

Supporting Information

A Highly Active PN^3 Manganese Pincer Complex Performing N-Alkylation of Amines Under Mild Conditions

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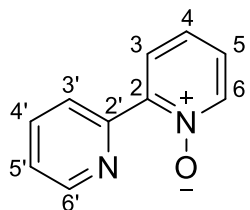
General Considerations

If not explicitly mentioned differently, all reactions were carried out in an inert gas atmosphere under exclusion of air and moisture at room temperature. These conditions were ensured by using the Schlenk-technique or working in a glove box. Solvents used for preparations or analytics were dried with sodium and benzophenone or calcium hydride, and distilled under inert gas atmosphere. Commercially obtained starting materials were purified if needed. GC analyses were carried out using an *Agilent Technologies 7890A* system equipped with a *HP-5* column (30 m, 320 μm , 0.25 μm) or *Shimadzu GC-2010 Plus* equipped with a *HP-5* column (30 m, 320 μm , 0.25 μm). GC-FID conditions: (Inlet temp.: 270 $^{\circ}\text{C}$, carrier gas flow: He at 34.9 cm s^{-1} ; oven temperature: 50 $^{\circ}\text{C}$ (2.25 min) to 300 $^{\circ}\text{C}$ at 25 $^{\circ}\text{C min}^{-1}$ (hold 5 min) for a total run time of 17.25 min). GC-MS analyses were carry out on an Agilent 7820A/MSD 5977B system equipped with a *HP-5MS* column (30 m, 250 μm , 0.25 μm). GC-MS conditions: Inlet temp.: 270 $^{\circ}\text{C}$, carrier gas flow: He at 39.8 cm s^{-1} ; oven temperature: 45 $^{\circ}\text{C}$ (2.25 min) to 300 $^{\circ}\text{C}$ at 25 $^{\circ}\text{C min}^{-1}$ (hold 0.55 min) for a total run time of 13 min). NMR-spectroscopic experiments were performed on *Bruker AVIII* and *Bruker AVIII HD* instruments (400, 600 & 700 MHz). Chemical shifts (δ in ppm) are indicated relative to TMS and were referenced to residual protons in the solvent. Air-tight sealed NMR tubes were used for NMR experiments on compounds that were air or moisture sensitive. NMR experiments were performed at room temperature (25 $^{\circ}\text{C}$) if not explicitly mentioned otherwise. *Merck* aluminum oxide 90 active basic (0.063–0.200 mm particle size, activity stage I) was used for column chromatography.

Table S1. Chemical shifts and multiplicities of used deuterated solvents.¹

solvent	δ (^1H) / ppm (multiplicity)	δ ($^{13}\text{C}\{^1\text{H}\}$) / ppm (multiplicity)
CDCl_3	7.26 (br s)	77.16 (t)
C_6D_6	7.16 (br s)	128.06 (t)
$\text{THF-}d_8$	1.72 (br s)	25.31 (quint)
	3.58 (br s)	67.21 (quint)
$\text{toluene-}d_8$	2.08 (quint)	20.43 (sept)
	6.97 (br s)	125.13 (t)
	7.01 (br s)	127.96 (t)
	7.09 (br s)	128.87 (t)
		137.48 (s)

Ligand Preparation

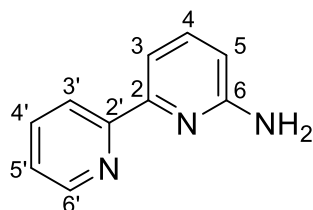


2,2'-bipyridine N monoxide (bpy-¹O):² A round bottom flask was charged with 2,2'-bipyridine (4.57 g, 29.3 mmol, 1.0 equiv), TFA (20 mL, 29.8 g, 261.4 mmol, 8.9 equiv) was added and then the reaction mixture was cooled to 0 °C. A septum was fitted on the round bottom flask and then H₂O₂ (4.5 mL, 30 wt% in H₂O, 1.50 g, 44.0 mmol, 1.5 equiv) was added dropwise over

15 min. The reaction was allowed to reach room temperature and was stirred for 2.5 h. CHCl₃ (100 mL) was added for dilution, the organic phase was collected by phase separation and carefully washed with NaOH (6 M, 4 × 30 mL). The combined aqueous phases were extracted with CH₂Cl₂ (3 × 50 mL), combined and dried over MgSO₄. All volatiles were removed under reduced pressure, leaving an off white product.

Yield: 4.54 g (26.3 mmol, 90%).

¹H-NMR (400.3 MHz, CDCl₃, 298 K): δ = 8.89–8.91 (m, 1H, ⁶Py-*H*), 8.71–8.72 (m, 1H, ⁶Py-*H*), 8.30–8.31 (m, 1H, ⁴Py-*H*), 8.16–8.19 (m, 1H, ⁴Py-*H*), 7.80–7.84 (m, 1H, ³Py-*H*), 7.32–7.37 (m, 2H, ⁴Py-*H* & ⁴Py-*H*), 7.24–7.28 (m, 1H, ³Py-*H*). The NMR spectroscopy data are in accordance with the literature.^[2]

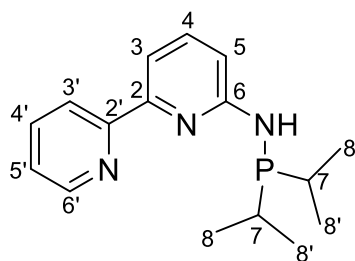


6-amino-2,2'-bipyridine (bpy-⁶NH₂):² bpy-¹O (4.50 g, 26.1 mmol, 1.0 equiv) and *t*BuNH₂ (17.3 mL, 12.11 g, 165.6 mmol, 6.3 equiv) were dissolved in CHCl₃ (100 mL) and degassed with 3 freeze-pump-thaw cycles. The mixture was cooled to 5 °C, TsCl (12.50 g, 65.6 mmol, 2.5 equiv) was added at once and then the reaction mixture was stirred for

2 h at 5 °C. TFA (50 mL, 74.50 g, 653.4 mmol, 25.0 equiv) was added at once and the reaction was heated to 65 °C for 20 h. The reaction mixture was let cool to room temperature and all volatiles were removed under reduced pressure, leaving a brown oily residue. The residue was dissolved in MTBE (20 mL), treated with HCl (4 M, 26 mL) and the aqueous phase was separated. The organic phase was extracted with H₂O (3 × 20 mL) and the combined aqueous phases were then treated with NaOH (2 M, 60 mL). Subsequently, saturated aqueous Na₂CO₃ solution was added to adjust the pH >7. The formed organic phase was diluted with CH₂Cl₂ (50 mL), separated and the aqueous phase was extracted with CH₂Cl₂ (3 × 50 mL). The combined organic phases were concentrated under reduced pressure. Purification by column chromatography (Al₂O₃, hept : EtOAc 99:1 to 1:99, then EtOAc : MeOH 99:1 to 80:20) provided analytically clean off-white product.

Yield: 4.26 g (24.9 mmol, 95%).

¹H-NMR (400.3 MHz, CDCl₃, 298 K): δ = 8.65–8.67 (m, 1H), 8.25–8.29 (m, 1H), 7.75–7.81 (m, 1H), 7.71–7.74 (m, 1H), 7.55–7.60 (m, 1H), 7.24–7.28 (m, 1H), 6.53–6.56 (m, 1H), 4.49 (br s, NH₂); **¹³C{¹H}-NMR** (100.6 MHz, CDCl₃, 298 K): δ = 158.1 (⁶C_q-NH₂), 156.6 (²C_q), 154.8 (²C_q), 149.3 (⁶CH), 138.7 (⁴CH), 136.8 (⁴CH), 123.4 (⁵CH), 121.1 (³CH), 111.8 (³CH), 109.0 (⁵CH). The NMR spectroscopic data are in accordance with the literature.²



***N*-(diisopropylphosphaneyl)-[2,2'-bipyridin]-6-amine**

(bpy-⁶NH-^{*i*Pr}P): Following a procedure for the synthesis of PyNHP(*i*Pr)₂:³ bpy-NH₂ (334 mg, 1.95 mmol, 1.0 equiv) was dissolved in THF (10 mL) and degassed, NEt₃ (0.25 mL, 238 mg, 2.35 mmol, 1.2 equiv) was added at once. *i*Pr₂PCl (0.34 mL, 326 mg, 2.14 mmol, 1.1 equiv) was added dropwise and the

reaction mixture was stirred at room temperature for 16 h. Precipitates were filtered off, the residue was extracted with THF (3 × 5 mL) and all volatiles were removed in *vacuo* at 60 °C. The product was obtained as slightly yellow oil that solidified and became an off-white powder upon scratching with a spatula.

Yield: 518 mg (1.80 mmol, 92%).

¹H-NMR (600.3 MHz, THF-*d*₈, 298 K): δ = 8.56–8.58 (m, 1H), 8.38–8.41 (m, 1H), 7.82–7.84 (m, 1H), 7.73–7.77 (m, 1H), 7.51–7.55 (m, 1H), 7.22–7.25 (m, 1H), 7.04–7.07 (m, 1H), 5.68 (d, ²J_{P,H} = 9.3 Hz, 1H, NH), 1.88–1.95 (m, 2H, 2 × CH(CH₃)₂), 1.06–1.14 (m, 12H, 2 × CH(CH₃)₂); **¹³C{¹H}-NMR** (150.9 MHz, THF-*d*₈, 298 K): 161.5 (d, ²J_{P,C} = 18.4 Hz, ⁶C_q), 157.5 (²C_q), 155.2 (d, ⁴J_{P,C} = 0.9 Hz, ²C_q), 149.7 (⁶CH), 138.4 (d, ⁴J_{P,C} = 1.9 Hz, ⁴CH), 136.8 (⁴CH), 123.8 (⁵CH), 121.1 (³CH), 111.9 (³CH), 109.9 (d, ³J_{P,C} = 15.2 Hz, ⁵CH), 27.2 (d, J_{P,C} = 12.4 Hz, ⁷CH), 19.3 (d, J_{P,C} = 21.2 Hz, ⁸CH₃), 17.8 (d, J_{P,C} = 8.5 Hz, ⁸CH₃); **³¹P{¹H}-NMR** (243.0 MHz, THF-*d*₈, 298 K): δ = 48.9.

HRMS (ESI) m/z calcd. for [C₁₆H₂₃N₃P, M+H]⁺: 288.1630; Found: 288.1620.

Procedure for preparation and crystallization of [(bpy-⁶NH-^{*i*Pr}P)Mn(CO)₃]⁺ X⁻ (Complex A)

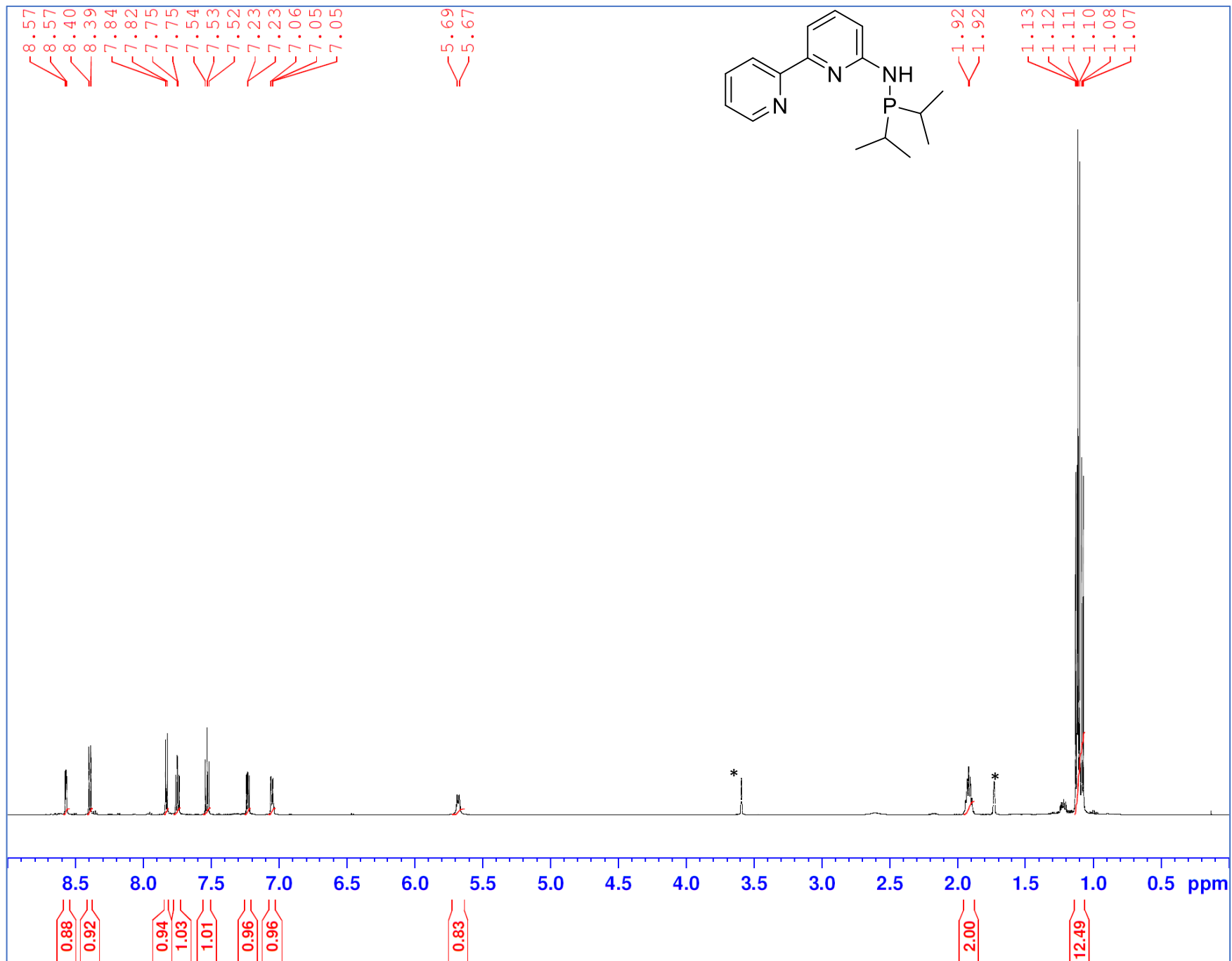
(X⁻ = Br⁻. ½ [Mn(Br₄)²⁻]): In the glovebox a 2 mL vial was charged with Mn(CO)₅Br (8.2 mg, 30 μmol, 1 equiv) and **bpy-⁶NH-^{*i*Pr}P** (8.6 mg, 30 μmol, 1 equiv), followed by addition of DME (0.6 mL). After 1 h of stirring at room temperature a distinct color change from light orange to brown was observed. Precipitates were filtered off and the solution was stored at –35 °C overnight to afford pale yellow crystals suitable for X-ray analysis.

Spectroscopic characterization of Complex A:

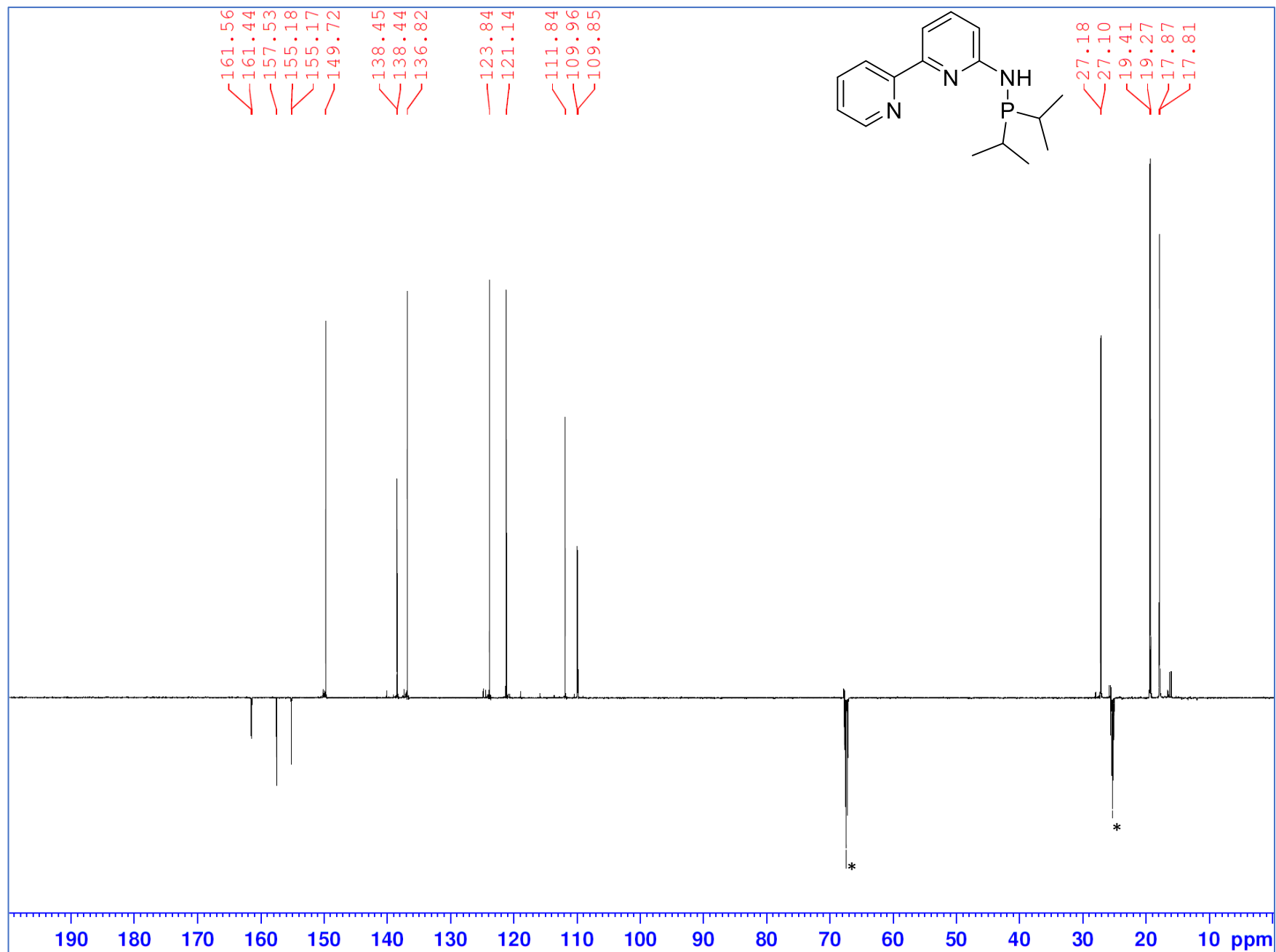
$^1\text{H-NMR}$ (400.3 MHz, THF- d_8 , 298 K): δ = 8.60–8.67 (br m, 1H), 8.14–8.21 (br m, 1H), 8.02–8.09 (br m, 1H), 7.79–7.89 (br m, 1H), 7.65–7.74 (br m, 1H), 7.27–7.35 (br m, 1H), 6.76–6.82 (br d, 1H), 6.63–6.72 (br d, 1H, NH), 3.68–3.82 (m, 2H, $2 \times \text{CH}(\text{CH}_3)_2$), 1.33–1.48 (m, 12H, $2 \times \text{CH}(\text{CH}_3)_2$); **$^{13}\text{C}\{^1\text{H}\}\text{-NMR}$** (100.6 MHz, THF- d_8 , 298 K): 185.1 (C_q), 157.5 (d, $^2J_{\text{P,C}} = 12$ Hz, C_q), 156.8 (C_q), 155.7 (C_q), 150.3 (CH), 139.9 (CH), 137.6 (CH), 124.4 (CH), 121.0 (CH), 114.8 (CH), 113.1 ($^3J_{\text{P,C}} = 5$ Hz, CH), 31.6 (d, $J_{\text{P,C}} = 24$ Hz, CH), 19.3, 18.7 (d, $J_{\text{P,C}} = 5$ Hz, CH_3); **$^{31}\text{P}\{^1\text{H}\}\text{-NMR}$** (162 MHz, THF- d_8 , 298 K): δ = 98.0.

Procedure for crystallization of $[(\text{bpy-}^6\text{NH-}^i\text{PrP})\text{MnBr}_2]$:

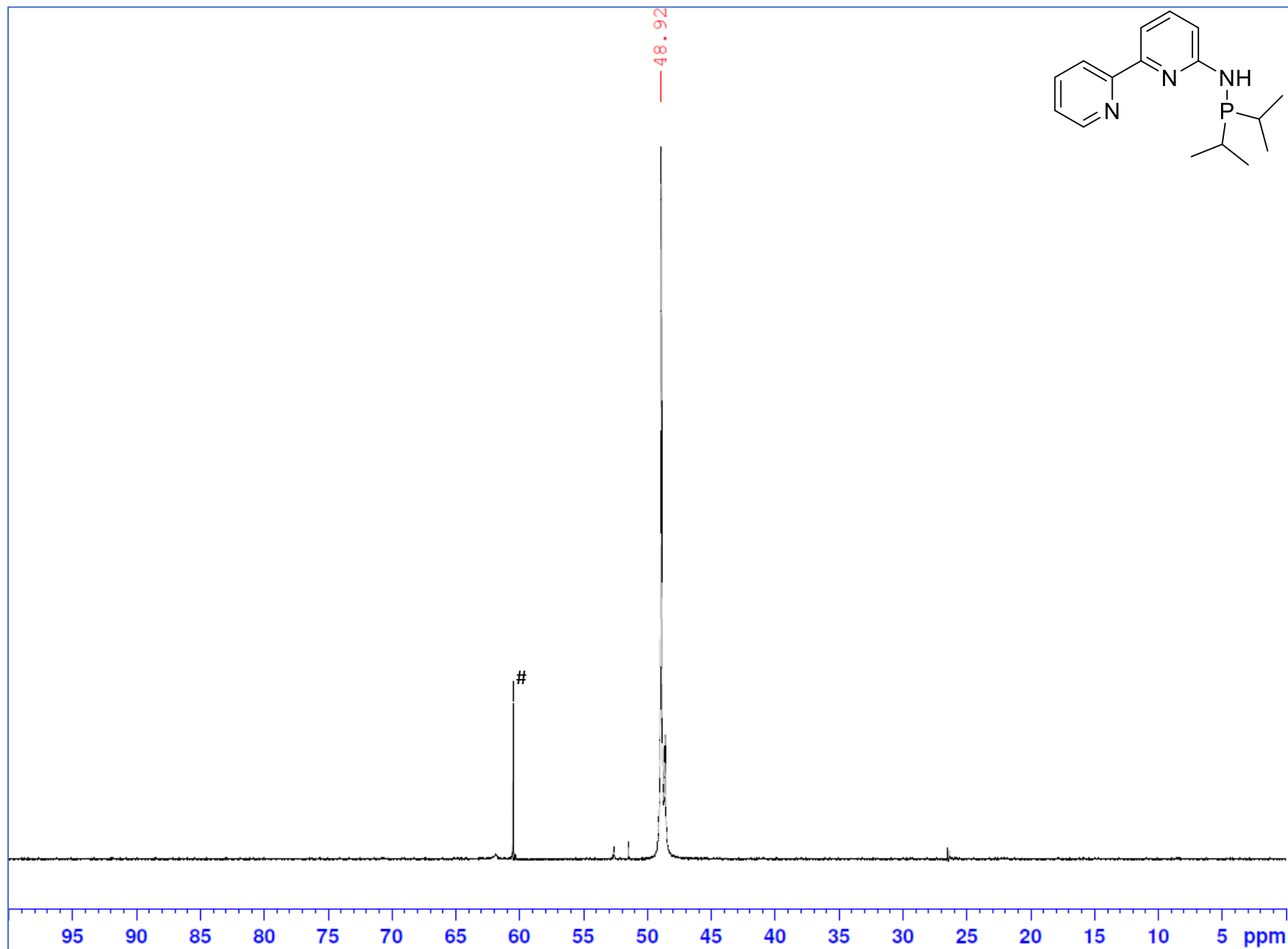
In the glovebox a screw cap NMR tube was charged with $\text{Mn}(\text{CO})_5\text{Br}$ (9.6 mg, 35 μmol , 1 equiv) dissolved in THF- d_8 (0.3 mL) and **$\text{bpy-}^6\text{NH-}^i\text{PrP}$** (10.0 mg, 35 μmol , 1 equiv) dissolved in THF- d_8 (0.3 mL). The NMR tube was slightly agitated to ensure mixing of the reactants. Storage at room temperature over 72 h afforded yellow crystals suitable for X-ray analysis.



Supplementary Figure S1. ¹H-NMR spectrum of **bpy**-⁶NH-ⁱPr₂P in THF-*d*₆; * ≡ deuterated solvent.

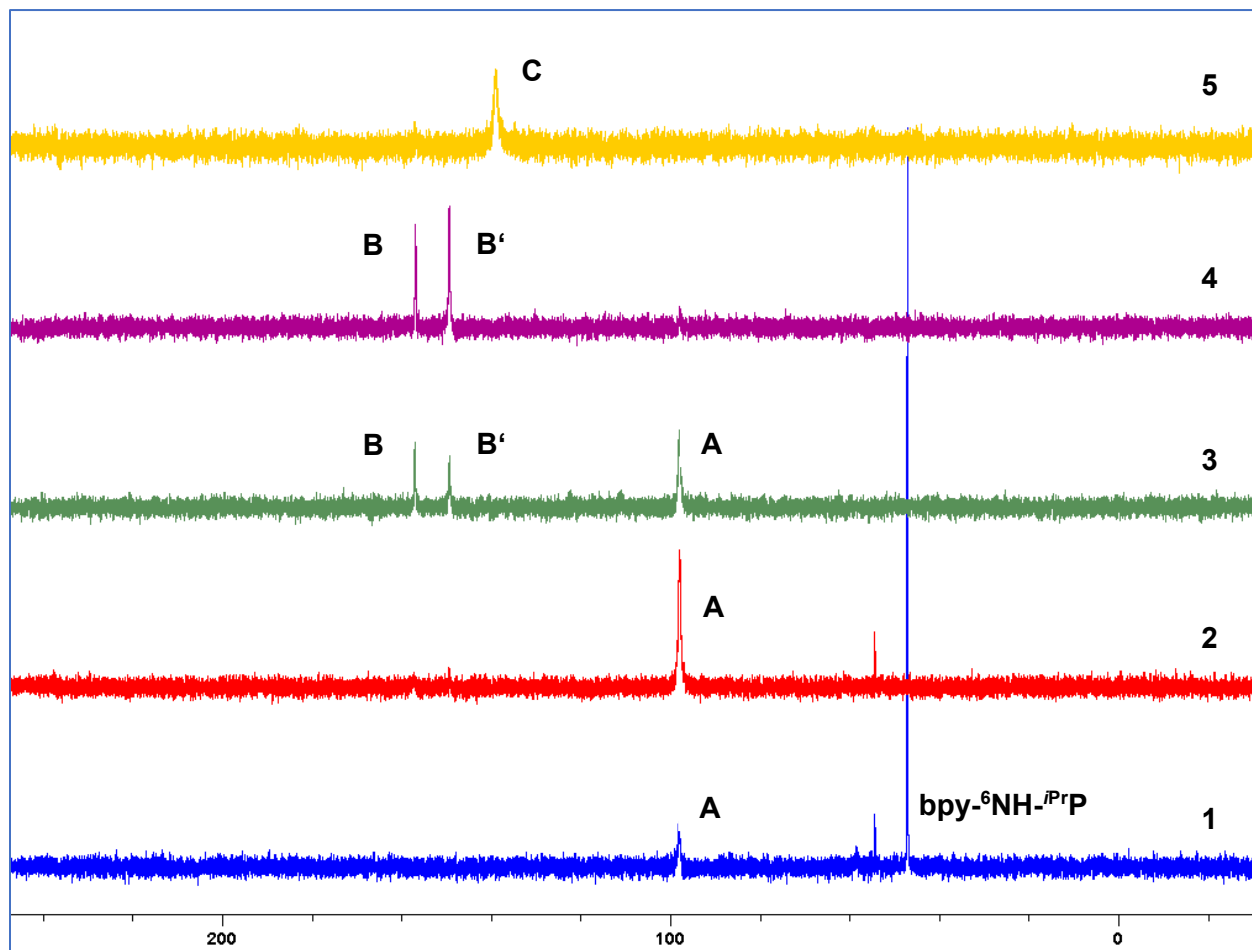


Supplementary Figure S2. ^{13}C (APT)-NMR spectrum of **bpy- ^6NH - $i\text{Pr}_2\text{P}$** in $\text{THF-}d_6$; * \equiv deuterated solvent.

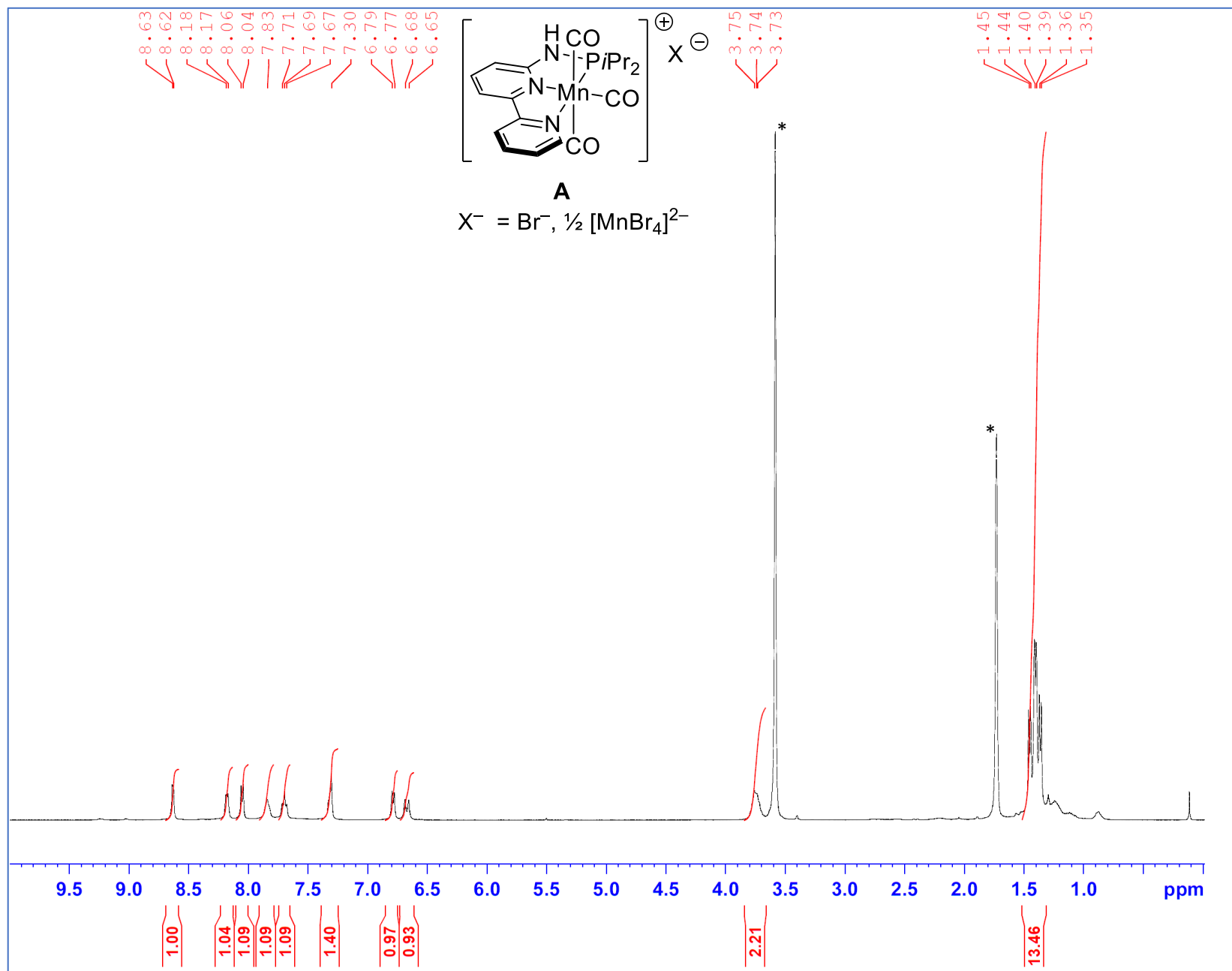


Supplementary Figure S3. $^{31}\text{P}\{^1\text{H}\}$ -NMR spectrum of **bpy-⁶NH-ⁱPrP** in $\text{THF-}d_6$; # \equiv signal vanishes upon complexation (see Supplementary Figure S4).

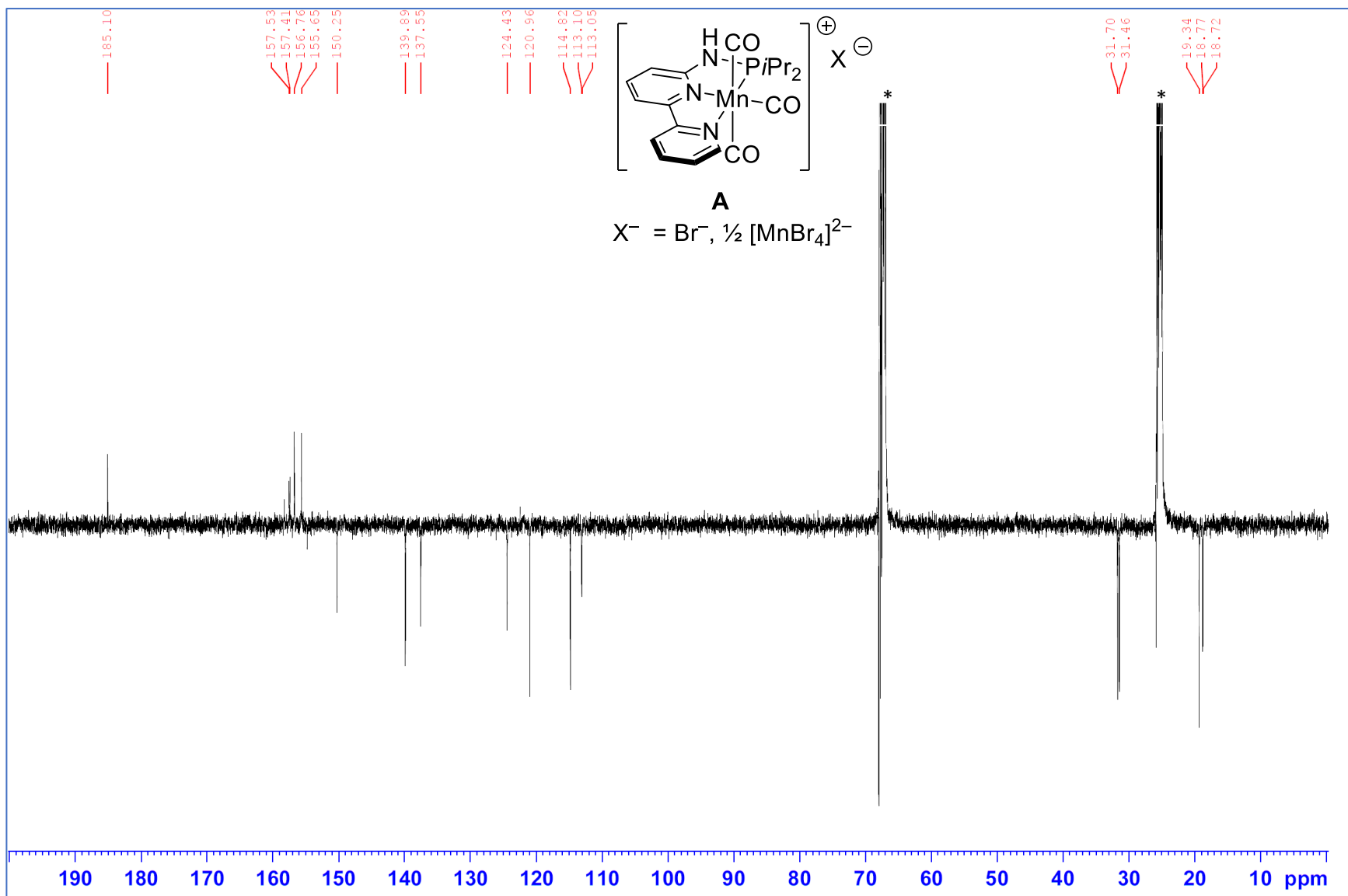
Complexation and ^{31}P -NMR spectroscopic investigation:



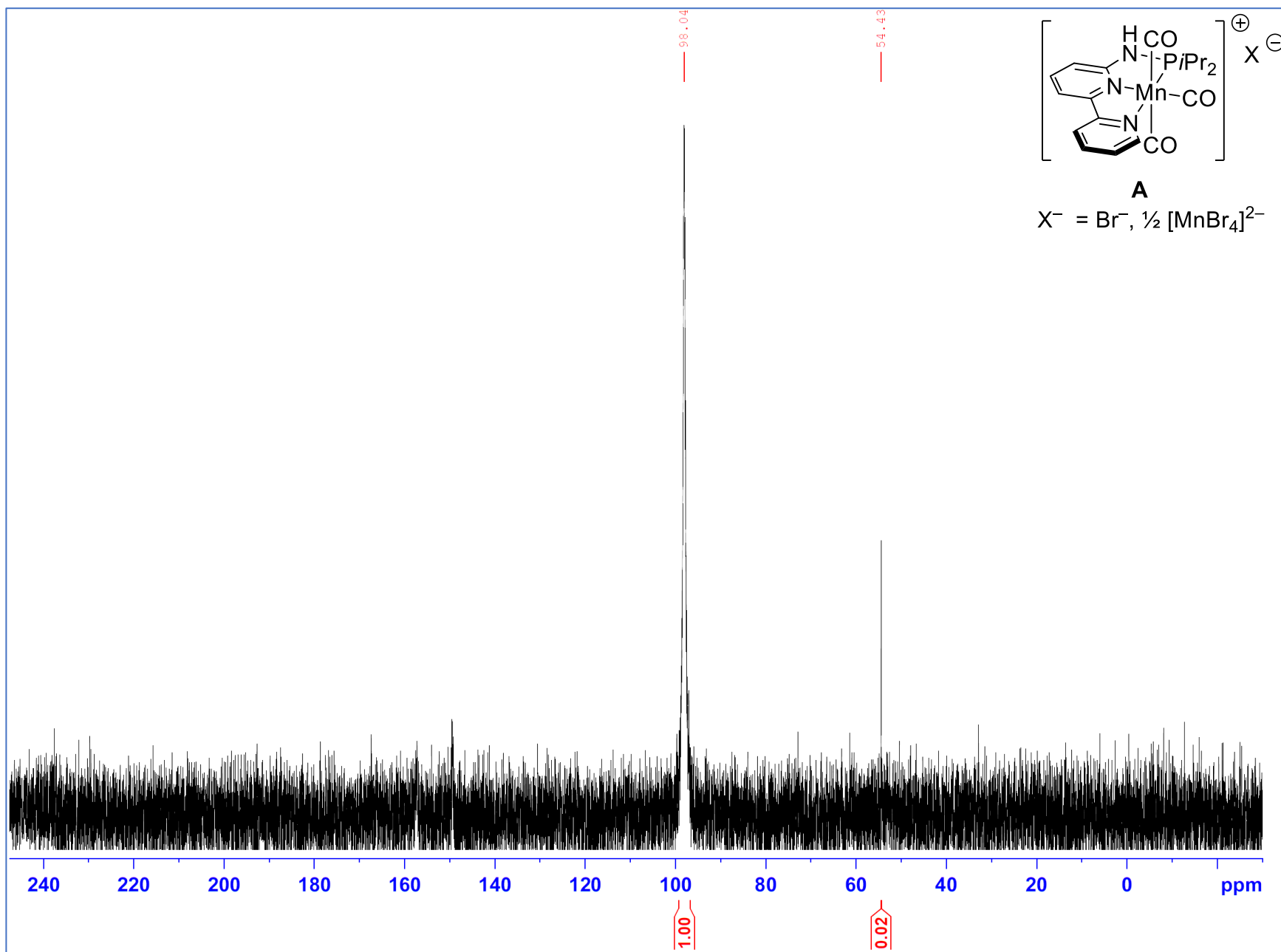
Supplementary Figure S4. Complexation reaction of $\text{Mn}(\text{CO})_5\text{Br}$ with $\text{bpy-}^6\text{NH-}^i\text{PrP}$ monitored by ^{31}P -NMR spectroscopy in $\text{THF-}d_6$. **1** 5 min at room temperature. **2** 2 h at room temperature. **3** 6 h at room temperature. **4** 24 h at room temperature. **5** 5 min after addition of 2 equiv KOtBu.



Supplementary Figure S5. 1H -NMR spectrum of **A** in $THF-d_8$; * \equiv deuterated solvent.



Supplementary Figure S6. ^{13}C (APT)-NMR spectrum of **A** in $\text{THF-}d_8$; * \equiv deuterated solvent.



Supplementary Figure S7. $^{31}\text{P}\{^1\text{H}\}$ -NMR spectrum of **A** in $\text{THF-}d_6$.

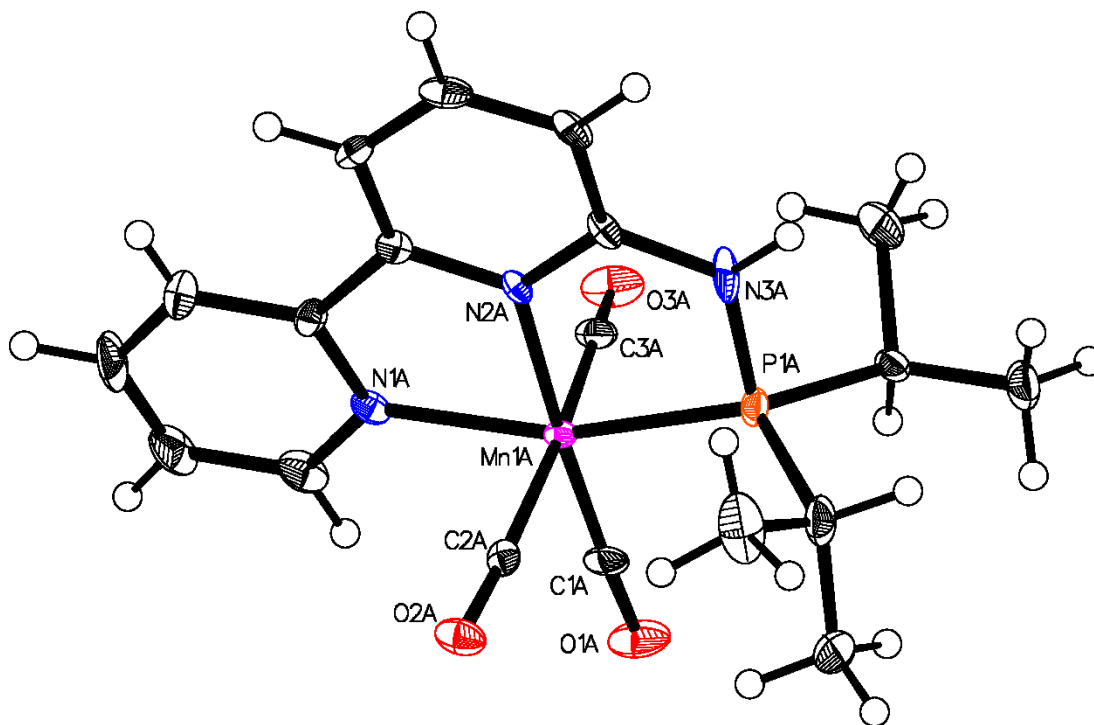
X-ray Analysis

The X-ray intensity data were measured on Bruker D8 Venture and X8 APEX2 diffractometer equipped with multilayer monochromators, Mo K α INCOATEC micro focus sealed tubes and Oxford and Cryoflex2 cooling systems. The structure was solved by *direct methods* and refined by *full-matrix least-squares techniques*. Non-hydrogen atoms were refined with *anisotropic displacement parameters*. Hydrogen atoms were inserted at calculated positions and refined with riding model. The following software was used: *Bruker SAINT software package*⁴ using a narrow-frame algorithm for frame integration, *SADABS*⁵ for absorption correction, *OLEX2*⁶ for structure solution, refinement, molecular diagrams and graphical user-interface, *Shelxle*⁷ for refinement and graphical user-interface *SHELXS-2015*⁸ for structure solution, *SHELXL-2015*⁹ for refinement, *Platon*¹⁰ for symmetry check. Experimental data and CCDC-Codes Experimental data and CCDC-Code (Available online: <http://www.ccdc.cam.ac.uk/conts/retrieving.html>) can be found in Table S2. Crystal data, data collection parameters, and structure refinement details are given in Tables S2–S5. Crystal structures and hydrogen bonds are visualized in Figures S8–S10.

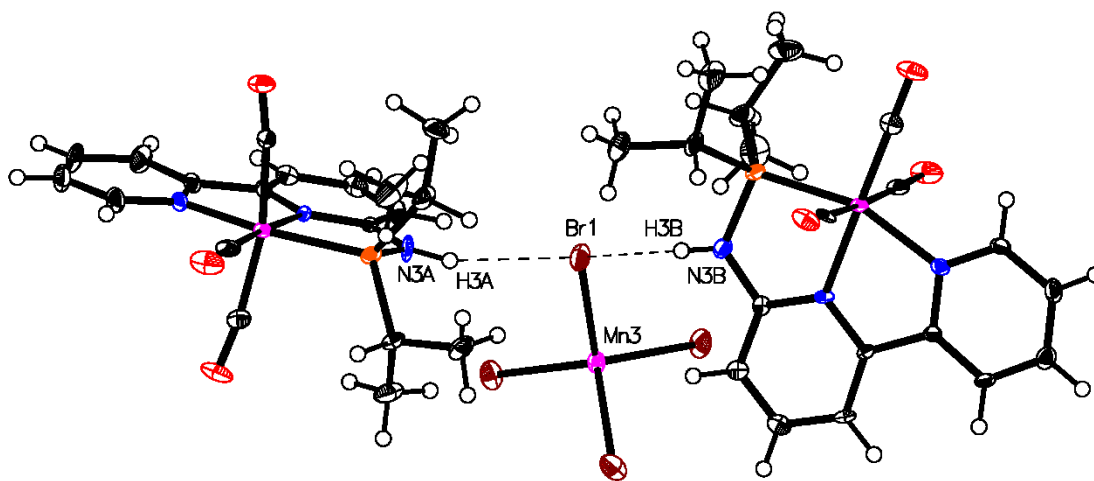
Table S2. Experimental parameter and CCDC-Code.

sample	machine	source	<i>t</i>	detector distance	time/frame	#frames	frame width	CCDC
	Bruker		(K)	(mm)	(s)		(deg)	
[(bpy- ⁶ NH- ⁱ PrP)Mn(CO) ₃] ₂ [MnBr ₄] (A)	D8	Mo	100	35	25	556	0.500	1900349
[(bpy- ⁶ N- ⁱ PrP)MnBr ₂]	X8	Mo	100	35	8	782	0.500	1900350

[(bpy-⁶NH-ⁱPrP)Mn(CO)₃]₂[MnBr₄] (A)



Supplementary Figure S8 Crystal structure, drawn with 50% displacement ellipsoid. The bond precision for C-C single bonds is 0.0064Å. Counter ion and second independent molecule (B) from asymmetric unit are omitted for clarity.



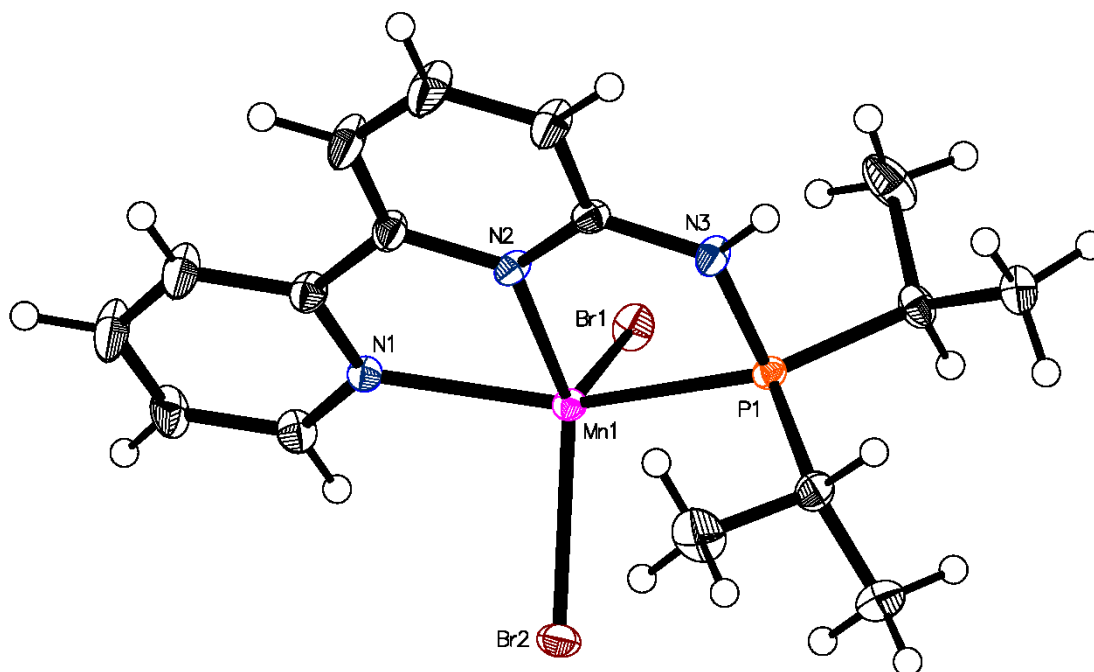
Supplementary Figure S9. Visualisation of weak to moderate hydrogen bonds N3A-H3A-Br1 and N3B-H3B-Br1 influencing the bond length of Mn3-Br1. In comparison to Mn3-Br2, Mn3-Br3 and Mn3-Br4, Mn3-Br1 is elongated.

Table S3. Sample and crystal data.

Chemical formula	C38H44Br4Mn3N6O6P2	Crystal system	monoclinic	
Formula weight [g/mol]	1227.19	Space group	<i>P21/c</i>	
Temperature [K]	100	Z	4	
Measurement method	ω and ω scans	Volume [Å³]	4754.20(18)	
Radiation (Wavelength [Å])	MoK α ($\lambda = 0.71073$)	Unit cell dimensions [Å] and [°]	17.2071(3)	90
Crystal size / [mm³]	0.251 × 0.184 × 0.006		12.2037(3)	96.3421(9)
Crystal habit	clear light yellow plate		22.7795(5)	90
Density (calculated) / [g/cm³]	1.715	Absorption coefficient / [mm⁻¹]	4.262	
Abs. correction Tmin	0.6235	Abs. correction Tmax	0.746	
Abs. correction type	multiscan	F(000) [e⁻]	2428	

Table S4. Data collection and structure refinement.

