Supporting Information

Iron-Catalyzed Hydroboration of Non-Activated Imines and Nitriles: Kinetic and Mechanistic Studies

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1. General Considerations

All reagents were purchased from commercial vendors and used without further purification unless otherwise noted. All reactions were performed under an atmosphere of dry argon using Schlenk line and inert atmosphere glove box techniques unless otherwise noted. $CDCl_3$ was used without drying. ^{1}H, ^{13}C, ^{11}B and ^{19}F NMR spectra were recorded on a Jeol 400 MHz spectrometer at 300K unless otherwise noted. ^{1}H NMR spectra were referenced to the solvent residual peak ($CDCl_3$, δ 7.26 ppm) and $^{13}C\{^{1}H\}$ NMR spectra were referenced to the solvent residual peak ($CDCl_3$, δ 77.16 ppm). Data for ^{1}H NMR are recorded as follows: the chemical shifts are reported in (δ, ppm), multiplicity (br = broad, s = singlet, d = doublet, t = triplet, q= quartet, m = multiplet), and coupling constants in Hz as absolute values.

2. General procedure for the synthesis of aldimines and ketimines

Imine substrates were synthesized using reported literature methods.[1] To an oven dried 50 mL round bottom flask, aldehyde (0.5 mmol), aniline (0.75 mmol), $NaHCO_3$ (5 equiv., 2.5 mmol), activated molecular sieves (7 g; 4 Å), and benzene (10 mL) were added under an argon atmosphere and the reaction mixture heated at reflux temperature overnight. After being allowed to cool to room temperature, the reaction mixture was filtered through Celite, the filtrate was collected, and the solvent removed under reduced pressure. Recrystallization of the crude solids was achieved from diethyl ether or hexanes.

3. Optimization of reaction conditions and control experiments

In an inert atmosphere glovebox, an oven dried J. Young NMR was charged with ^{dpp}BIANFe(Tol) (3.00 mg, 0.005 mmol), N-benzylideneaniline (0.5 mmol, 1 equiv.), HBpin (0.75 mmol, 1.5 equiv.), NaO^{t}Bu (1.00 mg, 0.01 mmol) and THF (0.7 mL). The reaction mixture was then placed in a preheated oil bath at 70 °C. The progress of the reaction was monitored using ^{11}B NMR spectroscopy. Upon completion, the reaction mixture was diluted with hexanes and filtered through silica gel (60 Å, 40-63 microns) using a filter pipette. Complete hydrolysis of the product was monitored by TLC and the solvent subsequently removed under reduced pressure. ^{1}H NMR yield was determined by dissolution in 0.5-0.6 mL of $CDCl_3$ and calculated based on an internal standard, mesitylene (10 μL). In all cases, the product peaks were integrated with respect to the -CH_3 peak of the internal standard which was normalized to 1.

Entry	^{dpp}BIANFe(Tol)	Activator (2 mol %)	Solvent (h)	Temperature (°C)	Yield %
1	No	NaO^{t}Bu	THF	70	30
2	No	No	THF	70	10
3	Yes	No	THF	70	87
4	Yes	NaO^{t}Bu	THF	70	95

Table S1. Control experiments. Reaction condition: imine (0.5 mmol), HBpin (1.5 equiv.), ^{dpp}BIANFe(Tol) (0.005 mmol), 20 hrs; Yield determined by ^{1}H NMR analysis using mesitylene as the internal standard.

Entry	Solvent	Temperature (°C)	Time (h)	Yield %
1	DCM	70	5	64
2	Hexanes	70	5	94
3	Toluene	70	1	97
4	THF	70	5	92

Table S2. Optimization of solvent. Reaction condition: imine (0.5 mmol), HBpin (1.5 equiv.), ^{dpp}BIANFe(Tol) (0.005 mmol), NaO^{t}Bu (0.01 mmol); Yields were determined by ^{1}H NMR employing mesitylene as internal standard.

Entry	Temperature (°C)	Solvent	Time (h)	Yield %
1	RT	Toluene	5	84
2	50	Toluene	1	91
3	70	Toluene	1	97
4	90	Toluene	5	97

Table S3. Optimization of temperature. Reaction condition: imine (0.5 mmol), HBpin (1.5 equiv.), ^{dpp}BIANFe(Tol) (0.005 mmol), NaO^{t}Bu (0.01 mmol); Yields were determined by ^{1}H NMR employing mesitylene as internal standard.

Entry	Activator	Temperature (°C)	Time (h)	Yield %
1	NaH	70	5	80
2	$NaBH(C_2H_5)_3$	70	5	90
3	KF	70	5	78
4	NaO^{t}Bu	70	1	97
5	KO^{t}Bu	70	5	84

Table S4. Optimization of activator. Reaction condition: imine (0.5 mmol), HBpin (1.5 equiv.), ^{dpp}BIANFe(Tol) (0.005 mmol), activator (0.01 mmol) in toluene; Yields were determined by ^{1}H NMR employing mesitylene as internal standard.

4. General procedure for the catalytic hydroboration of aldimines and ketimines

In an inert atmosphere glovebox, an oven dried J. Young NMR tube was charged with ^{dpp}BIANFe(Tol) (3.00 mg, 0.005 mmol), imine (0.5 mmol, 1 equiv), HBpin (109 µL, 0.75 mmol, 1.5 Equiv.), NaO^{t}Bu (1.00 mg, 0.01 mmol) and toluene (0.7 ml). The reaction mixture was then placed in a preheated oil bath at 70 °C. The progress of the reaction was monitored by ^{11}B NMR spectroscopy. Upon completion, the reaction mixture was treated with silica gel (60 Å, 40-63 Microns) and hexanes through a fliter pipette. Complete hydrolysis of the product was monitored by TLC and the solvent subsequently removed under reduced pressure. ^{1}H NMR yield in 0.5-0.6 ml of $CDCl_3$ was determined based on the internal standard, mesitylene (10 µL). In all cases, the product peaks were integrated with respect to the -CH_3 peak of the internal standard which was normalized to 1. To isolate the product, the reaction mixture was diluted with ethyl acetate (5 mL) and was stirred for 1 h at room temperature after the addition of 1M HCl in ether (2 mL). The resulting white solid precipitate was filtered over filter frit and washed with copious amount of ethyl acetate to yield pure product as an ammonium salt. The ^{1}H and ^{13}C NMR spectra of the

isolated ammonium salts are reported in D_2O. Free amines could be readily obtained by extraction with dichloromethane after stirring the ammonium salt with NaOH (2 mL, 2.0M) for 10 minutes.

5. General procedure for the catalytic hydroboration of nitriles

In an inert atmosphere glovebox, an oven dried screw cap vial was charged with ^{dpp}BIANFe(Tol) (1.62 mg, 0.0025 mmol), nitrile (0.25 mmol, 1 equiv), HBpin (91 μL, 0.625 mmol, 2.5 equiv) and a magnetic stir bar. The reaction mixture was then stirred on a preheated oil bath at 70 °C, or at room temperature, until the solid product precipitates out or the entire reaction mixture solidifies. Upon completion, the reaction mixture was filtered through celite. ^{1}H NMR yield in 0.5-0.6 ml of $CDCl_3$ was determined based on the internal standard, mesitylene (5 μL). In all cases, the product peaks were integrated with respect to the -CH_3 peak of the internal standard which was normalized to 1. To isolate the product, the reaction mixture was hydrolyzed by the addition of diethyl ether and deionized water followed by extraction with diethyl ether several times. The extract was then stirred for 1 h at room temperature after the addition of 1M HCl in ether (2 mL). The resulting white solid precipitate was filtered over filter frit and washed with copious amount of ethyl acetate to yield pure product as ammonium salt. The ^{1}H and ^{13}C NMR spectra of the isolated ammonium salts are reported in D_2O. Free amines could be readily obtained by extraction with dichloromethane after stirring the ammonium salt with NaOH (2 mL, 2.0M) for 10 minutes.

6. Preliminary study of reaction kinetics

^{dpp}BIANFe(η^6-C_7H_8), 4-fluorophenyl-*N*-phenylmethanimine (**1b**), HBpin, NaO^{t}Bu and 1,4-bis(trifluoromethyl)benzene (internal standard) were dissolved in ~ 0.7 mL toluene in a J. Young NMR tube in an inert atmosphere glove box and the tube sealed. Kinetics experiments were performed via changing concentration of e.g. ^{dpp}BIANFe(Tol), HBPin etc. while holding all other concentrations constant. The reaction progress was conveniently monitored employing ^{19}F NMR spectroscopy. The sample was heated to 70 °C within the NMR spectrometer and ^{19}F NMR spectra were recorded at 10 minutes intervals for ~13 hrs. For analysis of the spectra, the integral of the internal standard was set to 1 in each spectrum and the values for the starting material as well as the products were used without further manipulation.

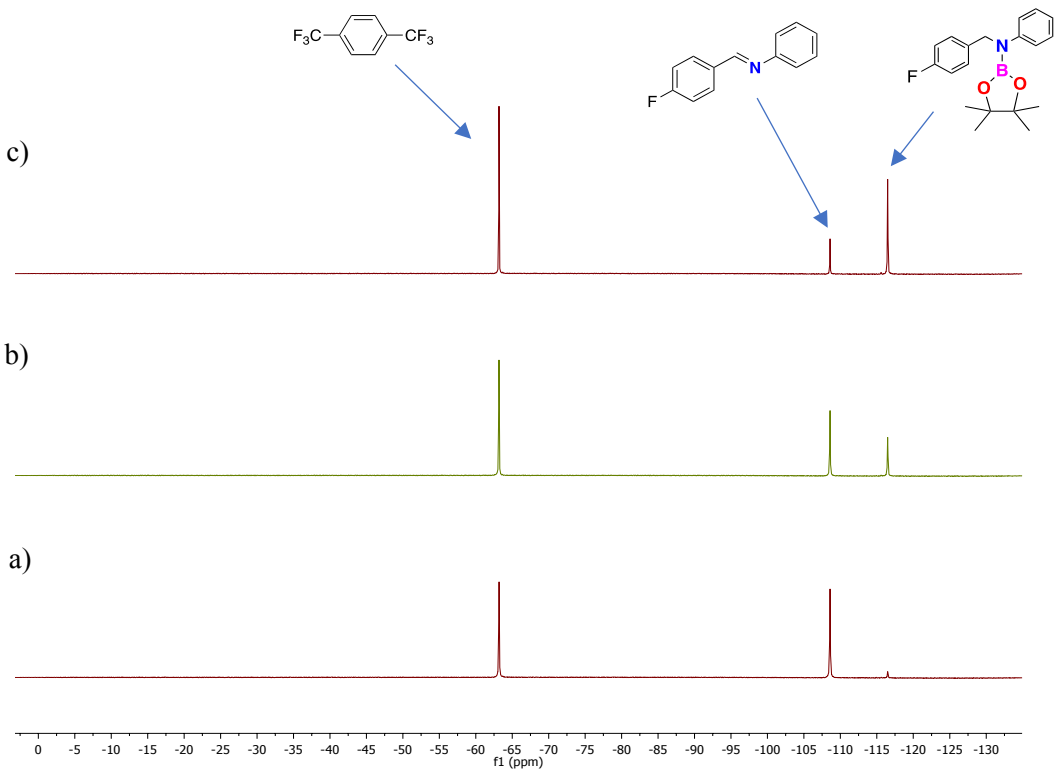


Figure S1. Typical ^{19}F NMR spectra recorded during a kinetic measurement run after a) 30 min. b) 6 hrs and c) 13 hrs.

Reaction rates were determined by least-square fit of the initial product concentration versus time. *K*max was determined by taking the maximum rate of the reaction, the relevant plots are shown in **Figures S2-S4**. Activation parameters including enthalpy ($\Delta H^{\ddagger}$), entropy ($\Delta S^{\ddagger}$) and activation energy (E_a) were calculated from kinetic data using Eyring and Arrhenius plots. In a typical sample, the J. Young NMR tube was loaded with ^{dpp}BIANFe(Tol) (0.0025 mmol), 4-fluorophenyl-*N*-phenylmethanimine (**1b**), (0.25 mmol), HBpin (0.375 mmol), NaO^{t}Bu (0.005 mmol) dissolved in ~ 0.7 mL toluene and sealed. All the experiments were carried out under the same conditions at different temperatures (50 °C, 60 °C, 70 °C, 80 °C) within the NMR spectrometer. ^{19}F NMR spectra were recorded at 10 minutes intervals for ~8 hrs. Reaction rates were determined by the least square fit of initial product concentration versus time, and Eyring and Arrhenius plots (shown in **Figure S6** and **Figure S7**). Enthalpy ($\Delta H^{\ddagger}$), entropy ($\Delta S^{\ddagger}$) and activation energy (E_a) were calculated from the slope and intercept of the least-square fit.

6.1. [HBpin] rate order assessment

HBpin (mmol)	^{dpp}BIANFe(Tol) (mmol)	Imine (mmol)	Kmax (mmol/min)	R^2
0.250	0.0025	0.25	0.0056	0.9804
0.375	0.0025	0.25	0.1960	0.9908
0.500	0.0025	0.25	0.5749	0.9971
0.625	0.0025	0.25	0.1500	0.9711
0.75	0.0025	0.25	0.0207	0.9861

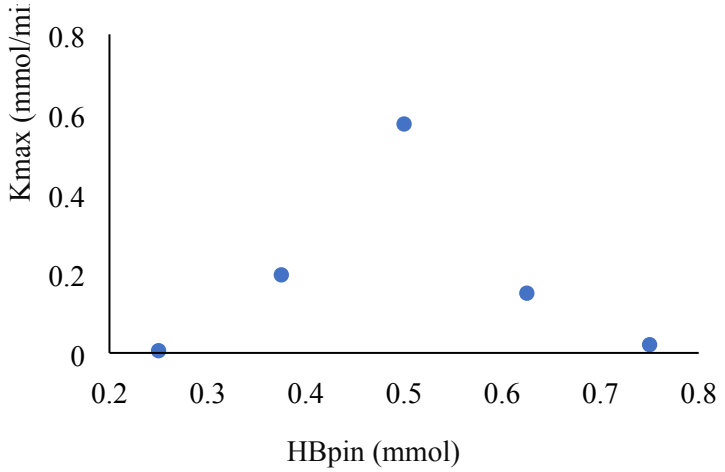


Figure S2. Plot of Initial rate vs. [HBpin] in the reaction of 4-fluorophenyl-N-phenylmethanimine and HBpin catalyzed by ^{dpp}BIANFe(Tol) at 70 °C.

6.2. [^{dpp}BIANFe(η^6-C_7H_8)] rate order assessment

HBpin (mmol)	^{dpp}BIANFe(Tol) (mmol)	Imine (mmol)	Kmax (mmol/min)	R^2
0.250	0.00125	0.25	0.0268	0.9764
0.250	0.00250	0.25	0.5076	0.9800
0.250	0.00500	0.25	1.2887	0.9855
0.250	0.00750	0.25	1.6630	0.9819
0.250	0.01250	0.25	3.5270	0.9929

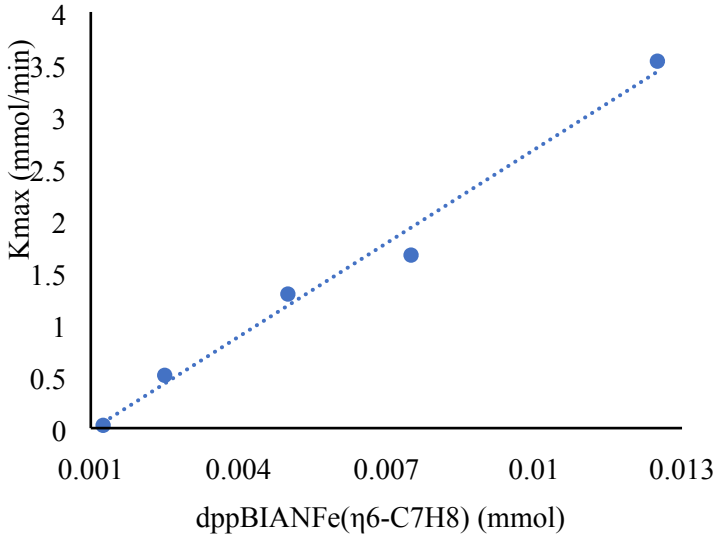


Figure S3. Plot of initial rate vs. ^{dpp}BIANFe(Tol) in the reaction of 4-fluorophenyl-N-phenylmethanimine and HBpin catalyzed by complex ^{dpp}BIANFe(Tol) at 70 °C.

6.3. [4-fluorophenyl-N-phenylmethanimine] rate order assessment

HBpin (mmol)	^{dpp}BIANFe(Tol) (mmol)	Imine (mmol)	K (mmol/min)	R^2
0.250	0.0025	0.25	0.0056	0.9804
0.250	0.0025	0.50	0.1552	1
0.250	0.0025	0.75	0.2752	0.9853
0.250	0.0025	1.00	0.0033	0.9747

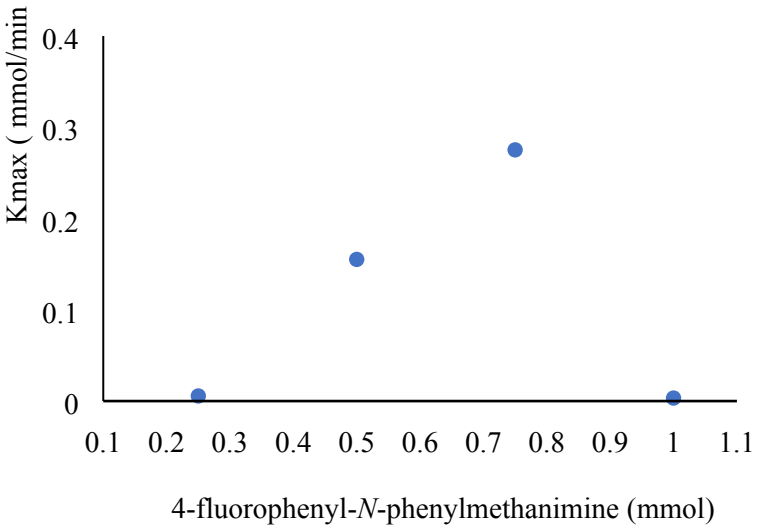


Figure S4. Plot of initial rate vs. [4-fluorophenyl-N-phenylmethanimine] in the reaction of 4-fluorophenyl-N-phenylmethanimine and HBpin catalyzed by complex ^{dpp}BIANFe(Tol) at 70 °C.

6.4. Temperature dependence experiments (Eyring and Arrhenius plots)

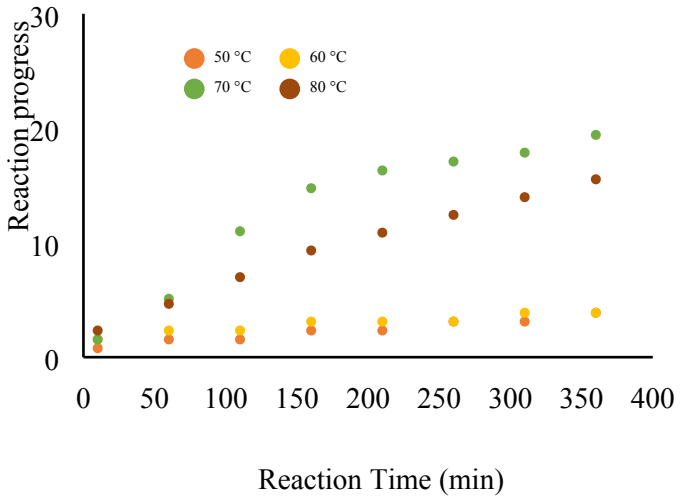


Figure S5. Reaction profile of catalytic hydroboration of 4-fluorophenyl-N-phenylmethanimine with HBpin using ^{dpp}BIANFe(Tol) at different temperatures.

k	ln (k/T)	ln (k)	T (K)	1/T × 10^{-3}
0.0071	-10.72	-4.95	323	3.09
0.0093	-10.49	-4.68	333	3.00
0.0240	-9.57	-3.73	343	2.91
0.0494	-9.11	-3.01	353	2.83
ln (k/T) vs. 1/T			ln (k) vs. 1/T	
Intercept	9.32±42.51		Intercept	18.59±46.54
Slope	-6516.62±19.42		Slope	-7657.50±46.30

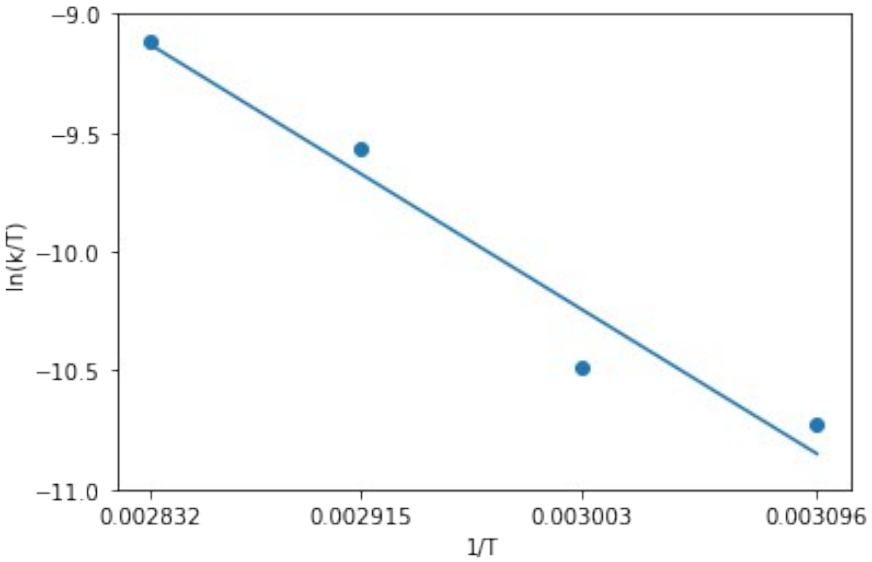


Figure S6. Eyring plot of ln(k/T) vs 1/T for hydroboration of 4-fluorophenyl-N-phenylmethanimine by ^{dpp}BIANFe(Tol)

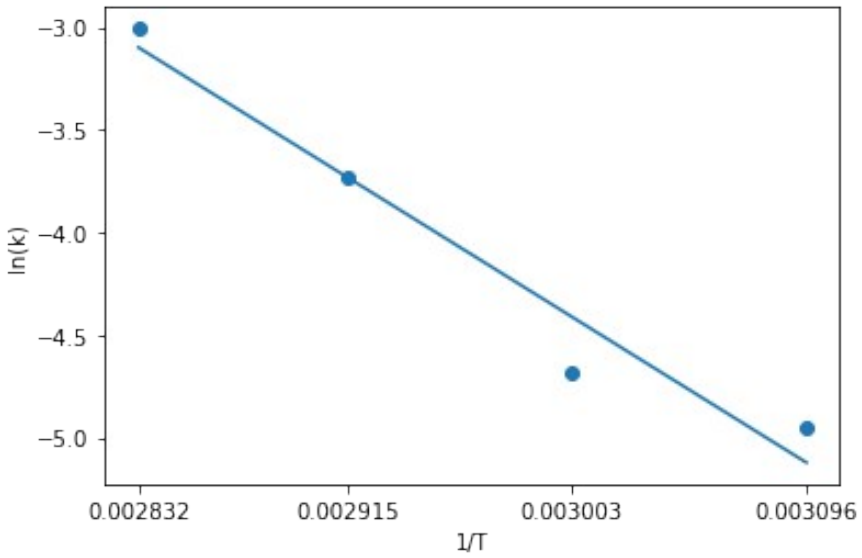
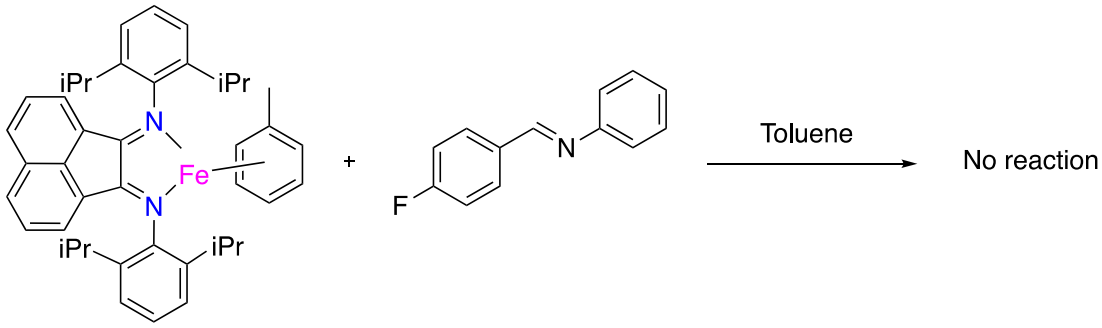


Figure S7. Arrhenius plot of ln(*k*) vs 1/T for hydroboration of 4-fluorophenyl-N-phenylmethanimine by ^{dpp}BIANFe(Tol)

7. Stoichiometric reactions

7.1. Reaction of ^{dpp}BIANFe(η^6-C_7H_8) and 4-fluorophenyl-N-phenylmethanimine



In an inert atmosphere glovebox, an oven dried J. Young NMR tube was charged with ^{dpp}BIANFe(η^6-C_7H_8) (32 mg, 0.05 mmol, 1 equiv.) and 4-fluorophenyl-N-phenylmethanimine (30 mg, 0.15 mmol, 3 equiv.) in ~ 0.7 ml toluene. The reaction mixture was then warmed in a preheated oil bath (70 °C). The progress of the reaction was monitored overnight by ^{19}F NMR spectroscopy.

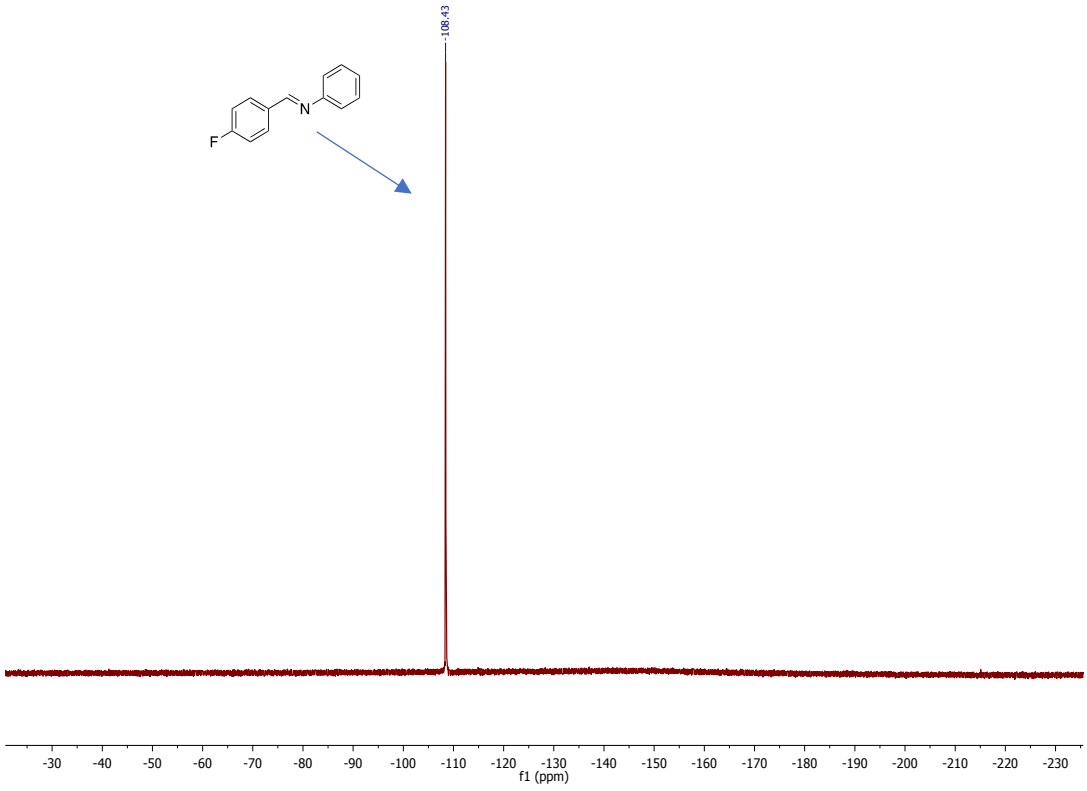
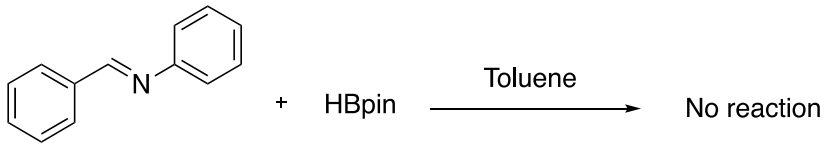


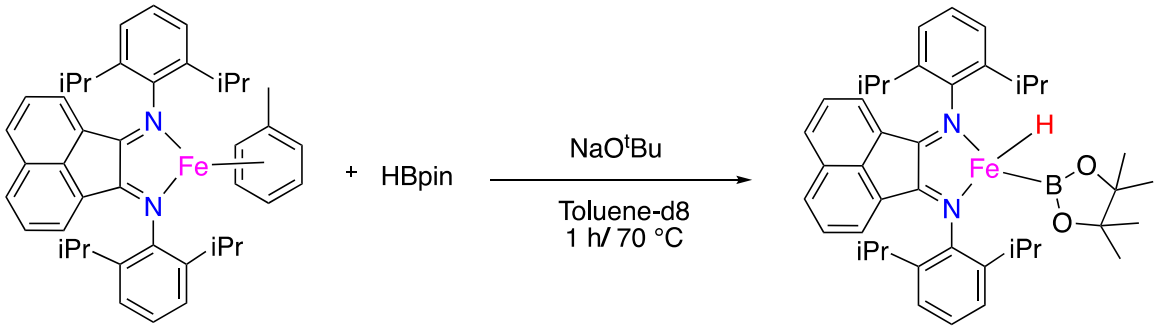
Figure S8. ^{19}F NMR spectra of the reaction between ^{dpp}BIANFe(η^6-C_7H_8) and 4-fluorophenyl-N-phenylmethanimine after 20 h at 70 °C.

7.2. Reaction of N-benzylideneaniline and HBpin



In an inert atmosphere glovebox, an oven dried J. Young NMR tube was charged with N-benzylideneaniline (91 mg, 0.5 mmol, 1equiv.) and HBpin (73 µL, 0.5 mmol, 1 equiv.) in ~ 0.7 ml toluene. The reaction mixture was then warmed in a preheated oil bath (70 °C). The progress of the reaction was monitored overnight by ^{11}B NMR spectroscopy.

7.3. Reaction of ^{dpp}BIANFe(η^6-C_7H_8)) and HBpin in the presence of NaO^{t}Bu



In an inert atmosphere glovebox, an oven dried J. Young NMR tube was charged with ^{dpp}BIANFe(η^6-C_7H_8) (64.80 mg, 0.1 mmol, 1equiv.), HBpin (14.5 µL, 0.1 mmol, 1 equiv.) and NaO^{t}Bu (9.6 mg, 1 equiv.) in ~ 0.7 ml toluene. The reaction mixture was then warmed in a preheated oil bath (70 °C). The progress of the reaction was monitored by proton parawide and ^{11}B NMR spectroscopy (**Figure 9-11**).

