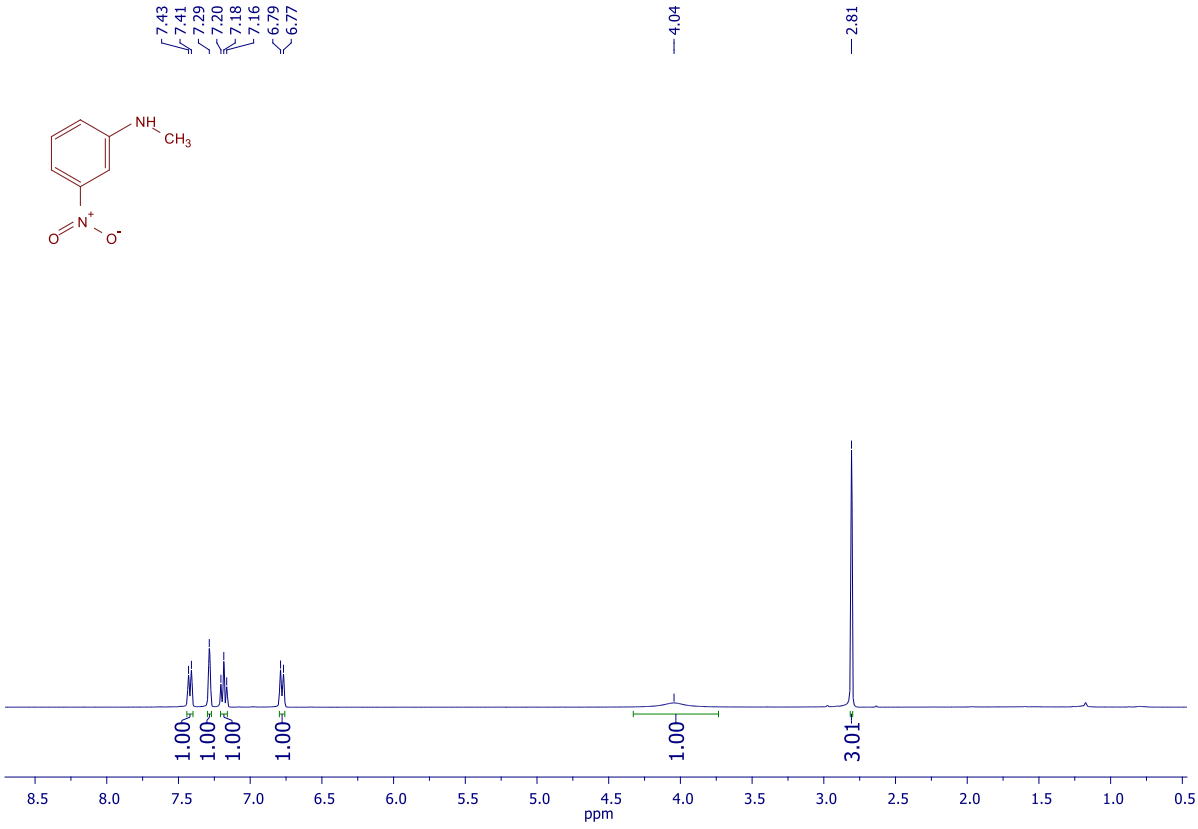
^{1}H NMR spectrum of 4-fluoro-N-methylaniline



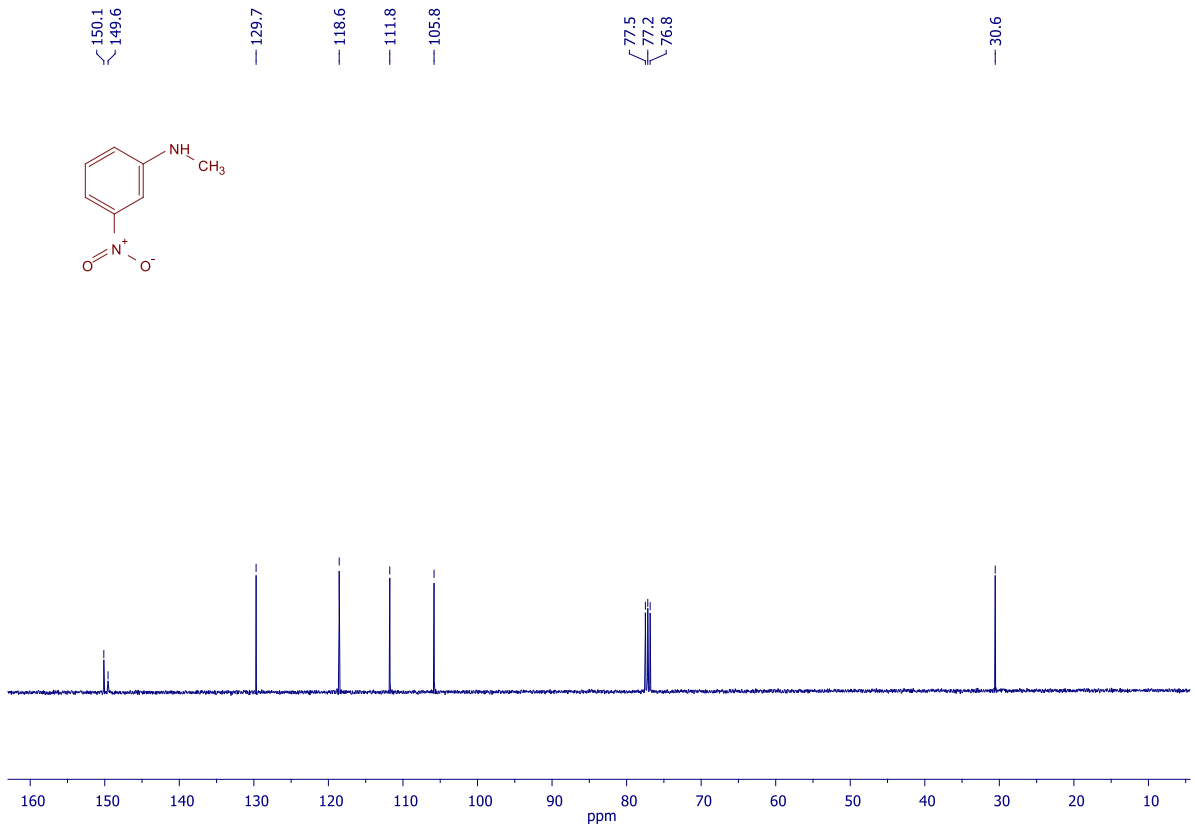
^{13}C {^{1}H} NMR spectrum of 4-fluoro-N-methylaniline



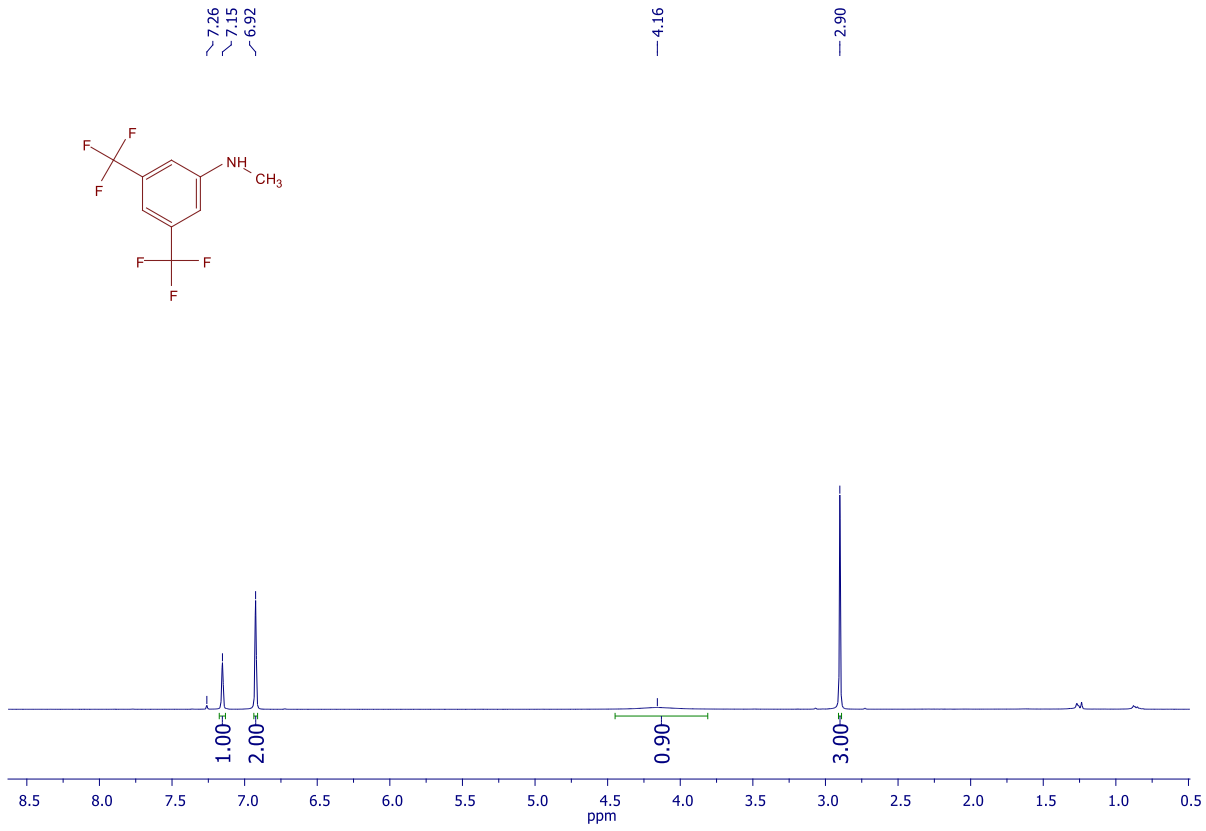
^{19}F NMR spectrum of 4-fluoro-N-methylaniline



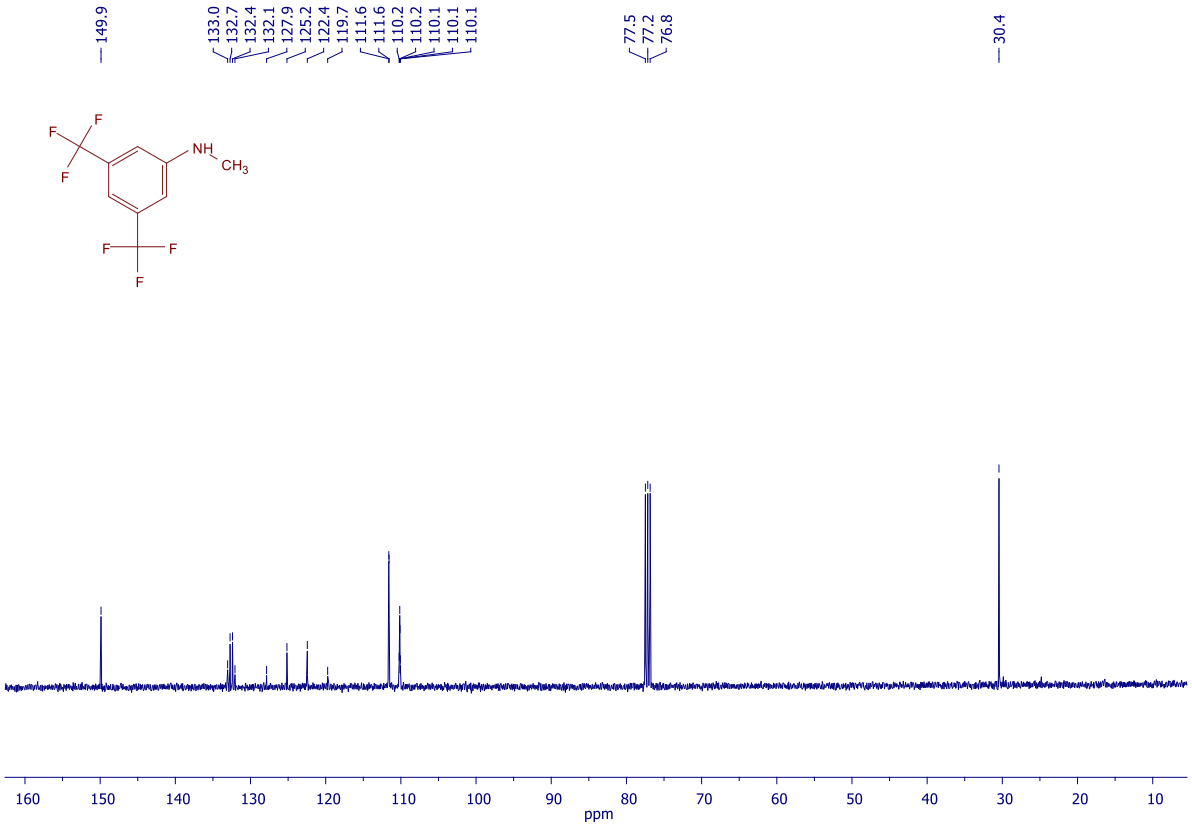
^{1}H NMR spectrum of N-methyl-3-nitroaniline



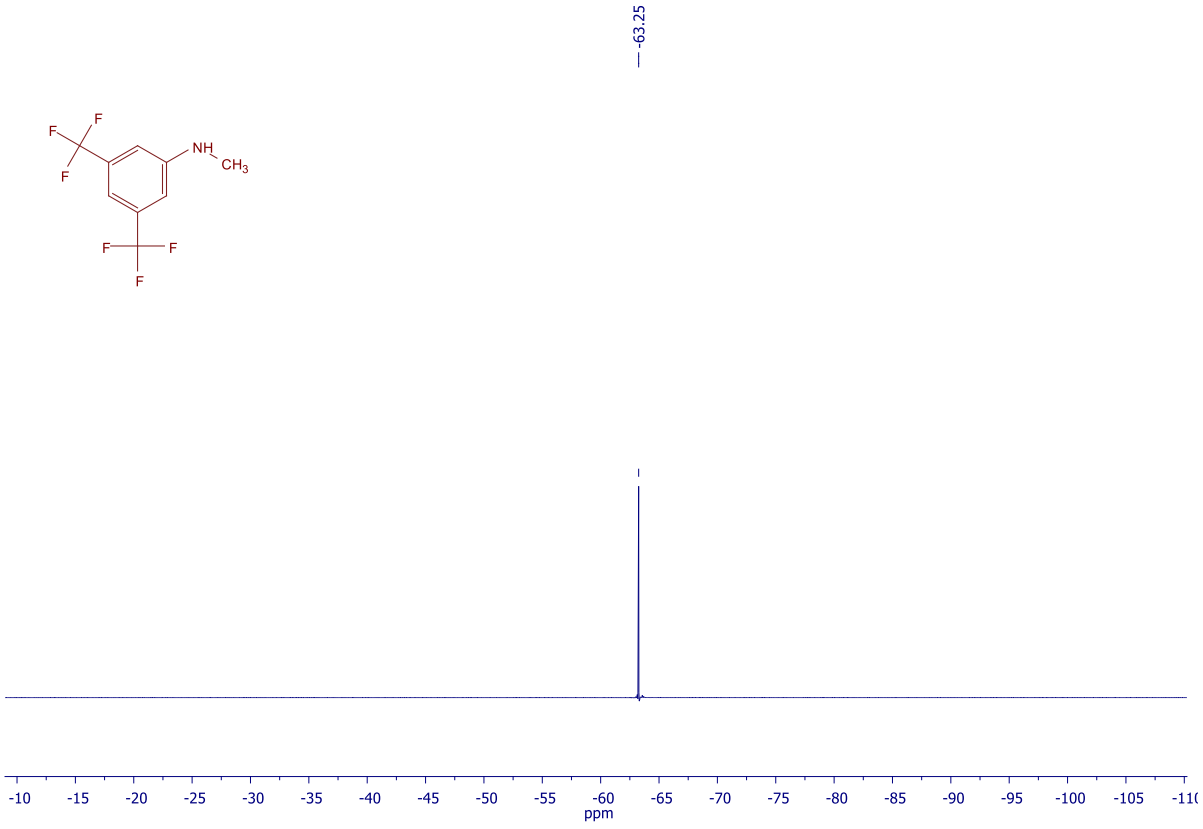
^{13}C {^{1}H} NMR spectrum of N-methyl-3-nitroaniline



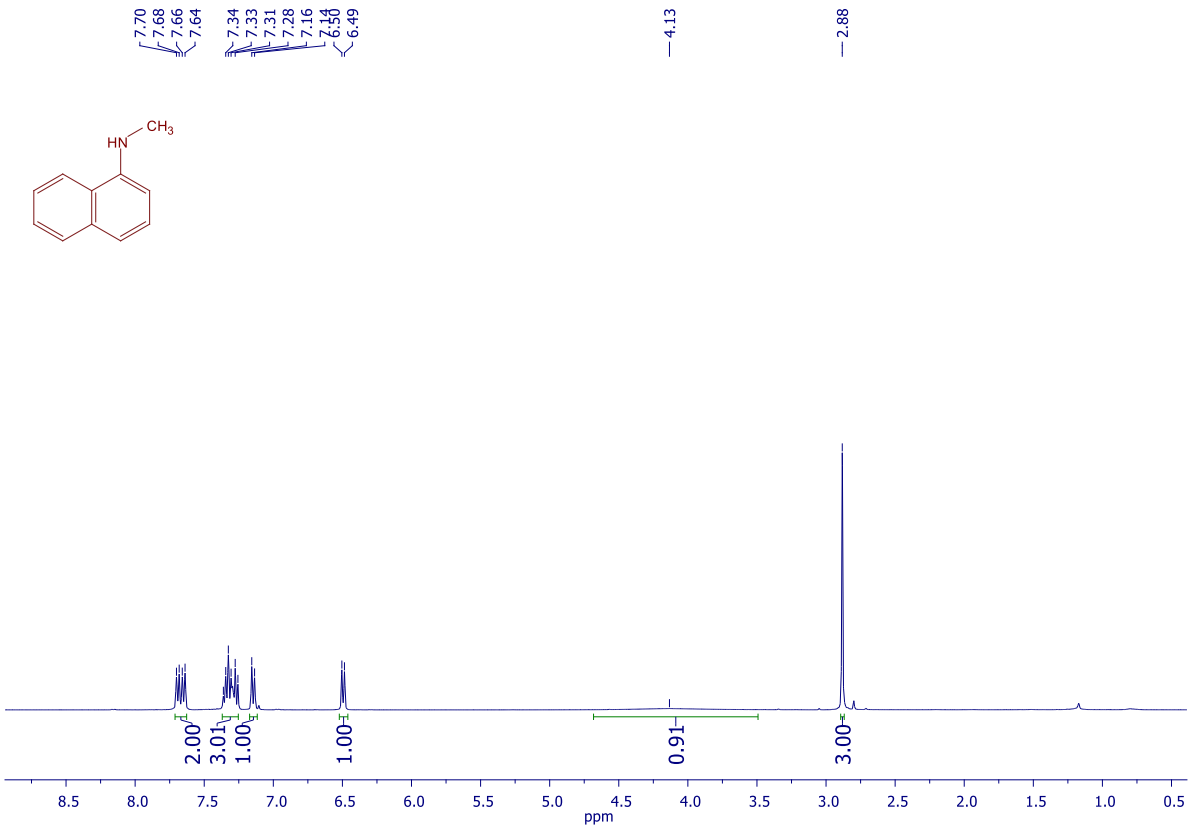
^{1}H NMR spectrum of N-methyl-3,5-bis(trifluoromethyl)aniline



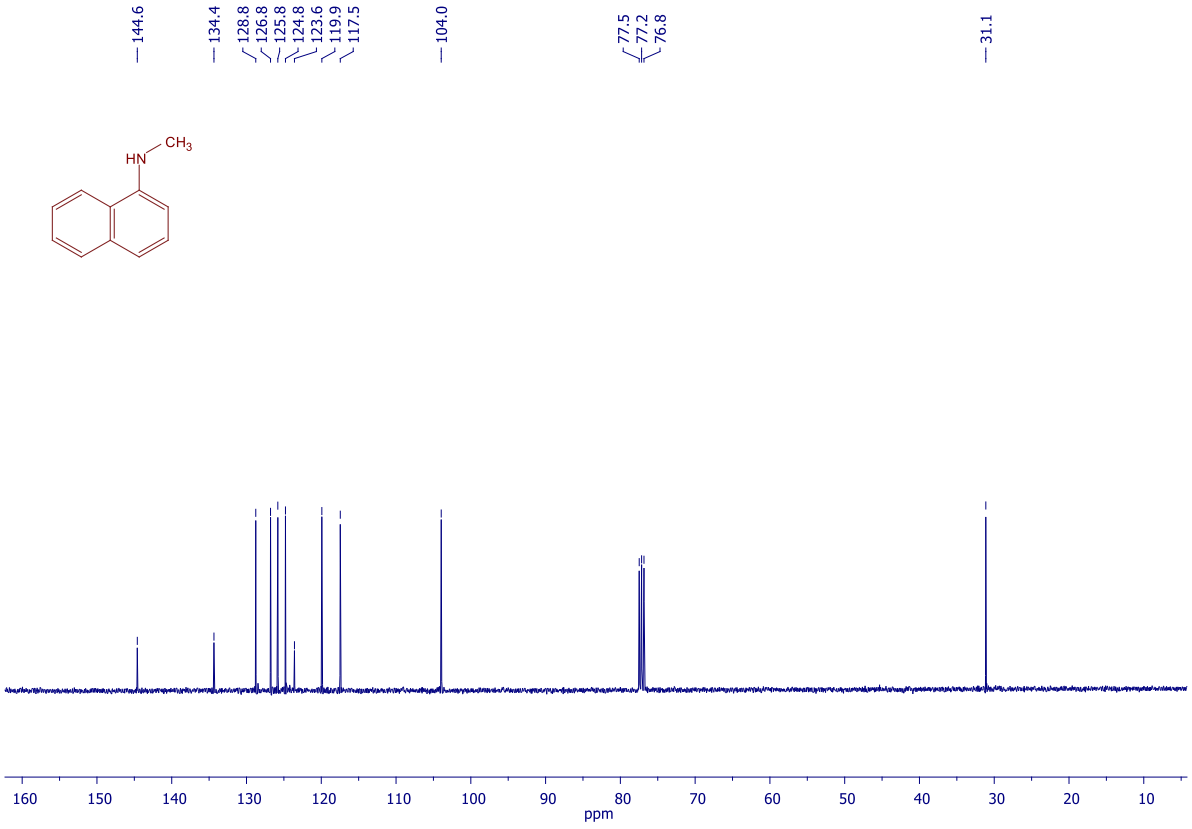
^{13}C {^{1}H} NMR spectrum of N-methyl-3,5-bis(trifluoromethyl)aniline