Index ranges	-24 ≤ h ≤ 23, -13 ≤ k ≤ 17, -28 ≤ l ≤ 32	Theta range for data collection [°]	4.37 to 60.068	
Reflections number	26011	Data / restraints / parameters	13888/0/540	
Refinement method	Least squares	Final R indices	all data	R1 = 0.1043, wR2 = 0.1318
Function minimized	$\sum w(F_o^2 - F_c^2)^2$		$l > 2\sigma(l)$	R1 = 0.0543, wR2 = 0.1144
Goodness-of-fit on F²	0.994	Weighting scheme	$w = 1/[\sigma^2(F_o^2) + (0.0434P)^2]$	
Largest diff. peak and hole [e Å⁻³]	1.02/-1.41		where $P = (F_o^2 + 2F_c^2)/3$	

[(bpy-⁶NH-ⁱPrP)MnBr₂]

Supplementary Figure S10. Crystal structure, drawn with 50% displacement ellipsoid. The bond precision for C-C single bonds is 0.0064Å. Counter ion and second independent molecule (B) from asymmetric unit are omitted for clarity.

Table S5. Sample and crystal data.

Chemical formula	C ₁₆ H ₂₂ Br ₂ MnN ₃ P	Crystal system	monoclinic	
Formula weight [g/mol]	502.23	Space group	<i>P</i> 2 ₁ / <i>n</i>	
Temperature [K]	100	Z	4	
Measurement method	ω and φ scans	Volume [Å³]	1970.4(3)	
Radiation (Wavelength [Å])	MoKα (λ = 0.71073)	Unit cell dimensions [Å] and [°]	10.0429(8)	90
Crystal size / [mm³]	0.3 × 0.2 × 0.2		13.6802(12)	104.517(3)
Crystal habit	clear yellow block		14.8147(11)	90
Density (calculated) / [g/cm³]	1.693	Absorption coefficient / [mm⁻¹]	4.81	
Abs. correction Tmin	0.6239	Abs. correction Tmax	0.746	
Abs. correction type	multiscan	F(000) [e⁻]	996	

Table S6. Sample and crystal data.

Index ranges	-14 ≤ h ≤ 12, -19 ≤ k ≤ 19, -20 ≤ l ≤ 20	Theta range for data collection [°]	4.114 to 60.158	
Reflections number	19948	Data / restraints / parameters	5700/0/213	
Refinement method	Least squares	Final R indices	all data	R1 = 0.0658, wR2 = 0.0739
Function minimized	$\sum w(F_o^2 - F_c^2)^2$		I > 2σ(I)	R1 = 0.0385, wR2 = 0.0669
Goodness-of-fit on F²	0.994	Weighting scheme	w=1/[σ ² (F _o ²)+(0.0255P) ²]	
Largest diff. peak and hole [e Å⁻³]	0.52/-0.56		where P=(F _o ² +2F _c ²)/3	

General Procedure for Catalysis

Exemplary preparation of stock solution: In the glovebox a 4 mL vial was charged with $\text{Mn}(\text{CO})_5\text{Br}$ (37.1 mg, 135 μmol , 1 equiv) and **bpy-⁶NH-ⁱPrP** (38.8 mg, 135 μmol , 1 equiv), followed by addition of DME (2.7 mL) to prepare a stock solution. After 30 min of stirring at room temperature a distinct color change from light orange to brown was observed and this stock solution was used without any further purification.

Standard procedure for N-alkylation reaction: In the glovebox, a 2 mL vial was charged with KH (20.0 mg, 0.5 mmol, 0.5 equiv) and catalyst stock solution (100 μL , $c = 50 \mu\text{mol mL}^{-1}$ in DME, 5 μmol , 0.005 equiv). Benzyl alcohol (104 μL , 108.1 mg, 1 mmol, 1.0 equiv) was added dropwise via syringe and hydrogen was allowed to evolve for 1 min. Aniline (99 μL , 102.0 mg, 1.1 mmol, 1.1 equiv) was added via syringe at once subsequently. The vial was capped and placed in a metal-block on a heated stirring plate. After the desired amount of reaction time, the vial was allowed to cool to ambient temperature. *p*-Xylene (100 μL) was added as standard, the reaction mixture was treated with H_2O (0.5 mL) and extracted with EtOAc ($3 \times 0.7 \text{ mL}$). The sample was analyzed by GC-MS and GC-FID. The product (**1a**) was isolated by flash column chromatography on Al_2O_3 using (9:1) heptanes/DCM, yielding 144.7 mg (0.79 mmol, 79%) of a colorless oil.

Upscaling procedure for N-alkylation reaction: In the glovebox a 25 mL Schlenk-tube was charged with $\text{Mn}(\text{CO})_5\text{Br}$ (6.9 mg, 25 μmol , 0.0025 equiv), **bpy-⁶NH-ⁱPrP** (7.2 mg, 25 μmol , 0.0025 equiv) and KH (160.0 mg, 0.4 mmol, 0.4 equiv), followed by DME (1 mL). The mixture was stirred for 30 min at room temperature. Benzyl alcohol (1.04 mL, 1.081 g, 10.0 mmol, 1.0 equiv) was added dropwise via syringe and hydrogen was allowed to evolve for 2 min. Aniline (0.95 μL , 978.5 mg, 10.5 mmol, 1.05 equiv) was added via syringe subsequently. The Schlenk tube was closed and placed in an oil bath at 60 °C on a heated stirring plate. After 24 h, the Schlenk-tube was allowed to cool to ambient temperature. The reaction mixture was treated with H_2O (2 mL) and extracted with EtOAc ($3 \times 10 \text{ mL}$). The product (**1a**) was isolated by flash column chromatography on Al_2O_3 using (9:1) heptanes/DCM yielding 1.79 g (9.77 mmol, 98%) of a colorless oil. The product was characterized with GC-FID and $^1\text{H}/^{13}\text{C}$ -NMR spectroscopy.

Optimization of Conditions

Table S7. Initial Metal Precursor Screening.^[a]

entry	metal precursor	MS 3Å (mg)	conv (%) ^[b]	ratio 1a:1b ^[b]
1	Mn(CO)₅Br	-	>99	only 1a
2	Mn(CO) ₅ Br	50	>99	only 1a
3	CoCl ₂	-	21	9:91
4	CoCl ₂	50	9	only 1b
5	Fe(CO) ₄ Br ₂	-	19	only 1b
6	Fe(CO) ₄ Br ₂	50	4	only 1b

[a] General conditions: 0.5 mmol of aniline, 0.6 mmol of benzyl alcohol, 0.5 mmol of KOtBu, 25 μmol of metal precursor, 25 μmol of **bpy-⁶NH-ⁱPrP**, 0.5 mL toluene, Ar. [b] Conversion to **1a** and **1b**, determined by GCMS, referenced to aniline consumption.

Table S8. Different catalyst and base loadings.^[a]

entry	x (mol %)	y (mol %)	conv (%) ^[b]	ratio 1a:1b ^[b]
1	3	100	84	98:2
2	3	50	38	85:15
3	1	100	78	99:1
4	1	50	41	81:19
5	1	10	8	only 1b
6 ^[c]	1	10	5	only 1b

[a] General conditions: 0.5 mmol of aniline, 0.6 mmol of benzyl alcohol, 0.5 mL (50 μmol mL⁻¹, 25 μmol) of Mn(CO)₅Br and **bpy-⁶NH-ⁱPrP** in toluene, Ar. [b] Conversion to **1a** and **1b**, determined by GCMS, referenced to aniline consumption. [c] 10 mol % CsF as further additive.

Table S9. Different amounts of solvent.[a]

$$\text{Ph-NH}_2 + \text{Ph-CH}_2\text{OH} \xrightarrow[\text{toluene, 50 }^\circ\text{C, 18 h}]{\text{Mn(CO)}_5\text{Br 1 mol \%}, \text{bpy-}^6\text{NH-}^i\text{Pr}^i\text{P 1 mol \%}, \text{KO}^t\text{Bu 100 mol \%}} \text{Ph-NH-CH}_2\text{Ph} + \text{Ph-N=CH-Ph}$$

1a **1b**

entry	toluene (mL)	conv (%) ^[b]	ratio 1a:1b ^[b]
1	1.5	39	89:11
2	1	60	96:4
3	0.5	76	97:3
4	0.1	93	>99:1
5	neat	94	only 1a

[a] General conditions: 0.5 mmol of aniline, 0.6 mmol of benzyl alcohol, 0.5 mL (c = 50 $\mu\text{mol mL}^{-1}$, 25 μmol) of $\text{Mn(CO)}_5\text{Br}$ and **bpy-⁶NH-ⁱPrⁱP** in toluene, Ar. [b] Conversion to **1a** and **1b**, determined by GCMS, referenced to aniline consumption.

Table S10. Solvent screening.^[a]

entry	solvent	conv (%) ^[b]	ratio 1a:1b ^[b]
1	toluene	86 ^[d]	99:1
2	tetrahydrofuran	98	only 1a
3	acetonitrile	– ^[c]	–
4	1,2-difluoro benzene	70 ^[c]	97:3
5	nitromethane	14	only 1a
6	1,2-dimethoxyethane (DME)	>99	only 1a
7	acetone	4	41:59
8	dimethyl formamide	75 ^[c]	89:11
9	dimethyl sulfoxide	12	only 1a
10	1,4-dioxane	85 ^[d]	only 1a
11	cyclic propylene carbonate	43 ^[c]	17:83
12	<i>n</i> -pentane	75	only 1a
13	nitrobenzene	86 ^[c]	only 1b
14	2-propanol	75 ^[c]	only 1a
15	neat	93	99:1

[a] General conditions: 1.0 mmol of aniline, 1.2 mmol of benzyl alcohol, 0.1 mL of solvent, 50 μmol of Mn(CO)₅Br, 50 μmol of **bpy-⁶NH-ⁱPrP**, Ar. [b] Conversion to **1a** and **1b**, determined by GCMS, referenced to aniline consumption. [c] Side reactions with solvent. [d] No benzyl alcohol left.

Table S11. Base screening with different loadings.^[a]

$$\text{Ph-NH}_2 + \text{Ph-CH}_2\text{OH} \xrightarrow[\text{DME, 50 }^\circ\text{C, 20 h}]{\text{Mn(CO)}_5\text{Br 0.5 mol \%}, \text{bpy-6-NH-}^i\text{PrP 0.5 mol \%}, \text{base}} \text{Ph-NH-CH}_2\text{Ph} + \text{Ph-N=CH-Ph}$$

1a
1b

entry	base	loading (mol %)	conv. (%) ^[b]	ratio 1a:1b ^[b]
1	KOH	10	3	only 1a
2	KOH	50	9	only 1a
3	NaOH	10	-	-
4	NaOH	50	9 ^[c]	86:14
5	KH	10	9	63:17
6	KH	20	25	90:10
7	KH	30	56	94:6
8	KH	40	78	97:3
9	KH	50	>99	only 1a
10	NaH	10	6	only 1a
11	NaH	50	58	96:4
12	NaNH ₂	10	2	only 1a
13	NaNH ₂	50	13 ^[c]	57:43
14	KO ^t Bu	10	5	38:62
15	KO ^t Bu	50	79	99:1
16	NaO ^t Bu	10	2	only 1a
17	NaO ^t Bu	50	62	96:4
18	Cs ₂ CO ₃	10	-	-
19	Cs ₂ CO ₃	50	2	only 1a
20	NaHDMS	50	-	-
21	LiBDMA	50	-	-
22	K ₂ CO ₃	100	-	-

[a] General conditions: 0.5 mmol of aniline, 0.6 mmol of benzyl alcohol, 0.1 mL (c = 250 μmol mL⁻¹, 25 μmol) of Mn(CO)₅Br and **bpy-6-NH-ⁱPrP** in DME, Ar. [b] Conversion to **1a** and **1b**, determined by GCMS, referenced to aniline consumption. [c] No benzyl alcohol left.

Table S12. Substrate ratio.[a]

entry	aniline (equiv)	benzyl alcohol (equiv)	conv (%) ^[b]	ratio 1a:1b ^[b]
1 ^[c,d]	1	1	22	91:9
2	1	1	99	99:1
3	1.5	1	92	only 1a
4	1	1.5	43	96:4
5 ^[e]	1	1	65	only 1b

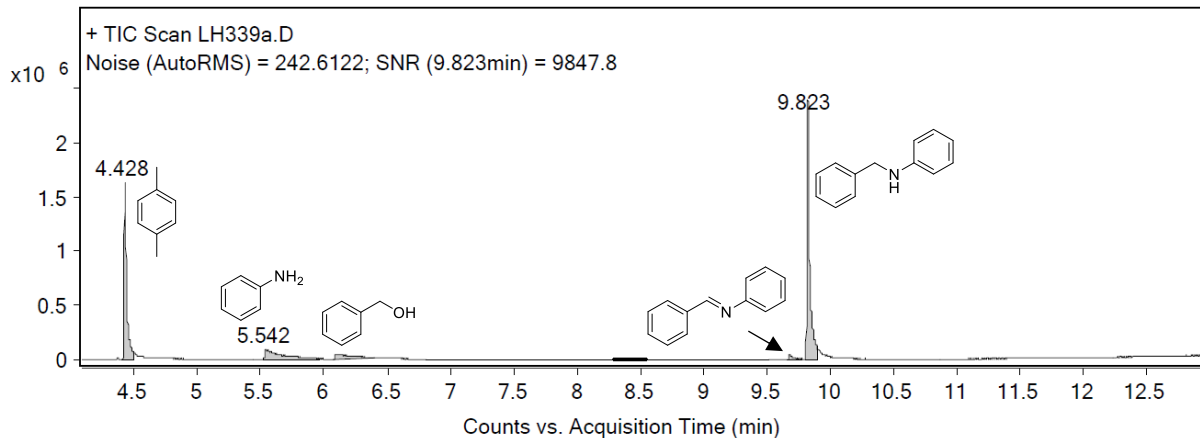
[a] General conditions: 1 equiv \equiv 0.5 mmol, 0.1 mL ($c = 250 \mu\text{mol mL}^{-1}$, 25 μmol) $\text{Mn}(\text{CO})_5\text{Br}$ and $\text{bpy-}^6\text{NH-}i\text{PrP}$ in DME, Ar. [b] Conversion to **1a** and **1b**, determined by GCMS, referenced to consumption of limiting reagent: [c] Aniline added first. [d] Reaction at 25 °C. [e] Open system.

Table S13. Cross check of optimized conditions.[a]

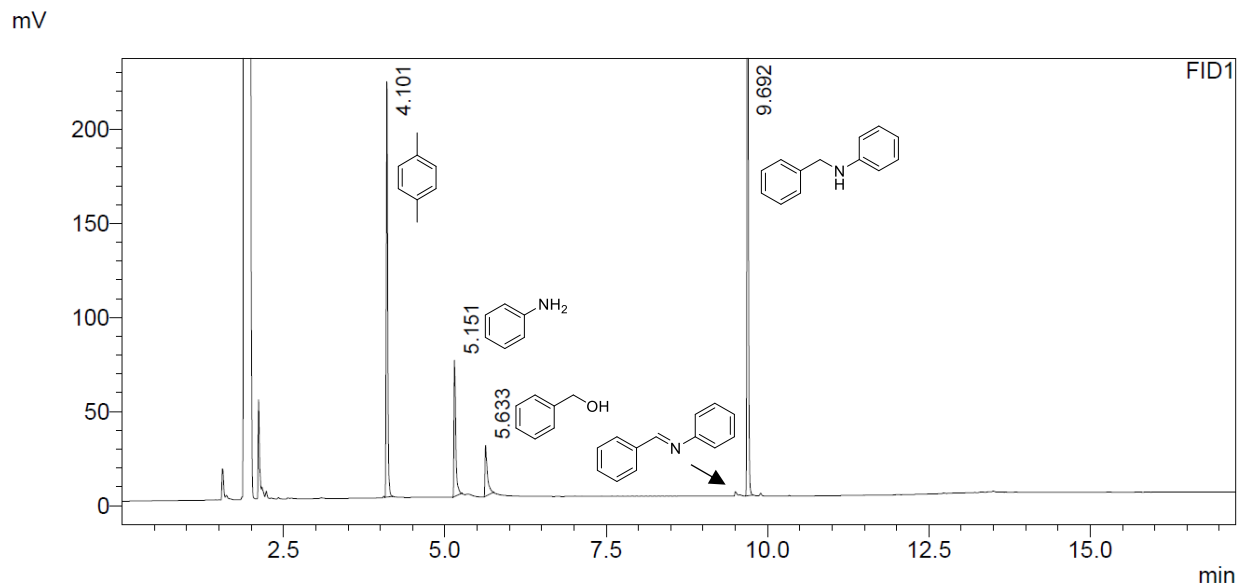
entry	precursor	loading (mol %)	conv (%) ^[b]	ratio 1a:1b ^[b]
1	$\text{Mn}(\text{CO})_5\text{Br}$	0.5	95	98:2
2	MnCl_2	1	1	only 1a
3	$\text{FeCl}_2(\text{THF})_{1.5}$	1	0	-
4	CoCl_2	1	1	38:62
5 ^[c]	$\text{Mn}(\text{CO})_5\text{Br}$	1	3	90:10
6 ^[d]	-	-	0	-
7 ^[e]	$\text{Mn}(\text{CO})_5\text{Br}$	1	0	-
8 ^[f]	-	-	4	only 1a

[a] General reaction conditions: 0.5 mmol of aniline, 0.6 mmol of benzyl alcohol, 0.1 mL of DME, 1:1 ratio metal precursor to $\text{bpy-}^6\text{NH-}i\text{PrP}$, Ar. [b] Conversion to **1a** and **1b**; Aniline consumption determined by GCMS. [c] No ligand added. [d] Without metal precursor. [e] No base added. [f] Without catalyst.

Representative GC-MS and GC-FID traces



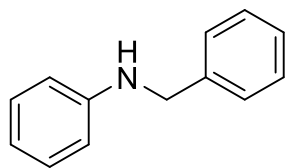
Supplementary Figure S11. GC-MS trace of the N-benylation of aniline.



Supplementary Figure S12. GC-FID trace of the N-benylation of aniline.

Analytical Data of N-alkylated anilines

N-benzylaniline (**1a**)



Pale yellow oil. Yield: 144.7 mg (0.79 mmol, 79%), GC-FID: 99%.

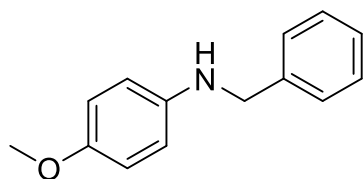
¹H-NMR (400.3 MHz, CDCl₃, 298 K): δ = 7.33–7.42 (m, 4H, Ar), 7.26–7.32 (m, 1H, Ar), 7.15–7.22 (m, 2H, Ar), 6.70–6.76 (m, 1H, Ar), 6.63–6.68 (m, 2H, Ar), 4.34 (s, 2H, Ar-CH₂-NH), 4.03 (br s, 1H, CH₂-NH-Ar);

¹³C{¹H}-NMR (100.6 MHz, CDCl₃, 298 K): δ = 148.3 (C_q), 139.6 (C_q), 129.4, 128.8, 127.7, 127.4, 117.7, 113.0 (aryl), 48.5 (CH₂). The NMR spectroscopic data are in accordance with the literature.¹¹

HRMS (ESI) m/z calcd. for [C₁₃H₁₄N, M+H]⁺: 184.1126; Found: 184.1118.

GC-FID Retention time (min): 9.692.

N-benzyl-4-methoxyaniline (**2a**)



Light brown oil. Yield: 107.7 mg (0.50 mmol, 50%), GC-FID: 97%.

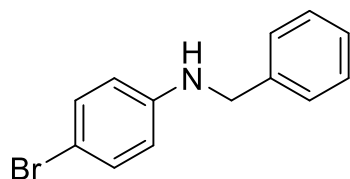
¹H-NMR (400.3 MHz, CDCl₃, 298 K): δ = 7.37–7.47 (m, 4H, Ar), 7.31–7.36 (m, 1H, Ar), 6.82–6.87 (m, 2H, Ar), 6.63–6.68 (m, 2H, Ar), 4.33 (s, 2H, Ar-CH₂-NH), 3.79 (br s, 4H, OCH₃ & CH₂-NH-Ar);

¹³C{¹H}-NMR (100.6 MHz, CDCl₃, 298 K): δ = 152.3 (C_q), 142.6 (C_q), 139.8 (C_q), 128.6, 127.6, 127.2, 115.0, 114.2 (aryl), 55.8 (OCH₃), 49.3 (CH₂). The NMR spectroscopic data are in accordance with the literature.¹¹

HRMS (ESI) m/z calcd. for [C₁₄H₁₆NO, M+H]⁺: 214.1232; Found: 214.1227.

GC-FID Retention time (min): 11.820.

N-benzyl-4-bromoaniline (**2b**)



Dark brown oil. Yield: 107.7 mg (0.50 mmol, 50%), GC-FID: 94%.

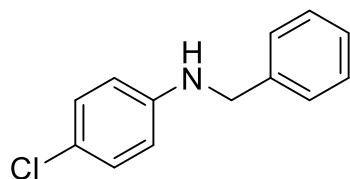
¹H-NMR (400.3 MHz, CDCl₃, 298 K): 7.32–7.36 (m, 4H, Ar), 7.26–7.31 (m, 1H, Ar), 7.21–7.26 (m, 2H, Ar), 6.48–6.52 (m, 2H, Ar), 4.30 (br s, 2H, Ar-CH₂-NH), 4.06 (br s, 1H, CH₂-NH-Ar); **¹³C{¹H}-NMR** (100.6 MHz, CDCl₃, 298 K): δ = 147.2 (C_q), 139.0 (C_q), 132.1, 128.8,

127.54, 127.53, 114.6 (C_q), 109.3 (aryl), 48.4 (CH₂). The NMR spectroscopic data are in accordance with the literature.¹¹

HRMS (ESI) m/z calcd. for [C₁₃H₁₃BrN, M+H]⁺: 262.0231; Found: 262.0221.

GC-FID Retention time (min): 12.280.

N-benzyl-4-chloroaniline (**2c**)



Orange-brown oil. Yield: 190.0 mg (0.87 mmol, 87%), GC-FID: 95%.

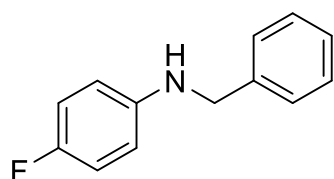
¹H-NMR (400.3 MHz, CDCl₃, 298 K): δ = 7.33–7.39 (m, 4H, Ar), 7.27–7.33 (m, 1H, Ar), 7.09–7.14 (m, 2H, Ar), 6.53–6.58 (m, 2H, Ar), 4.29–4.33 (m, 2H, Ar-CH₂-NH), 4.06 (br s, 1H, CH₂-NH-Ar);

¹³C{¹H}-NMR (100.6 MHz, CDCl₃, 298 K): δ = 146.8 (C_q), 139.1 (C_q), 129.2, 128.8, 127.6, 127.5, 122.3 (C_q), 114.1 (aryl), 48.5 (CH₂). The NMR spectroscopic data are in accordance with the literature.¹²

HRMS (ESI) m/z calcd. for [C₁₃H₁₃ClN, M+H]⁺: 218.0736; Found: 218.0728.

GC-FID Retention time (min): 11.797.

N-benzyl-4-fluoroaniline (**2d**)



Dark yellow oil. Yield: 198.7 mg (0.99 mmol, 99%), GC-FID: >99%.

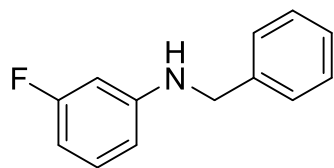
¹H-NMR (400.3 MHz, CDCl₃, 298 K): δ = 7.34–7.47 (m, 4H, Ar), 7.27–7.32 (m, 1H, Ar), 6.85–6.93 (m, 2H, Ar), 6.55–6.61 (m, 2H, Ar), 4.30 (s, 2H, Ar-CH₂-NH), 3.93 (br s, 1H, CH₂-NH-Ar);

¹³C{¹H}-NMR (100.6 MHz, CDCl₃, 298 K): δ = 156.0 (C_q, d, ¹J_{F,C} = 234.9 Hz), 144.6 (C_q, d, ⁴J_{F,C} = 2.1 Hz), 139.4 (C_q), 128.8, 127.6, 127.4, 115.8 (d, ²J_{F,C} = 22.3 Hz), 113.8 (d, ³J_{F,C} = 7.3 Hz, aryl), 49.0 (CH₂); **¹⁹F-NMR** (659.0 MHz, CDCl₃, 298 K): –127.96 (m). The NMR spectroscopic data are in accordance with the literature.¹³

HRMS (ESI) m/z calcd. for [C₁₃H₁₃FN, M+H]⁺: 202.1032; Found: 202.1026.

GC-FID Retention time (min): 10.660.

N-benzyl-3-fluoroaniline (**2e**)



Orange oil. Yield: 199.0 mg (0.99 mmol, 99%), GC-FID: >99%.

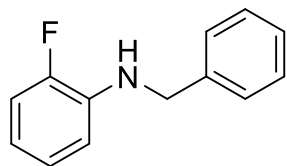
¹H-NMR (400.3 MHz, CDCl₃, 298 K): δ = 7.42–7.49 (m, 4H, Ar), 7.36–7.42 (m, 1H, Ar), 7.15–7.22 (m, 1H, Ar), 6.45–6.55 (m, 2H, Ar), 6.38–6.44 (m, 1H, Ar), 4.37 (s, 2H, Ar-CH₂-NH), 4.20 (br s, 1H, CH₂-NH-Ar);

¹³C{¹H}-NMR (100.6 MHz, CDCl₃, 298 K): δ = 164.2 (C_q, d, ¹J_{F,C} = 242.8 Hz); 150.0 (C_q, d, ³J_{F,C} = 10.4 Hz), 138.9 (C_q), 130.4 (d, ³J_{F,C} = 10.2 Hz), 128.8, 127.5, 127.4, 108.8 (d, ⁴J_{F,C} = 2.2 Hz), 103.9 (d, ²J_{F,C} = 21.5 Hz), 99.6 (d, ²J_{F,C} = 25.3 Hz, aryl), 48.2 (CH₂); **¹⁹F-NMR** (659.0 MHz, CDCl₃, 298 K): –112.78 (m). The NMR spectroscopic data are in accordance with the literature.¹⁴

HRMS (ESI) m/z calcd. for [C₁₃H₁₃FN, M+H]⁺: 202.1032; Found: 202.1025.

GC-FID Retention time (min): 10.760.

N-benzyl-2-fluoroaniline (**2f**)



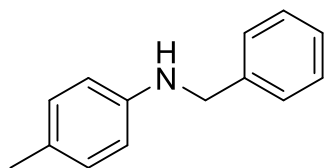
Pale yellow oil. Yield: 184.8 mg (0.92 mmol, 92%), GC-FID: 93%.

¹H-NMR (400.3 MHz, CDCl₃, 298 K): δ = 7.44–7.53 (m, 4H, Ar), 7.37–7.44 (m, 1H, Ar), 7.05–7.16 (m, 2H, Ar), 6.72–6.84 (m, 2H, Ar), 4.46 (br s, 3H, Ar-CH₂-NH & CH₂-NH-Ar); **¹³C{¹H}-NMR** (100.6 MHz, CDCl₃, 298 K): δ = 151.6 (C_q, d, ¹J_{F,C} = 238.4 Hz), 139.0 (C_q), 136.7 (C_q, d, ²J_{F,C} = 18.5 Hz), 128.8, 127.42, 127.40, 124.7 (d, ³J_{F,C} = 3.7 Hz), 116.9 (d, ³J_{F,C} = 11.2 Hz), 114.5 (d, ²J_{F,C} = 18.5 Hz), 112.4 (d, ⁴J_{F,C} = 2.9 Hz, aryl), 47.9 (CH₂); **¹⁹F-NMR** (659.0 MHz, CDCl₃, 298 K): –136.50 (m). The NMR spectroscopic data are in accordance with the literature.¹³

HRMS (ESI) m/z calcd. for [C₁₃H₁₃FN, M+H]⁺: 202.1032; Found: 202.1024.

GC-FID Retention time (min): 10.356.

N-benzyl-4-methylaniline (**2g**)



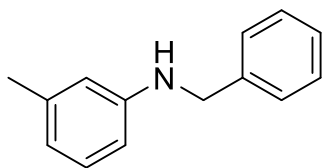
Orange oil. Yield: 135.8 mg (0.69 mmol, 69%), GC-FID: 91%.

¹H-NMR (400.3 MHz, CDCl₃, 298 K): δ = 7.46–7.57 (m, 4H, Ar), 7.39–7.46 (m, 1H, Ar), 7.12–7.19 (m, 2H, Ar), 6.67–6.76 (m, 2H, Ar), 4.43 (s, 2H, Ar-CH₂-NH), 4.00 (br s, 1H, CH₂-NH-Ar), 2.42 (s, 3H, CH₃); **¹³C{¹H}-NMR** (100.6 MHz, CDCl₃, 298 K): δ = 146.0 (C_q), 139.8 (C_q), 129.8, 128.6, 127.5, 127.2, 126.7 (C_q), 113.1 (aryl), 48.6 (CH₂), 20.5 (CH₃). The NMR spectroscopic data are in accordance with the literature.¹¹

HRMS (ESI) m/z calcd. for [C₁₄H₁₆N, M+H]⁺: 198.1283; Found: 198.1279.

GC-FID Retention time (min): 11.106.

N-benzyl-3-methylaniline (**2h**)



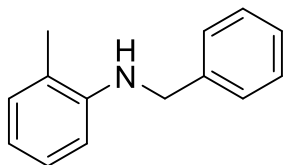
Brown oil. Yield: 166.7 mg (0.85 mmol, 85%), GC-FID: 90%.

¹H-NMR (400.3 MHz, CDCl₃, 298 K): δ = 7.45–7.53 (m, 4H, Ar), 7.39–7.44 (m, 1H, Ar), 7.18–7.24 (m, 1H, Ar), 6.68–6.72 (m, 1H, Ar), 6.55–6.61 (m, 2H, Ar), 4.43 (s, 2H, Ar-CH₂-NH), 4.04 (br s, 1H, CH₂-NH-Ar), 2.42 (s, 3H, CH₃); **¹³C{¹H}-NMR** (100.6 MHz, CDCl₃, 298 K): δ = 148.3 (C_q), 139.7 (C_q), 139.0 (C_q), 129.2, 128.7, 127.6, 127.2, 118.6, 113.7, 110.0 (aryl), 48.4 (CH₂), 21.7 (CH₃). The NMR spectroscopic data are in accordance with the literature.¹⁴

HRMS (ESI) m/z calcd. for [C₁₄H₁₆N, M+H]⁺: 198.1283; Found: 198.1277.

GC-FID Retention time (min): 11.070.

N-benzyl-2-methylaniline (**2i**)



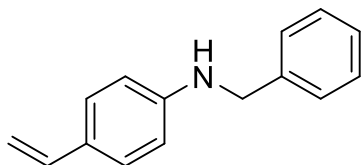
Pale yellow oil. Yield: 123.1 mg (0.62 mmol, 62%), GC-FID: 76%.

¹H-NMR (400.3 MHz, CDCl₃, 298 K): δ = 7.33–7.42 (m, 2H, Ar), 7.26–7.32 (m, 1H, Ar), 7.06–7.14 (m, 2H, Ar), 6.65–6.71 (m, 1H, Ar), 6.60–6.65 (m, 1H, Ar), 4.38 (s, 2H, Ar-CH₂-NH), 3.86 (br s, 1H, CH₂-NH-Ar), 2.18 (s, 3H, CH₃); **¹³C{¹H}-NMR** (100.6 MHz, CDCl₃, 298 K): δ = 146.2 (C_q), 139.7 (C_q), 130.2, 128.8, 127.7, 127.4, 127.3, 122.1 (C_q), 117.3, 110.1 (aryl), 48.5 (CH₂), 17.7 (CH₃). The NMR spectroscopic data are in accordance with the literature.¹²

HRMS (ESI) m/z calcd. for [C₁₄H₁₆N, M+H]⁺: 198.1283; Found: 198.1275.

GC-FID Retention time (min): 10.972.

N-benzyl-4-vinylaniline (**2j**)



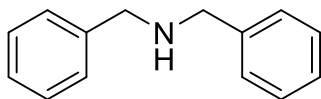
Orange oil. Yield: 91.2 mg (0.44 mmol, 44%), GC-FID: 89%.

¹H-NMR (400.3 MHz, CDCl₃, 298 K): δ = 7.26–7.41 (m, 7H, Ar), 6.64 (t, ³J_{H,H} = 11.0 Hz, 1H, CH=CH₂), 6.59–6.64 (m, 2H, Ar), 5.54 (dd, ³J_{transH,H} = 17.6 Hz, ²J_{H,H} = 1.0 Hz, 1H, CH=CH₂), 5.04 (dd, ³J_{cisH,H} = 10.9 Hz, ²J_{H,H} = 1.0 Hz, 1H, CH=CH₂), 4.37 (s, 2H, Ar-CH₂-NH), 4.12 (br s, 1H, CH₂-NH -Ar); **¹³C{¹H}-NMR** (100.6 MHz, CDCl₃, 298 K): δ = 148.0 (C_q), 139.4 (C_q), 136.8 (CH, vinyl), 128.8, 127.59, 127.58, 127.51, 127.4, 112.9 (aryl), 109.7 (CH₂, vinyl), 48.3 (CH₂). The NMR spectroscopic data are in accordance with the literature.¹¹

HRMS (ESI) m/z calcd. for [C₁₅H₁₆N, M+H]⁺: 210.1283; Found: 210.1269.

GC-FID Retention time (min): 10.869.

Dibenzylamine (**2k**)



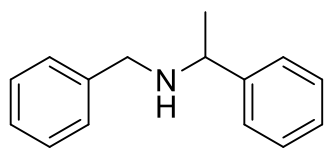
Pale yellow oil. Yield: 127.0 mg (0.64 mmol, 64%), GC-FID: 92%.

¹H-NMR (400.3 MHz, CDCl₃, 298 K): δ = 7.28–7.34 (m, 8H, Ar), 7.22–7.27 (m, 2H, Ar), 3.81 (s, 4H, 2 CH₂), 1.60 (br s, 1H); **¹³C{¹H}-NMR** (100.6 MHz, CDCl₃, 298 K): δ = 140.6 (C_q), 128.6, 128.4, 127.2 (aryl), 53.4 (CH₂). The NMR spectroscopic data are in accordance with the literature.¹⁵

HRMS (ESI) m/z calcd. for [C₁₄H₁₆N, M+H]⁺: 198.1277; Found: 198.1277.

GC-FID Retention time (min): 9.646.

N-benzyl-1-phenylethan-1-amine (2l)



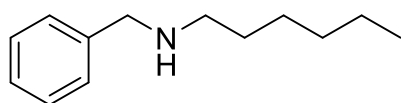
Pale yellow oil. Yield: GC-FID: 65%.

¹H-NMR (400.3 MHz, CDCl₃, 298 K): δ = 7.19–7.37 (m, 10H, Ar), 3.79 (q, ²J_{H,H} = 6.6 Hz, 1H, CH₃-CH), 3.61 (q, J_{H,H} = 13.7 Hz 2H, CH-NH-CH₂), 1.63 (br s, 1H, CH-NH-CH₂), 1.35 (d, ²J_{H,H} = 6.6 Hz, 3H, CH₃-CH); **¹³C{¹H}-NMR** (100.6 MHz, CDCl₃, 298 K): δ = 145.7 (C_q), 140.8 (C_q), 128.6, 128.5, 128.3, 127.1, 127.0, 126.9 (aryl), 57.6 (CH), 51.8 (CH₂), 24.6 (CH₃). The NMR spectroscopic data are in accordance with the literature.¹⁶

HRMS (ESI) m/z calcd. for [C₁₅H₁₈N, M+H]⁺: 212.1434; Found: 212.1434.

GC-FID Retention time (min): 9.706.

N-benzylhexan-1-amine (2m)



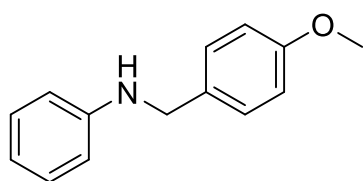
Pale yellow oil. Yield: GC-FID: 81%.

¹H-NMR (600.3 MHz, CDCl₃, 298 K): δ = 7.29–7.35 (m, 4H, Ar), 7.21–7.28 (m, 1H, Ar), 3.79 (s, 2H, CH₂), 2.63 (t, J=7.15 Hz, 2H, CH₂), 1.47–1.33 (m, 2H, CH₂), 1.25–1.39 (br s partially overlapped by other signal (m), 7H, 3 CH₂, CH₂-NH-Ar), 0.86–0.90 (m, 3H, CH₃); **¹³C{¹H}-NMR** (150.9 MHz, CDCl₃, 298 K): δ = 140.7 (C_q), 128.5, 128.2, 127.0 (aryl), 44.3, 49.7, 31.9, 30.2, 27.2, 22.8 (CH₂), 14.2 (CH₃). The NMR spectroscopic data are in accordance with the literature.¹⁷

HRMS (ESI) m/z calcd. for [C₁₃H₂₂N, M+H]⁺: 192.1747; Found: 192.1745.

GC-FID Retention time (min): 8.717.

N-(4-methoxybenzyl)aniline (3a)



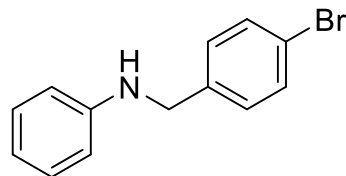
Orange oil. Yield: 105.5 mg (0.50 mmol, 50%), GC-FID: 95%.

¹H-NMR (400.3 MHz, CDCl₃, 298 K): δ = 7.27–7.32 (m, 2H, Ar), 7.15–7.21 (m, 2H, Ar), 6.86–6.91 (m, 2H, Ar), 6.69–6.75 (m, 1H, Ar), 6.62–6.67 (m, 2H, Ar), 4.26 (s, 2H, Ar-CH₂-NH), 3.94 (br s, 1H, CH₂-NH-Ar), 3.81 (s, 3H, OCH₃); **¹³C{¹H}-NMR** (100.6 MHz, CDCl₃, 298 K): δ = 159.0 (C_q), 148.4 (C_q), 131.6 (C_q), 129.4, 128.9, 117.6, 114.2, 113.0 (aryl), 55.5 (OCH₃), 48.0 (CH₂). The NMR spectroscopic data are in accordance with the literature.¹¹

HRMS (ESI) m/z calcd. for [C₁₄H₁₆NO, M+H]⁺: 214.1232; Found: 214.1227.

GC-FID Retention time (min): 11.900.

N-(4-bromobenzyl)aniline (**3b**)



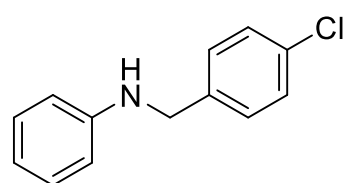
Dark orange oil. Yield: 99.0 mg (0.38 mmol, 38%), GC-FID: 83%.

¹H-NMR (400.3 MHz, CDCl₃, 298 K): δ = 7.28–7.50 (m, 3H, Ar), 7.22–7.28 (m, 1H, Ar), 7.14–7.22 (m, 2H, Ar), 6.69–6.77 (m, 1H, Ar), 6.58–6.68 (m, 2H, Ar), 4.30 (br s, 2H, Ar-CH₂-NH), 4.05 (br s, 1H, CH₂-NH-Ar); **¹³C{¹H}-NMR** (100.6 MHz, CDCl₃, 298 K): δ = 148.0 (C_q), 138.7 (C_q), 131.9, 129.4, 129.2, 121.1 (C_q), 118.0, 113.0 (aryl), 47.8 (CH₂). The NMR spectroscopic data are in accordance with the literature.¹²

HRMS (ESI) *m/z* calcd. for [C₁₃H₁₃BrN, M+H]⁺: 262.0231; Found: 262.0222.

GC-FID Retention time (min): 11.091.

N-(4-chlorobenzyl)aniline (**3c**)



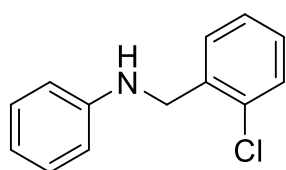
Orange oil. Yield: 76.1 mg (0.35 mmol, 35%), GC-FID: 90%.

¹H-NMR (400.3 MHz, CDCl₃, 298 K): δ = 7.32 (br s, 4H, Ar), 7.15–7.21 (m, 2H, Ar), 6.71–6.77 (m, 1H, Ar), 6.60–6.65 (m, 2H, Ar), 4.32 (br s, 2H, Ar-CH₂-NH), 4.05 (br s, 1H, CH₂-NH-Ar); **¹³C{¹H}-NMR** (100.6 MHz, CDCl₃, 298 K): δ = 148.0 (C_q), 138.2 (C_q), 133.0, 129.4, 128.9, 128.8 (C_q), 118.0, 113.0 (aryl), 47.8 (CH₂). The NMR spectroscopic data are in accordance with the literature.¹¹

HRMS (ESI) *m/z* calcd. for [C₁₃H₁₃ClN, M+H]⁺: 218.0736; Found: 218.0724.

GC-FID Retention time (min): 10.661.

N-(2-chlorobenzyl)aniline (**3d**)



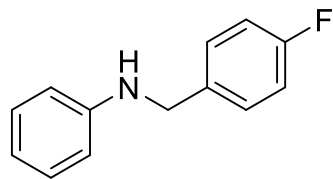
Light orange oil. Yield: 133.3 mg (0.61 mmol, 61%), GC-FID: 90%.

¹H-NMR (400.3 MHz, CDCl₃, 298 K): δ = 7.25–7.33 (m, 2H, Ar), 7.05–7.12 (m, 4H, Ar), 6.60–6.68 (m, 1H, Ar), 6.48–6.54 (m, 2H, Ar), 4.31 (s, 2H, Ar-CH₂-NH), 4.00 (s, br 1H, CH₂-NH-Ar); **¹³C{¹H}-NMR** (100.6 MHz, CDCl₃, 298 K): δ = 147.8 (C_q), 136.8 (C_q), 133.3 (C_q), 129.6, 129.4, 129.1, 128.4, 127.0, 117.8, 113.0 (aryl), 45.9 (CH₂). The NMR spectroscopic data are in accordance with the literature.¹²

HRMS (ESI) *m/z* calcd. for [C₁₃H₁₃ClN, M+H]⁺: 218.0736; Found: 218.0730.

GC-FID Retention time (min): 10.439.

N-(4-fluorobenzyl)aniline (**3e**)



Light brown oil. Yield: 81.4 mg (0.40 mmol, 40%), GC-FID: 72%.

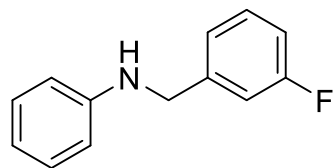
¹H-NMR (400.3 MHz, CDCl₃, 298 K): δ = 7.23–7.29 (m, 2H, Ar), 7.07–7.17 (m, 2H, Ar), 6.93–7.00 (m, 2H, Ar), 6.65–6.72 (m, 1H, Ar), 6.53–6.60 (m, 2H, Ar), 4.21 (s, 2H, Ar-CH₂-NH), 3.91 (br s, 1H, CH₂-NH-Ar); **¹³C{¹H}-NMR** (100.6 MHz, CDCl₃, 298 K): δ = 162.1 (C_q, d, ¹J_{F,C} = 244.9 Hz), 148.1 (C_q), 135.2 (C_q, d, ⁴J_{F,C} = 2.9 Hz), 129.4, 129.1 (d, ³J_{F,C} = 8.1 Hz), 117.8, 115.5 (d, ²J_{F,C} = 22.1 Hz), 113.0 (aryl), 47.6 (CH₂); **¹⁹F-NMR** (659.0 MHz, CDCl₃, 298 K): –115.63 (m).

The NMR spectroscopic data are in accordance with the literature.¹²

HRMS (ESI) m/z calcd. for [C₁₃H₁₃FN, M+H]⁺: 202.1032; Found: 202.1023.

GC-FID Retention time (min): 11.771.

N-(3-fluorobenzyl)aniline (**3f**)



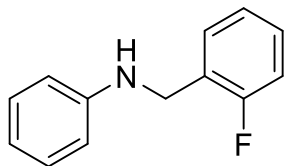
Dark brown oil. Yield: 71.3 mg (0.35 mmol, 35%), GC-FID: 94%.

¹H-NMR (400.3 MHz, CDCl₃, 298 K): δ = 7.29–7.36 (m, 1H, Ar), 7.16–7.25 (m, 3H, Ar), 7.10–7.15 (m, 1H, Ar), 6.96–7.02 (m, 1H, Ar), 6.74–6.80 (m, 1H, Ar), 6.62–6.69 (m, 2H, Ar), 4.36 (s, 2H, Ar-CH₂-NH), 4.10 (br s, 1H, CH₂-NH-Ar); **¹³C{¹H}-NMR** (100.6 MHz, CDCl₃, 298 K): δ = 163.3 (C_q, d, ¹J_{F,C} = 247.3 Hz), 148.0 (C_q), 142.5 (C_q, d, ³J_{F,C} = 6.7 Hz), 130.2 (d, ³J_{F,C} = 8.7 Hz), 129.4, 122.9 (d, ⁴J_{F,C} = 2.9 Hz), 117.9, 114.3 (d, ²J_{F,C} = 21.5 Hz), 114.1 (d, ²J_{F,C} = 21.1 Hz), 113.0 (aryl), 47.9 (d, ⁴J_{F,C} = 1.5 Hz, CH₂); **¹⁹F-NMR** (659.0 MHz, CDCl₃, 298 K): –112.95 (m). The NMR spectroscopic data are in accordance with the literature.¹⁸

HRMS (ESI) m/z calcd. for [C₁₃H₁₃FN, M+H]⁺: 202.1032; Found: 202.1029.

GC-FID Retention time (min): 10.622.

N-(2-fluorobenzyl)aniline (**3g**)



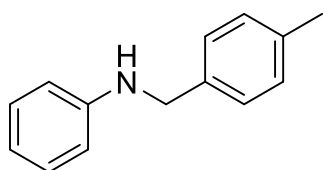
Yellow oil. Yield: 71.6 mg (0.36 mmol, 36%), GC-FID: 65%.

¹H-NMR (400.3 MHz, CDCl₃, 298 K): δ = 7.30–7.36 (m, 1H, Ar), 7.16–7.23 (m, 1H, Ar), 7.10–7.16 (m, 2H, Ar), 6.98–7.07 (m, 2H, Ar), 6.66–6.72 (m, 1H, Ar), 6.57–6.62 (m, 2H, Ar), 4.35 (s, 2H, Ar-CH₂-NH), 3.98 (br s, 1H, CH₂-NH-Ar); **¹³C{¹H}-NMR** (100.6 MHz, CDCl₃, 298 K): δ = 161.0 (C_q, d, ¹J_{F,C} = 245.7 Hz), 147.9 (C_q), 129.5 (d, ³J_{F,C} = 4.4 Hz), 129.4, 128.9 (d, ³J_{F,C} = 8.2 Hz), 126.5 (C_q, d, ²J_{F,C} = 14.7 Hz), 124.3 (d, ⁴J_{F,C} = 3.7 Hz), 117.8, 115.4 (d, ²J_{F,C} = 21.3 Hz), 113.0 (aryl), 41.9 (d, ³J_{F,C} = 4.4 Hz, CH₂); **¹⁹F-NMR** (659.0 MHz, CDCl₃, 298 K): –119.05 (m). The NMR spectroscopic data are in accordance with the literature.¹²

HRMS (ESI) m/z calcd. for [C₁₃H₁₃FN, M+H]⁺: 202.1032; Found: 202.1027.

GC-FID Retention time (min): 9.592.

N-(4-methylbenzyl)aniline (**3h**)



Orange oil. Yield: 88.1 mg (0.45 mmol, 45%), GC-FID: 93%.

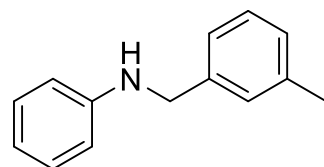
¹H-NMR (400.3 MHz, CDCl₃, 298 K): δ = 7.17–7.22 (m, 2H, Ar), 7.06–7.14 (m, 4H, Ar), 6.63–6.70 (m, 1H, Ar), 6.53–6.59 (m, 2H, Ar), 4.19 (s, 2H, Ar-CH₂-NH), 3.86 (br s, 1H, CH₂-NH-Ar), 2.29 (s, 3H, CH₃);

¹³C{¹H}-NMR (100.6 MHz, CDCl₃, 298 K): δ = 148.3 (C_q), 136.9 (C_q), 136.5 (C_q), 129.4, 129.3, 127.6, 117.5, 112.9 (aryl), 48.1 (CH₂), 21.1 (CH₃). The NMR spectroscopic data are in accordance with the literature.¹¹

HRMS (ESI) *m/z* calcd. for [C₁₄H₁₆N, M+H]⁺: 198.1283; Found: 198.1280.

GC-FID Retention time (min): 11.164.

N-(3-methylbenzyl)aniline (**3i**)



Yellow oil. Yield: 123.8 mg (0.63 mmol, 63%), GC-FID: 88%.

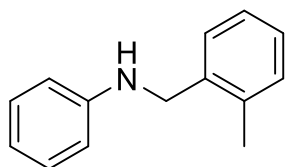
¹H-NMR (400.3 MHz, CDCl₃, 298 K): δ = 7.04–7.17 (m, 5H, Ar), 6.98–7.02 (m, 1H, Ar), 6.61–6.67 (m, 1H, Ar), 6.49–6.55 (m, 2H, Ar), 4.15 (s, 2H, Ar-CH₂-NH), 3.82 (br s, 1H, CH₂-NH-Ar), 2.26 (s, 3H, CH₃);

¹³C{¹H}-NMR (100.6 MHz, CDCl₃, 298 K): δ = 148.3 (C_q), 139.4 (C_q), 138.2 (C_q), 129.3, 128.6, 128.3, 128.0, 124.6, 117.5, 112.9 (aryl), 48.3 (CH₂), 21.5 (CH₃). The NMR spectroscopic data are in accordance with the literature.¹³

HRMS (ESI) *m/z* calcd. for [C₁₄H₁₆N, M+H]⁺: 198.1283; Found: 198.1278.

GC-FID Retention time (min): 11.087.

N-(2-methylbenzyl)aniline (**3j**)



Orange oil. Yield: 84.4 mg (0.43 mmol, 43%), GC-FID: 79%.