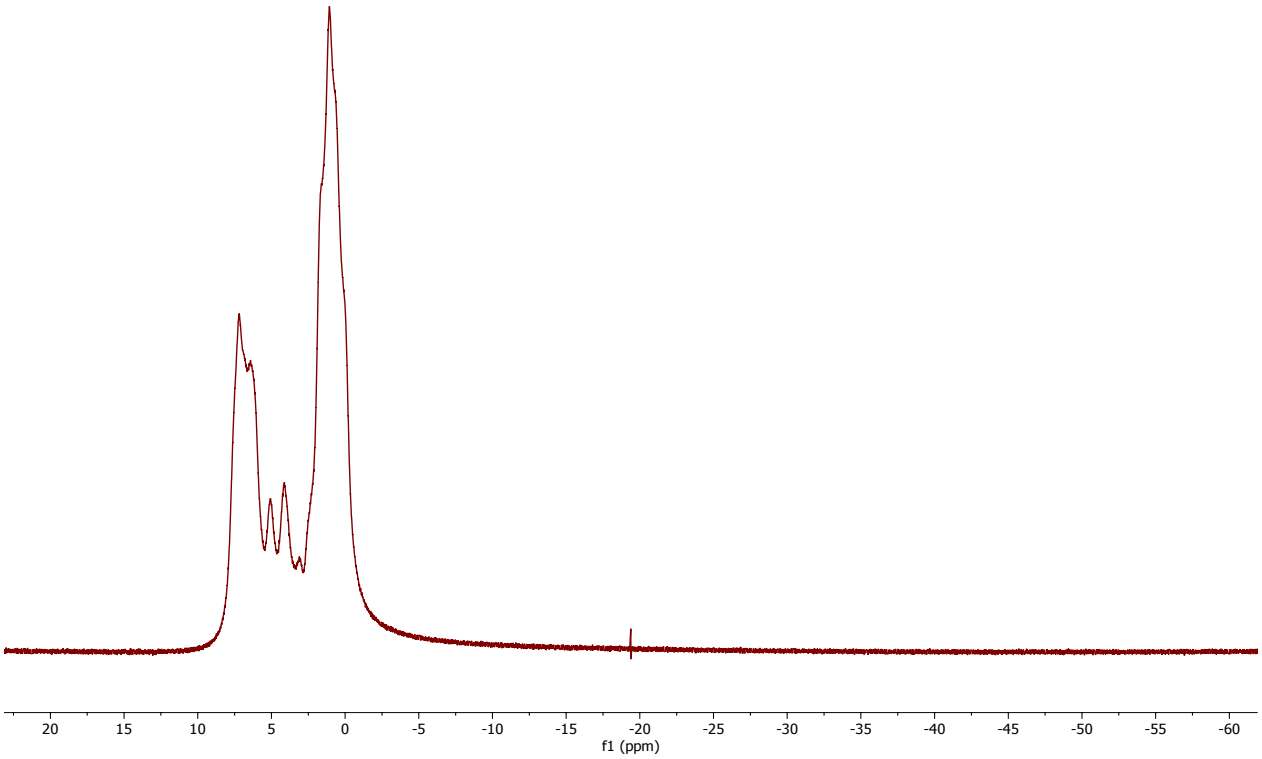


Figure S9. ^{1}H NMR spectra of the stoichiometric reaction between ^{dpp}BIANFe(Tol) and HBpin and NaO^{t}Bu after 1 h at 70 °C.

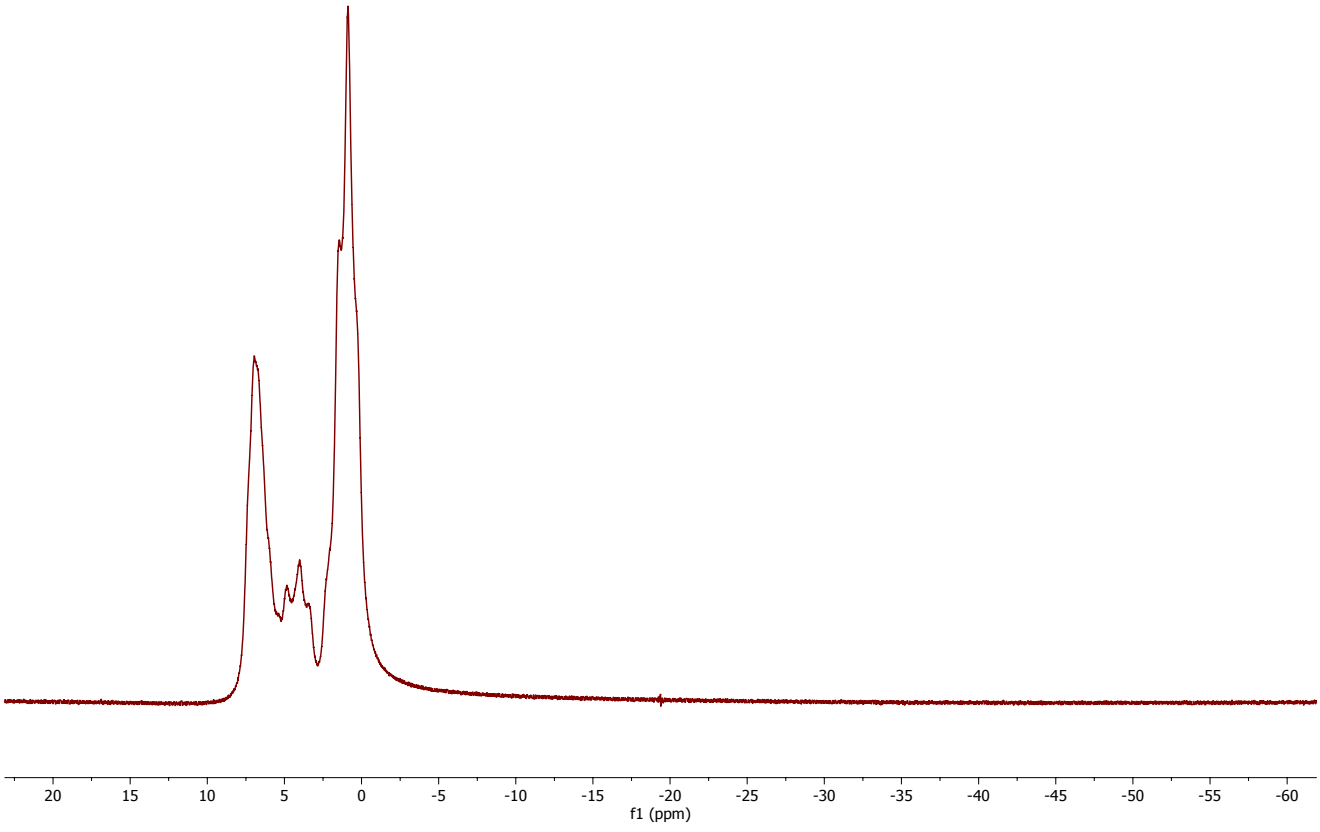


Figure S10. ^{1}H NMR spectra of the stoichiometric reaction between ^{dpp}BIANFe(Tol) and HBpin and NaO^{t}Bu after 30 min at 70 °C.

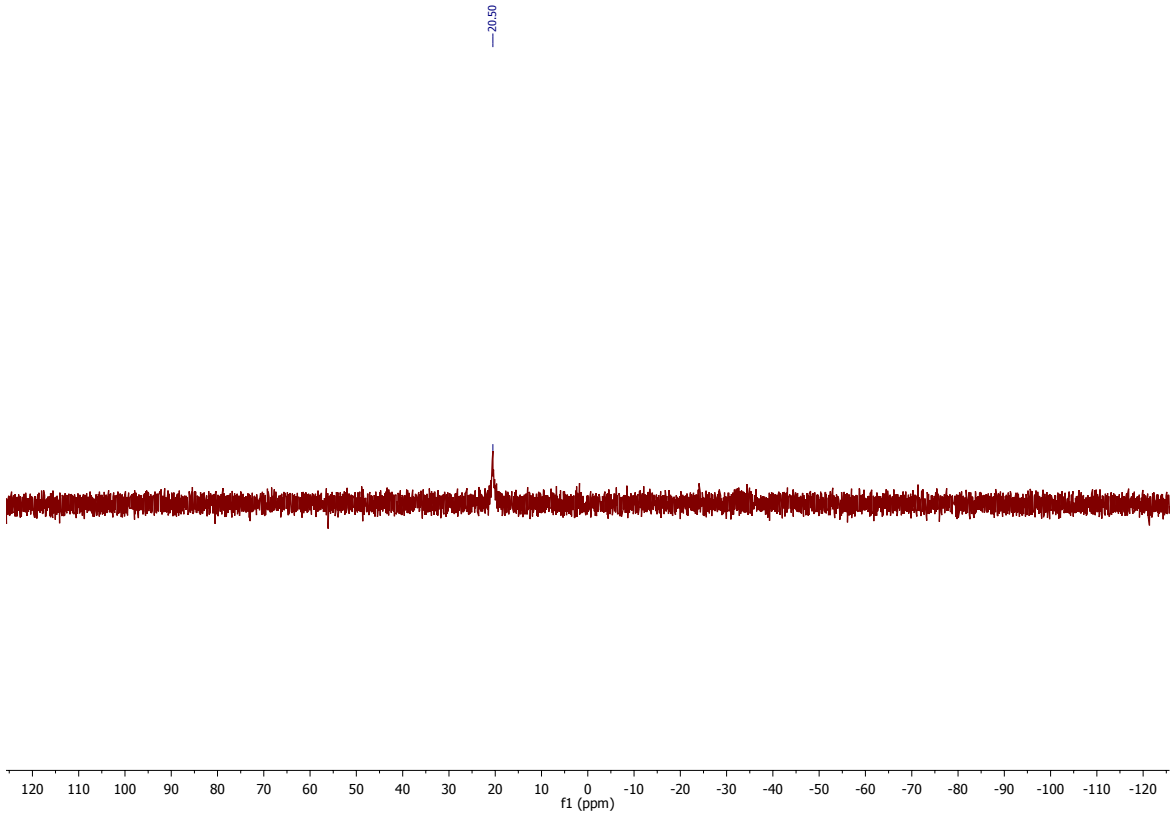
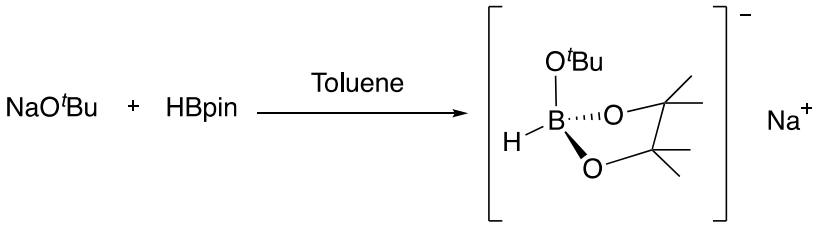


Figure S11. ^{11}B NMR spectra of the reaction between ^{dpp}BIANFe(Tol) and HBpin and NaO^{t}Bu after 1 h at 70 °C.

7.4. Reaction of NaO^{t}Bu and HBpin



In an inert atmosphere glovebox, an oven dried J. Young NMR tube was charged with HBpin (73

μL, 0.5 mmol, 1 equiv.) and NaO^{t}Bu (48 mg, 0.5 mmol, 1 equiv.) in ~ 0.7 ml toluene. The reaction mixture was then warmed in a preheated oil bath (70 °C). The progress of the reaction was monitored by ^{11}B NMR.

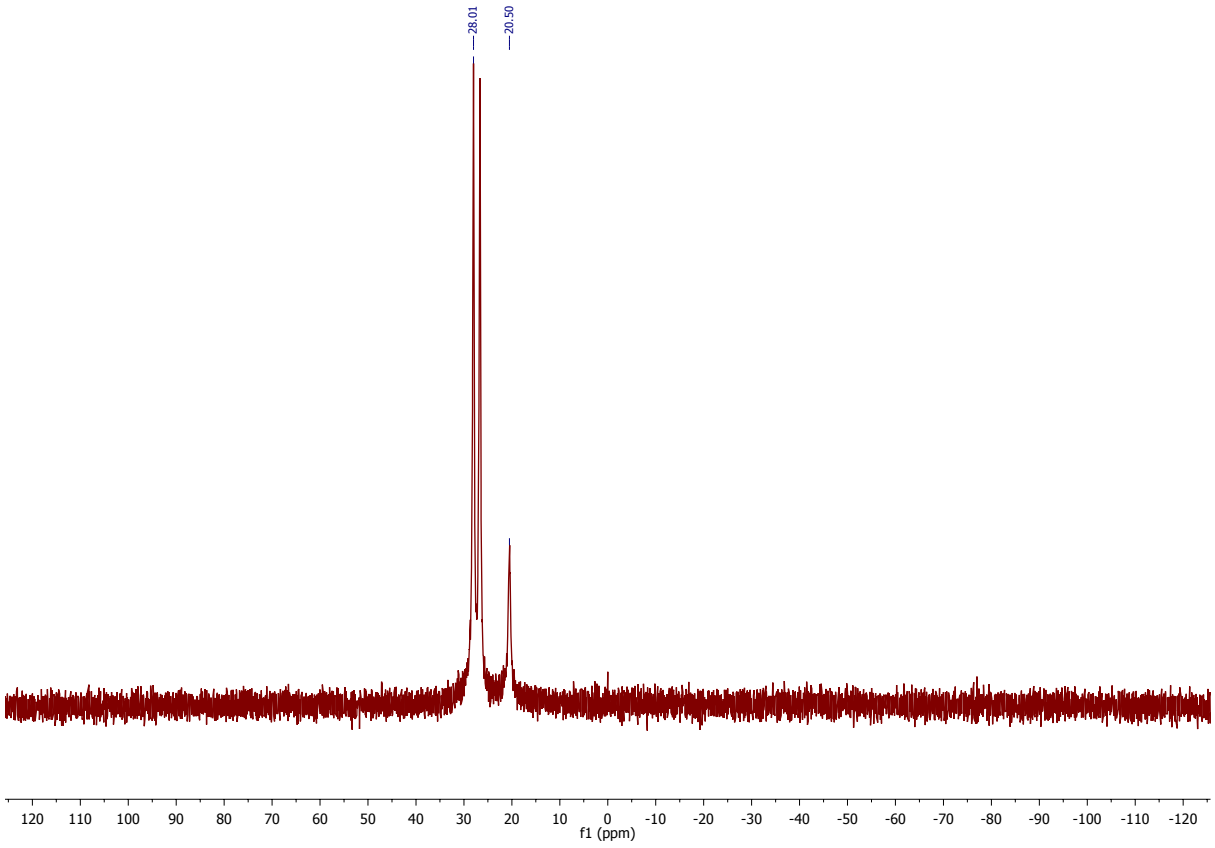
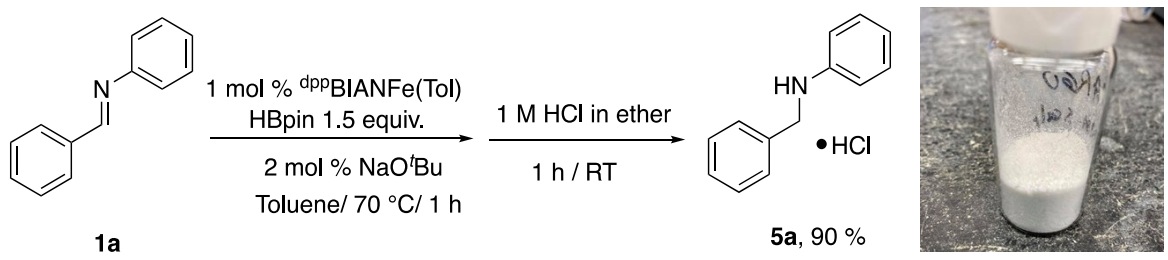


Figure S12. ^{11}B NMR spectrum of the reaction between HBpin and NaO^{t}Bu after 1 h at 70 °C.

8. Procedure for gram scale reaction



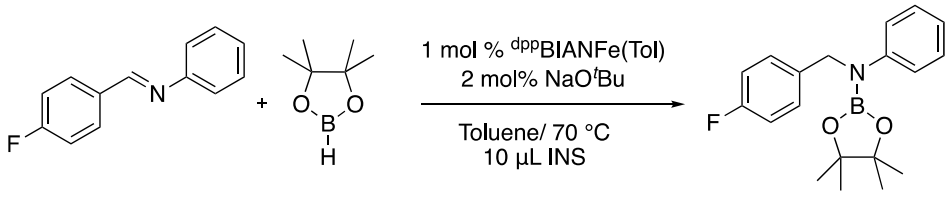
An oven dried 20 mL scintillation vial containing a magnet was charged with N-benzylideneaniline (1 g, 5.52 mmol), ^{dpp}BIANFe(Tol) (35.8 mg, 0.0552 mmol), HBpin (8.28 mmol, 1.5 equiv.), NaO^{t}Bu (10.6 mg, 0.11 mmol) and Toluene (7 mL) in an inert atmosphere glovebox. The reaction mixture was stirred in a preheated oil bath at 70 °C for 1 h. The reaction mixture was then hydrolyzed by the addition of diethyl ether and deionized water followed by extraction with diethyl ether several times. The extract was stirred for 1 h at room temperature after the addition of 1M HCl in ether (5 mL). The resulting white solid precipitate was filtered over filter frit and washed with copious amount of ethyl acetate to yield pure product as an ammonium salt. The ^{1}H and ^{13}C NMR of the isolated ammonium salt is reported in D_2O. Free amine could be readily obtained by extraction with dichloromethane after stirring the ammonium salt with NaOH (5 mL, 2.0M) for 10 minutes.

***N*-Benzylanilinium chloride (5a)** (90 %, white solid)

^{1}H NMR (400 MHz, D_2O): δ = 4.43 (s, 2H), 7.12 (m, 4H), 7.22 (m, 3H), 7.3 (m, 3H). ^{13}C NMR (101 MHz, D_2O): δ = 133.87, 130.34, 130.17, 129.91, 129.86, 129.76, 129.06, 122.92, 55.55.[10]

9. Hg poisoning of catalyst

An oven dried 20 mL scintillation vial containing a magnet was charged with ^{dpp}BIANFe(η^6-C_7H_8) (3.00 mg, 0.005 mmol), NaO^{t}Bu (1 mg, 0.01 mmol), HBpin (0.75 mmol, 1.5 equiv.), 4-fluorophenyl-*N*-phenylmethanimine (0.5 mmol, 1 equiv.), 1,4-bis(trifluoromethyl)benzene as internal standard (10 µL), Hg^0 (1.00 g, 4.98 mmol) in Toluene (0.7 mL). The reaction mixture placed on a preheated oil bath at 70 °C with vigorous stirring. The reaction was stopped after 1 h of heating and allowed to cool down to room temperature. The reaction mixture was then transferred to an oven dried J-Young tube in glove box. The crude yield, as determined by ^{19}F NMR was 76%.



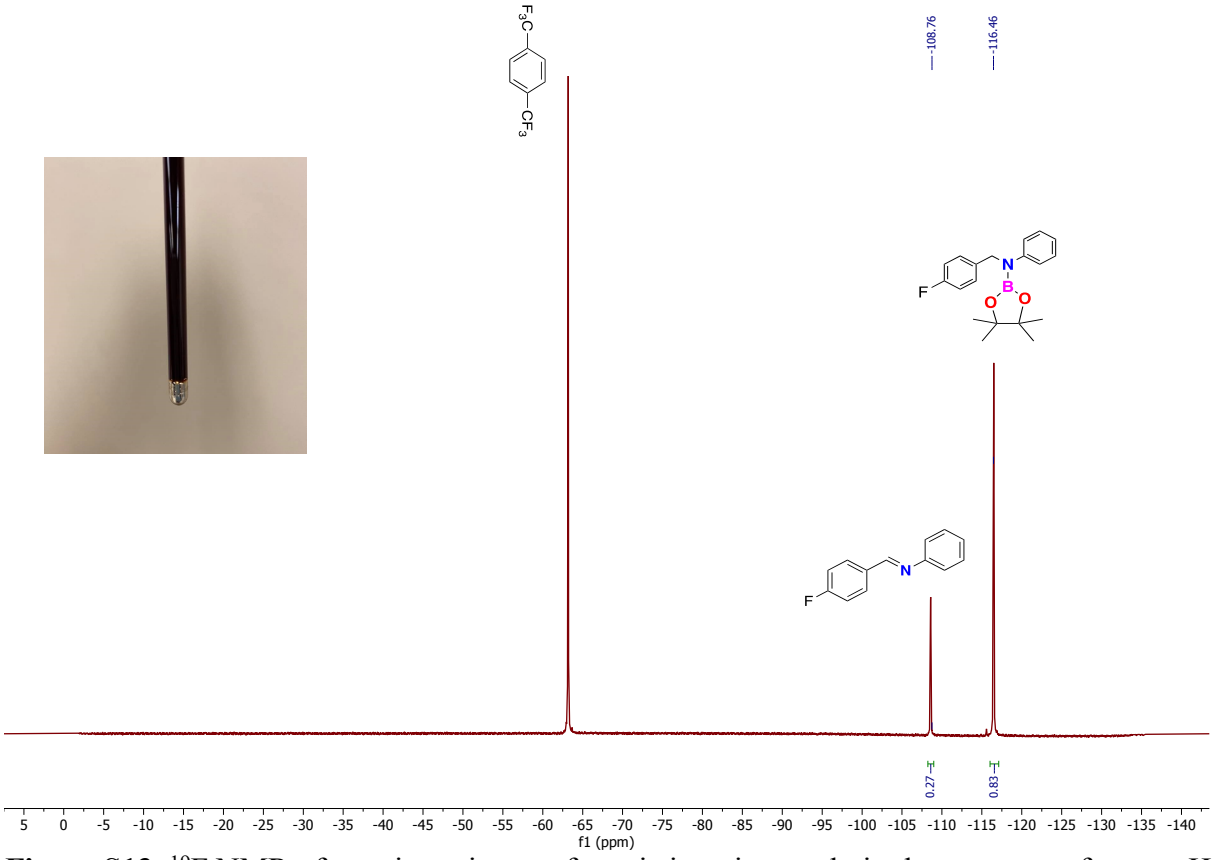
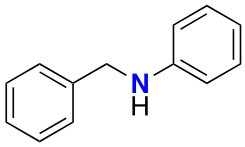


Figure S13. ^{19}F NMR of reaction mixture after stirring vigorously in the presence of excess Hg^0.

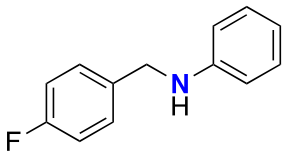
10. ^{1}H, ^{13}C NMR spectra



N-benzylaniline (2a) (97 %)

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.47-7.41 (m, 4H), 7.37 (t, 1H), 7.27 (t, 2H, *J* = 8.48 Hz), 6.82 (t, 1H, *J* = 8 Hz*),*), 6.71 (d, 2H, *J* = 7.68 Hz), 4.39 (s, 2H) ^{13}C NMR (101 MHz, $CDCl_3$): δ = 147.53, 138.82, 128.65, 128.02, 126.89, 126.61, 116.95, 112.25, 47.67. Spectral data matches the literature report.[2]

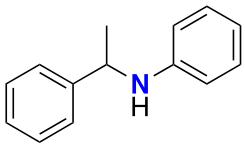
2,2-oxybis(4,4,5,5-tetramethyl-1,3,2-dioxoboralane: ^{1}H NMR (400 MHz; $CDCl_3$): δ= 1.38 (s, 24H). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 82.56, 24.19.[6]



N-(4-fluorobenzyl)aniline (2b) (77 %)

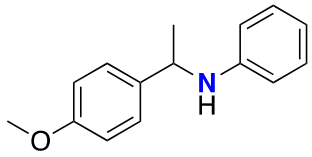
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.24-7.20 (m, 4H), 7.06 (t, 2H, *J*=8.72 Hz), 6.78 (t, 1H, *J* = 7.36 Hz), 6.66 (d, 2H, *J*= 7.88 Hz), 4.31 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 163.25, 147.94, 129.28, 126.92, 117.73, 115.53, 115.32, 112.89, 47.58. Spectral data matches the literature report.[2]

2,2-oxybis(4,4,5,5-tetramethyl-1,3,2-dioxoboralane: ^{1}H NMR (400 MHz; $CDCl_3$): δ= 1.38 (s, 24H). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 83.19, 24.49.[6]



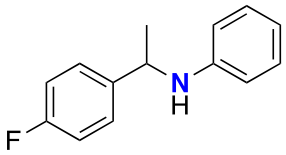
N-(1-phenylethyl)aniline (2c) (84 %)

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.47-7.38 (m, 4H), 7.31 (m, 1H), 7.18 (t, 2H, *J* = 8.36 Hz), 6.75 (t, 1H, *J* = 8 Hz), 6.61 (d, 2H, *J* = 8.6 Hz), 4.57 (q, 1H, *J* = 6.72 Hz), 1.59 (d, 3H, *J* = 6.76 Hz). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 147.33, 145.30, 129.13, 128.67, 126.93, 125.87, 119.44, 113.32, 53.45. Spectral data matches the literature report.[3]



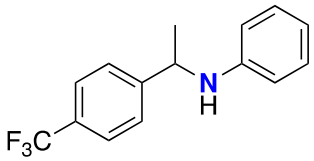
N-(1-(4-methoxyphenyl)ethyl)aniline (2d) (88 %)

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.33 (d, 2H, *J* = 8.16 Hz), 7.14 (t, 2H, *J* = 8 Hz), 6.90 (d, 2H, *J* = 12 Hz), 6.69 (t, 1H, *J* = 8 Hz), 6.57 (d, 2H, *J* = 8.52 Hz), 4.49 (q, 1H, *J* = 8 Hz), 3.80 (s, 3H), 1.53 (d, 3H, *J* = 6.72 Hz). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 158.62, 147.51, 137.42, 129.25, 127.05, 117.32, 114.15, 113.46, 55.37, 52.95, 25.17, 27.72. Spectral data matches the literature report.[3]



N-(1-(4-fluorophenyl)ethyl)aniline (2e) (99 %)

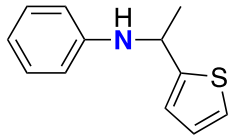
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.38- 7.34 (m, 2H), 7.14 (t, 2H, *J* =8.48 Hz), 7.03 (t, 2H, *J* = 8.72 Hz), 6.71 (t, 1H, *J* = 7.32 Hz), 6.54 (d, 2H, *J* = 7.68 Hz), 4.49 (q, 1H, *J* = 6.72 Hz), 1.52 (d, 3H, *J* = 6.76 Hz). ^{3}C NMR (101 MHz, $CDCl_3$): δ = 147.09, 140.89, 137.74, 129.13, 127.27, 126.92, 119.40, 113.30, 52.87, 25.18. Spectral data matches the literature report.[3]



N-(1-(4-(trifluoromethyl)phenyl)ethyl)aniline (2f) (99 %)

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.60 (d, 2H, *J* =8 Hz), 7.51 (d, 2H, *J* =8 Hz), 7.13 (t, 2H, *J* = 7.88 Hz), 6.71 (t, 1H, *J* =8 Hz), 6.52 (d, 2H, *J* =8 Hz), 4.55 (q, 1H, *J* = 6.72 Hz), 1.54 (d, 3H, *J* = 6.76 Hz). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 149.59, 146.86, 129.21, 126.21, 125.69, 117.68, 113.34, 53.30, 24.63. Spectral data matches the literature report.[4]

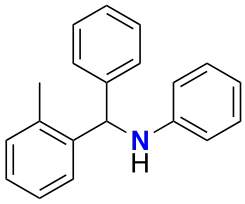
2,2-oxybis(4,4,5,5-tetramethyl-1,3,2-dioxoboralane: ^{1}H NMR (400 MHz; $CDCl_3$): δ= 1.38 (s, 24H). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 83.32, 24.63.[6]



N-(1-(thiophen-2-yl)ethyl)aniline (2g) (88 %)

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.10- 7.08 (m, 2H), 6.95-6.93 (m, 1H), 6.82 (d, 2H), 6.72 (t, 1H, *J* =8 Hz), 6.63 (d, 2H, *J* =7.64 Hz), 4.82 (q, 1H, *J* =6.6 Hz), 1.62 (d, 3H, *J* =6.64 Hz). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 150.31, 129.11, 128.89, 127.52, 126.96, 126.73, 119.82, 113.60, 49.41, 24.45.[7]

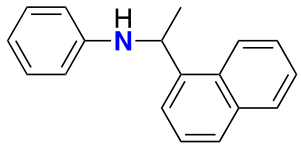
2,2-oxybis(4,4,5,5-tetramethyl-1,3,2-dioxoboralane: ^{1}H NMR (400 MHz; $CDCl_3$): δ= 1.38 (s, 24H). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 83.33, 24.45.[6]



N-(phenyl(o-tolyl)methyl)aniline (2h) (46 %)

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.26-7.22 (m, 4H), 7.20- 7.14 (m, 6H), 6.96 (t, 1H, *J* = 8 Hz), 6.74 (t, 1H, *J* = 7.36 Hz), 6.55 (d, 2H, *J* = 8.48 Hz). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 151.08, 147.54, 142.16, 136.08, 130.94, 128.58, 125.42, 123.66, 120.80, 117.67, 113.27, 59.64, 24.74.[8]

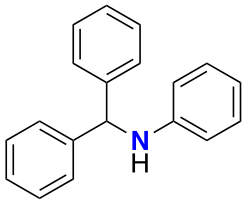
2,2-oxybis(4,4,5,5-tetramethyl-1,3,2-dioxoboralane: ^{1}H NMR (400 MHz; $CDCl_3$): δ= 1.38 (s, 24H). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 83.28, 24.74.[6]



N-(1-(naphthalen-1-yl)ethyl)aniline (2i) (50 %)

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.52- 7.43 (m, 4H), 7.38- 7.29 (m, 1H), 7.18- 7.13 (m, 3H), 6.93 (d, 1H, *J* = 7.68 Hz), 6.71 (t, 1H, *J* = 7.24 Hz), 6.62 (d, 2H, *J* = 7.96 Hz), 4.68 (q, 1H, *J* = 6.6 Hz), 1.62 (d, 3H, *J* = 6.68 Hz). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 146.71, 142.20, 128.45, 127.82, 127.20, 127.03, 125.35, 124.85, 123.79, 123.61, 116.65, 112.82, 53.02, 24.34. Spectral data matches the literature report.[1]

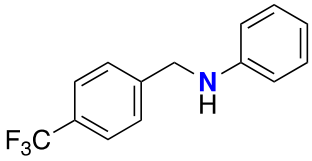
2,2-oxybis(4,4,5,5-tetramethyl-1,3,2-dioxoboralane: ^{1}H NMR (400 MHz; $CDCl_3$): δ= 1.38 (s, 24H). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 82.47, 24.34.[6]



N-benzhydrylaniline (2j) (63 %)

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.38 (t, 4H, *J* = 7.12 Hz), 7.33- 7.99 (m, 3H), 7.2- 7.15 (m, 4H), 6.82 (d, 1H, *J* = 7.32 Hz), 6.76 (t, 1H, *J* = 7.32 Hz), 6.61 (d, 2H, *J* = 7.72 Hz), 5.58 (s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 147.94, 129.28, 126.92, 117.72, 115.52, 115.32, 112.89, 47.58. Spectral data matches the literature report.[1]

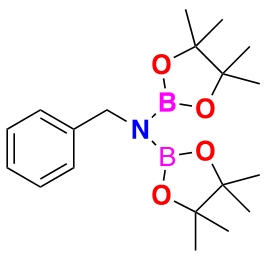
2,2-oxybis(4,4,5,5-tetramethyl-1,3,2-dioxoboralane: ^{1}H NMR (400 MHz; $CDCl_3$): δ= 1.38 (s, 24H). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 83.19, 24.49.[6]



***N*-(4-(trifluoromethyl)benzyl)aniline (2k) (99 %)**

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.62 (d, 2H, *J* = 8 Hz), 7.5 (d, 2H, *J* = 8 Hz), 7.24- 7.20 (m, 2H), 6.79 (t, 1H, *J* = 8 Hz), 6.64 (d, 2H, *J* = 8 Hz), 4.42 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 147.53, 138.82, 128.65, 128.02, 126.89, 126.61, 116.95, 112.25, 47.67. Spectral data matches the literature report.[9]

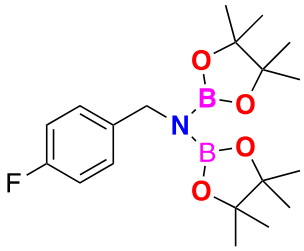
2,2-oxybis(4,4,5,5-tetramethyl-1,3,2-dioxoboralane: ^{1}H NMR (400 MHz; $CDCl_3$): δ= 1.32 (s, 24H). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 82.56, 24.19.[6]



N-benzyl-4,4,5,5-tetramethyl-N-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1,3,2-dioxaborolan-2-amie (4a) (98 %)

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.31- 7.29 (m, 2H), 7.24 (br. d, 2H), 7.15 (br. t, 1H), 4.23 (s, 2H), 1.19 (s, 24H). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 142.55, 127.01, 126.43, 125.59, 81.82, 46.76, 24.02. Spectral data matches the literature report.[5]

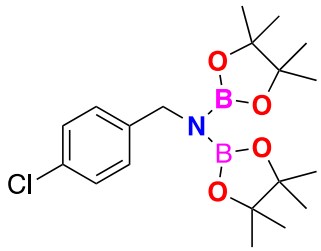
2,2-oxybis(4,4,5,5-tetramethyl-1,3,2-dioxoboralane: ^{13}C NMR (101 MHz, $CDCl_3$): δ = 81.82, 24.02.[6] The methyl peaks of $O(Bpin)_2$ in ^{1}H NMR are overlapping in the region 1.26-1.19 ppm.