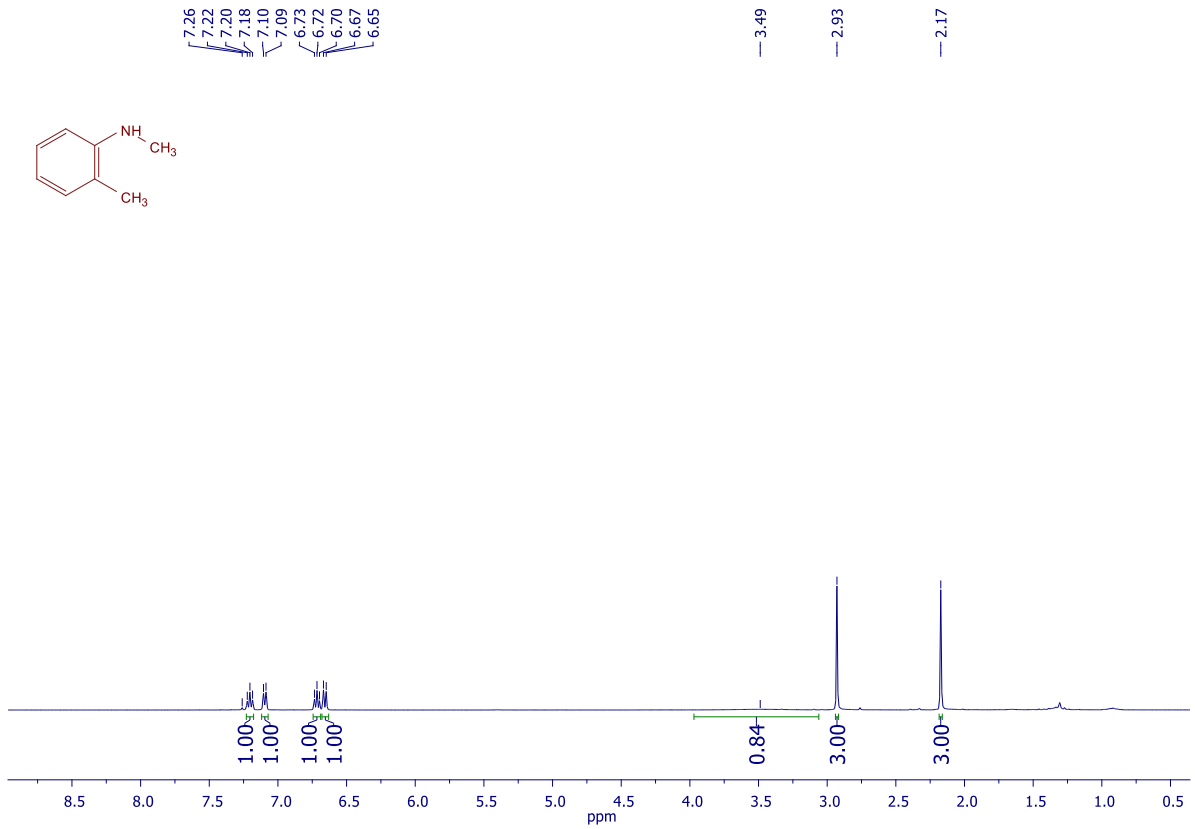
^{19}F NMR spectrum of N-methyl-3,5-bis(trifluoromethyl)aniline



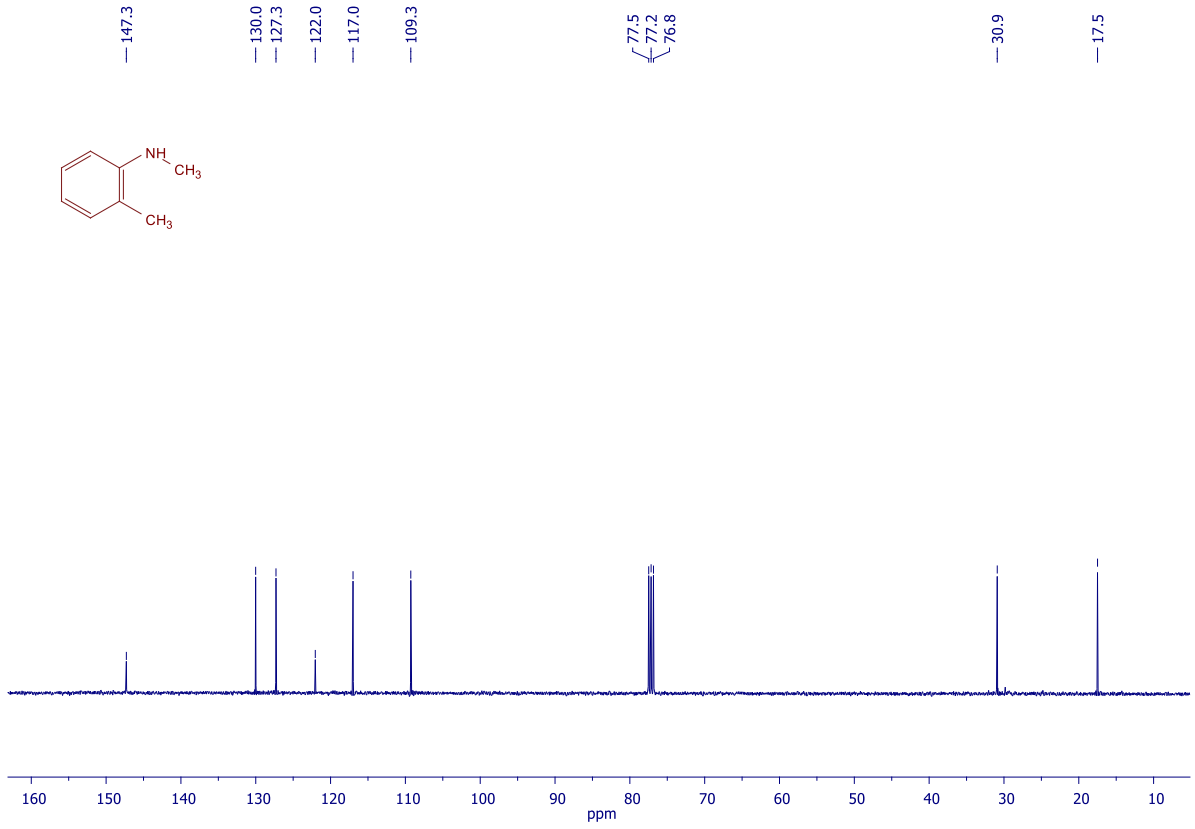
^{1}H NMR spectrum of N-methylnaphthalen-1-amine



^{13}C {^{1}H} NMR spectrum of N-methylnaphthalen-1-amine

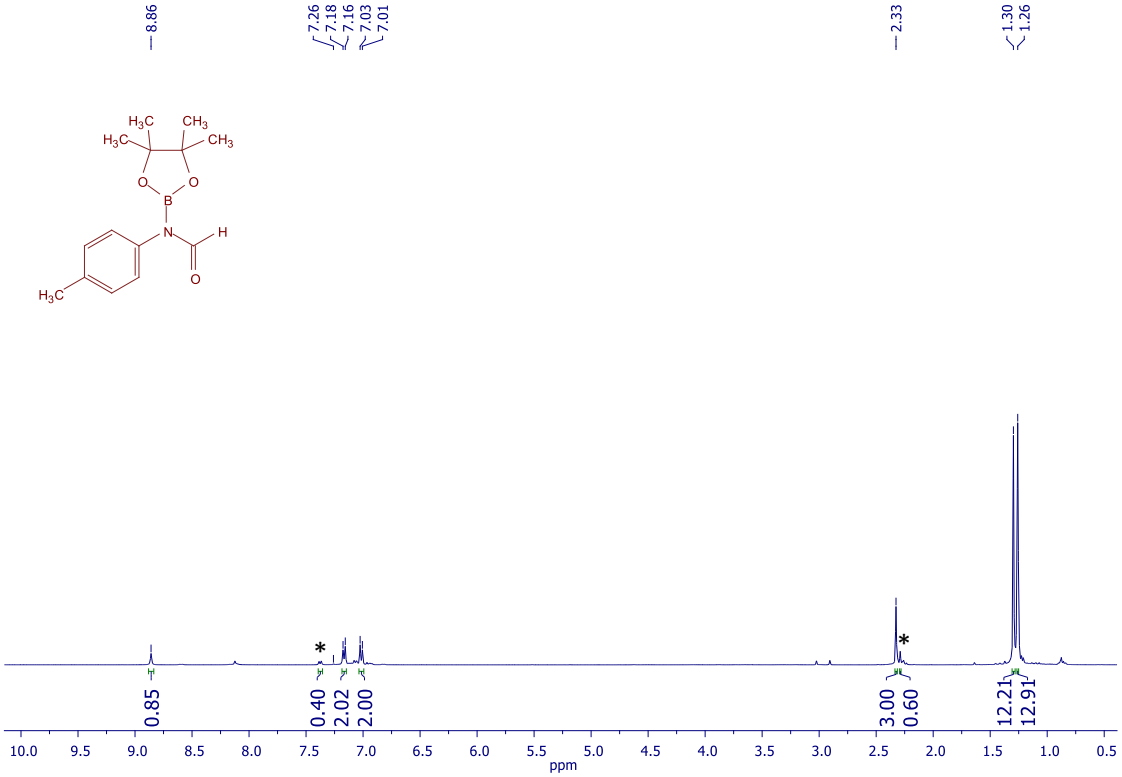


^{1}H NMR spectrum of N,2-dimethylaniline

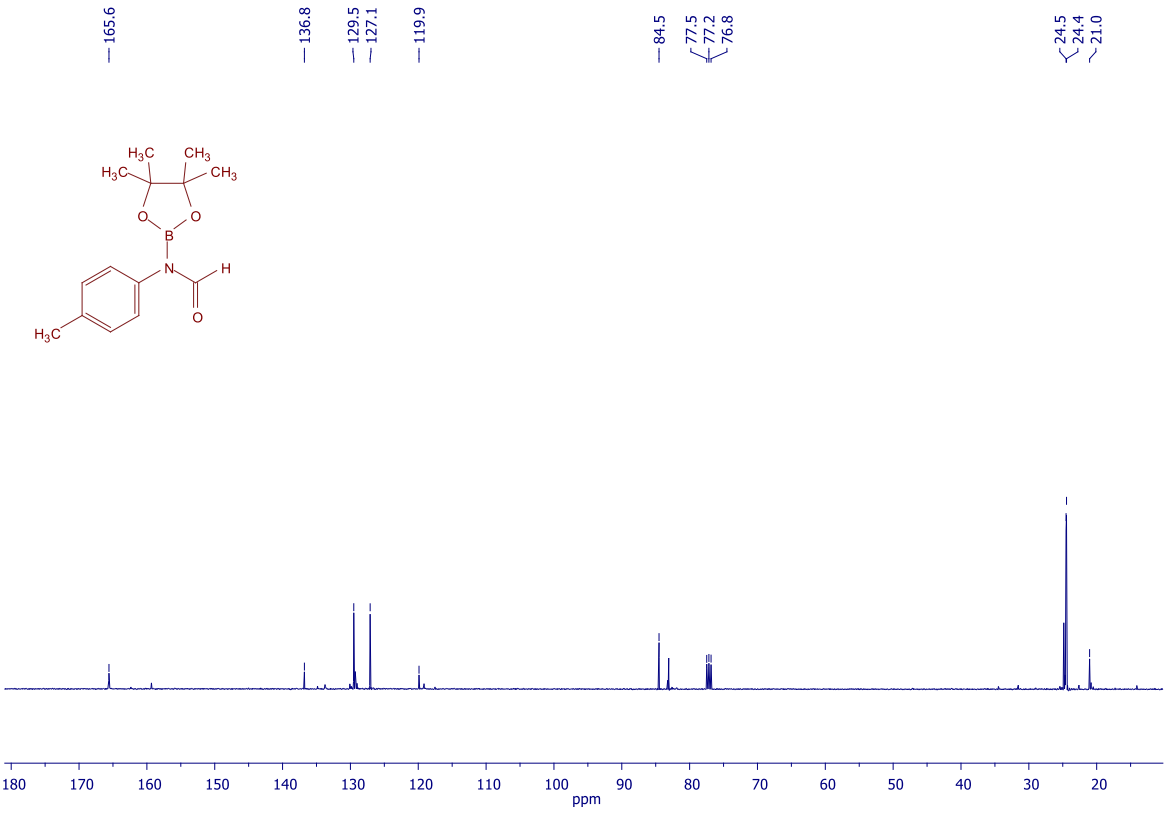


^{13}C {^{1}H} NMR spectrum of N,2-dimethylaniline

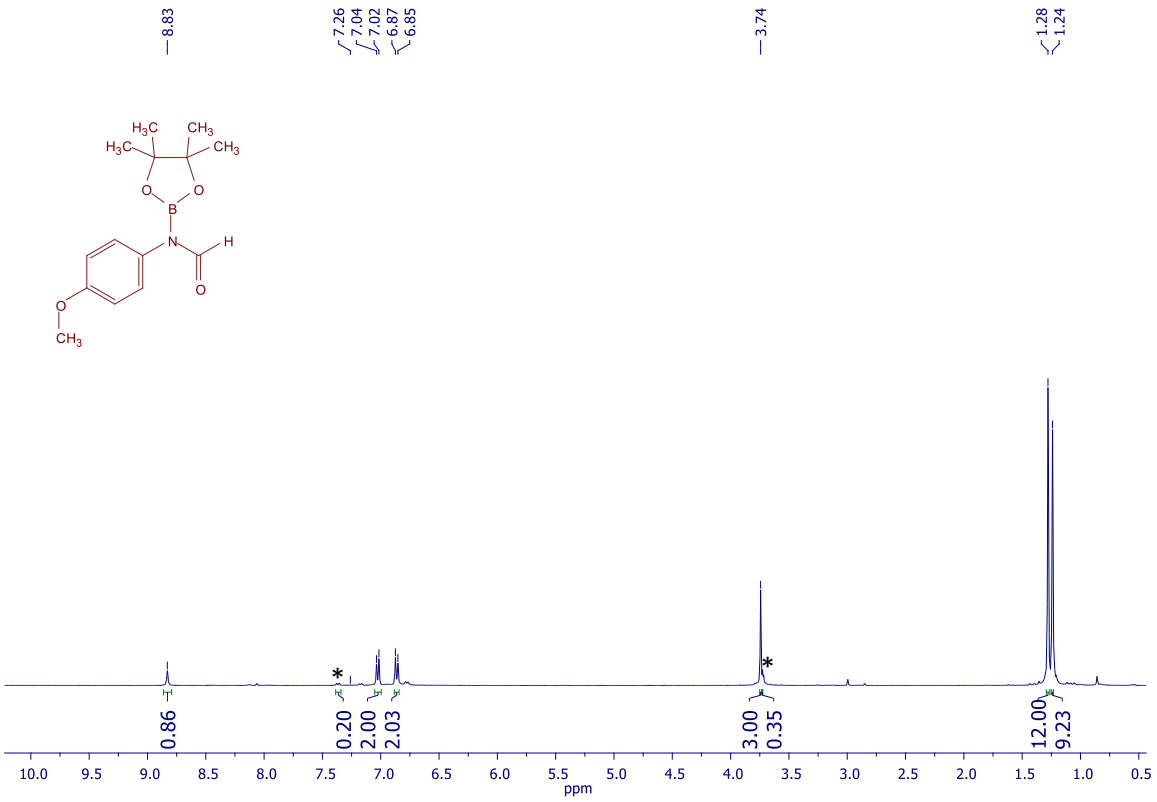
NMR spectra of monohydroboration reaction in $CDCl_3$:



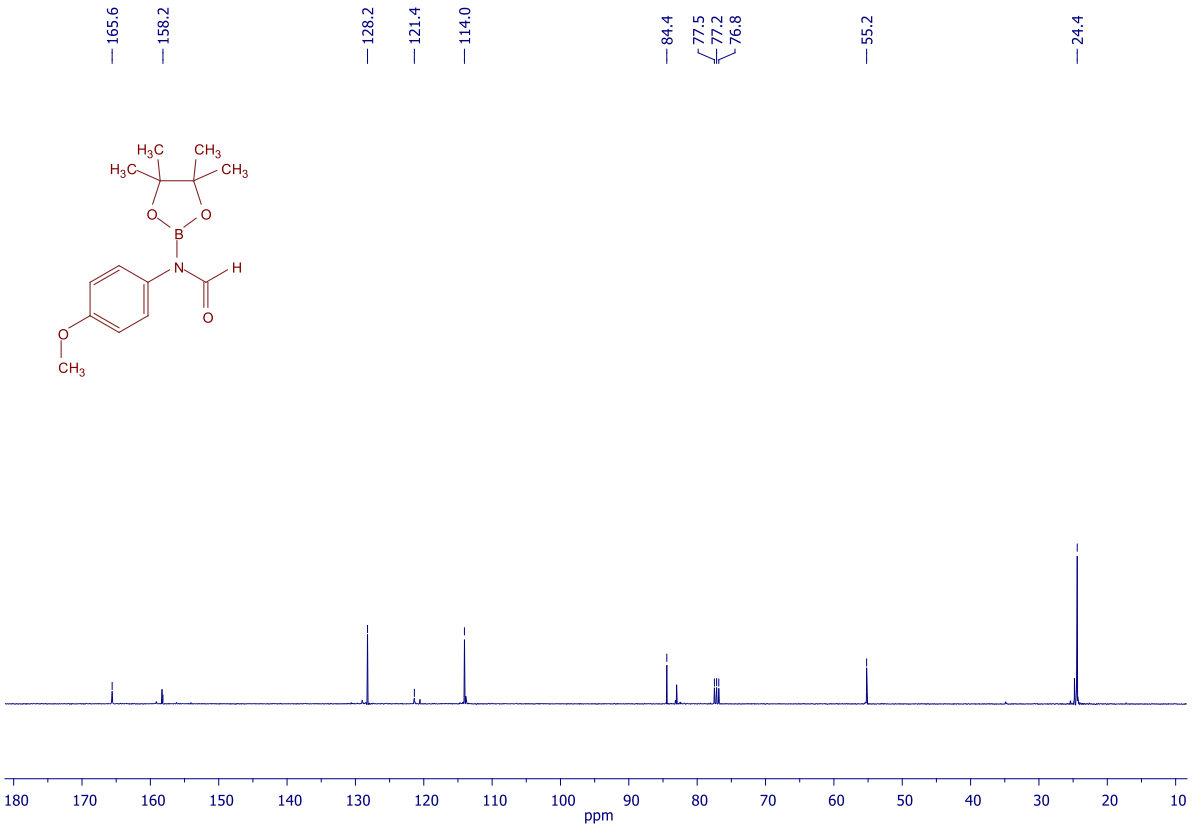
*^1H NMR spectrum of N-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-N-(p-tolyl)formamide (Compound-**3a**), (* represents starting isocyanate in the reaction mixture)*



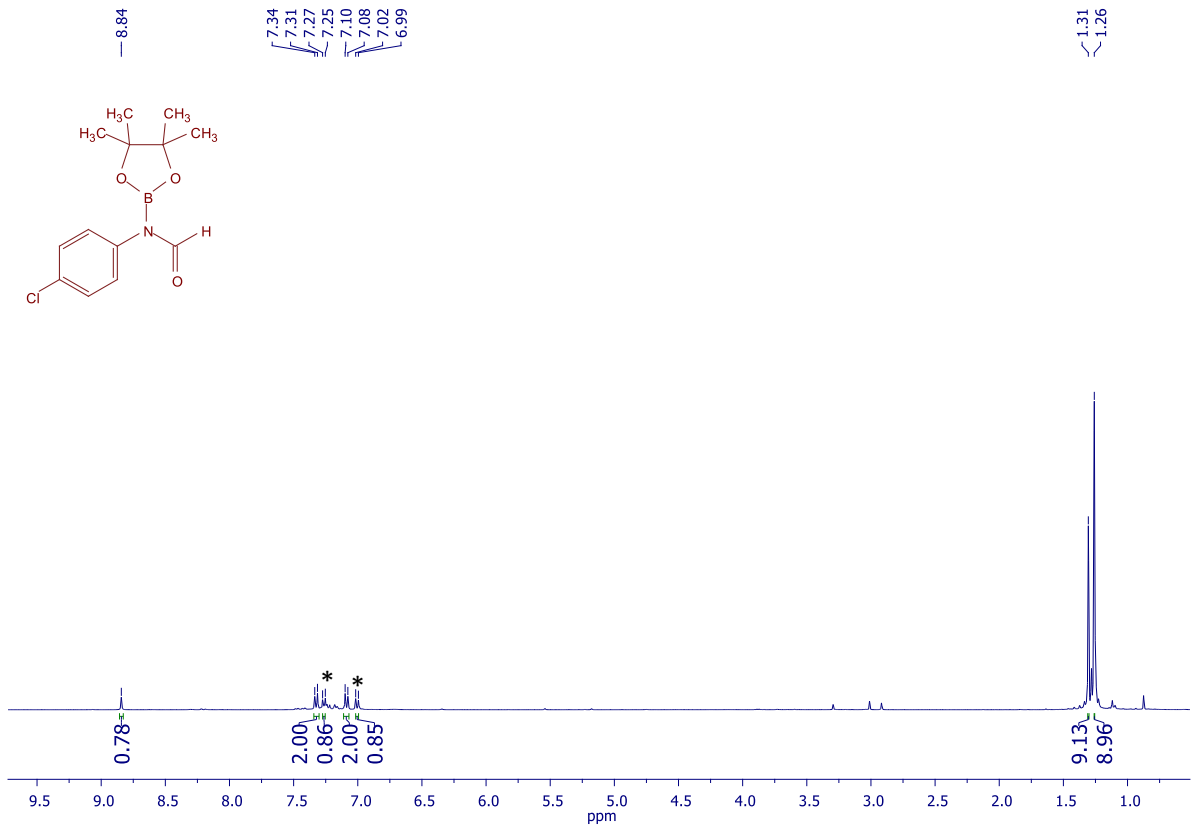
*^{13}C {^1H} NMR spectrum of N-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-N-(p-tolyl)formamide (Compound-**3a**)*



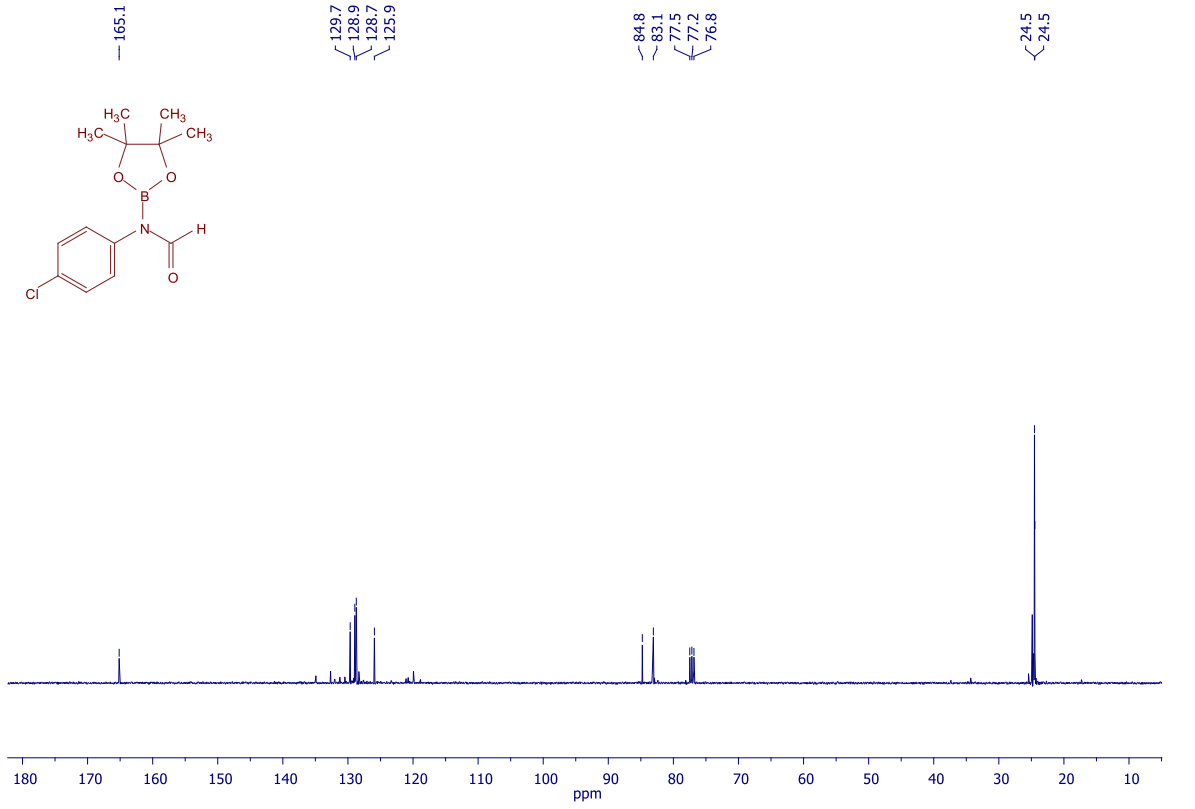
*^{1}H NMR spectrum of N-(4-methoxyphenyl)-N-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)formamide (Compound-**3b**), (* represents starting isocyanate in the reaction mixture)*