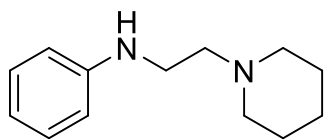
¹H-NMR (400.3 MHz, CDCl₃, 298 K): δ = 7.26–7.30 (m, 1H, Ar), 7.09–7.19 (m, 5H, Ar), 6.65–6.71 (m, 1H, Ar), 6.55–6.60 (m, 2H, Ar), 4.20 (s, 2H, Ar-CH₂-NH), 3.74 (br s, 1H, CH₂-NH-Ar), 2.32 (s, 3H, CH₃);

¹³C{¹H}-NMR (100.6 MHz, CDCl₃, 298 K): δ = 148.4 (C_q), 137.1 (C_q), 136.4 (C_q), 130.5, 129.4, 128.3, 127.5, 126.2, 117.5, 112.8 (aryl), 46.5 (CH₂), 19.0 (CH₃). The NMR spectroscopic data are in accordance with the literature.¹²

HRMS (ESI) *m/z* calcd. for [C₁₄H₁₆N, M+H]⁺: 198.1283; Found: 198.1274.

GC-FID Retention time (min): 11.106.

N-(2-(piperidin-1-yl)ethyl)aniline (**3k**)



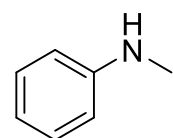
Yellow oil. Yield: 65.7 mg (0.32 mmol, 32%), GC-FID: 32%.

¹H-NMR (400.3 MHz, CDCl₃, 298 K): δ = 7.16–7.23 (m, 2H, Ar), 6.68–6.74 (m, 1H, Ar), 6.62–6.68 (m, 2H, Ar), 4.34 (s, 1H, Ar-CH₂-NH), 3.17 (t, ³J_{H,H} = 6.1 Hz, 2H, NH-CH₂-CH₂-Pip), 2.59 (t, ³J_{H,H} = 6.1 Hz, 2H, NH-CH₂-CH₂-Pip), 2.23–2.52 (m, 4H, 2 × CH₂), 1.53–1.66 (m, 4H, 2 × CH₂), 1.40–1.52 (m, 2H, CH₂); **¹³C{¹H}-NMR** (100.6 MHz, CDCl₃, 298 K): δ = 148.8 (C_q), 129.3, 117.2, 113.0 (aryl), 57.6 (N-((CH₂)₂-(CH₂)₂)-CH₂), 54.5 (NH-CH₂-CH₂-N), 40.6 (NH-CH₂-CH₂-N), 26.1 (N-((CH₂)₂-(CH₂)₂)-CH₂), 24.6 (N-((CH₂)₂(CH₂)₂)-CH₂). The NMR spectroscopic data are in accordance with the literature.¹⁹

HRMS (ESI) m/z calcd. for [C₁₃H₂₁N₂, M+H]⁺: 205.1705; Found: 205.1701.

GC-FID Retention time (min): 9.879.

N-methylaniline (**3l**)



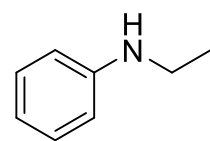
Dark yellow liquid. Yield: GC-FID: 16%.

¹H-NMR (400.3 MHz, CDCl₃, 298 K): δ = 7.17–7.23 (m, 2H, Ar), 6.69–6.74 (m, 1H, Ar), 6.60–6.65 (m, 2H, Ar), 3.87 (br s, 1H, NH), 2.84 (s, 3H, CH₃); **¹³C{¹H}-NMR** (100.6 MHz, CDCl₃, 298 K): δ = 149.5 (C_q), 129.3, 117.4, 112.6 (aryl), 30.9 (CH₃). The NMR spectroscopic data are in accordance with the literature.¹¹

HRMS (ESI) m/z calcd. for [C₇H₁₀N, M+H]⁺: 108.0813; Found: 108.0811.

GC-FID Retention time (min): 5.900.

N-ethylaniline (**3m**)



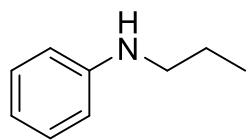
Dark yellow liquid. Yield: GC-FID: 82%.

¹H-NMR (400.3 MHz, CDCl₃, 298 K): δ = 7.32–7.41 (m, 2H, Ar), 6.87–6.92 (m, 1H, Ar), 6.77–6.82 (m, 2H, Ar), 3.75 (br s, 1H, NH), 3.33 (q, ³J_{H,H} = 7.1 Hz, 2H, CH₂-CH₃), 1.43 (t, ³J_{H,H} = 7.1 Hz, 3H, CH₂CH₃); **¹³C{¹H}-NMR** (100.6 MHz, CDCl₃, 298 K): δ = 148.5 (C_q), 129.3, 117.3, 112.8 (aryl), 38.5 (CH₂), 14.9 (CH₃). The NMR spectroscopic data are in accordance with the literature.¹¹

HRMS (ESI) m/z calcd. for [C₈H₁₂N, M+H]⁺: 122.0970; Found: 122.0960.

GC-FID Retention time (min): 6.359.

N-propylaniline (**3n**)



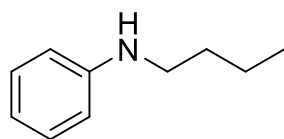
Orange oil. Yield: GC-FID: 65%.

¹H-NMR (400.3 MHz, CDCl₃, 298 K): δ = 7.17–7.23 (m, 2H, Ar), 6.67–6.72 (m, 1H, Ar), 6.59–6.64 (m, 2H, Ar), 3.63 (br s, 1H, NH), 3.11 (t, ³J_{H,H} = 7.1 Hz, 2H, CH₂-CH₂-CH₃), 1.61–1.73 (m, 2H, CH₂-CH₂-CH₃), 1.03 (t, ³J_{H,H} = 7.4 Hz, 3H, (CH₂)₂-CH₃); **¹³C{¹H}-NMR** (100.6 MHz, CDCl₃, 298 K): δ = 148.7 (C_q), 129.3, 117.2, 112.8 (aryl), 45.9 (CH₂-CH₂-CH₃), 22.9 (CH₂-CH₂-CH₃), 11.8 ((CH₂)₂-CH₃). The NMR spectroscopic data are in accordance with the literature.²⁰

HRMS (ESI) m/z calcd. for [C₉H₁₄N, M+H]⁺: 136.1126; Found: 136.1119.

GC-FID Retention time (min): 6.997.

N-butylaniline (**3o**)



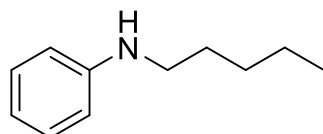
Orange oil. Yield: GC-FID: 72%.

¹H-NMR (400.3 MHz, CDCl₃, 298 K): δ = 7.15–7.21 (m, 2H, Ar), 6.67–6.72 (m, 1H, Ar), 6.59–6.64 (m, 2H, Ar), 3.59 (br s, 1H, NH), 3.12 (t, ³J_{H,H} = 7.1 Hz, CH₂-(CH₂)₂-CH₃), 1.57–1.67 (m, 2H, CH₂-CH₂-CH₂-CH₃), 1.39–1.50 (m, 2H, (CH₂)₂-CH₂-CH₃), 0.97 (t, ³J_{H,H} = 7.3 Hz, (CH₂)₃-CH₃); **¹³C{¹H}-NMR** (100.6 MHz, CDCl₃, 298 K): δ = 148.7 (C_q), 129.4, 117.2, 112.8 (aryl), 43.8 (CH₂-(CH₂)₂-CH₃), 31.8 (CH₂-CH₂-CH₂-CH₃), 20.4 ((CH₂)₂-CH₂-CH₃), 14.0 ((CH₂)₃-CH₃). The NMR spectroscopic data are in accordance with the literature.¹¹

HRMS (ESI) m/z calcd. for [C₁₀H₁₆N, M+H]⁺: 150.1283; Found: 150.1274.

GC-FID Retention time (min): 7.630.

N-pentylaniline (**3p**)



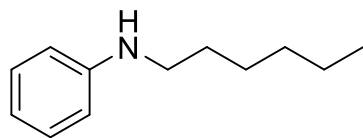
Dark yellow oil. Yield: GC-FID: 63%.

¹H-NMR (400.3 MHz, CDCl₃, 298 K): δ = 7.15–7.23 (m, 2H, Ar), 6.67–6.73 (m, 1H, Ar), 6.60–6.65 (m, 2H, Ar), 3.60 (br s, 1H, NH), 3.12 (t, ³J_{H,H} = 7.1 Hz, 2H, CH₂-(CH₂)₃-CH₃), 1.59–1.69 (m, 2H, CH₂-CH₂-(CH₂)₂-CH₃), 1.34–1.46 (m, 4H, (CH₂)₂-(CH₂)₂-CH₃), 0.94 (t, ³J_{H,H} = 7.1 Hz, 3H, (CH₂)₄-CH₃); **¹³C{¹H}-NMR** (100.6 MHz, CDCl₃, 298 K): δ = 148.7 (C_q), 129.3, 117.2, 112.8 (aryl), 44.1 (CH₂-(CH₂)₃-CH₃), 29.5 (CH₂-CH₂-(CH₂)₂-CH₃), 29.4 ((CH₂)₂-CH₂-CH₂-CH₃), 22.7 ((CH₂)₃-CH₂-CH₃), 14.2 ((CH₂)₄-CH₃). The NMR spectroscopic data are in accordance with the literature.²¹

HRMS (ESI) m/z calcd. for [C₁₁H₁₈N, M+H]⁺: 164.1439; Found: 164.1432.

GC-FID Retention time (min): 8.206.

N-hexylaniline (**3q**)



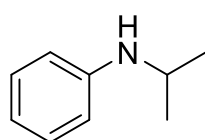
Orange oil. Yield: 53.7 mg (0.30 mmol, 30%), GC-FID: 64%.

¹H-NMR (400.3 MHz, CDCl₃, 298 K): δ = 7.18–7.26 (m, 2H, Ar), 6.71–6.77 (m, 1H, Ar), 6.63–6.68 (m, 2H, Ar), 3.61 (br s, 1H, NH), 3.15 (t, ³J_{H,H} = 7.2 Hz, 2H, CH₂- (CH₂)₄-CH₃), 1.62–1.71 (m, 2H, CH₂-CH₂-(CH₂)₃-CH₃), 1.33–1.51 (m, 6H, (CH₂)₂-(CH₂)₃-CH₃), 0.94–1.02 (m, 3H, (CH₂)₅-CH₃); **¹³C{¹H}-NMR** (100.6 MHz, CDCl₃, 298 K): δ = 148.7 (C_q), 129.3, 117.2, 112.8 (aryl), 44.1 (CH₂- (CH₂)₄-CH₃), 31.8 (CH₂-CH₂-(CH₂)₃-CH₃), 29.7 ((CH₂)₂-CH₂-(CH₂)₂-CH₃), 27.0 ((CH₂)₃-CH₂-CH₂-CH₃), 22.7 ((CH₂)₄-CH₂-CH₃), 14.1 ((CH₂)₅-CH₃). The NMR spectroscopic data are in accordance with the literature.¹¹

HRMS (ESI) m/z calcd. for [C₁₂H₂₀N, M+H]⁺: 178.1596; Found: 178.1588.

GC-FID Retention time (min): 8.742.

N-(*iso*-propyl)aniline (**3r**)



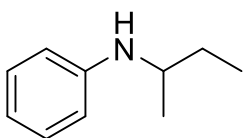
Brown oil. Yield: 100.3 mg (0.74 mmol, 74%), GC-FID: 82%.

¹H-NMR (400.3 MHz, CDCl₃, 298 K): δ = 7.14–7.21 (m, 2H, Ar), 6.66–6.72 (m, 1H, Ar), 6.57–6.62 (m, 2H, Ar), 3.64 (sept, ³J_{H,H} = 6.2 Hz, 1H, CH-(CH₃)₂), 3.44 (br s, 1H, CH-NH-Ar), 1.22 (d, ³J_{H,H} = 6.2 Hz, 6H, CH-(CH₃)₂); **¹³C{¹H}-NMR** (100.6 MHz, CDCl₃, 298 K): δ = 147.7 (C_q), 129.4, 117.1, 113.4 (aryl), 44.3 (CH-(CH₃)₂), 23.2 (CH-(CH₃)₂). The NMR spectroscopic data are in accordance with the literature.²⁰

HRMS (ESI) m/z calcd. for [C₉H₁₄N, M+H]⁺: 136.1126; Found: 136.1118.

GC-FID Retention time (min): 8.524.

N-(*sec*-butyl)aniline (**3s**)



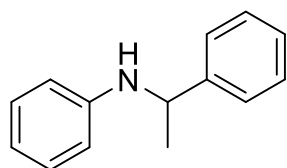
Orange oil. Yield: 82.4 mg (0.55 mmol, 55%), GC-FID: 55%.

¹H-NMR (400.3 MHz, CDCl₃, 298 K): δ = 7.13–7.21 (m, 2H, Ar), 6.64–6.70 (m, 1H, Ar), 6.56–6.62 (m, 2H, Ar), 3.36–3.50 (m, 2H, CH-NH-Ar & CH₃-CH-CH₂-CH₃), 1.43–1.68 (m, 2H, CH₃-CH-CH₂-CH₃), 1.19 (d, ³J_{H,H} = 6.5 Hz, 3H, CH₃-CH-CH₂-CH₃), 0.97 (t, ³J_{H,H} = 7.5 Hz, 3H, CH₃-CH-CH₂-CH₃); **¹³C{¹H}-NMR** (100.6 MHz, CDCl₃, 298 K): δ = 147.9 (C_q), 129.4, 116.9, 113.3 (aryl), 49.9 (CH₃-CH-CH₂-CH₃), 29.8 (CH₃-CH-CH₂-CH₃), 20.4 (CH₃-CH-CH₂-CH₃), 10.5 (CH₃-CH-CH₂-CH₃). The NMR spectroscopic data are in accordance with the literature.²²

HRMS (ESI) m/z calcd. for [C₁₀H₁₆N, M+H]⁺: 150.1283; Found: 150.1274.

GC-FID Retention time (min): 7.144.

N-(1-phenylethyl)aniline (**3t**)



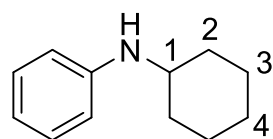
Brown oil. Yield: 51.5 mg (0.26 mmol, 26%), GC-FID: 49%.

¹H-NMR (400.3 MHz, CDCl₃, 298 K): δ = 7.35–7.40 (m, 2H, Ar), 7.29–7.35 (m, 2H, Ar), 7.20–7.25 (m, 1H, Ar), 7.06–7.12 (m, 2H, Ar), 6.62–6.67 (m, 1H, Ar), 6.49–6.54 (m, 2H, Ar), 4.49 (q, ³J_{H,H} = 6.7 Hz, 1H, CH₃-CH-Ar), 4.03 (br s, 1H, CH-NH-Ar), 1.52 (d, ³J_{H,H} = 6.7 Hz, 3H, CH₃-CH-Ar); **¹³C{¹H}-NMR** (100.6 MHz, CDCl₃, 298 K): δ = 147.4 (C_q), 145.4 (C_q), 129.2, 128.8, 127.0, 126.0, 117.4, 113.4 (aryl), 53.6 (CH₃-CH-Ar), 25.1 (CH₃-CH-Ar). The NMR spectroscopic data are in accordance with the literature.²¹

HRMS (ESI) m/z calcd. for [C₁₄H₁₆N, M+H]⁺: 198.1283; Found: 198.1284.

GCMS Retention time (min): 10.624

N-cyclohexylaniline (**3u**)



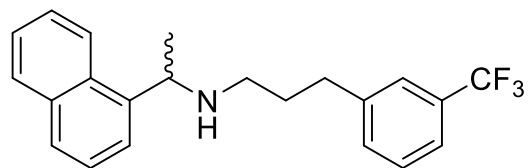
Orange oil. Yield: 45.2 mg (0.26 mmol, 26%), GC-FID: 61%.

¹H-NMR (400.3 MHz, CDCl₃, 298 K): δ = 7.16–7.23 (m, 2H, Ar), 6.68–6.75 (m, 1H, Ar), 6.60–6.66 (m, 2H, Ar), 3.54 (br s, 1H, CH-NH-Ar), 3.25–3.36 (m, 1H, CH), 2.06–2.15 (m, 2H, 2 × CH_{equatorial,2}), 1.75–1.84 (m, 2H, 2 × CH_{equatorial,3}), 1.67–1.75 (m, 1H, CH_{equatorial,4}), 1.35–1.48 (m, 2H, 2 × CH_{axial,3}), 1.13–1.34 (m, 3H, 3 × CH_{axial,2&4}); **¹³C{¹H}-NMR** (100.6 MHz, CDCl₃, 298 K): δ = 147.5 (C_q), 129.4, 116.9, 113.2 (aryl), 51.8 (CH-((CH₂)₂-(CH₂)₂)-CH₂), 33.6 (CH-((CH₂)₂-(CH₂)₂)-CH₂), 26.1 (CH-((CH₂)₂-(CH₂)₂)-CH₂), 25.1 (CH-((CH₂)₂-(CH₂)₂)-CH₂). The NMR spectroscopic data are in accordance with the literature.²²

HRMS (ESI) m/z calcd. for [C₁₂H₁₈N, M+H]⁺: 176.1439; Found: 176.1433.

GC-FID Retention time (min): 8.937.

N-(1-(naphthalen-1-yl)ethyl)-3-(3-(trifluoromethyl)phenyl)propan-1-amine (cinacalcet) (**4**)



Orange oil. Yield: GC-FID: 50%.

¹H-NMR (400.3 MHz, toluene-*d*₈, 298 K): δ = 8.13–8.18 (m, 1H, Ar), 7.62–7.68 (m, 2H, Ar), 7.53–7.58 (m, 1H, Ar), 7.19–7.36 (m, 5H, Ar), 6.87–6.93 (m, 2H, Ar), 3.80 (q, ²J_{H,H} = 6.6 Hz, 1H, CH₃-CH), 4.36 (q, J_{H,H} = 13.7 Hz, 2H, CH-NH-CH₂), 2.22–2.43 (m, 4H, NH-CH₂-CH₂-CH₂-Ar), 1.39–1.49 (m, 2H, NH-CH₂-CH₂-CH₂-Ar), 1.36 (br s, 1H, CH-NH-CH₂), 1.34 (d, ²J_{H,H} = 6.5 Hz, 3H, CH₃-CH); **¹³C{¹H}-NMR** (100.6 MHz, toluene-*d*₈, 298 K): δ = 143.8 (C_q), 141.9 (C_q), 134.8, 132.06, 132.02, 130.9 (q, J_{C,F} = 31.5 Hz, CF₃), 129.4, 129.2, 127.6, 125.93, 125.86, 125.5, 123.5, 123.4, 122.8 (q, J_{C,F} = 3.7 Hz, aryl), 54.7 (CH), 47.4, 33.5, 32.2 (CH₂), 23.9 (CH₃). The NMR spectroscopic data are in accordance with the literature.²³

HRMS (ESI) m/z calcd. for [C₂₂H₂₃F₃N, M+H]⁺: 358.1777; Found: 358.1778.

GC-FID Retention time (min): 12.430.

References

- (1) Fulmer, G. R.; Miller, A. J. M.; Sherden, N. H.; Gottlieb, H. E.; Nudelman, A.; Stoltz, B. M.; Bercaw, J. E.; Goldberg, K. I. NMR Chemical Shifts of Trace Impurities: Common Laboratory Solvents, Organics, and Gases in Deuterated Solvents Relevant to the Organometallic Chemist. *Organometallics* **2010**, *29*, 2176–2179.
- (2) Smith, A. J.; Kalkman, E. D.; Gilbert, Z. W.; Tonks, I. A. ZnCl₂ Capture Promotes Ethylene Polymerization by a Salicylaldiminato Ni Complex Bearing a Pendent 2,2'-Bipyridine Group. *Organometallics* **2016**, *35*, 2429–2432.
- (3) Michlik, S.; Kempe, R. A sustainable catalytic pyrrole synthesis. *Nat. Chem.* **2016**, *5*, 140–144.
- (4) Bruker SAINT v8.38B/A Copyright © 2005-2019 Bruker AXS.
- (5) Sheldrick, G. M. *SADABS*. University of Göttingen, 1996, Germany.
- (6) Dolomanov, O. V.; Bourhis, L. J.; Gildea, R. J.; Howard, J. A. K.; Puschmann, H. OLEX2: a complete structure solution, refinement and analysis program. *J. Appl. Cryst.* **2009**, *42*, 339–341.
- (7) Huebschle, C. B.; Sheldrick, G. M.; Dittrich, B. ShelXle: a Qt graphical user interface for SHELXL. *J. Appl. Cryst.* **2011**, *44*, 1281–1284.
- (8) Sheldrick, G. M. *SHELXS v 2016/4* University of Göttingen, 2015, Germany.
- (9) Sheldrick, G. M. *SHELXL v 2016/4* University of Göttingen, 2015, Germany.
- (10) Spek, A. L. Structure validation in chemical crystallography. *Acta Cryst.* **2009**, *D65*, 148–155.
- (11) Elangovan, S.; Neumann, J.; Sortais, J. B.; Junge, K.; Darcel, C.; Beller, M. Efficient and selective N-alkylation of amines with alcohols catalysed by manganese pincer complexes *Nat. Commun.* **2016**, *7*, 12641.
- (12) Zhang M.; Yang H.; Zhang Y.; Zhu C.; Li W.; Cheng Y.; Hu H. Direct reductive amination of aromatic aldehydes catalyzed by gold(I) complex under transfer hydrogenation conditions. *Chem. Commun.* **2011**, *47*, 6605–6607.
- (13) Midya S. P.; Mondal A.; Begum A.; Balaraman E. A Simple Cobalt(II) Chloride Catalyzed N-Alkylation of Amines with Alcohols. *Synthesis* **2017**, *49*, 3957–3961.
- (14) Landge V. G.; Mondal A.; Kumar V.; Nandakumar A.; Balaraman E. Manganese catalyzed N-alkylation of anilines with alcohols: ligand enabled selectivity. *Org. Biomol. Chem.* **2018**, *16*, 8175–8180.
- (15) Adamczyk-Woźniak A.; Maduraa I.; Velders A. H.; Sporyński A. Diverse reactivity of 2-formylphenylboronic acid with secondary amines: synthesis of 3-amino-substituted benzoxaboroles. *Tetrahedron Lett.* **2010**, *51*, 6181–6185.
- (16) Hollmann D.; Tillack A.; Michalik D.; Jackstell R.; Beller M. An Improved Ruthenium Catalyst for the Environmentally Benign Amination of Primary and Secondary Alcohols. *Chem. Asian J.* **2007**, *2*, 403–410.
- (17) Giovenzana G. B.; Imperio D.; Penoni A.; Palmisano G.; Reductive amination with zinc powder in aqueous media. *Beilstein J. Org. Chem.* **2011**, *7*, 1095–1099.
- (18) Wei D.; Bruneau-Voisine A.; Valyaev D. A.; Lugan N.; Sortais J.-B. Manganese catalyzed reductive amination of aldehydes using hydrogen as a reductant. *Chem. Commun.* **2018**, *54*, 4302–4305.

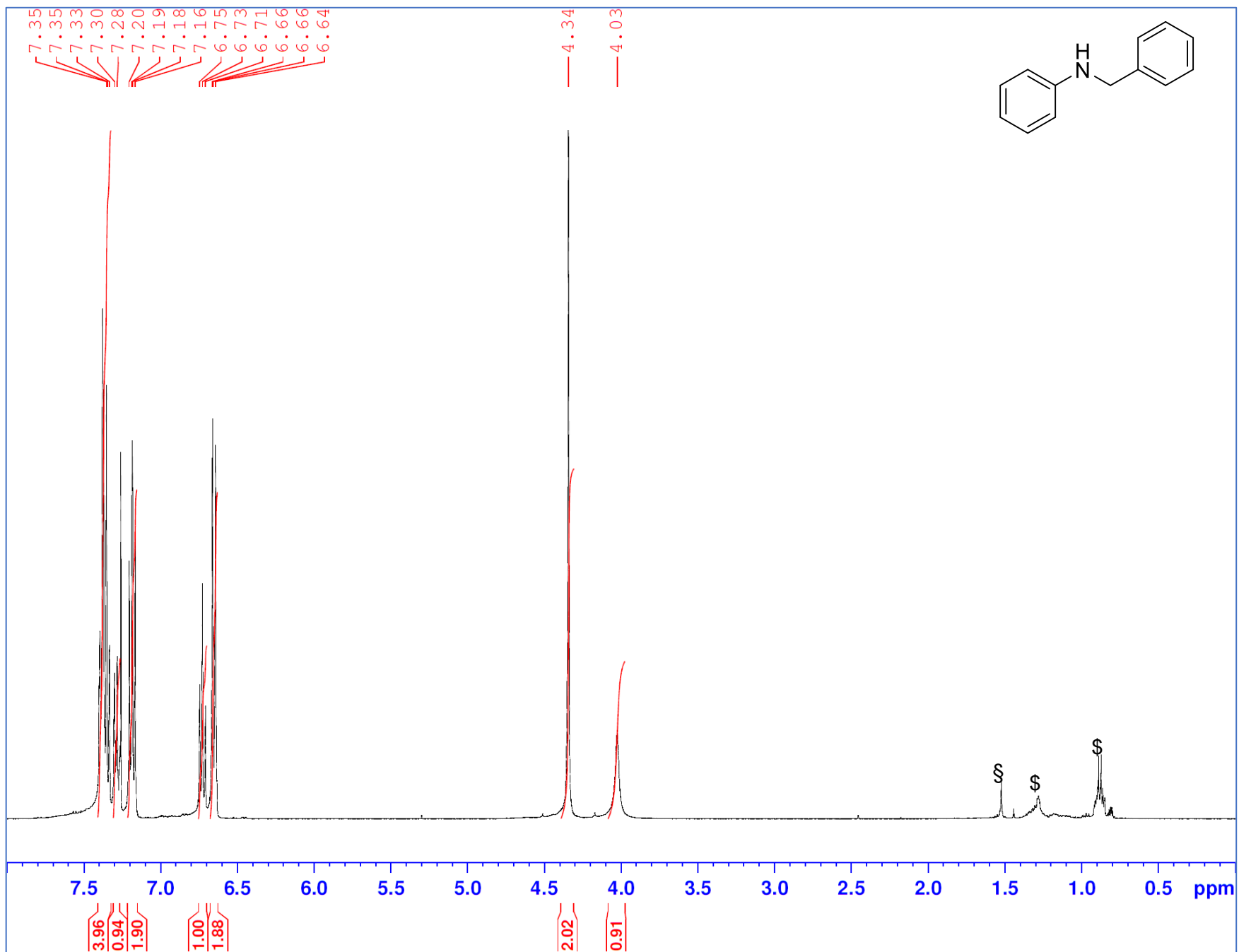
(19) Morita Y.; Ishigaki T.; Kawamura K.; Iseki K. Short and Practical Synthesis of N',N'-Disubstituted N-Aryl-1,2-Ethylenediamines by a Decarboxylative Ring-Opening Reaction under Nucleophilic Conditions. *Synthesis* **2007**, *16*, 2517–2523.

(20) Hollmann D.; Bähn S.; Tillack A.; Beller M. N-Dealkylation of aliphatic amines and selective synthesis of monoalkylated aryl amines. *Chem. Commun.* **2008**, 3199–3201.

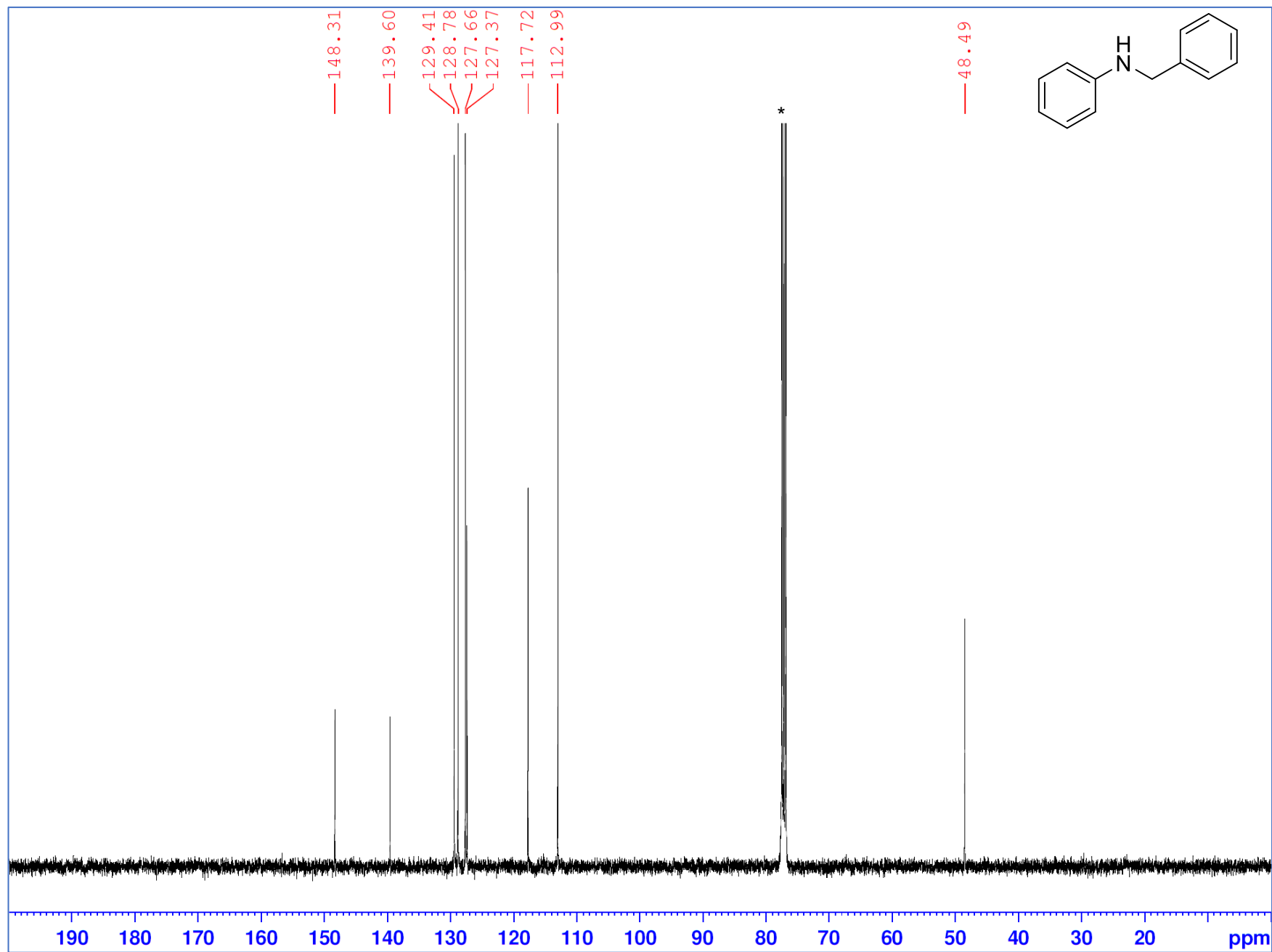
(21) Kumar A.; Sharma S.; Maurya R. A. Single Nucleotide-Catalyzed Biomimetic Reductive Amination. *Adv. Synth. Catal.* **2010**, *352*, 2227–2232.

(22) Barker T. J.; Jarvo E. R.; Titanium-Mediated Amination of Grignard Reagents Using Primary and Secondary Amines. *Angew. Chem., Int. Ed.* **2011**, *50*, 8325–8328.

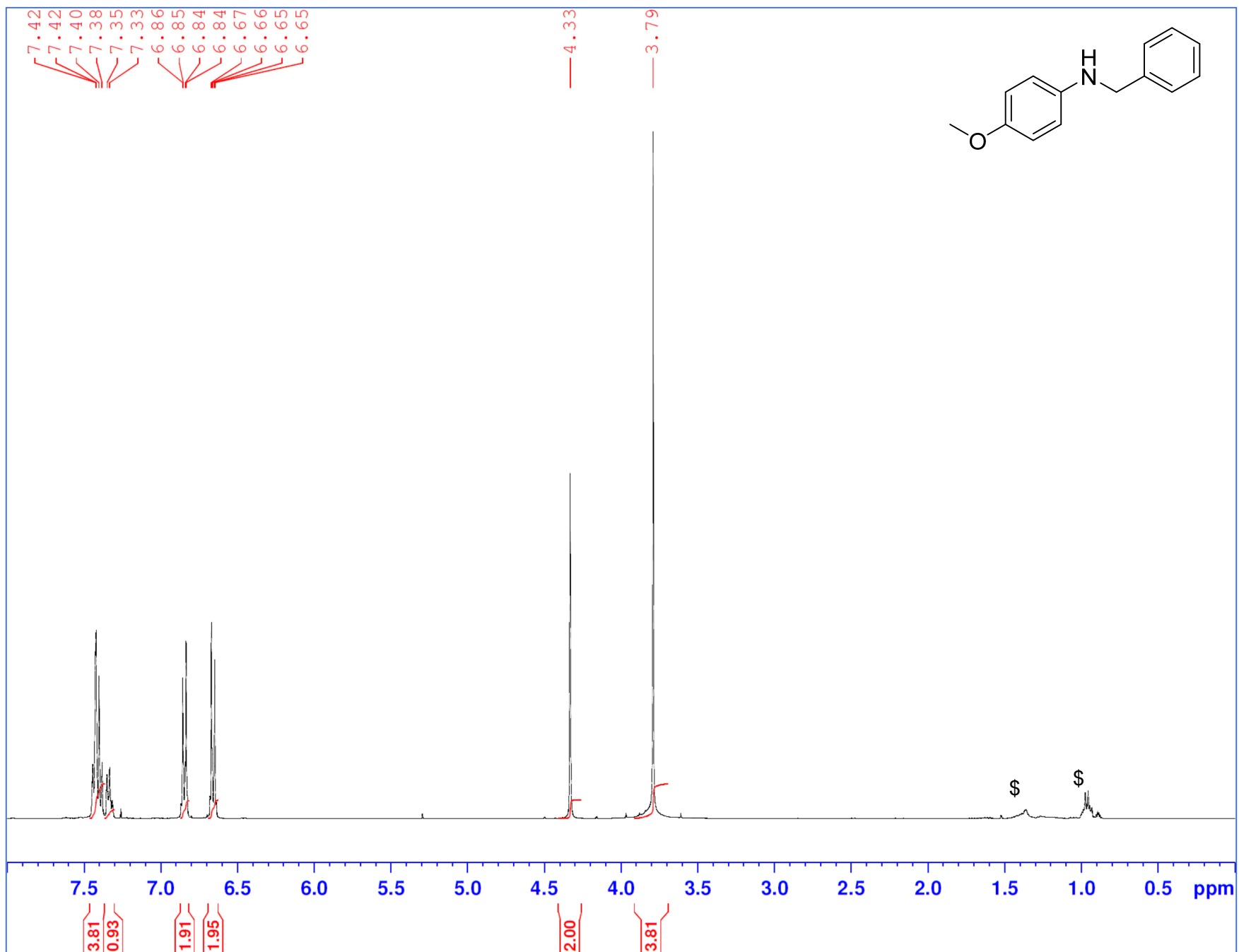
(23) Geoghegan K.; Kelleher S.; Evans P. An Investigation into the One-Pot Heck Olefination – Hydrogenation Reaction. *J. Org.Chem.* **2011**, *76*, 2187–2194.



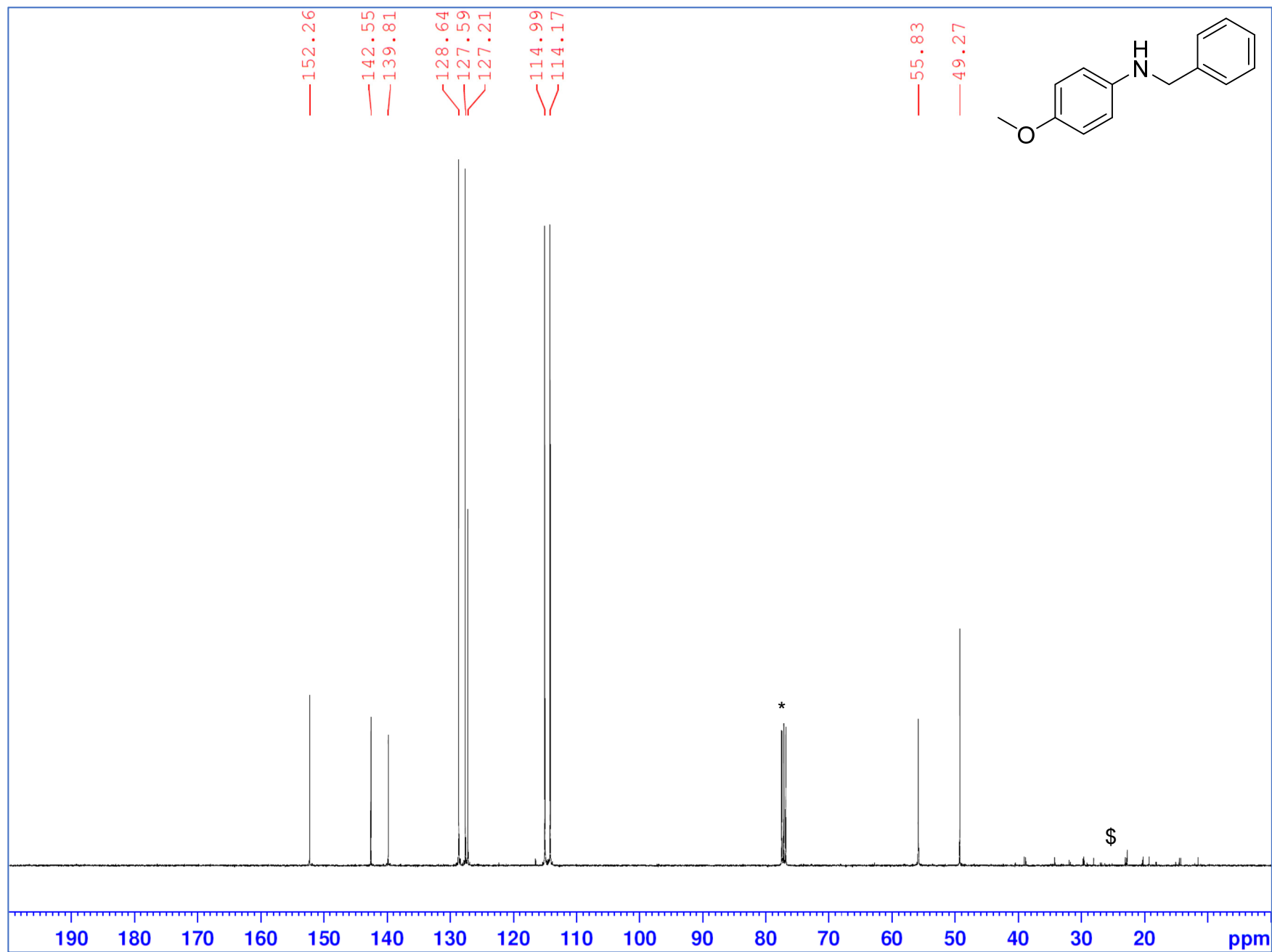
Supplementary Figure S13. ¹H-NMR spectrum of **1a** in CDCl₃, § ≡ residual water; \$ ≡ residual petrol ether.



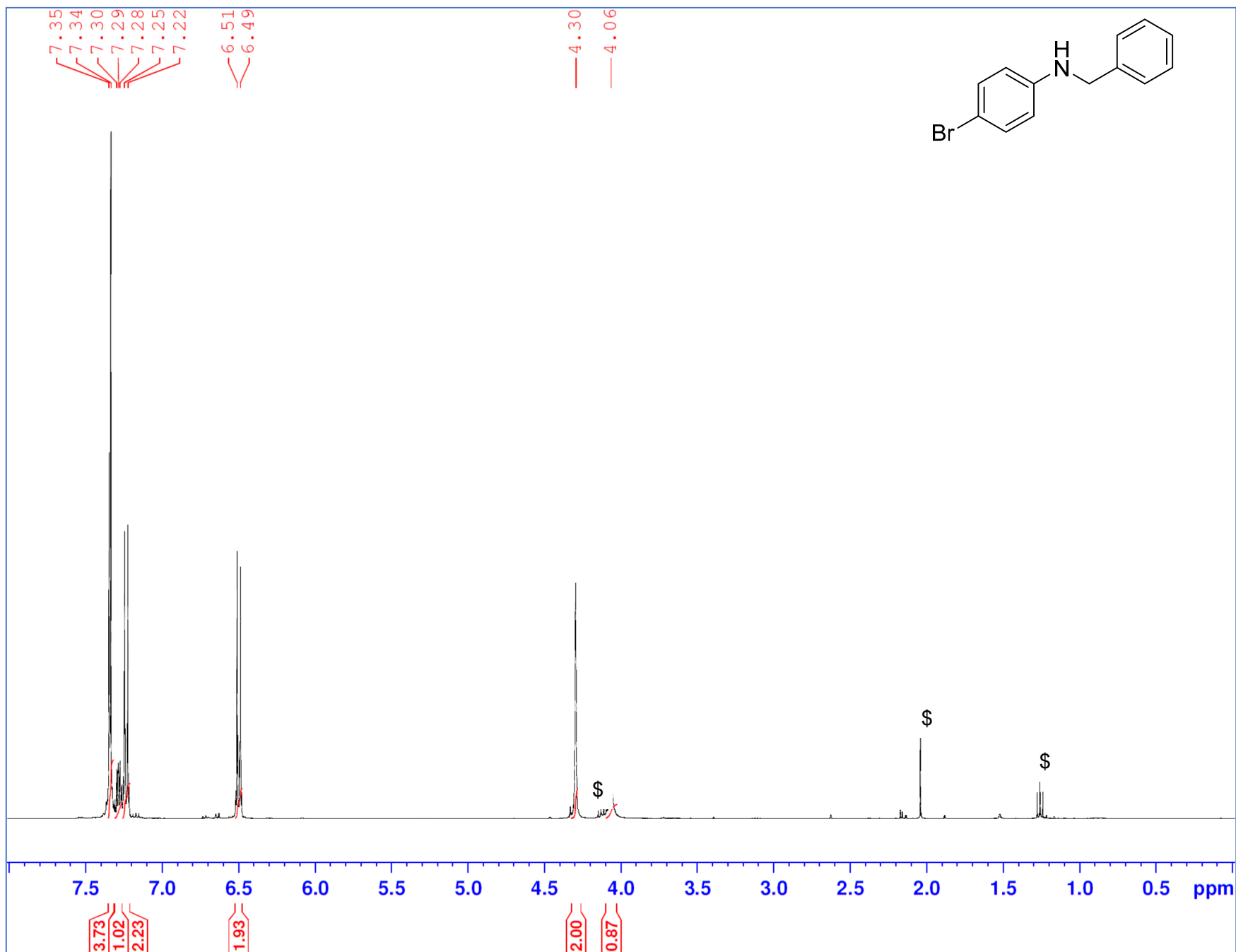
Supplementary Figure S14. $^{13}\text{C}\{^1\text{H}\}$ -NMR spectrum of **1a** in CDCl_3 , * \equiv deuterated solvent.



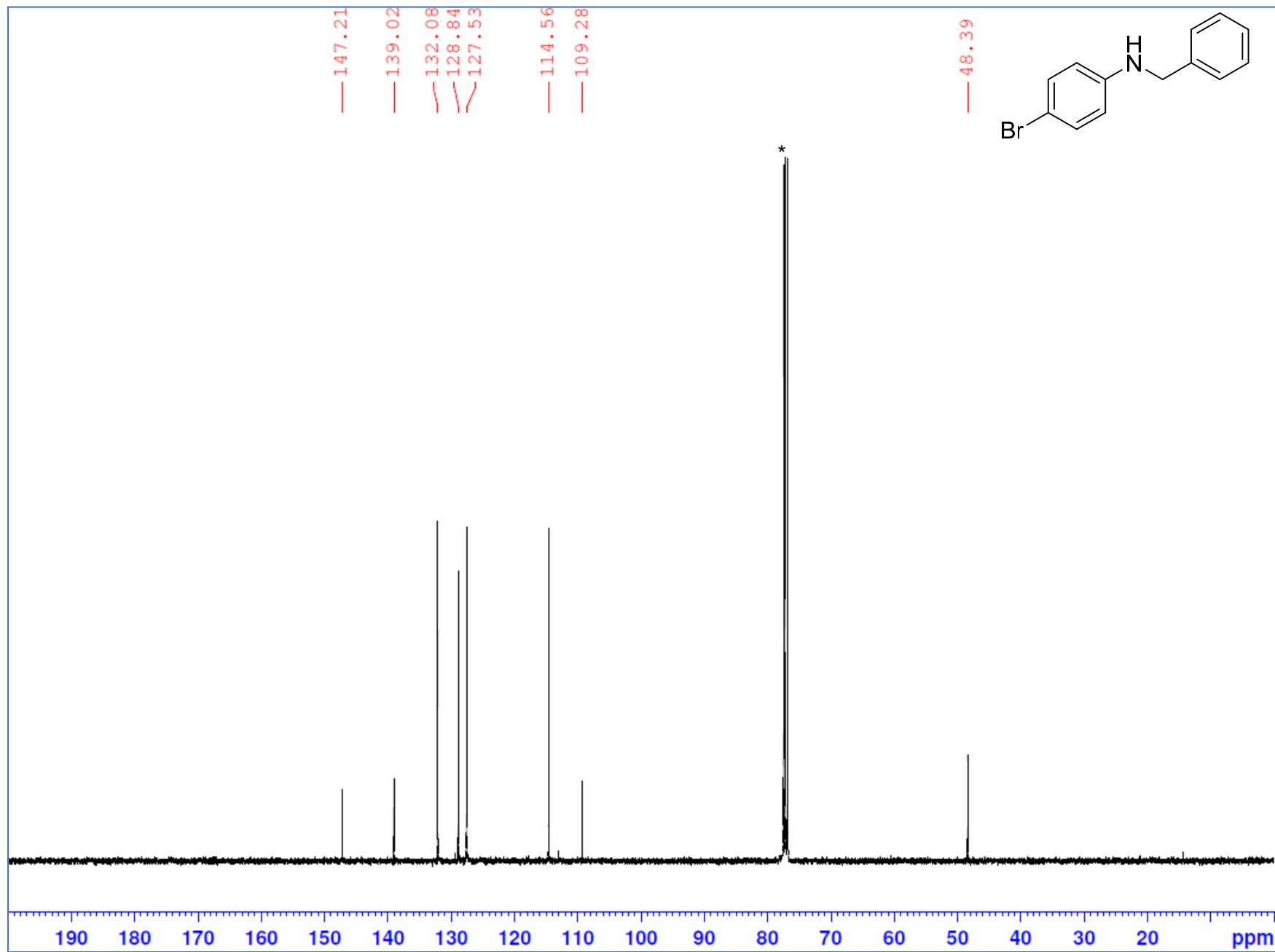
Supplementary Figure S15. ¹H-NMR spectrum of 2a in CDCl₃; \$ ≡ residual petrol ether.



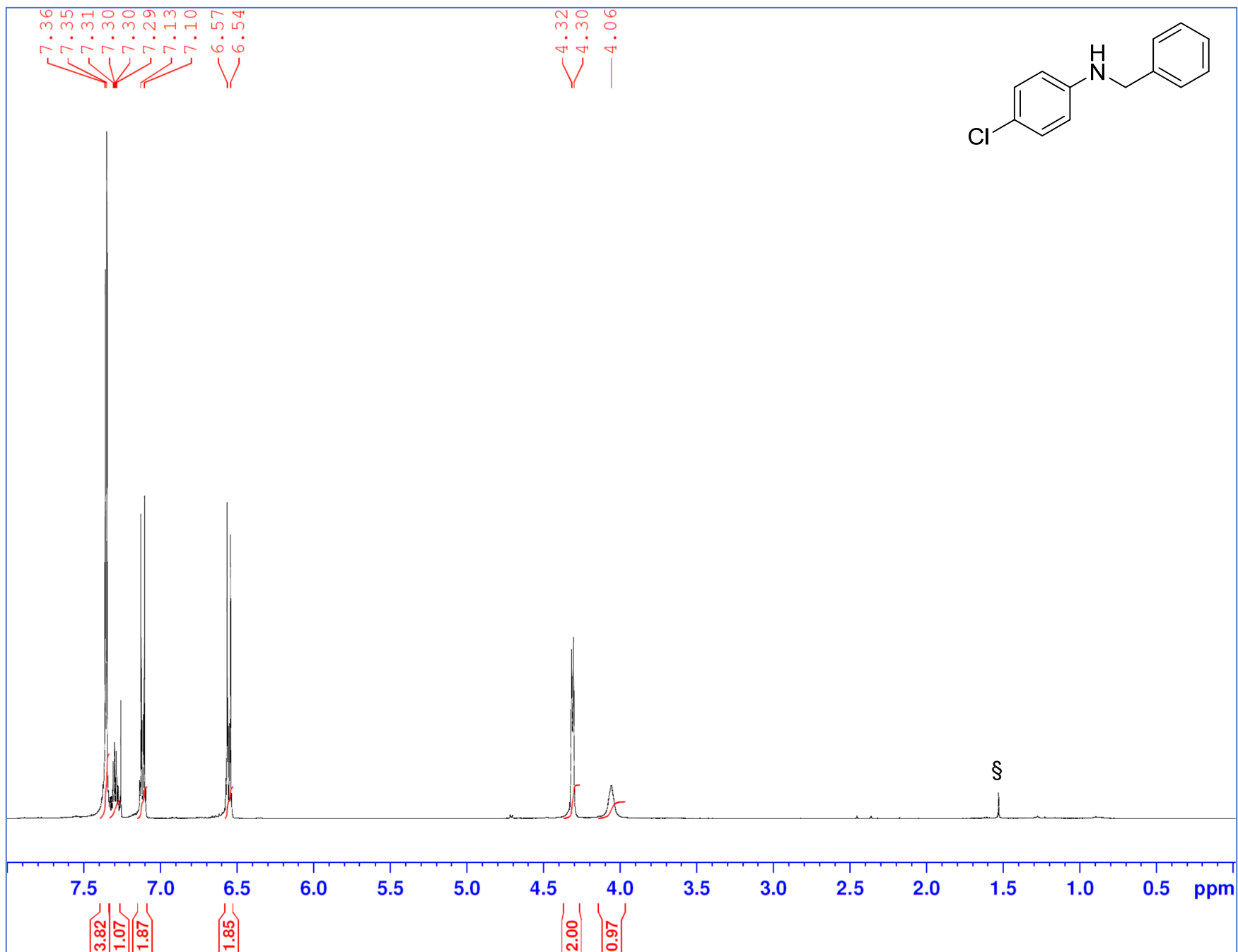
Supplementary Figure S16. $^{13}\text{C}\{^1\text{H}\}$ -NMR spectrum of **2a** in CDCl_3 , * \equiv deuterated solvent; \$ \equiv residual petrol ether.