N-(4-fluorobenzyl)-4,4,5,5-tetramethyl-N-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1,3,2-dioxaborolan-2-amine (4b) (95 %)

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.37- 7.33 (m, 2H), 6.84- 6.79 (m, 2H), 4.41 (s, 2H), 0.95 (s, 24H). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 138.91, 129.29, 127.00, 114.64, 82.45, 46.65, 24.59. Spectral data matches the literature report.[5]

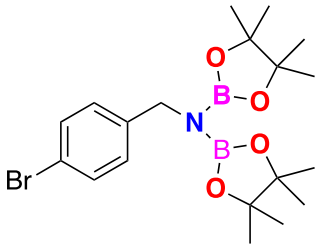
2,2-oxybis(4,4,5,5-tetramethyl-1,3,2-dioxoboralane: ^{1}H NMR (400 MHz; $CDCl_3$): ^{13}C NMR (101 MHz, $CDCl_3$): δ = 82.45, 24.59.[6] The methyl peaks of $O(Bpin)_2$ in ^{1}H NMR are overlapping in the region 0.95- 0.91 ppm.



N-(4-chlorobenzyl)-4,4,5,5-tetramethyl-N-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1,3,2-dioxaborolan-2-amine (4c) (81 %)

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.23- 7.17 (m, 4H), 4.15 (s, 2H), 1.17 (s, 24H). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 131.79, 129.02, 127.98, 82.51, 46.72, 24.58. Spectral data matches the literature report.[5]

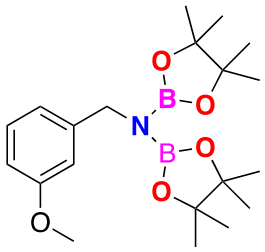
2,2-oxybis(4,4,5,5-tetramethyl-1,3,2-dioxoboralane: ^{1}H NMR (400 MHz; $CDCl_3$): ^{13}C NMR (101 MHz, $CDCl_3$): δ = 82.51, 24.58.[6] The methyl peaks of $O(Bpin)_2$ in ^{1}H NMR are overlapping in the region 1.25-1.17 ppm.



N-(4-bromobenzyl)-4,4,5,5-tetramethyl-N-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1,3,2-dioxaborolan-2-amine (4d) (84 %)

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.33 (d, 2H, *J* = 8.4 Hz), 7.15 (d, 2H, *J* = 8.16 Hz), 4.14 (s, 2H), 1.17 (s, 24H). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 142.17, 130.93, 129.40, 126.98, 82.53, 46.76, 24.58. Spectral data matches the literature report.[5]

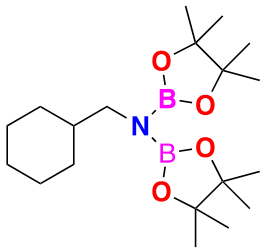
2,2-oxybis(4,4,5,5-tetramethyl-1,3,2-dioxoboralane: ^{1}H NMR (400 MHz; $CDCl_3$): ^{13}C NMR (101 MHz, $CDCl_3$): δ = 82.53, 24.58.[6] The methyl peaks of $O(Bpin)_2$ in ^{1}H NMR are overlapping in the region 1.24- 1.16 ppm.



N-(3-methoxybenzyl)-4,4,5,5-tetramethyl-N-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1,3,2-dioxaborolan-2-amine (4e) (99 %)

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.13 (t, 1H, *J* = 8.7 Hz), 6.88 (br. d, 2H), 6.71- 6.68 (m, 1H), 4.18 (s, 2H), 3.76 (s, 3H), 1.18 (s, 24H). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 159.31, 144.69, 128.72, 119.94, 112.65, 112.05, 82.30, 55.06, 47.24, 24.49. Spectral data matches the literature report.[5]

2,2-oxybis(4,4,5,5-tetramethyl-1,3,2-dioxoboralane: ^{1}H NMR (400 MHz; $CDCl_3$): ^{13}C NMR (101 MHz, $CDCl_3$): δ = 82.30, 24.49.[6] The methyl peaks of $O(Bpin)_2$ in ^{1}H NMR are overlapping in the region 1.25- 1.18 ppm.

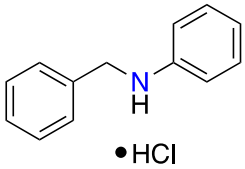


N-(cyclohexylmethyl)-4,4,5,5-tetramethyl-N-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1,3,2-dioxaborolan-2-amine (4f) (83 %)

^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.83 (br. d, 2H), 1.73- 1.58 (m, 5H), 1.41- 1.24 (m, 4H), 1.18 (s, 24H), 1.12 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 82.05, 49.77, 40.57, 30.61, 26.85, 26.23, 24.53. Spectral data matches the literature report.[5]

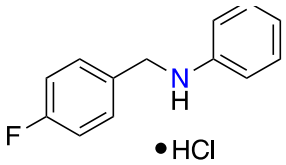
2,2-oxybis(4,4,5,5-tetramethyl-1,3,2-dioxoboralane: ^{1}H NMR (400 MHz; $CDCl_3$): ^{13}C NMR (101 MHz, $CDCl_3$): δ = 82.05, 24.53.[6] The methyl peaks of $O(Bpin)_2$ in ^{1}H NMR are overlapping in the region 1.24-1.18 ppm.

11. ^{1}H, ^{13}C NMR spectra of isolated products as ammonium salt



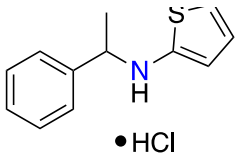
***N*-Benzylanilinium chloride (5b)** (85 %, white solid)

^{1}H NMR (400 MHz, D_2O): δ = 4.40 (s, 2H), 7.10 (m, 4H), 7.2 (m, 3H), 7.29 (m, 3H). ^{13}C NMR (101 MHz, D_2O): δ = 133.87, 130.34, 130.17, 129.91, 129.86, 129.76, 129.06, 122.92, 55.55.[10]



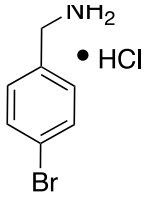
***N*-(4-fluorobenzyl) anilinium chloride (5c)** (65 %, white solid)

^{1}H NMR (400 MHz, D_2O): δ = 4.46 (s, 2H), 6.97 (t, 2H, *J* = 8 Hz), 7.15 (m, 4H), 7.37 (m, 3H). ^{13}C NMR (101 MHz, D_2O): δ = 164.68, 162.06, 133.70, 132.56, 130.22, 129.94, 125.89, 123.01, 116.02, 115.80, 54.80. GC-MS (M-HCl)= 201.10. HRMS [M-Cl] (calculated): 202.1032 HRMS [M-Cl] (found): 202.1030



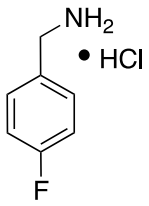
***N*-(1-phenylethyl)thiophen-2-aminium chloride (5d)** (75 %, white solid)

^{1}H NMR (400 MHz, D_2O): δ = 1.69 (d, 3H, *J* = 8 Hz), 4.98 (q, 1H, *J* = 4 Hz), 6.84 (m, 1H), 7.07 (m, 1H), 7.25 (m, 2H), 7.37 (m, 4H). ^{13}C NMR (101 MHz, D_2O): δ = 137.01, 132.89, 130.14, 130.04, 129.72, 129.26, 127.84, 127.42, 123.47, 122.91, 58.39, 18.67. GC-MS (M-HCl)= 203.05. HRMS [M-Cl] (calculated): 204.0848 HRMS [M-Cl] (found): 204.0844



(4-bromophenyl)methanaminium chloride (5e) (77 %, white solid)

^{1}H NMR (400 MHz, D_2O): δ = 3.98 (s, 2H), 7.18 (d, 2H, *J* = 8 Hz), 7.46 (d, 2H, *J* = 8 Hz). ^{13}C NMR (101 MHz, D_2O): δ = 132.01, 131.51, 130.53, 122.60, 42.32.[11]



(4-fluorophenyl)methanaminium chloride (5f) (84 %, white solid)

^{1}H NMR (400 MHz, D_2O): δ = 3.99 (s, 2H), 7.01 (t, 2H, *J* = 8 Hz), 7.28 (m, 2H). ^{13}C NMR (101 MHz, D_2O): δ = 164.10, 161.65, 131.13, 131.04, 128.54, 116.09, 115.87, 42.44.[12]

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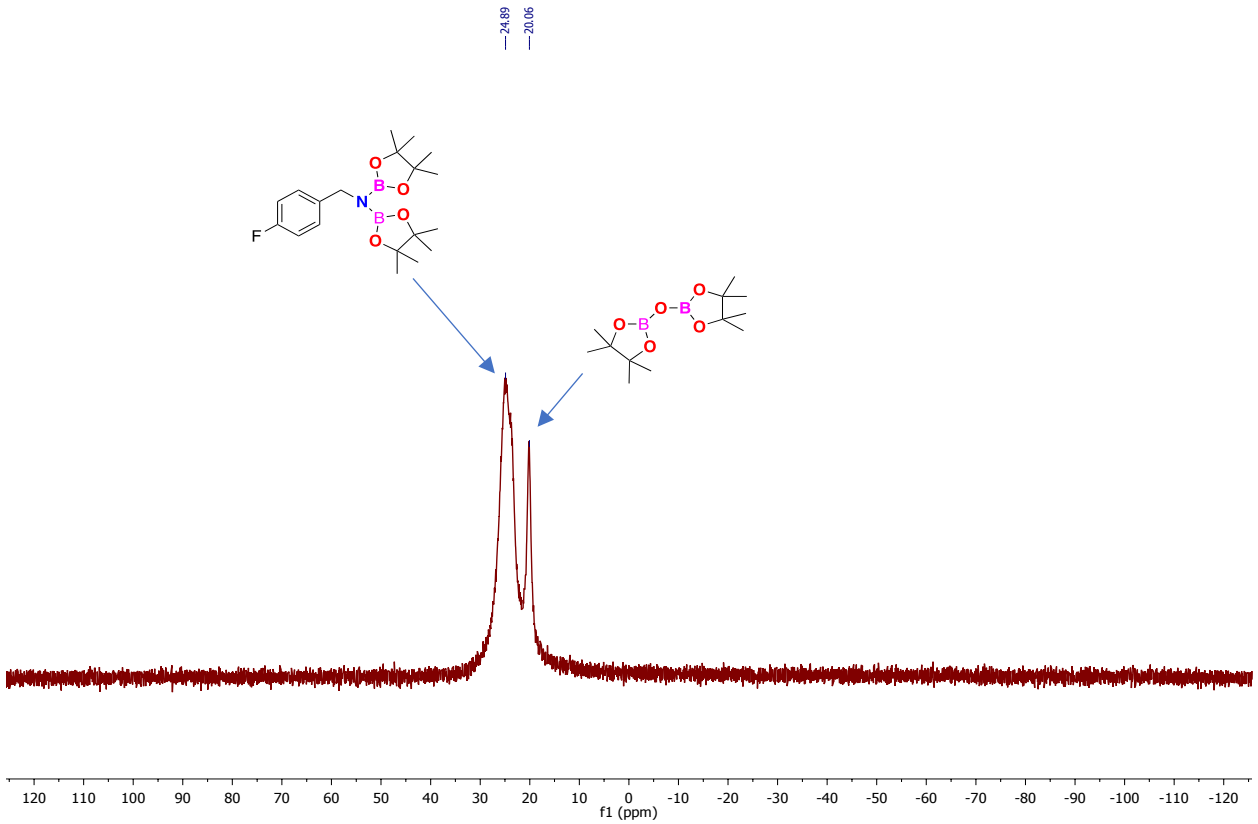

Figure S14. Typical ^{11}B NMR spectra recorded after catalytic hydroboration of a nitrile to diboryl amine.

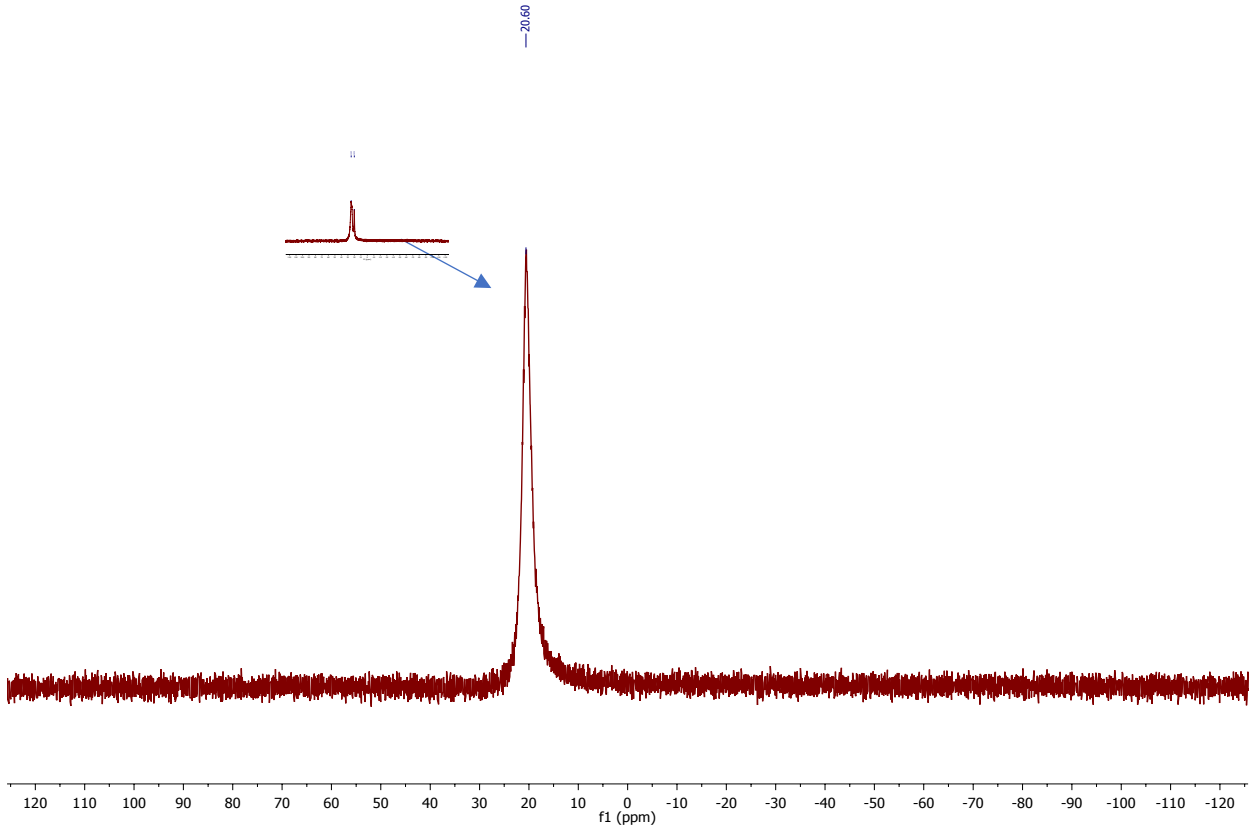

Figure S15. Typical ^{11}B NMR spectra recorded after catalytic hydroboration of an imine to amine after hydrolysis.

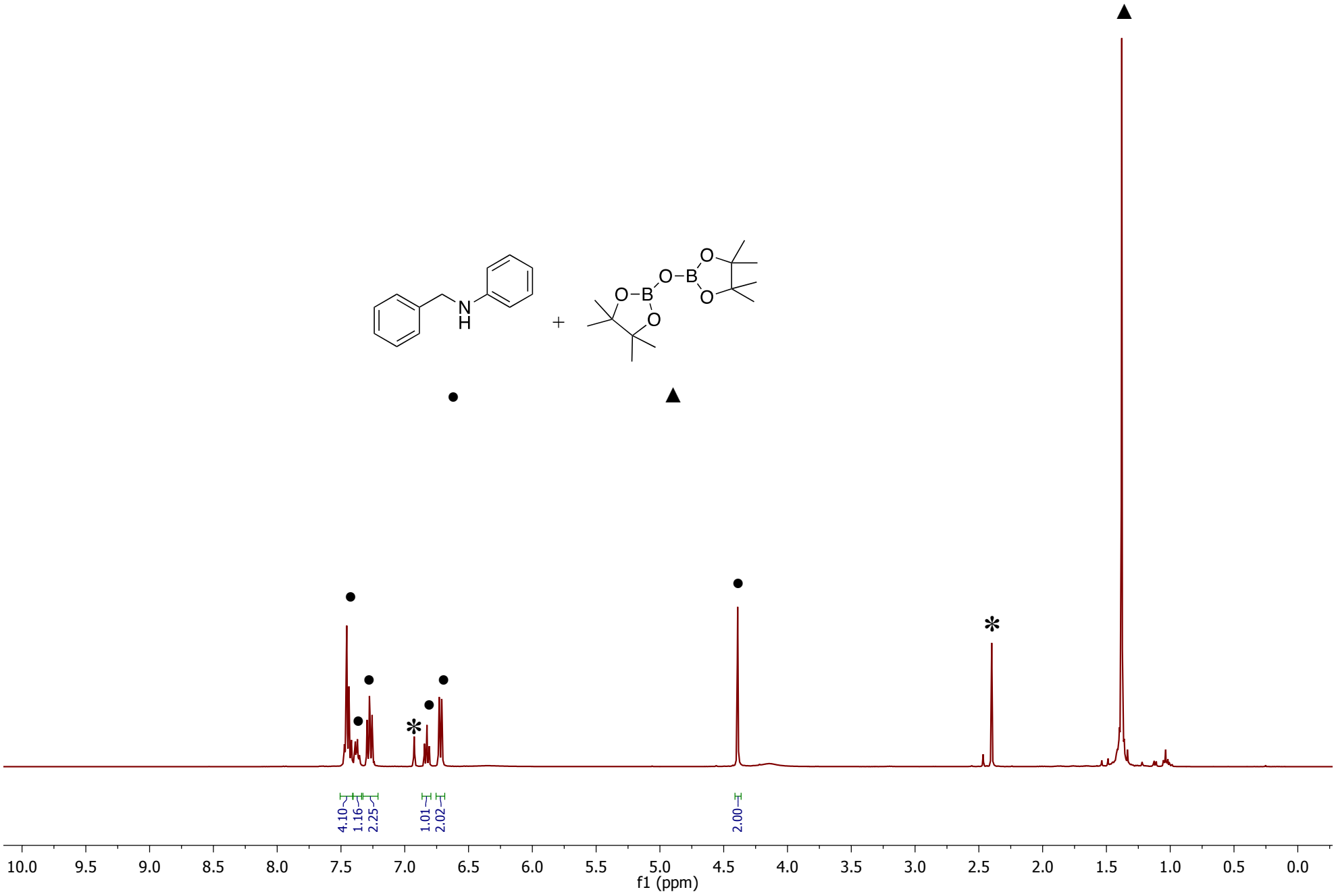

Figure S16 : ^{1}H NMR of *N*-benzylaniline: (ꕥ) and 2,2-oxybis(4,4,5,5-tetramethyl-1,3,2-dioxoboralane): (①)

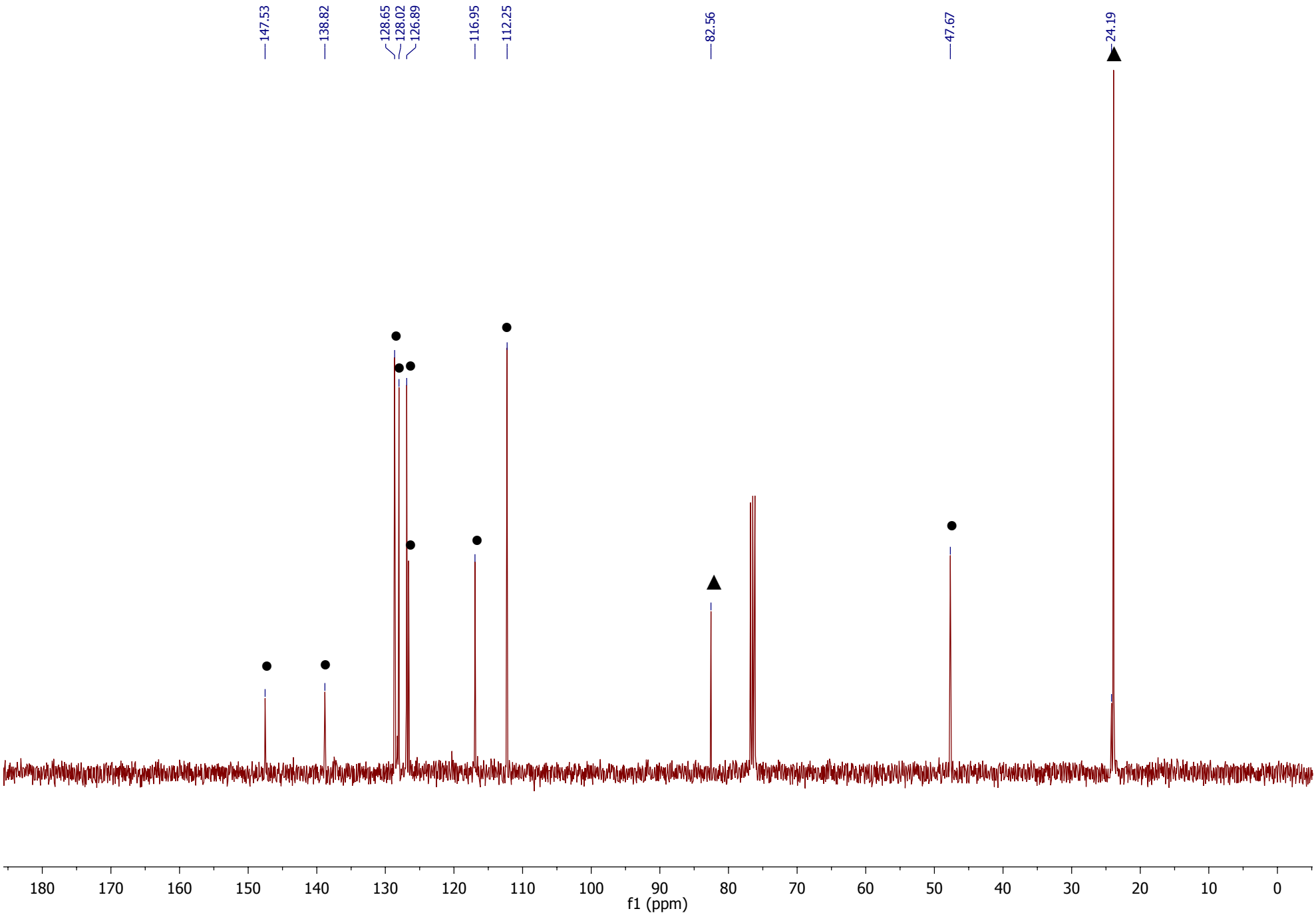

Figure S17 : ^{13}C NMR of *N*-benzylaniline: (ꙮ) and 2,2-oxybis(4,4,5,5-tetramethyl-1,3,2-dioxoboralane): (①)

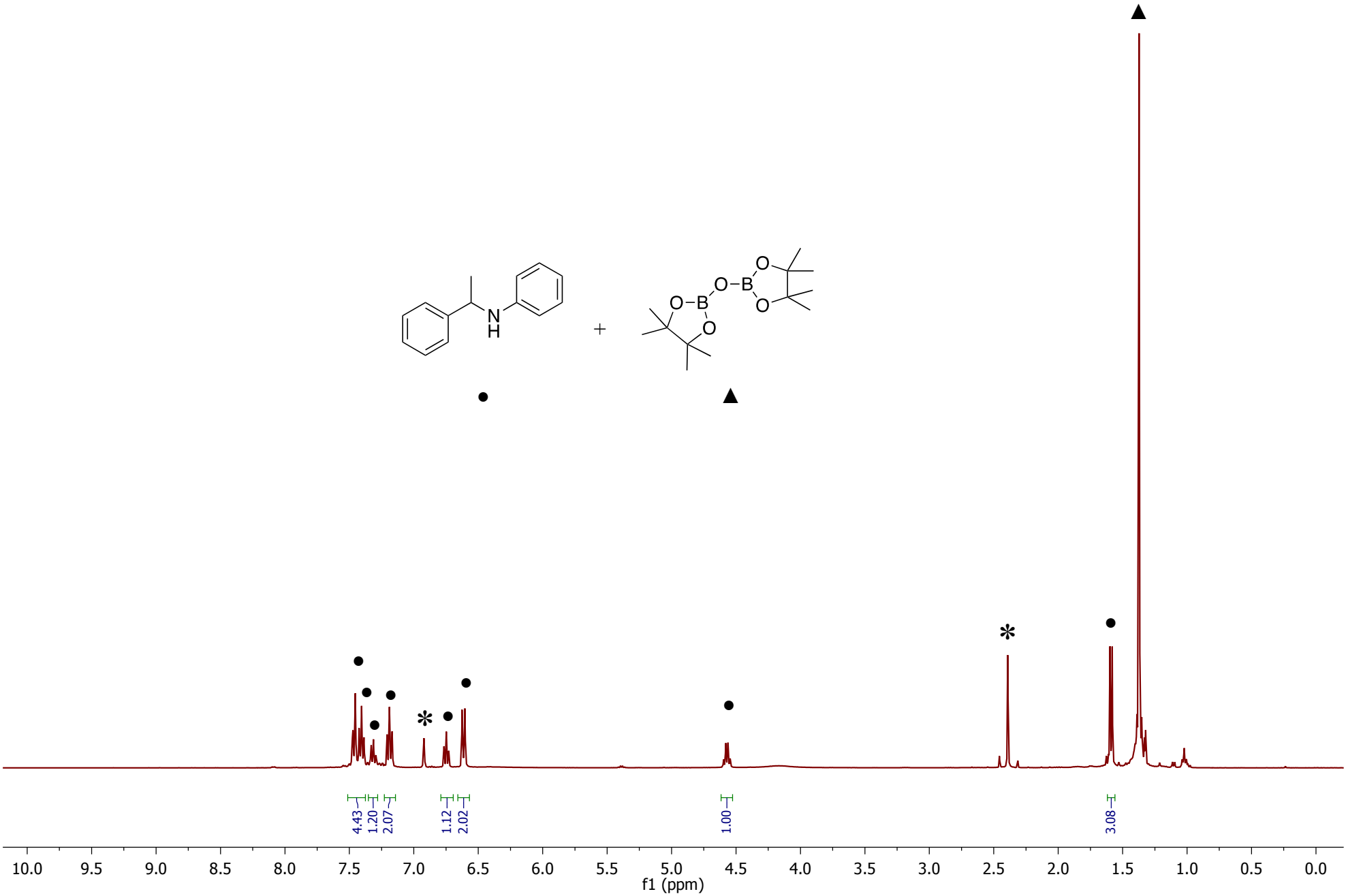

Figure S18 : ^{1}H NMR of *N*-(1-phenylethyl)aniline: (ꝏ) and 2,2-oxybis(4,4,5,5-tetramethyl-1,3,2-dioxoboralane): (①)

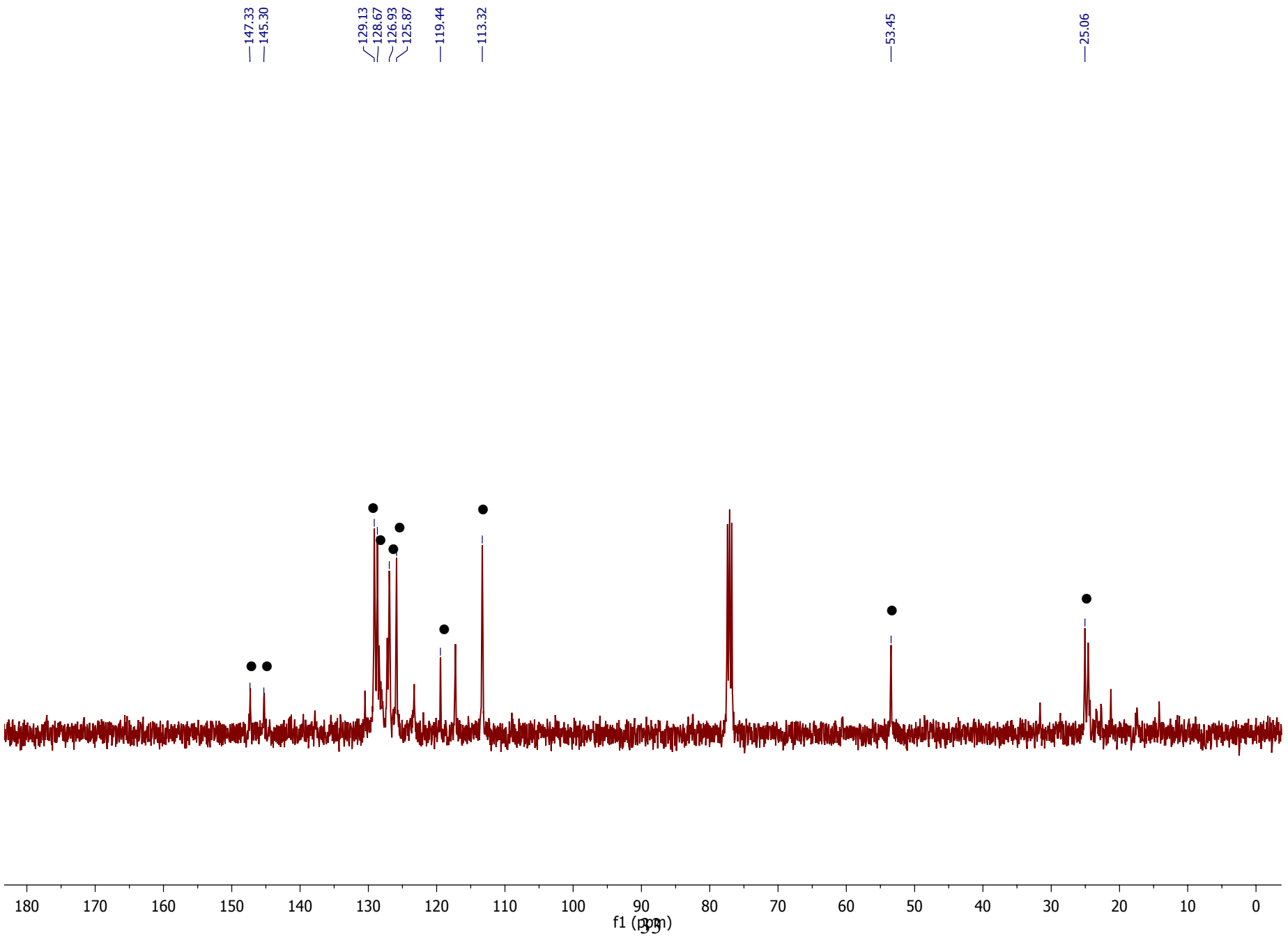

Figure S19 : ^{13}C NMR of *N*-(1-phenylethyl)aniline: (ಐ)