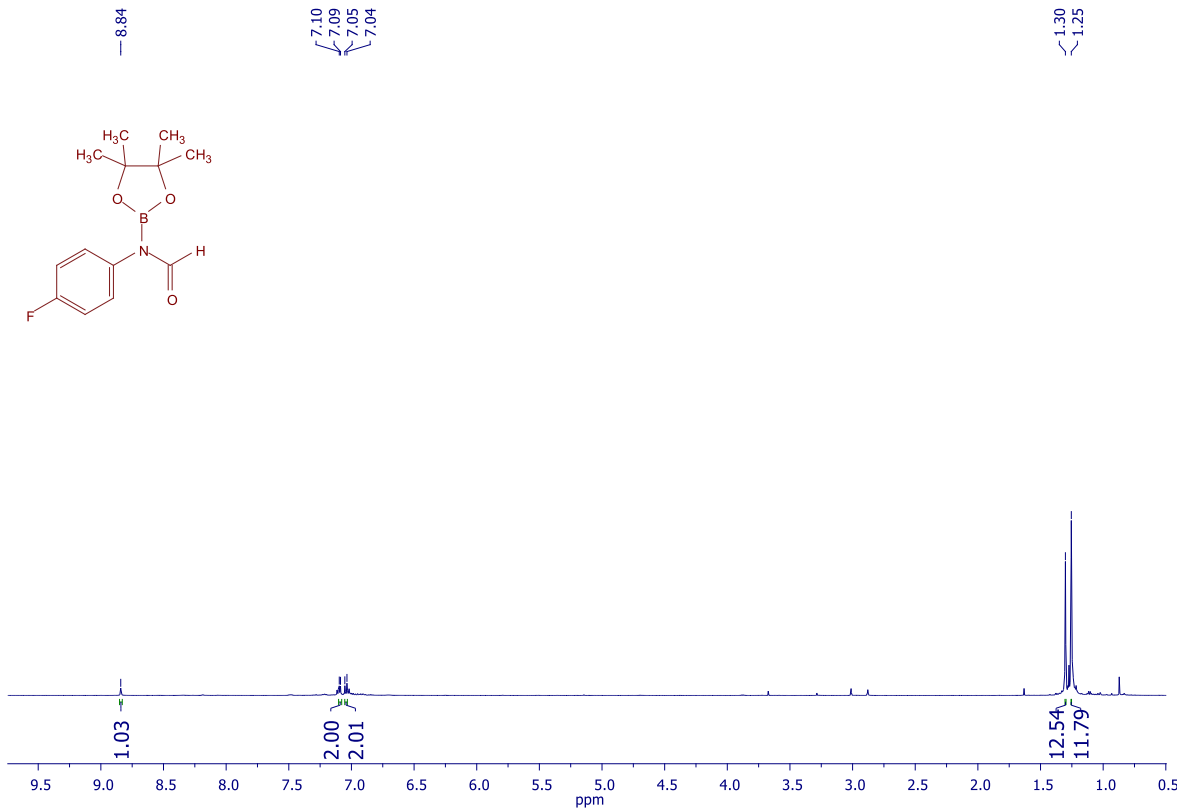
*^{13}C {^{1}H} NMR spectrum of N-(4-methoxyphenyl)-N-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)formamide (Compound-**3b**)*



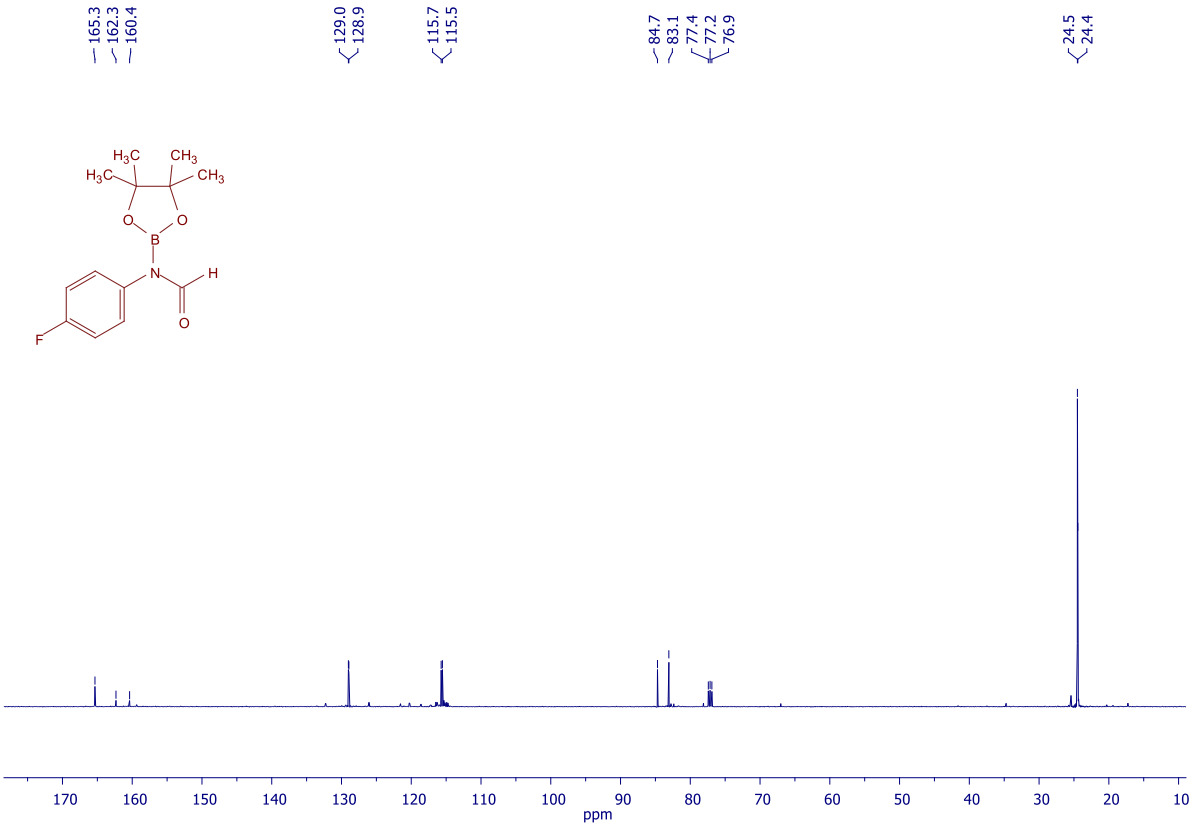
*^{1}H NMR spectrum of N-(4-chlorophenyl)-N-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)formamide (Compound-**3c**) (* represents starting isocyanate in the reaction mixture)*



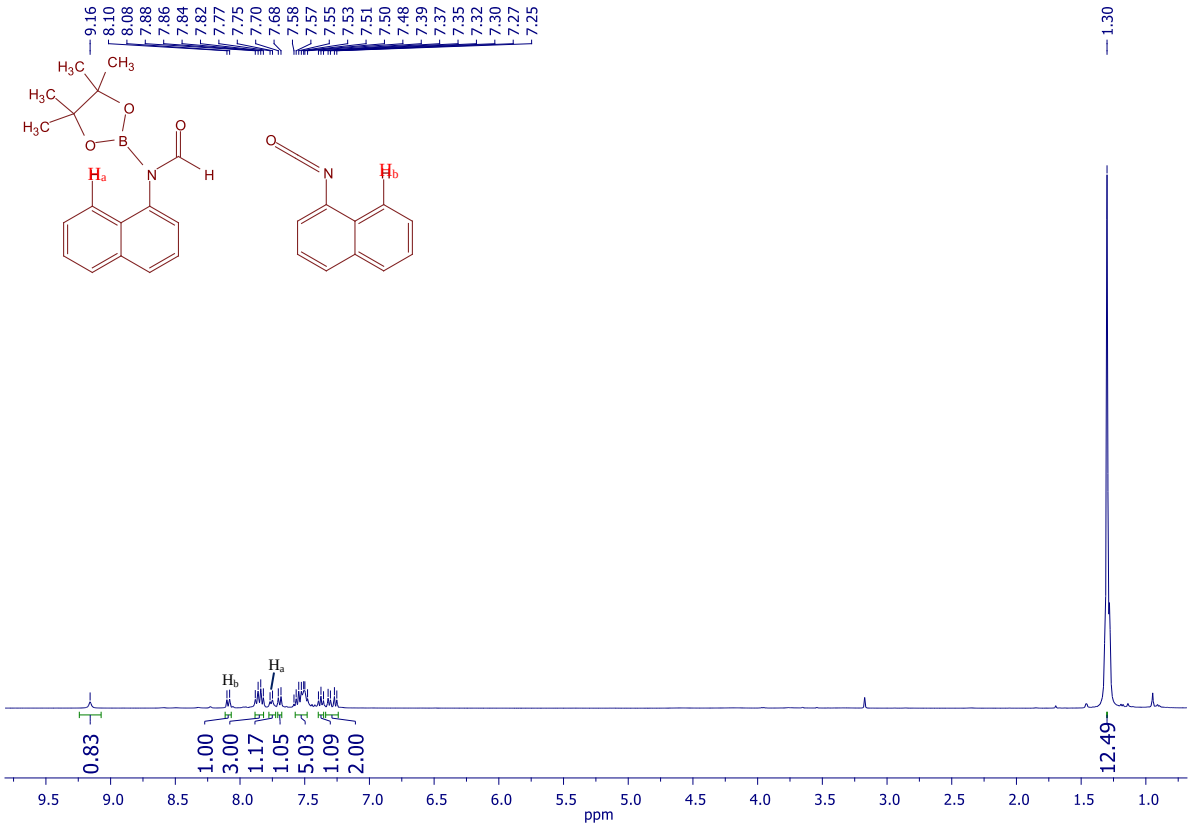
*^{13}C {^{1}H} NMR spectrum of N-(4-chlorophenyl)-N-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)formamide (Compound-**3c**)*



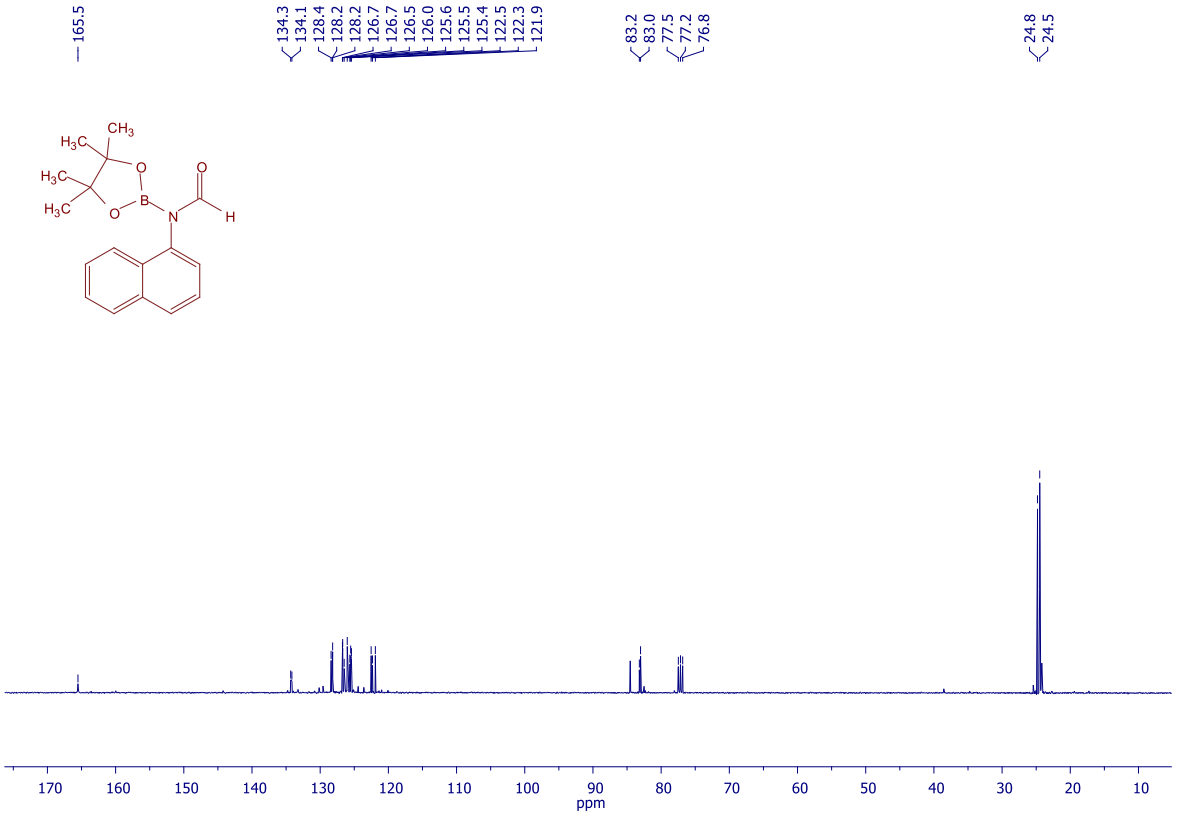
*^{1}H NMR spectrum of N-(4-fluorophenyl)-N-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)formamide (Compound-**3d**)*



*^{13}C {^{1}H} NMR spectrum of N-(4-fluorophenyl)-N-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)formamide (Compound-**3d**)*

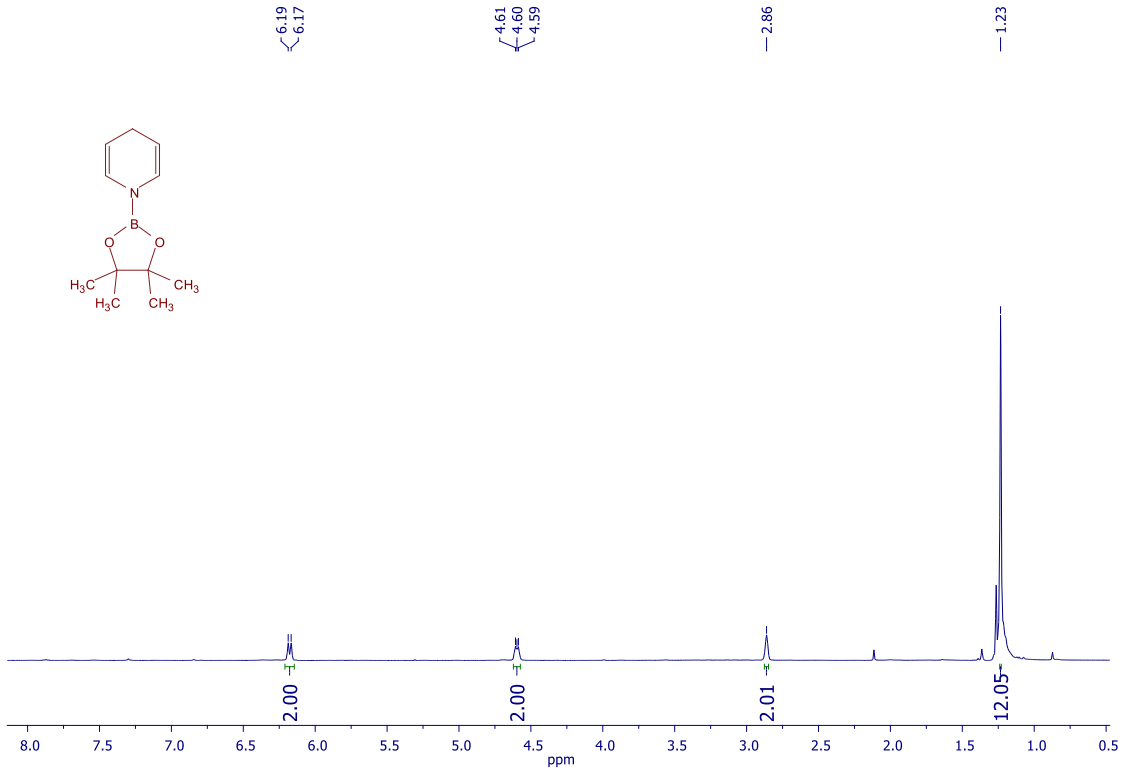


*^{1}H NMR spectrum of N-(naphthalen-1-yl)-N-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)formamide (Compound-**3j**)*

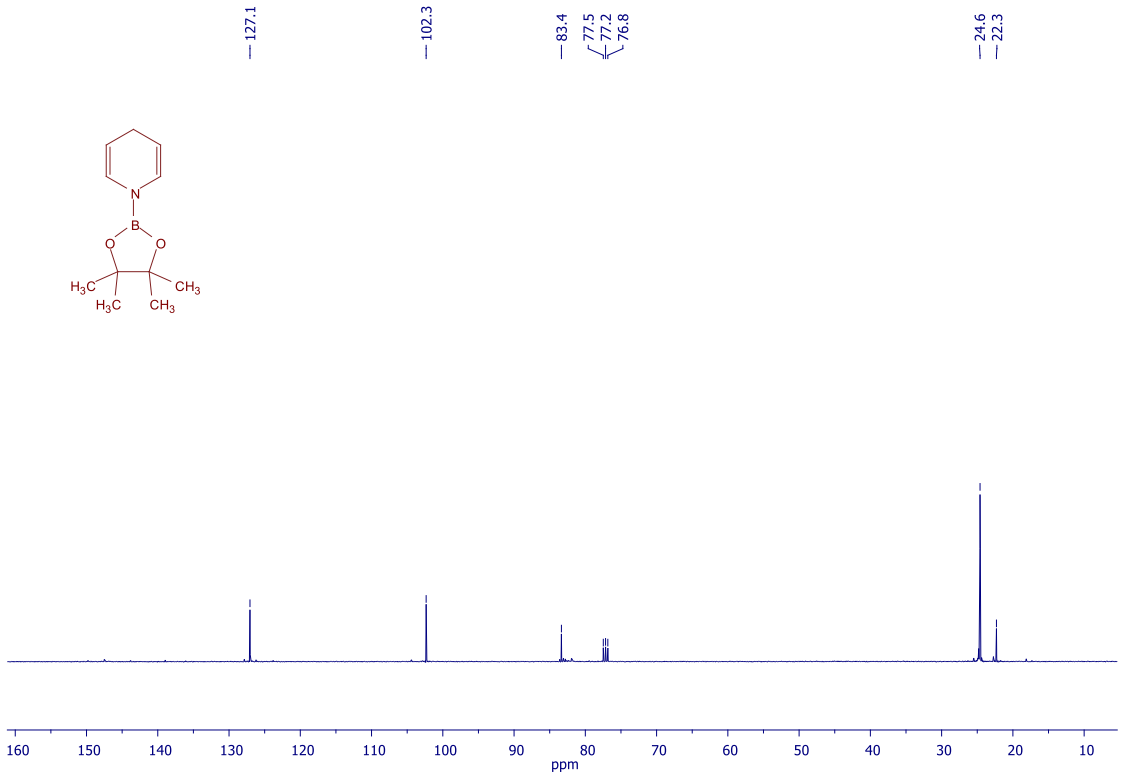


*^{13}C {^{1}H} NMR spectrum of N-(naphthalen-1-yl)-N-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)formamide (Compound-**3j**)*

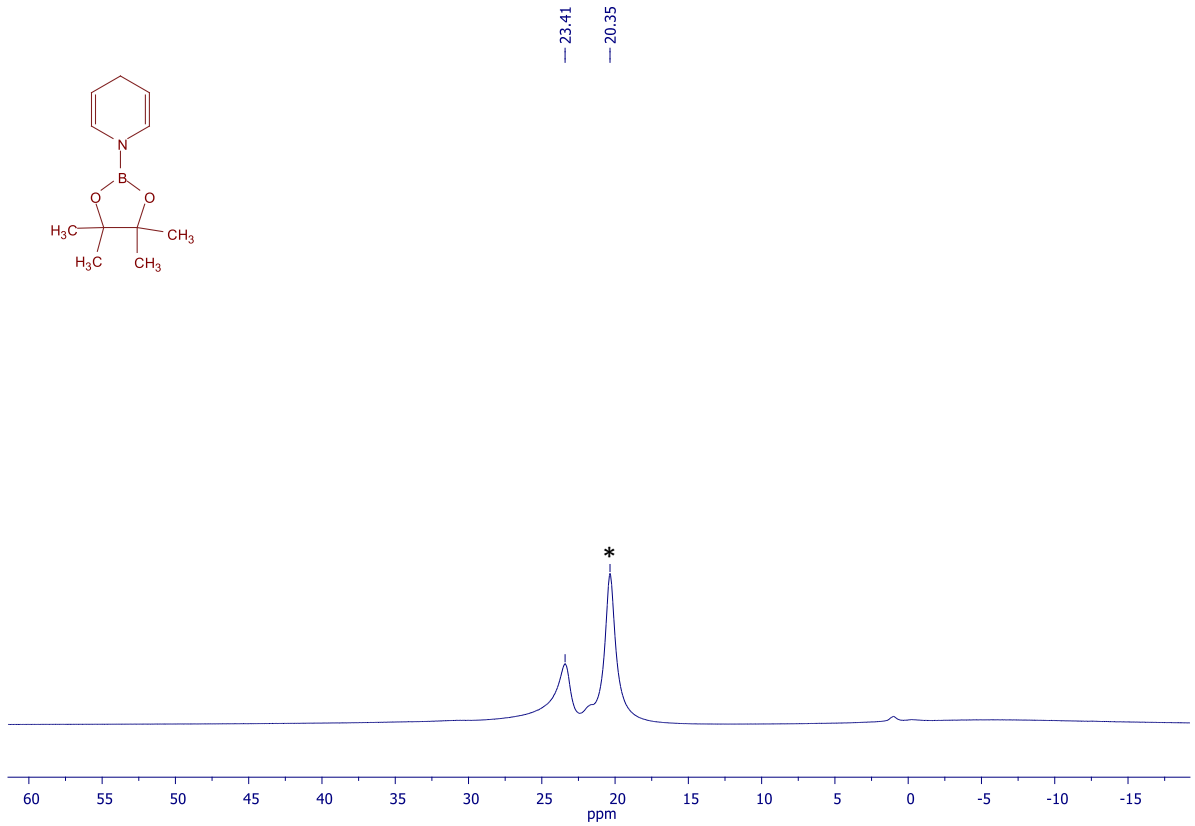
NMR spectra of pyridine hydroboration and hydrogenation of quinoline derivatives:



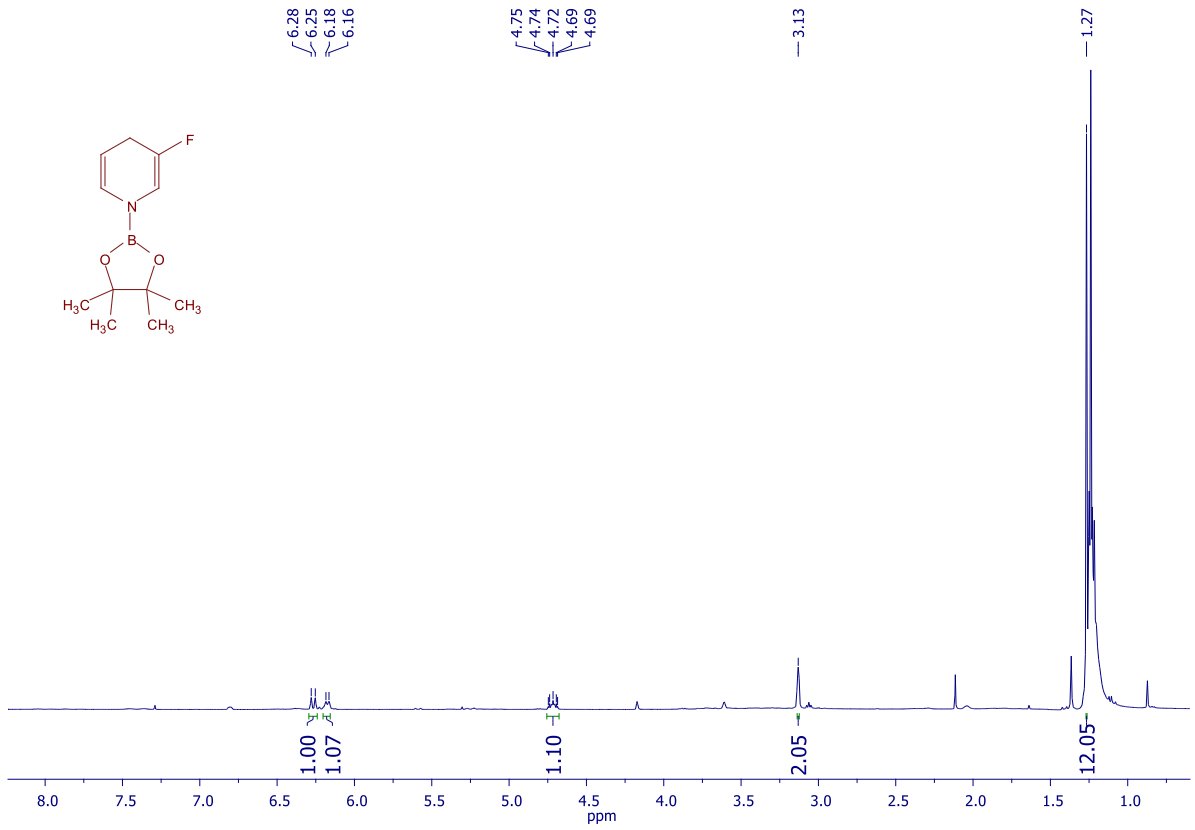
*^{1}H NMR spectrum of 1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1,4-dihydropyridine (Compound-**5a**)*