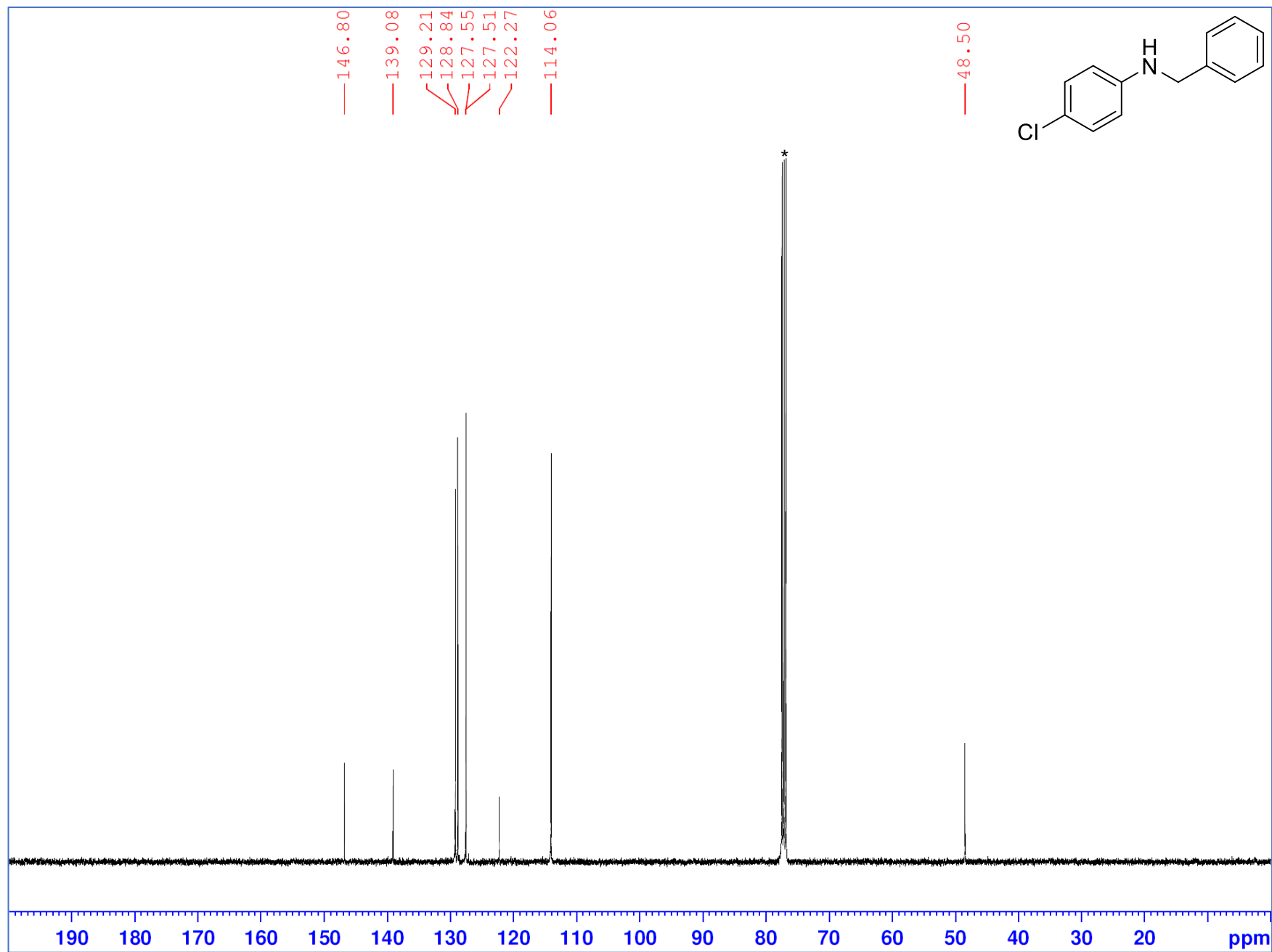
Supplementary Figure S17. ¹H-NMR spectrum of **2b** in CDCl₃; \$ ≡ residual EtOAc.



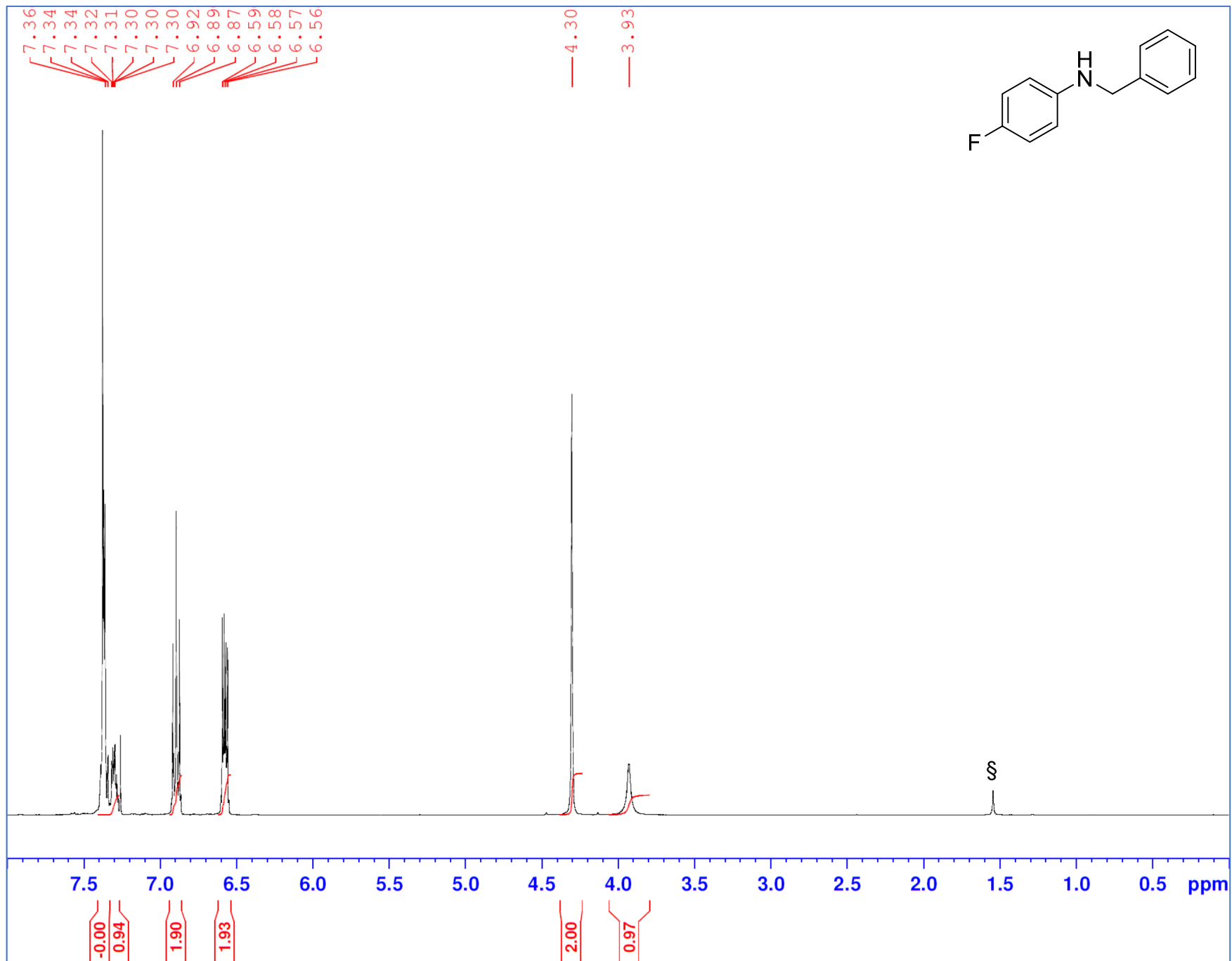
Supplementary Figure S18. $^{13}\text{C}\{^1\text{H}\}$ -NMR spectrum of **2b** in CDCl_3 , * \equiv deuterated solvent.



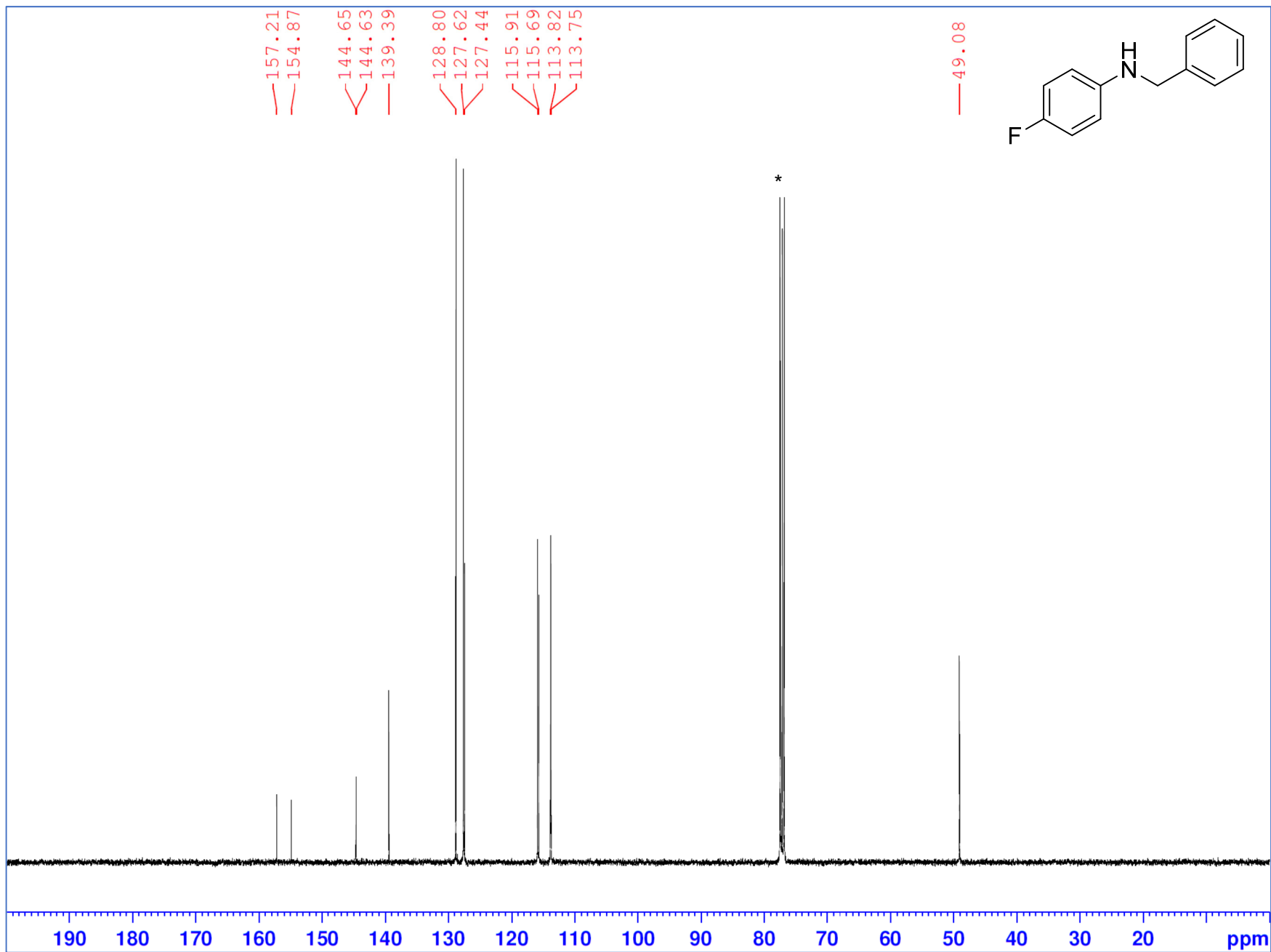
Supplementary Figure S19. $^1\text{H-NMR}$ spectrum of **2c** in CDCl_3 ; § \equiv residual water.



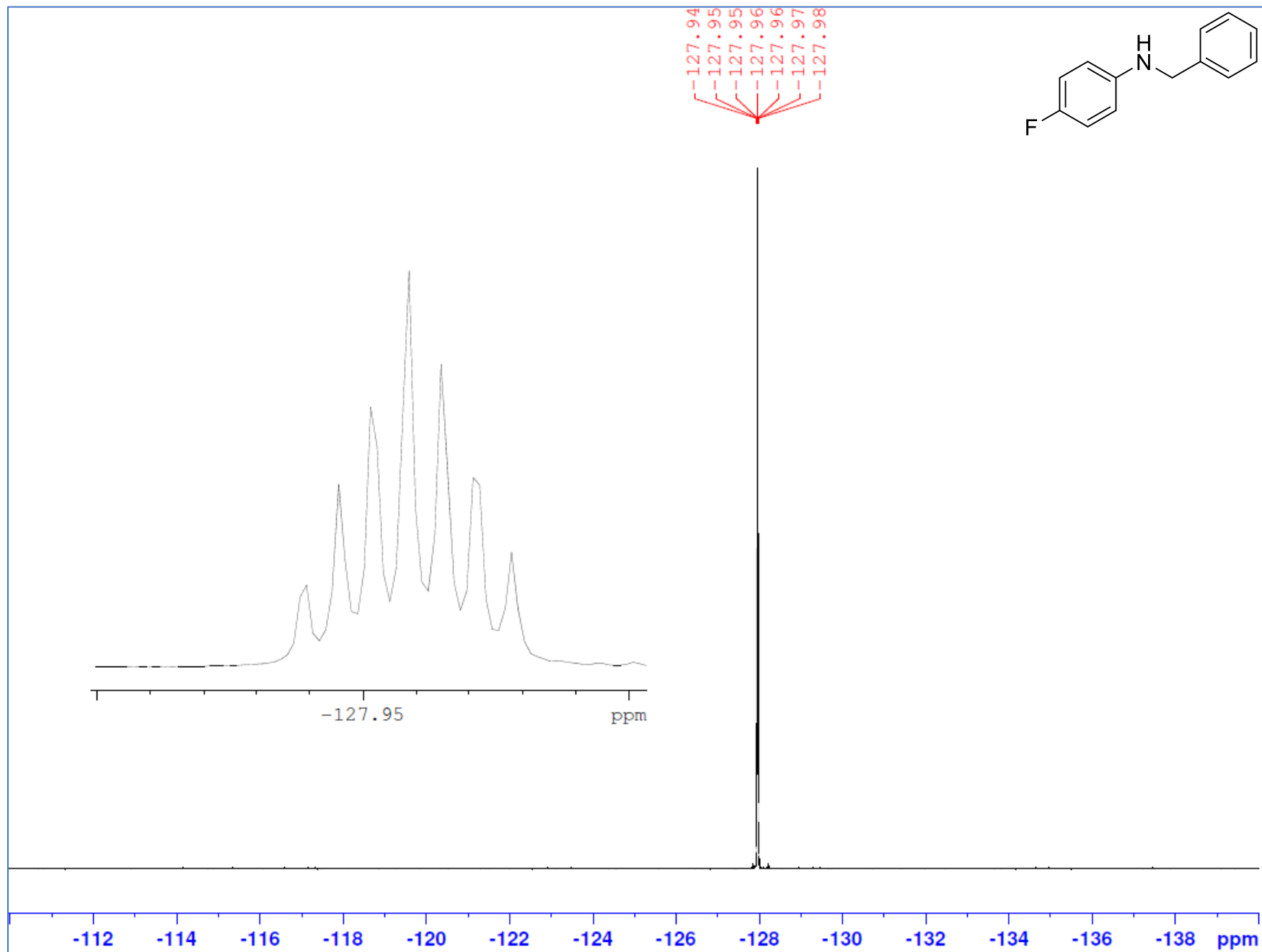
Supplementary Figure S20. $^{13}\text{C}\{^1\text{H}\}$ -NMR spectrum of **2c** in CDCl_3 , * \equiv deuterated solvent.



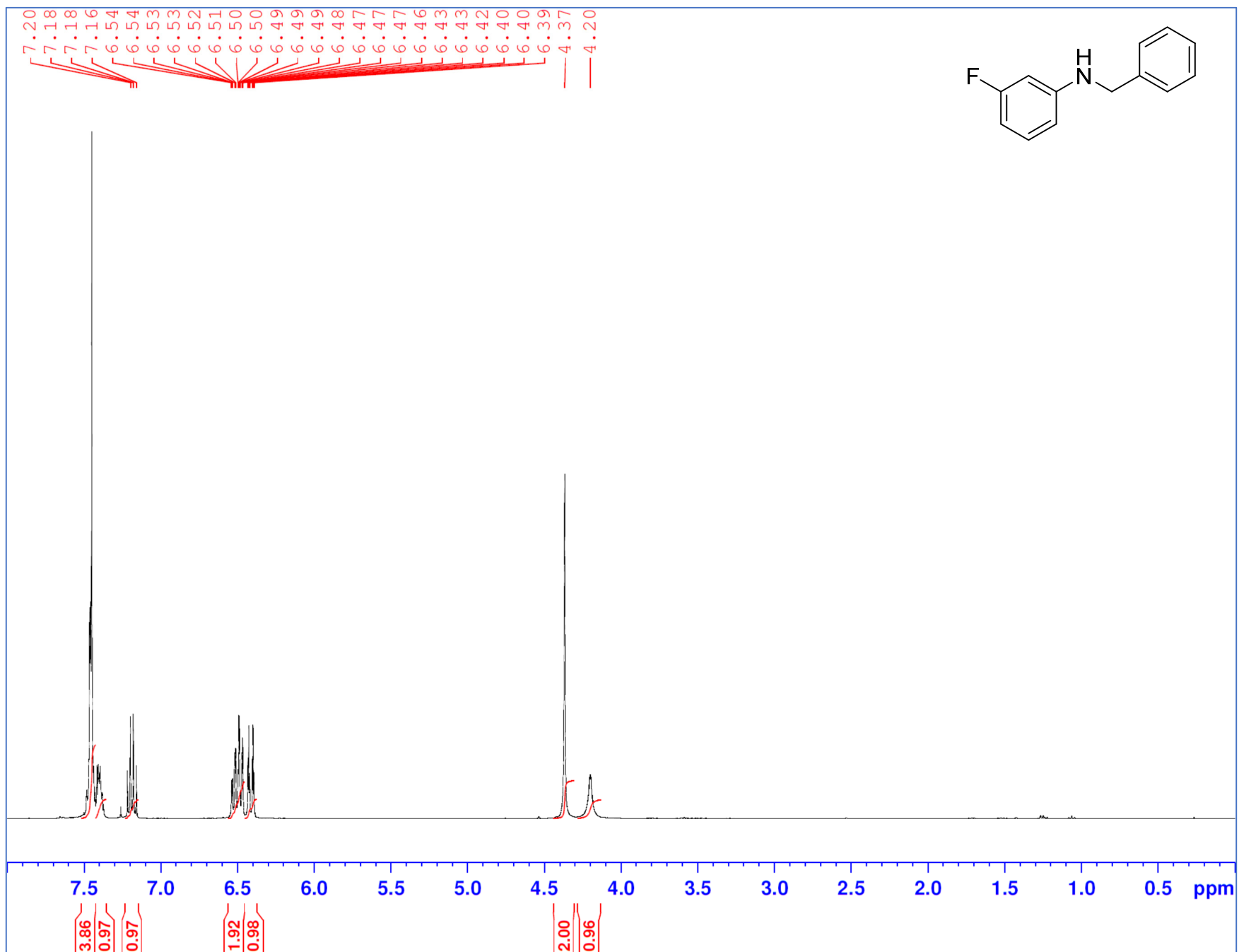
Supplementary Figure S21. ¹H-NMR spectrum of 2d in CDCl₃; § ≡ residual water.



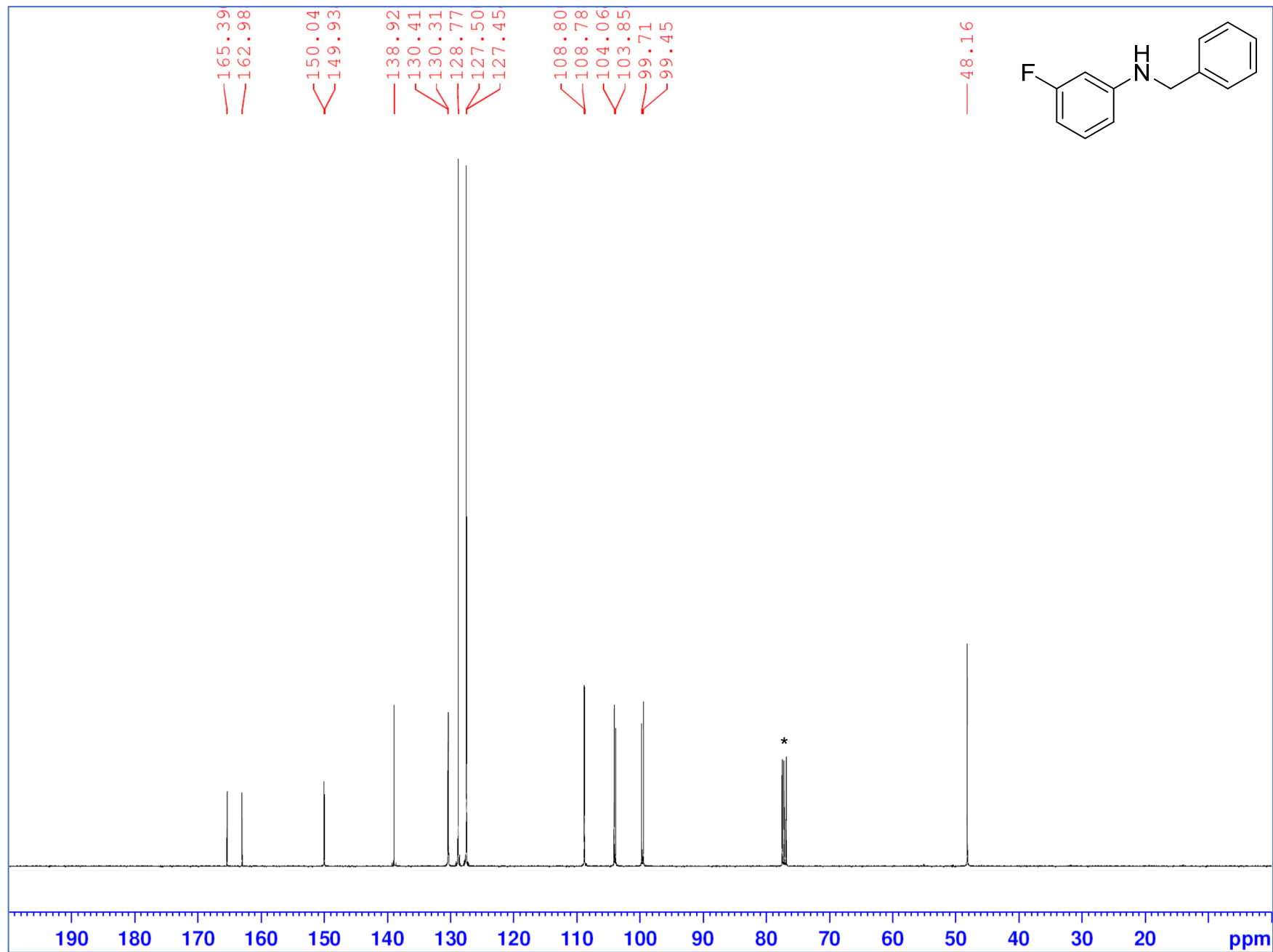
Supplementary Figure S22. ¹³C{¹H}-NMR spectrum of **2d** in CDCl₃, * ≡ deuterated solvent.



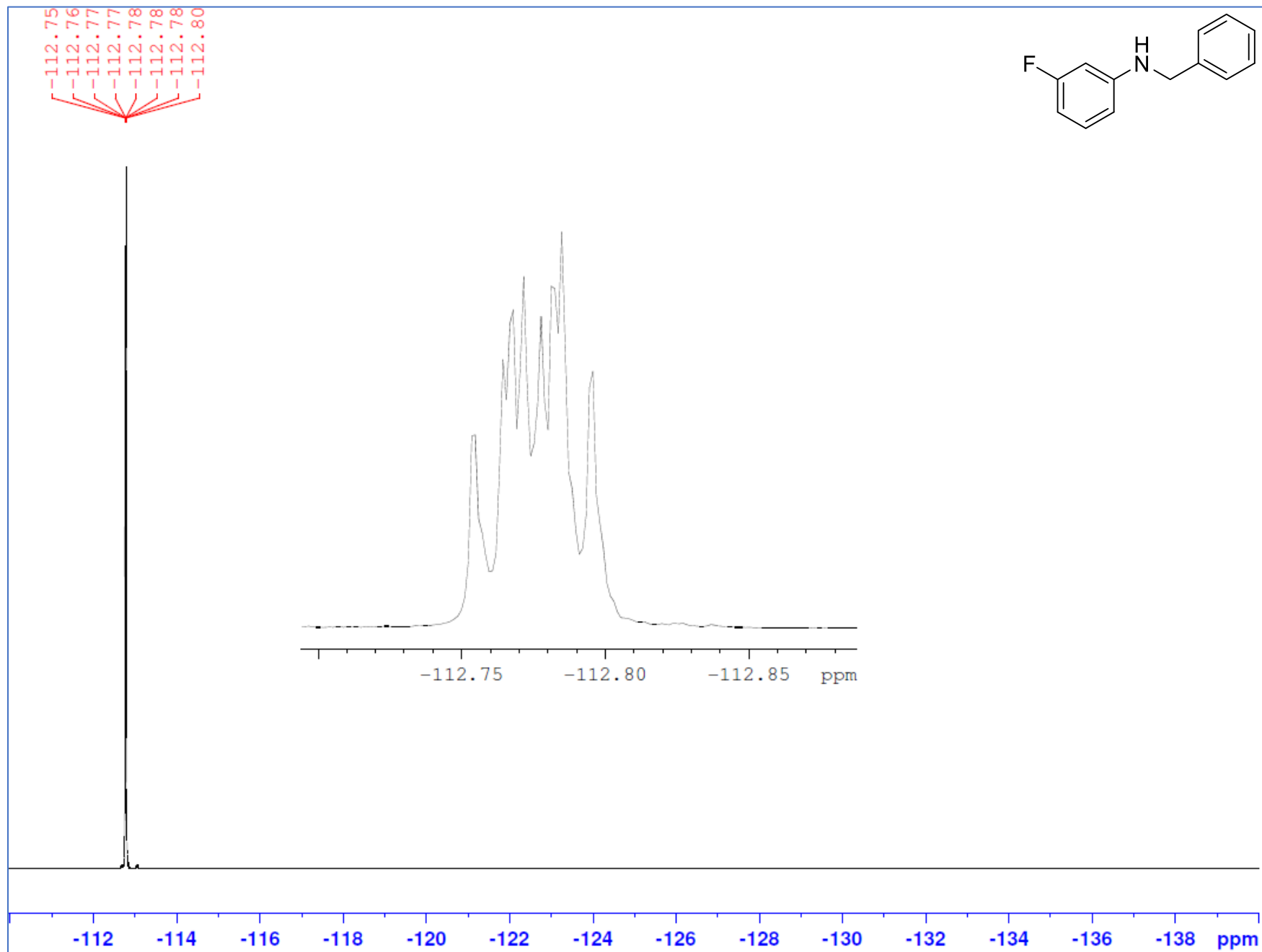
Supplementary Figure S23. ^{19}F -NMR spectrum of **2d** in CDCl_3 .



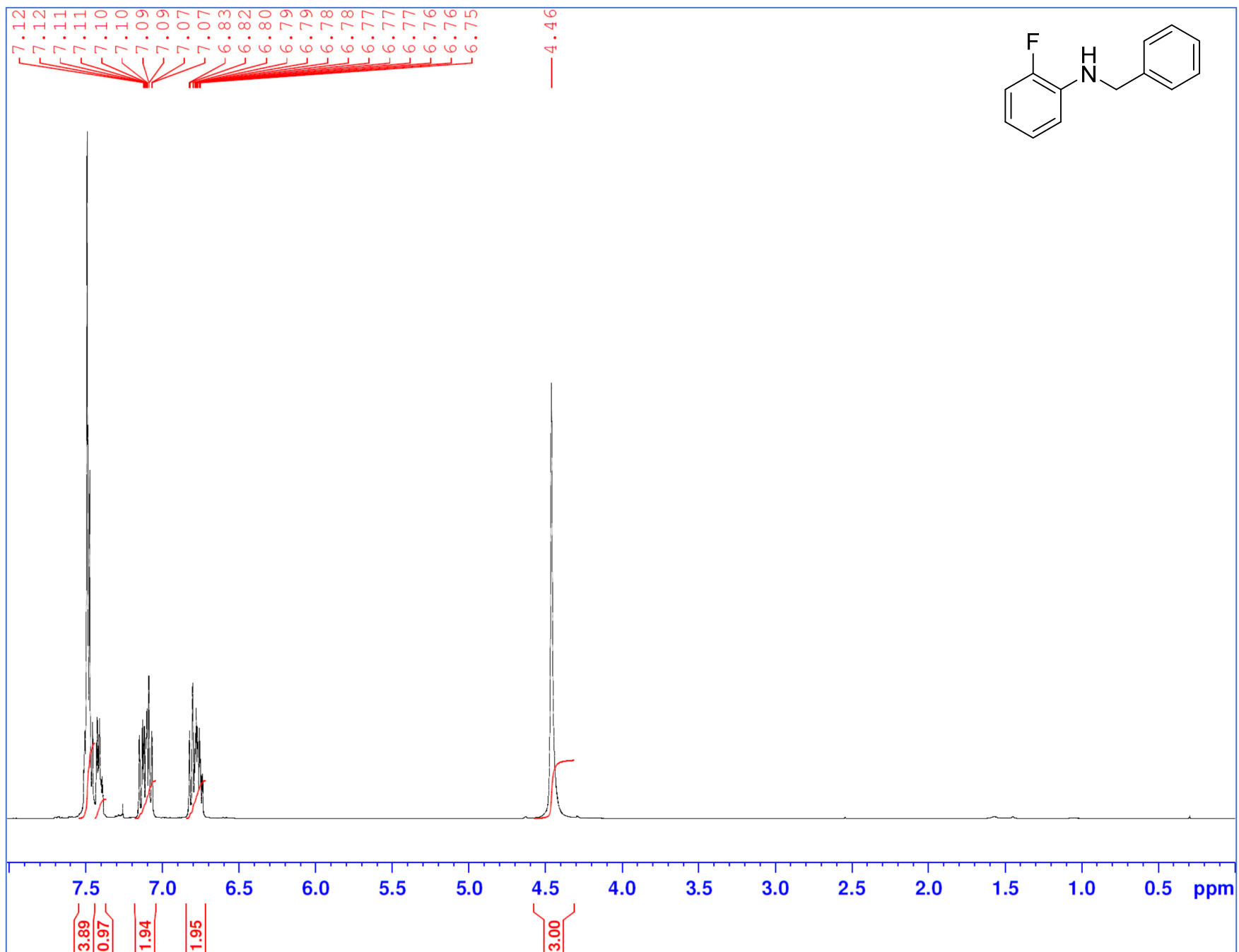
Supplementary Figure S24. ¹H-NMR spectrum of 2e in CDCl₃.



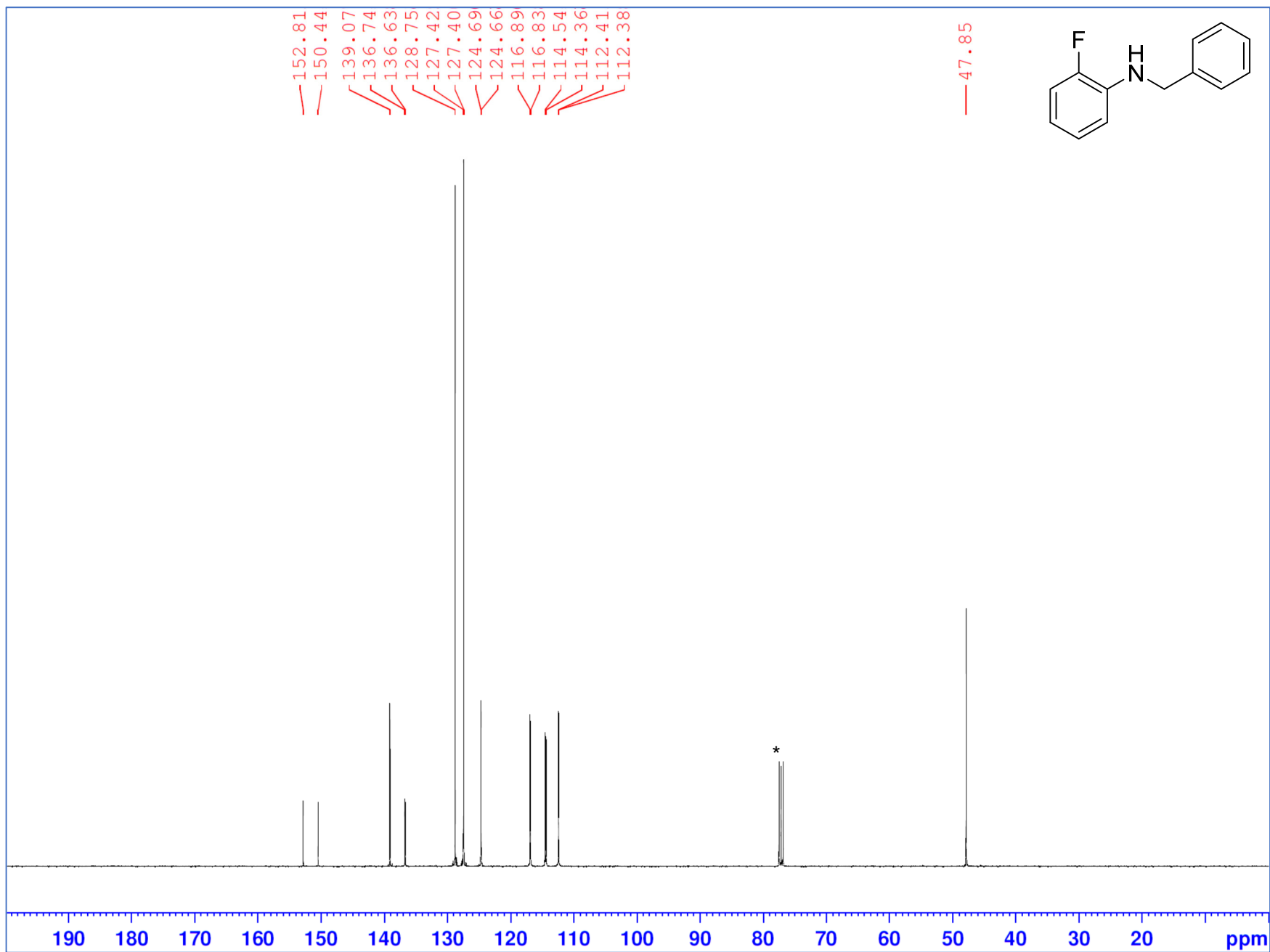
Supplementary Figure S25. $^{13}\text{C}\{^1\text{H}\}$ -NMR spectrum of **2e** in CDCl_3 ; * \equiv deuterated solvent.



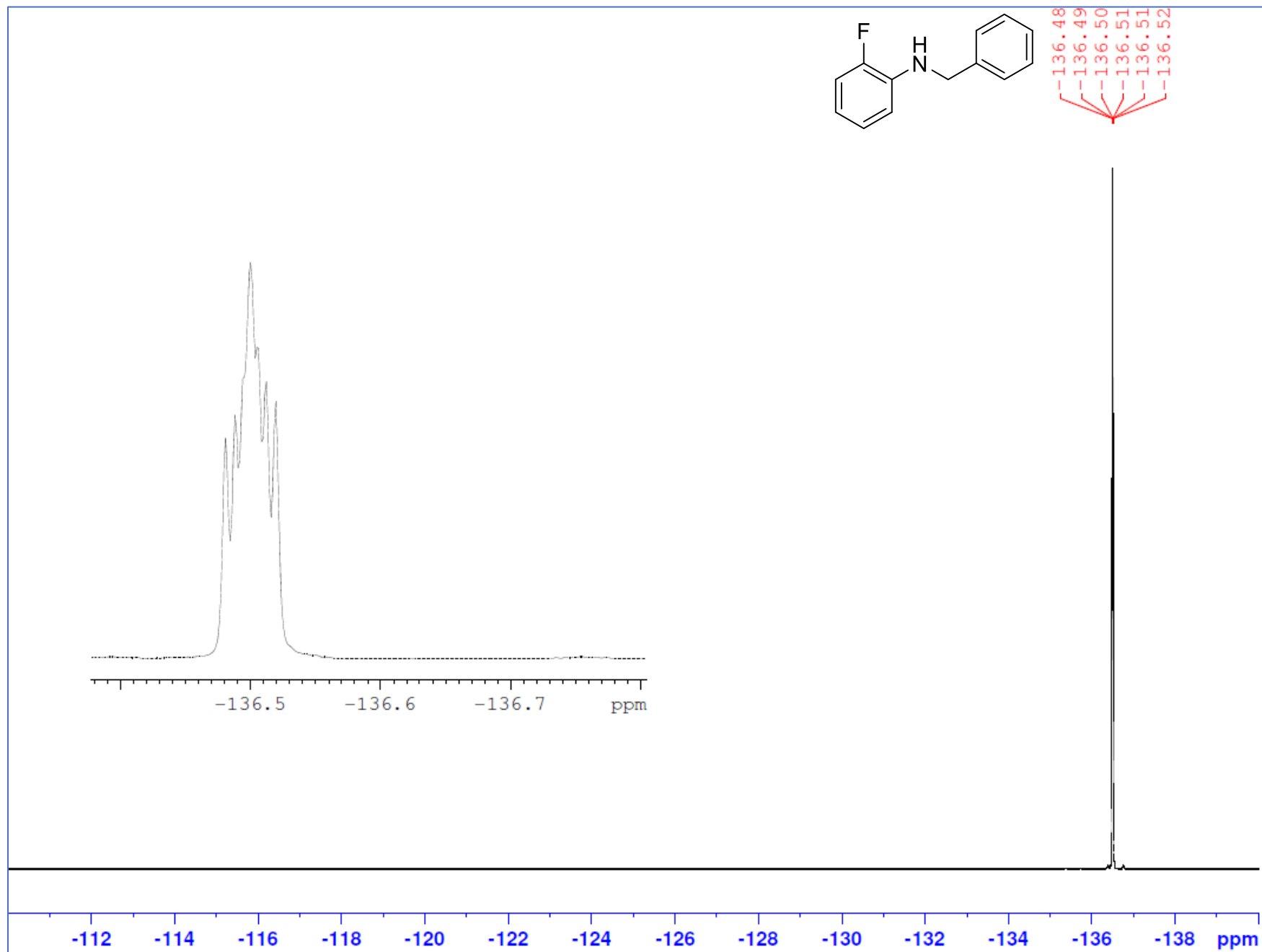
Supplementary Figure S26. ^{19}F -NMR spectrum of **2e** in CDCl_3 .



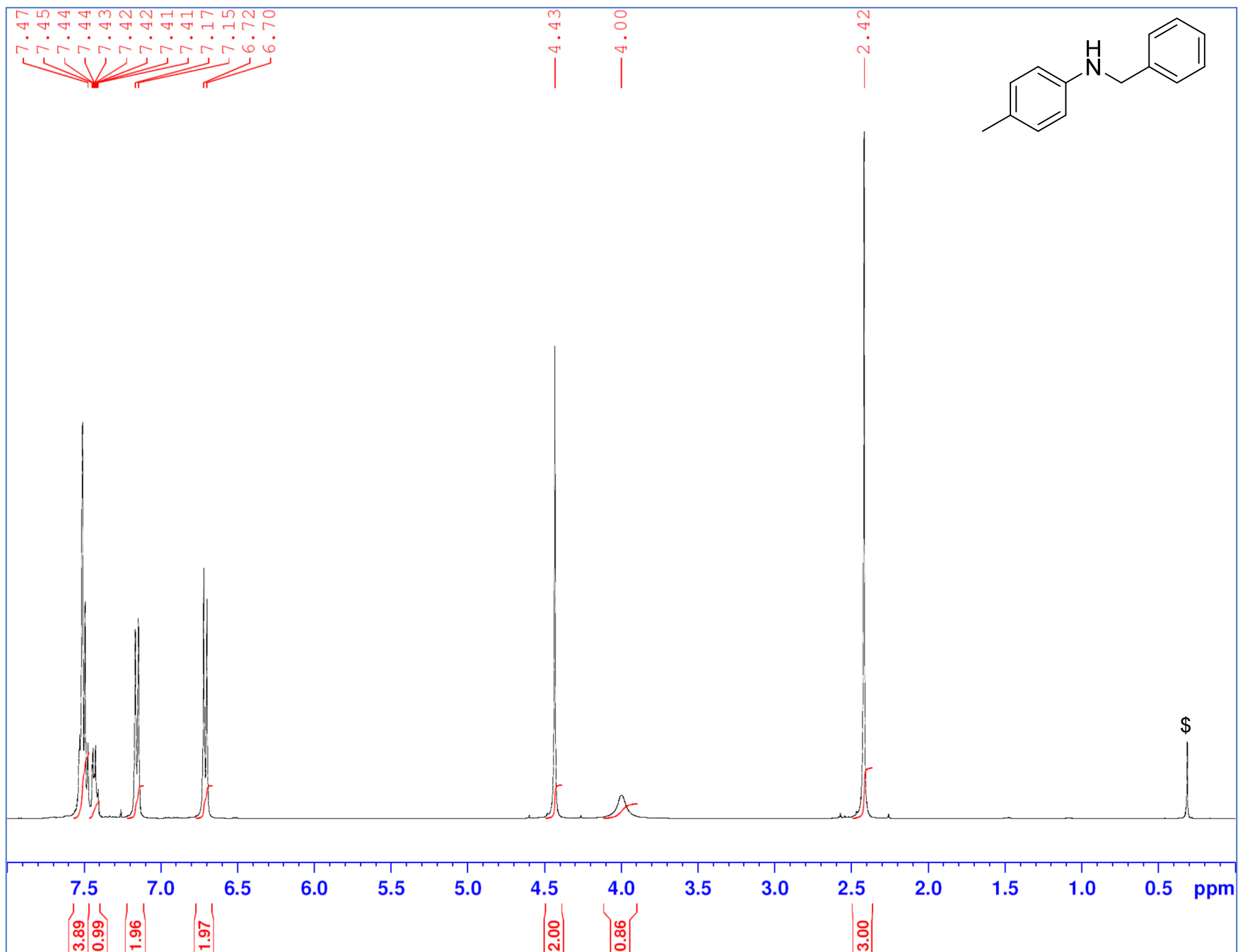
Supplementary Figure S27. ¹H-NMR spectrum of **2f** in CDCl₃.



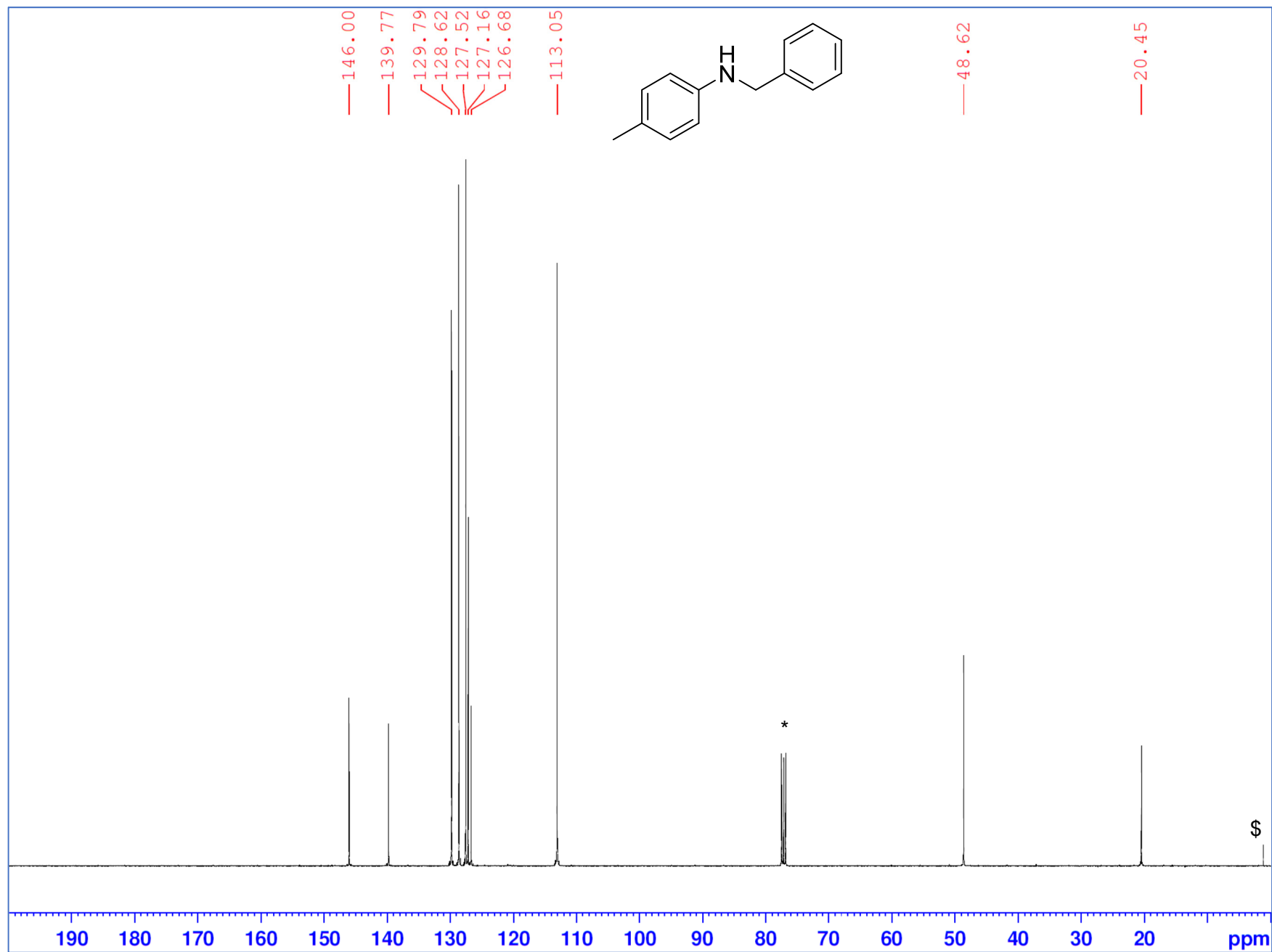
Supplementary Figure S28. $^{13}\text{C}\{^1\text{H}\}$ -NMR spectrum of **2f** in CDCl_3 ; * \equiv deuterated solvent.



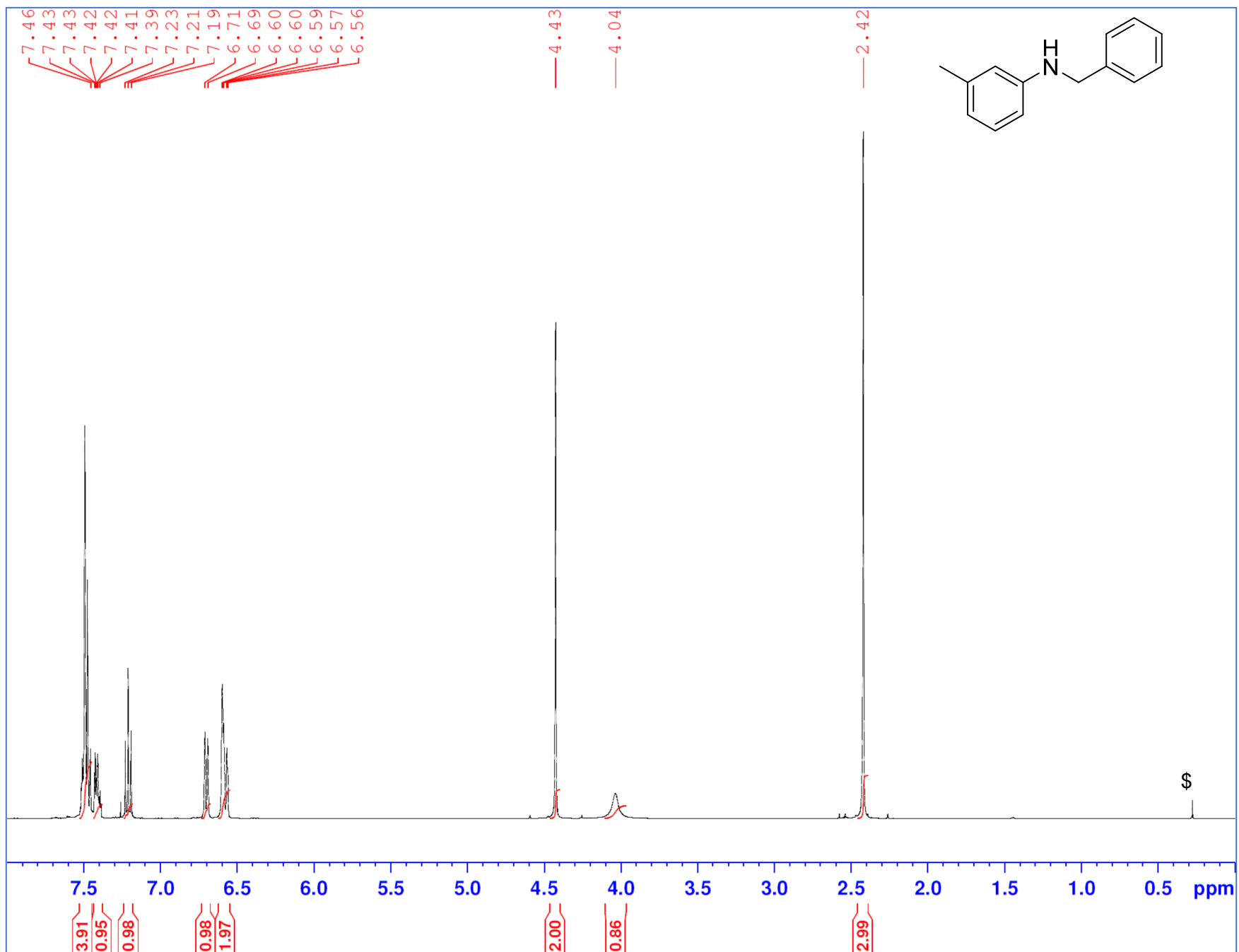
Supplementary Figure S29. ^{19}F -NMR spectrum of **2f** in CDCl_3 .