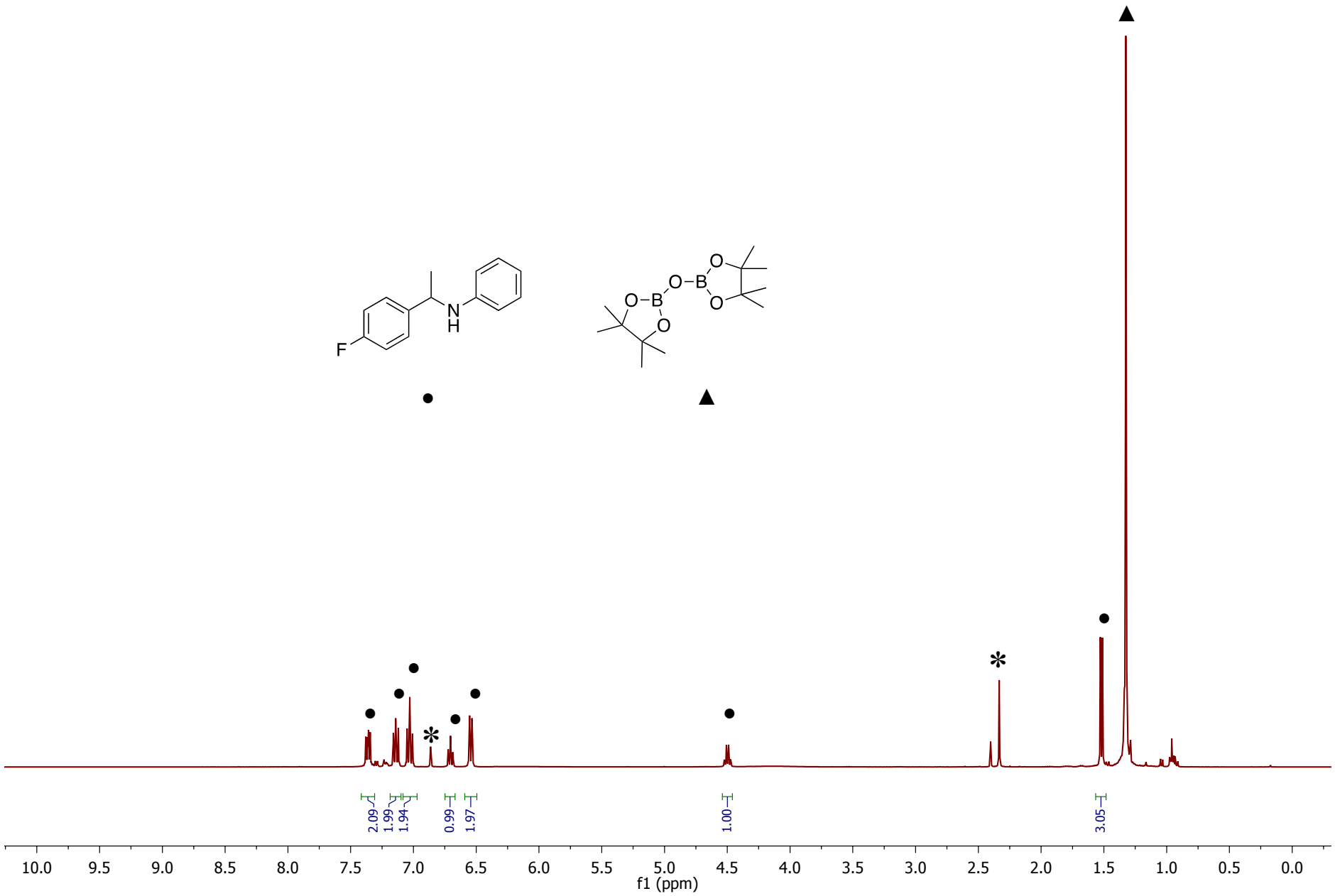

Figure S20 : ^{1}H NMR of *N*-(1-(4-fluorophenyl)ethyl)aniline: (ᴓ) and 2,2-oxybis(4,4,5,5-tetramethyl-1,3,2-dioxoboralane): (①)

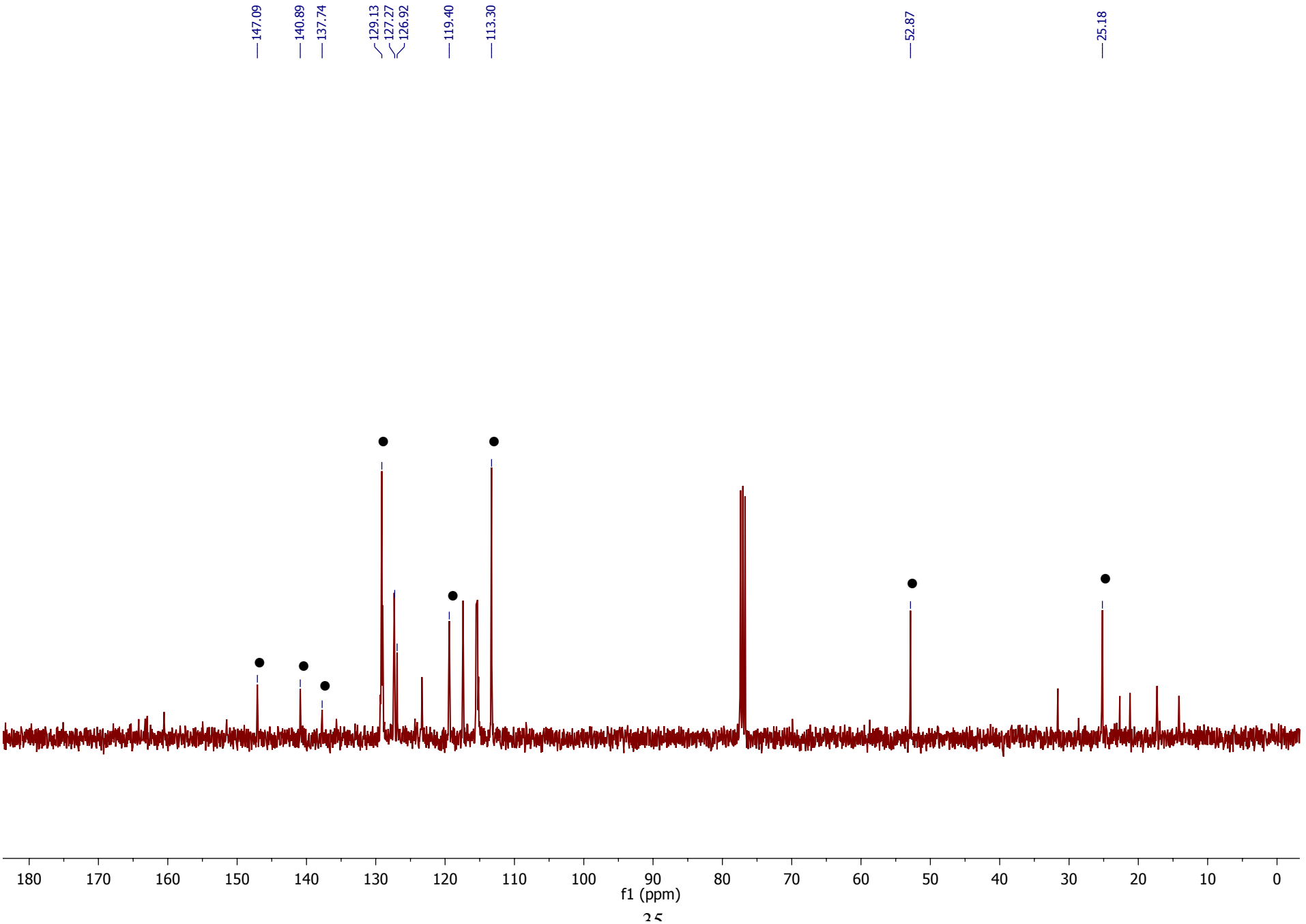

Figure S21 : ^{13} C NMR of *N*-(1-(4-fluorophenyl)ethyl)aniline: (ꭤ)

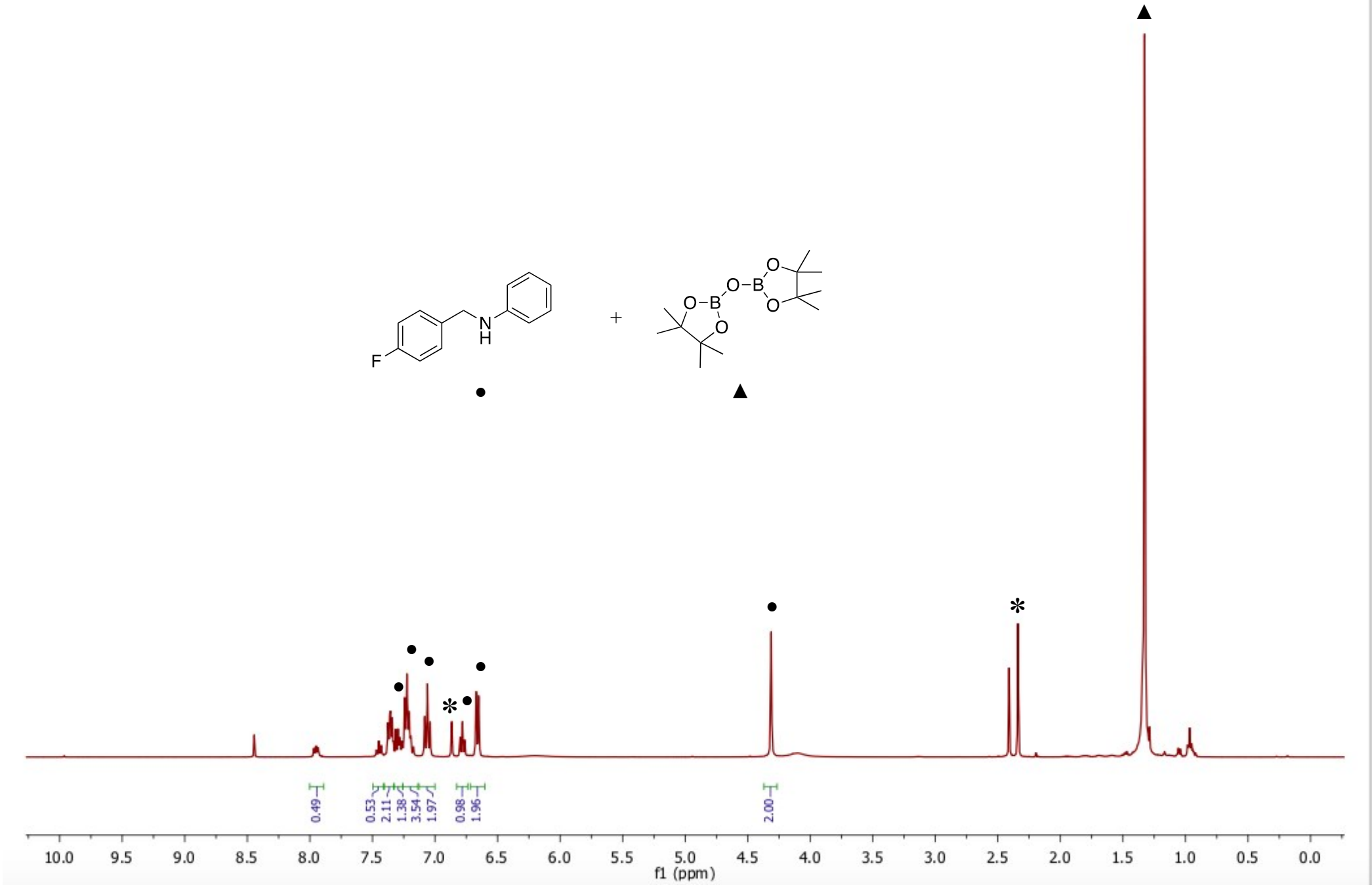

Figure S22 : ^{1}H NMR of *N*-(4-fluorobenzyl)aniline: (ꝏ) and 2,2-oxybis(4,4,5,5-tetramethyl-1,3,2-dioxoboralane): (①)

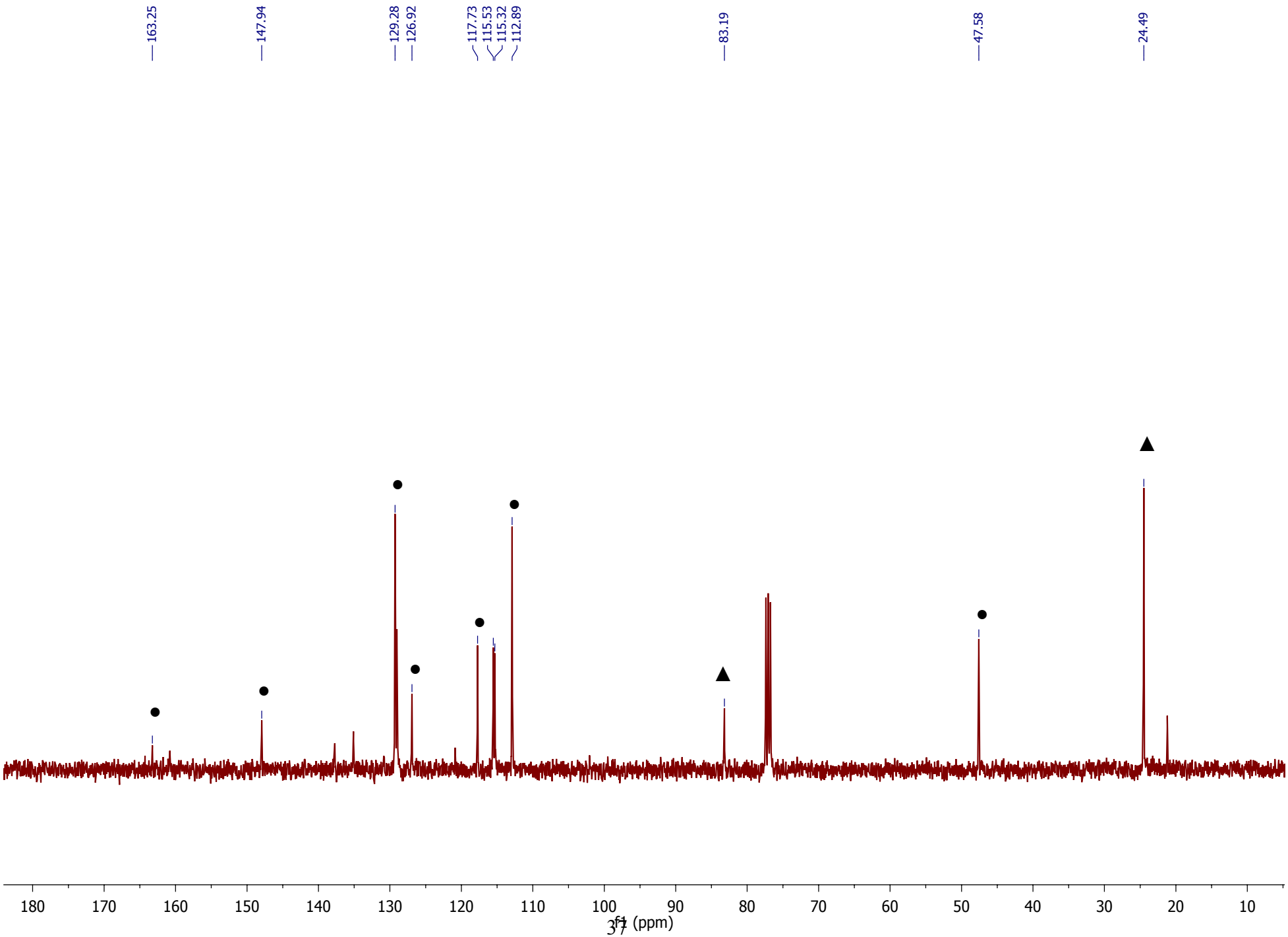

Figure S23 : ^{13}C NMR of *N*-(4-fluorobenzyl)aniline: (ꙮ) and 2,2-oxybis(4,4,5,5-tetramethyl-1,3,2-dioxoboralane): (①)

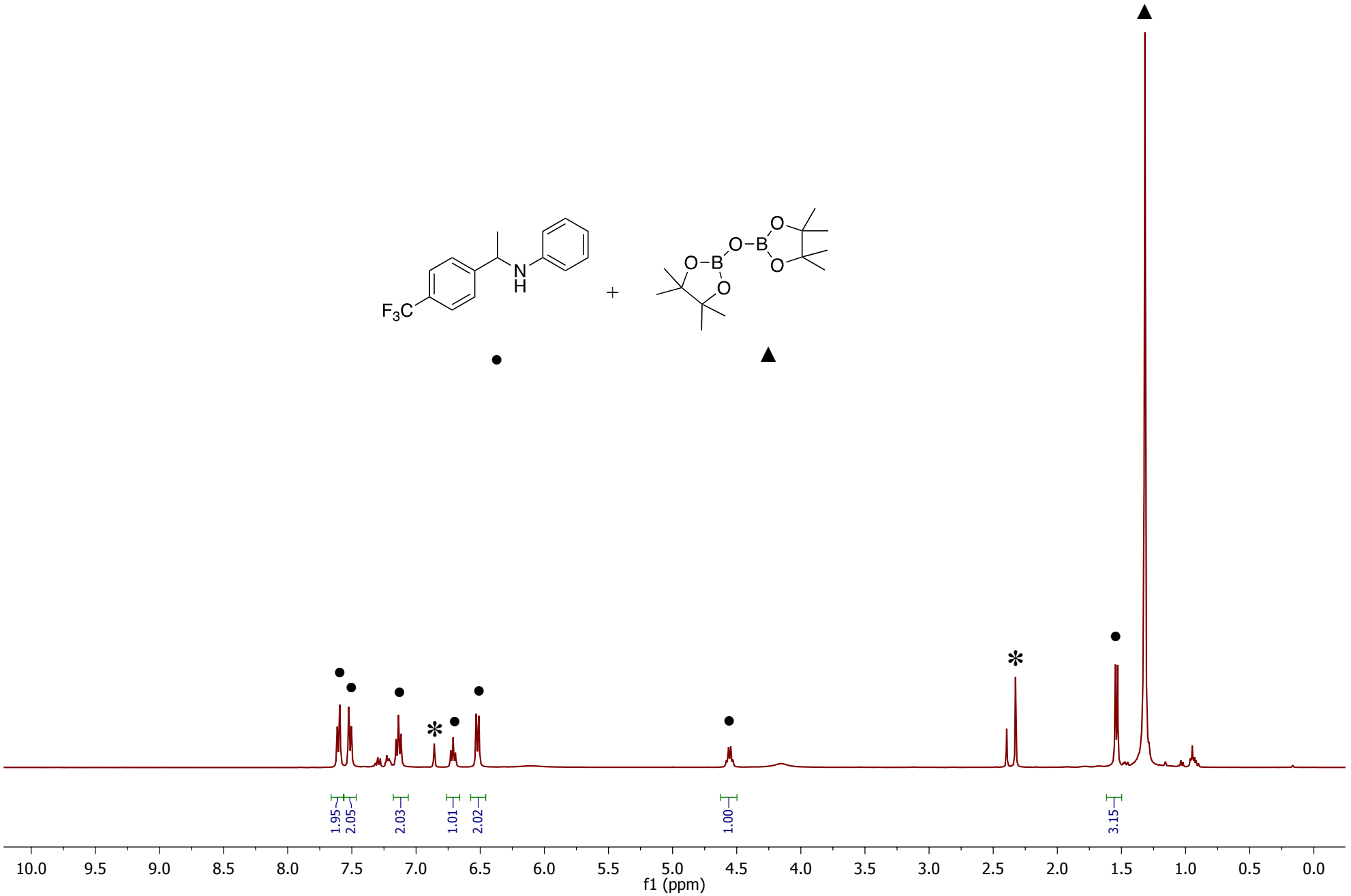

Figure S24 : ^{1}H NMR of *N*-(1-(4-trifuoromethyl)phenyl)ethylaniline: (ᔓ) and 2,2-oxybis(4,4,5,5-tetramethyl-1,3,2-dioxoboralane): (①)

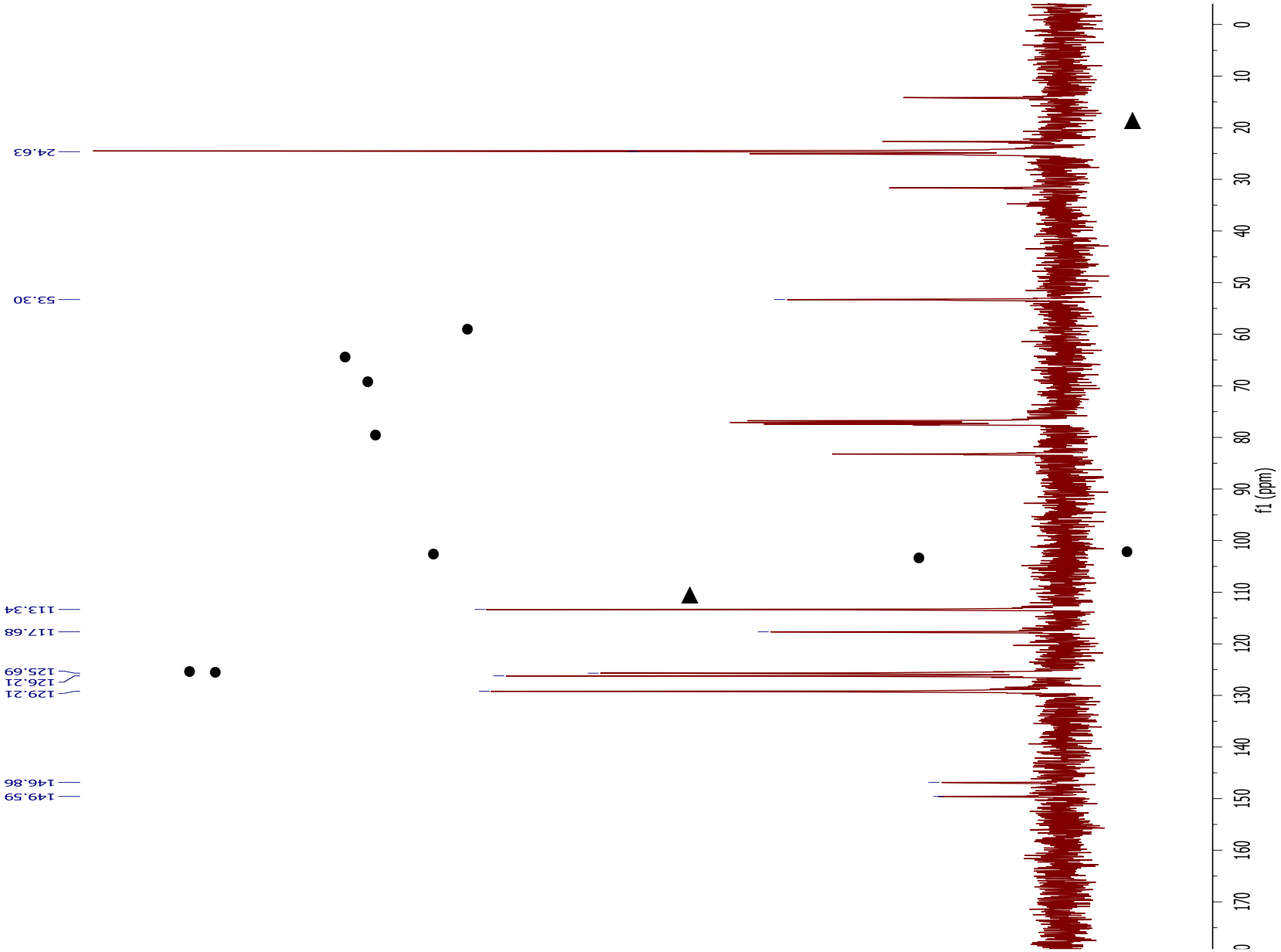

Figure S25 : ^{13}C NMR of *N*-(1-(4-trifuoromethyl)phenyl)ethylaniline: (ᘐ) and 2,2-oxybis(4,4,5,5-tetramethyl-1,3,2-dioxoboralane): (①)

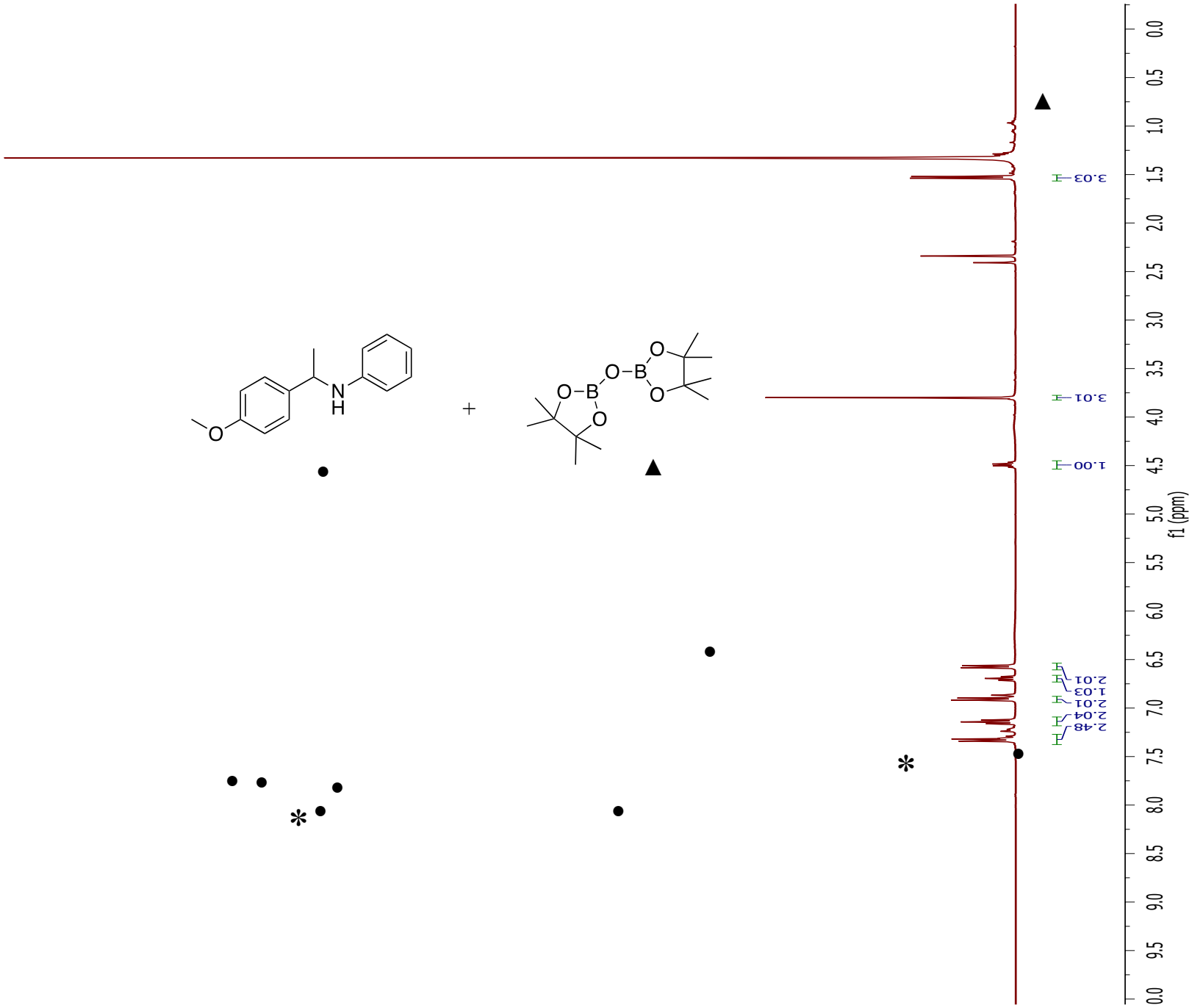

Figure S26 : ^{1}H NMR of *N*-(1-(4-methoxyphenyl)phenyl)ethylaniline: (ᔓ) and 2,2-oxybis(4,4,5,5-tetramethyl-1,3,2-dioxoboralane): (①)

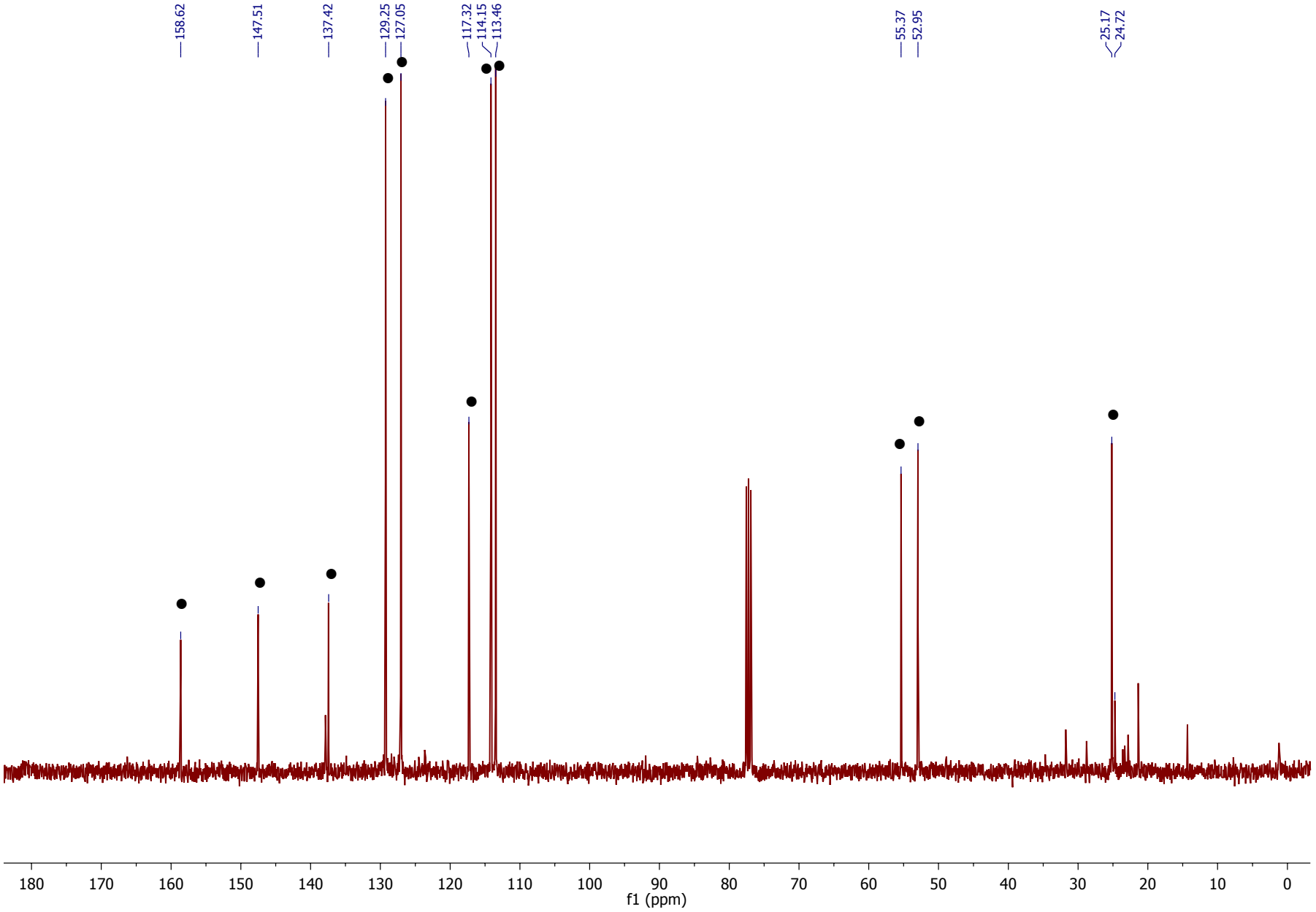

Figure S27 : ^{13}C NMR of *N*-(1-(4-methoxyphenyl)phenyl)ethylaniline: (ꝏ)