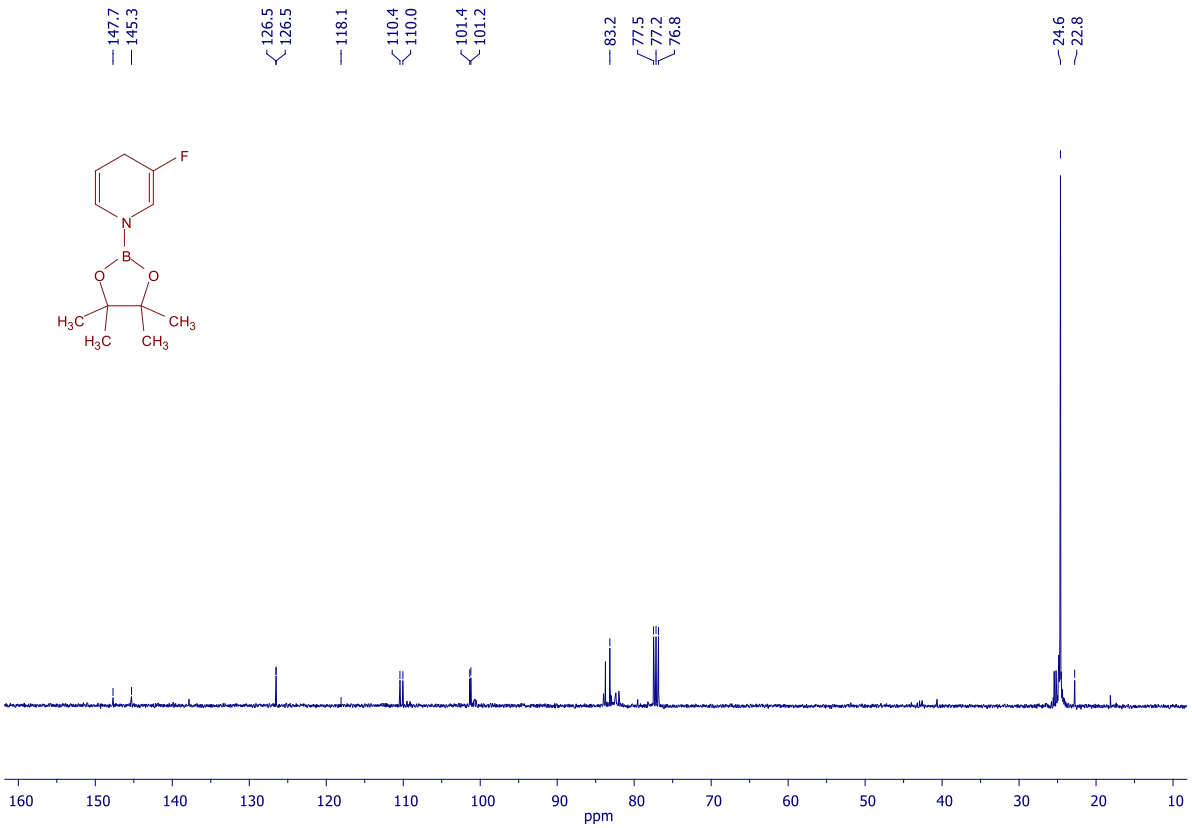
*^{13}C {^{1}H} NMR spectrum of 1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1,4-dihydropyridine (Compound-**5a**)*



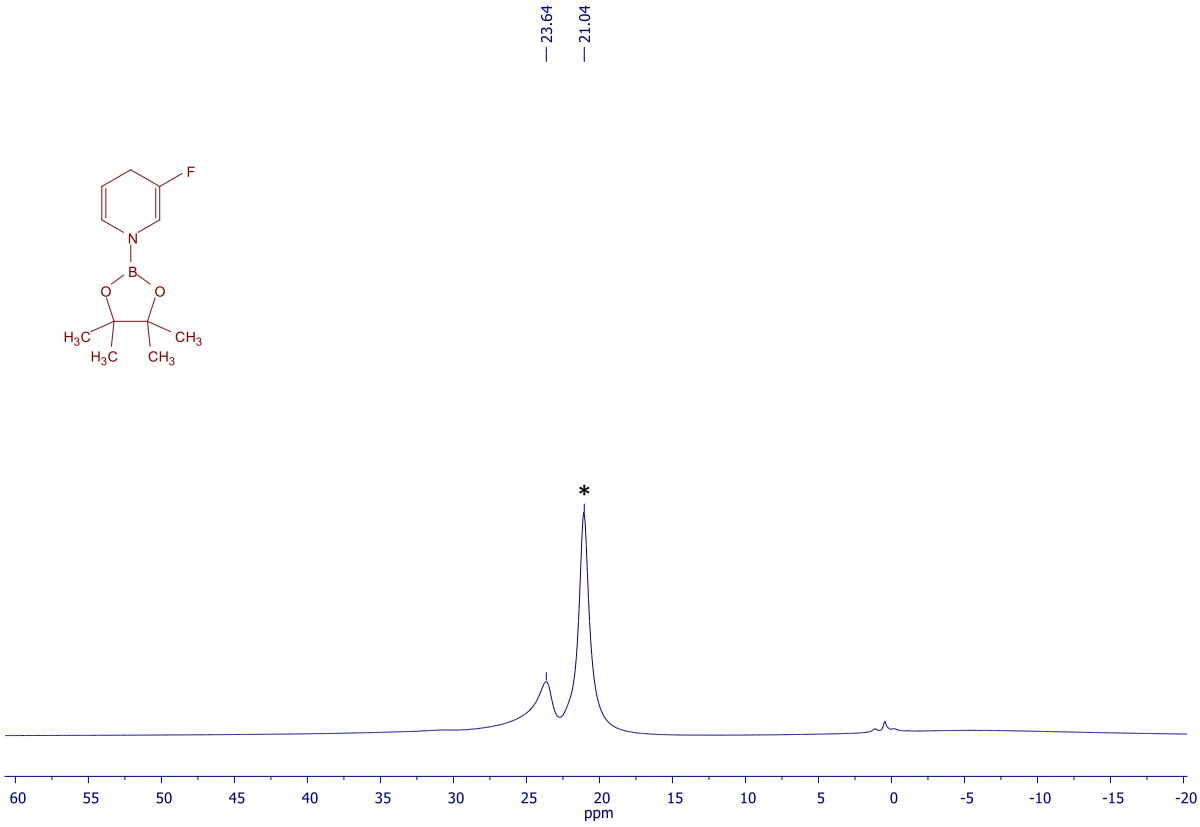
*^{11}B NMR spectrum of 1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1,4-dihydropyridine (Compound-**5a**) * indicates the decomposition product B_2pin_3*



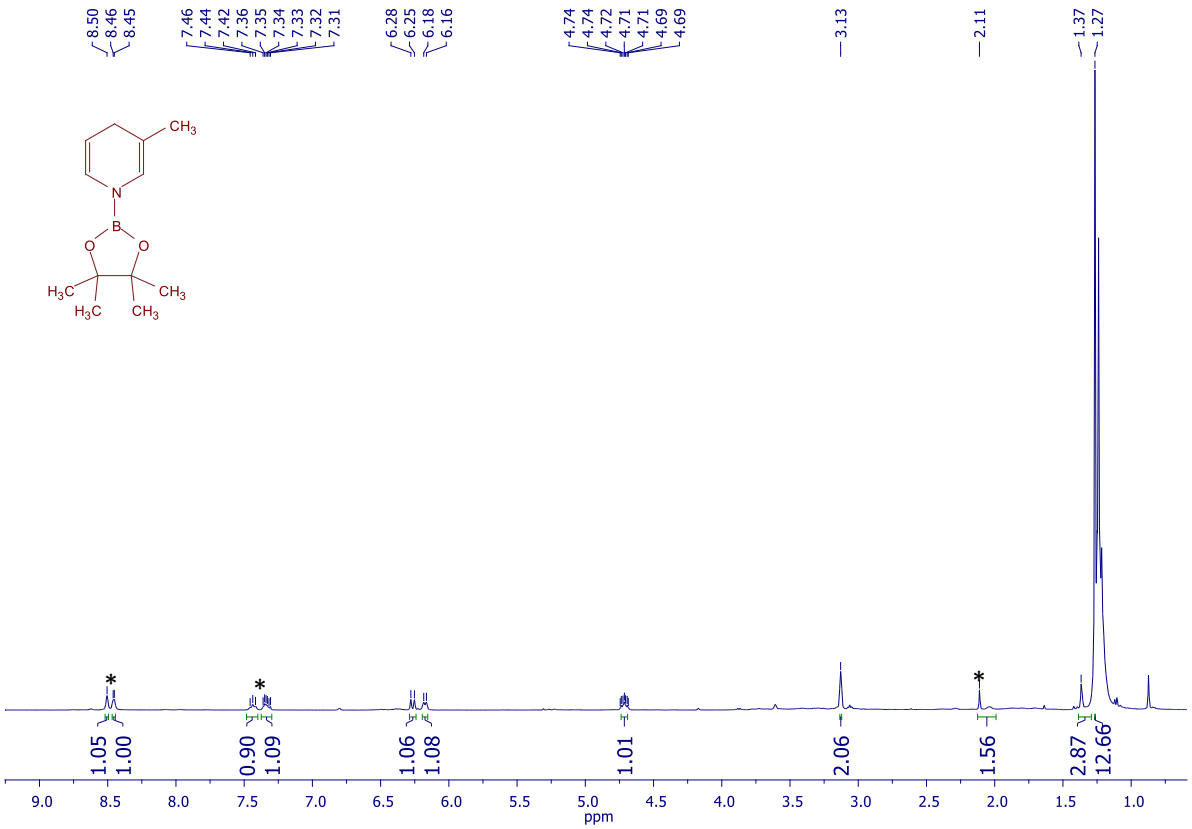
*^{1}H NMR spectrum of 3-fluoro-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1,4-dihydropyridine (Compound-**5b**)*



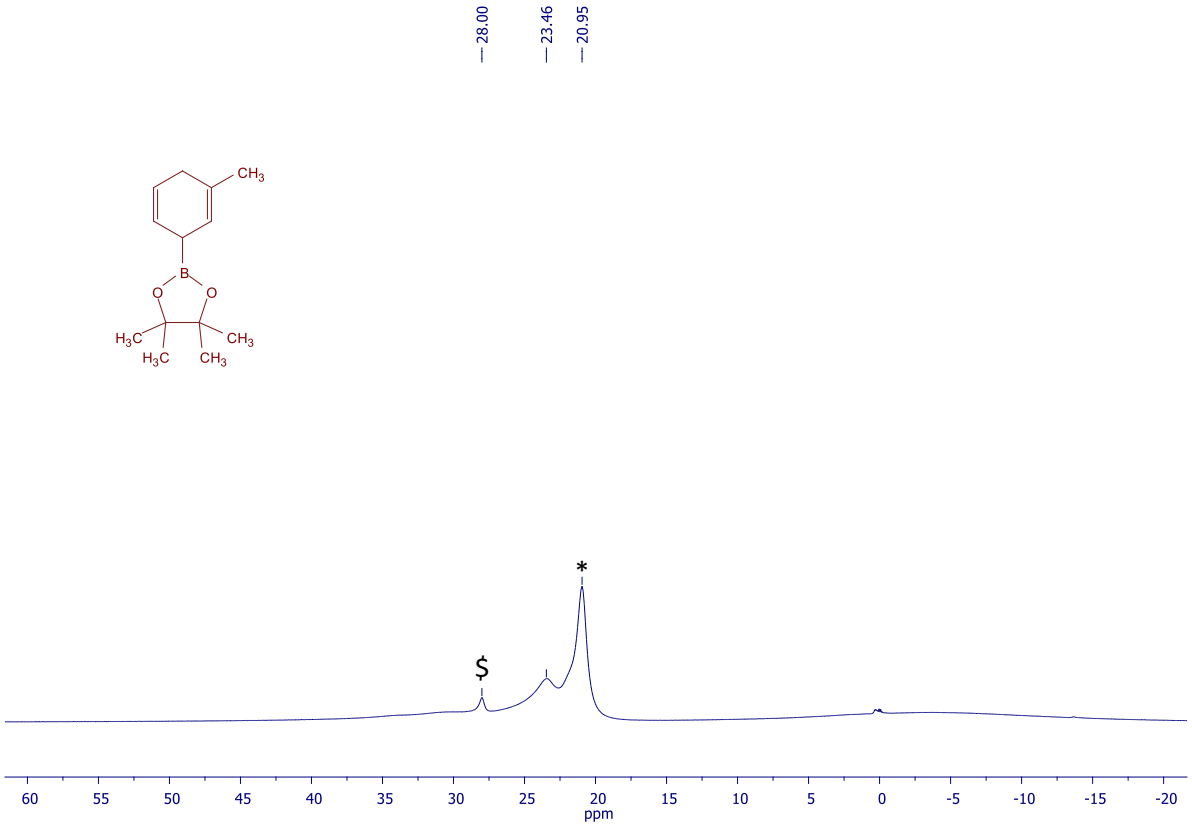
*^{13}C {^{1}H} NMR spectrum of 3-fluoro-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1,4-dihydropyridine (Compound-**5b**)*



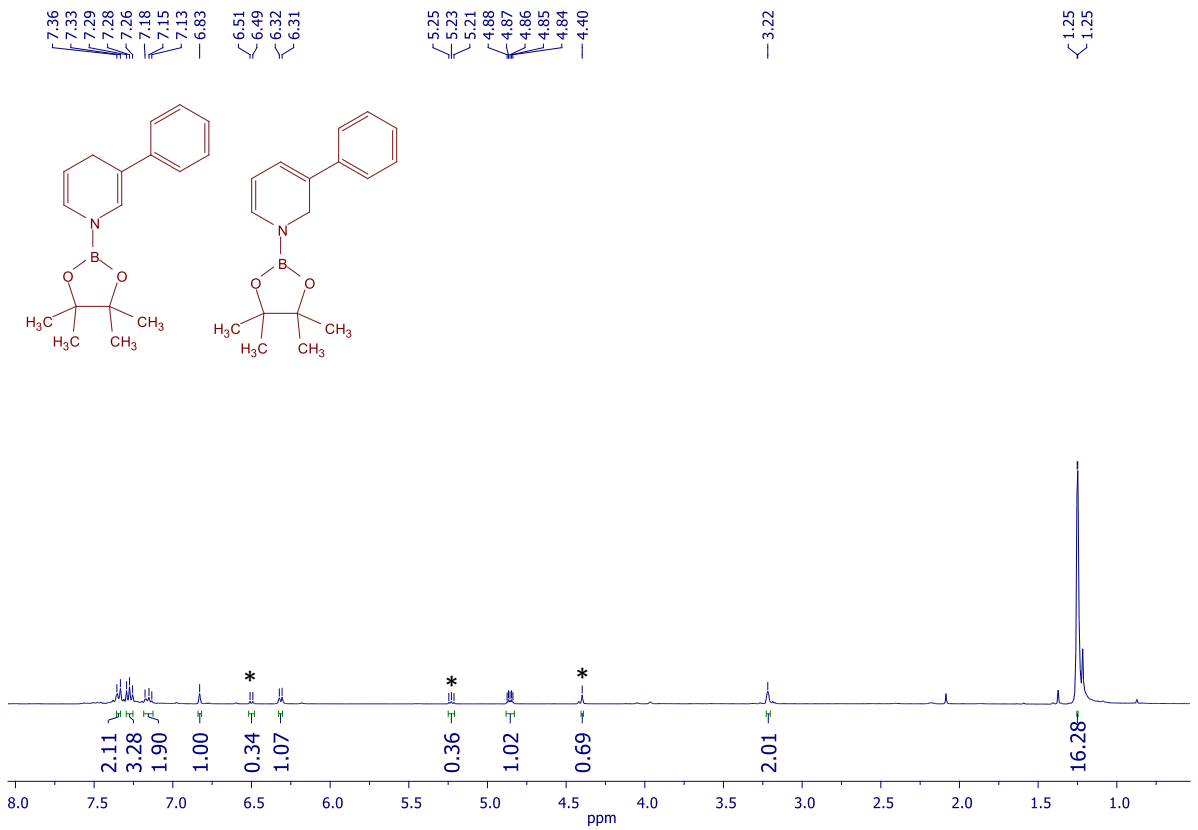
*^{11}B NMR spectrum of 3-fluoro-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1,4-dihydropyridine (Compound-**5b**) * indicates the decomposition product B_2pin_3*



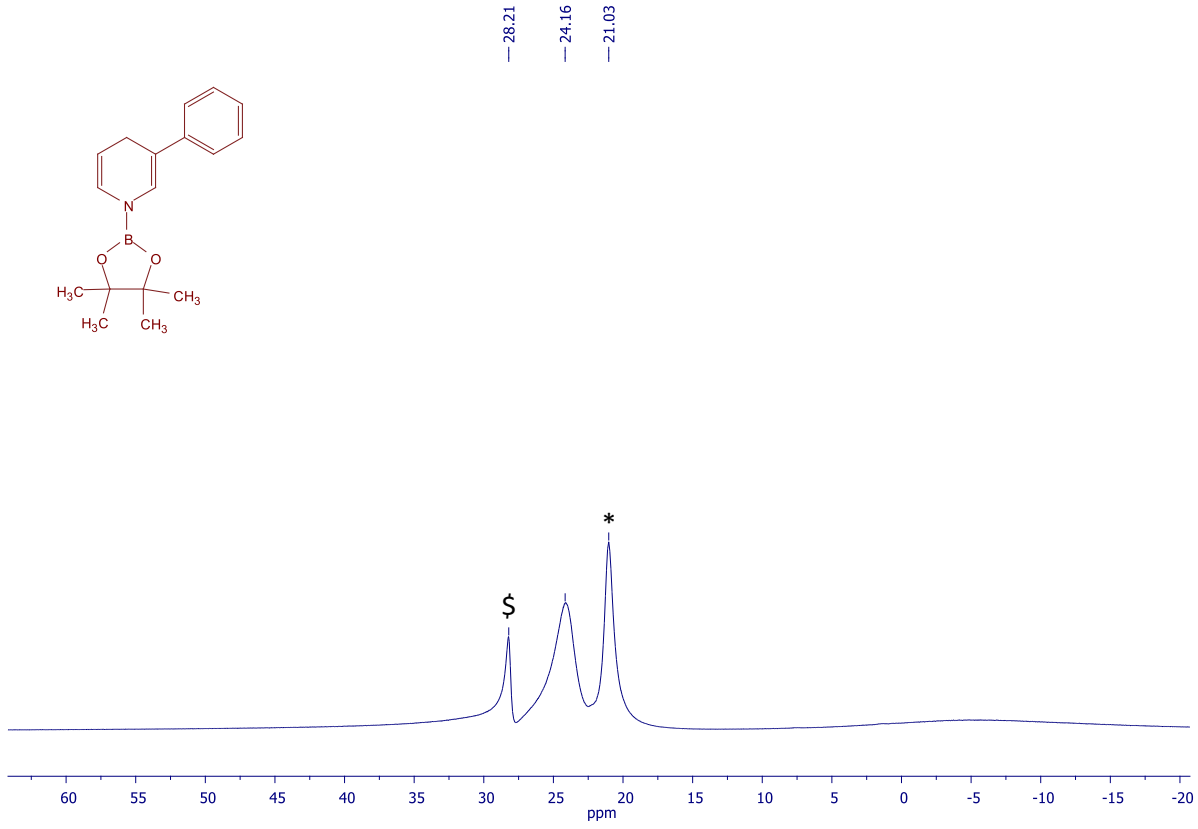
*[1]H NMR spectrum of 3-methyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1,4-dihydropyridine (Compound-**5c**), (* represents starting material in the reaction mixture)*



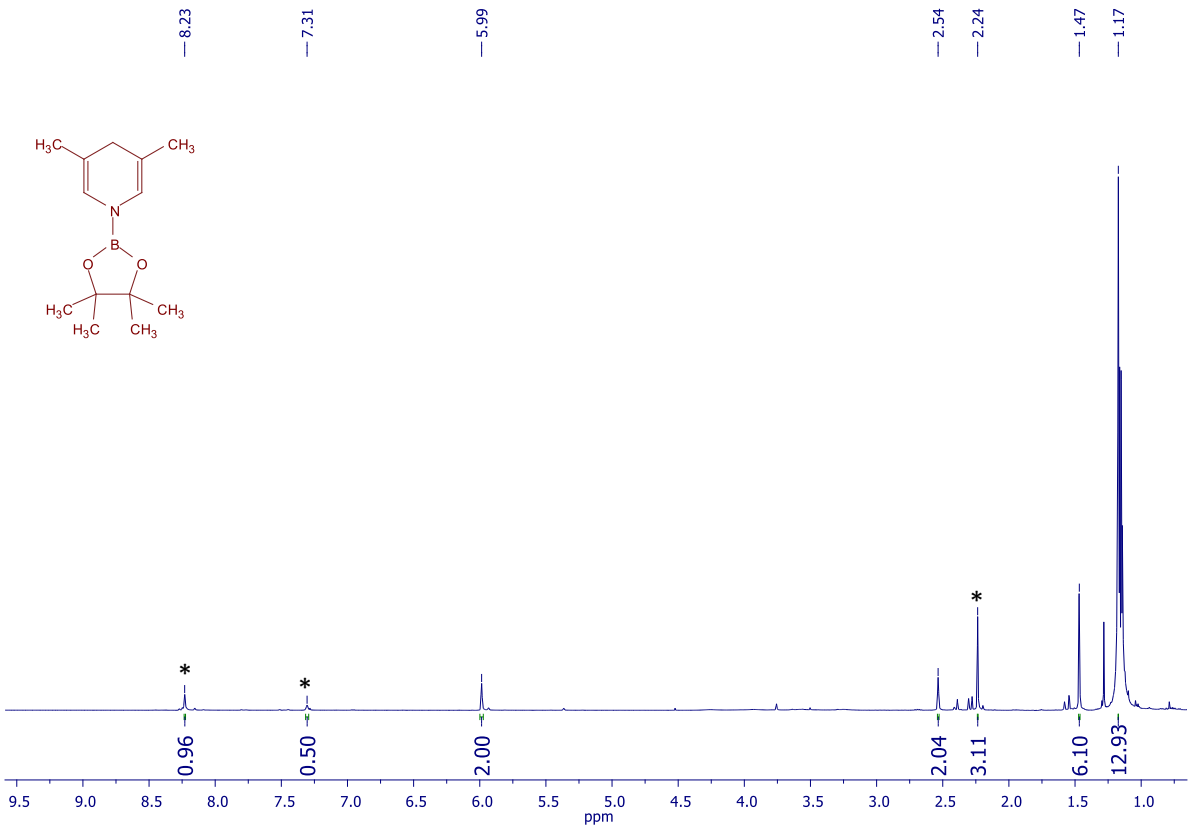
*[11]B NMR spectrum of 3-methyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1,4-dihydropyridine (Compound-**5c**) $ indicates the excess of HBpin and * indicates the decomposition product B_2pin_3*