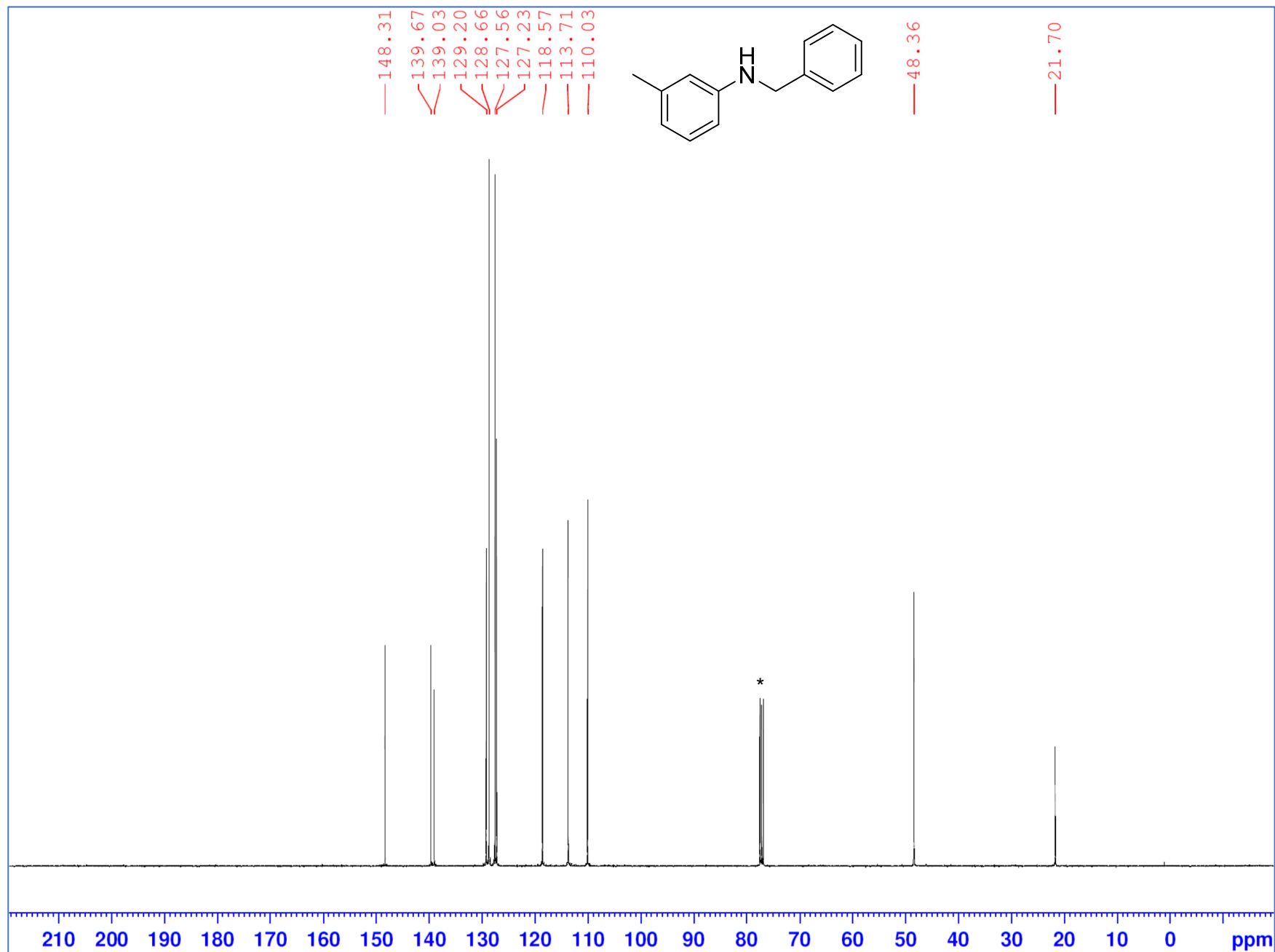
Supplementary Figure S30. $^1\text{H-NMR}$ spectrum of **2g** in CDCl_3 ; \$ \equiv silicon grease.



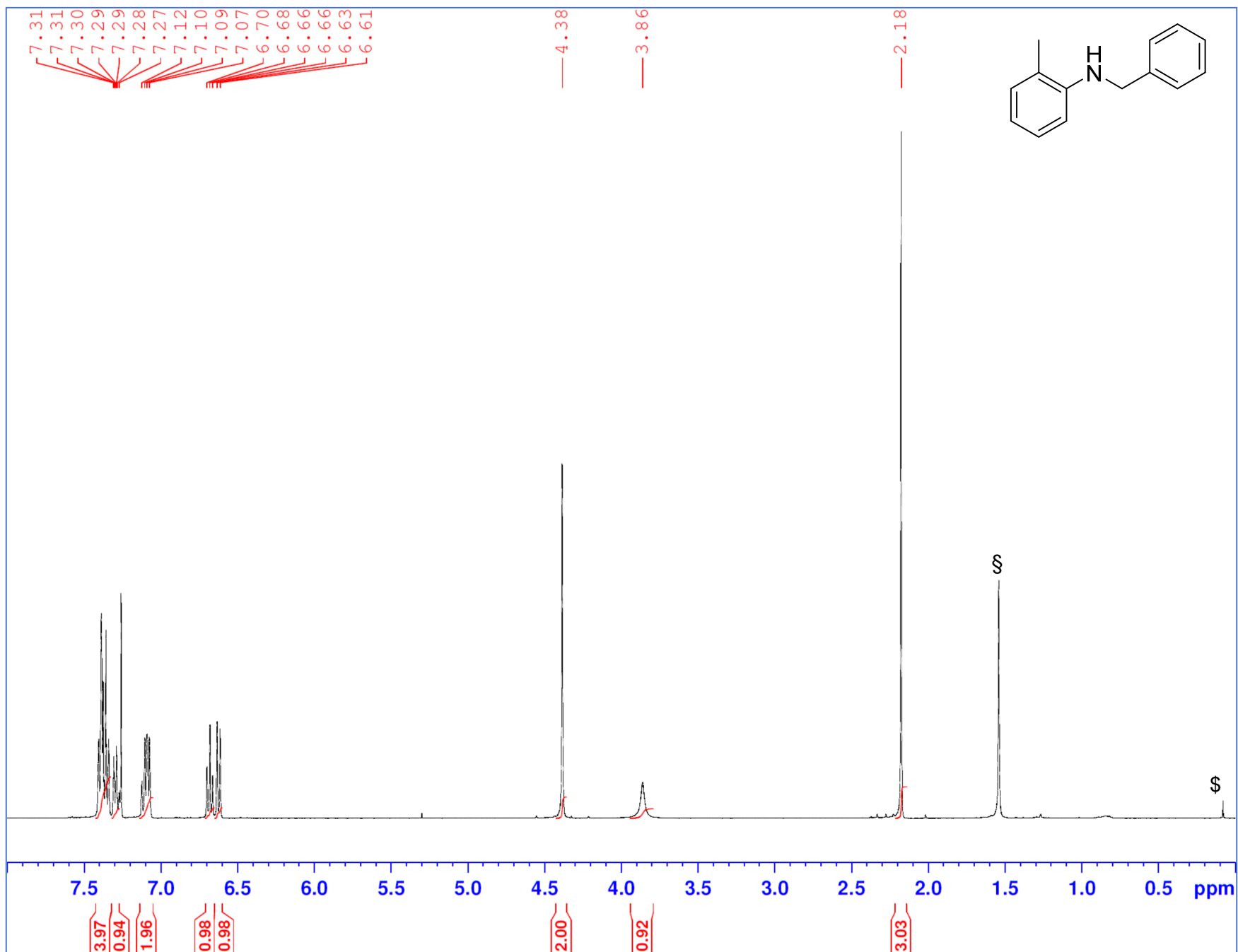
Supplementary Figure S31. $^{13}\text{C}\{^1\text{H}\}$ -NMR spectrum of **2g** in CDCl_3 ; * \equiv deuterated solvent; \$ \equiv silicon grease.



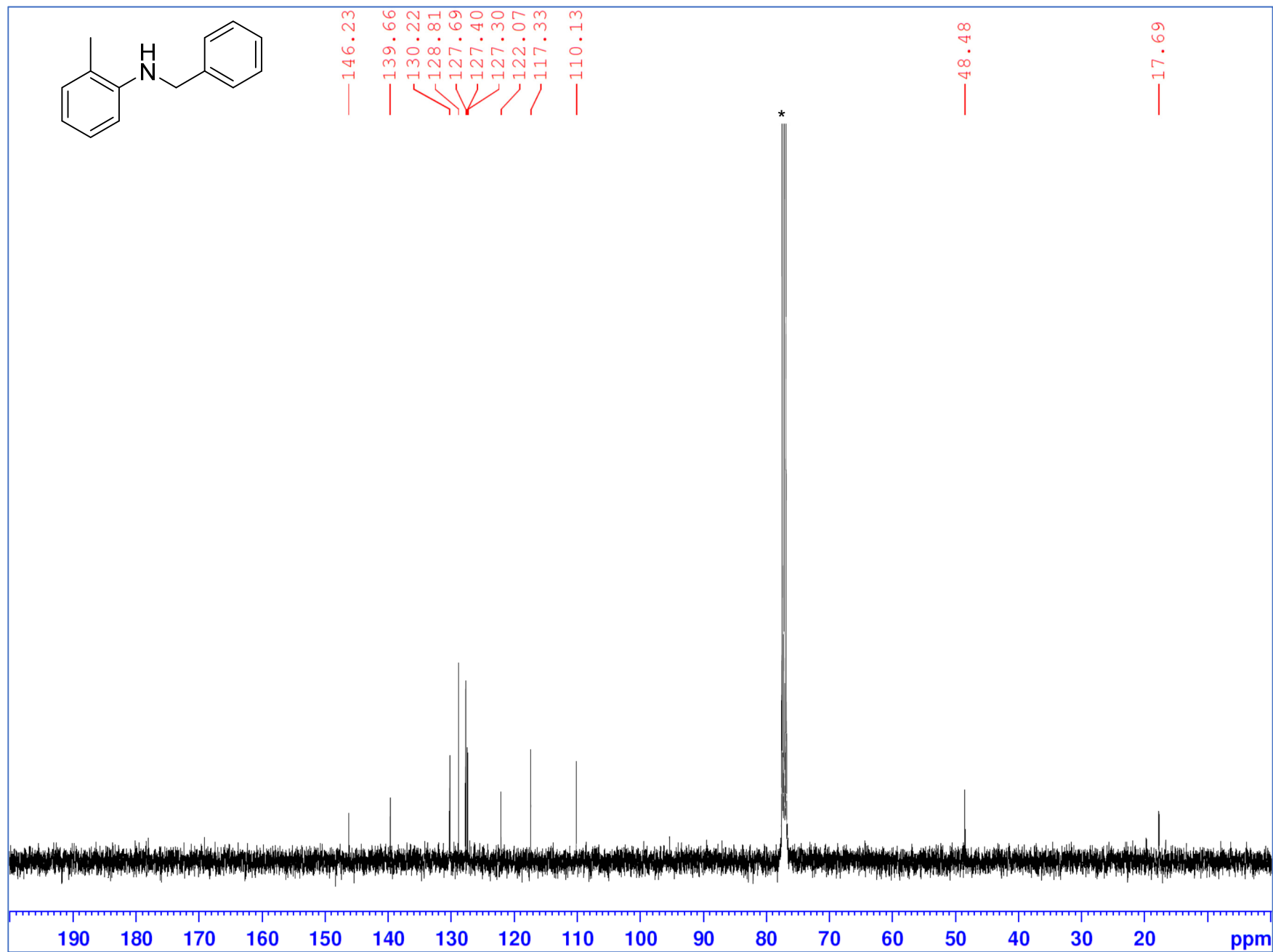
Supplementary Figure S32. ¹H-NMR spectrum of **2h** in CDCl₃; \$ ≡ silicon grease.



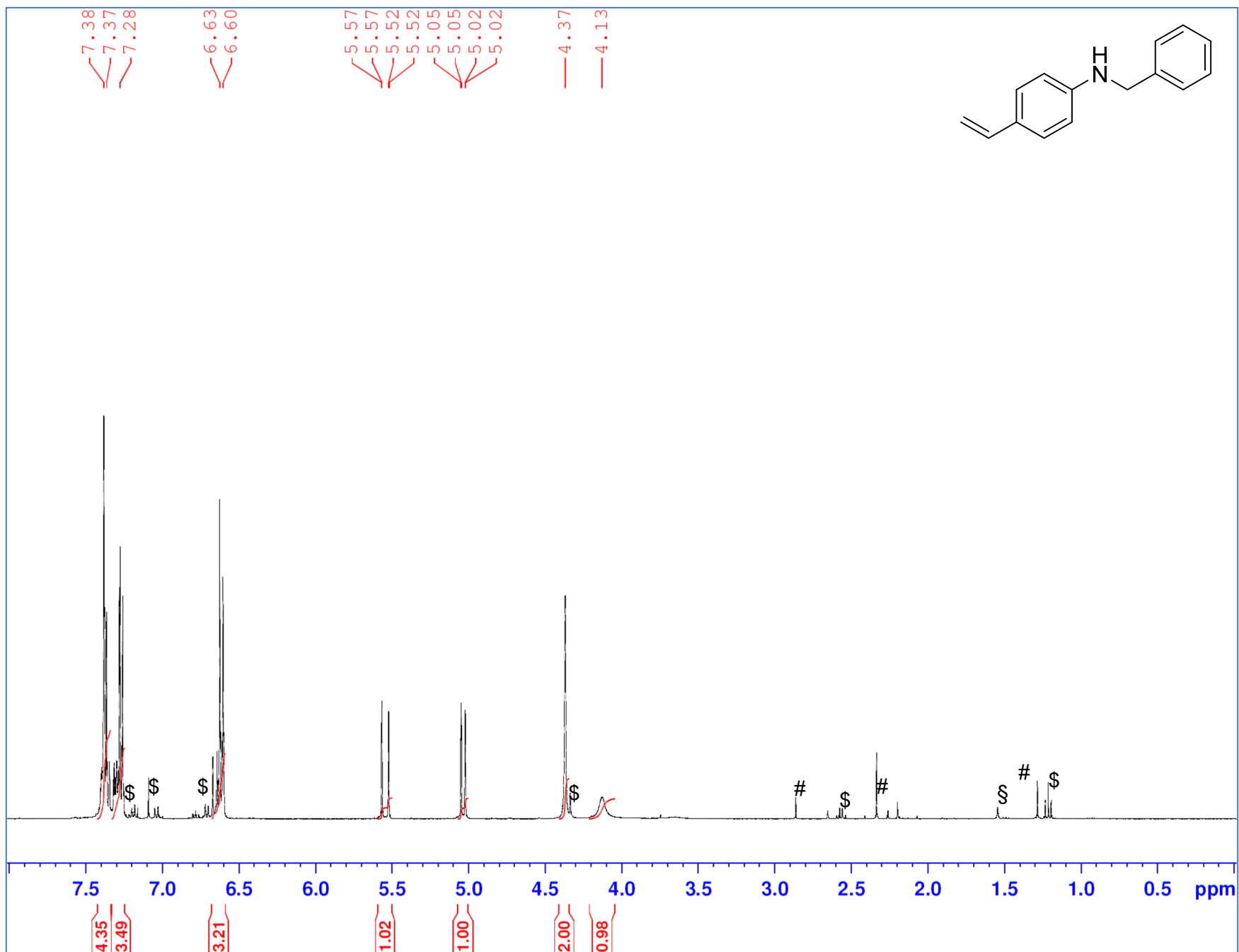
Supplementary Figure S33. $^{13}\text{C}\{^1\text{H}\}$ -NMR spectrum of **2h** in CDCl_3 ; * \equiv deuterated solvent.



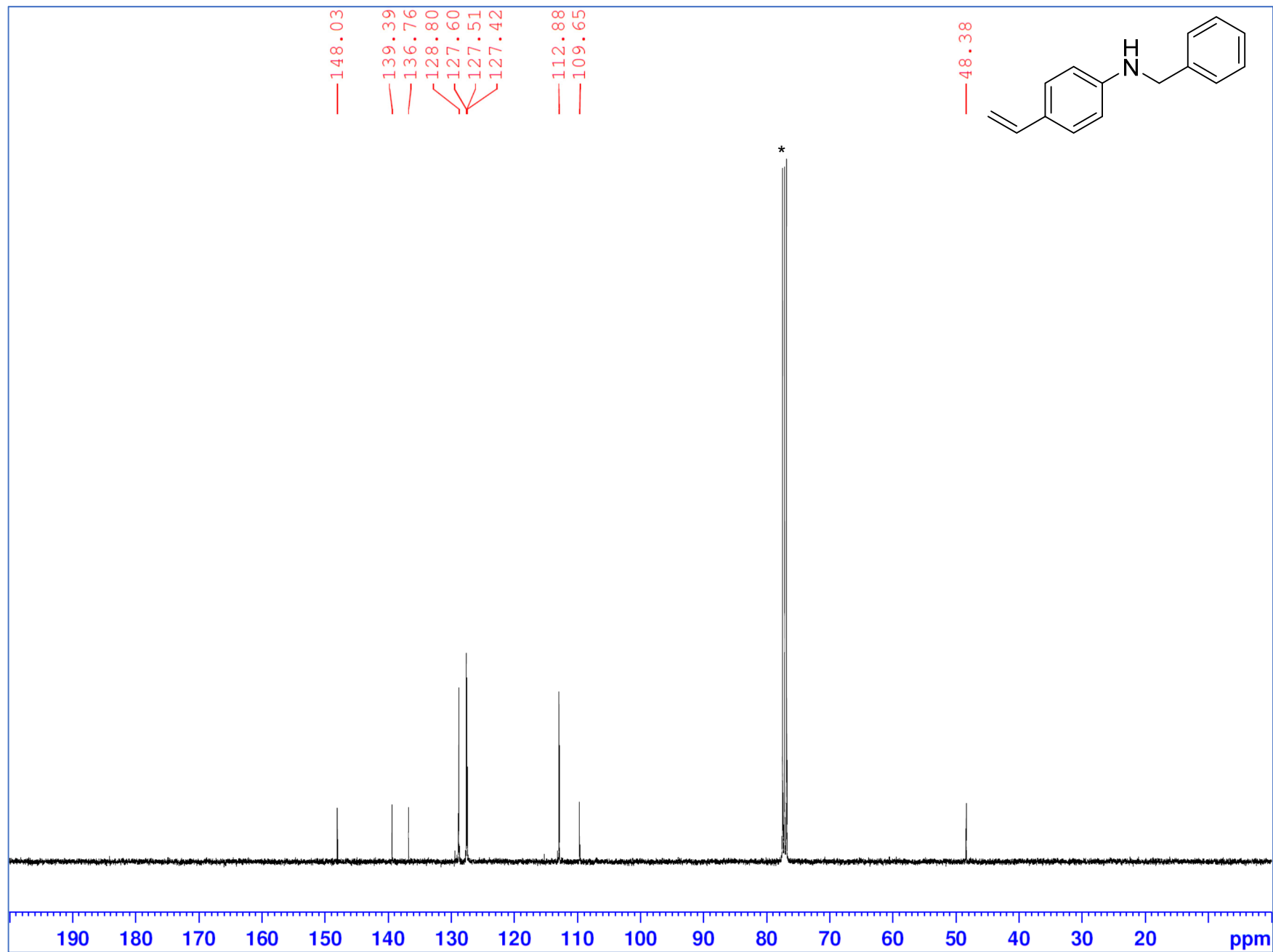
Supplementary Figure S34. $^1\text{H-NMR}$ spectrum of **2i** in CDCl_3 ; § ≡ residual water; \$ ≡ silicon grease.



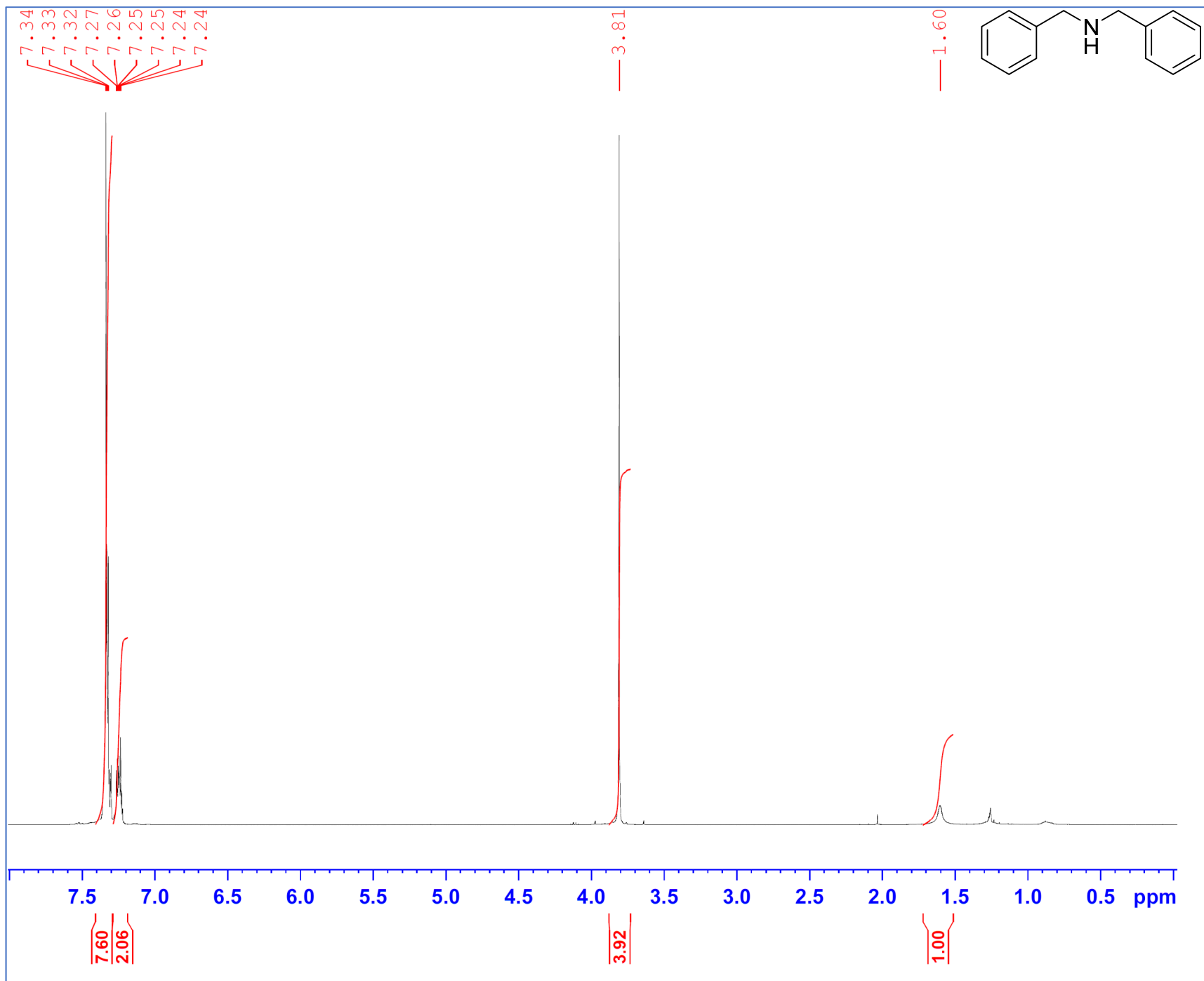
Supplementary Figure S35. $^{13}\text{C}\{^1\text{H}\}$ -NMR spectrum of 2i in CDCl_3 ; * \equiv deuterated solvent.



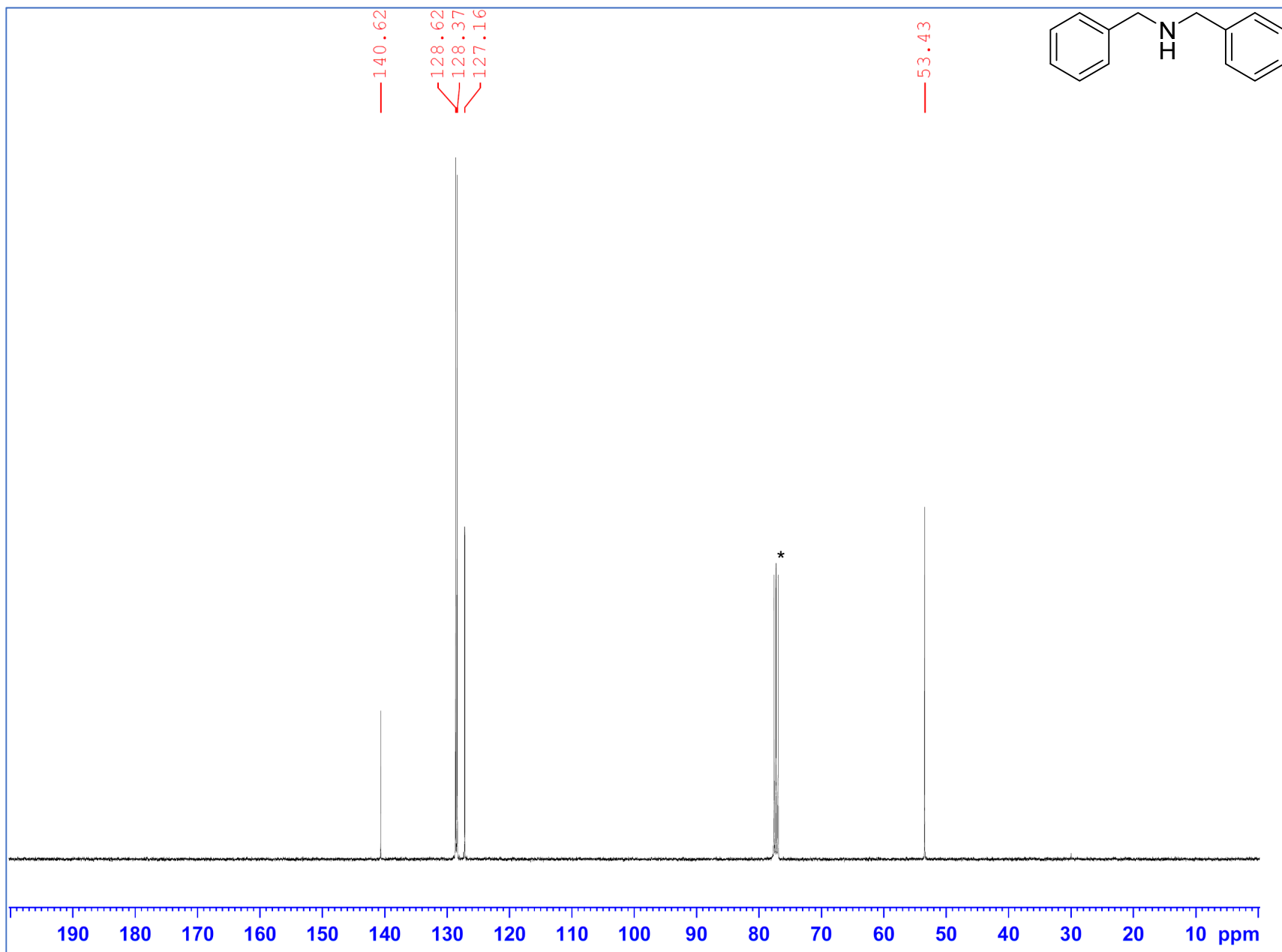
Supplementary Figure S36. ¹H-NMR spectrum of **2j** in CDCl₃; § ≡ residual water; § ≡ *N*-benzyl-4-ethylaniline; # = non-identified impurity.



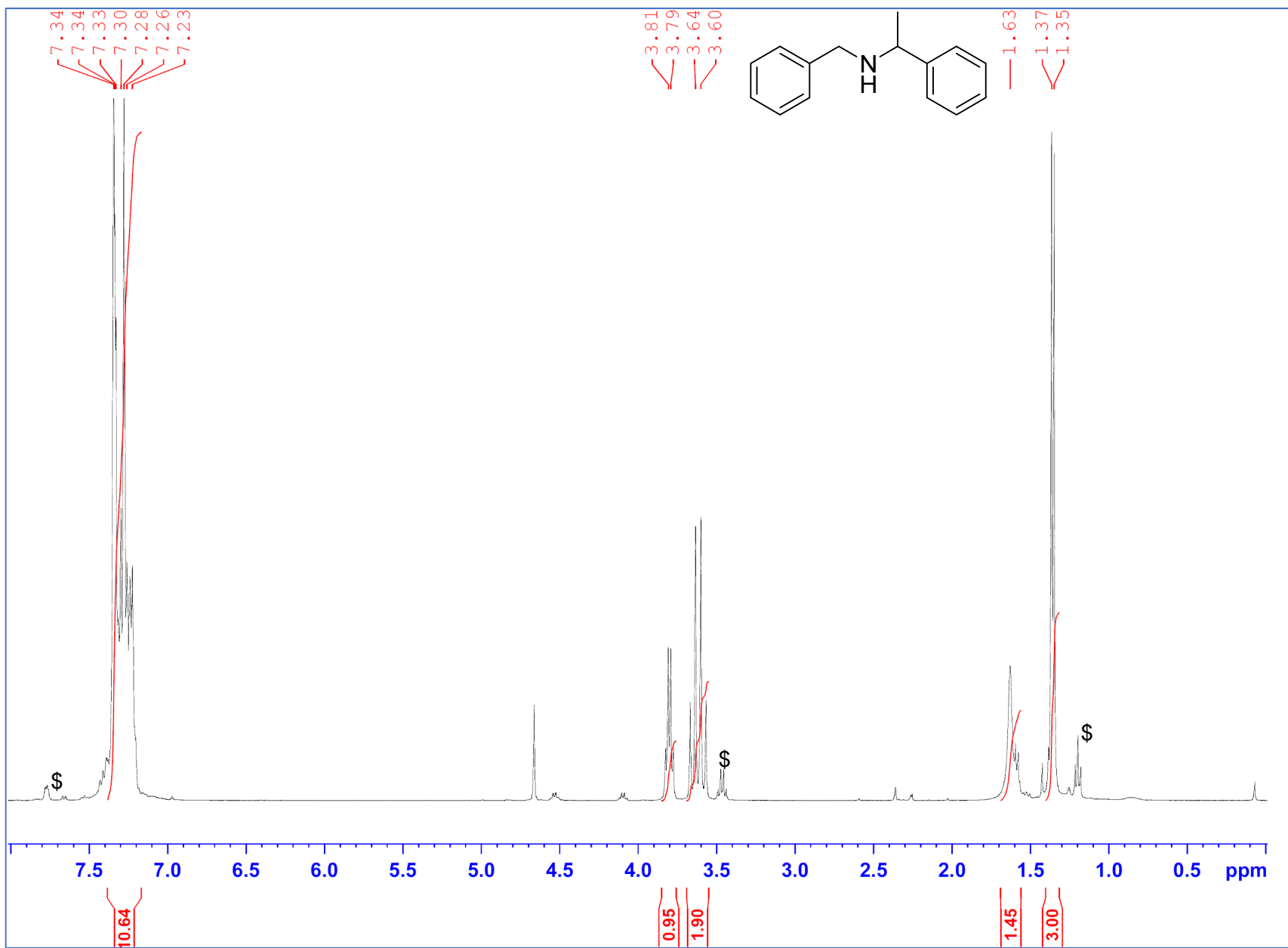
Supplementary Figure S37. $^{13}\text{C}\{^1\text{H}\}$ -NMR spectrum of **2j** in CDCl_3 ; * \equiv deuterated solvent.



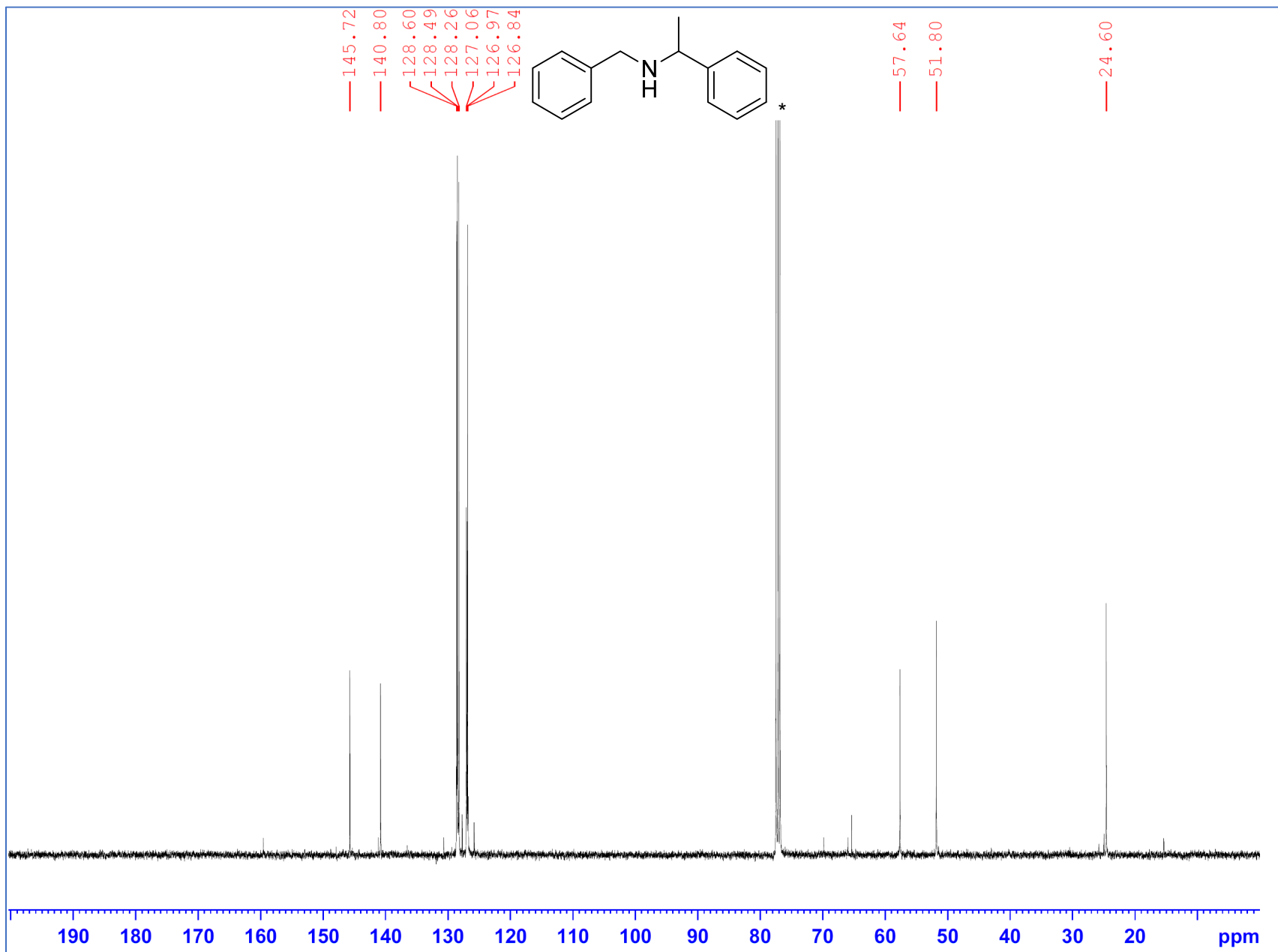
Supplementary Figure S38. ¹H-NMR spectrum of 2k in CDCl₃.



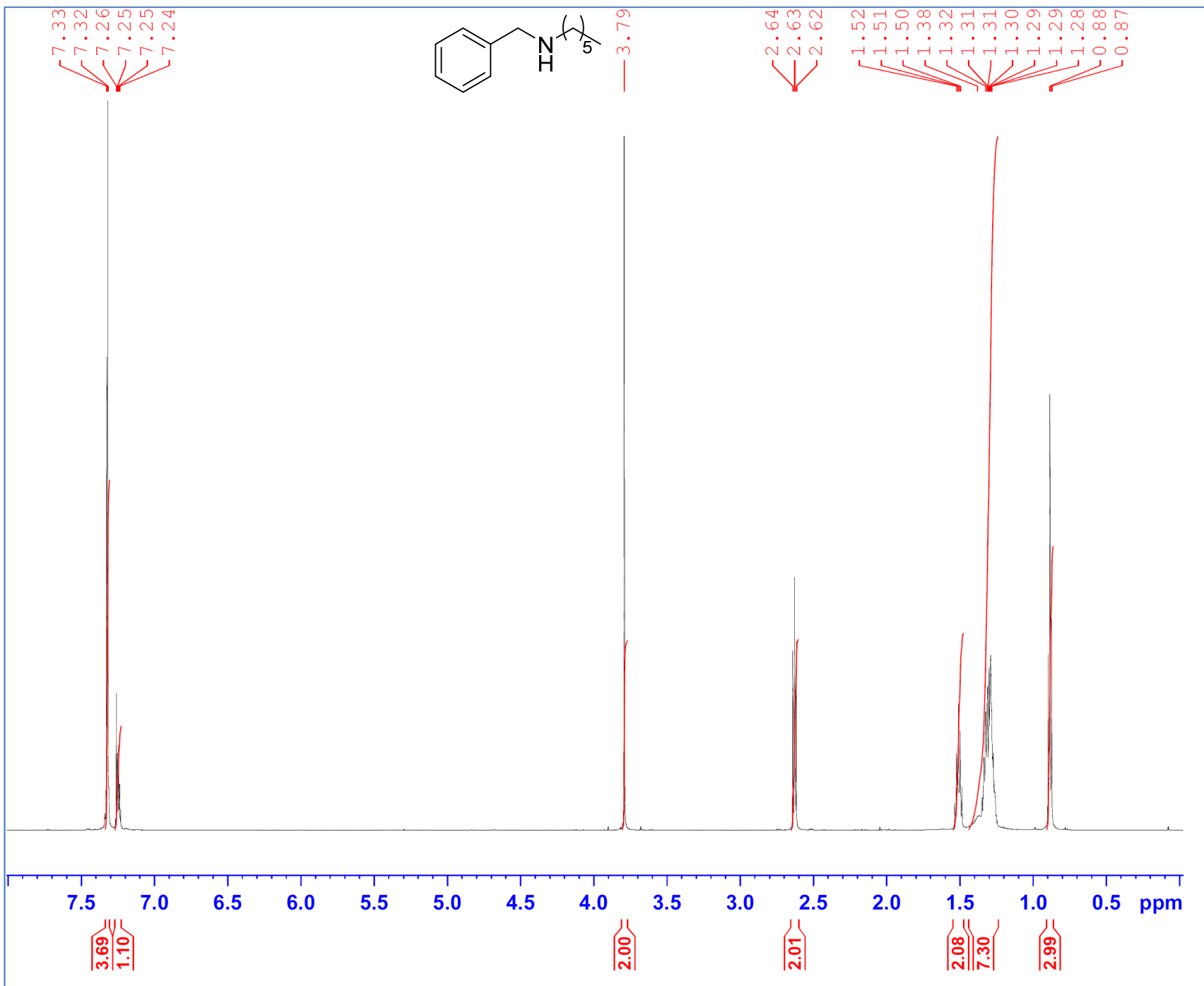
Supplementary Figure S39. $^{13}\text{C}\{^1\text{H}\}$ -NMR spectrum of **2k** in CDCl_3 ; * \equiv deuterated solvent.



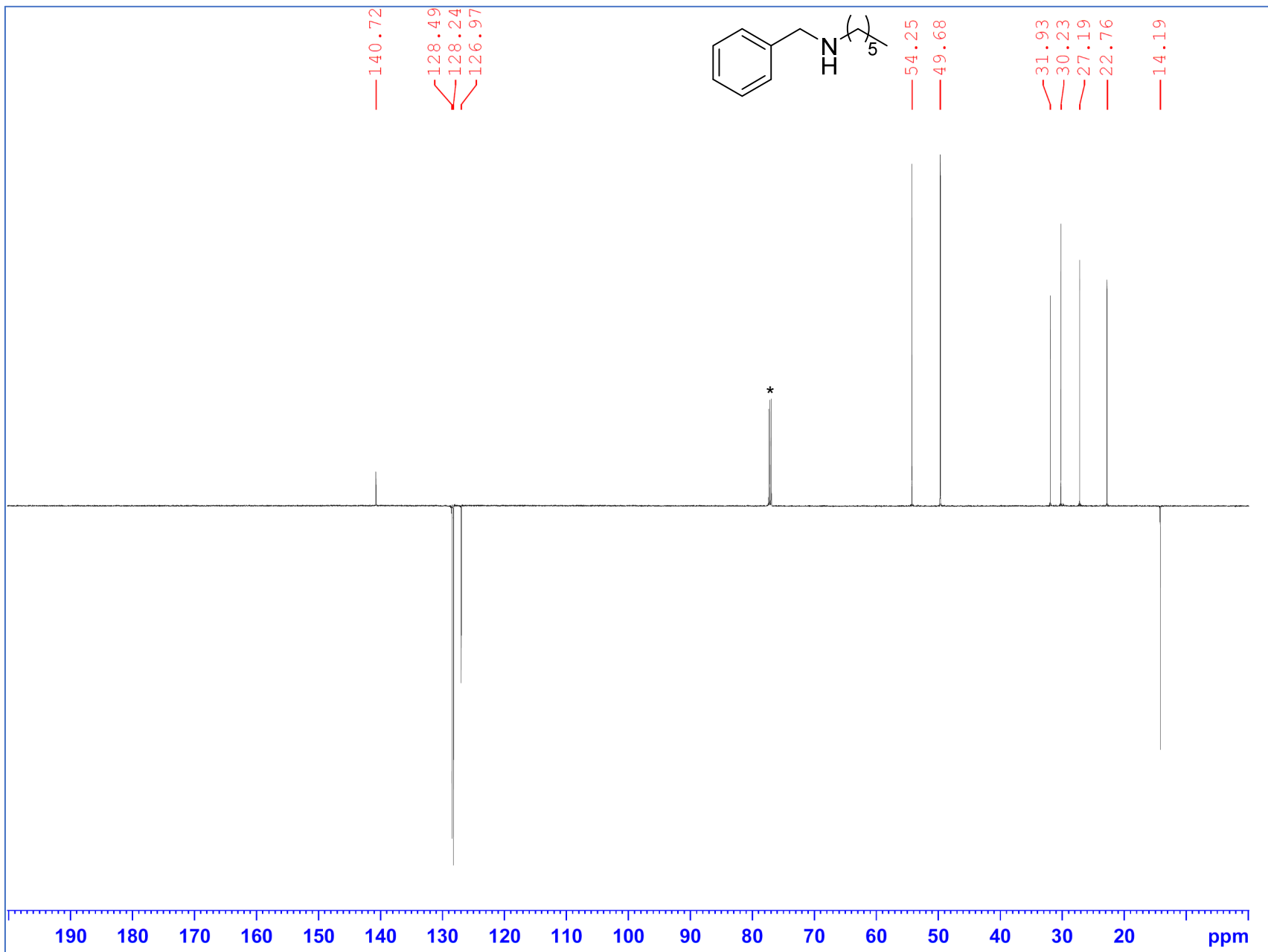
Supplementary Figure S40. ¹H-NMR spectrum of **2I** in CDCl₃; $\$$ \equiv (E)-N-benzyl-1-phenylethan-1-imine.



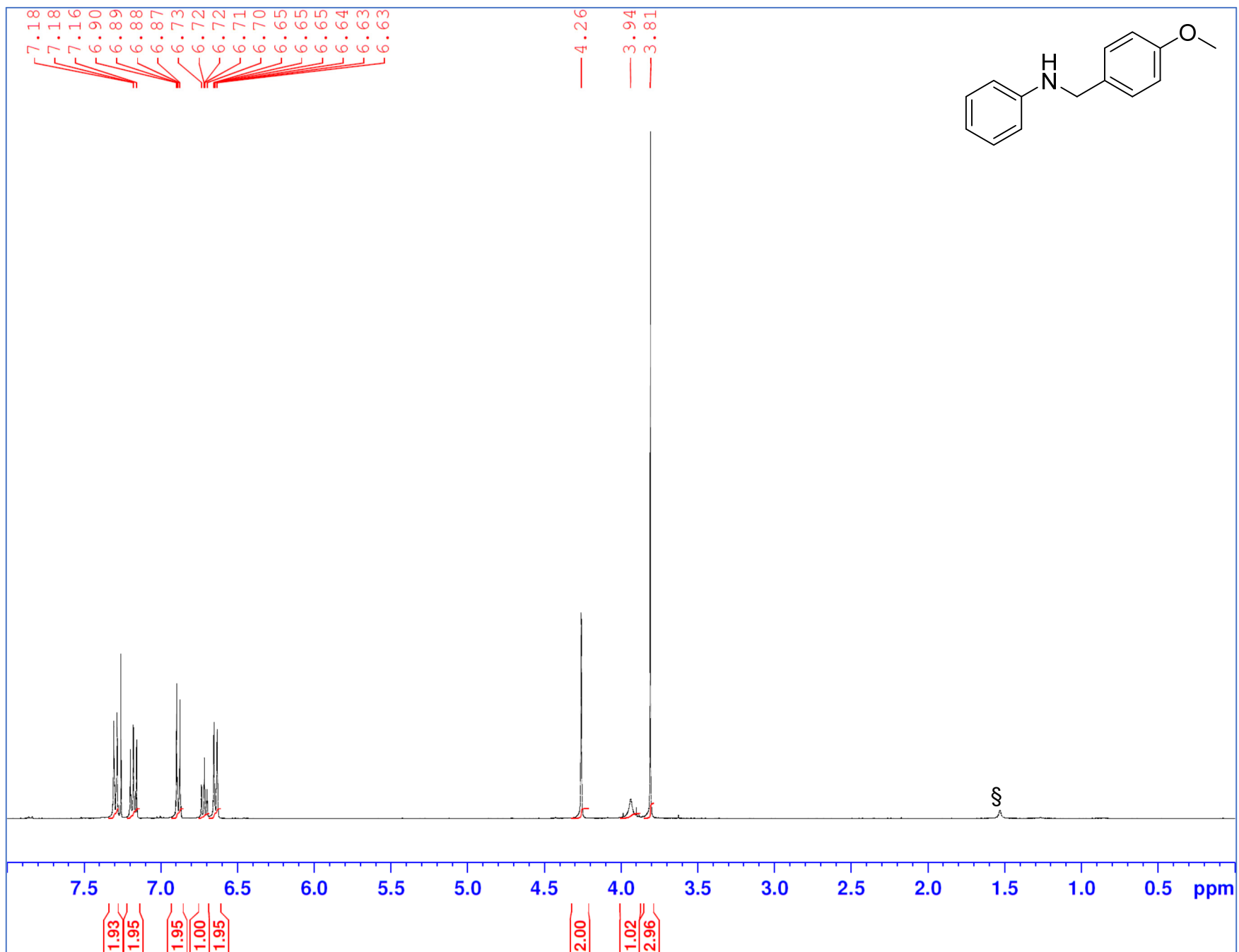
Supplementary Figure S41. $^{13}\text{C}\{^1\text{H}\}$ -NMR spectrum of 2l in CDCl_3 ; * ≡ deuterated solvent.



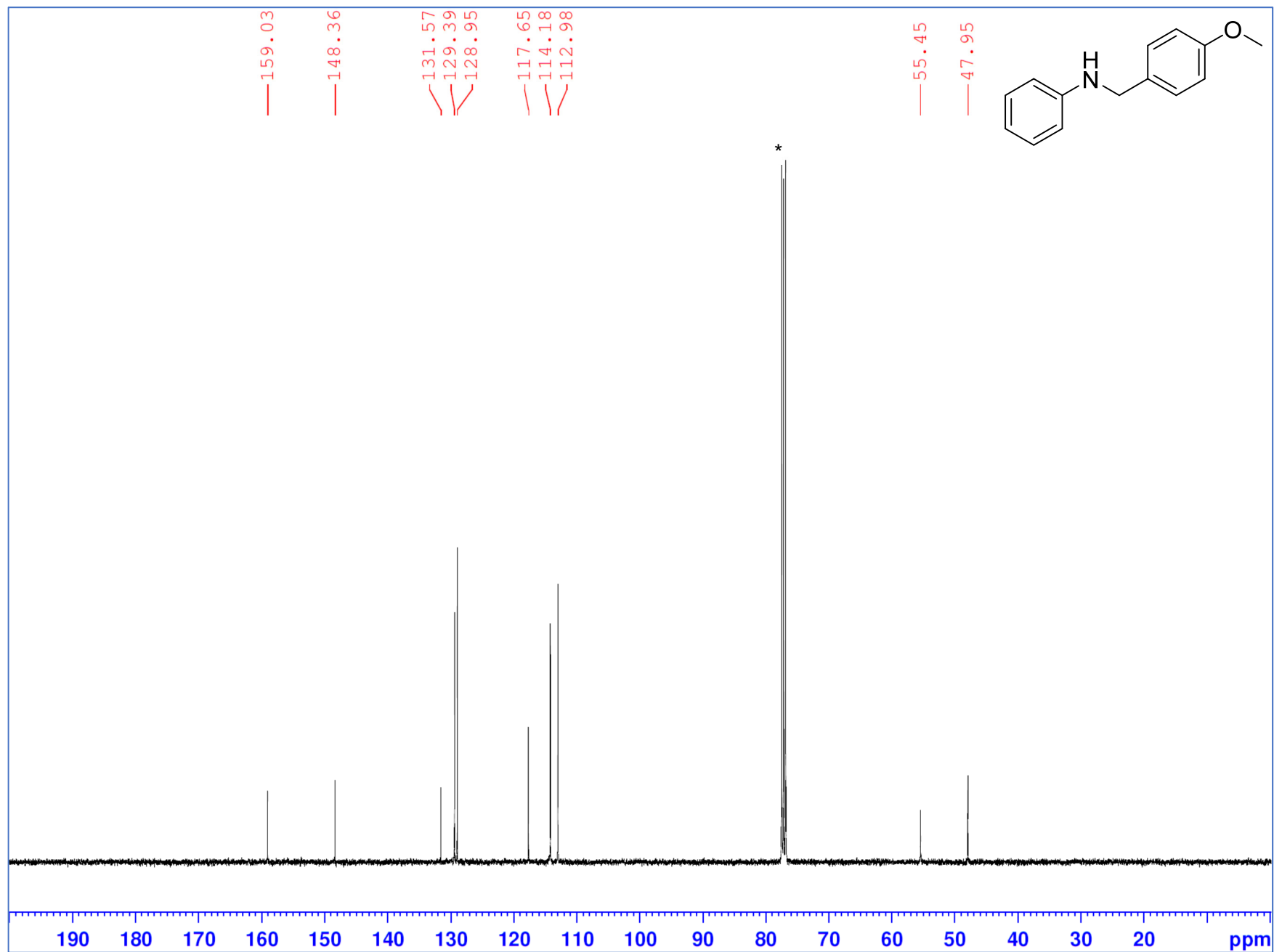
Supplementary Figure S42. ¹H-NMR spectrum (600.3 MHz) of 2m in CDCl₃.