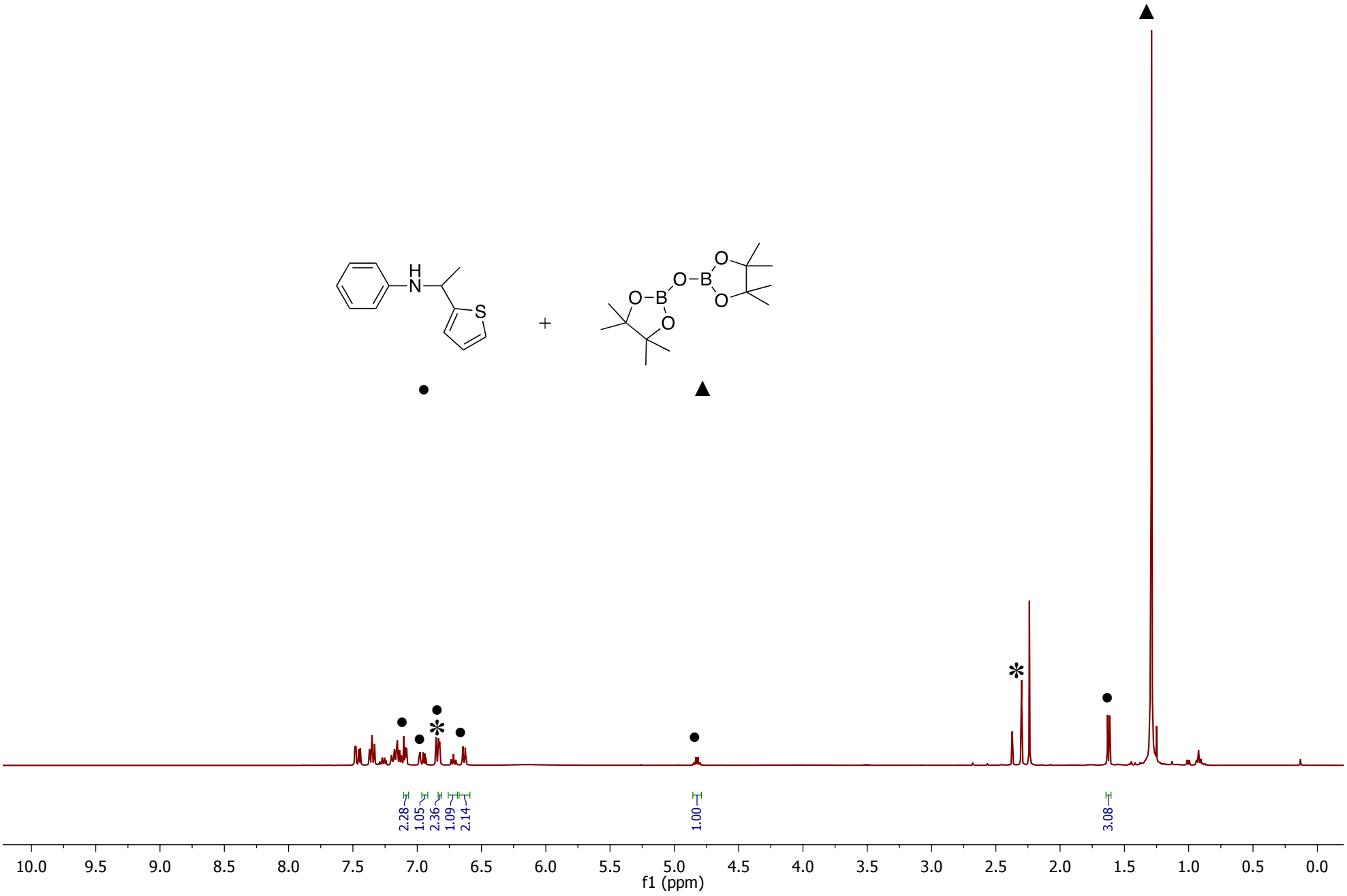

Figure S28 : ^{1}H NMR of *N*-(1-(thiophen-2-yl)ethyl)aniline: (ᘐ) and 2,2-oxybis(4,4,5,5-tetramethyl-1,3,2-dioxoboralane): (①)

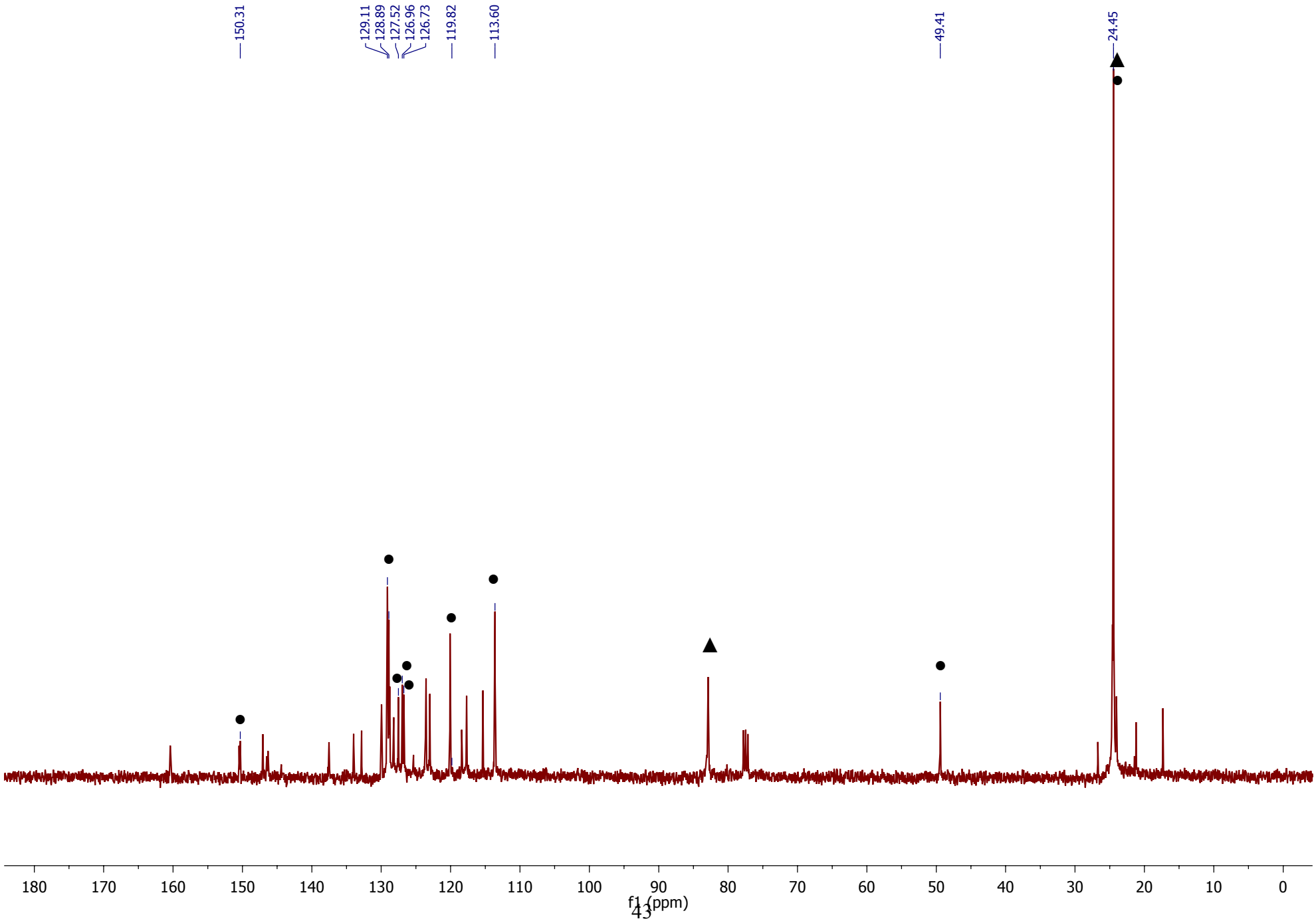

Figure S29 : ^{13}C NMR of *N*-(1-(thiophen-2-yl)ethyl)aniline: (ꝏ) and 2,2-oxybis(4,4,5,5-tetramethyl-1,3,2-dioxoboralane): (①)

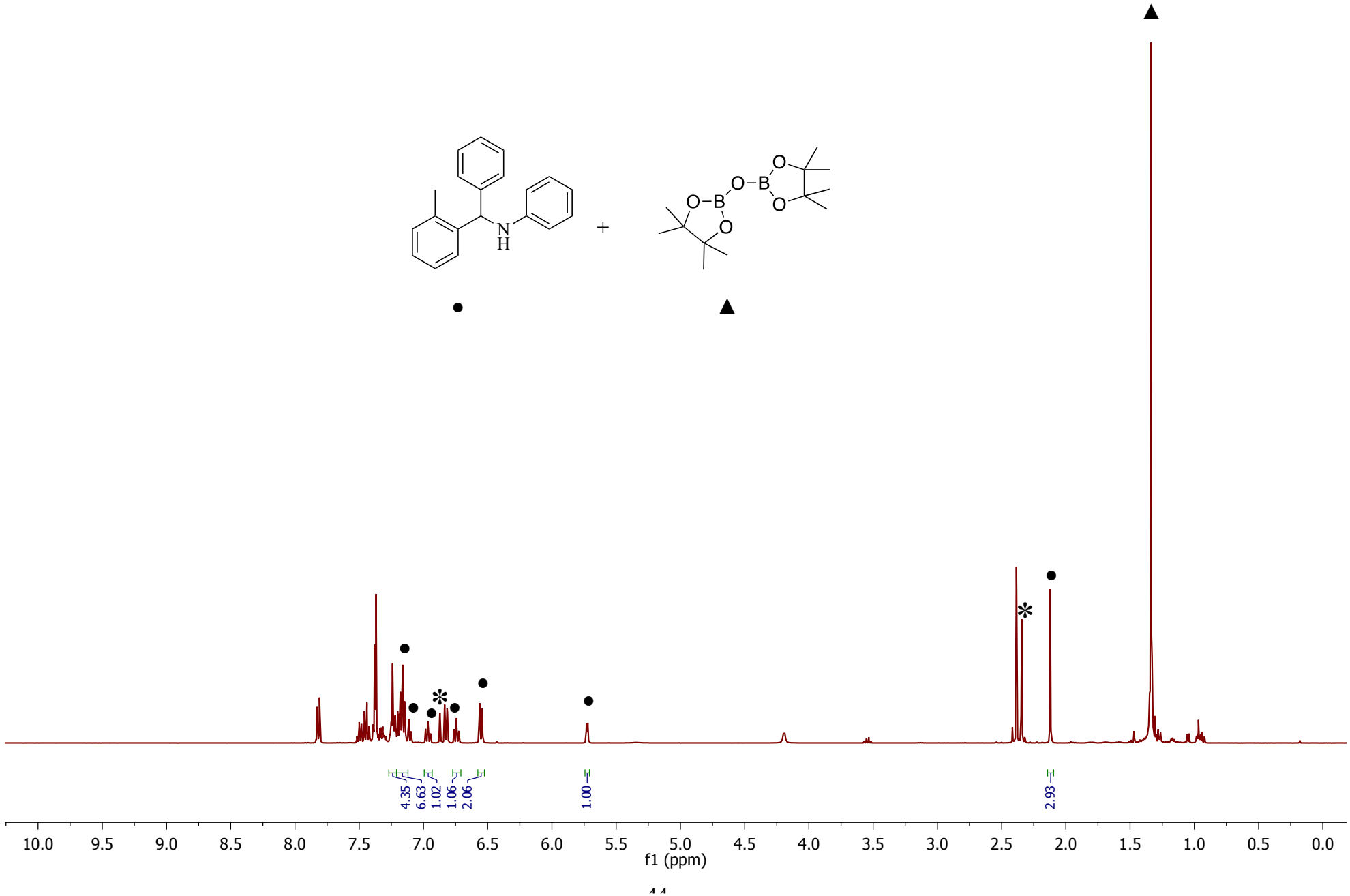

Figure S30 : ^{1}H NMR of *N*-(phenyl(o-toly1)methyl)aniline: (ᔓ) and 2,2-oxybis(4,4,5,5-tetramethyl-1,3,2-dioxoboralane): (①)

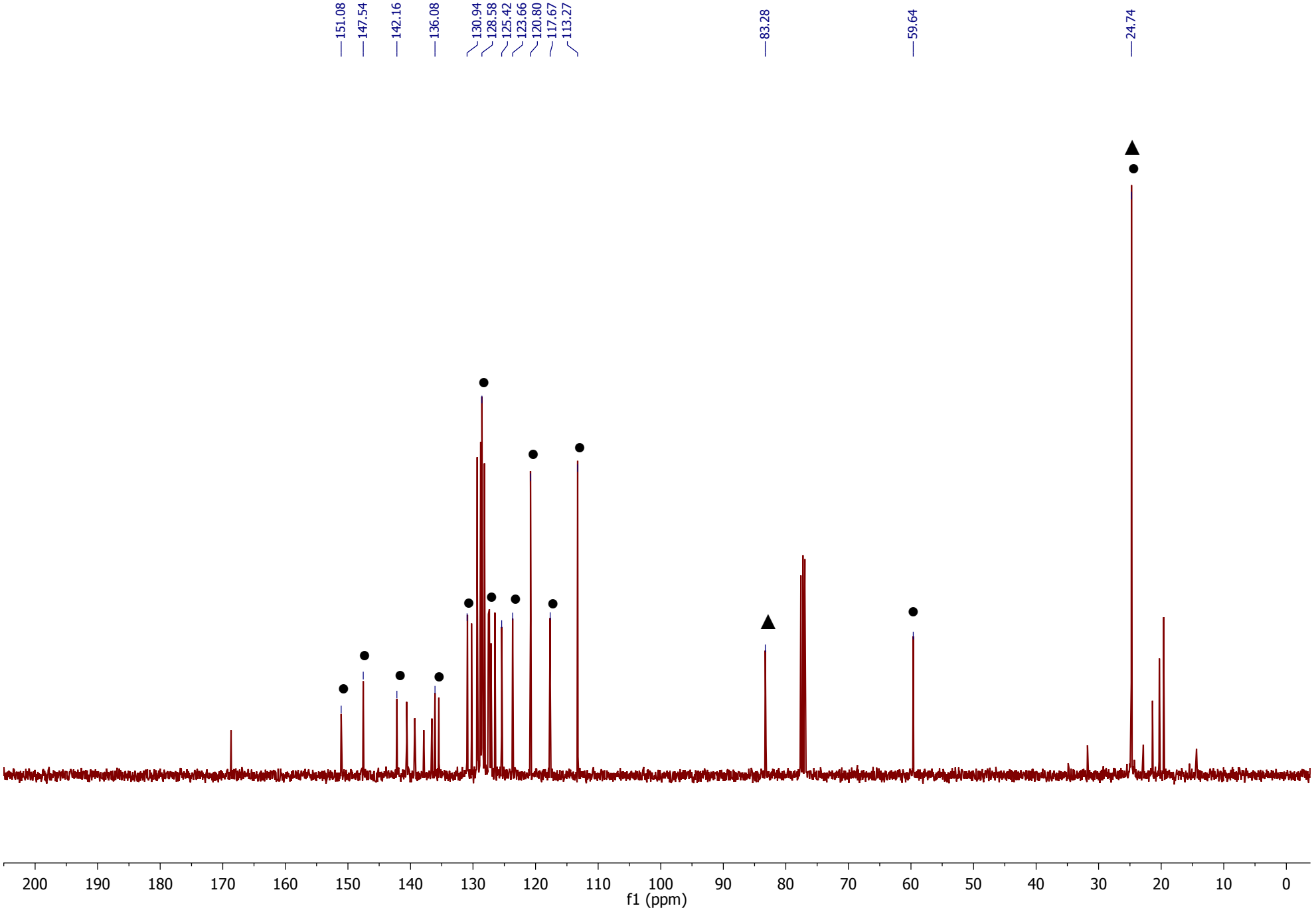

Figure S31 : ^{13}C NMR of *N*-(phenyl(o-toly1)methyl)aniline: (ꙮ) and 2,2-oxybis(4,4,5,5-tetramethyl-1,3,2-dioxoboralane): (①)

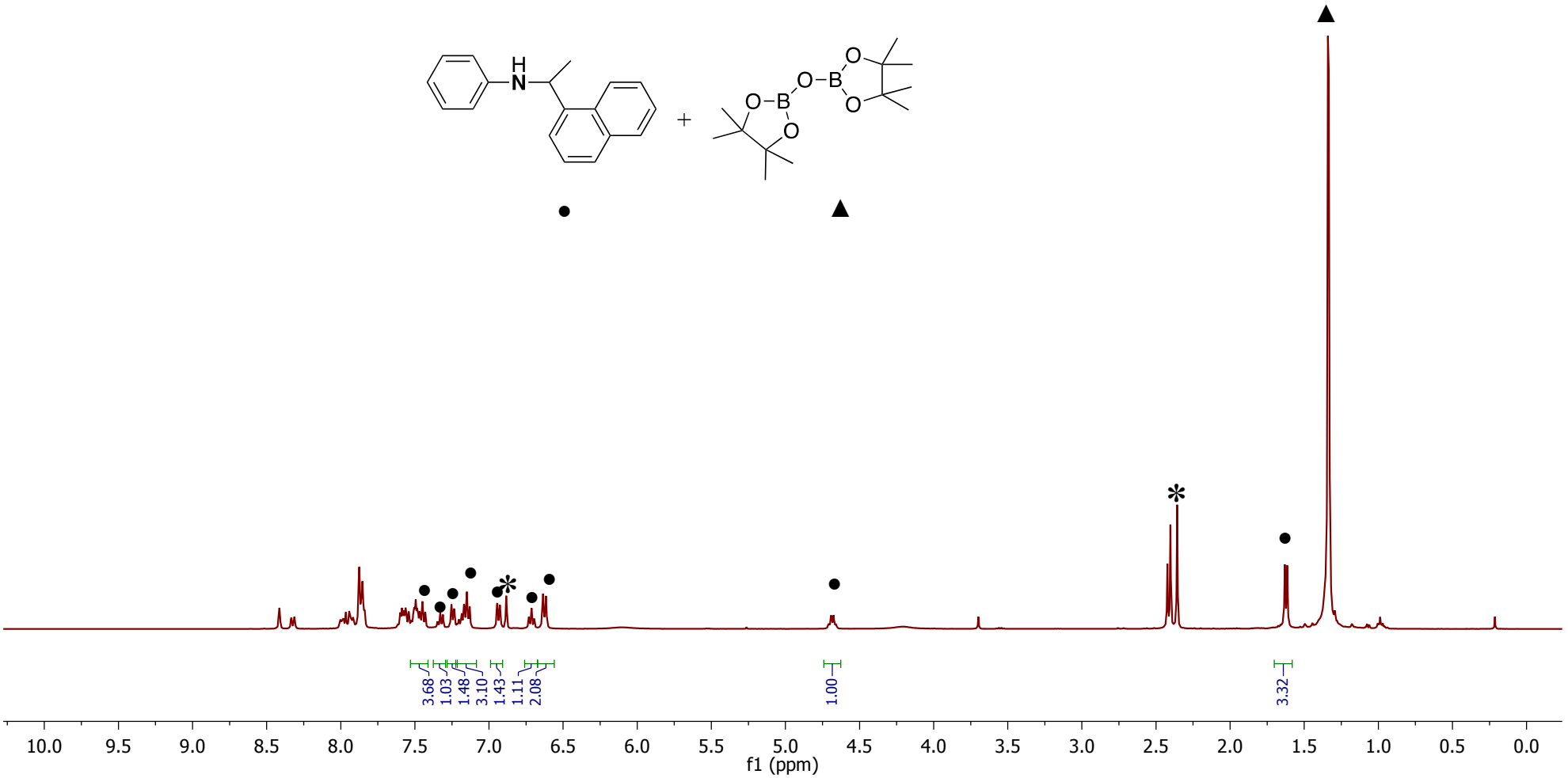

Figure S32 : ^{1}H NMR of *N*-(1-(naphthalen-1-yl)ethyl)aniline: (ᔓ) and 2,2-oxybis(4,4,5,5-tetramethyl-1,3,2-dioxoboralane): (①)

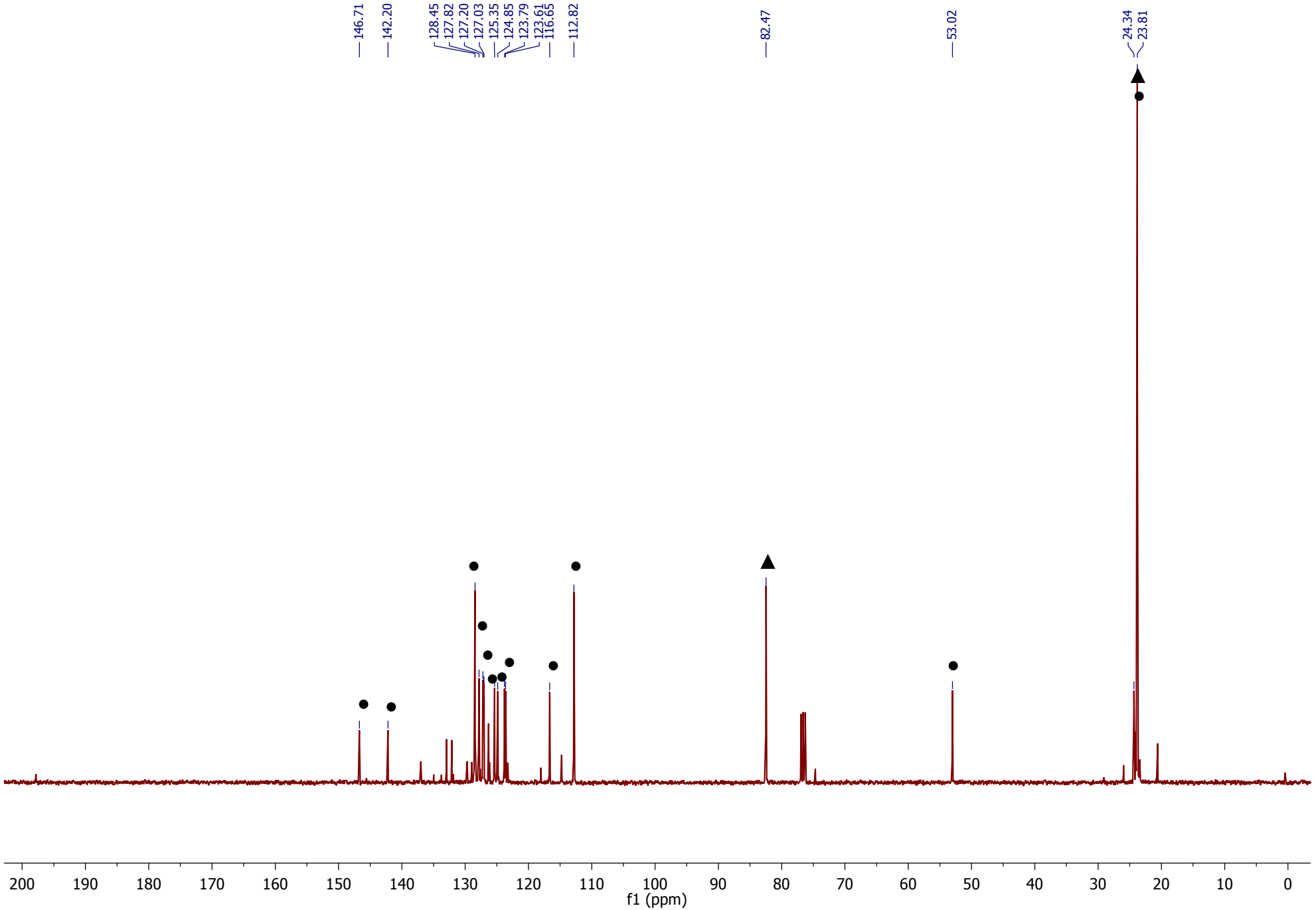

Figure S33 : ^{13}C NMR of *N*-(1-(naphthalen-1-yl)ethyl)aniline: (ꝏ) and 2,2-oxybis(4,4,5,5-tetramethyl-1,3,2-dioxoboralane): (①)

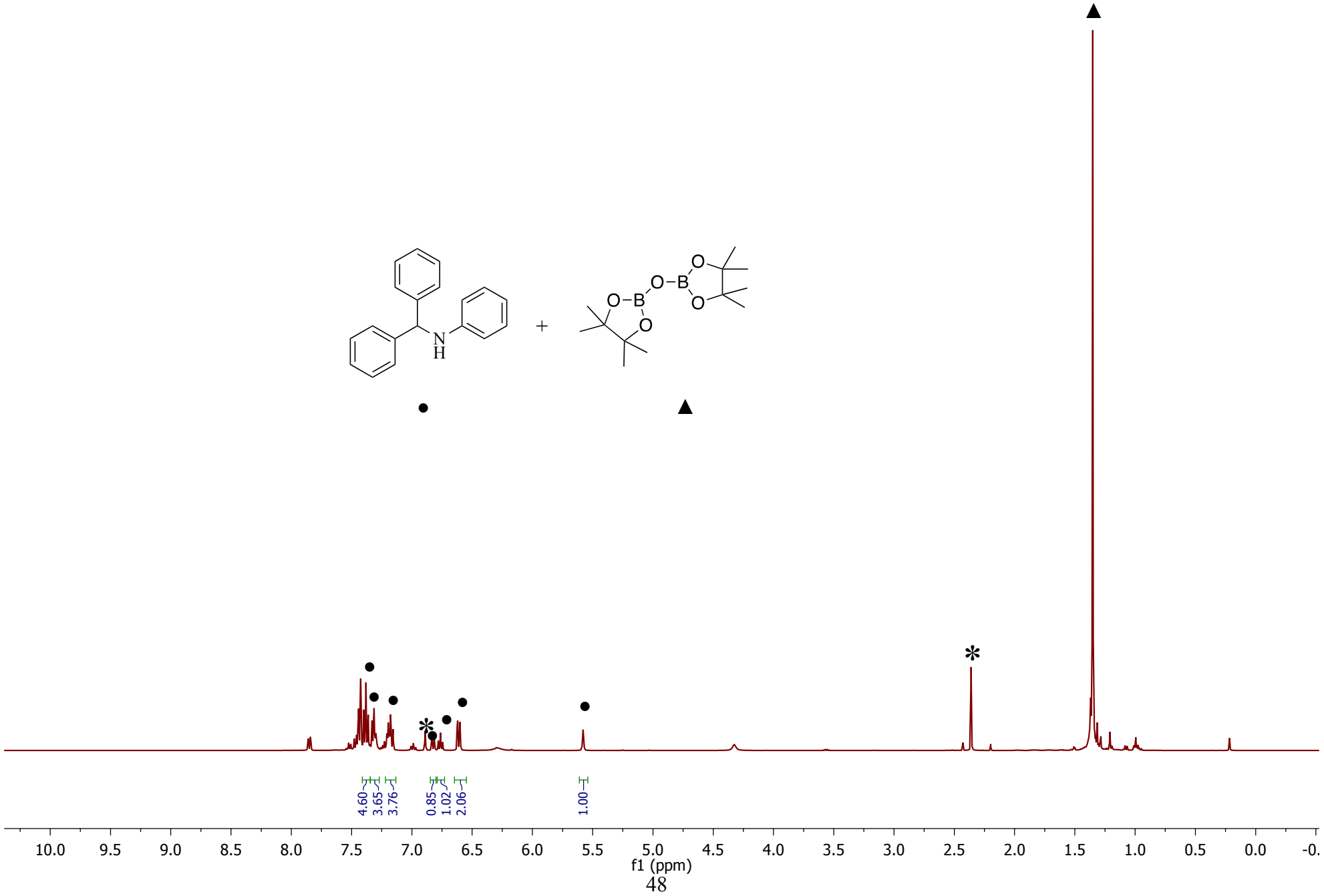

Figure S34 : ^{1}H NMR of *N*-(benzhyldryl)aniline: (ꙮ) and 2,2-oxybis(4,4,5,5-tetramethyl-1,3,2-dioxoboralane): (①)

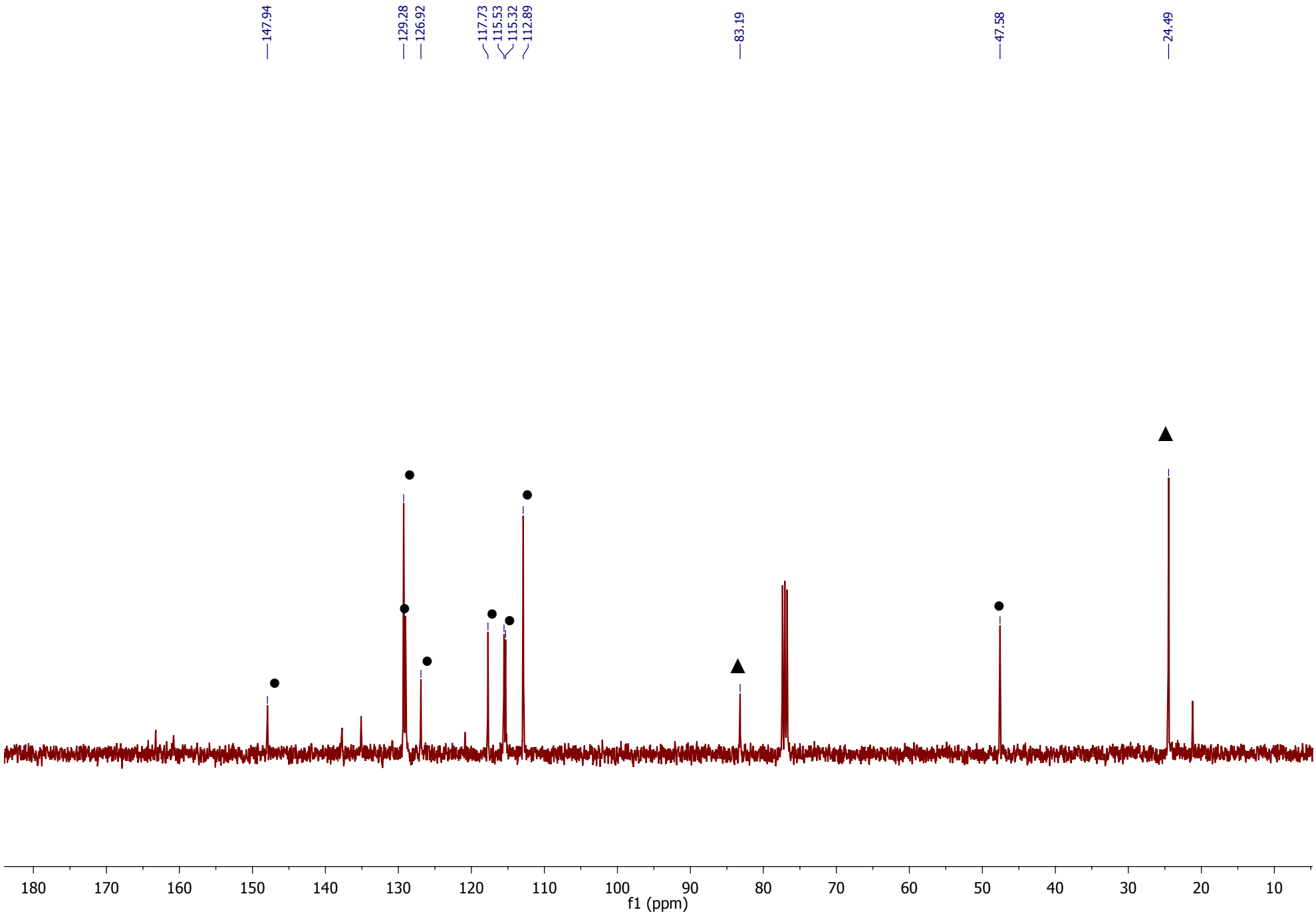

Figure S35 : ^{13}C NMR of *N*-(benzhyldryl)aniline: (ꕤ) and 2,2-oxybis(4,4,5,5-tetramethyl-1,3,2-dioxoboralane): (①)