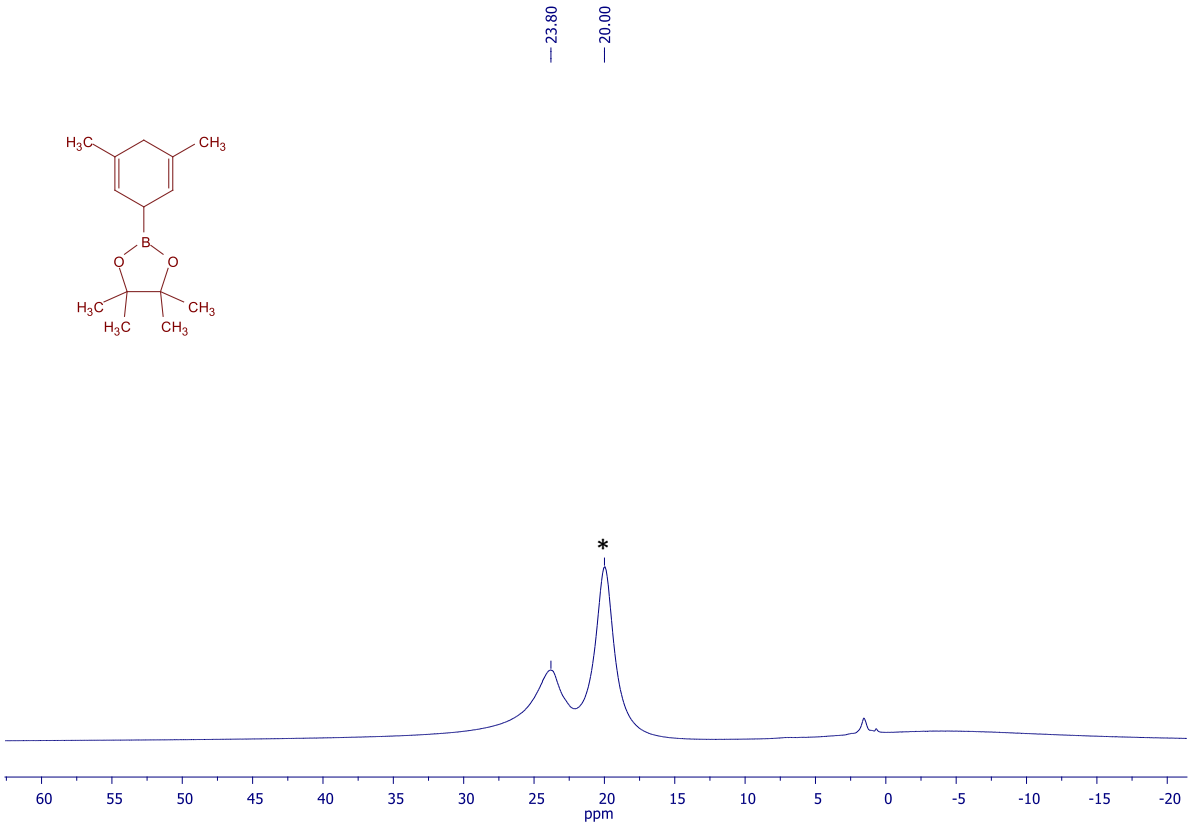
*^{1}H NMR spectrum of 3-phenyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1,4-dihydropyridine (Compound-**5d**), (* represents 1,2- dihydroborated product in the reaction mixture)*



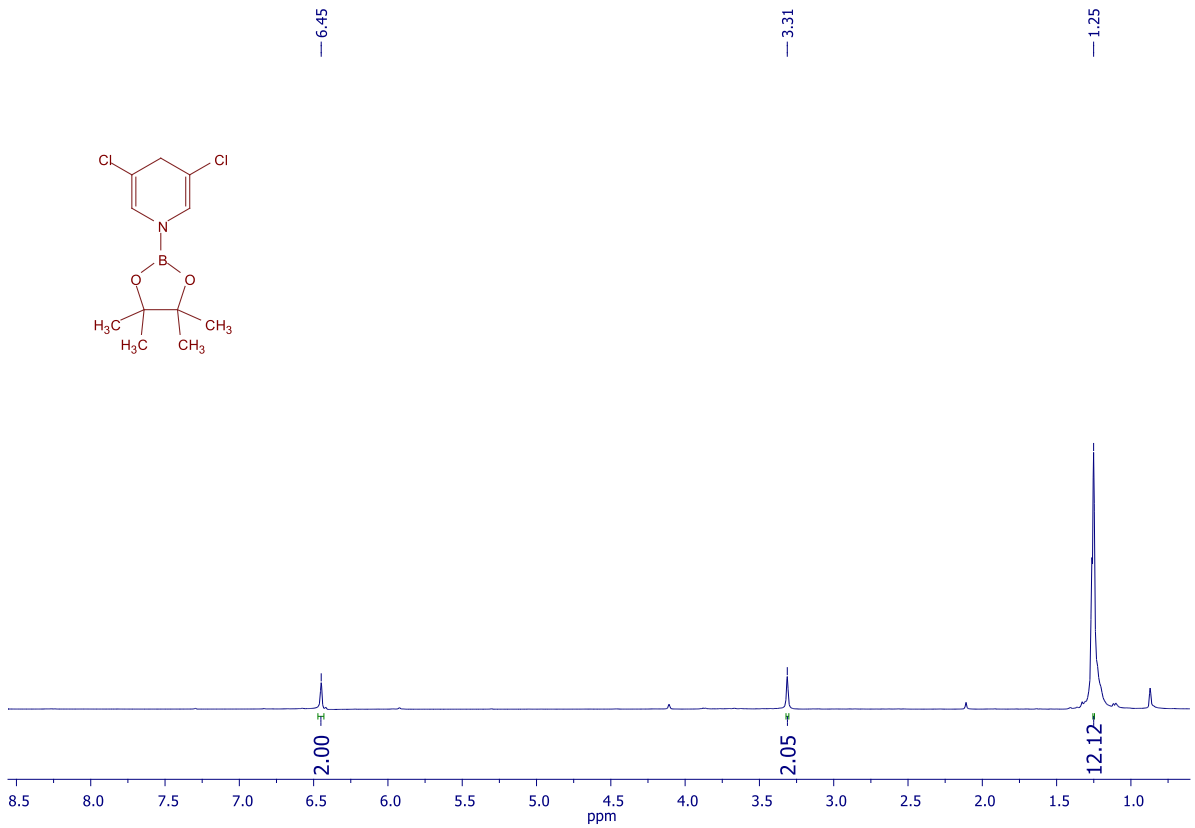
*^{11}B NMR spectrum of 3-phenyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1,4-dihydropyridine (Compound-**5d**) $ indicates the excess of HBpin * indicates the decomposition product B_2pin_3*



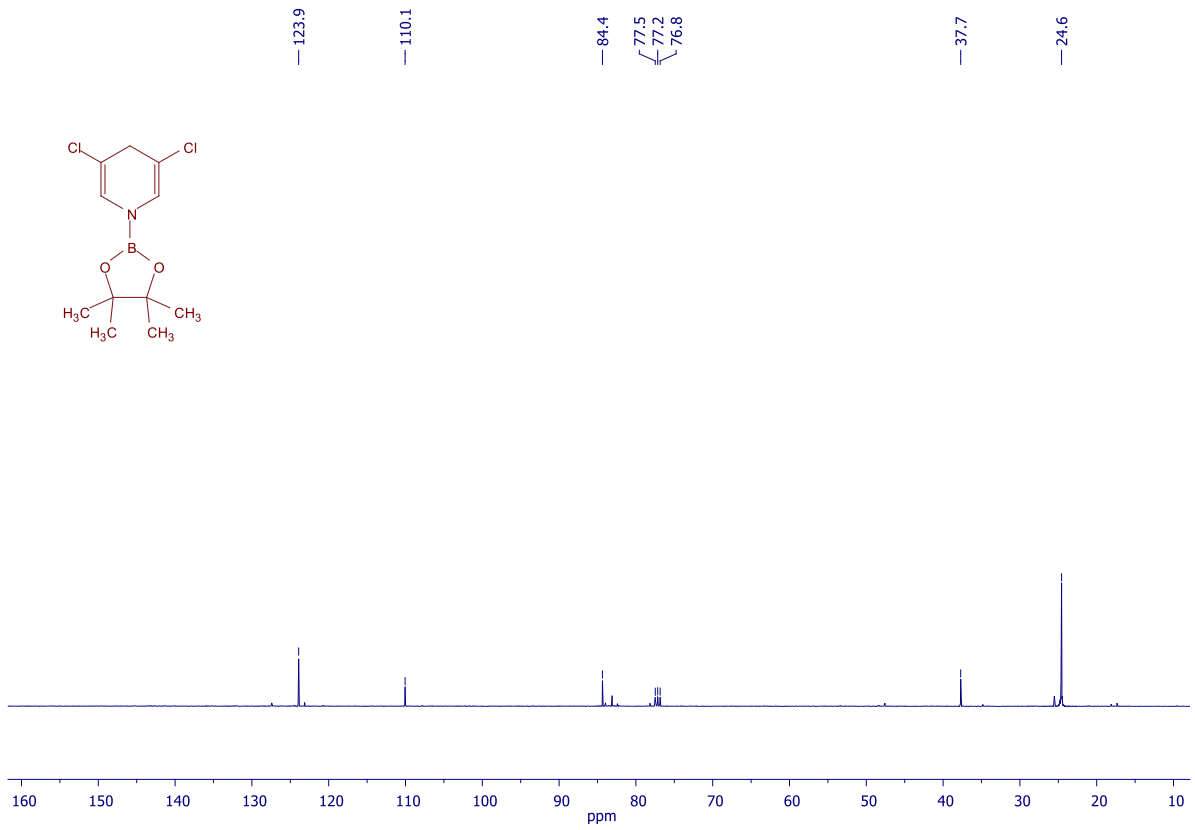
*^{1}H NMR spectrum of 3,5-dimethyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1,4-dihydropyridine (Compound-**5e**), (* represents starting material in the reaction mixture)*



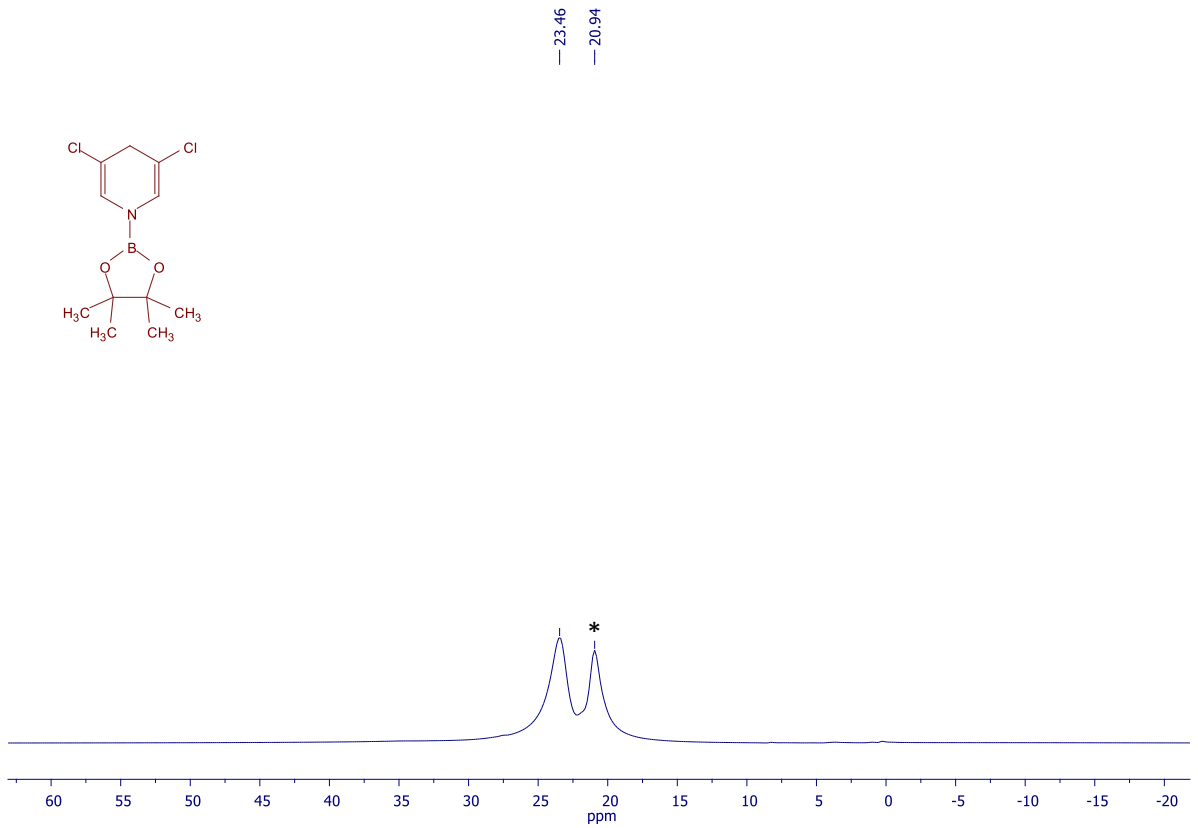
*^{11}B NMR spectrum of 3,5-dimethyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1,4-dihydropyridine (Compound-**5e**) * indicates the decomposition product B_2pin_3*



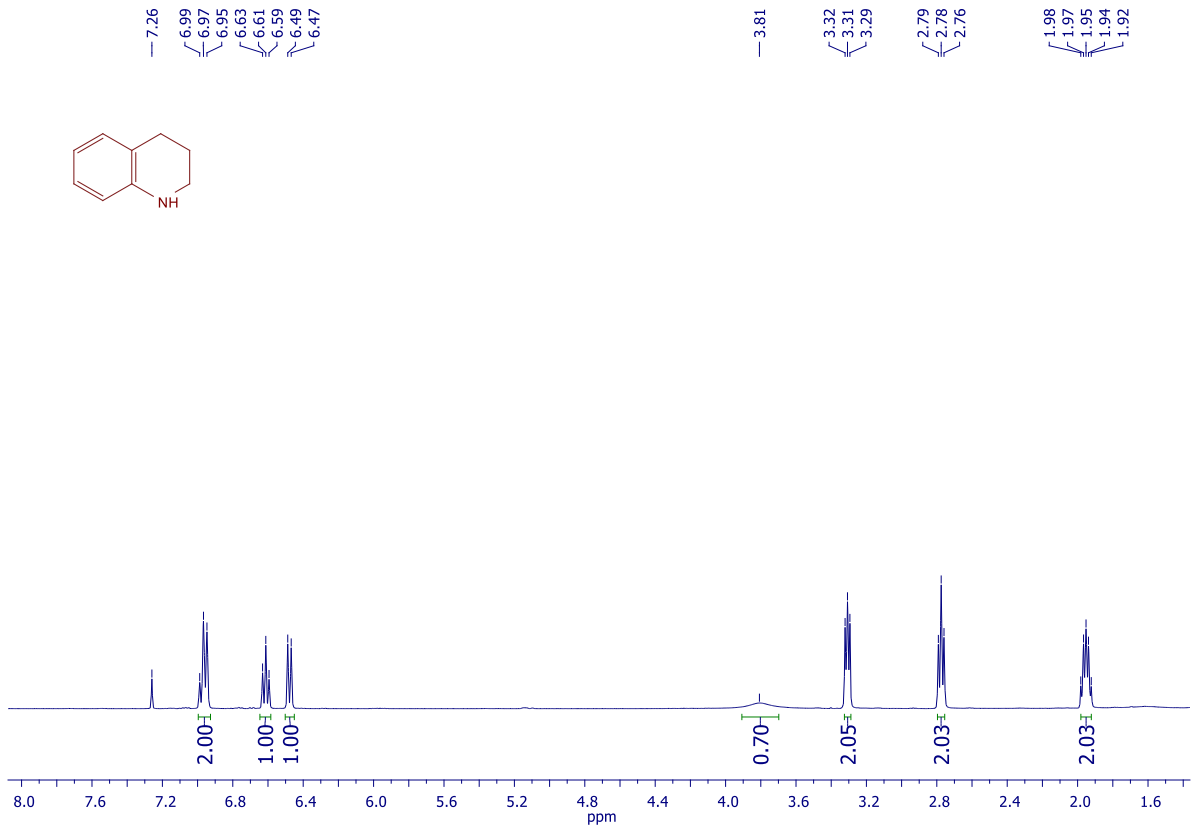
*[1]H NMR spectrum of 3,5-dichloro-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1,4-dihydropyridine (Compound-**5f**)*



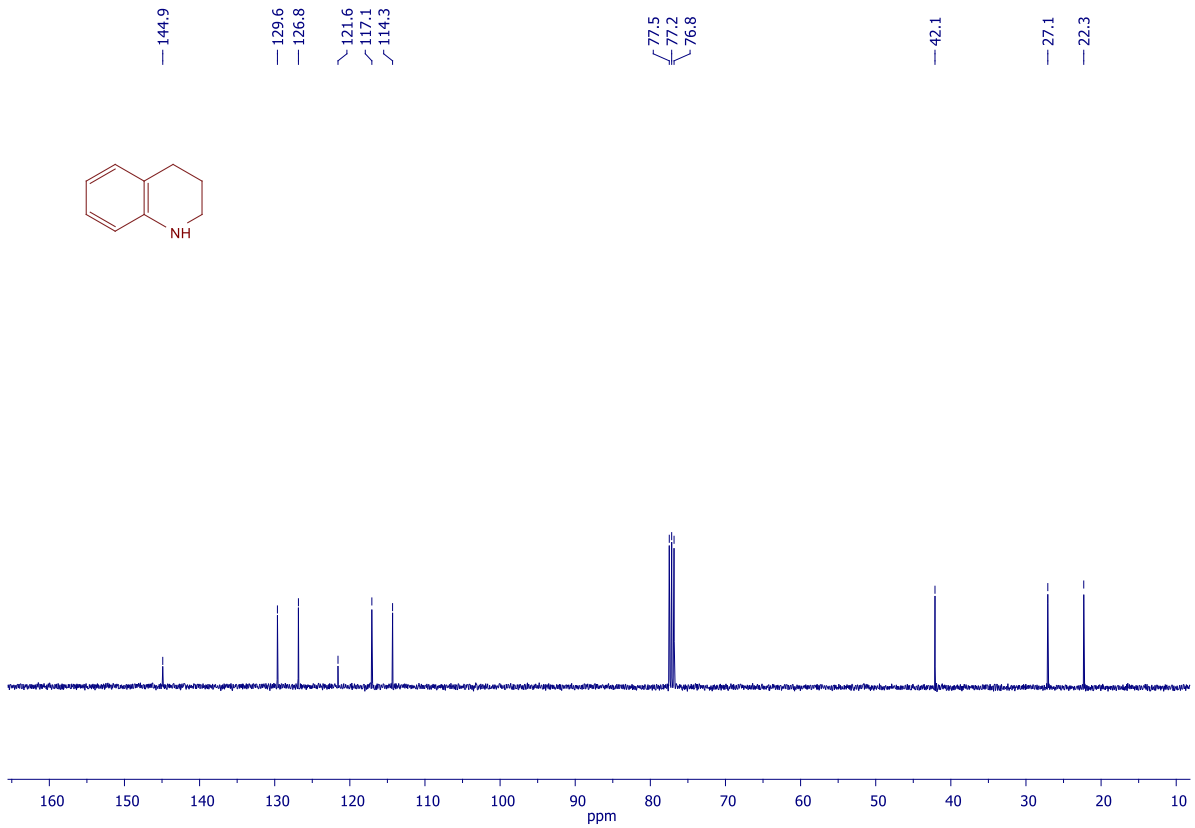
*[13]C {[1]H} NMR spectrum of 3,5-dichloro-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1,4-dihydropyridine (Compound-**5f**)*



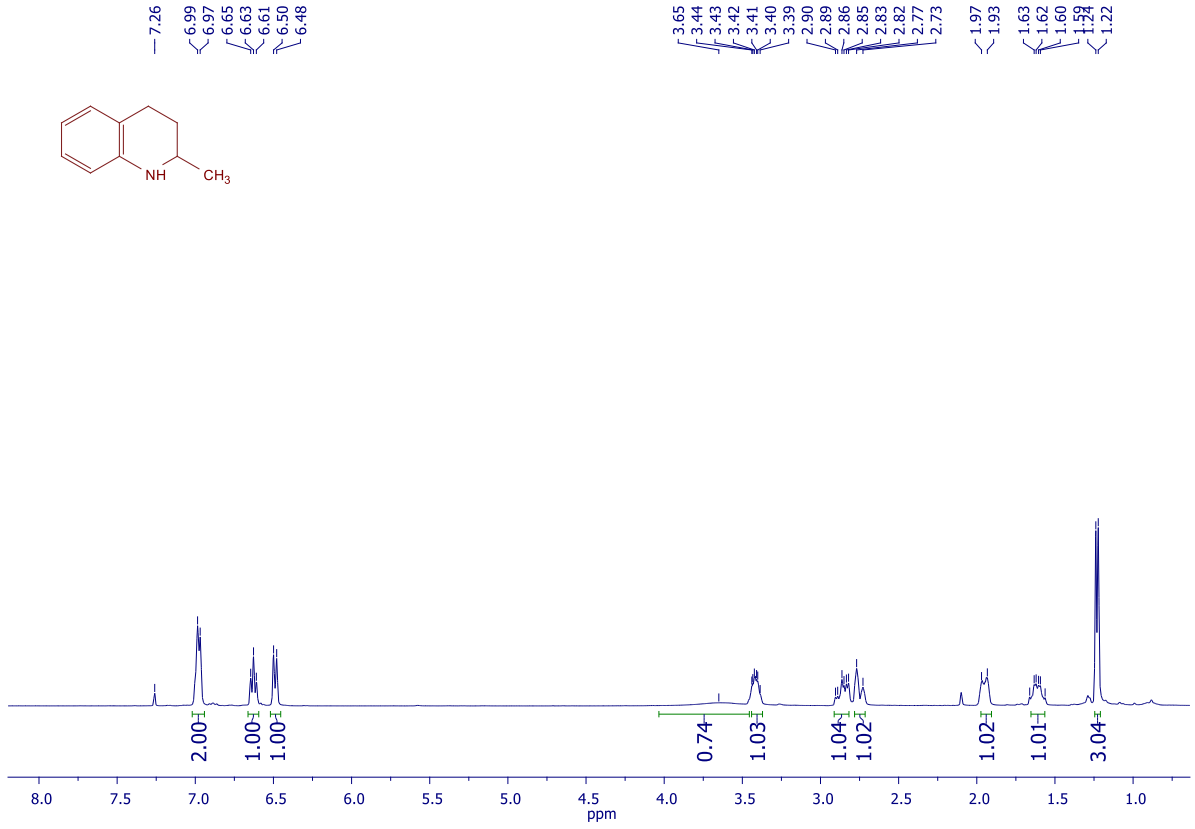
*^{11}B NMR spectrum of 3,5-dichloro-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1,4-dihydropyridine (Compound-**5f**) * indicates the decomposition product B_2pin_3*