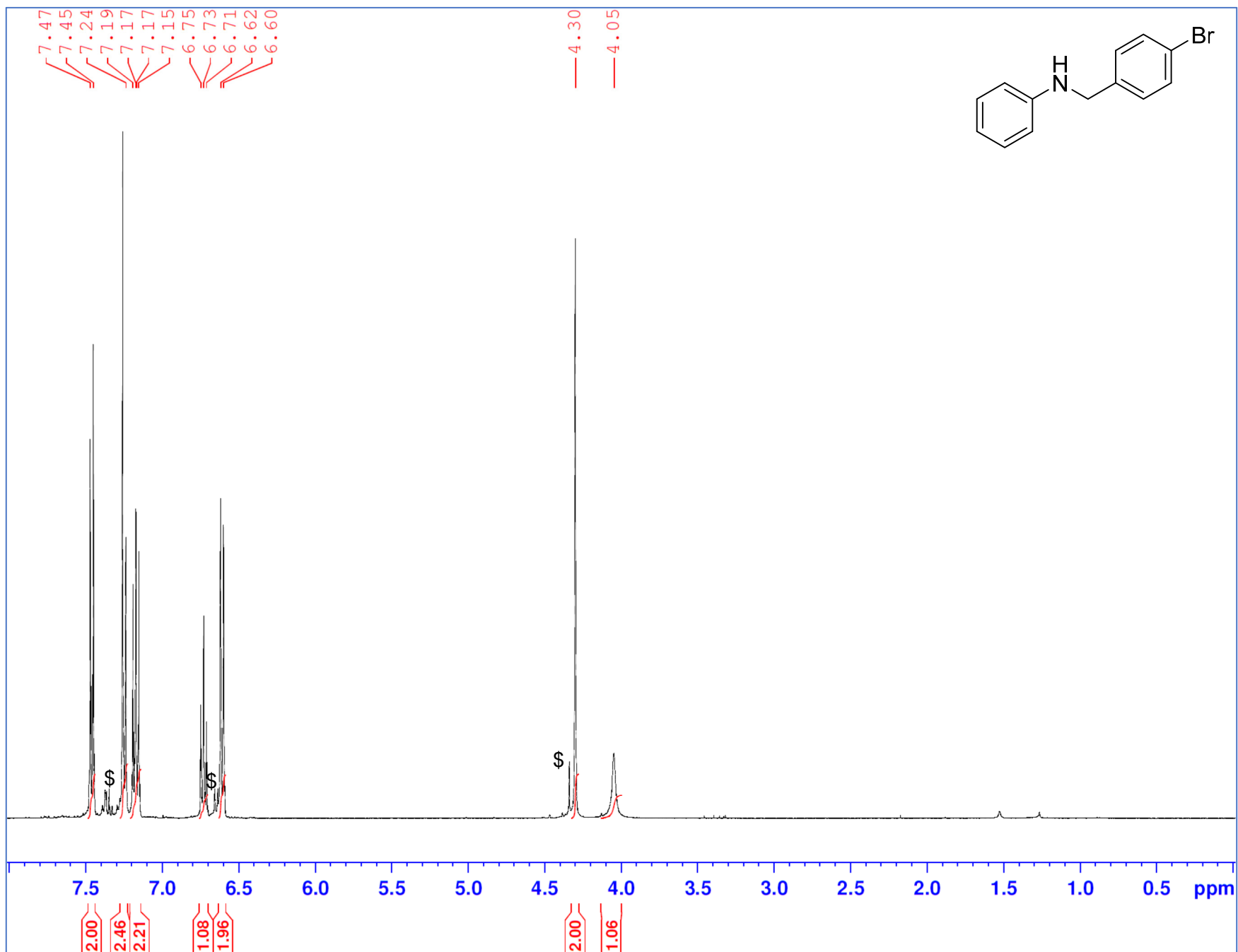
Supplementary Figure S43. ^{13}C (APT)-NMR spectrum (150.9 MHz) of **2m** in CDCl_3 ; * ≡ deuterated solvent.



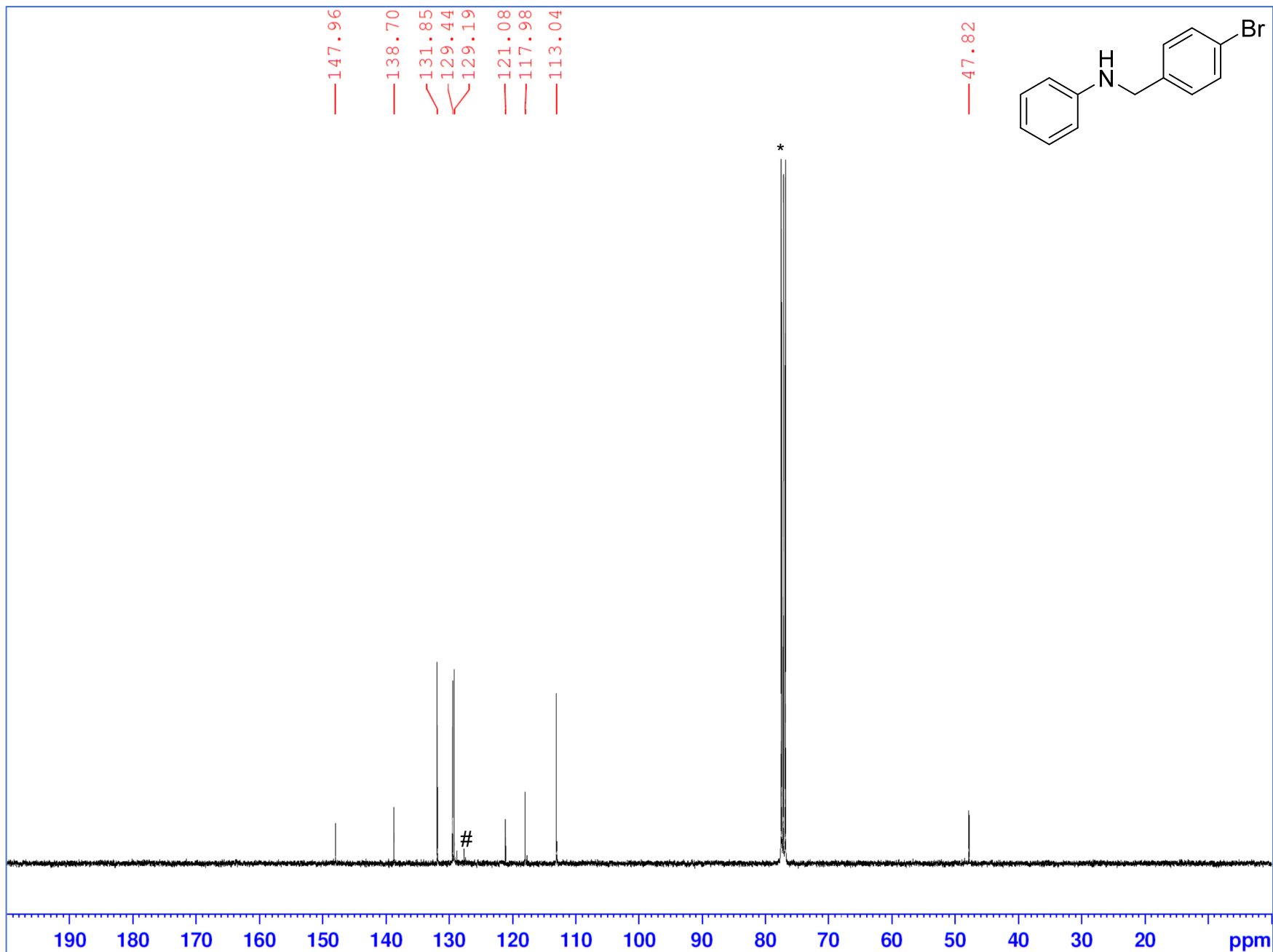
Supplementary Figure S44. ¹H-NMR spectrum of 3a in CDCl₃; § ≡ residual water.



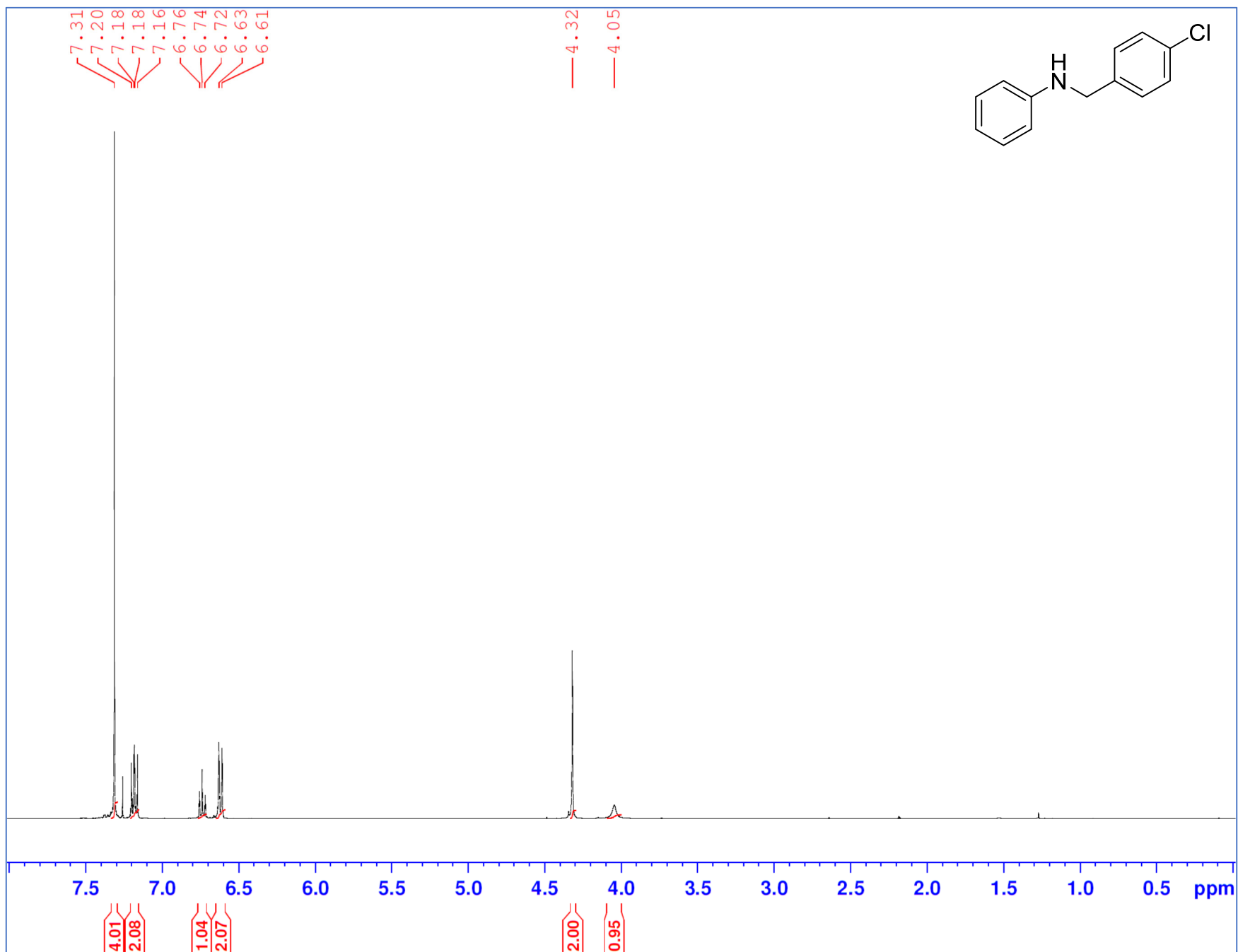
Supplementary Figure S45. $^{13}\text{C}\{^1\text{H}\}$ -NMR spectrum of **3a** in CDCl_3 ; * \equiv deuterated solvent.



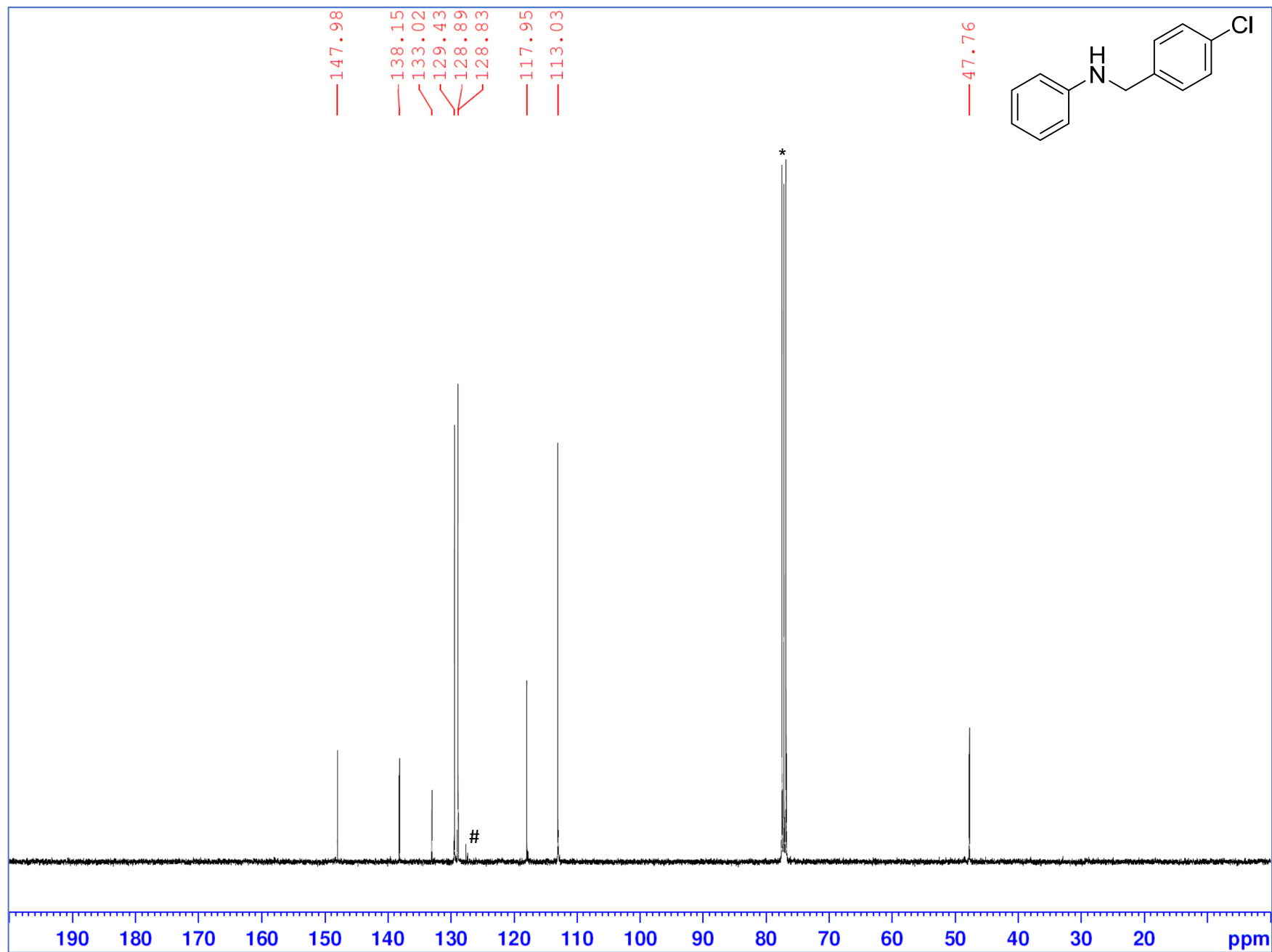
Supplementary Figure S46. ¹H-NMR spectrum of **3b** in CDCl₃; § ≡ 1-(4-bromophenyl)-*N*-phenylmethanimine.



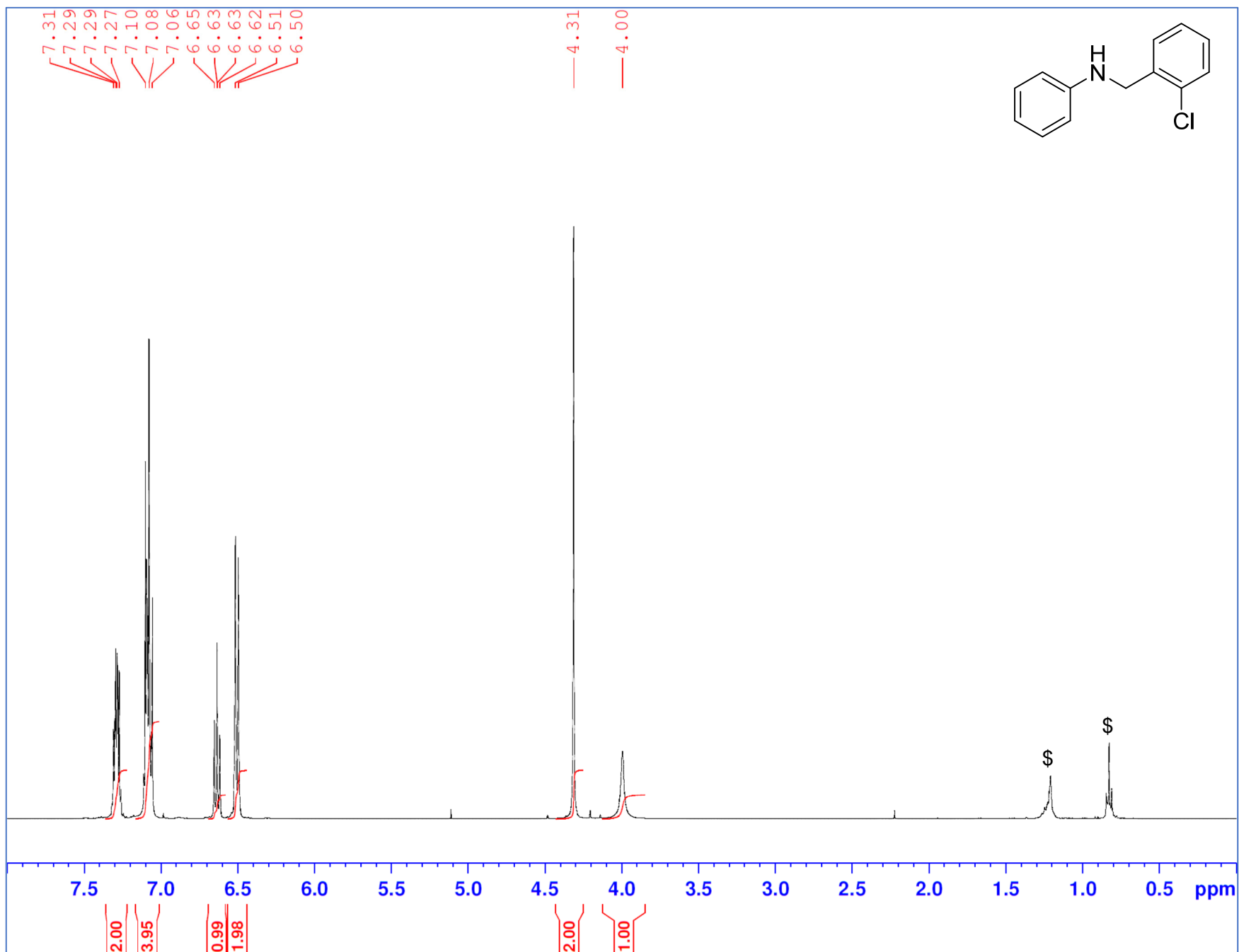
Supplementary Figure S47. $^{13}\text{C}\{^1\text{H}\}$ -NMR spectrum of **3b** in CDCl_3 ; * \equiv deuterated solvent; # \equiv non-identified impurity.



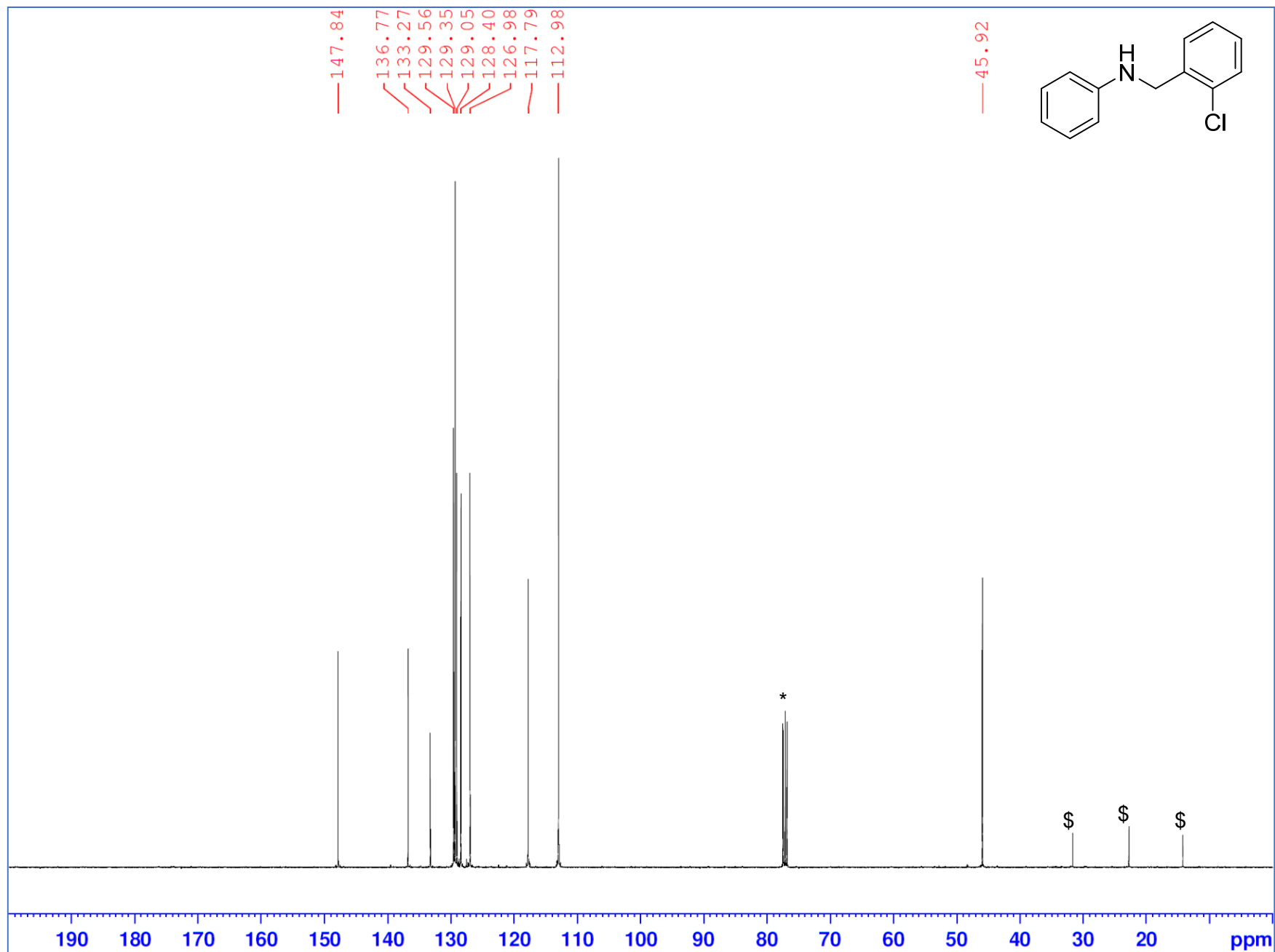
Supplementary Figure S48. ¹H-NMR spectrum of 3c in CDCl₃.



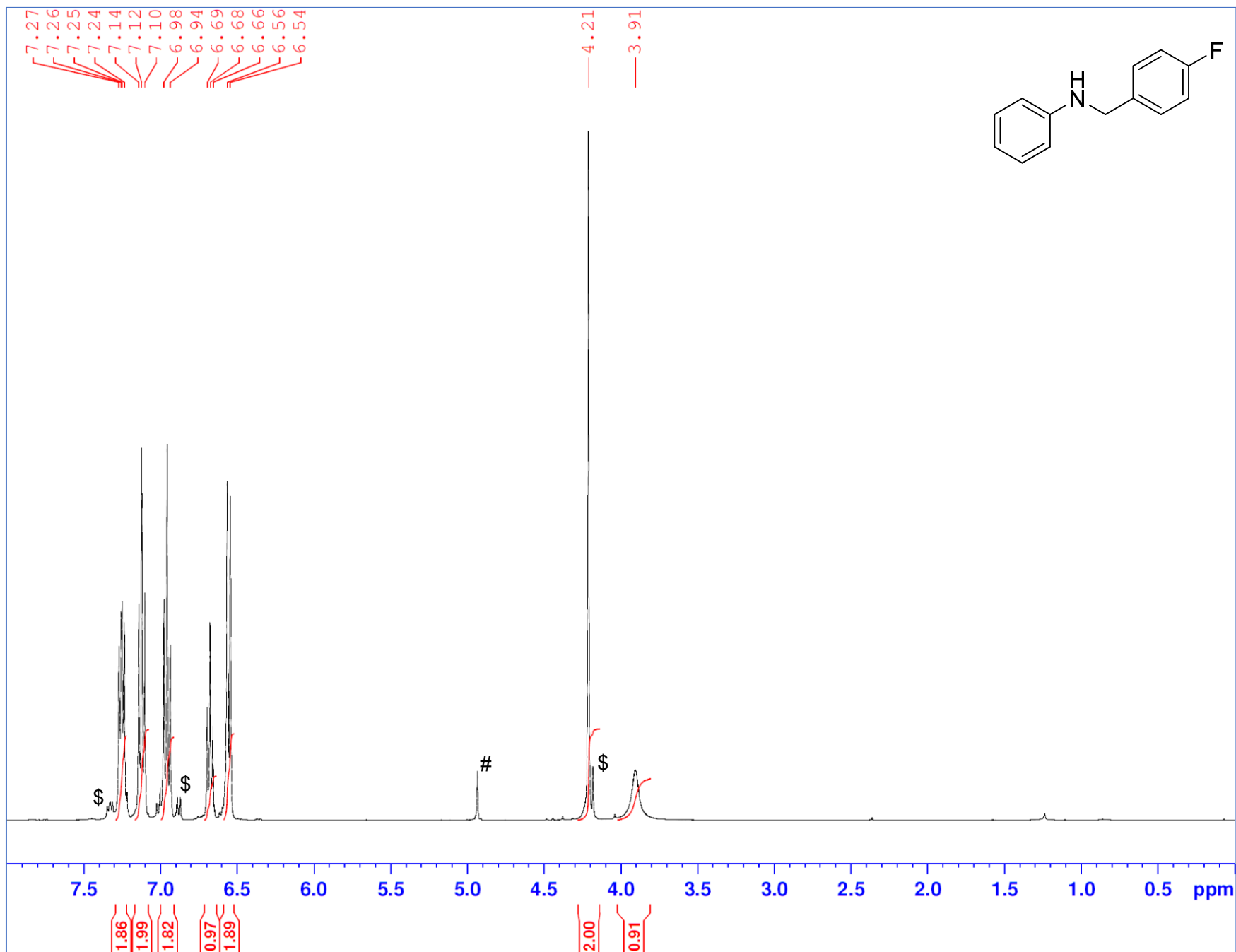
Supplementary Figure S49. $^{13}\text{C}\{^1\text{H}\}$ -NMR spectrum of **3c** in CDCl_3 ; * \equiv deuterated solvent; # \equiv non-identified impurity.



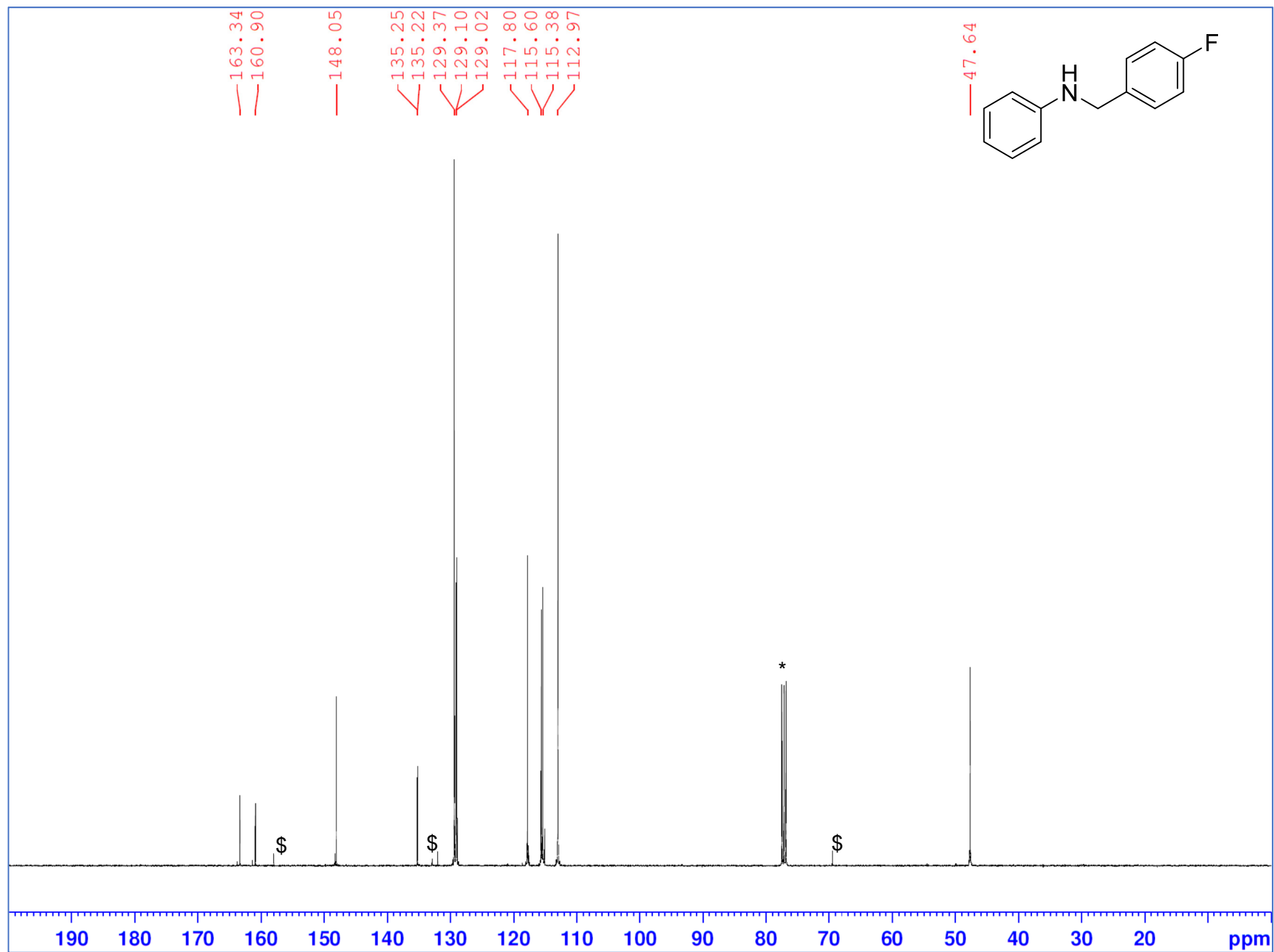
Supplementary Figure S50. ¹H-NMR spectrum of 3d in CDCl₃; \$ ≡ residual heptanes.



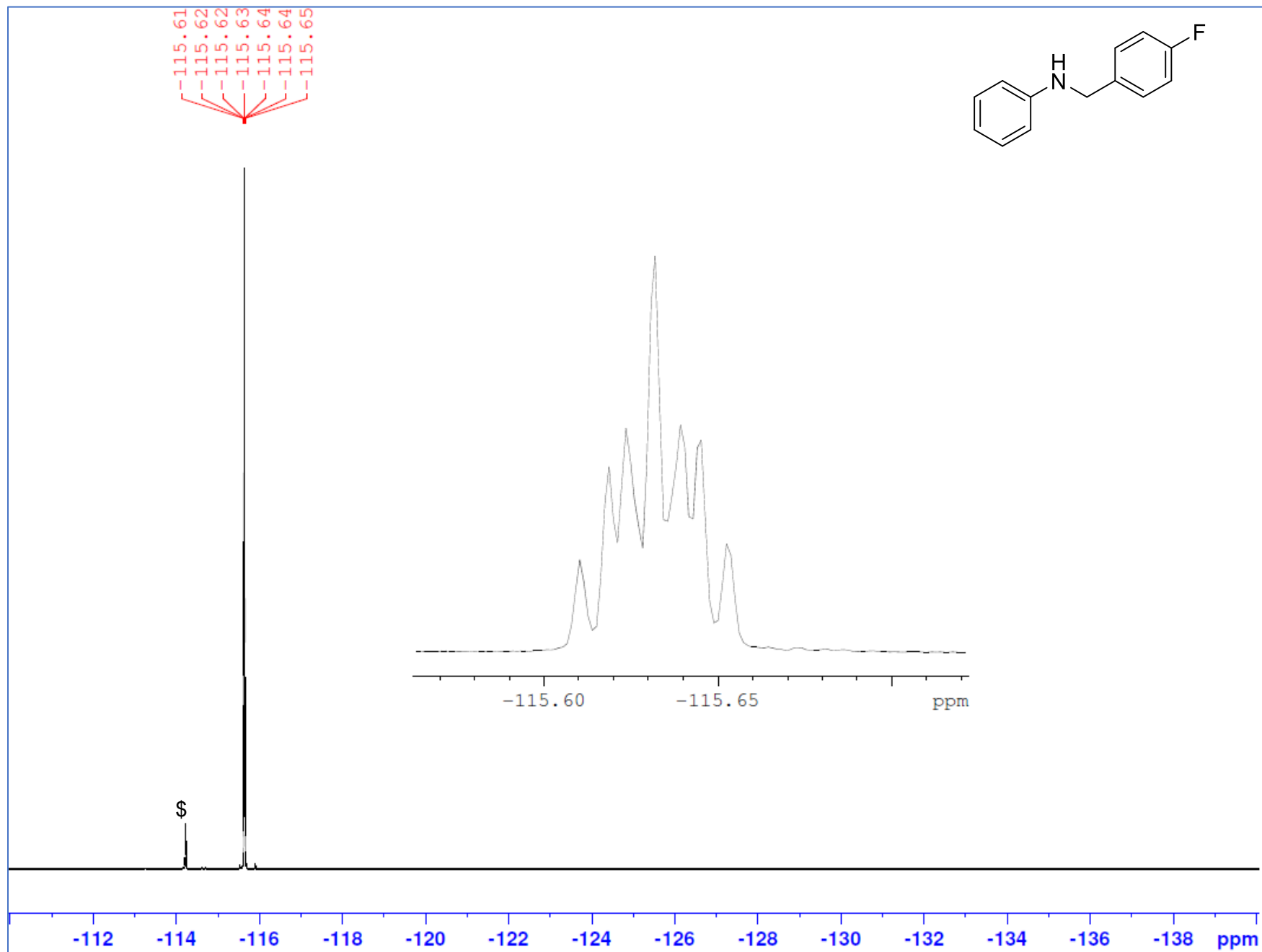
Supplementary Figure S51. $^{13}\text{C}\{^1\text{H}\}$ -NMR spectrum of 3d in CDCl_3 ; * \equiv deuterated solvent; \$ \equiv residual heptanes.



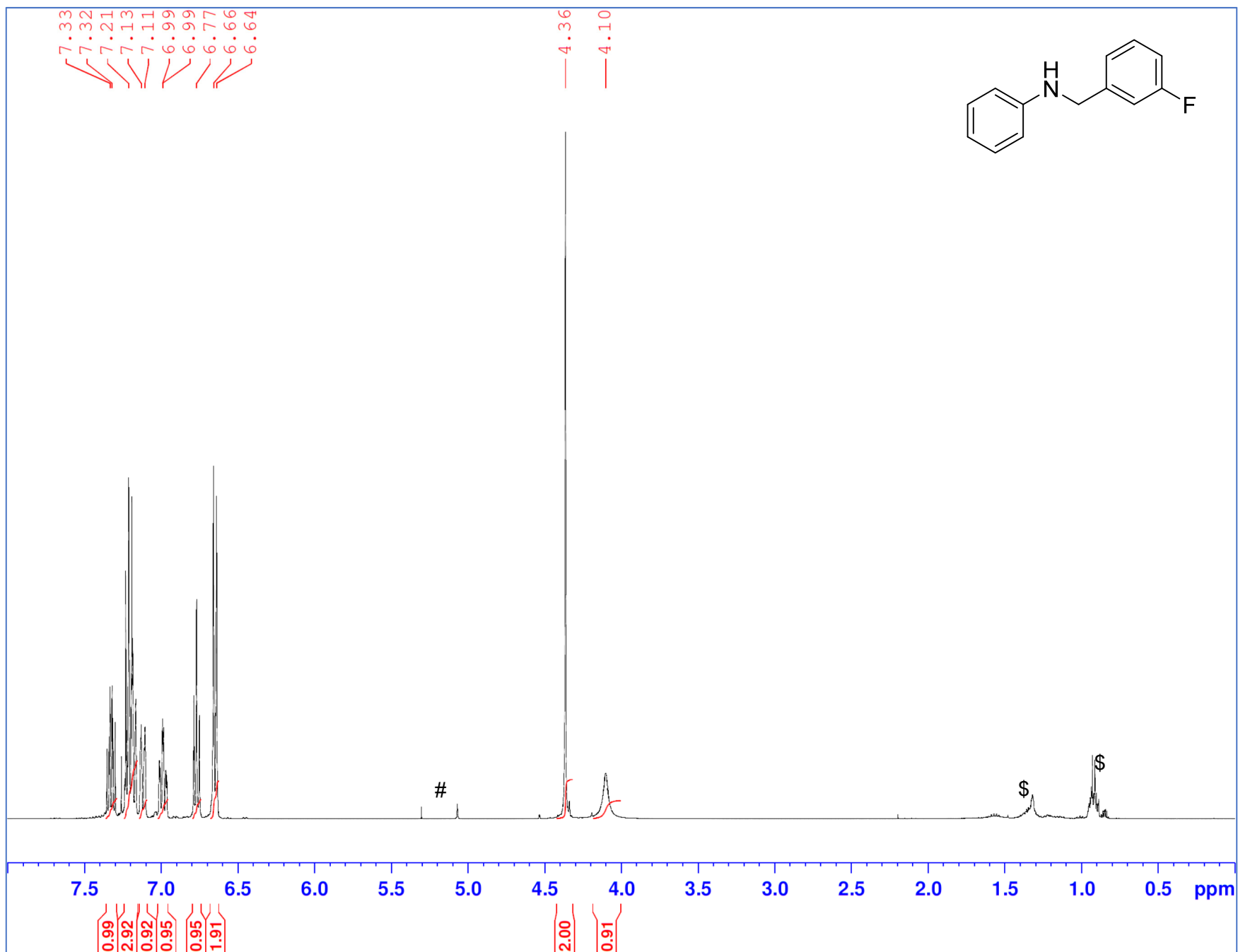
Supplementary Figure S52. ¹H-NMR spectrum of **3e** in CDCl₃; \$ ≡ 1-(4-fluorophenyl)-N-phenylmethanimine; # ≡ non-identified impurity.



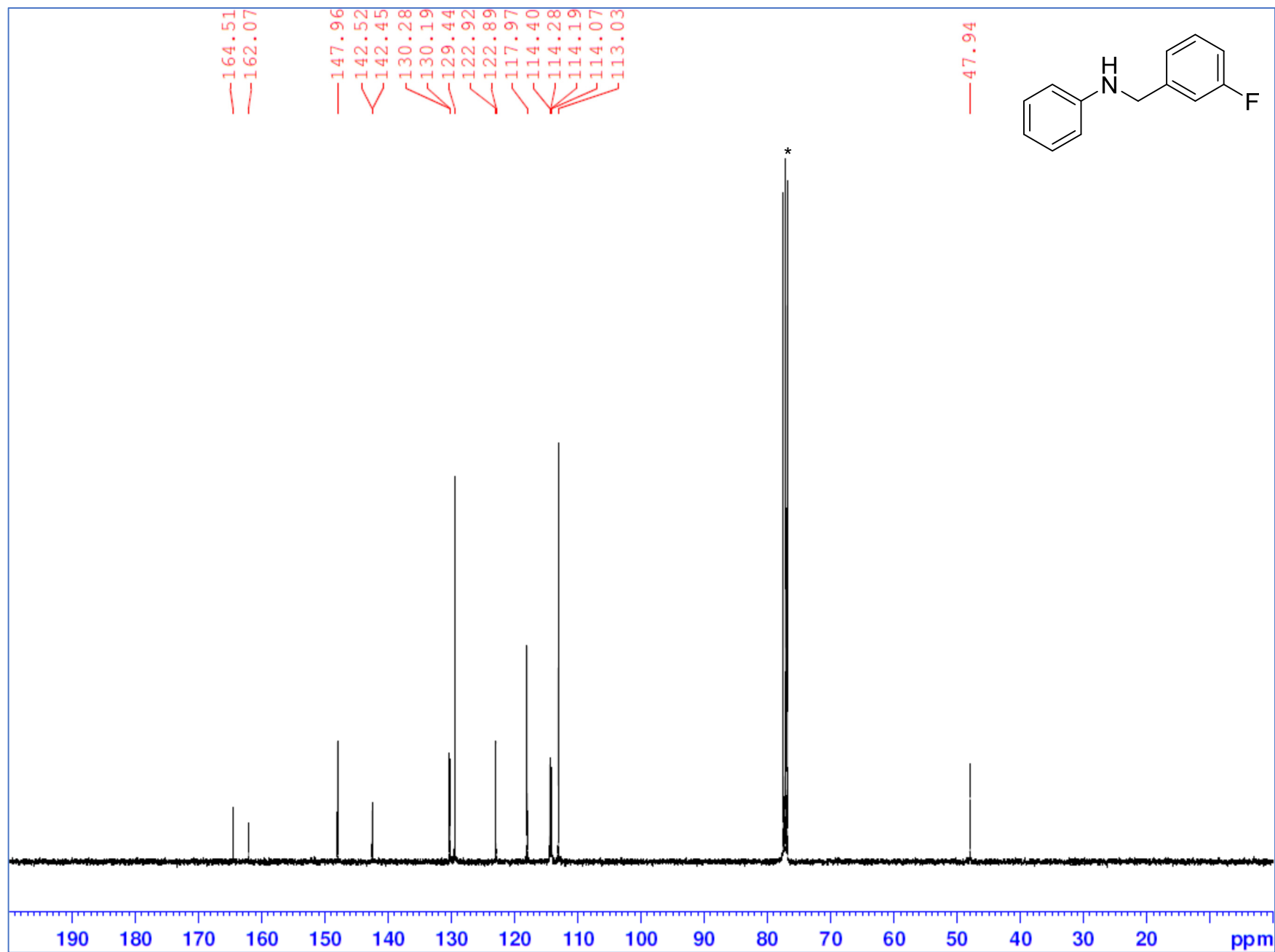
Supplementary Figure S53. ¹³C{¹H}-NMR spectrum of **3e** in CDCl₃; * ≡ deuterated solvent; \$ ≡ 1-(4-fluorophenyl)-*N*-phenylmethanimine.



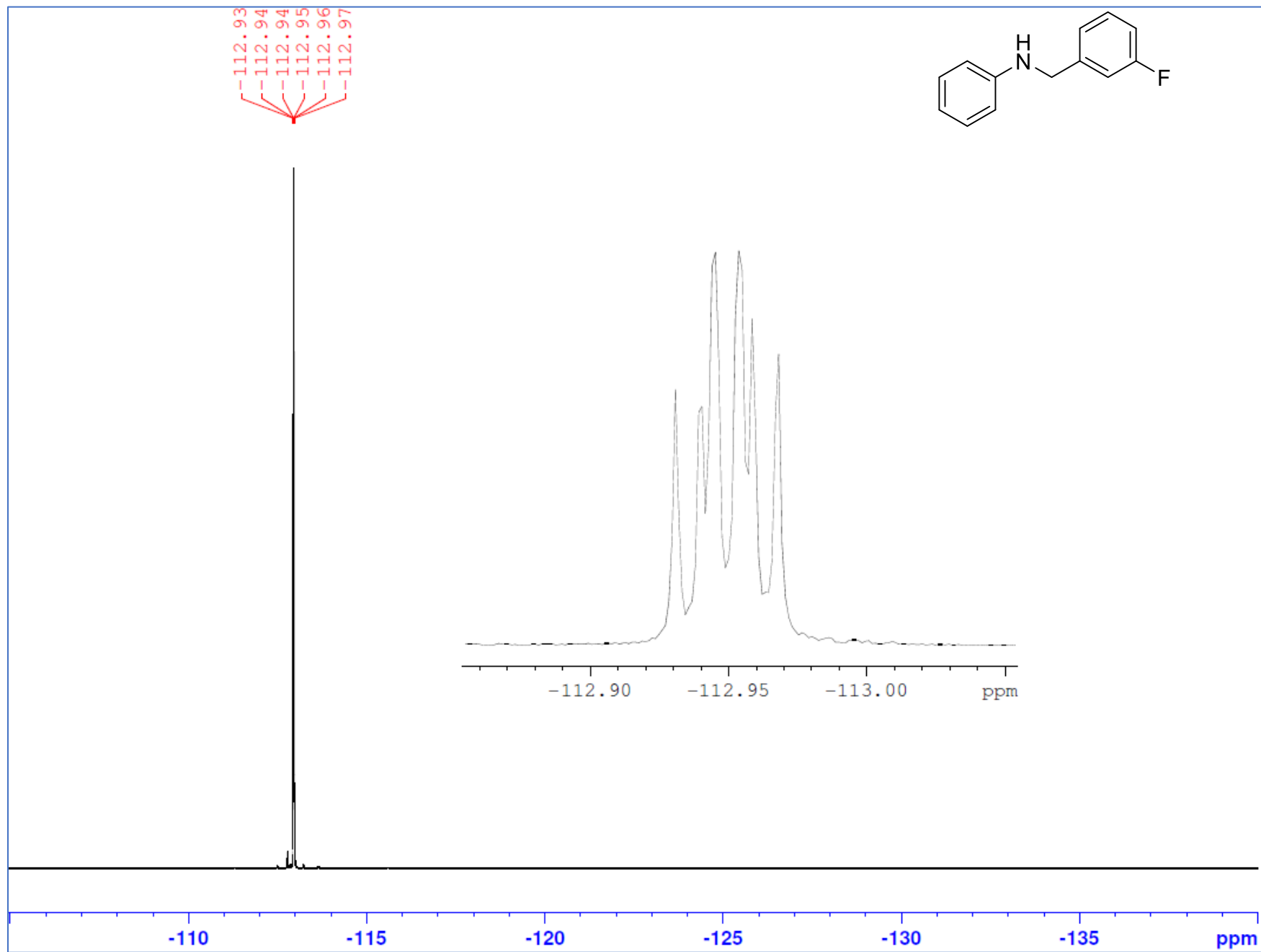
Supplementary Figure S54. ^{19}F -NMR spectrum of 3e in CDCl_3 ; \$ \equiv 1-(4-fluorophenyl)-*N*-phenylmethanimine.



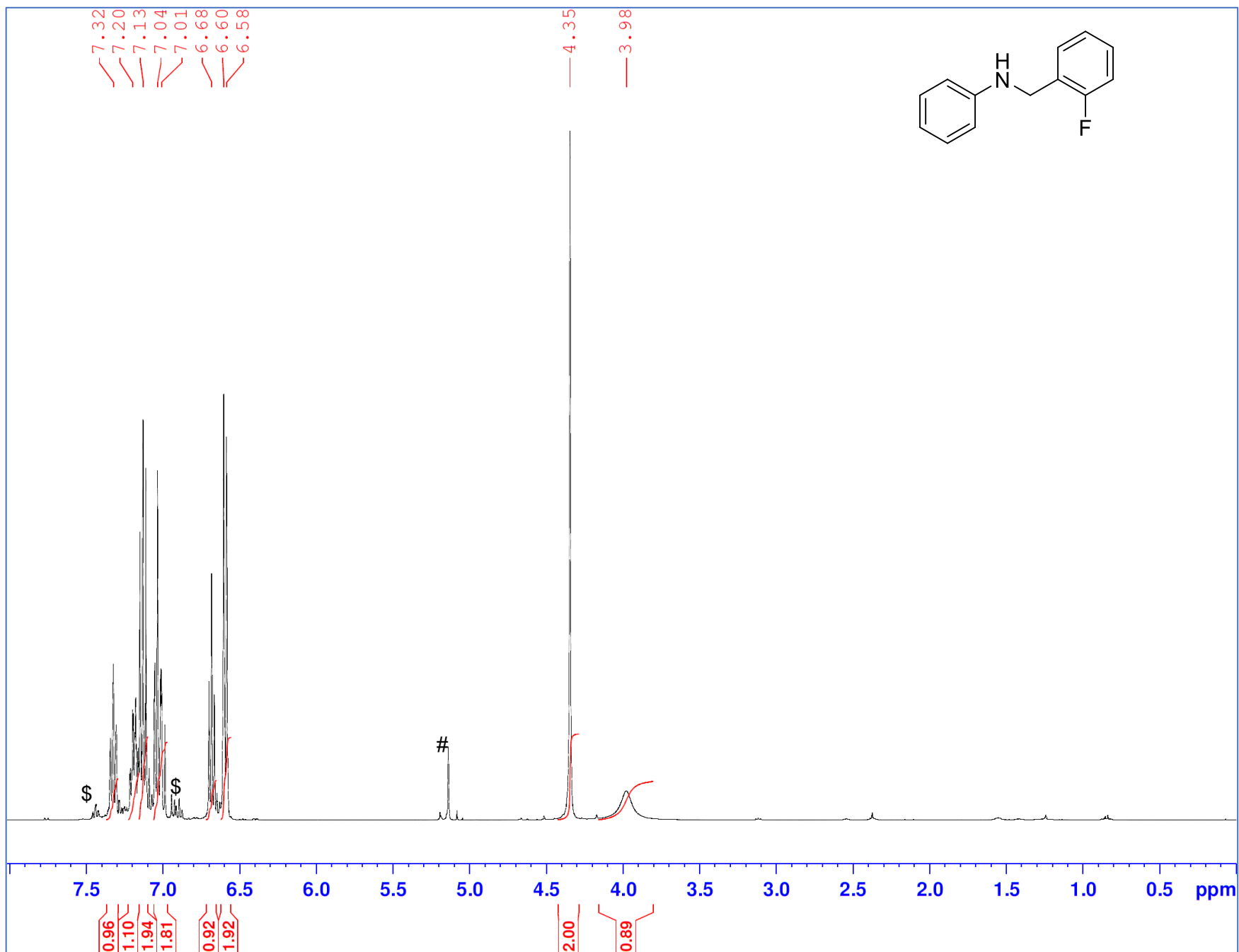
Supplementary Figure S55. ¹H-NMR spectrum of **3f** in CDCl₃; \$ ≡ residual petrol ether; # ≡ non-identified impurity.