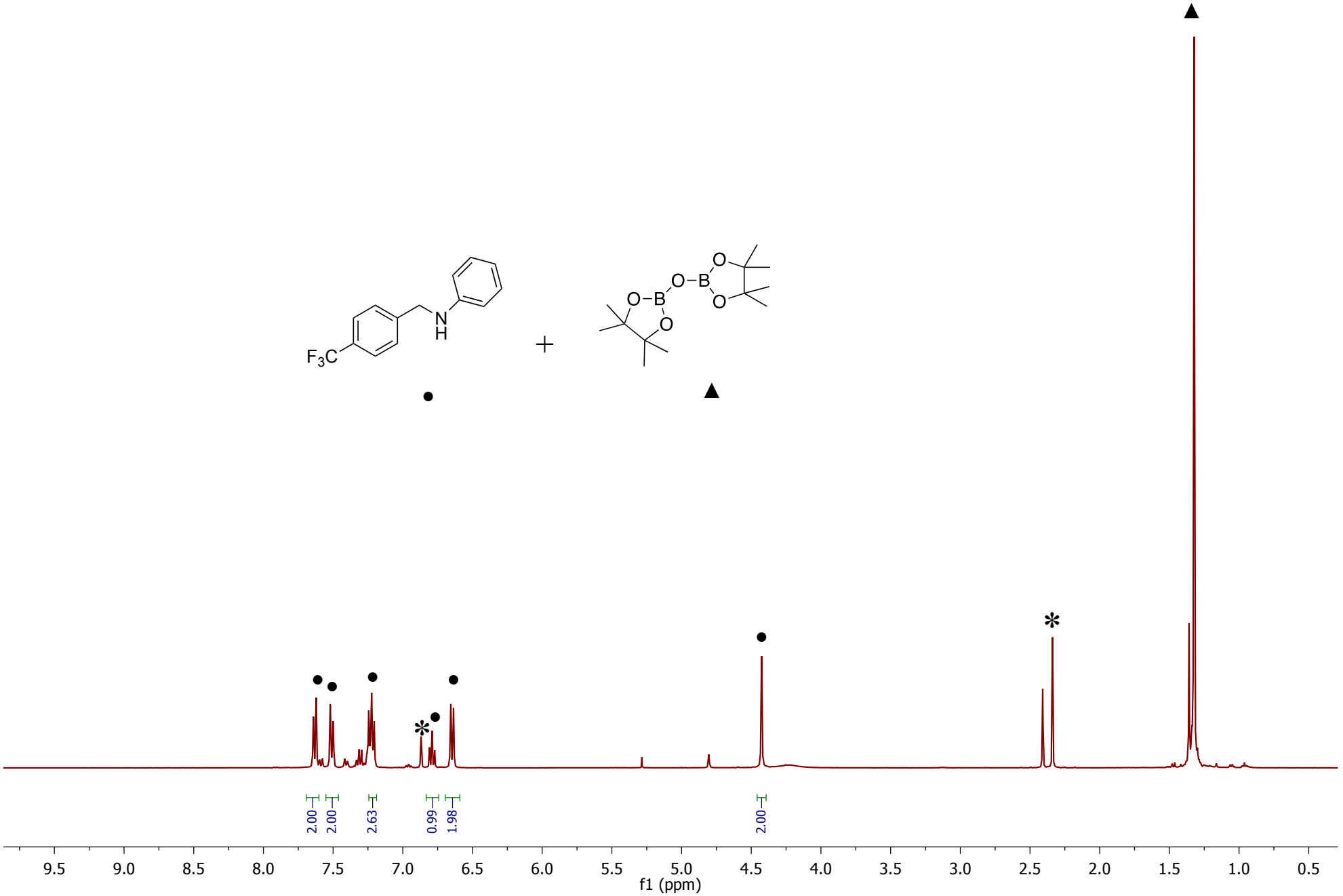

Figure S36 : ^{1}H NMR *N*-(4-(trifluoromethyl)benzyl)aniline: (ꕥ) and 2,2-oxybis(4,4,5,5-tetramethyl-1,3,2-dioxoboralane): (①)

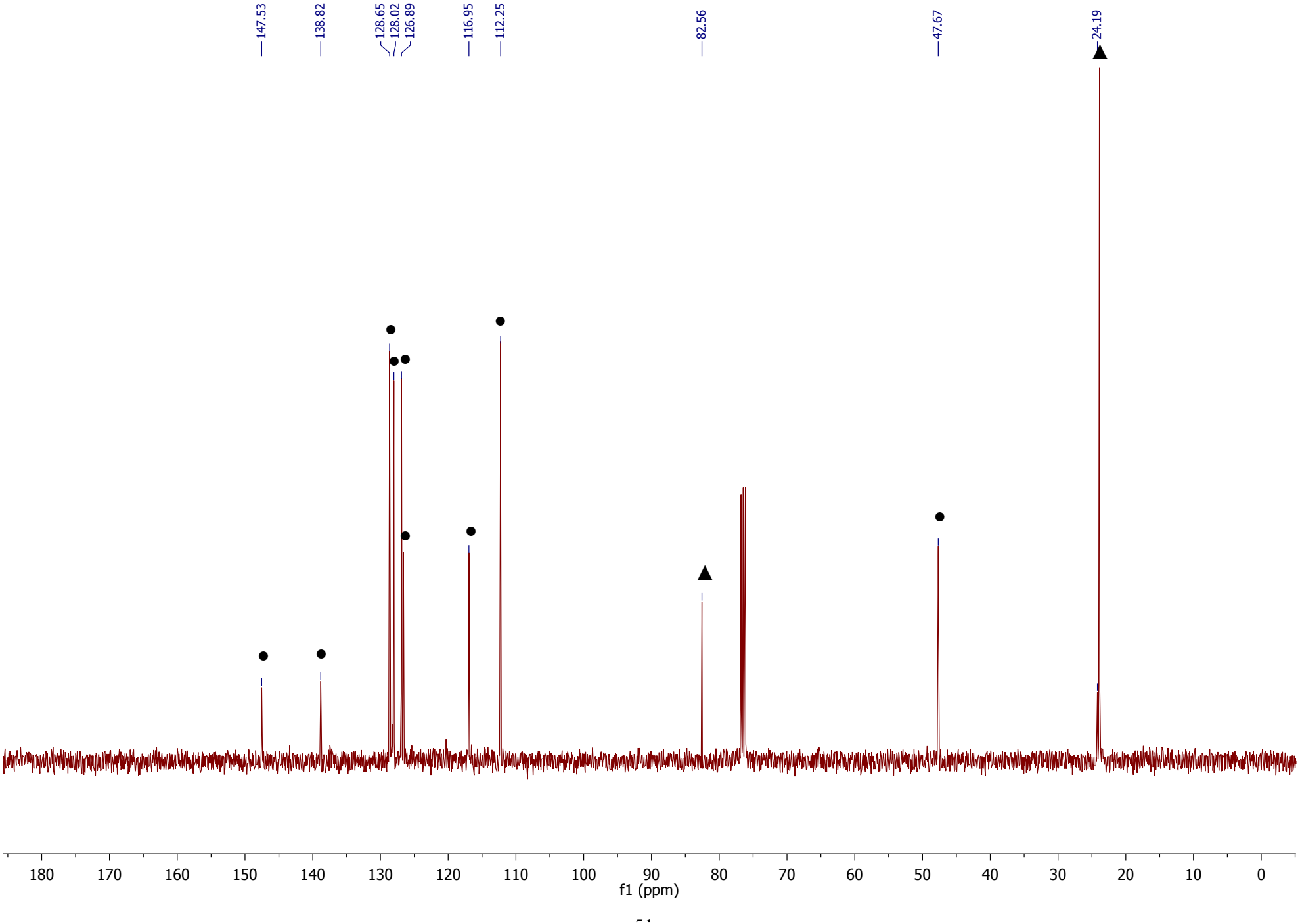

Figure S37 : ^{13}C NMR of *N*-(4-(trifluoromethyl)benzyl)aniline: (ᴓ) and 2,2-oxybis(4,4,5,5-tetramethyl-1,3,2-dioxoboralane): (①)

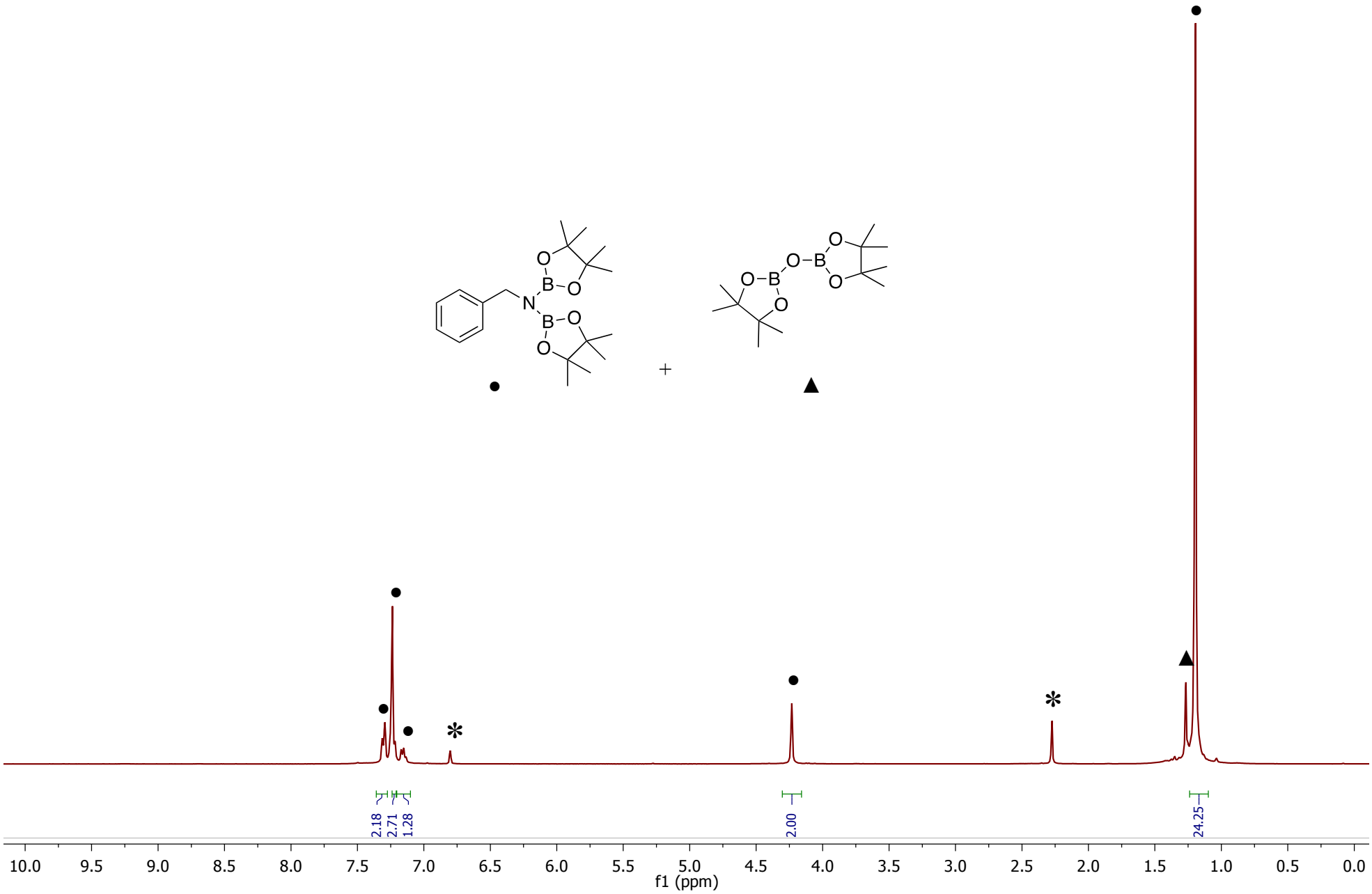

Figure S38 : ^{1}H NMR of *N*-benzyl-4,4,5,5-tetramethyl-*N*-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1,3,2-dioxaborolan-2-amine : (ꕥ) and 2,2-oxybis(4,4,5,5-tetramethyl-1,3,2-dioxoboralane): (①)

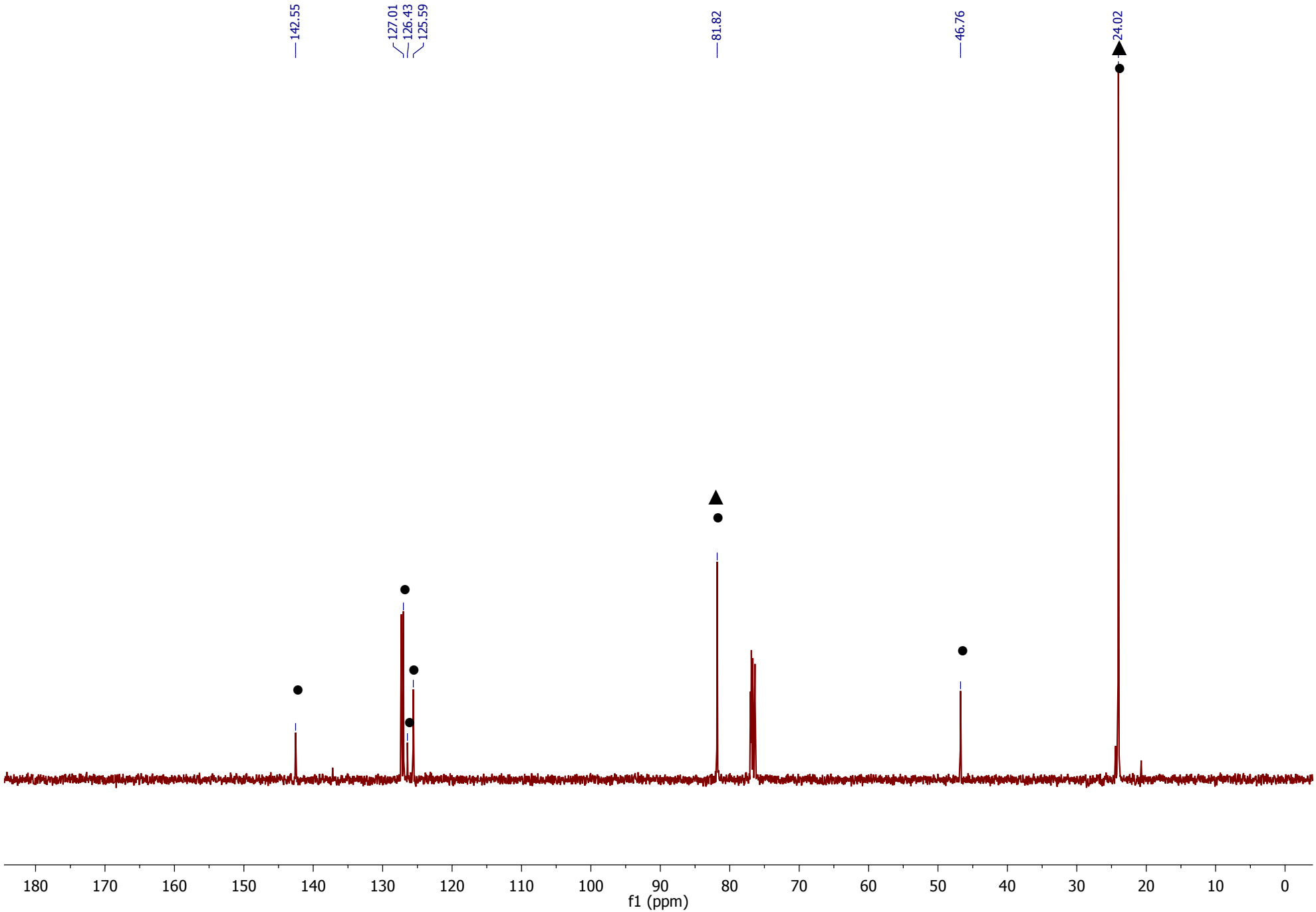

Figure S39 : ^{13}C NMR of *N*-benzyl-4,4,5,5-tetramethyl-*N*-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1,3,2-dioxaborolan-2-amine : (ꝏ) and 2,2-oxybis(4,4,5,5-tetramethyl-1,3,2-dioxoboralane): (①)

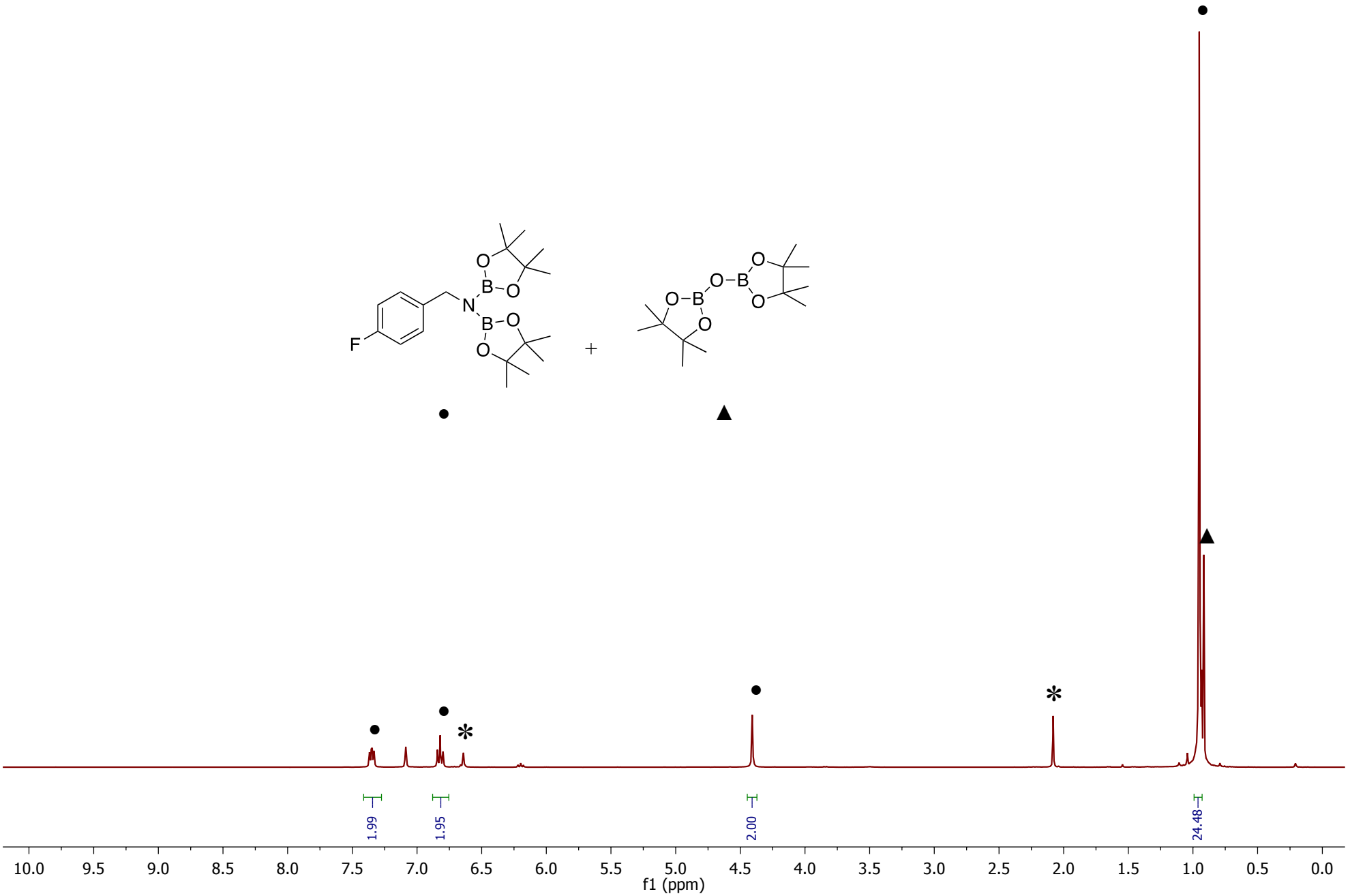

Figure S40 : ^{1}H NMR of *N-(*4-fluorobenzyl-4,4,5,5-tetramethyl-*N*-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1,3,2-dioxaborolan-2-amine : (ᴓ) and 2,2-oxybis(4,4,5,5-tetramethyl-1,3,2-dioxoboralane): (①)

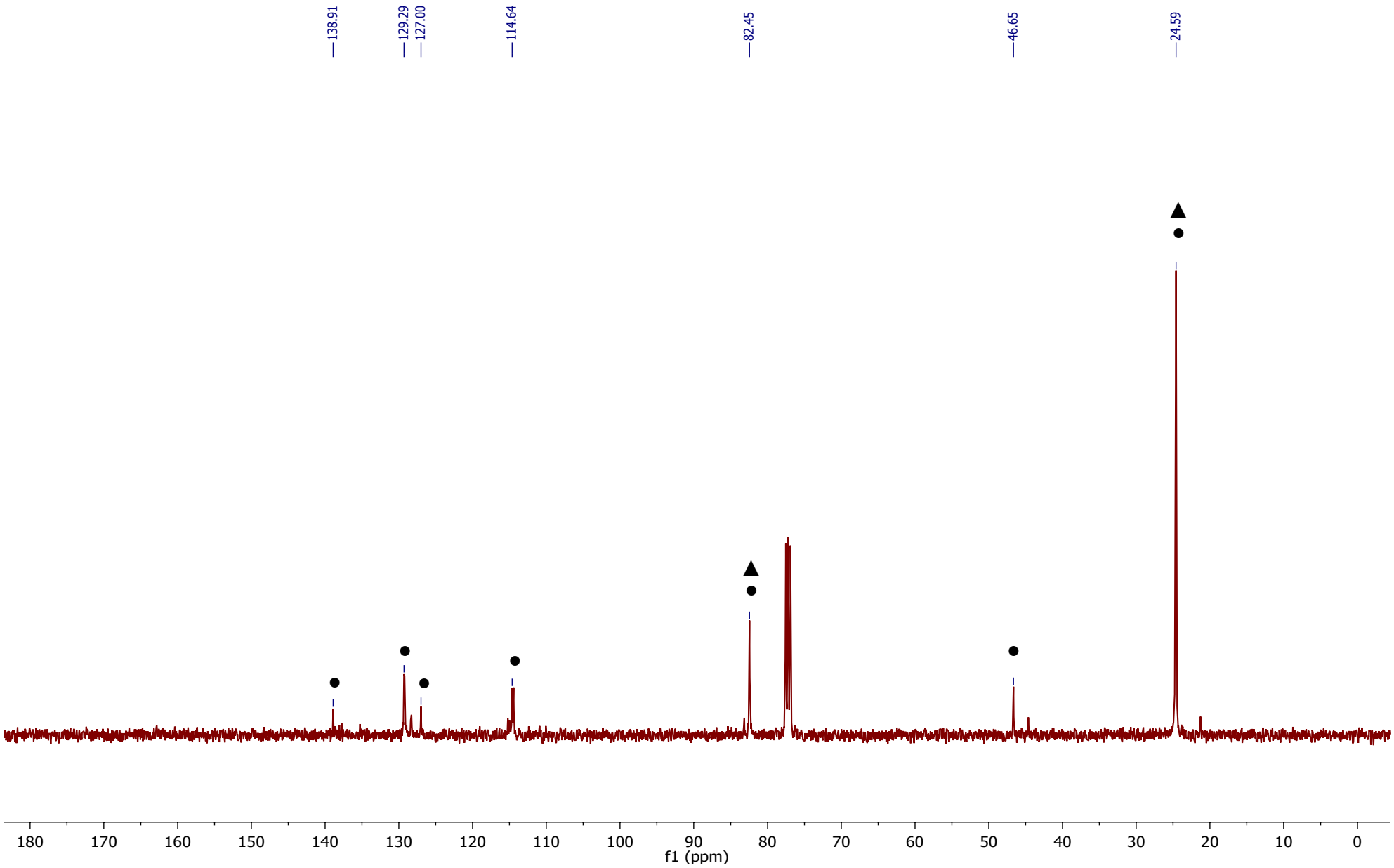

Figure S41 : ^{13}C NMR of *N-(*4-fluorobenzyl-4,4,5,5-tetramethyl-*N*-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1,3,2-dioxaborolan-2-amine : (ᴓ) and 2,2-oxybis(4,4,5,5-tetramethyl-1,3,2-dioxoboralane): (①)

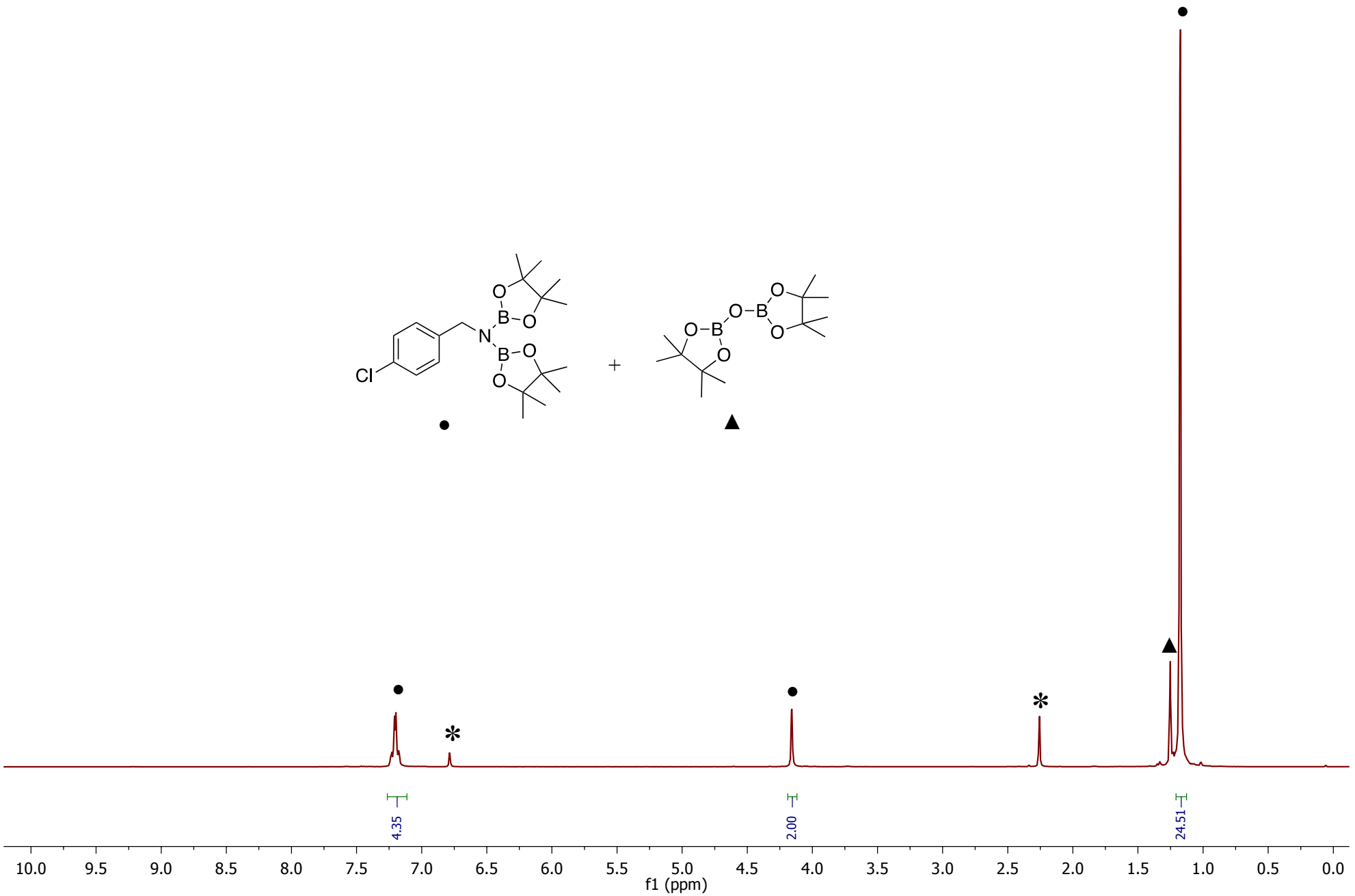

Figure S42 : ^{1}H NMR of *N-(*4-chlorobenzyl-4,4,5,5-tetramethyl-*N*-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1,3,2-dioxaborolan-2-amine : (ಜ) and 2,2-oxybis(4,4,5,5-tetramethyl-1,3,2-dioxoboralane): (①)

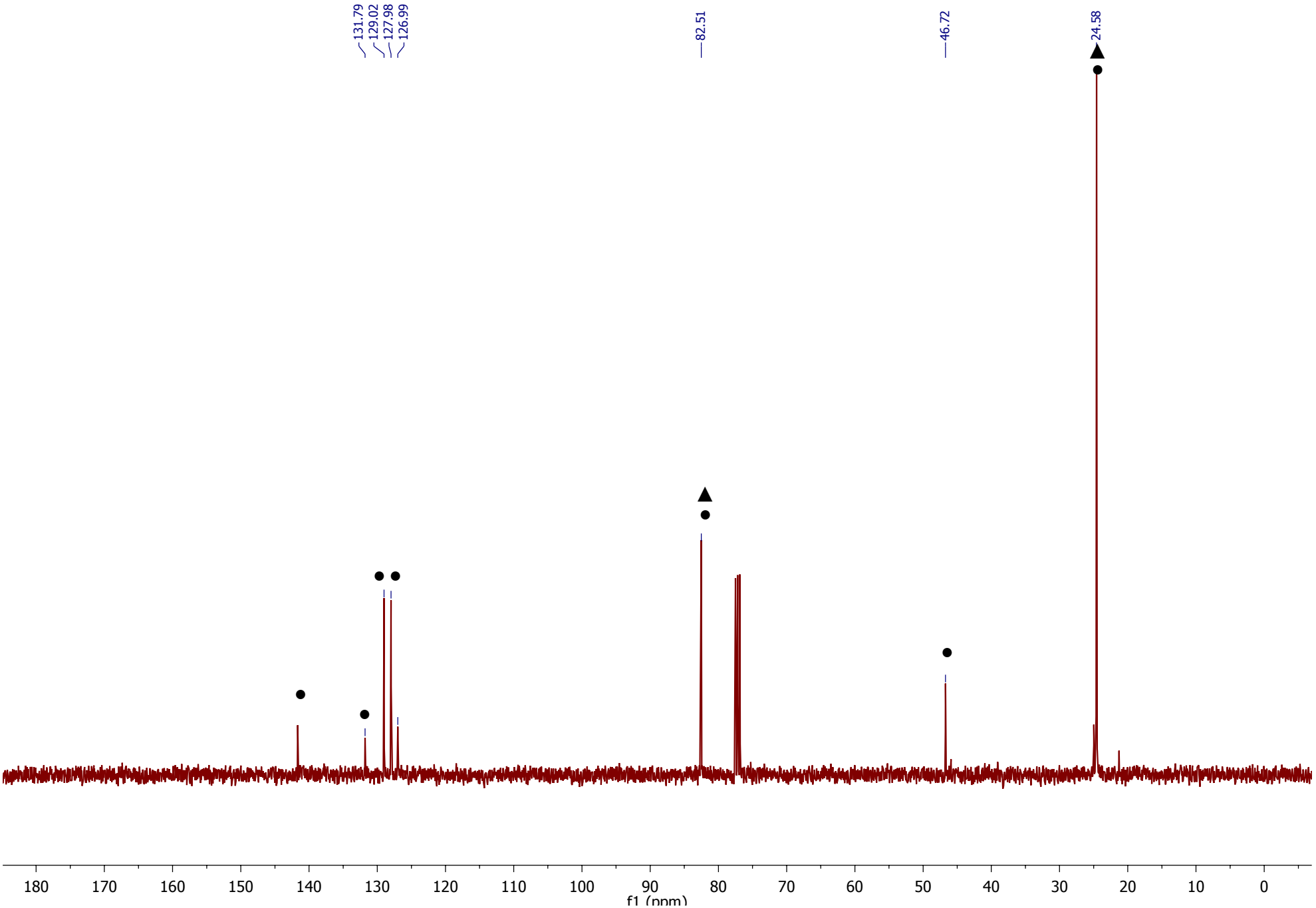

Figure S43 : ^{13}C NMR of *N-(*4-chlorobenzyl-4,4,5,5-tetramethyl-*N*-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1,3,2-dioxaborolan-2-amine : (ꝏ) and 2,2-oxybis(4,4,5,5-tetramethyl-1,3,2-dioxoboralane): (①)