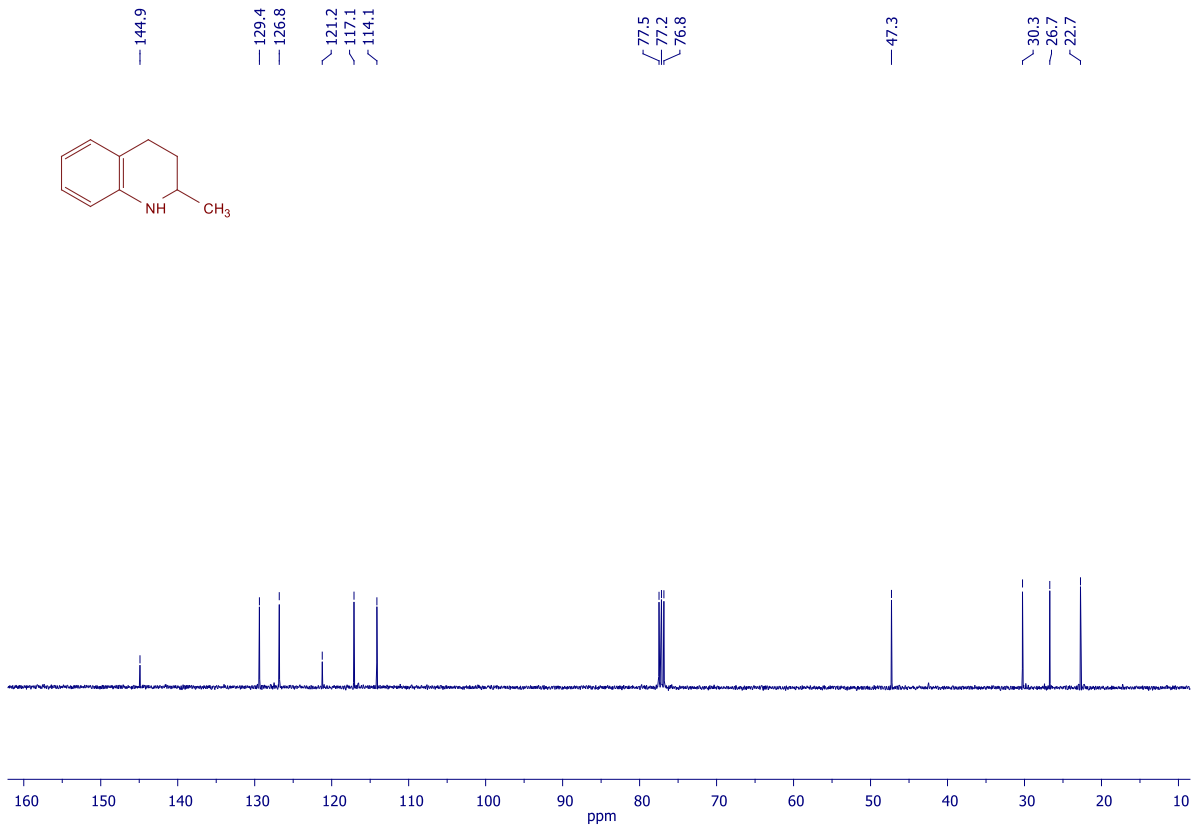
*^{1}H NMR spectrum of 1,2,3,4-tetrahydroquinoline (compound-**5g**)*



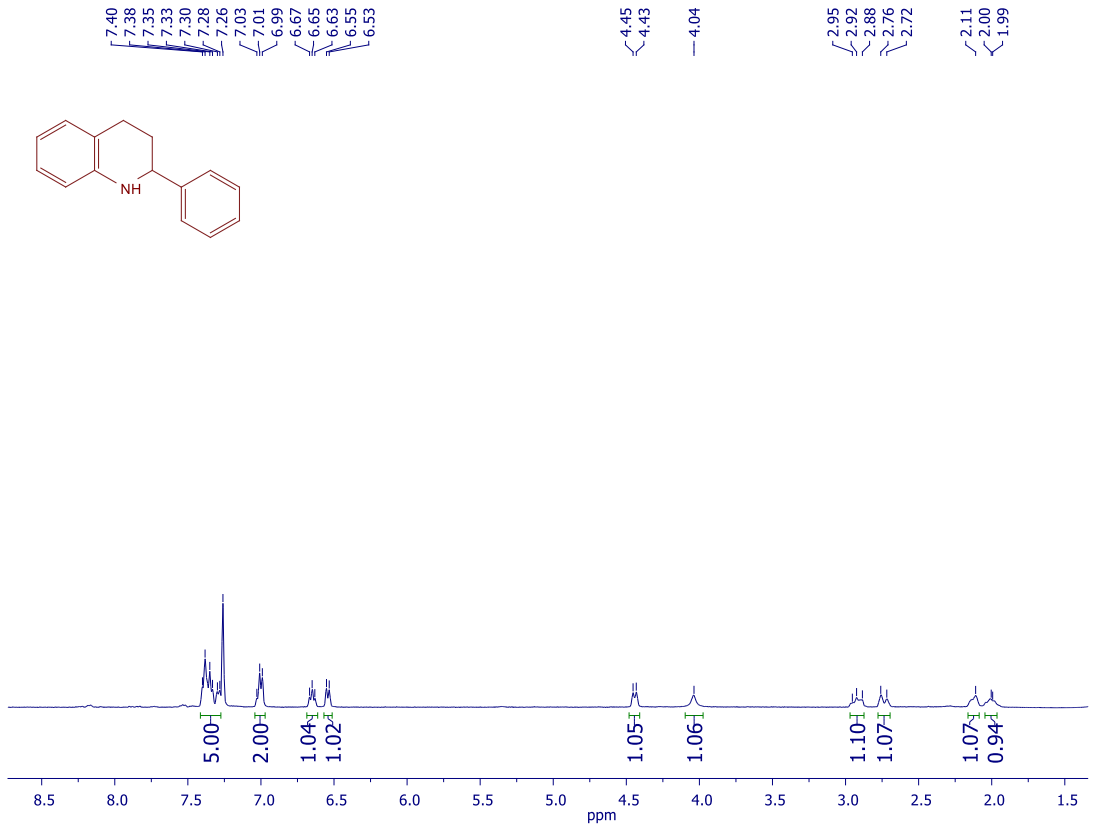
*[13] C{[1]H} NMR spectrum of 1,2,3,4-tetrahydroquinoline (compound-**5g**)*



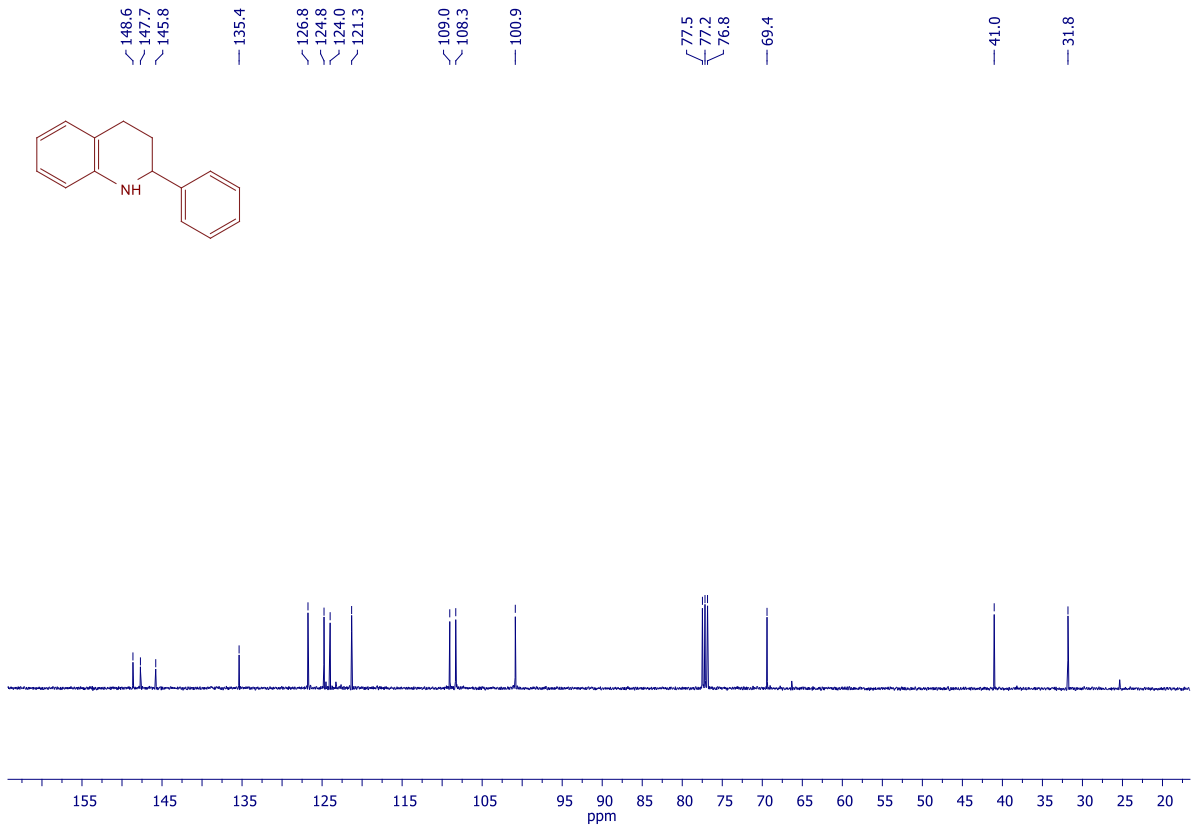
*[1]H NMR spectrum of 2-methyl-1,2,3,4-tetrahydroquinoline (compound-**5h**)*



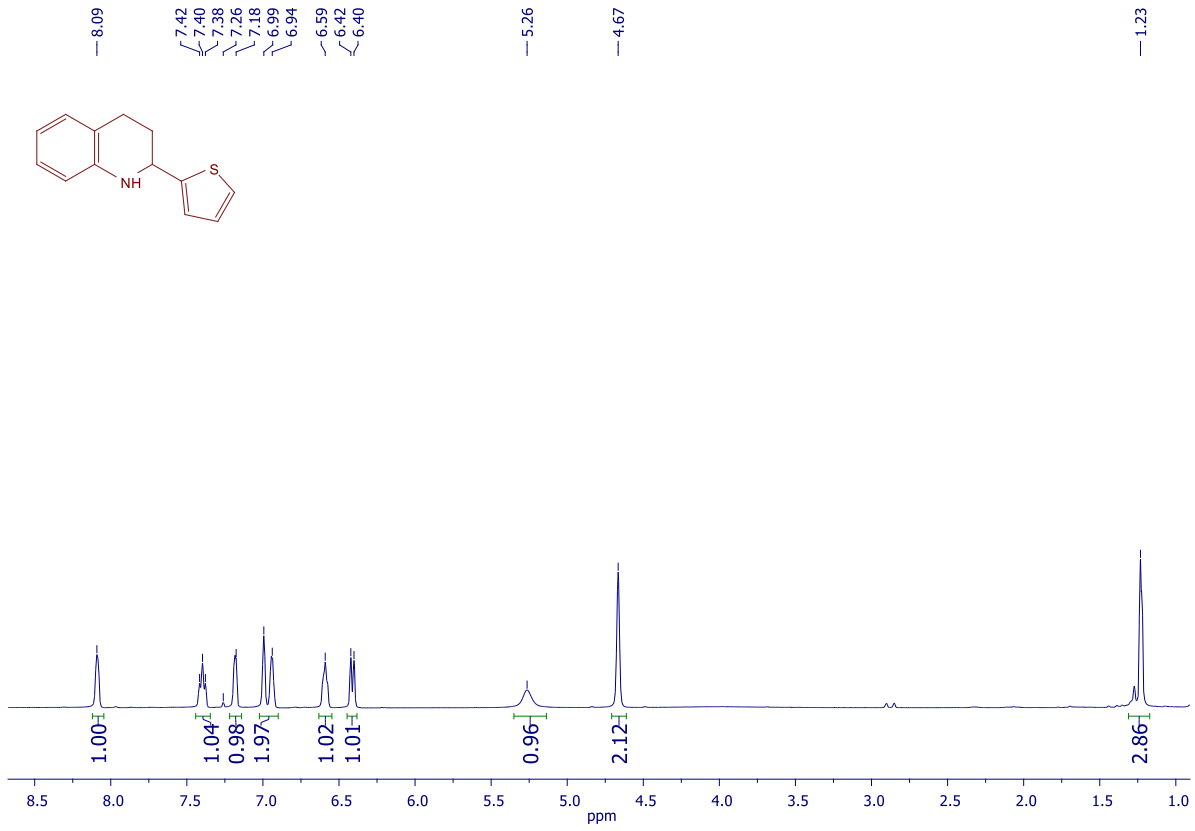
*^{13}C {^{1}H} NMR spectrum of 2-methyl-1,2,3,4-tetrahydroquinoline (compound-**5h**)*



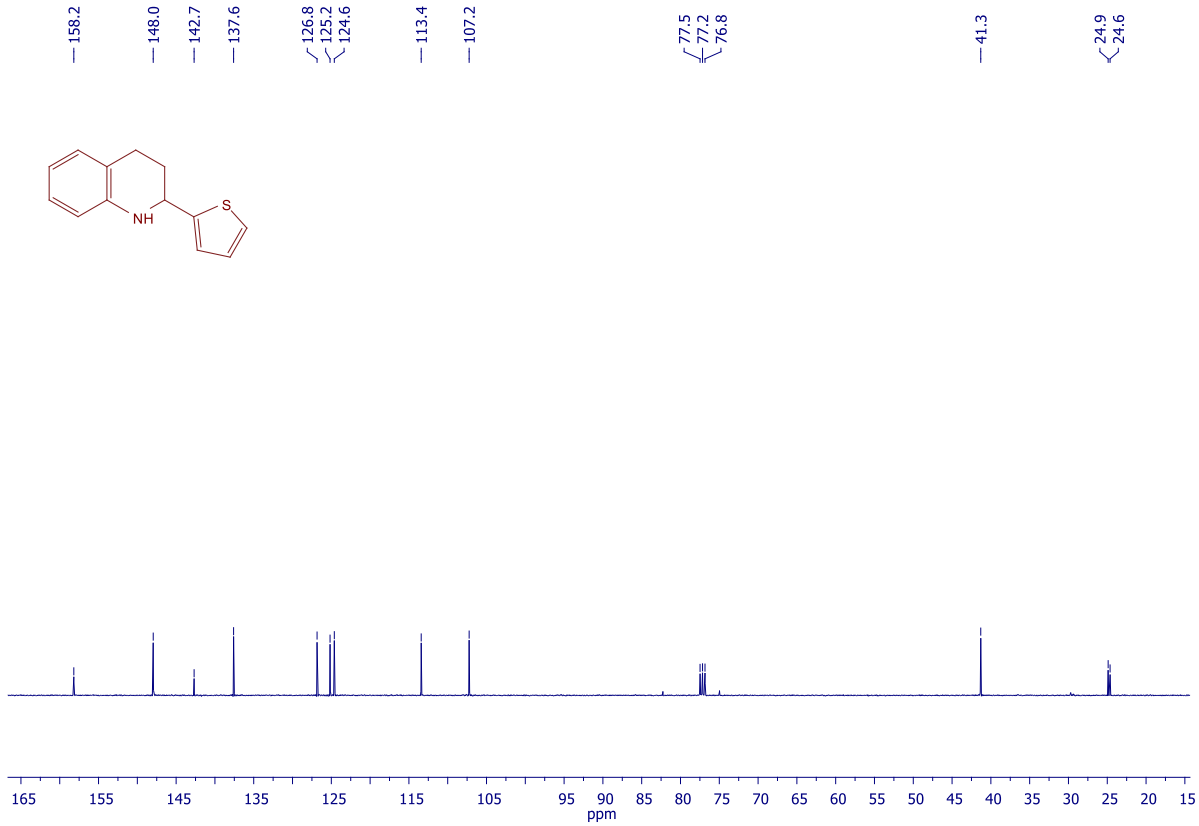
*^{1}H NMR spectrum of 2-phenyl-1,2,3,4-tetrahydroquinoline (compound-**5i**)*



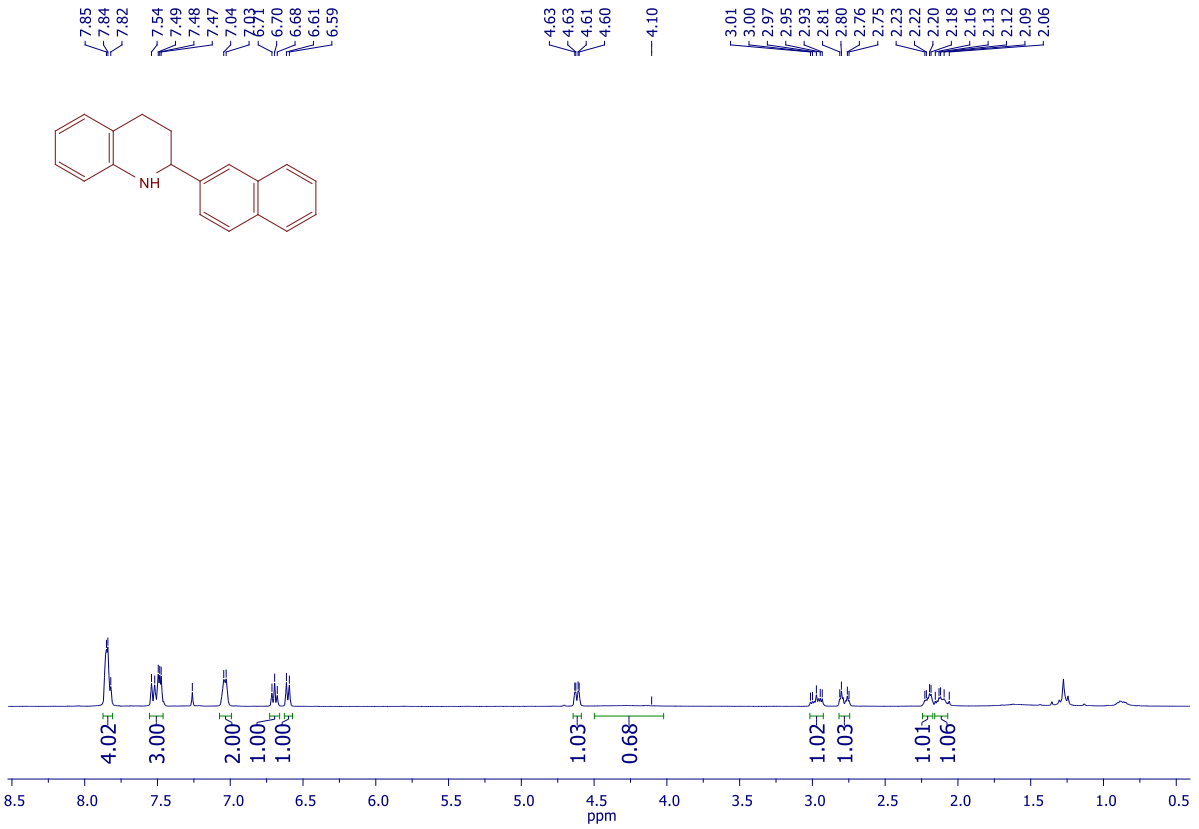
*^{13}C {^{1}H} NMR spectrum of 2-phenyl-1,2,3,4-tetrahydroquinoline (compound-**5i**)*



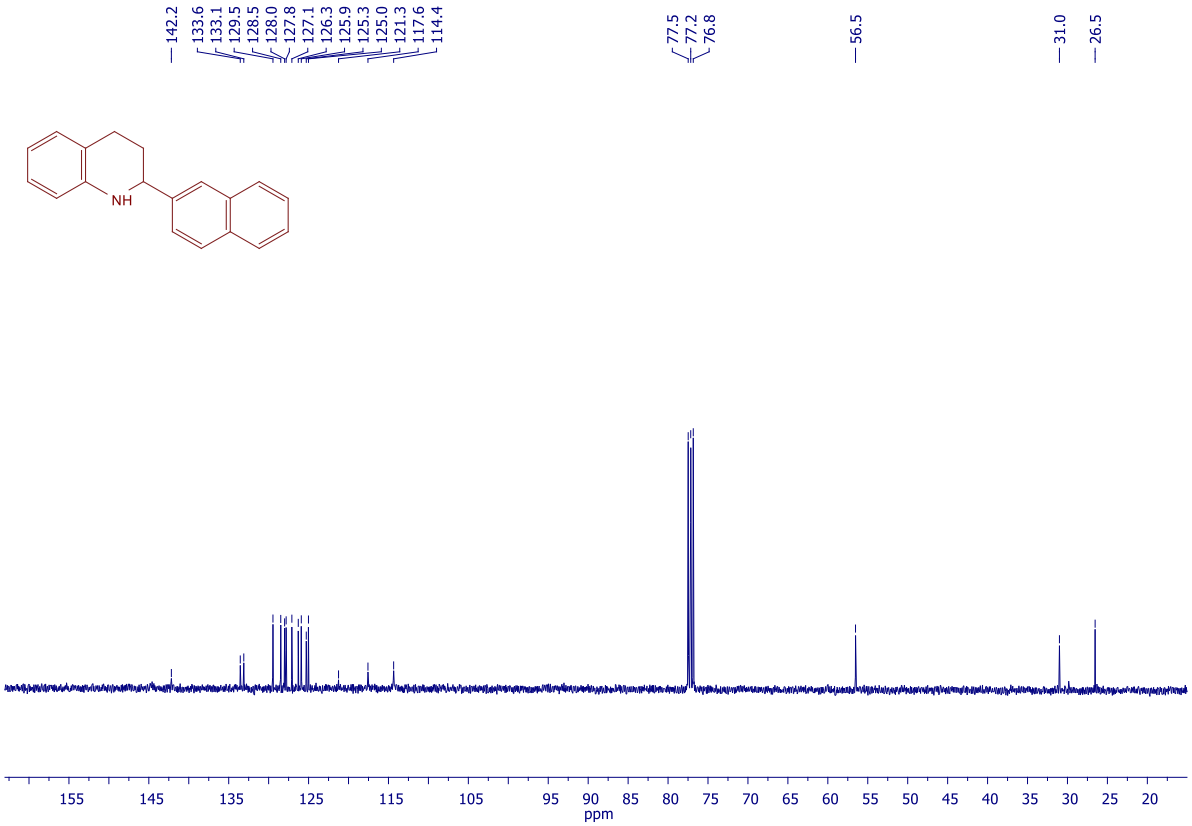
*^{1}H NMR spectrum of 2-(thiophen-2-yl)-1,2,3,4-tetrahydroquinoline (compound-**5j**)*



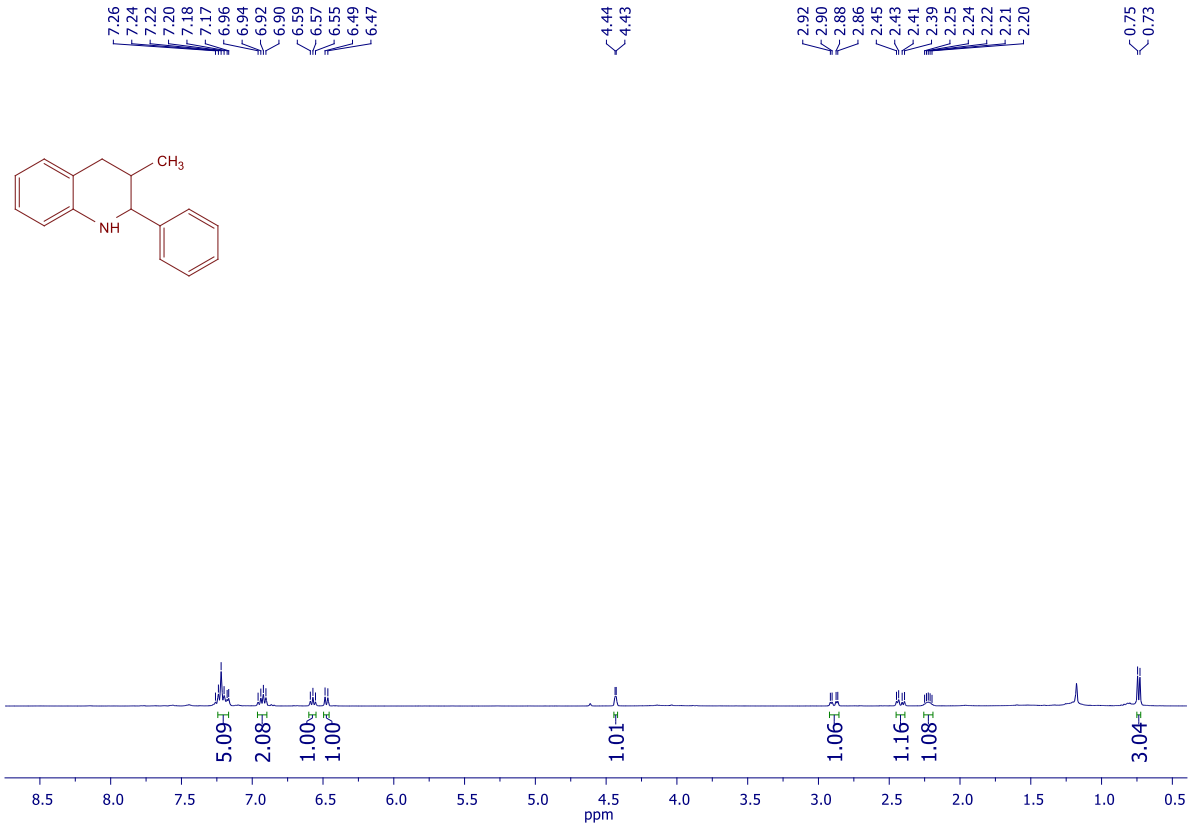
*^{13}C {^{1}H} NMR spectrum of 2-(thiophen-2-yl)-1,2,3,4-tetrahydroquinoline (compound-**5j**)*