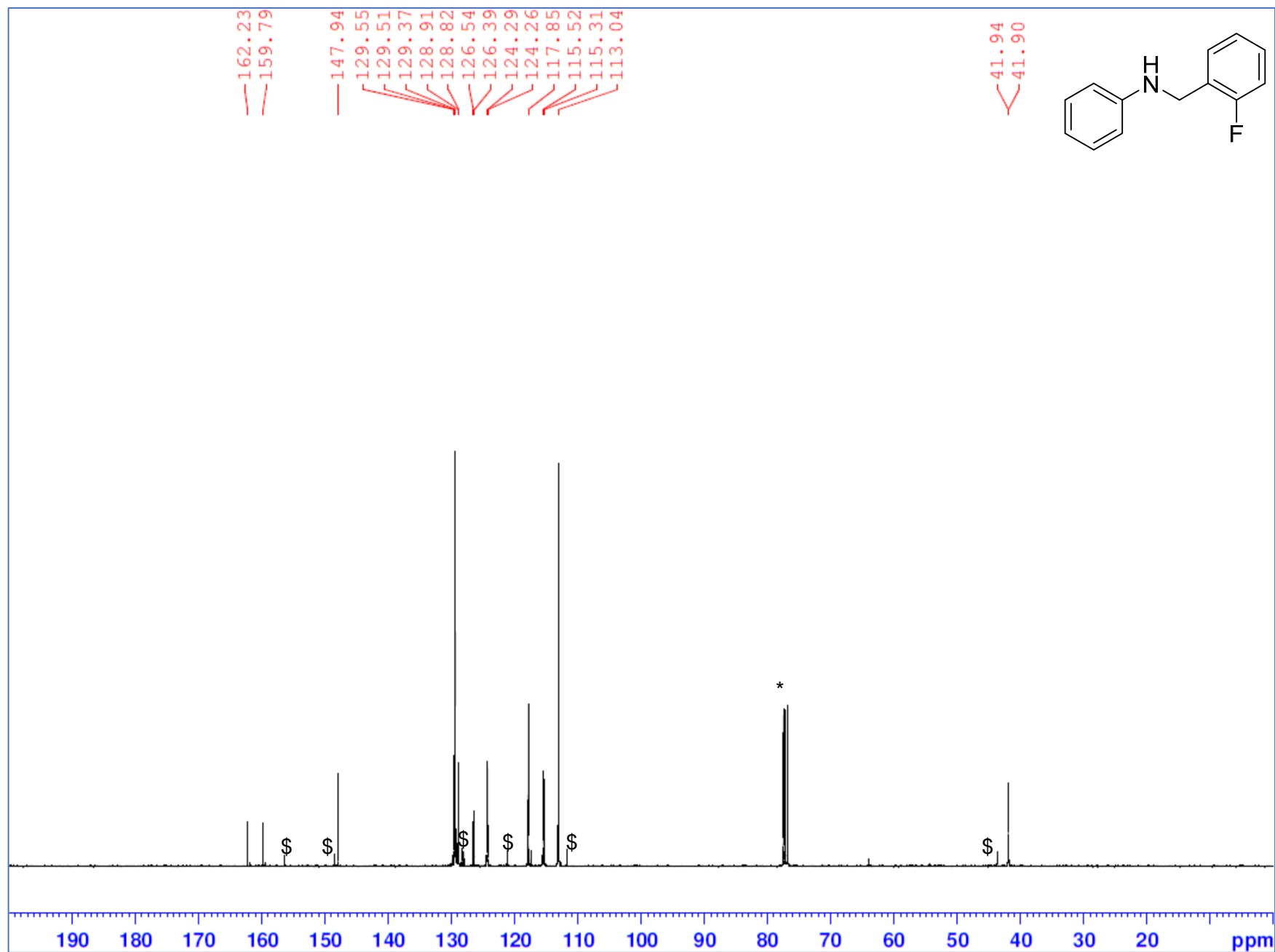
Supplementary Figure S56. $^{13}\text{C}\{^1\text{H}\}$ -NMR spectrum of **3f** in CDCl_3 ; * \equiv deuterated solvent.



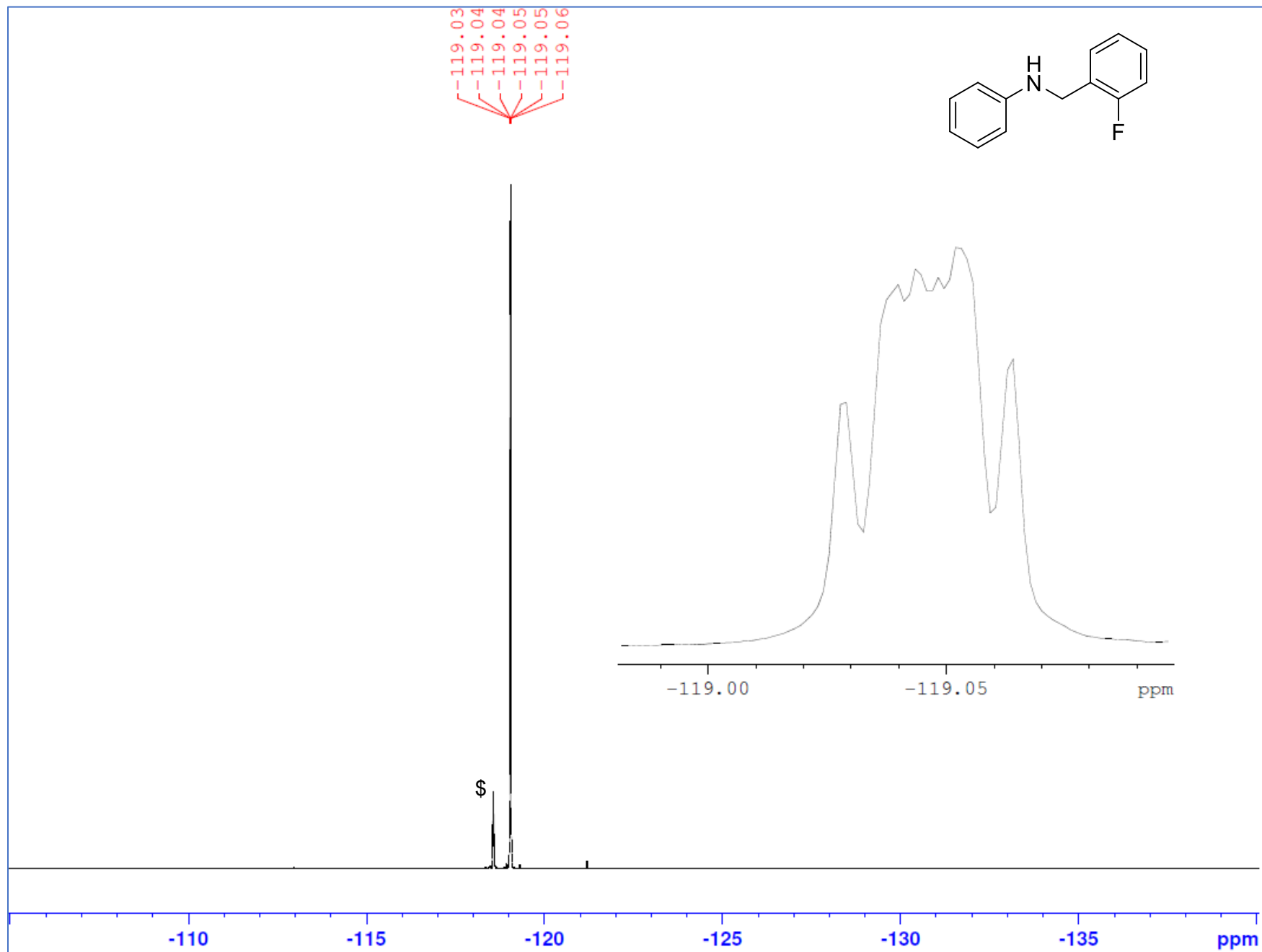
Supplementary Figure S57. ^{19}F -NMR spectrum of **3f** in CDCl_3 .



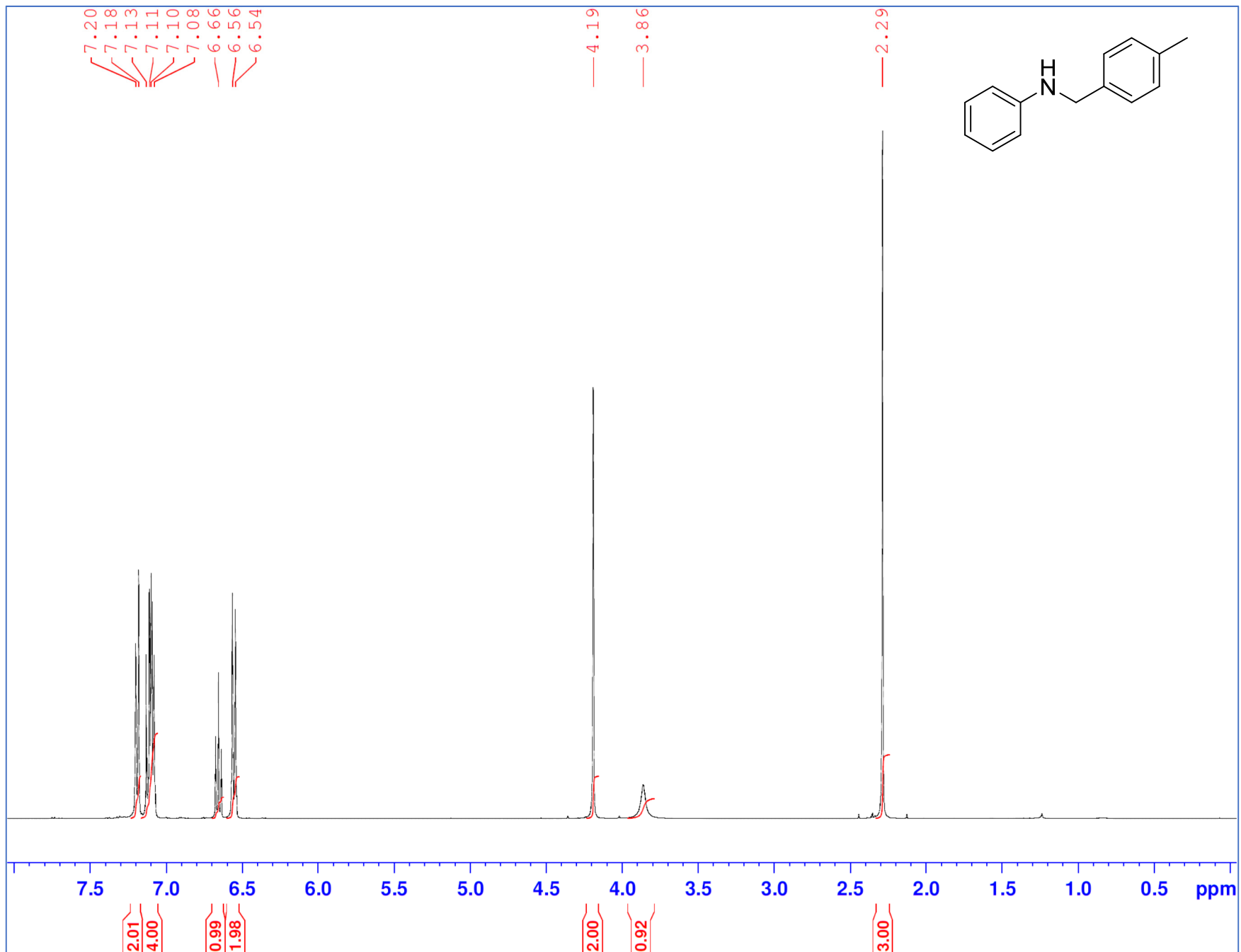
Supplementary Figure S58. ¹H-NMR spectrum of **3g** in CDCl₃; \$ ≡ 1-(2-fluorophenyl)-N-phenylmethanimine; # ≡ non-identified impurity.



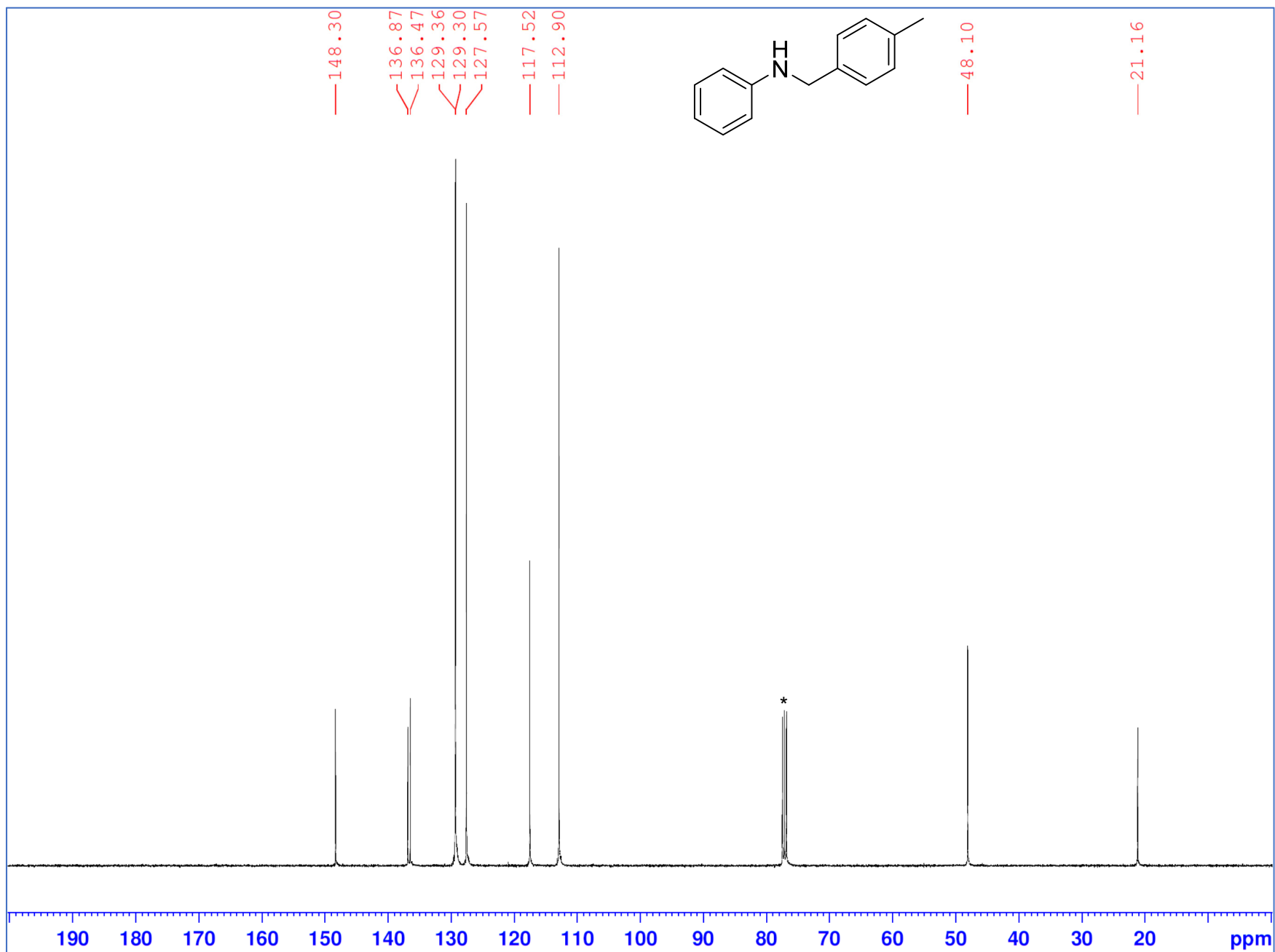
Supplementary Figure S59. ¹³C{¹H}-NMR spectrum of **3g** in CDCl₃; * ≡ deuterated solvent; § ≡ 1-(2-fluorophenyl)-N-phenylmethanimine.



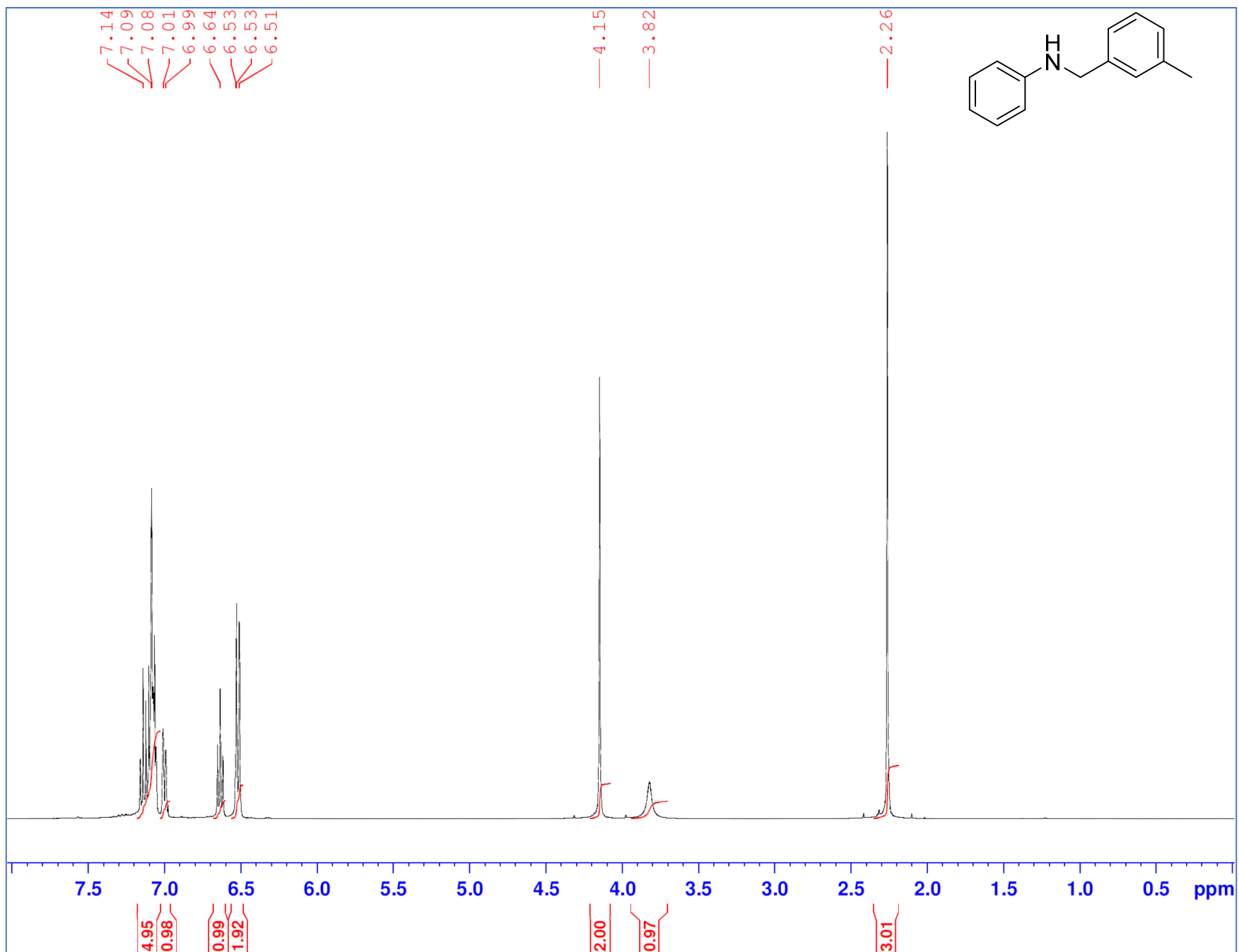
Supplementary Figure S60. ^{19}F -NMR spectrum of **3g** in CDCl_3 ; $\text{\$}$ = 1-(2-fluorophenyl)-*N*-phenylmethanimine.



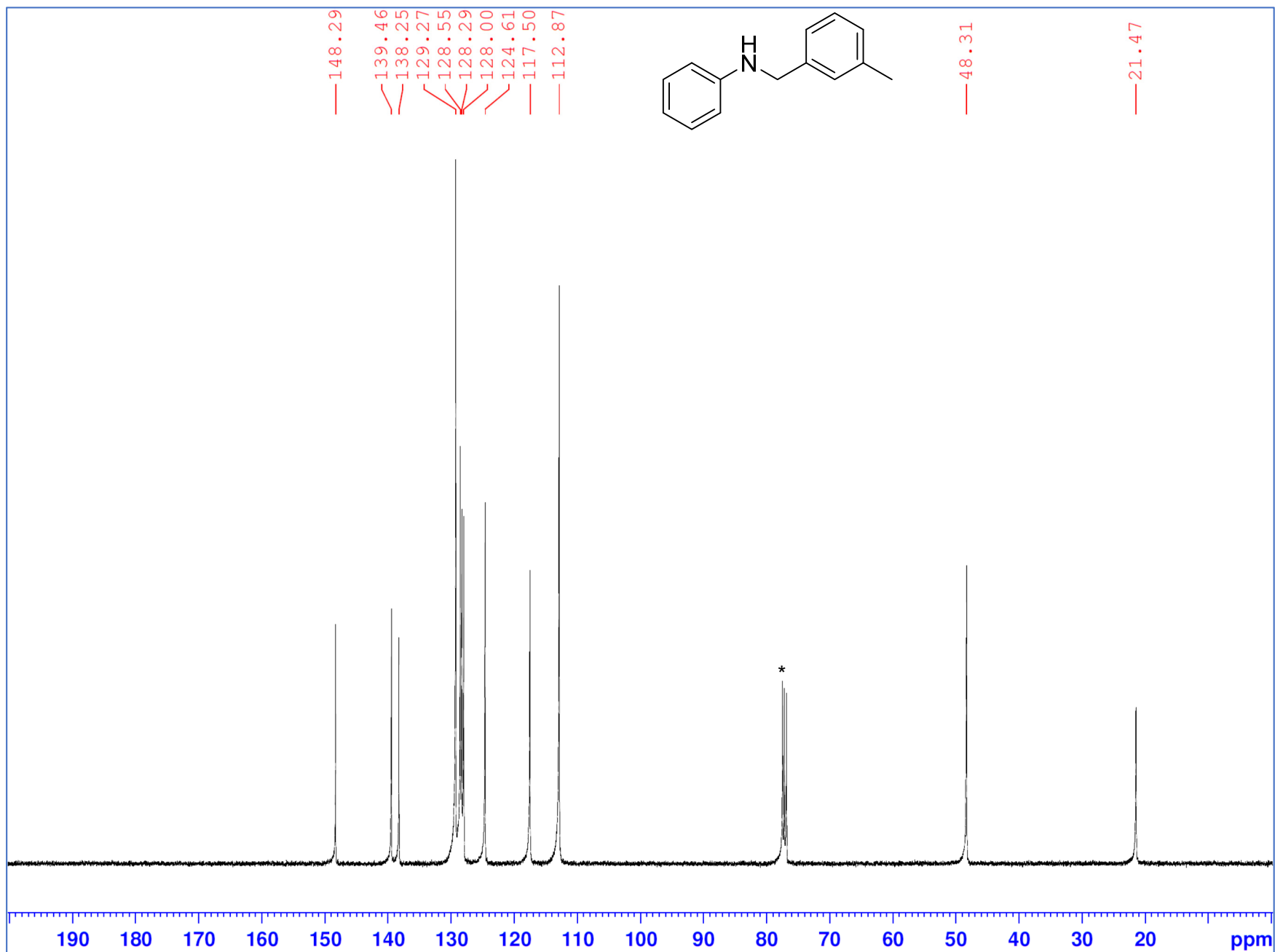
Supplementary Figure S61. ¹H-NMR spectrum of 3h in CDCl₃.



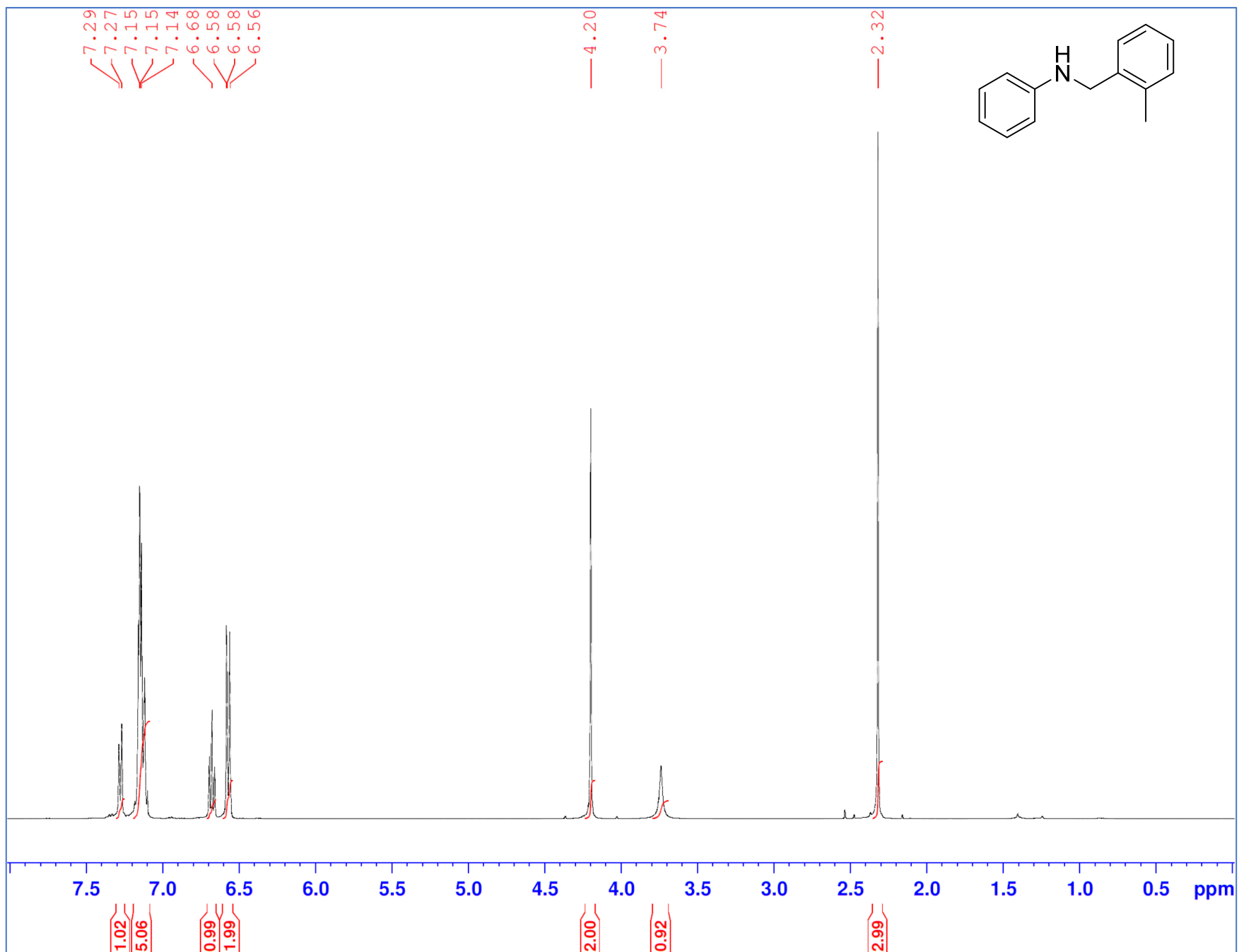
Supplementary Figure S62. $^{13}\text{C}\{^1\text{H}\}$ -NMR spectrum of **3h** in CDCl_3 ; * \equiv deuterated solvent.



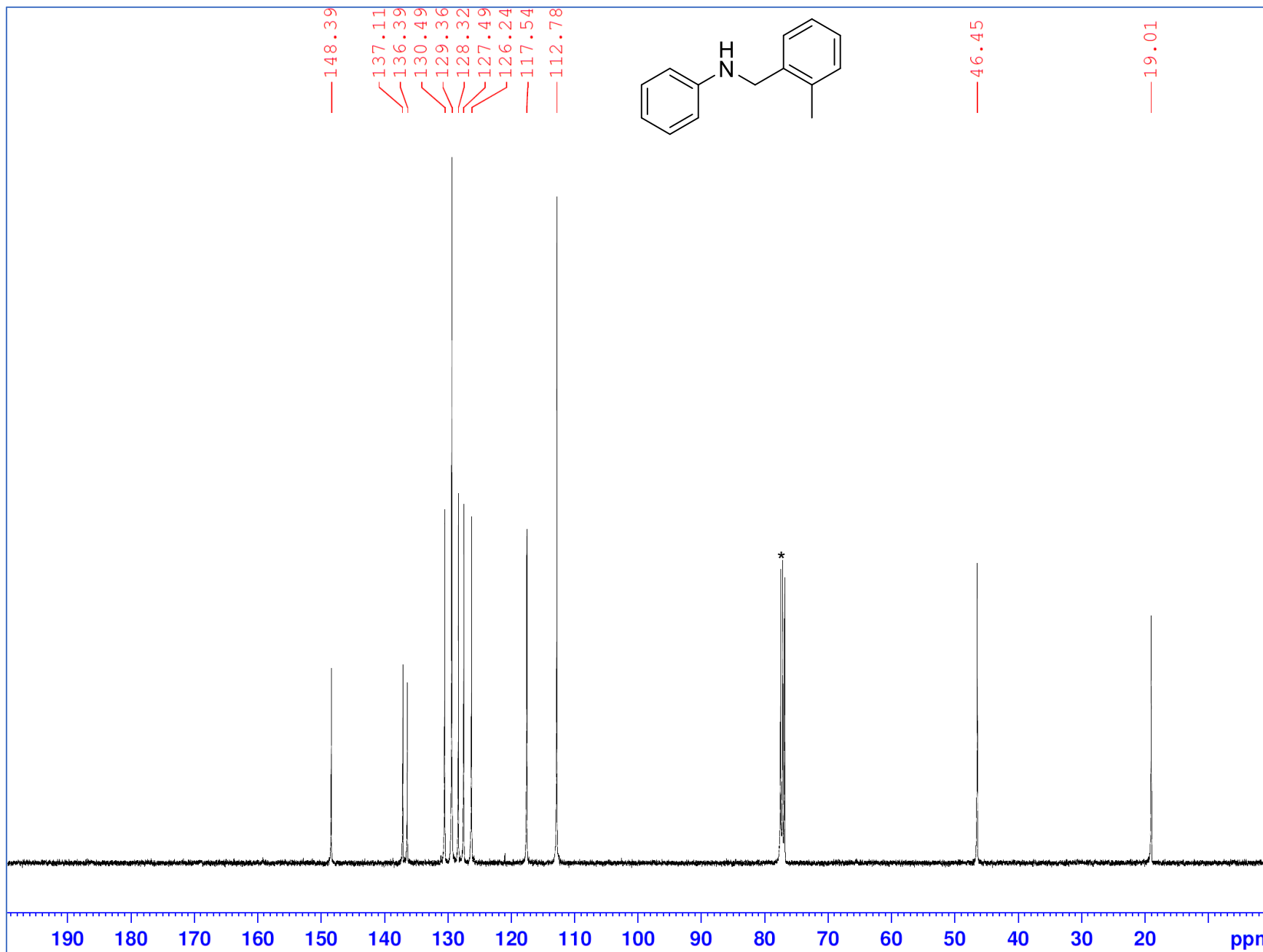
Supplementary Figure S63. ¹H-NMR spectrum of **3i** in CDCl₃.



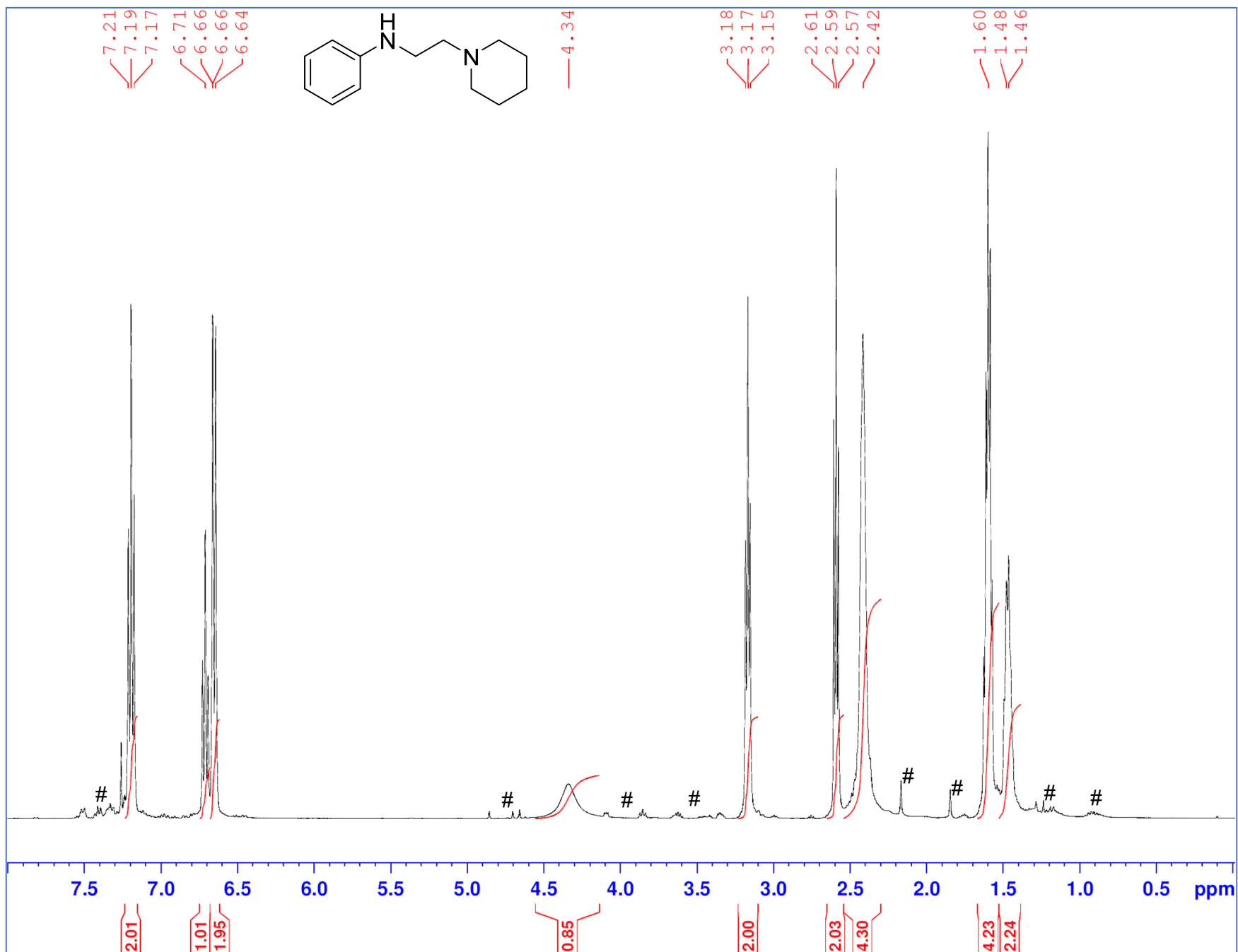
Supplementary Figure S64. $^{13}\text{C}\{^1\text{H}\}$ -NMR spectrum of **3i** in CDCl_3 ; * \equiv deuterated solvent.



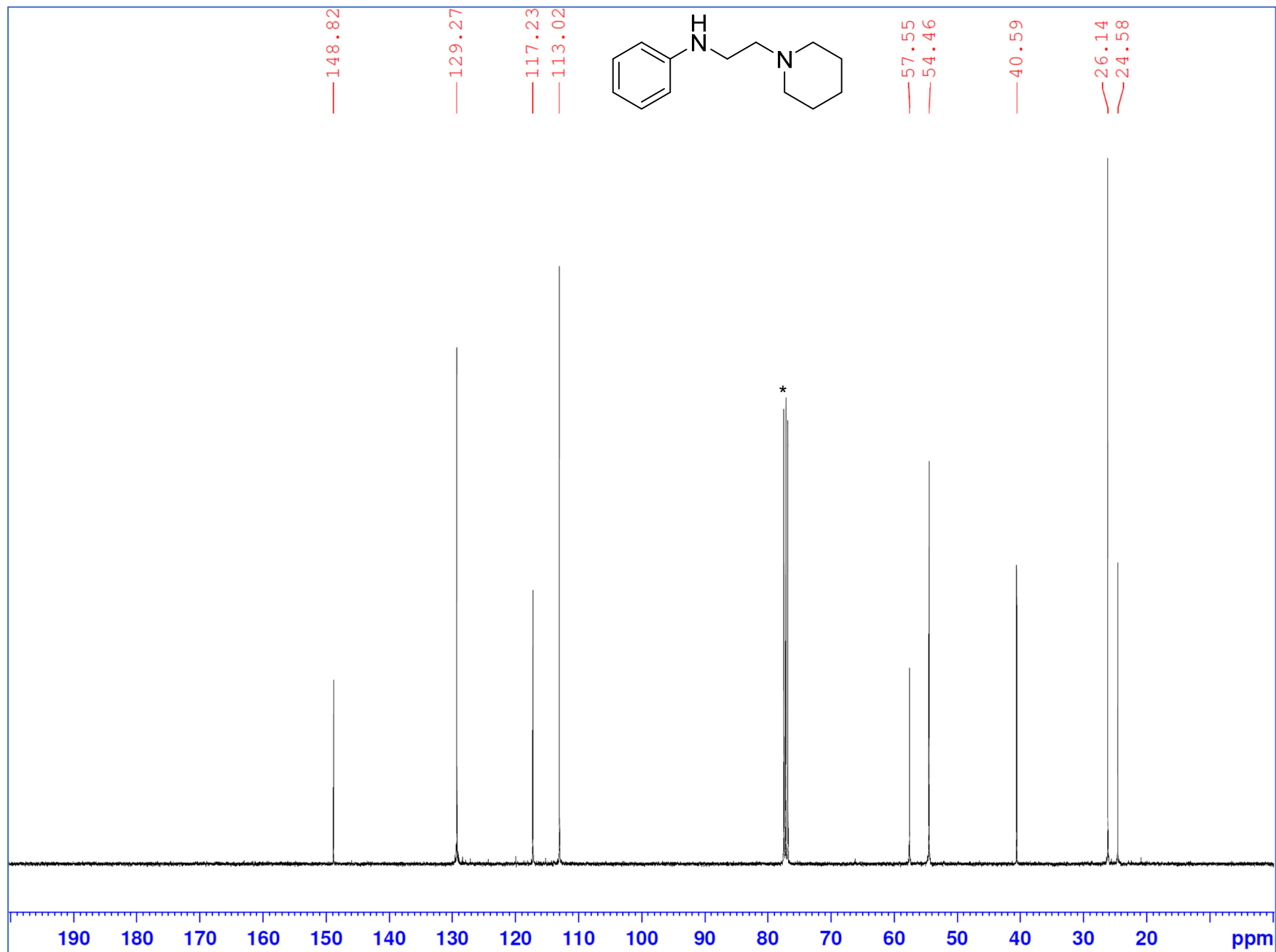
Supplementary Figure S65. ¹H-NMR spectrum of **3j** in CDCl₃.



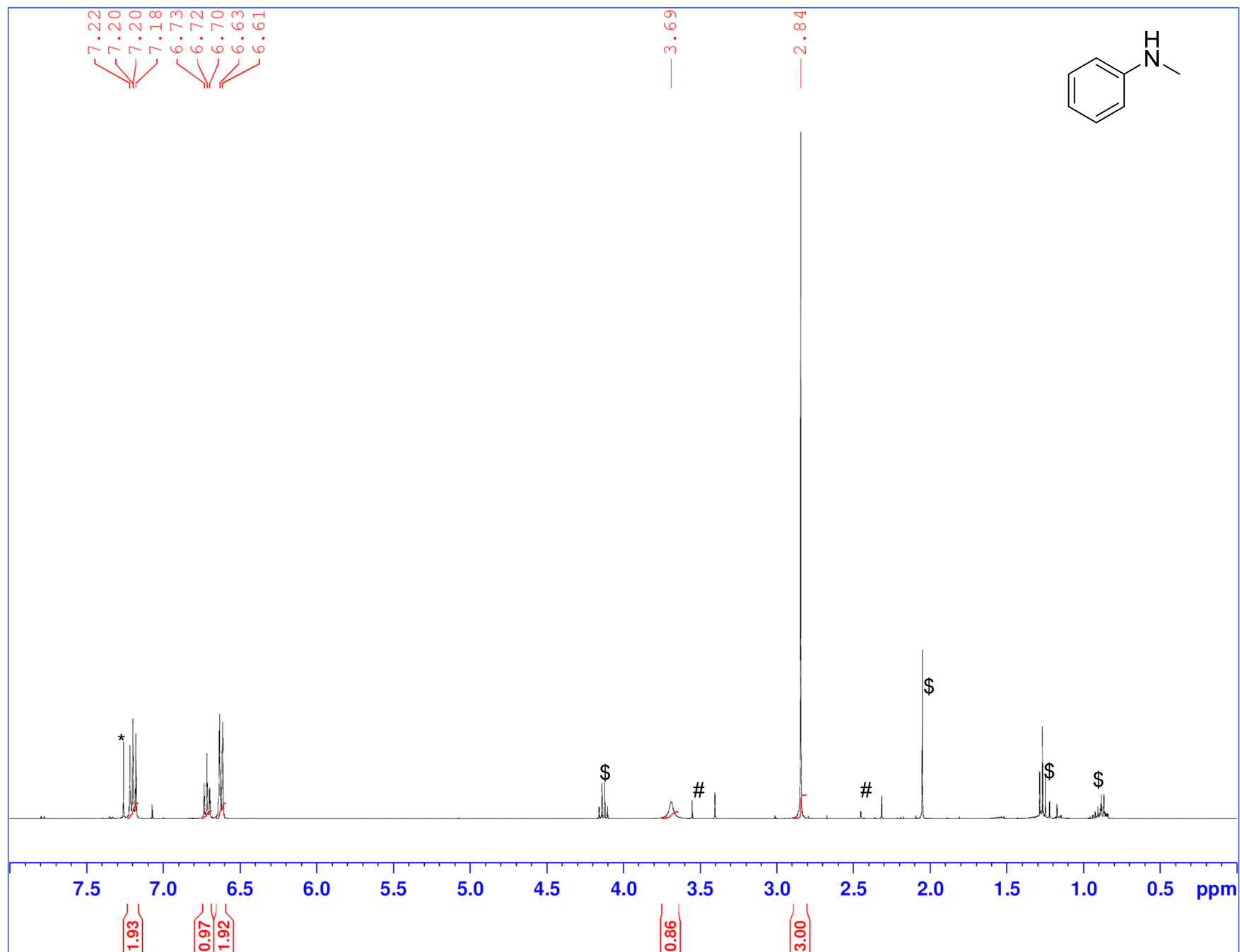
Supplementary Figure S66. $^{13}\text{C}\{^1\text{H}\}$ -NMR spectrum of **3j** in CDCl_3 ; * \equiv deuterated solvent.



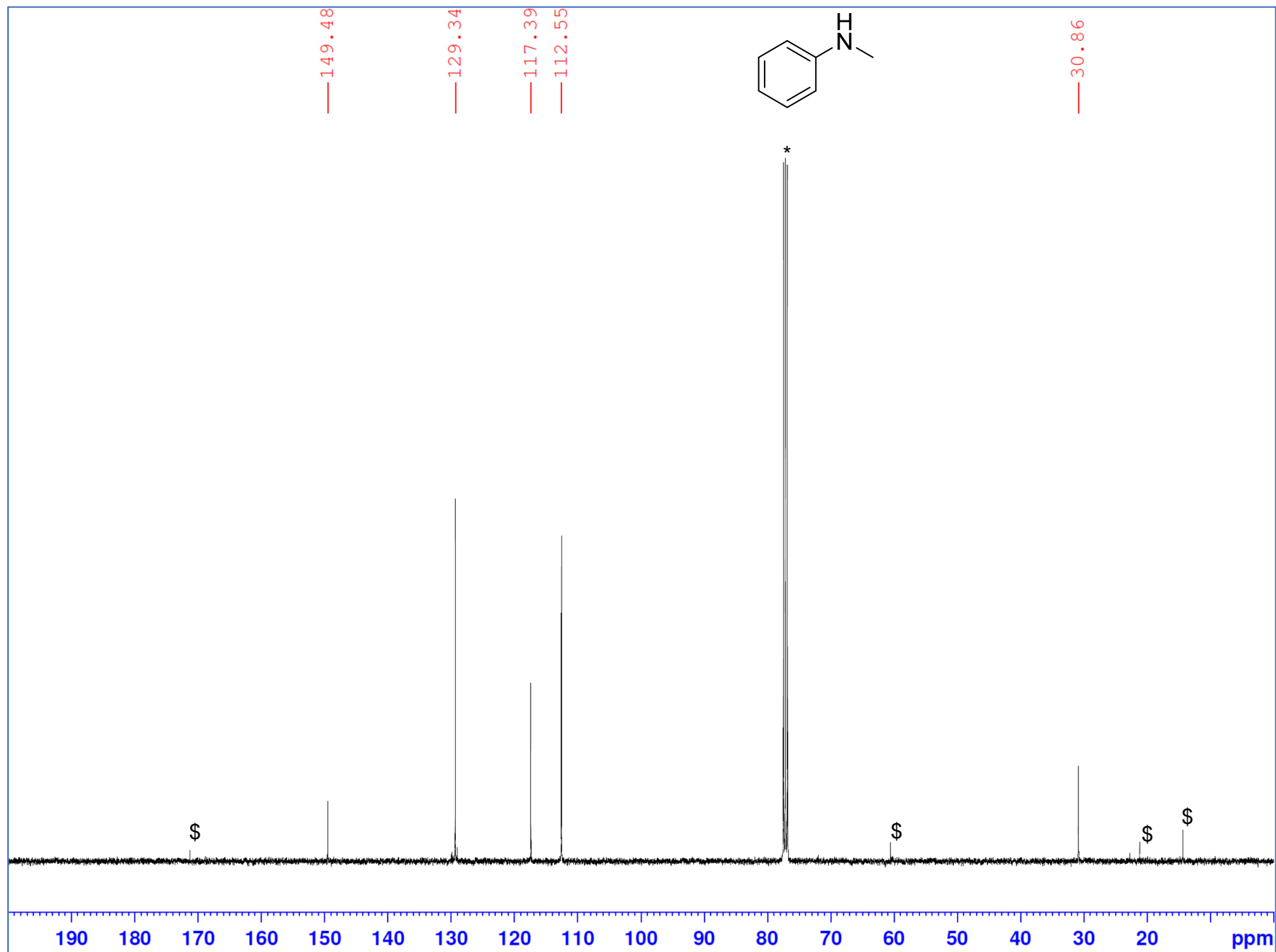
Supplementary Figure S67. ¹H-NMR spectrum of 3k in CDCl₃; # ≡ non-identified impurity.



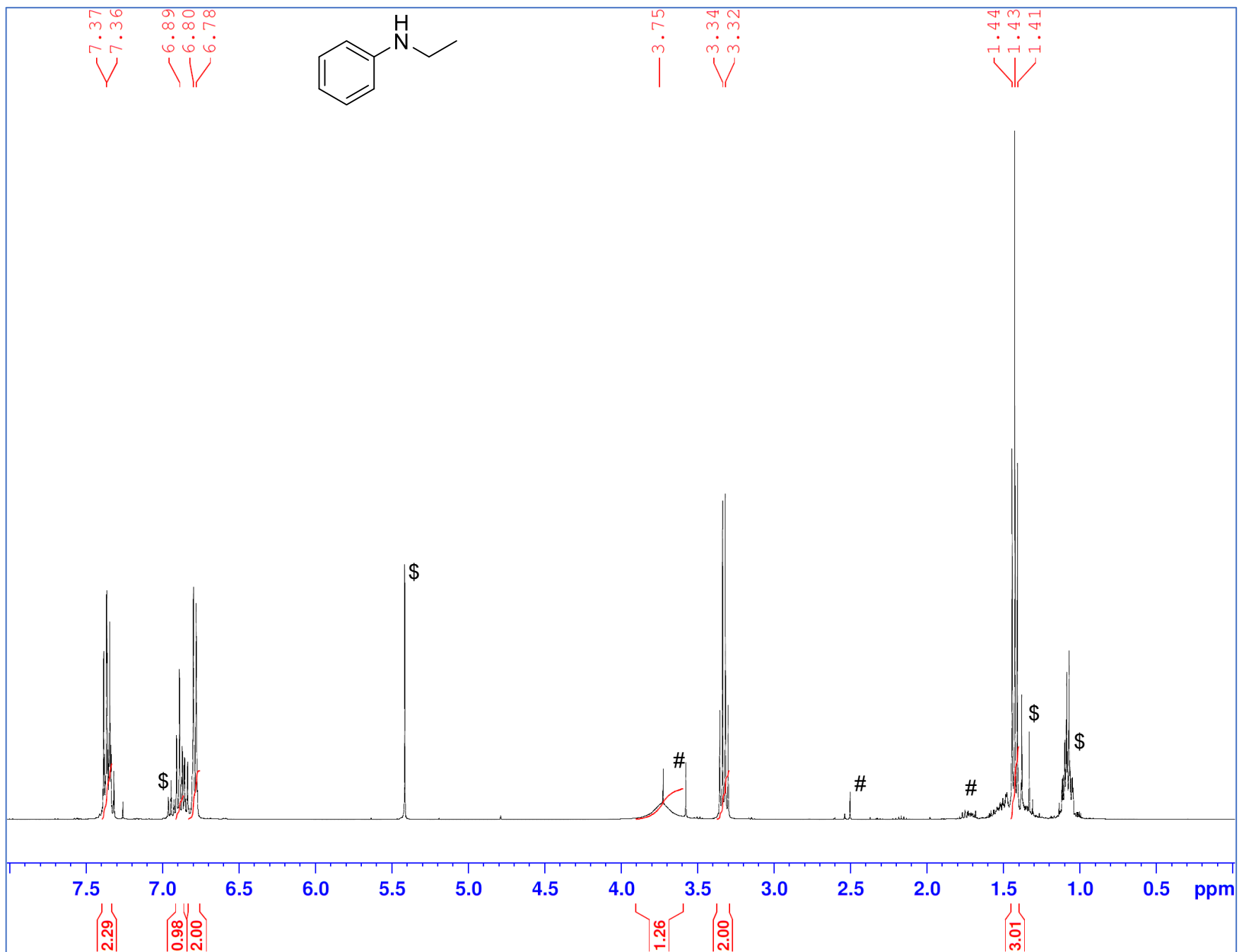
Supplementary Figure S68. $^{13}\text{C}\{^1\text{H}\}$ -NMR spectrum of 3k in CDCl_3 ; * \equiv deuterated solvent.