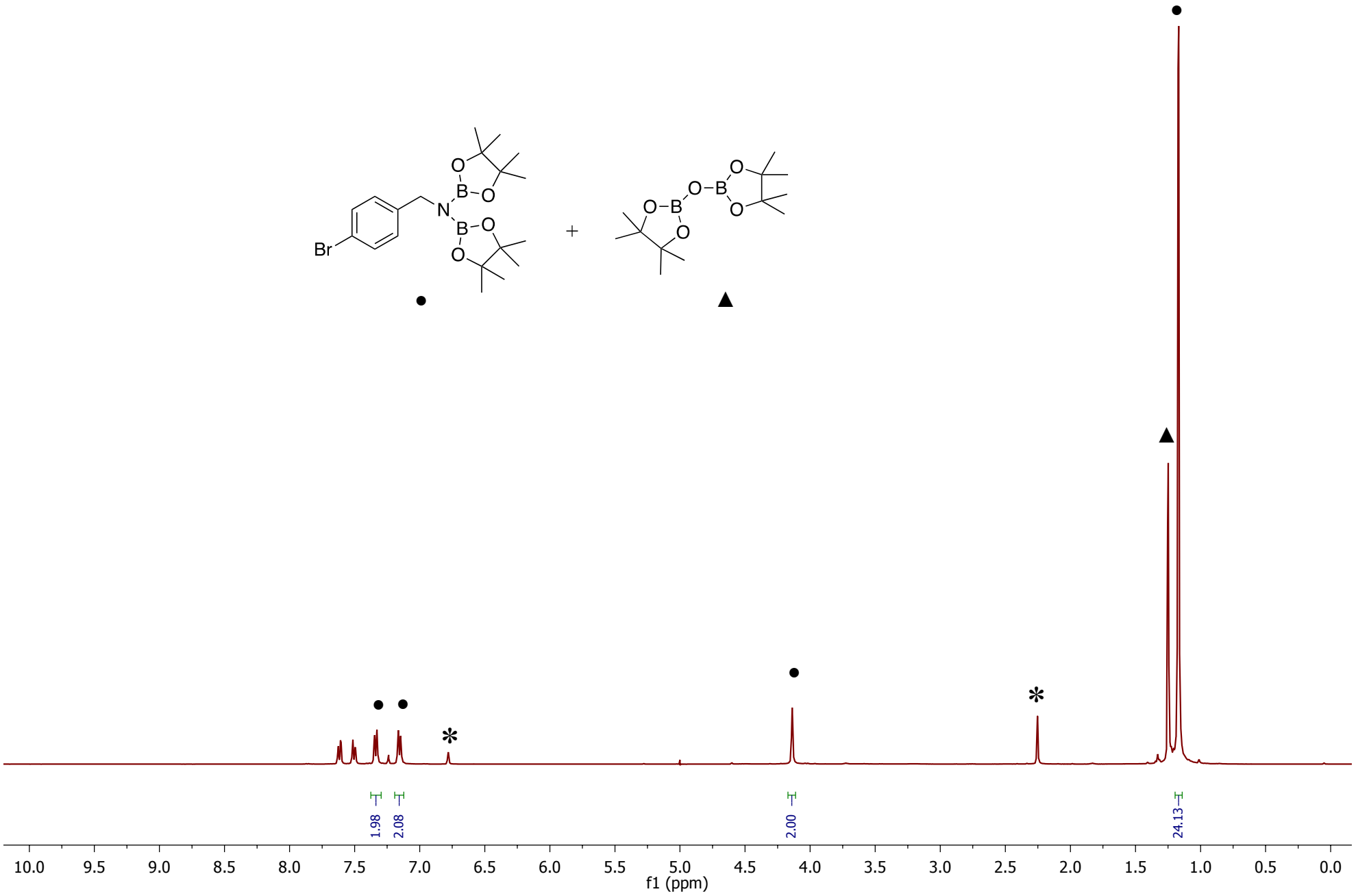

Figure S44 : ^{1}H NMR of *N-(*4-bromobenzyl-4,4,5,5-tetramethyl-*N*-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1,3,2-dioxaborolan-2-amine : (ꕥ) and 2,2-oxybis(4,4,5,5-tetramethyl-1,3,2-dioxoboralane): (①)

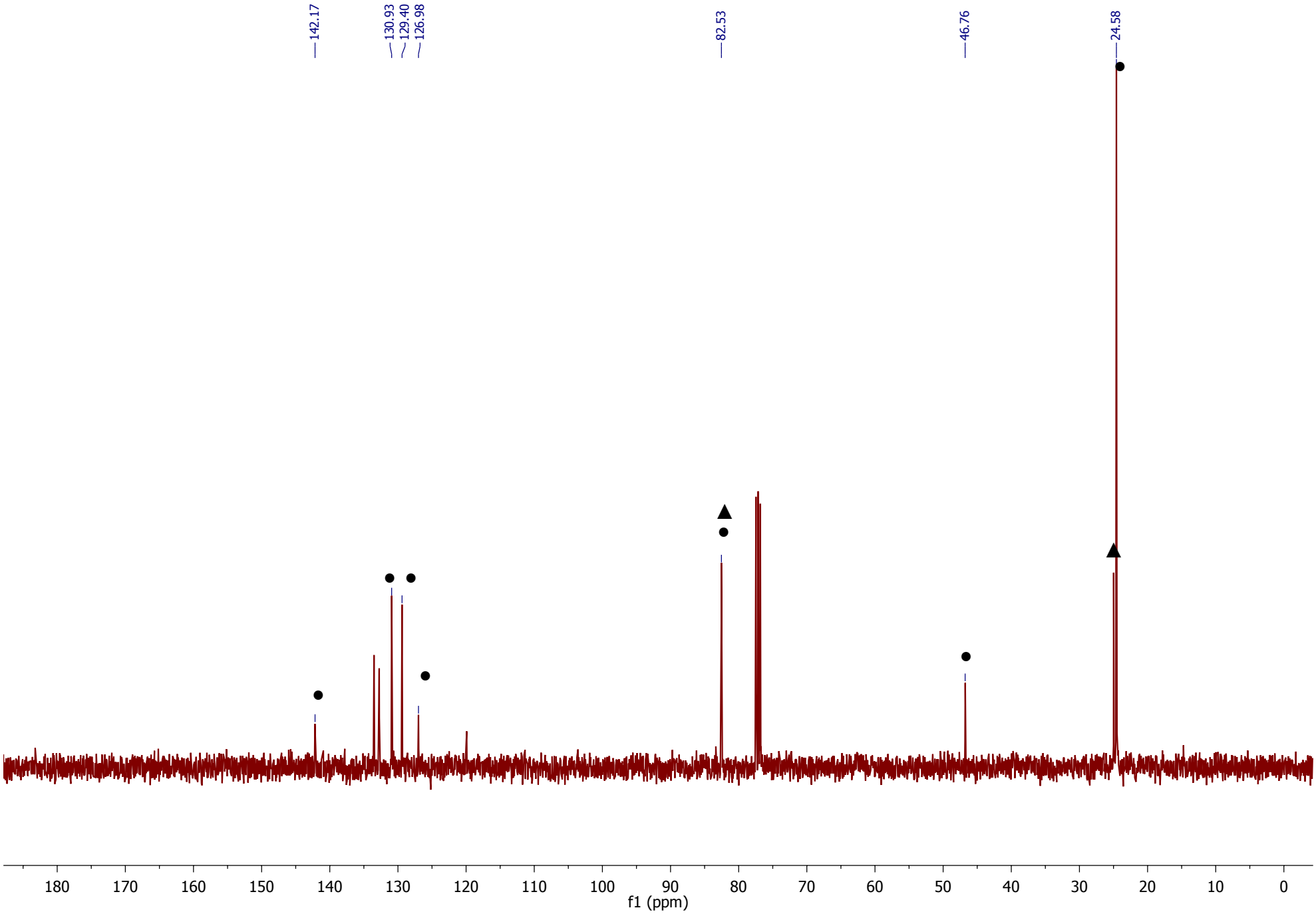

Figure S45 : ^{13}C NMR of *N-(*4-bromobenzyl-4,4,5,5-tetramethyl-*N*-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1,3,2-dioxaborolan-2-amine : (ᘐ) and 2,2-oxybis(4,4,5,5-tetramethyl-1,3,2-dioxoboralane): (①)

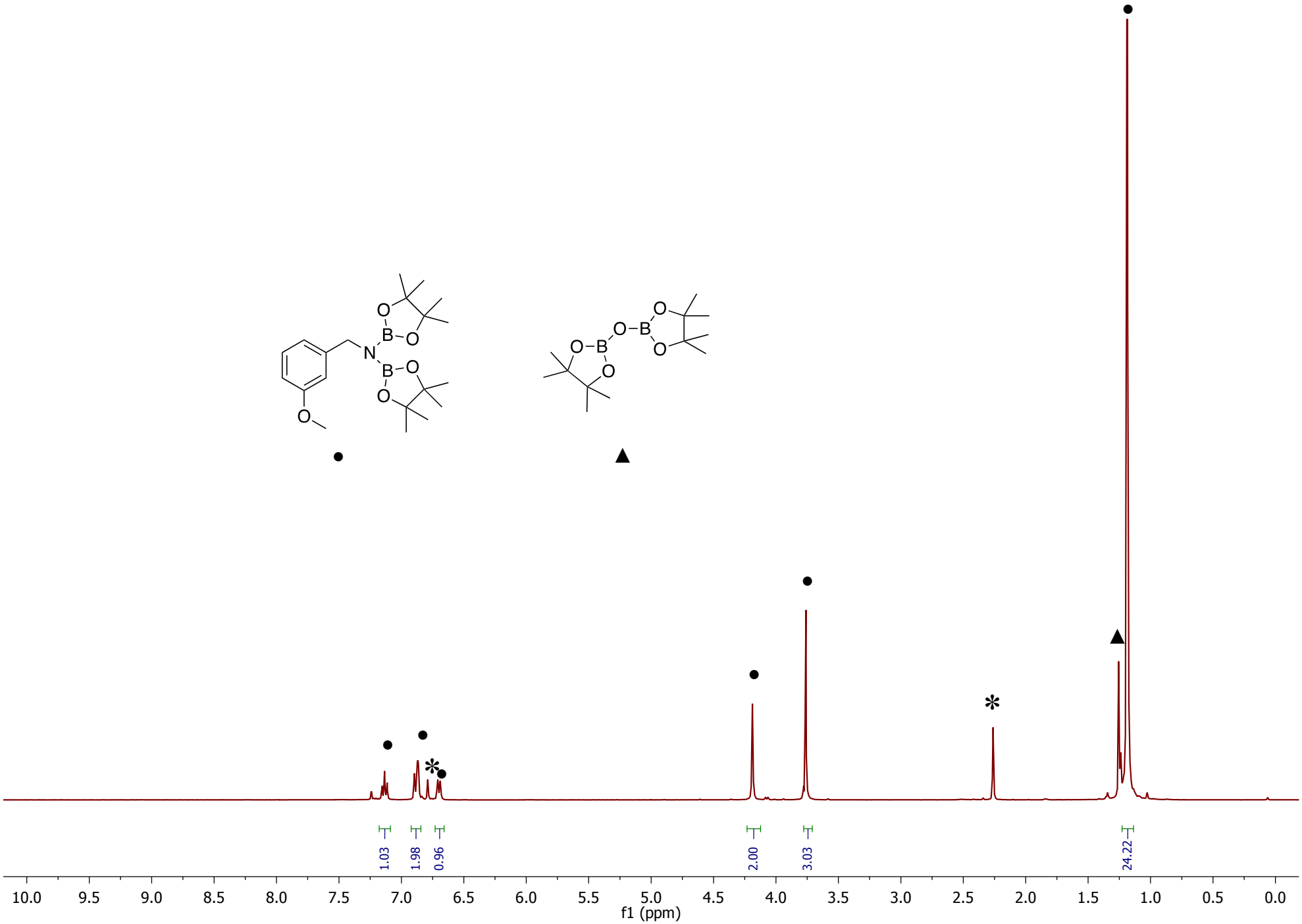

Figure S46 : ^{1}H NMR of *N-(*3-methoxybenzyl-4,4,5,5-tetramethyl-*N*-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1,3,2-dioxaborolan-2-amine : (ꕥ) and 2,2-oxybis(4,4,5,5-tetramethyl-1,3,2-dioxoboralane): (①)

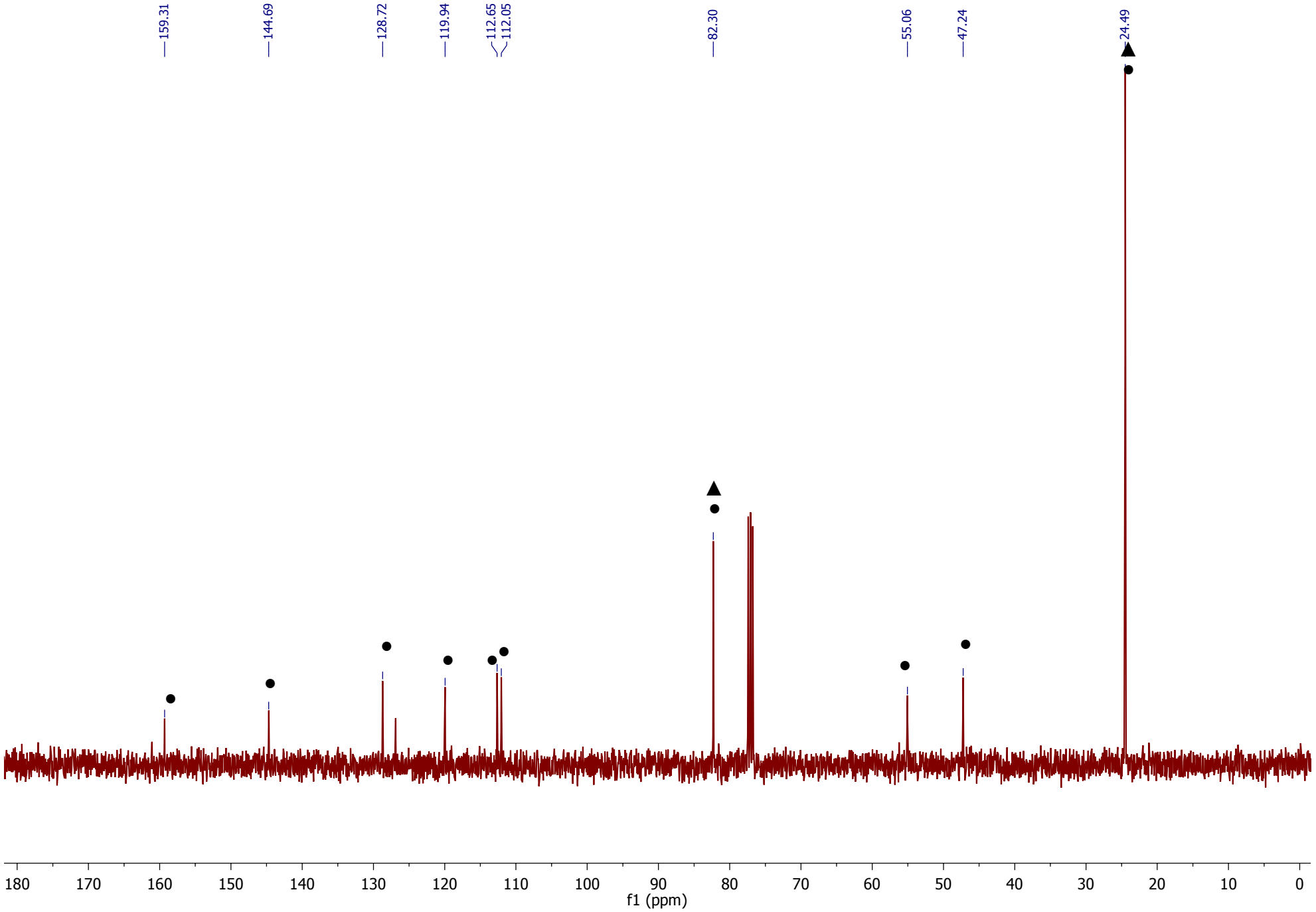

Figure S47: ^{13}C NMR of *N-(*3-methoxybenzyl-4,4,5,5-tetramethyl-*N*-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1,3,2-dioxaborolan-2-amine : (ꕤ) and 2,2-oxybis(4,4,5,5-tetramethyl-1,3,2-dioxoboralane): (①)

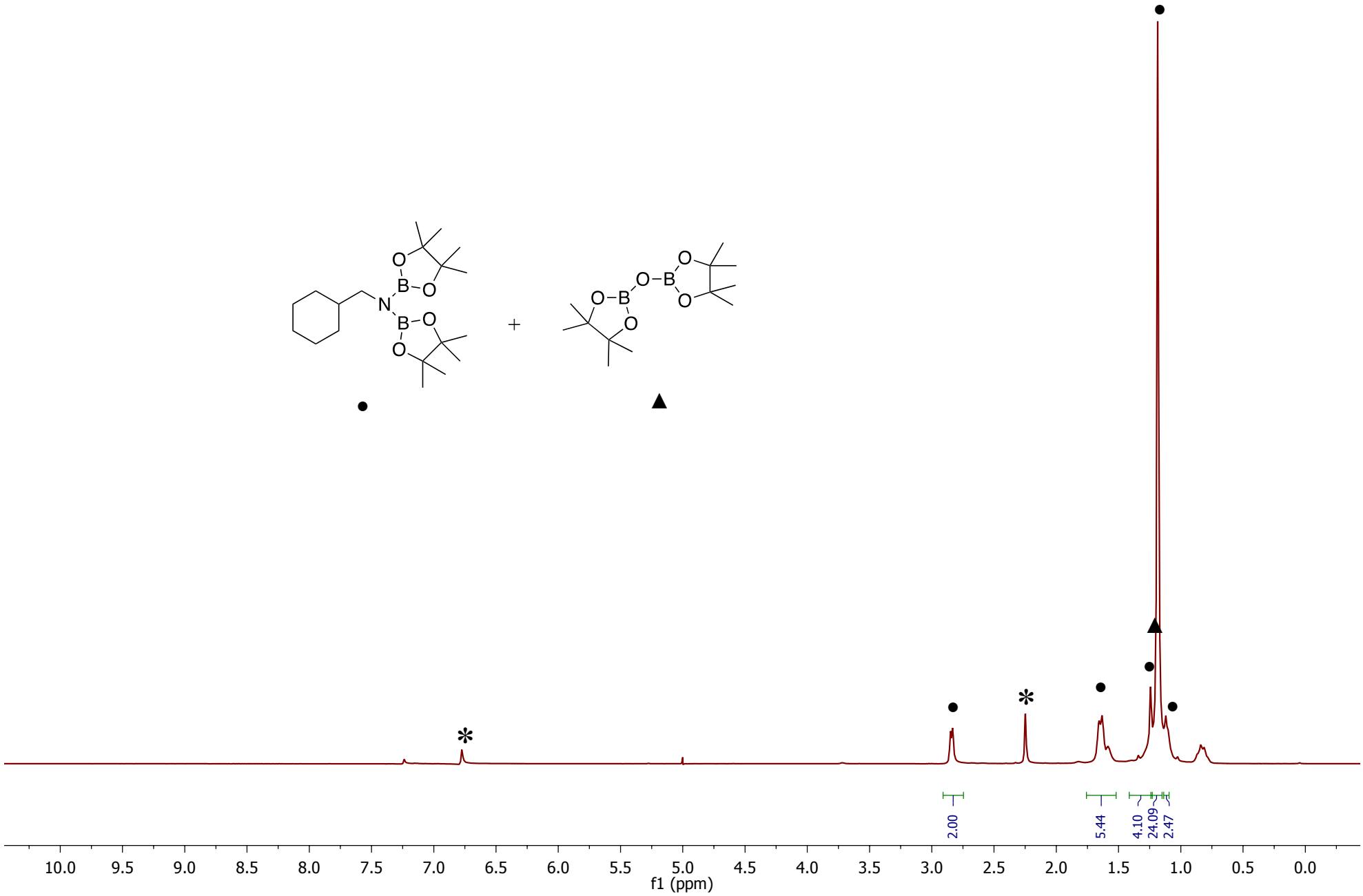

Figure S48 : ^{1}H NMR of *N*-*(*cyclohexylmethyl)-4,4,5,5-tetramethyl-*N*-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1,3,2-dioxaborolan-2-amine : (ꙮ) and 2,2-oxybis(4,4,5,5-tetramethyl-1,3,2-dioxoboralane): (①)

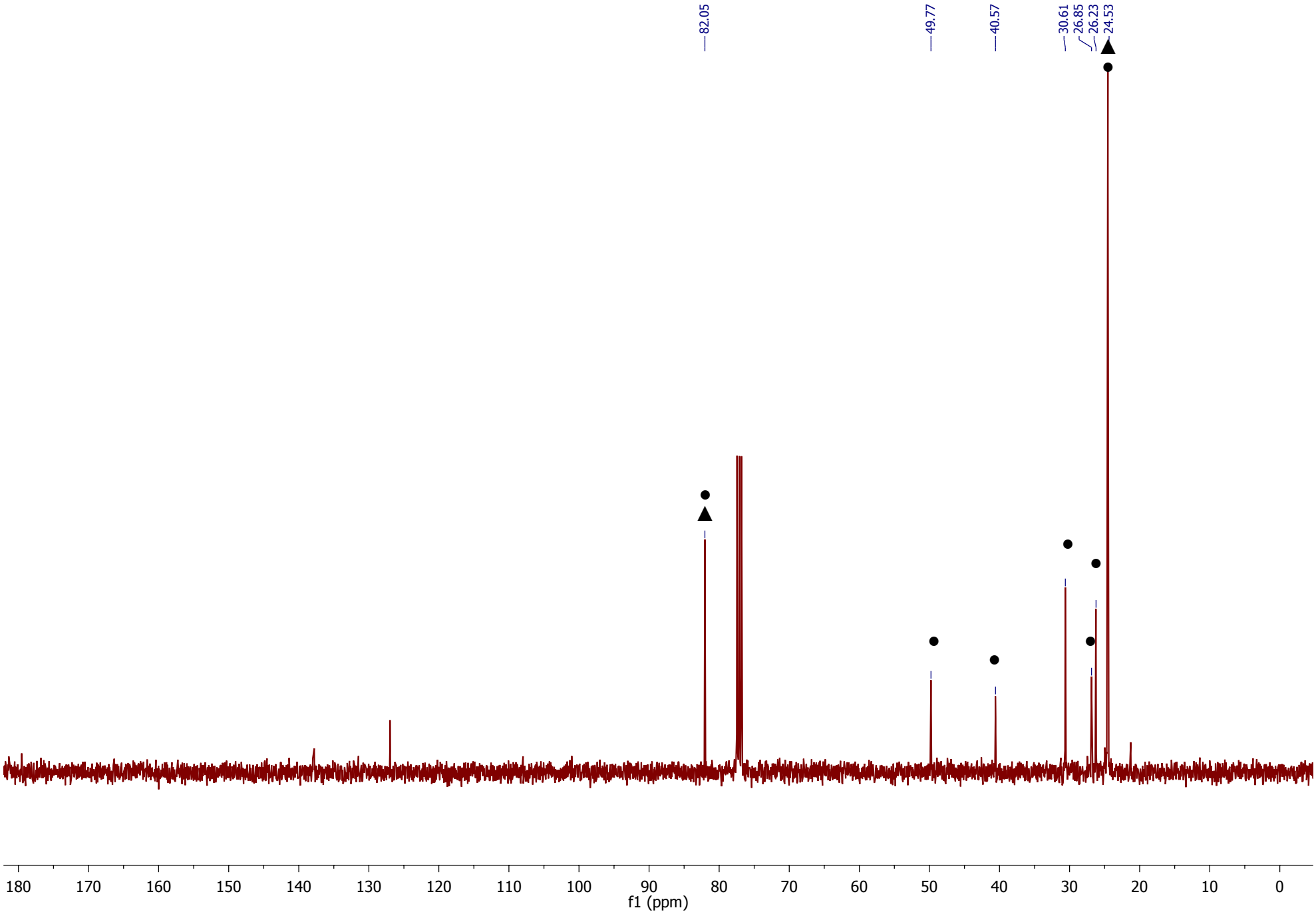

Figure S49 : ^{13}C NMR of *N-(*cyclohexylmethyl)-4,4,5,5-tetramethyl-*N*-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1,3,2-dioxaborolan-2-amine: (ಜ) and 2,2-oxybis(4,4,5,5-tetramethyl-1,3,2-dioxoboralane): (①)

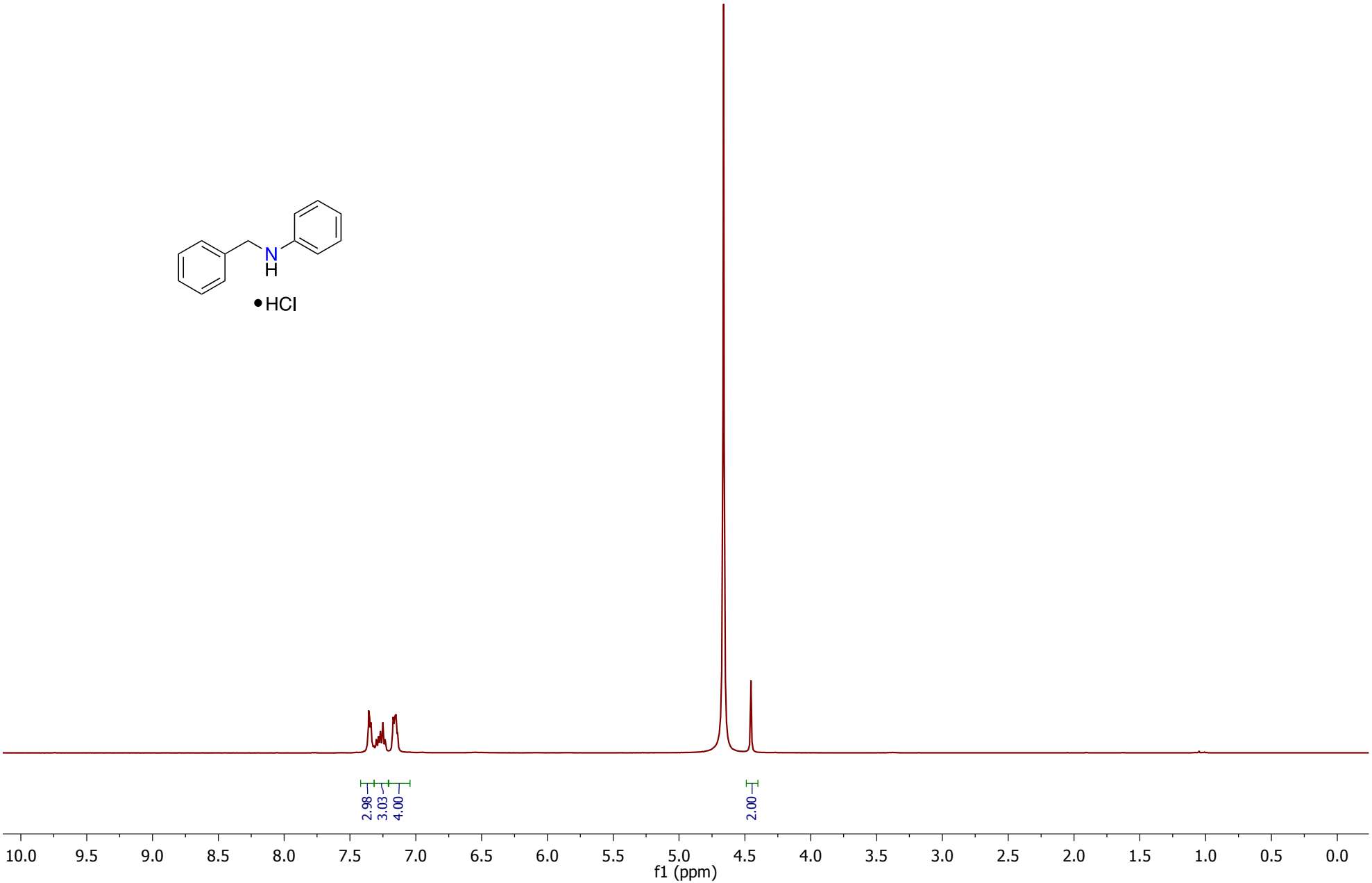

Figure S50 : ^{1}H NMR of *N*-Benzylanilinium chloride.

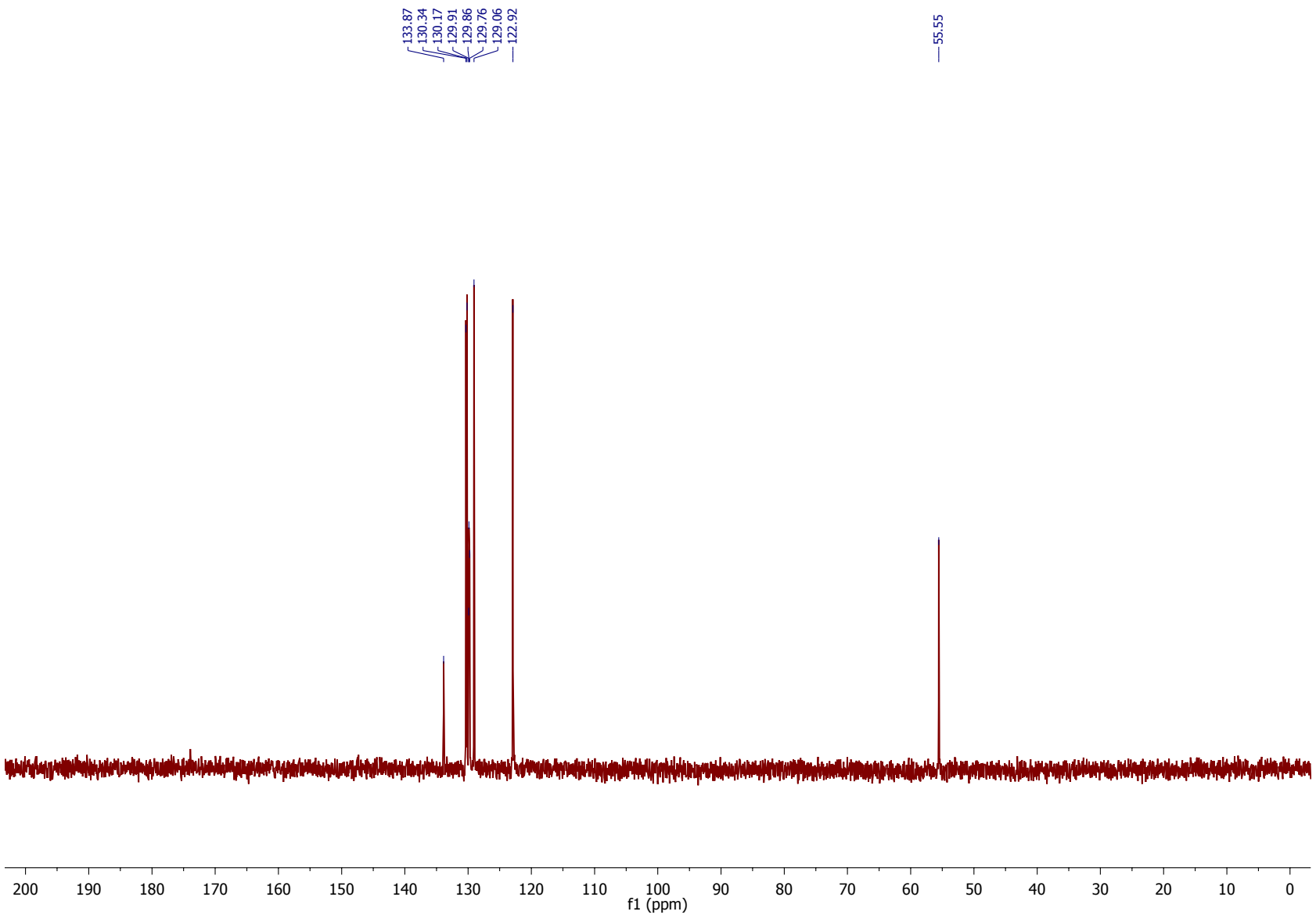

Figure S51 : ^{13}C NMR of *N*-Benzylanilinium chloride.