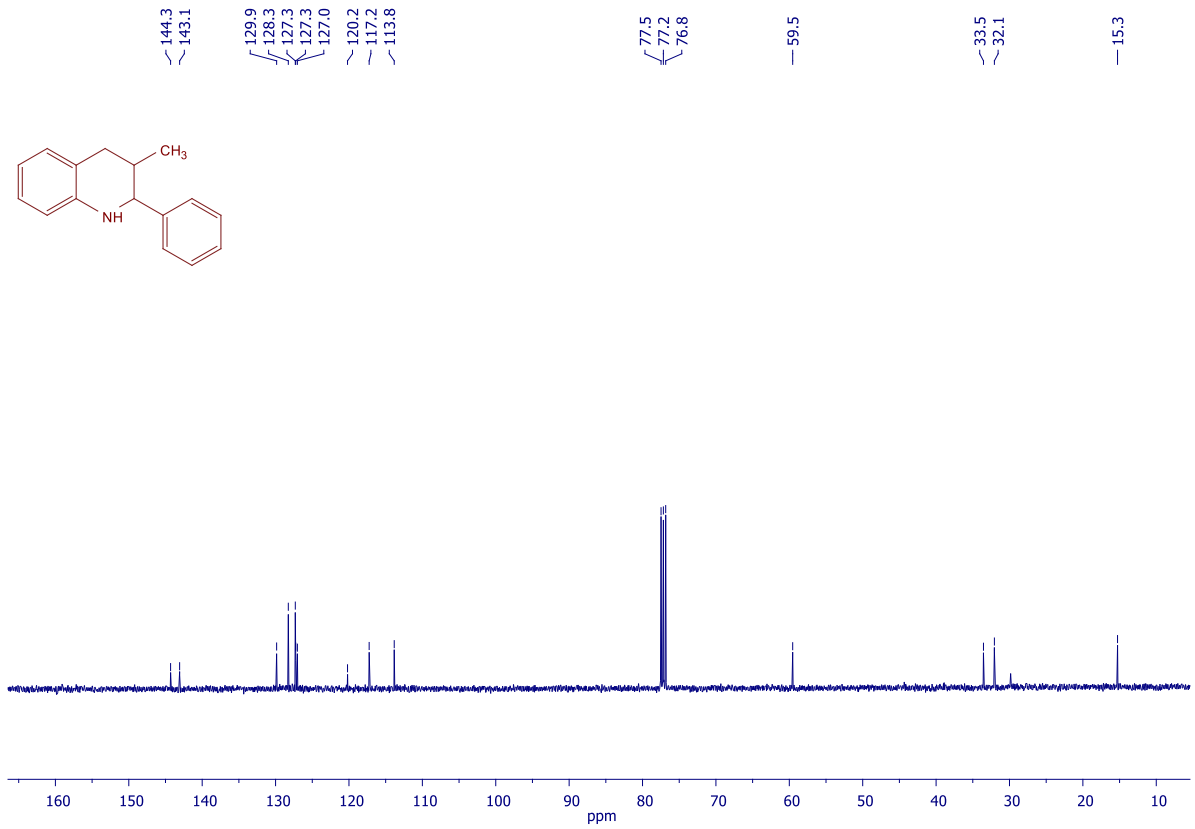
*^{1}H NMR spectrum of 2-(naphthalen-2-yl)-1,2,3,4-tetrahydroquinoline (compound-**5k**)*



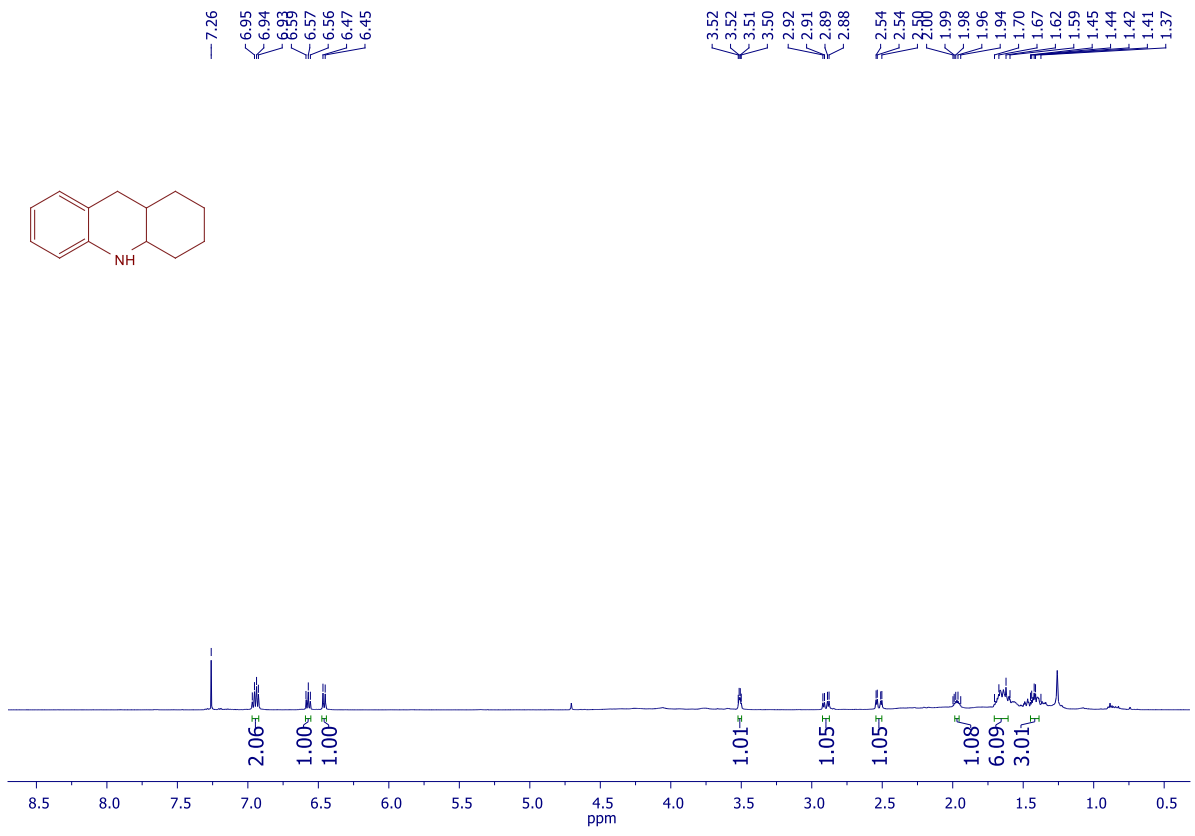
*^{13}C {^{1}H} NMR spectrum of 2-(naphthalen-2-yl)-1,2,3,4-tetrahydroquinoline (compound-**5k**)*



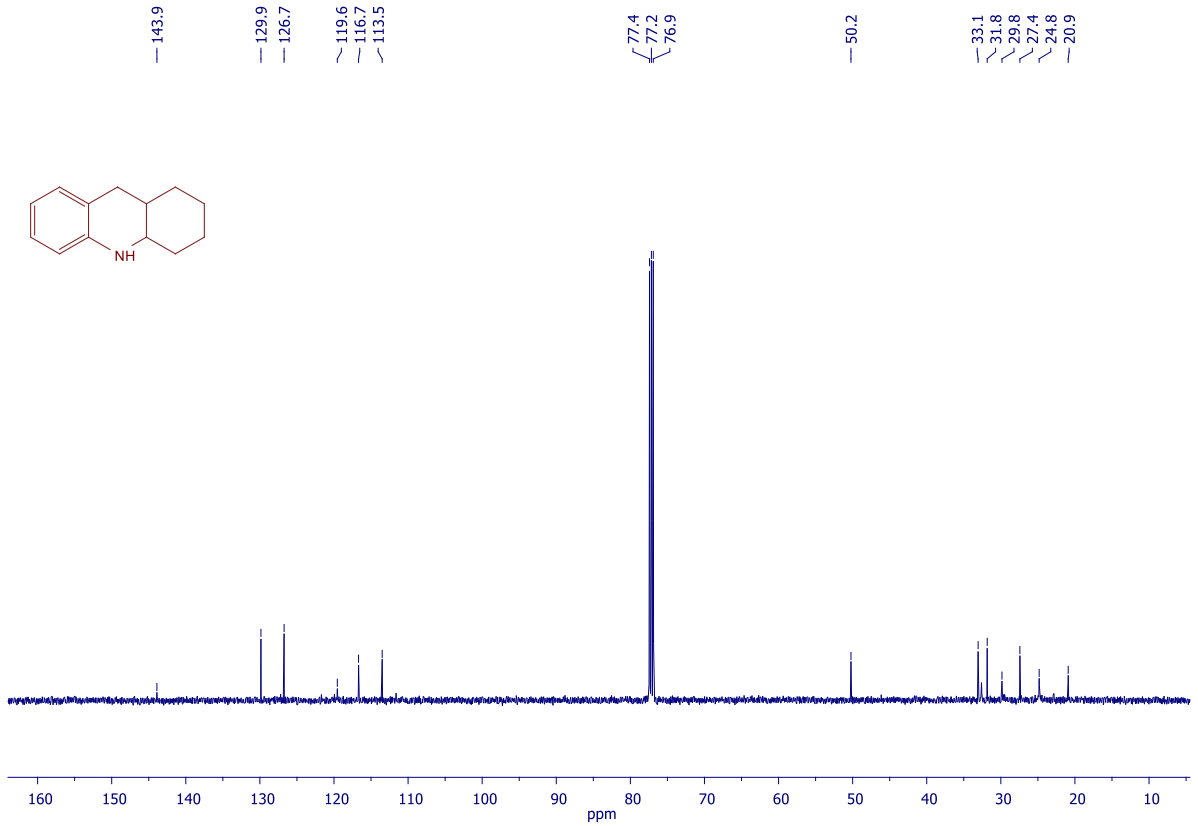
*^{1}H NMR spectrum of 3-methyl-2-phenyl-1,2,3,4-tetrahydroquinoline (compound-**5l**)*



*^{13}C {^{1}H} NMR spectrum of 3-methyl-2-phenyl-1,2,3,4-tetrahydroquinoline (compound-**5l**)*



*^{1}H NMR spectrum of 1,2,3,4,4^{a},9,9^{a},10-octahydroacridine (compound-**5m**)*



*^{13}C {^{1}H} NMR spectrum of 1,2,3,4,4^{a},9,9^{a},10-octahydroacridine (compound-**5m**)*

Procedure for chemoselective hydroboration of isocyanate:

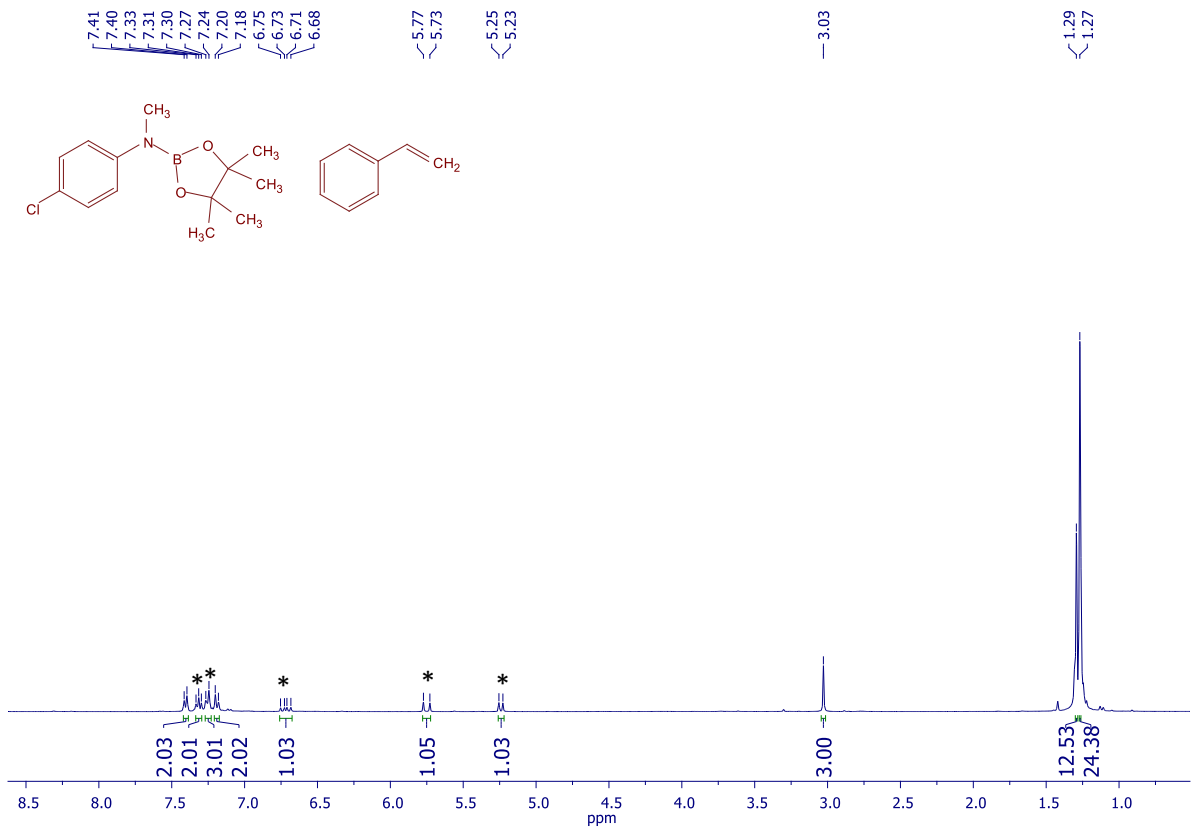
4-chlorophenyl isocyanate and styrene: $AgSbF_6$ (1.7 mg, 0.005 mmol, 1 mol%) and pinacolborane (225 µL, 1.55 mmol) were taken in a Schlenk tube. After that 4-chlorophenyl isocyanate (77 mg, 0.5 mmol) and styrene (52 mg, 0.5 mmol) were added to the reaction mixture and was then allowed to stir at 60 ºC for 6 hours. Upon completion of the reaction, $CDCl_3$ was added to the reaction mixture and ^{1}H NMR was recorded which shows only the hydroboration of isocyanate (>99%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 (d, J = 7.7 Hz, 2H), 7.33-7.30 (m, 2H), 7.27-7.24 (m, 3H), 7.19 (d, J = 8.8 Hz, 2H), 6.75-6.68 (m, 1H), 5.75 (d, J = 17.6 Hz, 1H), 5.24 (d, J = 10.9 Hz, 1H), 3.03 (s, 3H), 1.29 (s, 12H) ppm.

4-chlorophenyl isocyanate and 2-pyridinecarbonitrile: $AgSbF_6$ (1.7 mg, 0.005 mmol, 1 mol%) and pinacolborane (225 µL, 1.55 mmol) were taken in a Schlenk tube. After that 4-chlorophenyl isocyanate (77 mg, 0.5 mmol) and 2-pyridinecarbonitrile (52 mg, 0.5 mmol) were added to the reaction mixture and was then allowed to stir at 60 ºC for 6 hours. Upon completion of the reaction, $CDCl_3$ was added to the reaction mixture and ^{1}H NMR was recorded which shows only the hydroboration of isocyanate (>99%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.62 (d, J

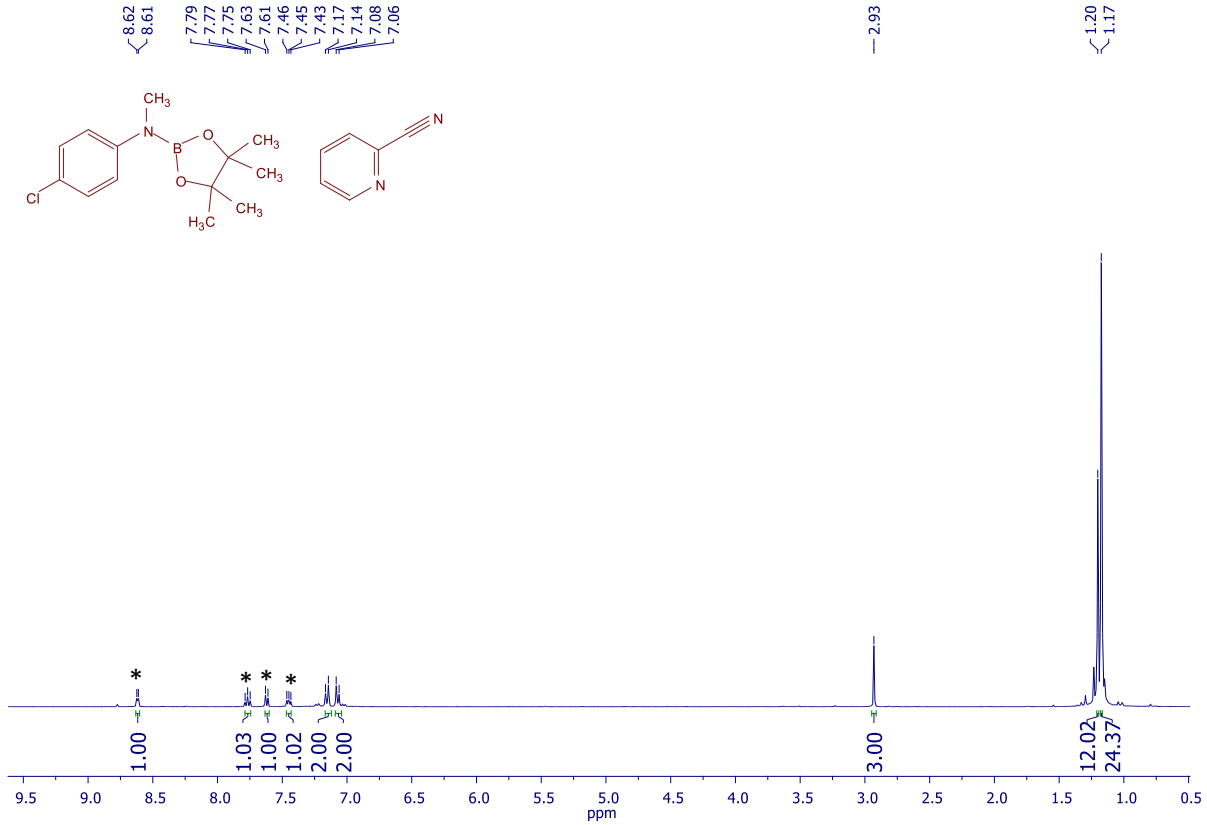
= 5.3 Hz, 1H), 7.77 (t, *J* = 7.8 Hz, 1H), 7.62 (d, *J* = 7.8 Hz, 1H), 7.46-7.43 (m, 1H), 7.16 (d, *J* = 8.9 Hz, 2H), 7.07 (d, *J* = 8.9 Hz, 2H), 2.93 (s, 3H), 1.20 (s, 12H) ppm.

4-methylphenyl isocyanate and 2-pyridinecarbonitrile: $AgSbF_6$ (3.4 mg, 0.01 mmol, 2 mol%) and pinacolborane (109 μL, 0.75 mmol) were taken in a Schlenk tube. After that 4-methylphenyl isocyanate (66.5 mg, 0.5 mmol) and 2-pyridinecarbonitrile (52 mg, 0.5 mmol) were added to the reaction mixture and was then allowed to stir at room temperature for 12 hours. Upon completion of the reaction, $CDCl_3$ was added to the reaction mixture and ^1H NMR was recorded which shows only the hydroboration of isocyanate (86%). ^1H NMR (400 MHz, $CDCl_3$) δ 8.83 (s, 1H), 8.66 (d, *J* = 4.8 Hz, 1H), 7.82-7.78 (m, 1H), 7.65 (d, *J* = 7.8 Hz, 1H), 7.50-7.47 (m, 1H), 7.13 (d, *J* = 8.0 Hz, 2H), 6.99 (d, *J* = 8.0 Hz, 2H), 2.28 (s, 3H), 1.22 (s, 12H) ppm.

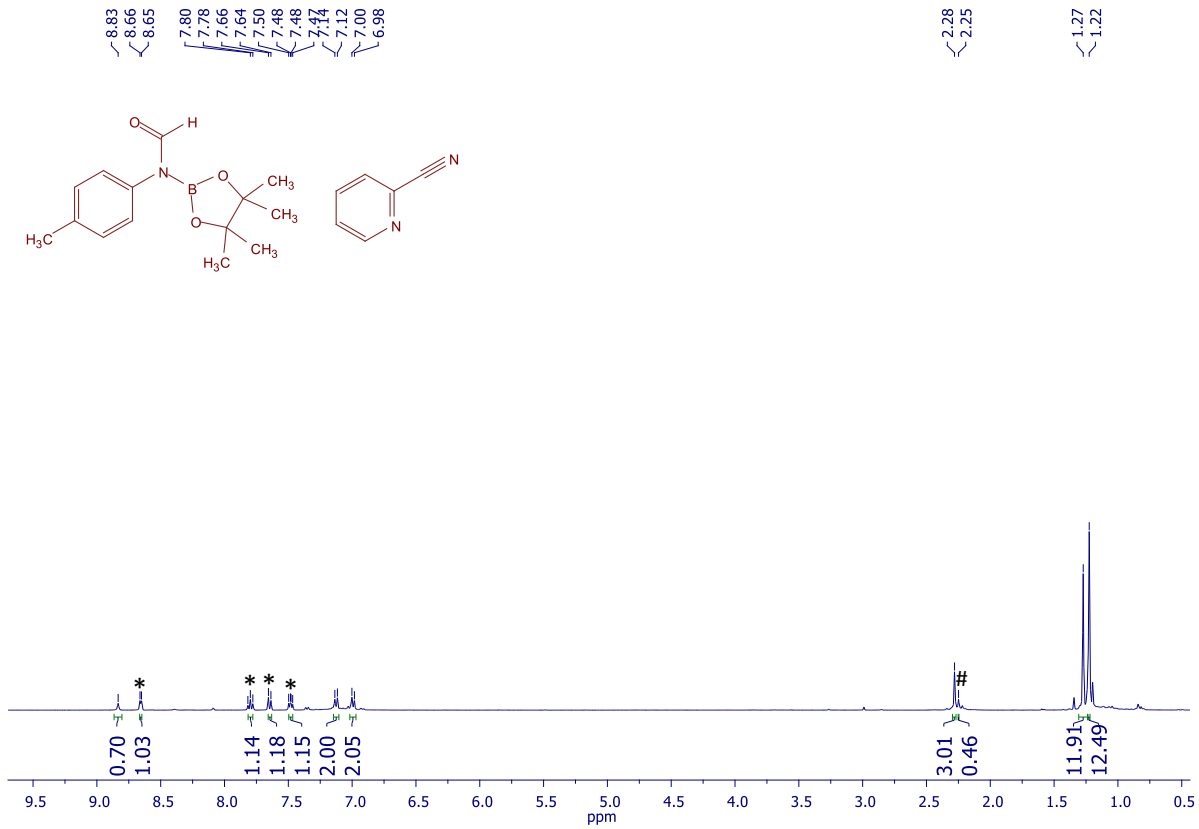
4-methylphenyl isocyanate and quinoline: $AgSbF_6$ (3.4 mg, 0.01 mmol, 2 mol%) and pinacolborane (109 μL, 0.75 mmol) were taken in a Schlenk tube. After that 4-methylphenyl isocyanate (66.5 mg, 0.5 mmol) and quinoline (64.5 mg, 0.5 mmol) were added to the reaction mixture and was then allowed to stir at room temperature for 12 hours. Upon completion of the reaction, $CDCl_3$ was added to the reaction mixture and ^1H NMR was recorded which shows only the hydroboration of isocyanate (90%). ^1H NMR (400 MHz, $CDCl_3$) δ 8.88 (s, 1H), 8.08 (t, *J* = 9.2 Hz, 2H), 7.75 (d, *J* = 8.1 Hz, 1H), 7.66 (t, *J* = 7.7 Hz, 1H), 7.48 (t, *J* = 7.5 Hz, 1H), 7.43-7.30 (m, 2H), 7.13 (d, *J* = 7.9 Hz, 2H), 7.02 (d, *J* = 7.9 Hz, 2H), 2.28 (s, 3H), 1.24 (s, 12H) ppm.



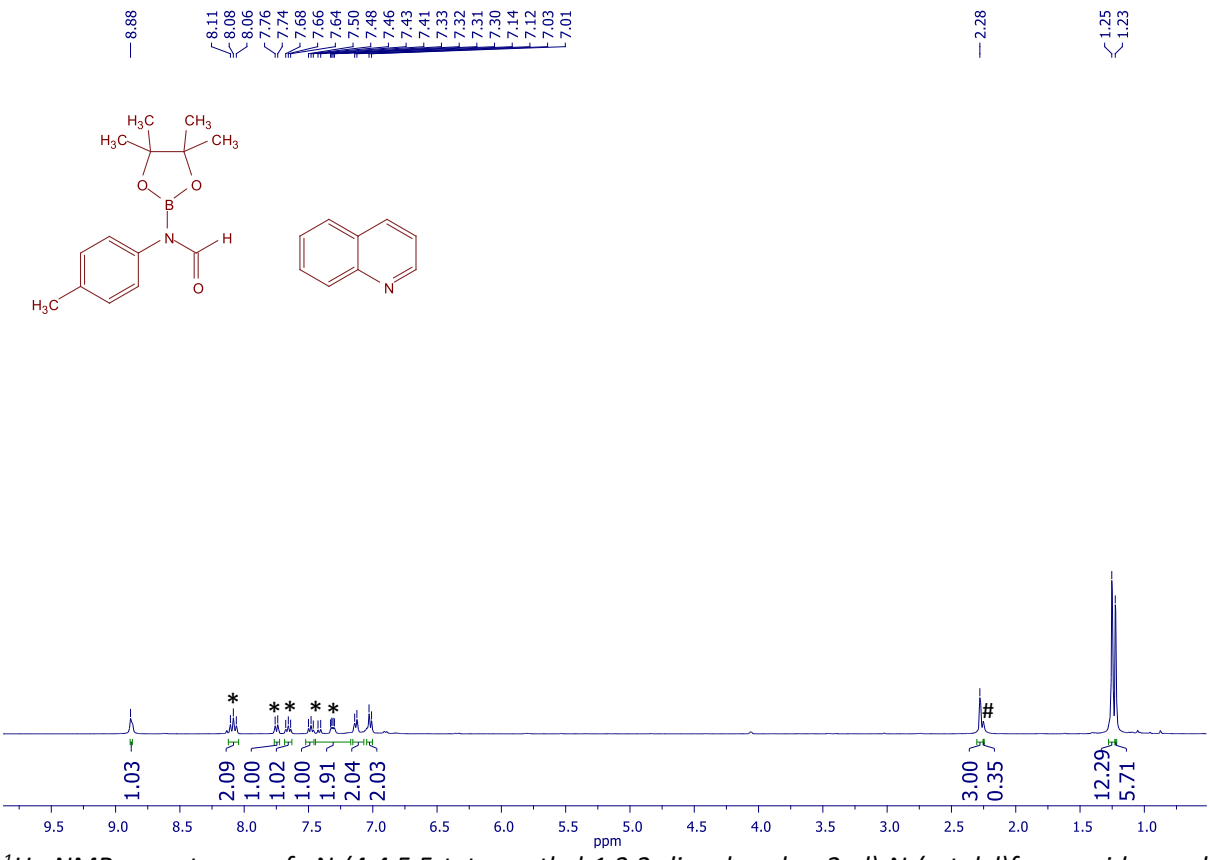
^{1}H NMR spectrum of N-(4-chlorophenyl)-N,4,4,5,5-pentamethyl-1,3,2-dioxaborolan-2-amine and styrene (represents styrene in the reaction mixture)*



^{1}H NMR spectrum of N-(4-chlorophenyl)-N,4,4,5,5-pentamethyl-1,3,2-dioxaborolan-2-amine and picolinonitrile (represents 2-cyano pyridine in the reaction mixture)*



^{1}H NMR spectrum of N-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-N-(p-tolyl)formamide and picolinonitrile (and # represent 2-cyano pyridine and p-tolyl isocyanate, respectively in the reaction mixture)*

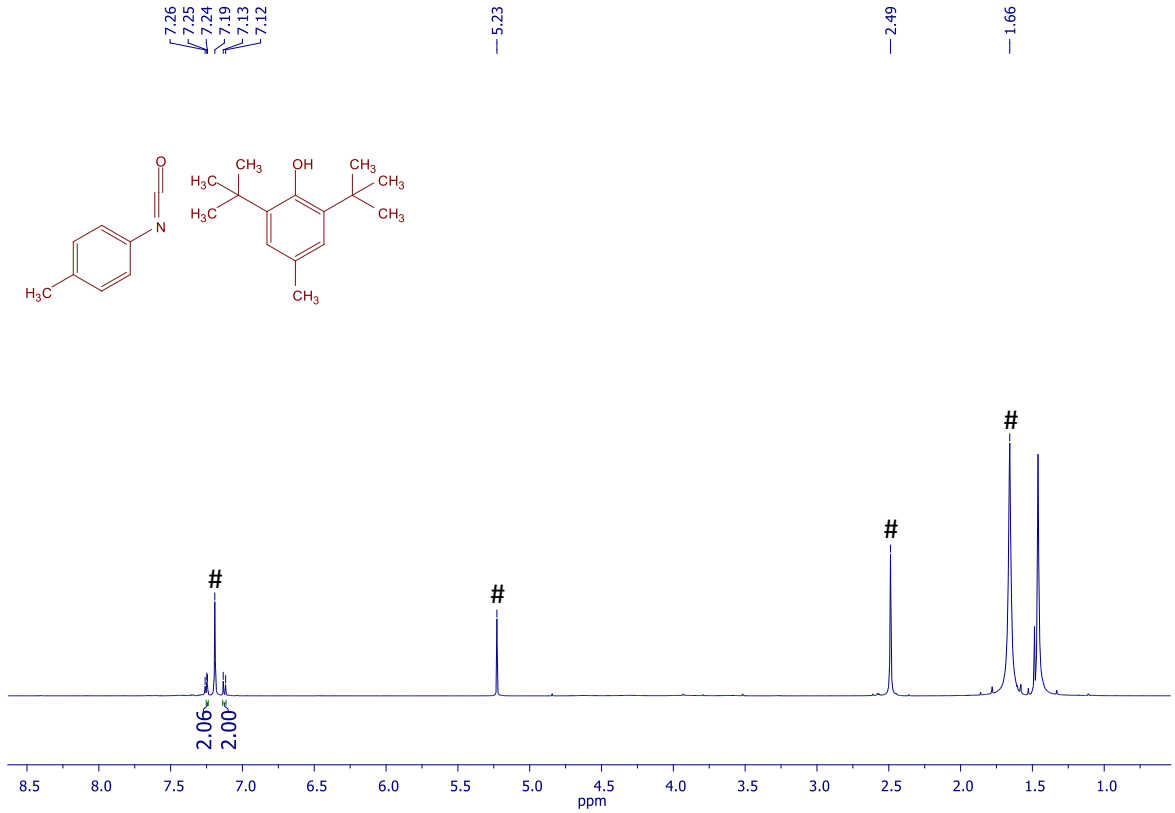


^{1}H NMR spectrum of N-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-N-(p-tolyl)formamide and quinoline (and # represent quinoline and p-tolyl isocyanate, respectively in the reaction mixture)*

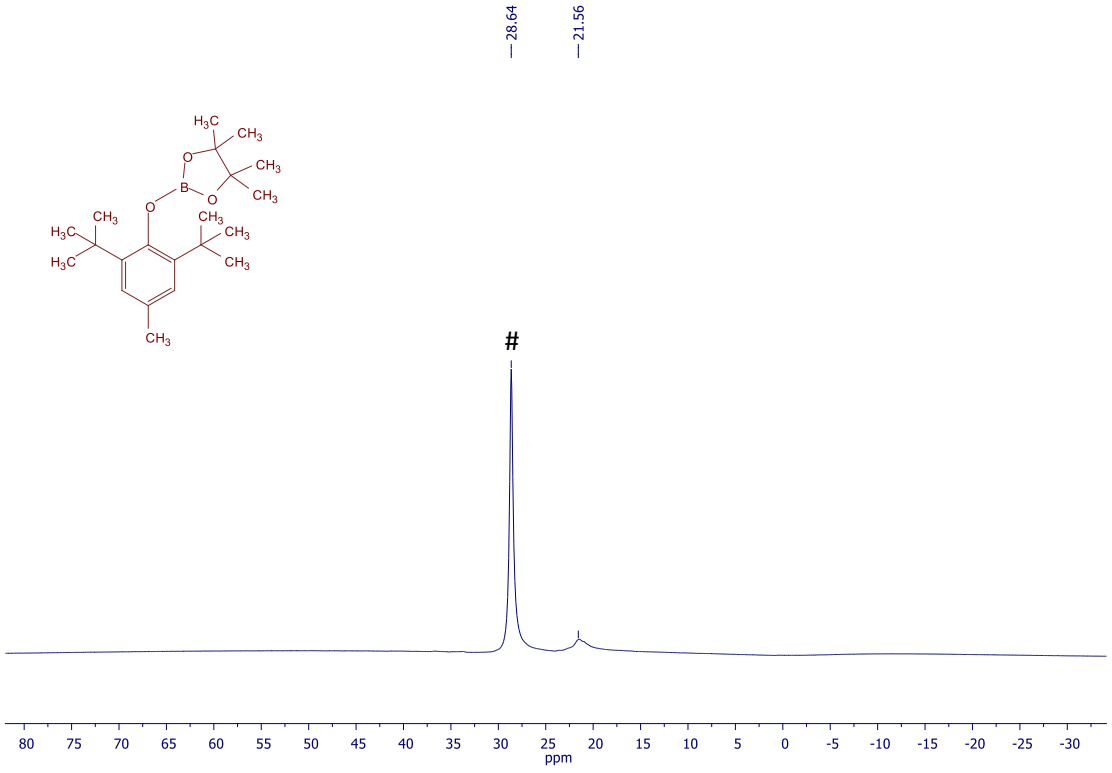
Radical scavenger experiments: $AgSbF_6$ (1.7 mg, 0.005 mmol, 1.0 mol%) and pinacolborane (225 µL, 1.55 mmol) were taken in a Schlenk tube. After that, 4-methylphenyl isocyanate (66.5 mg, 0.5 mmol) and radical scavenger (0.5 mmol to 1.5 mmol) were added to the reaction mixture and then heated to 60 ºC for 6 hours (our standard deoxygenative hydroboration condition). The progress of the reaction was monitored by ^{1}H NMR spectroscopy.

Procedure for mercury dropping test: $AgSbF_6$ (1.7 mg, 0.005 mmol, 1.0 mol%) and pinacolborane (225 µL, 1.55 mmol) were taken in a pressure tube. After that, 4-methylphenyl isocyanate (66.5 mg, 0.5 mmol) and mercury (40 mg, 2 mmol) were added to the reaction mixture and then allowed to stir at 60 ºC for 6 hours. After the reaction mercury drop was separated out and outcome of the reaction was monitored by ^{1}H NMR spectroscopy.

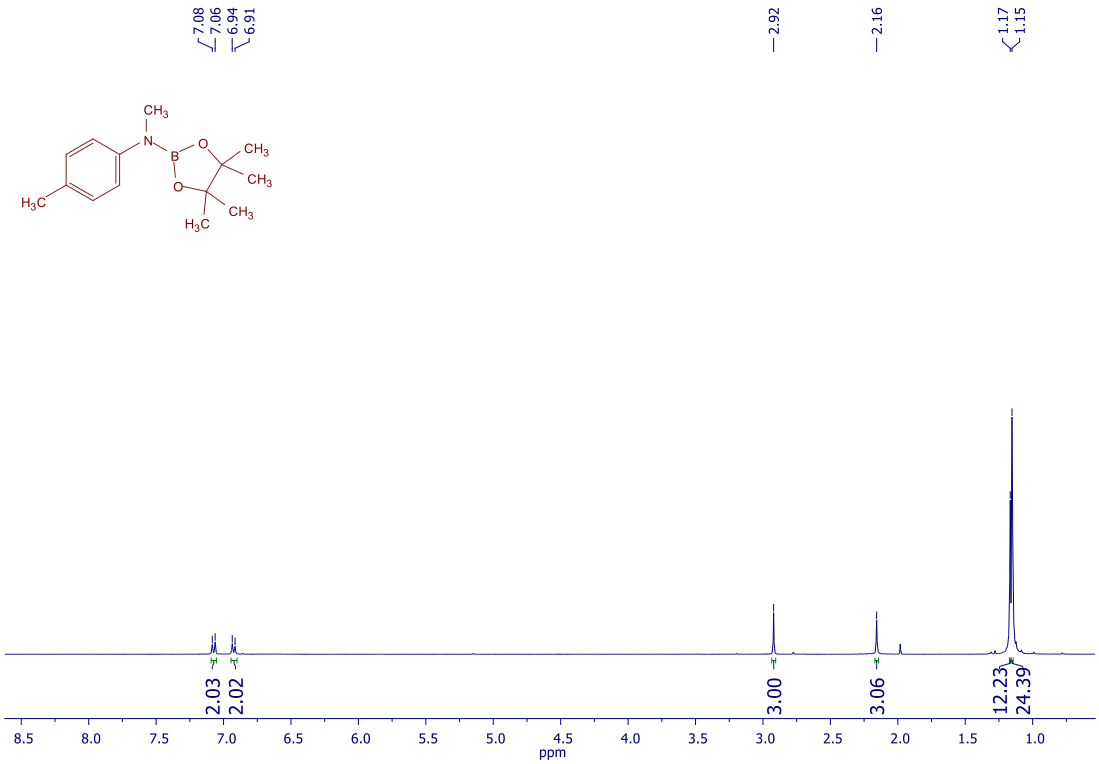
^{1}H NMR of control experiments:



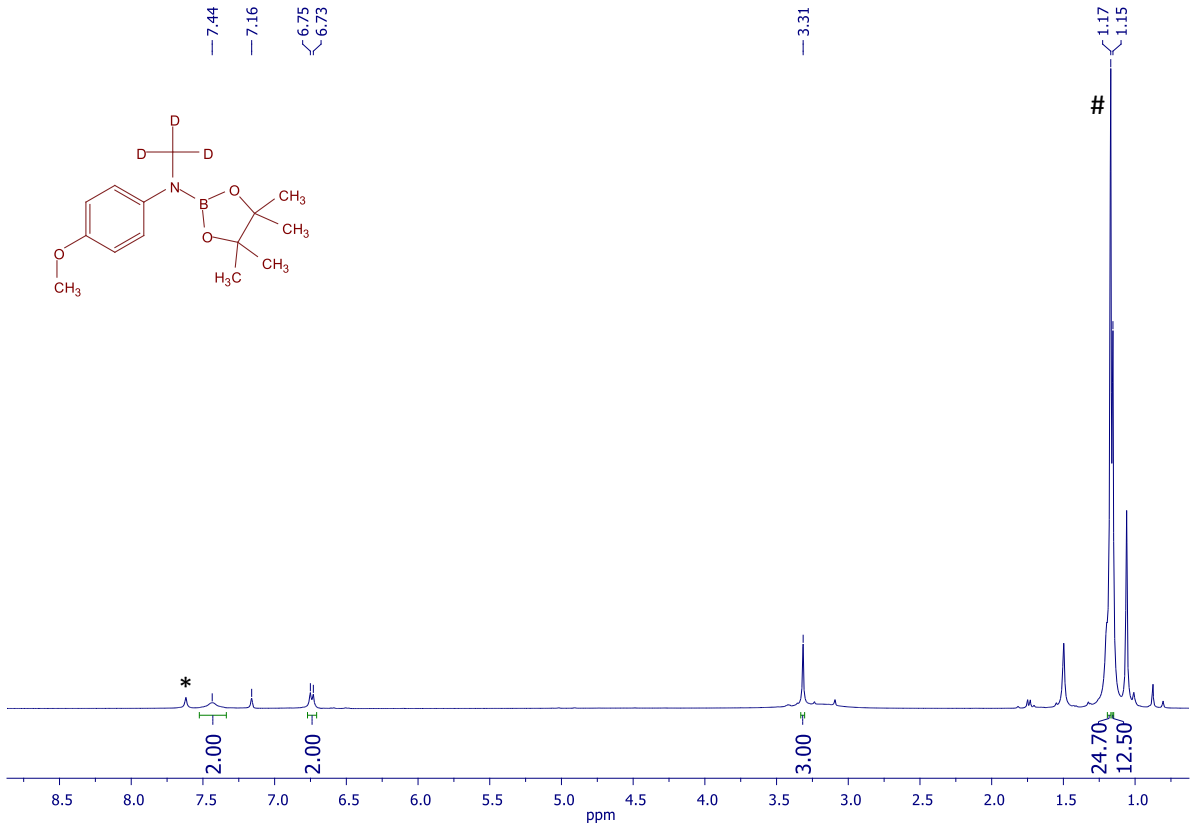
^{1}H NMR spectrum of the reaction mixture of 4-methylphenyl isocyanate *hydroboration under standard condition in presence of BHT. # indicates peaks corresponding to BHT*



^{11}B NMR (160 MHz, $CDCl_3$) spectrum of the reaction mixture of 4-methylphenyl hydroboration under standard condition in presence of BHT. # indicates resonance for H-Bpin.



^{1}H NMR spectrum of the reaction mixture of 4-methylphenyl isocyanate hydroboration under standard condition in presence of mercury.



^{1}H NMR spectrum of the reaction mixture of 4-methoxyphenyl isocyanate hydroboration under standard condition in presence of D-Bpin. (and # represent unknown impurity and byproduct $(Bpin)_2O$, respectively in the reaction mixture)*

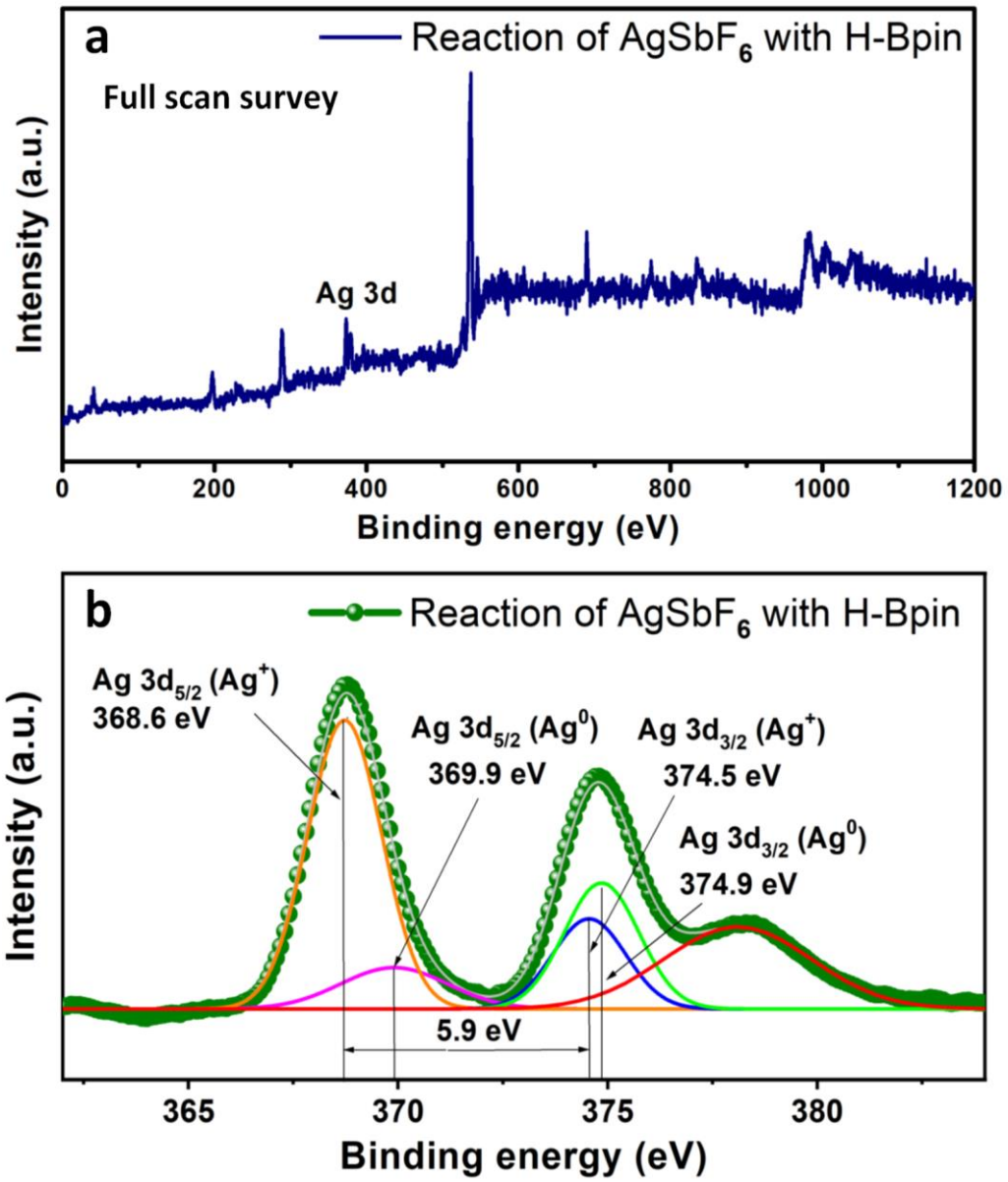


Figure S3. The full-scan XPS survey (a) and XPS spectrum (b, Ag 3d, narrow scan) of a reaction between $AgSbF_6$ and H-Bpin.

The full-scan XPS survey of a reaction between $AgSbF_6$ and H-Bpin (Figure **S3a**) shows the presence of Ag constituent as expected. Further, the high-resolution Ag 3d signals ($Ag_{5/2}$ and $Ag_{3/2}$) were well deconvoluted (Figure **S3b**) into four peaks at 368.6 eV (Ag $3d_{5/2}$, Ag^+), 369.9 eV (Ag $3d_{5/2}$, Ag^0), 374.5 eV (Ag $3d_{3/2}$, Ag^+), and 374.9 eV (Ag $3d_{3/2}$, Ag^0) which clearly supports the formation of Ag^0 from the reaction of $AgSbF_6$ and H-Bpin.[8]

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