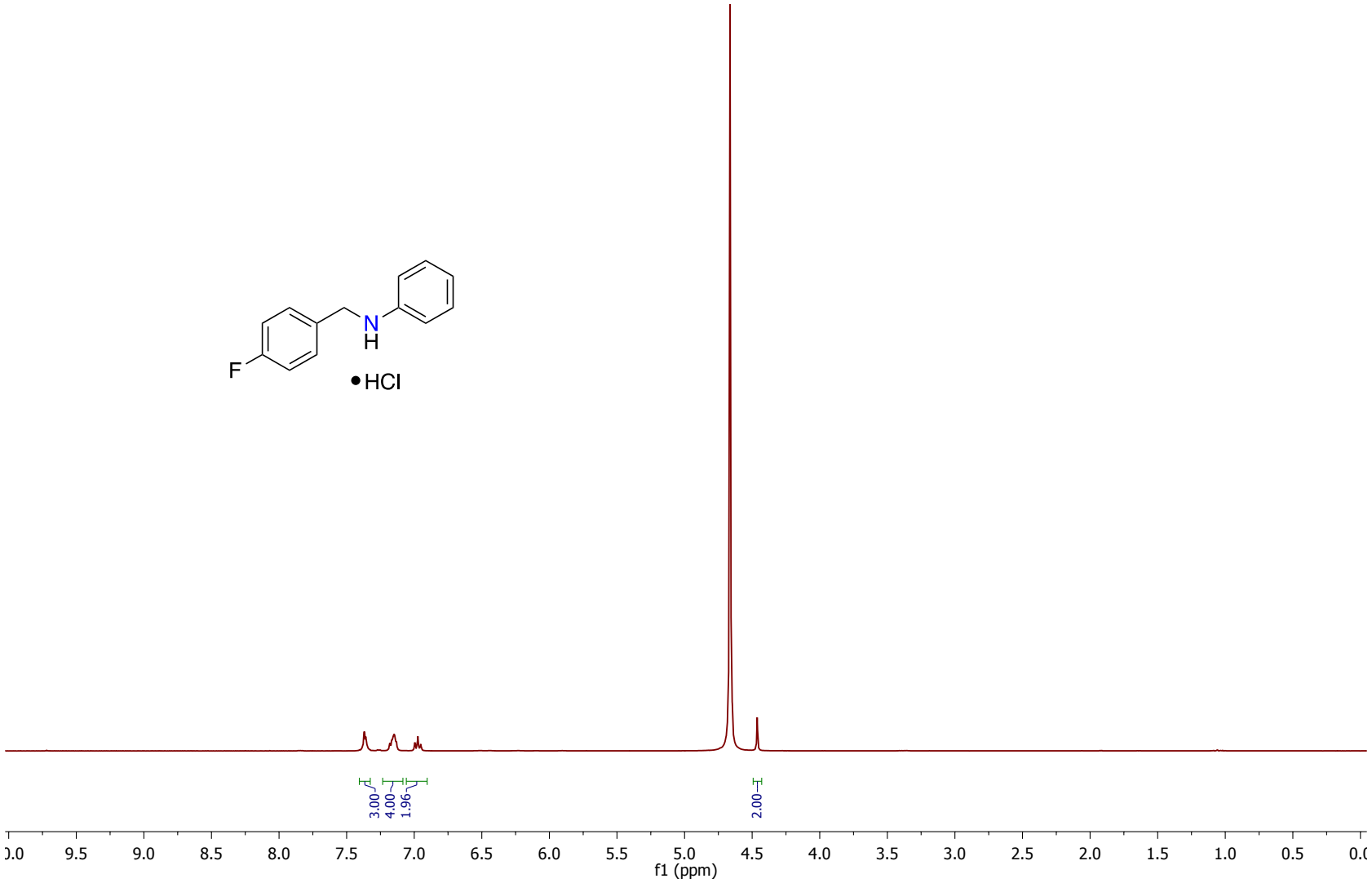

Figure S52 : ^{1}H NMR of *N*-(4-fluorobenzyl) anilinium chloride.

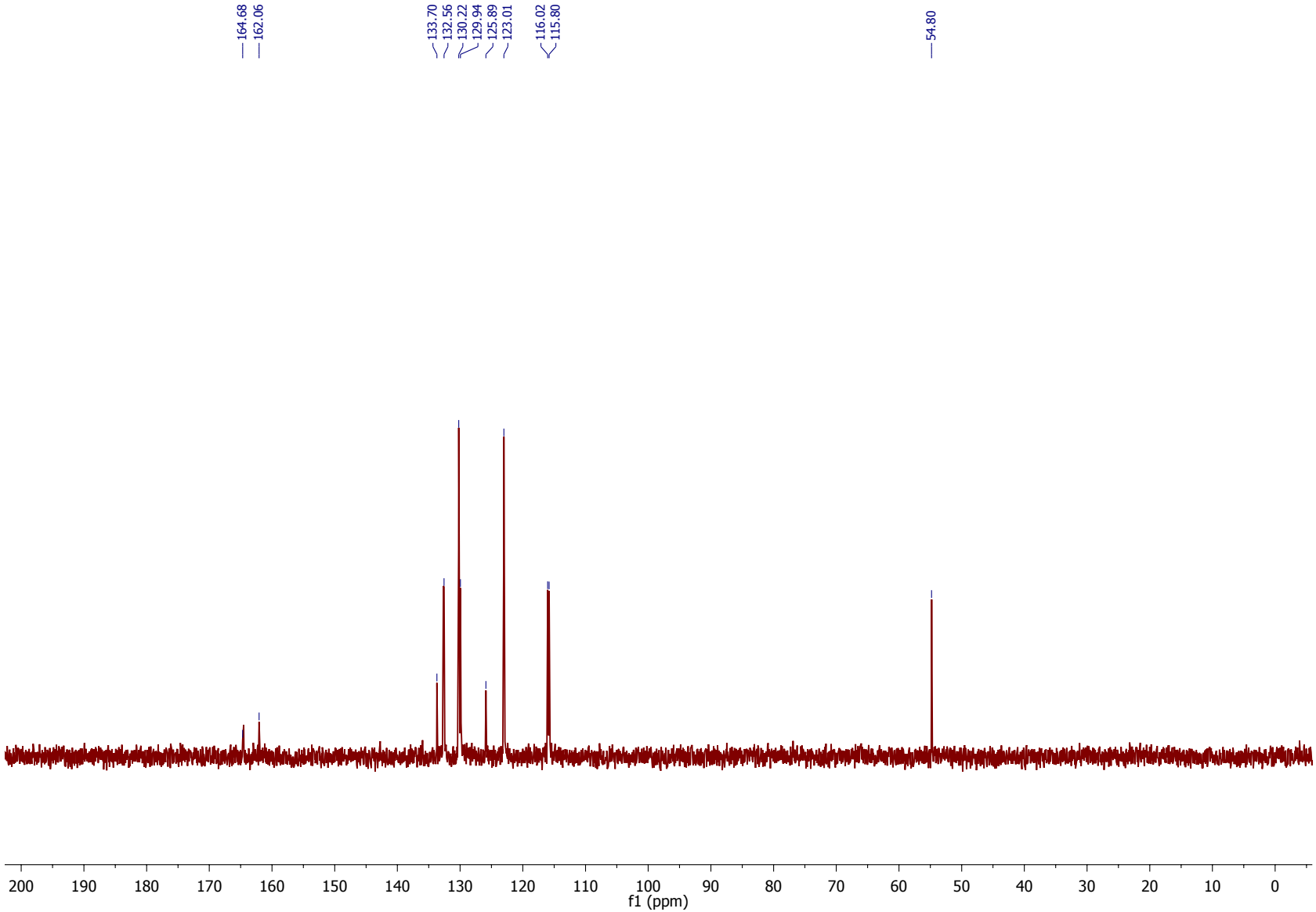

Figure S53 : ^{13}C NMR of *N*-(4-fluorobenzyl) anilinium chloride.

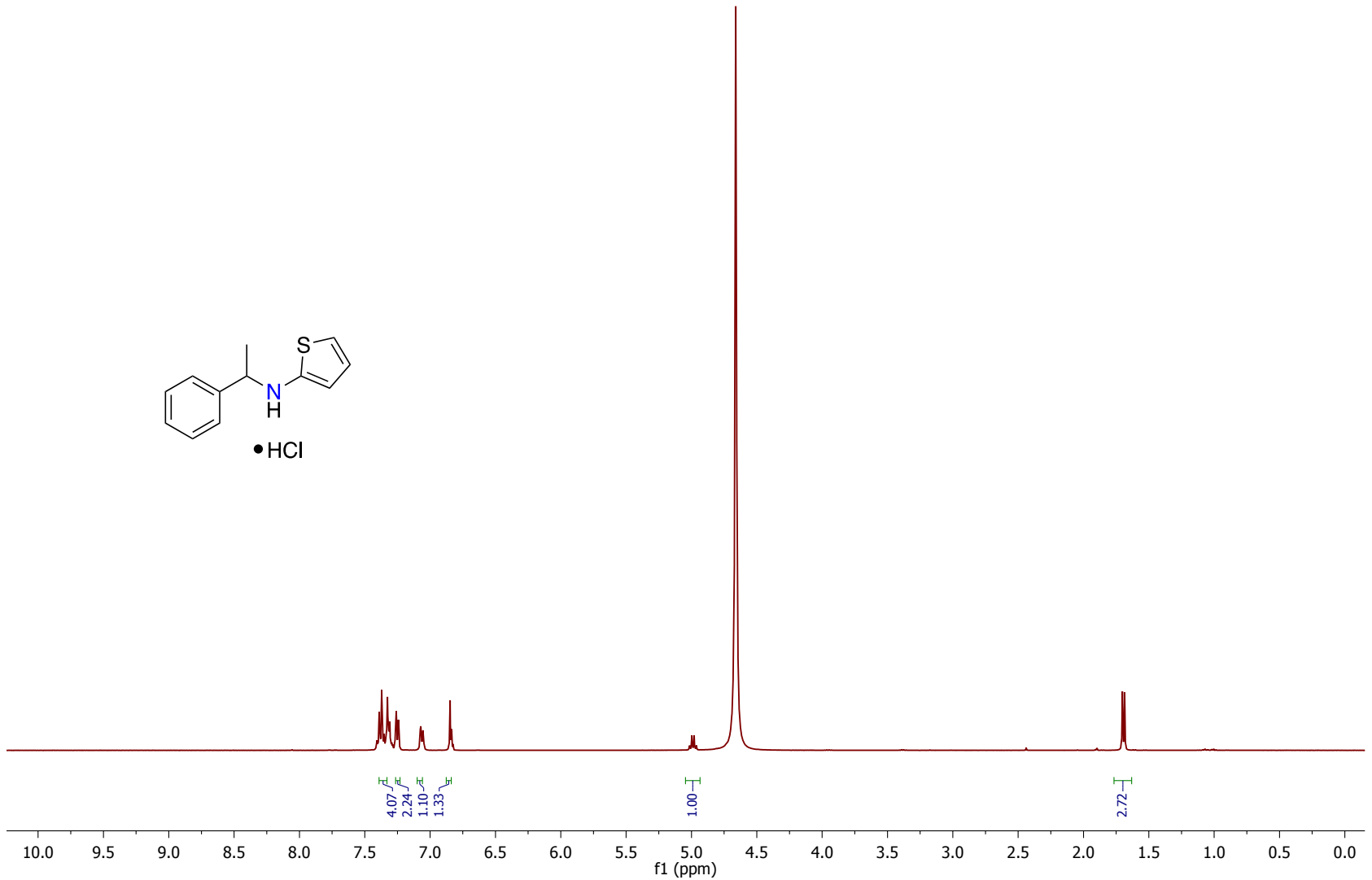

Figure S54 : ^{1}H NMR of *N*-(1-phenylethyl)thiophen-2-aminium chloride.

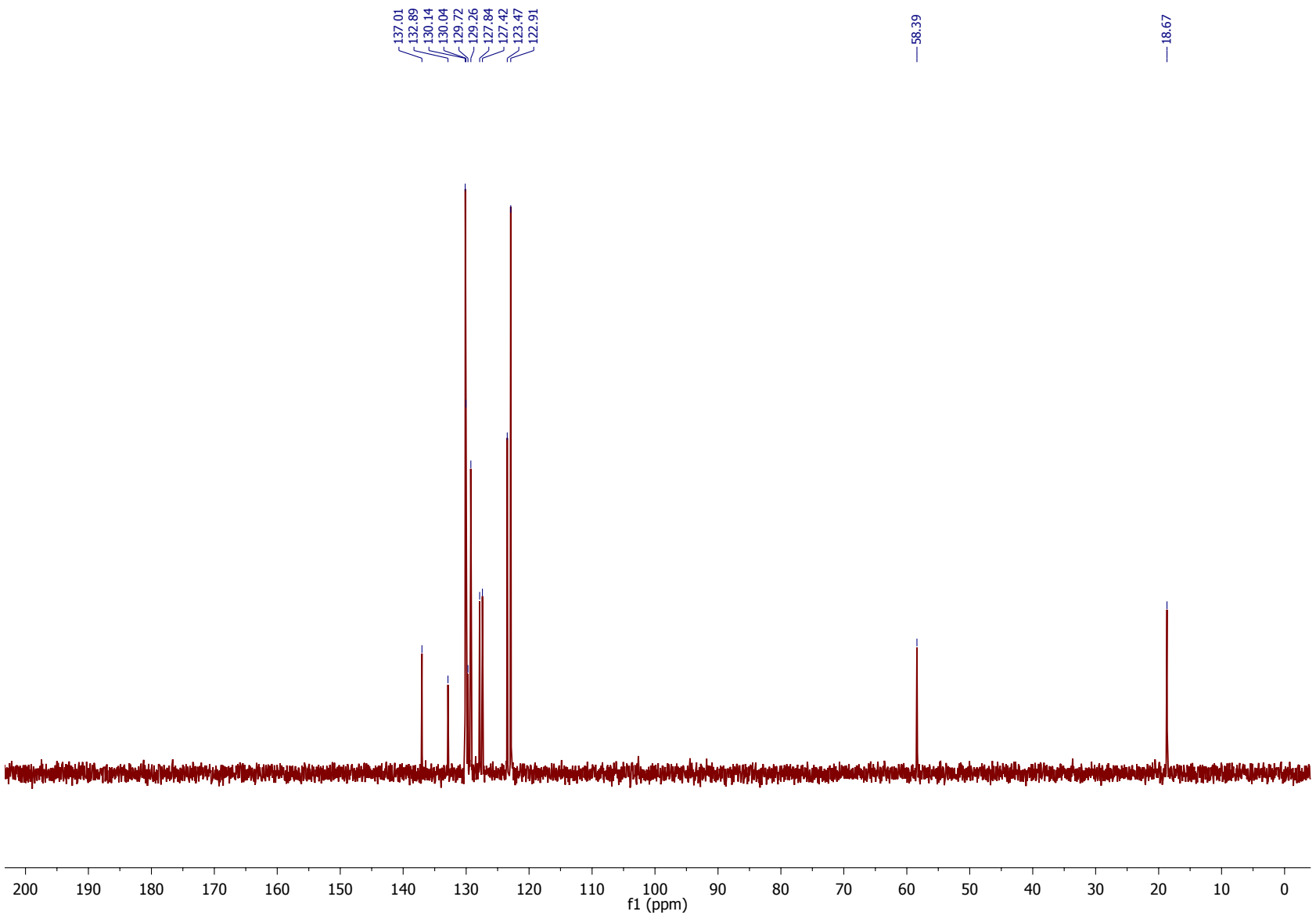

Figure S55 : ^{13}C NMR of *N*-(1-phenylethyl)thiophen-2-aminium chloride.

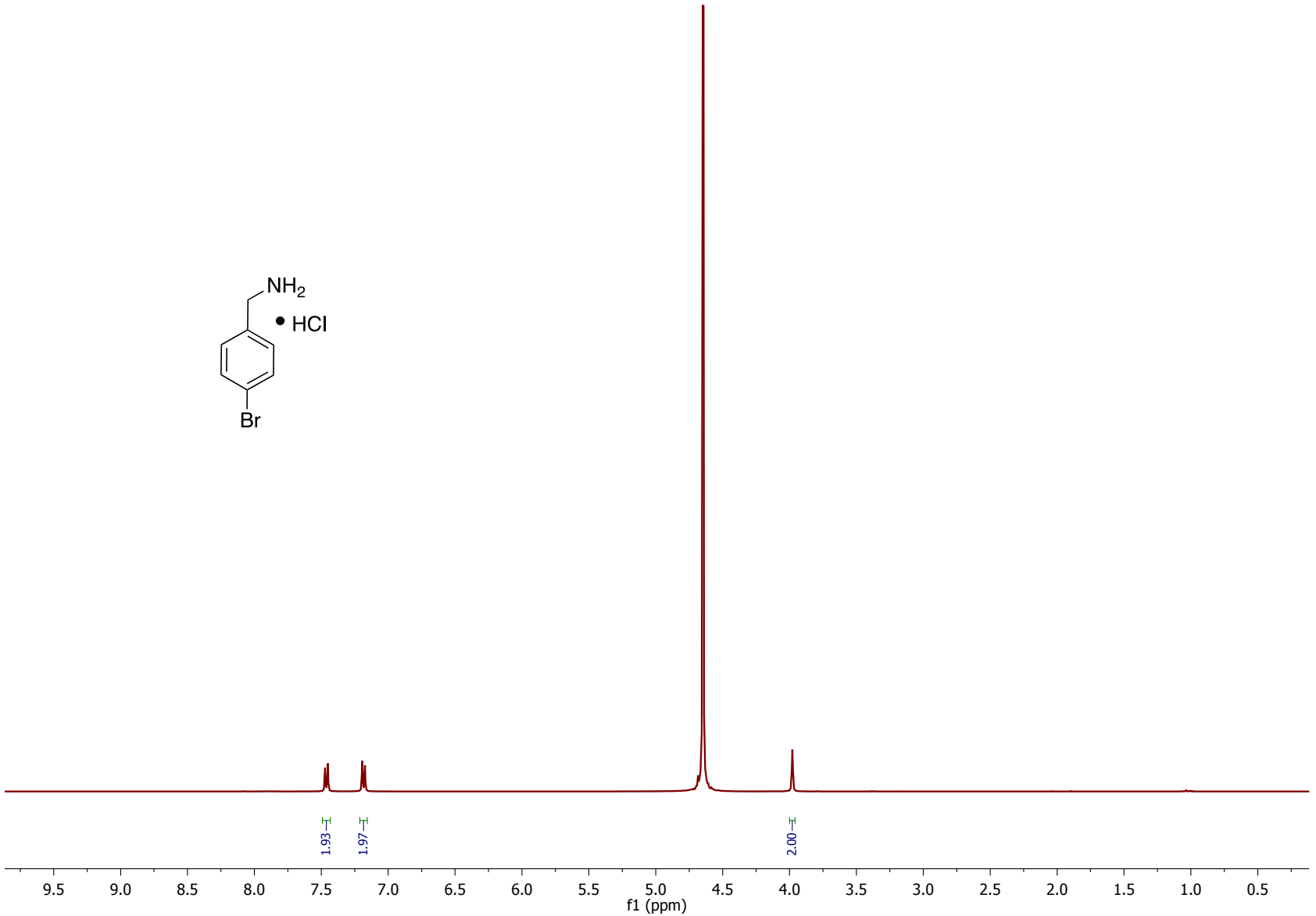

Figure S56 : ^{1}H NMR of (4-bromophenyl)methanaminium chloride.

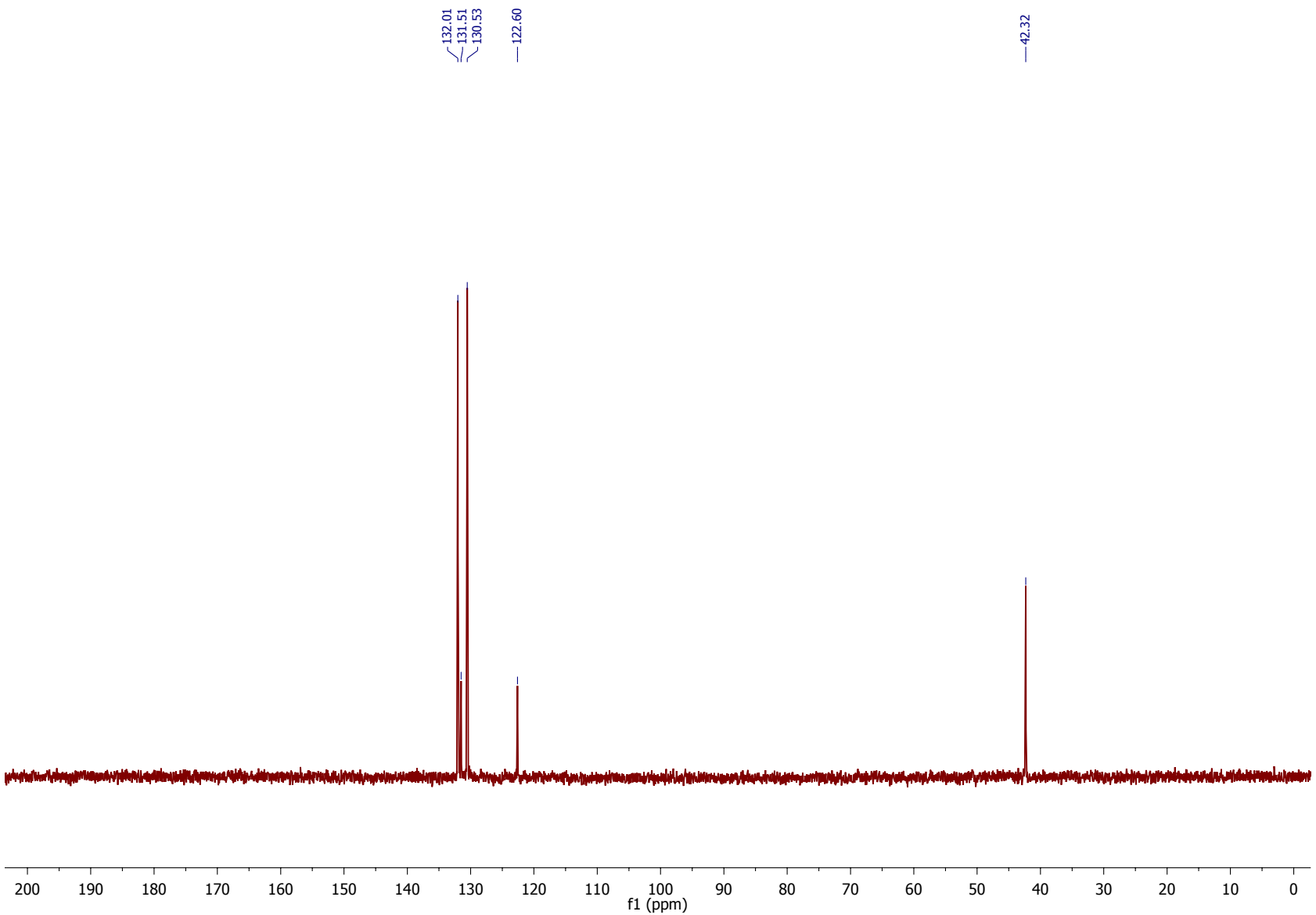

Figure S57 : ^{13}C NMR of (4-bromophenyl)methanaminium chloride.

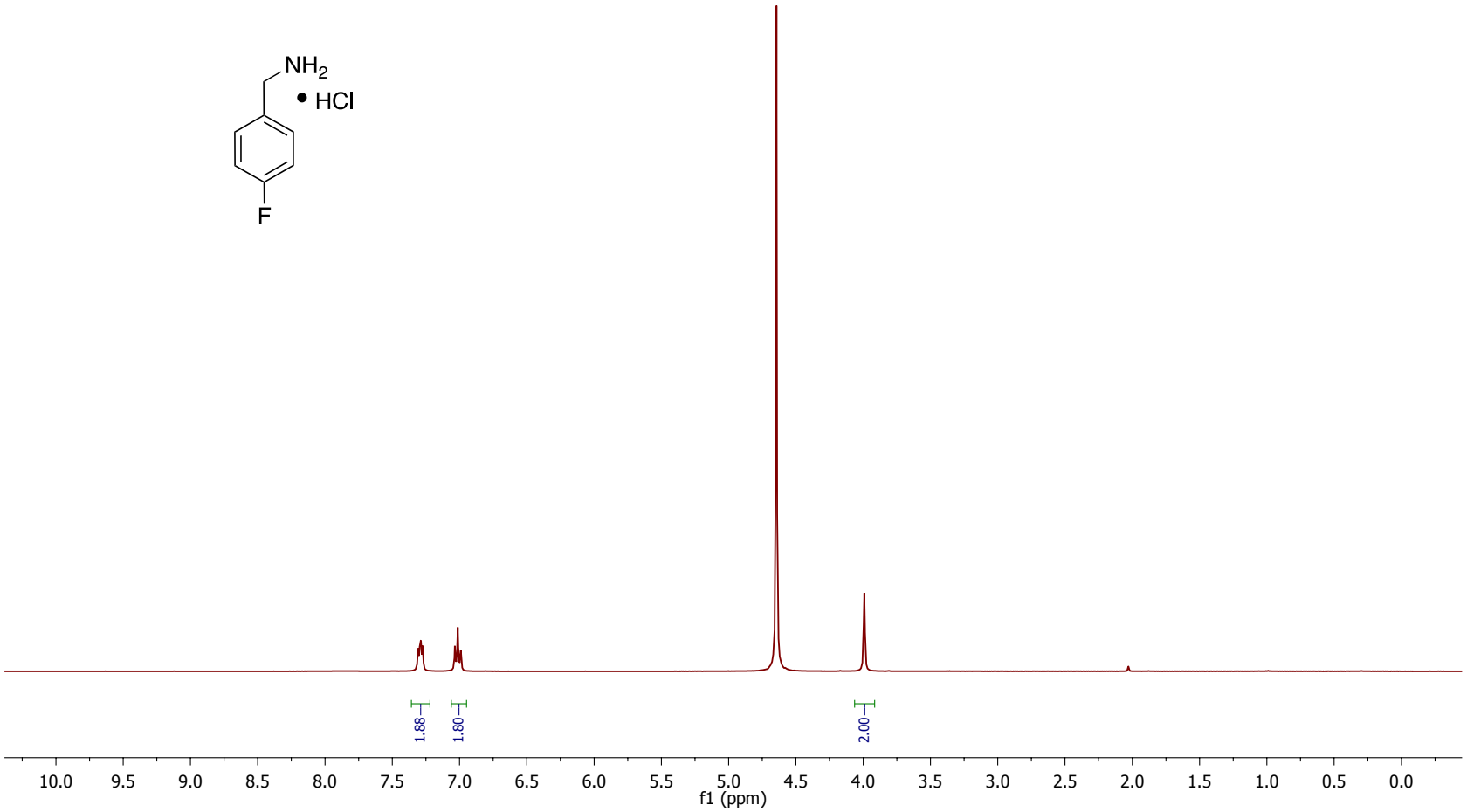

Figure S58 : ^{1}H NMR of (4-fluorophenyl)methanaminium chloride.

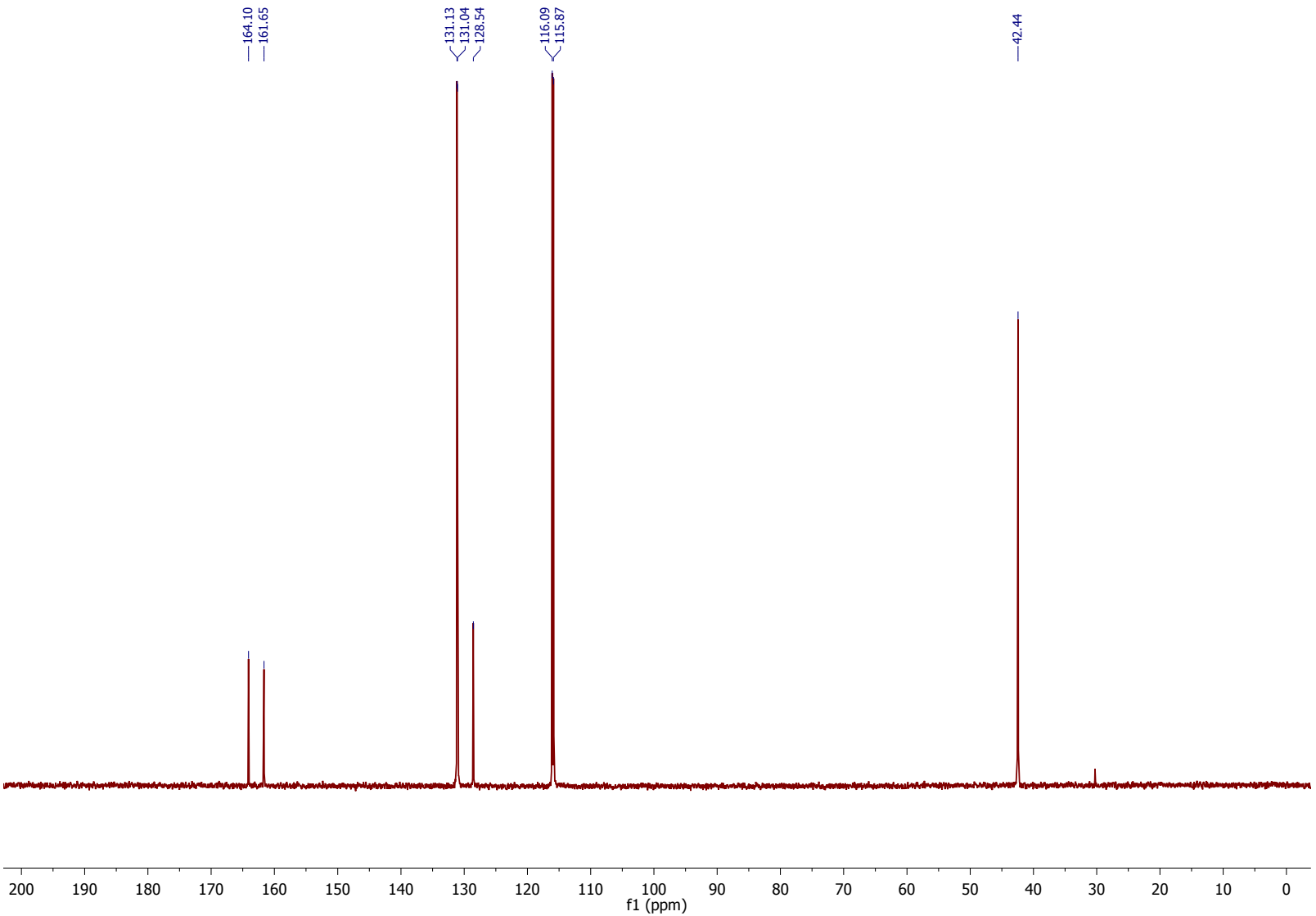

Figure S59 : ^{13}C NMR of (4-fluorophenyl) methanaminium chloride.