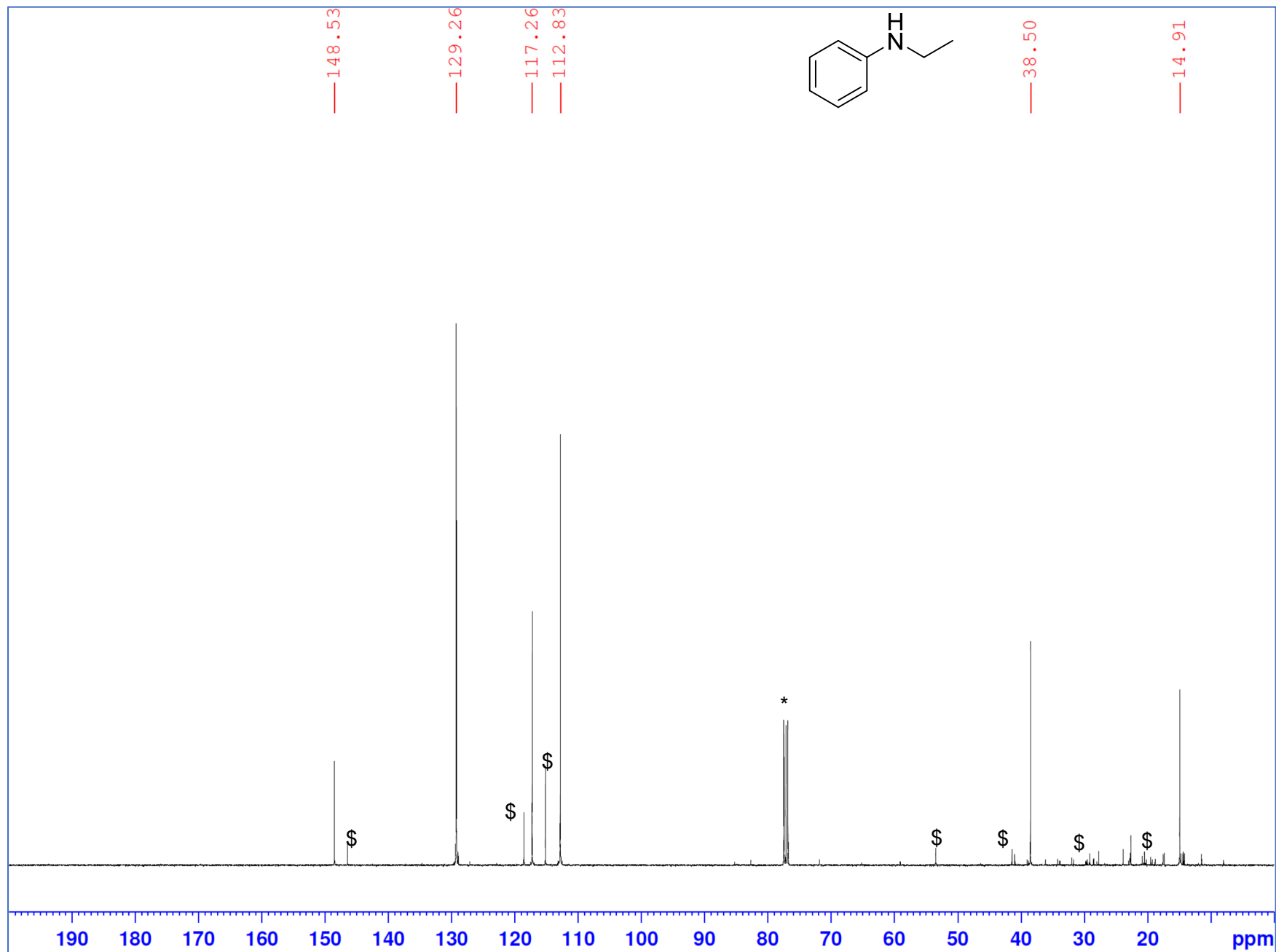
Supplementary Figure S69. $^1\text{H-NMR}$ spectrum of **3I** in CDCl_3 ; * \equiv deuterated solvent; \$ \equiv residual EtOAc and heptanes; # \equiv non-identified impurity.



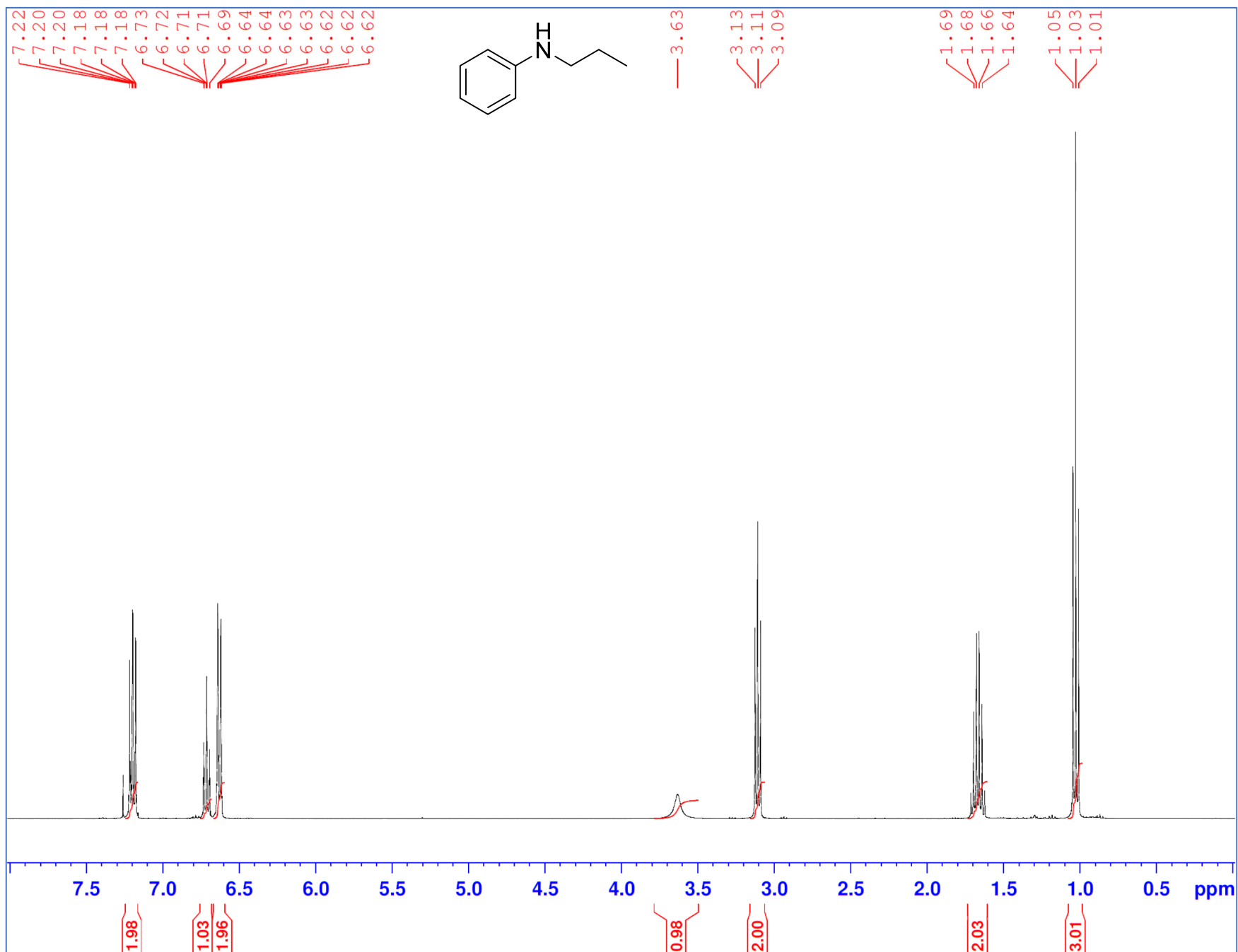
Supplementary Figure S70. $^{13}\text{C}\{^1\text{H}\}$ -NMR spectrum of **31** in CDCl_3 ; * \equiv deuterated solvent; \$ \equiv residual EtOAc.



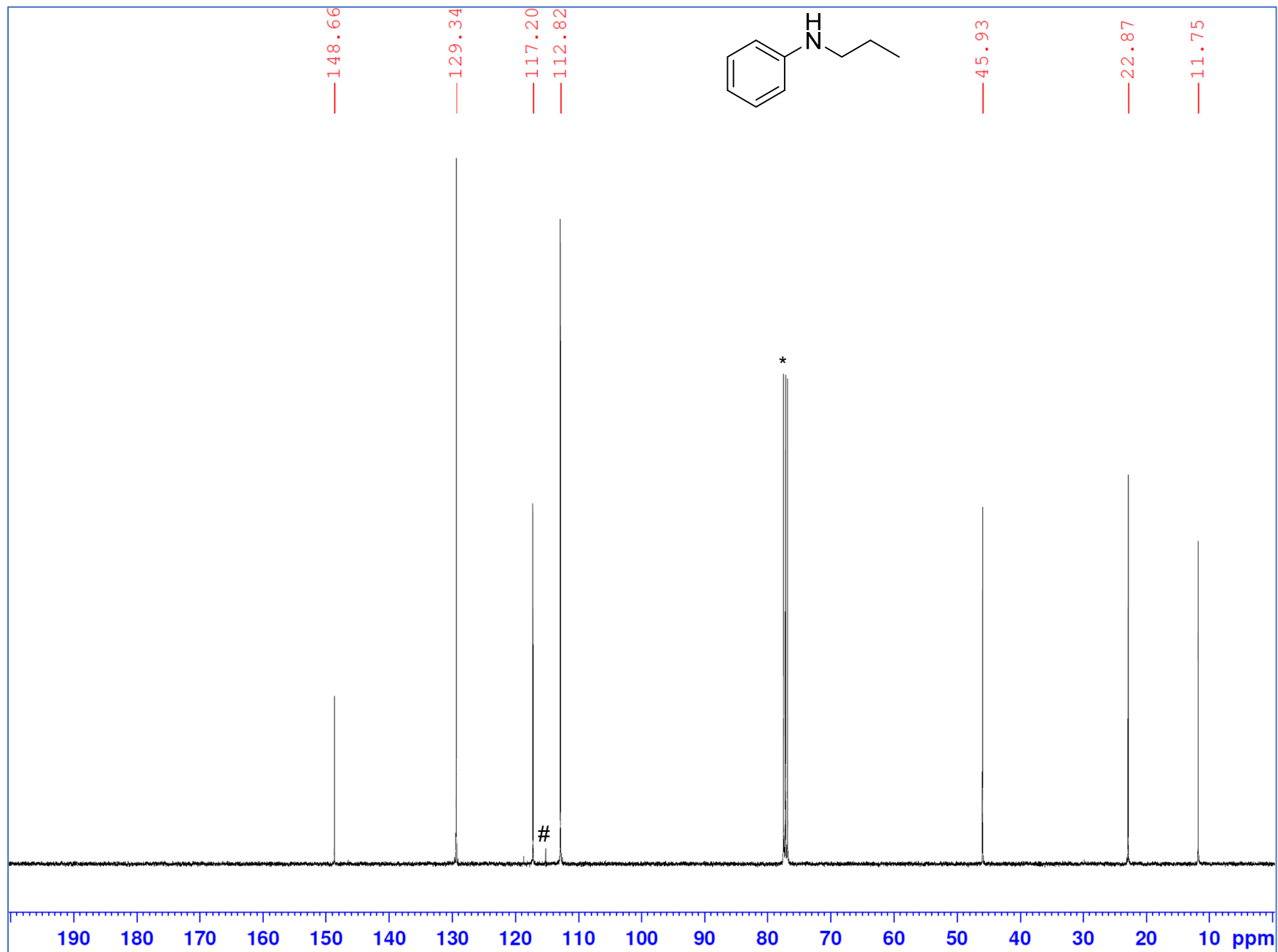
Supplementary Figure S71. ¹H-NMR spectrum of **3m** in CDCl₃; \$ ≡ residual aniline, CH₂Cl₂ and petrol ether; # ≡ non-identified impurity.



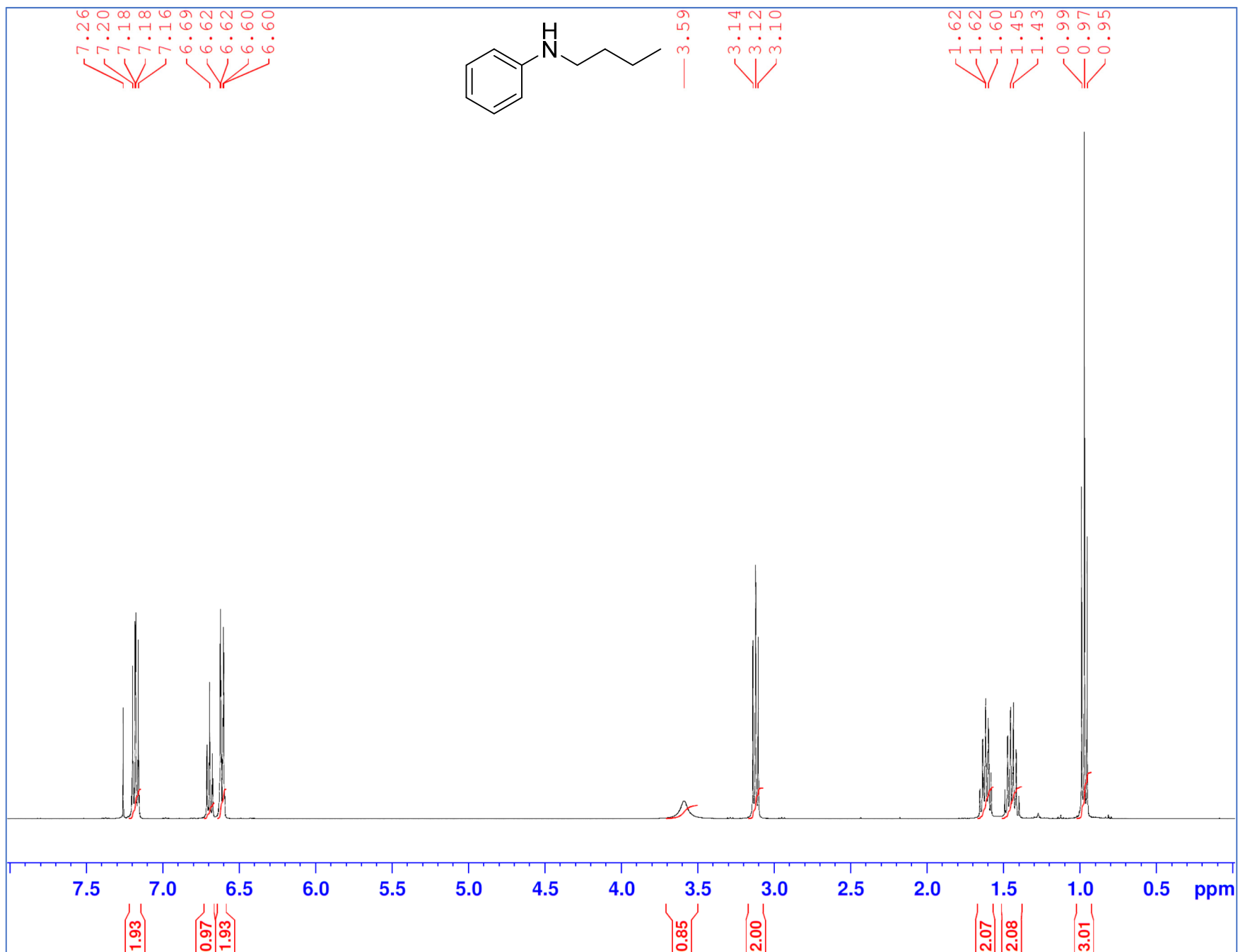
Supplementary Figure S72. $^{13}\text{C}\{^1\text{H}\}$ -NMR spectrum of **3m** in CDCl_3 ; * \equiv deuterated solvent; \$ \equiv residual aniline, CH_2Cl_2 and petrol ether.



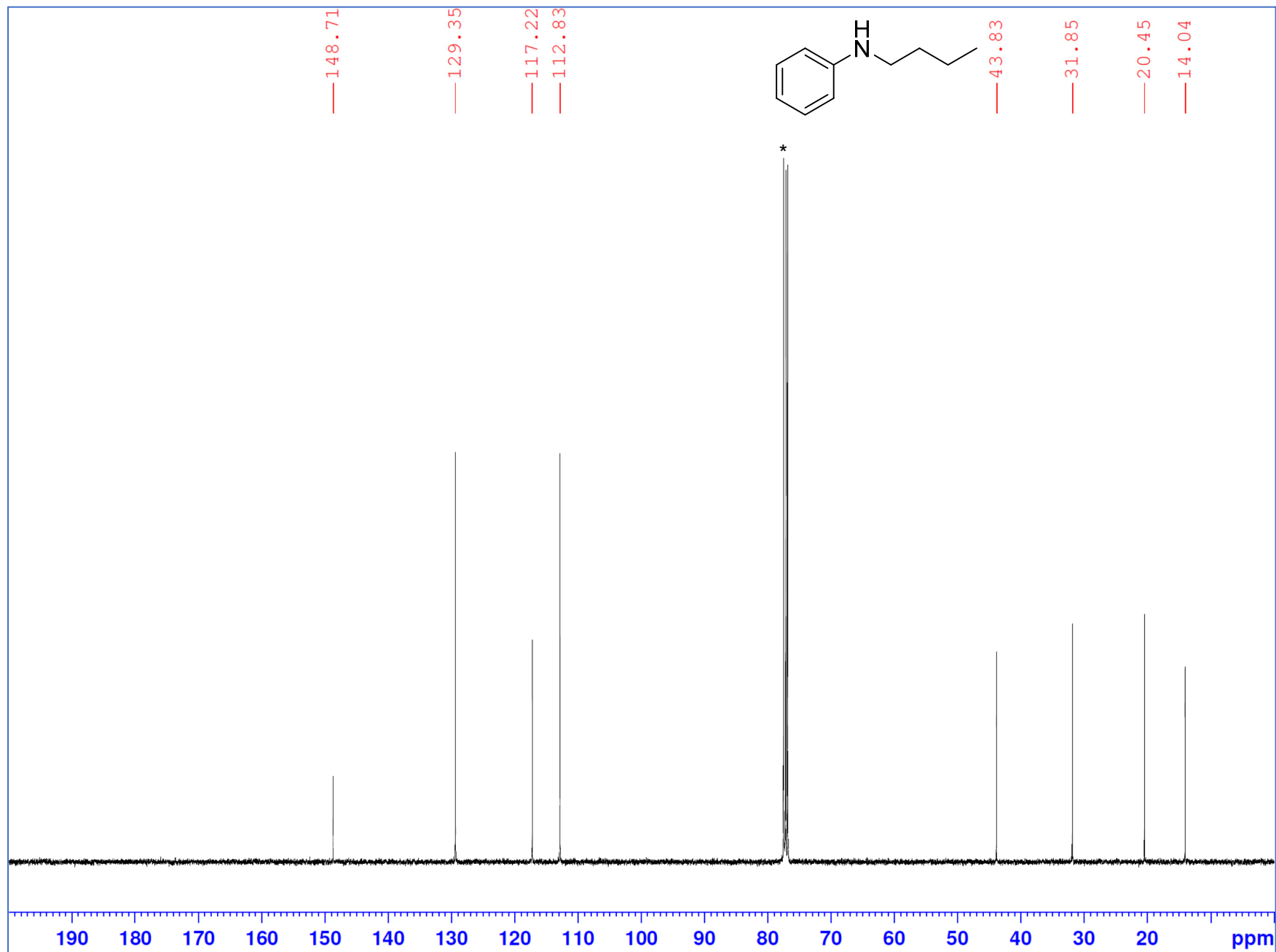
Supplementary Figure S73. ¹H-NMR spectrum of **3n** in CDCl₃.



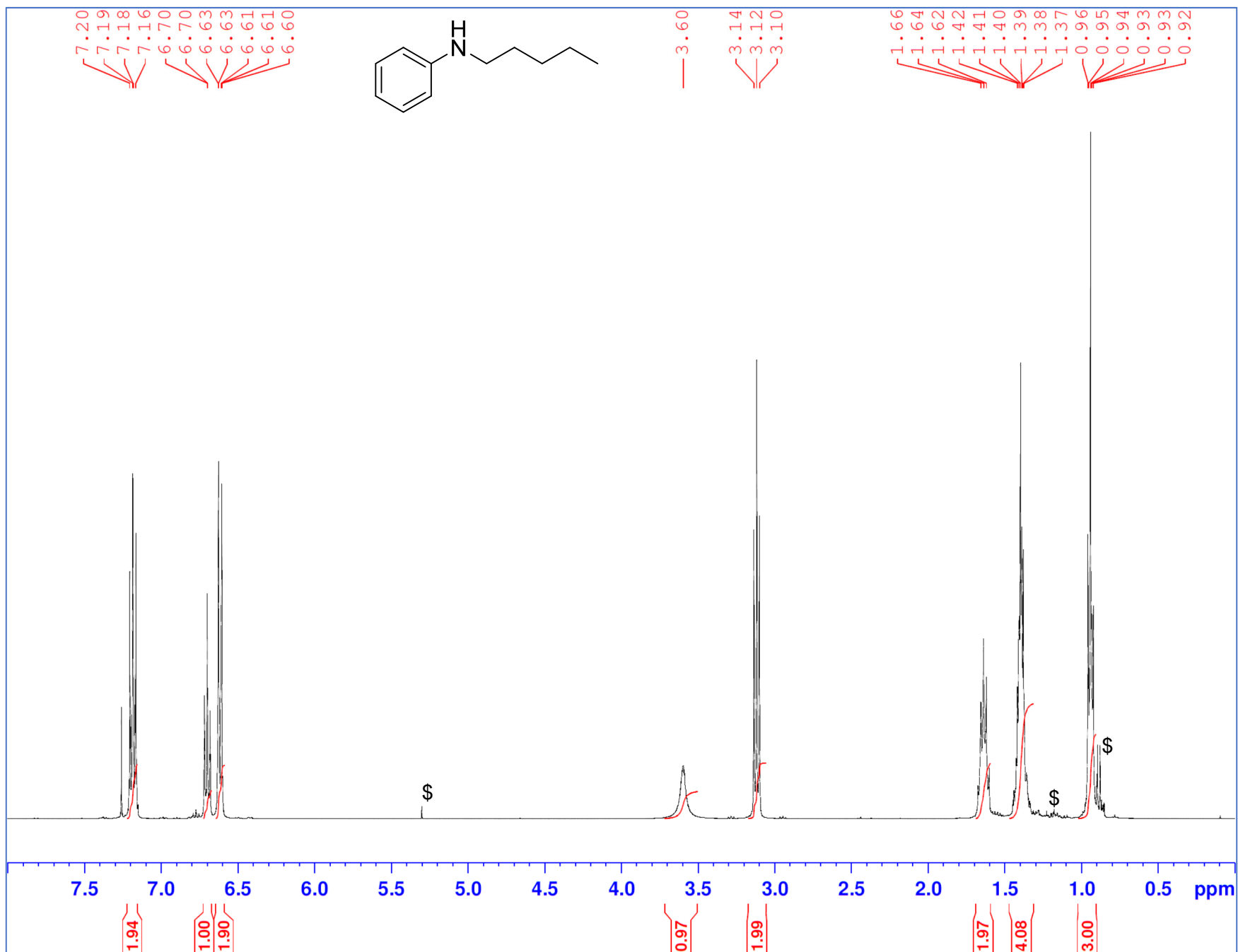
Supplementary Figure S74. $^{13}\text{C}\{^1\text{H}\}$ -NMR spectrum of **3n** in CDCl_3 ; * \equiv deuterated solvent; # \equiv non-identified impurity.



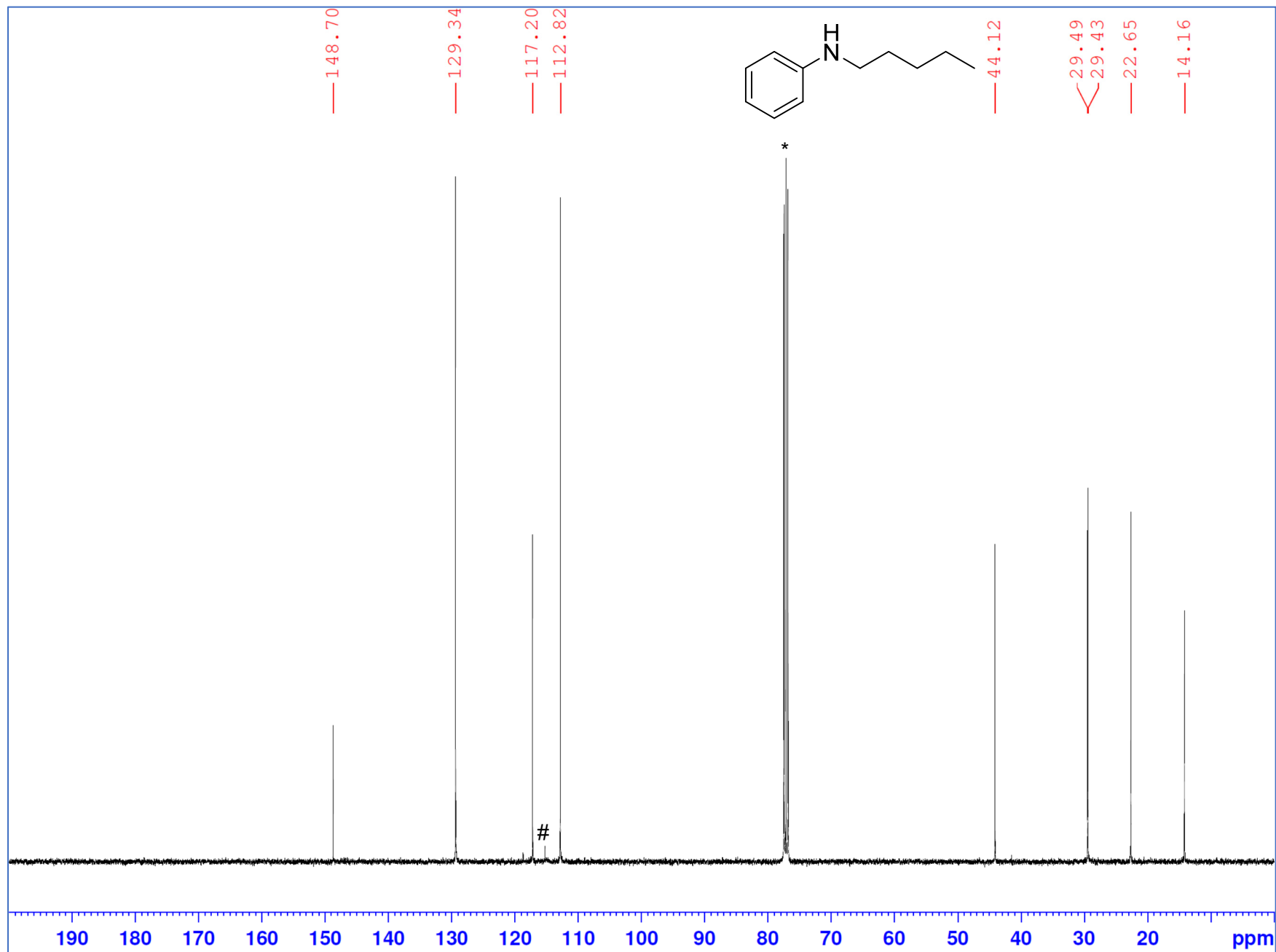
Supplementary Figure S75. ¹H-NMR spectrum of 3o in CDCl₃.



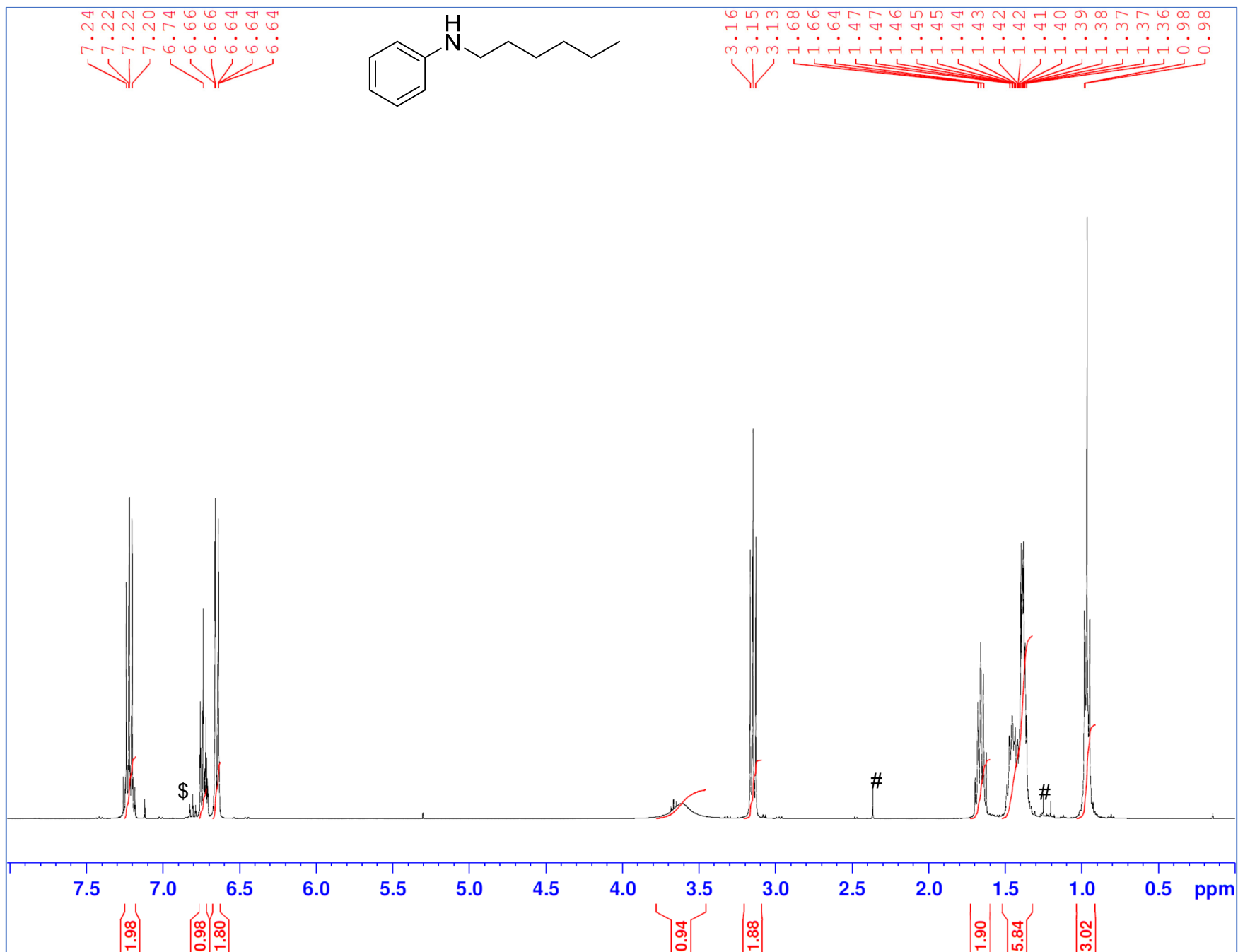
Supplementary Figure S76. $^{13}\text{C}\{^1\text{H}\}$ -NMR spectrum of **3o** in CDCl_3 ; * \equiv deuterated solvent.



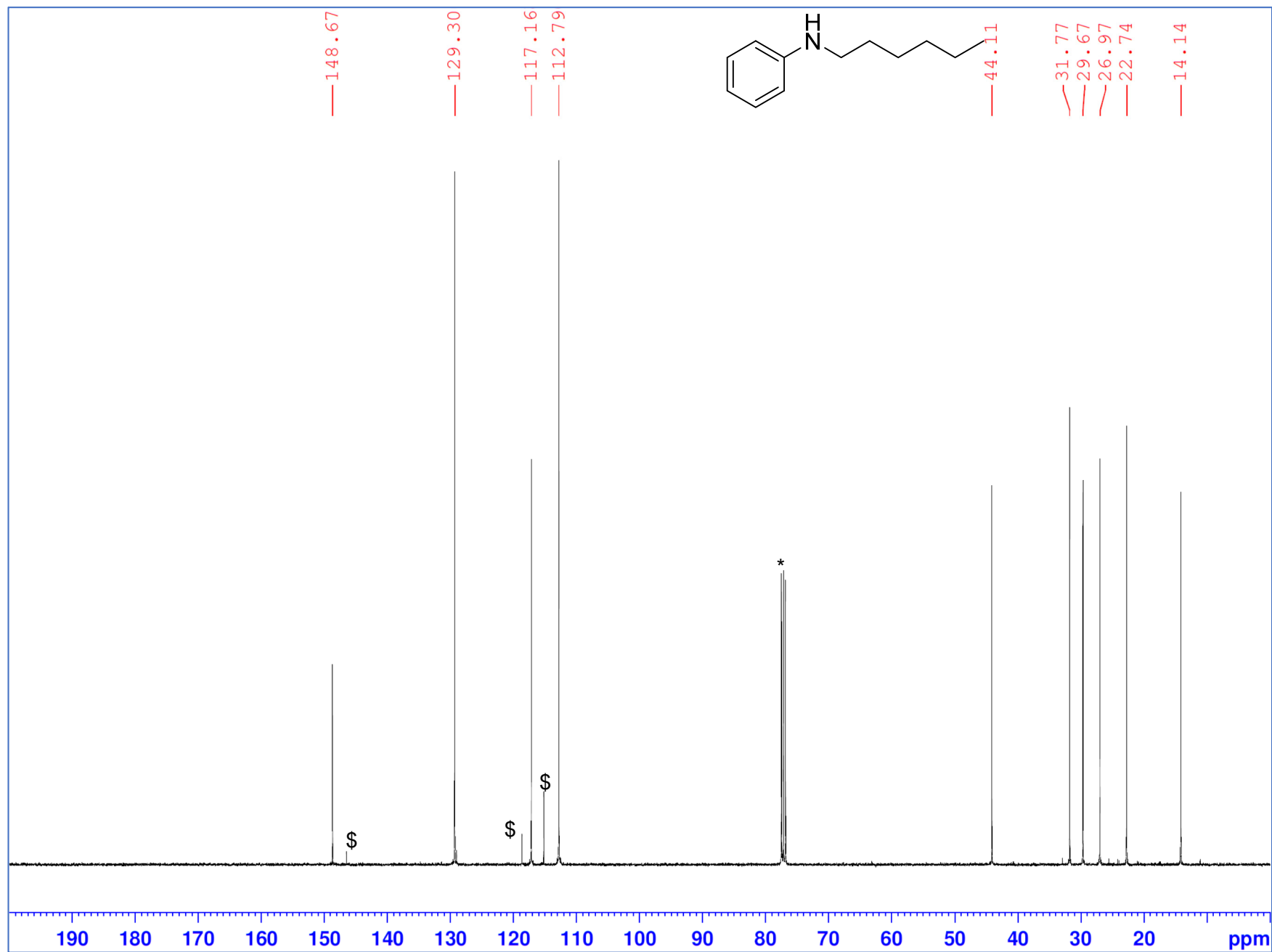
Supplementary Figure S77. ¹H-NMR spectrum of **3p** in CDCl₃; \$ ≡ residual CH₂Cl₂ and petrol ether.



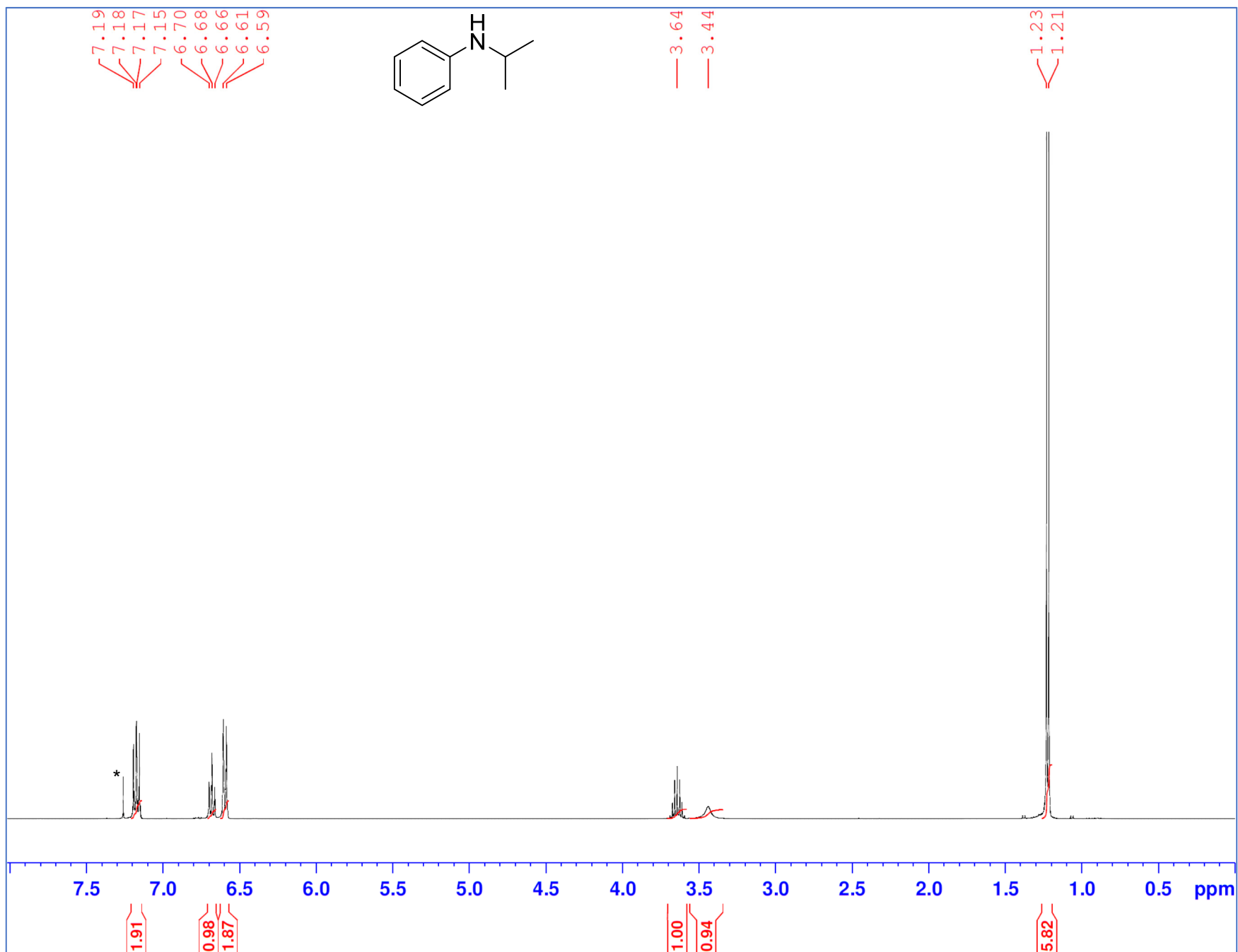
Supplementary Figure S78. $^{13}\text{C}\{^1\text{H}\}$ -NMR spectrum of **3p** in CDCl_3 ; * \equiv deuterated solvent; # \equiv non-identified impurity.



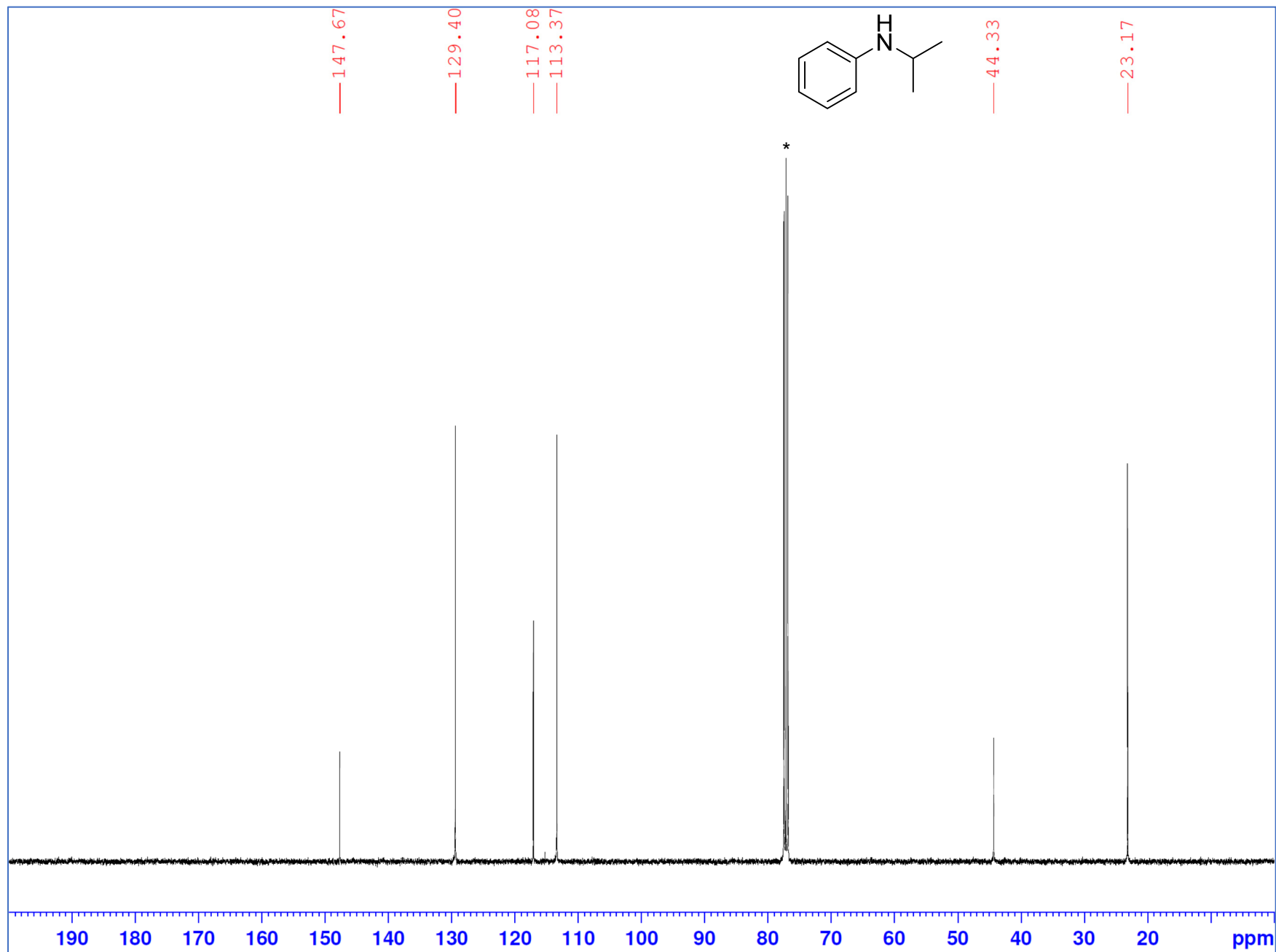
Supplementary Figure S79. $^1\text{H-NMR}$ spectrum of **3q** in CDCl_3 ; \$ \equiv residual aniline, # \equiv non-identified impurity.



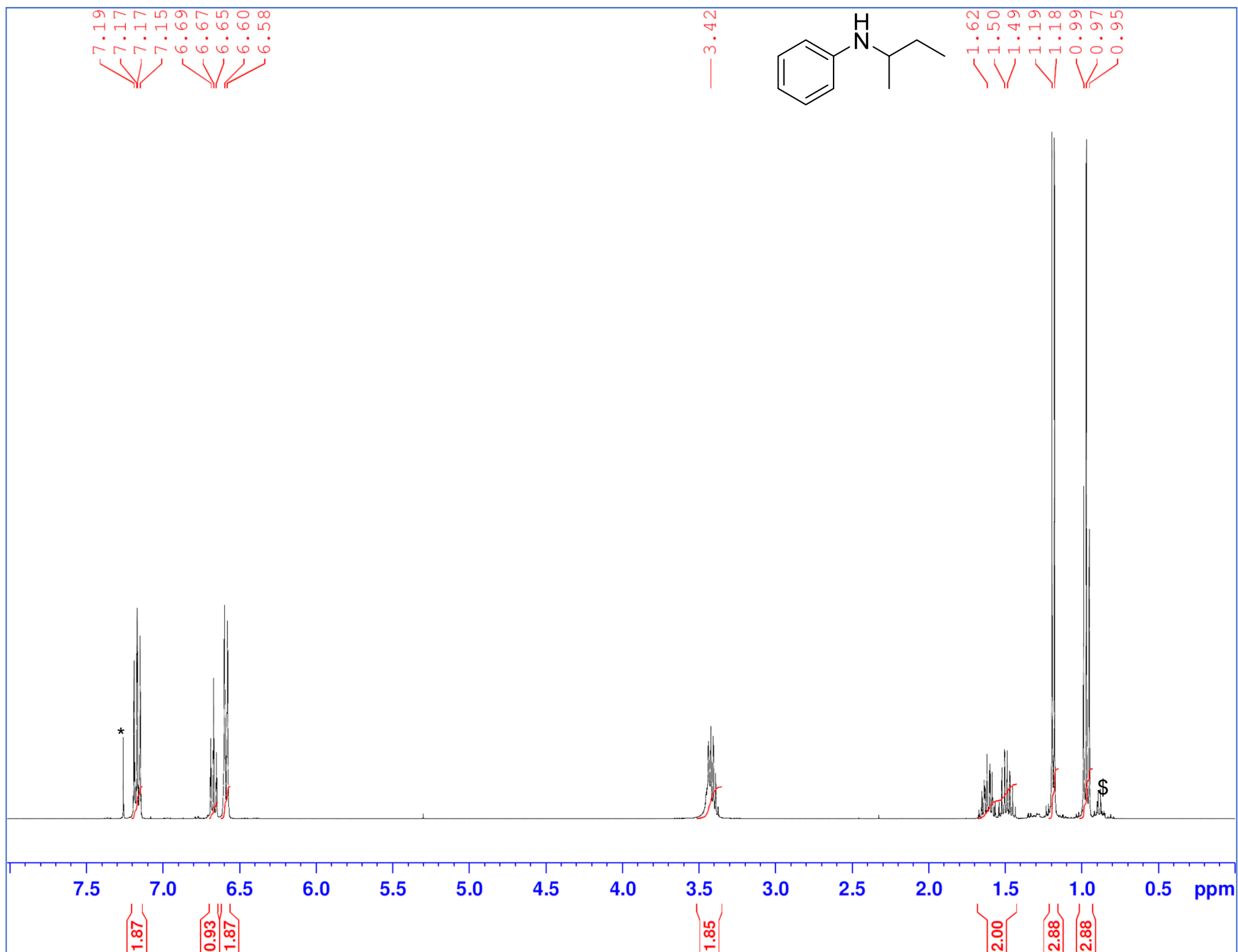
Supplementary Figure S80. $^{13}\text{C}\{^1\text{H}\}$ -NMR spectrum of **3q** in CDCl_3 ; * \equiv deuterated solvent; \$ \equiv residual aniline.



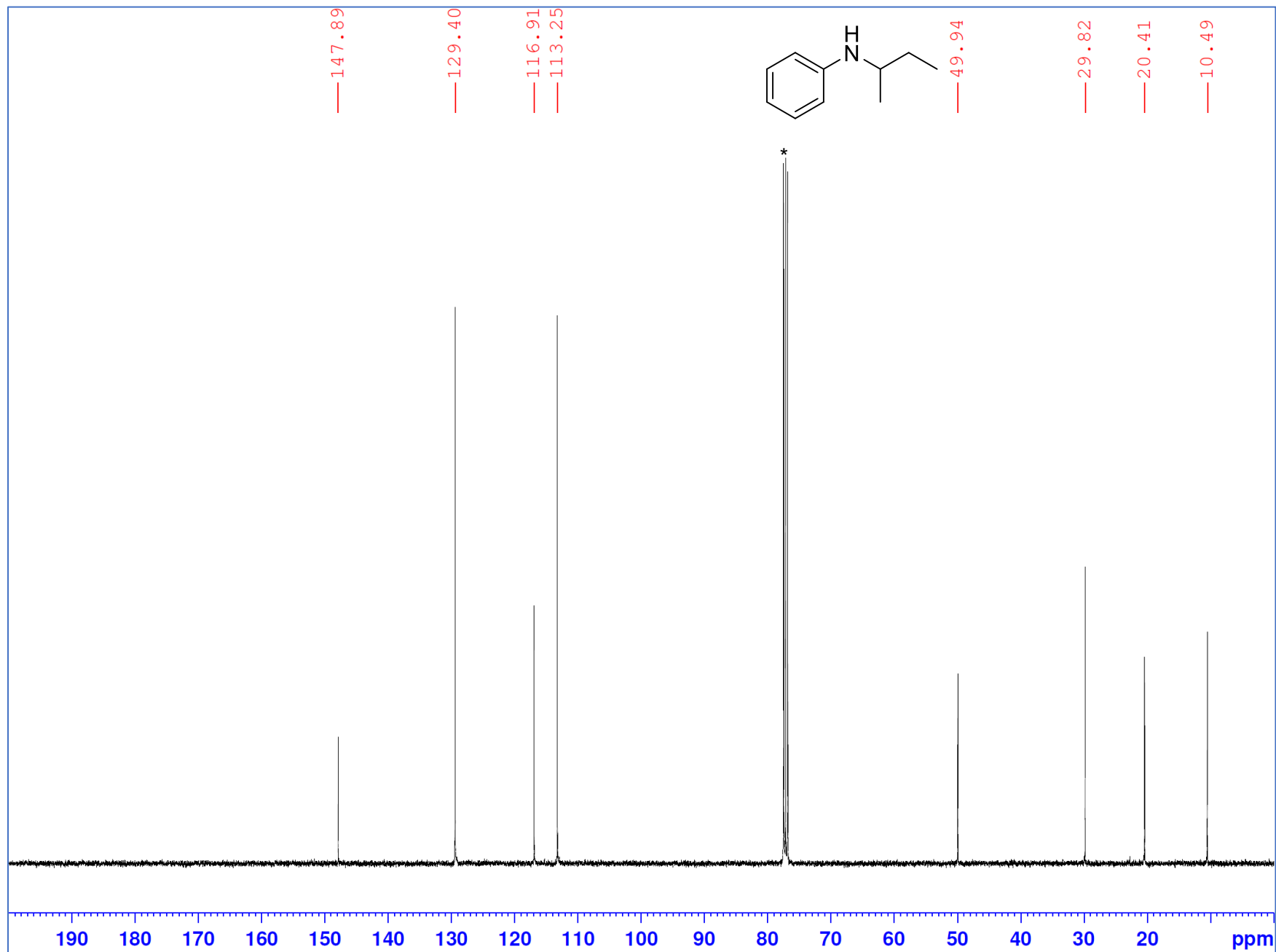
Supplementary Figure S81. ¹H-NMR spectrum of **3r** in CDCl₃; * ≡ deuterated solvent.



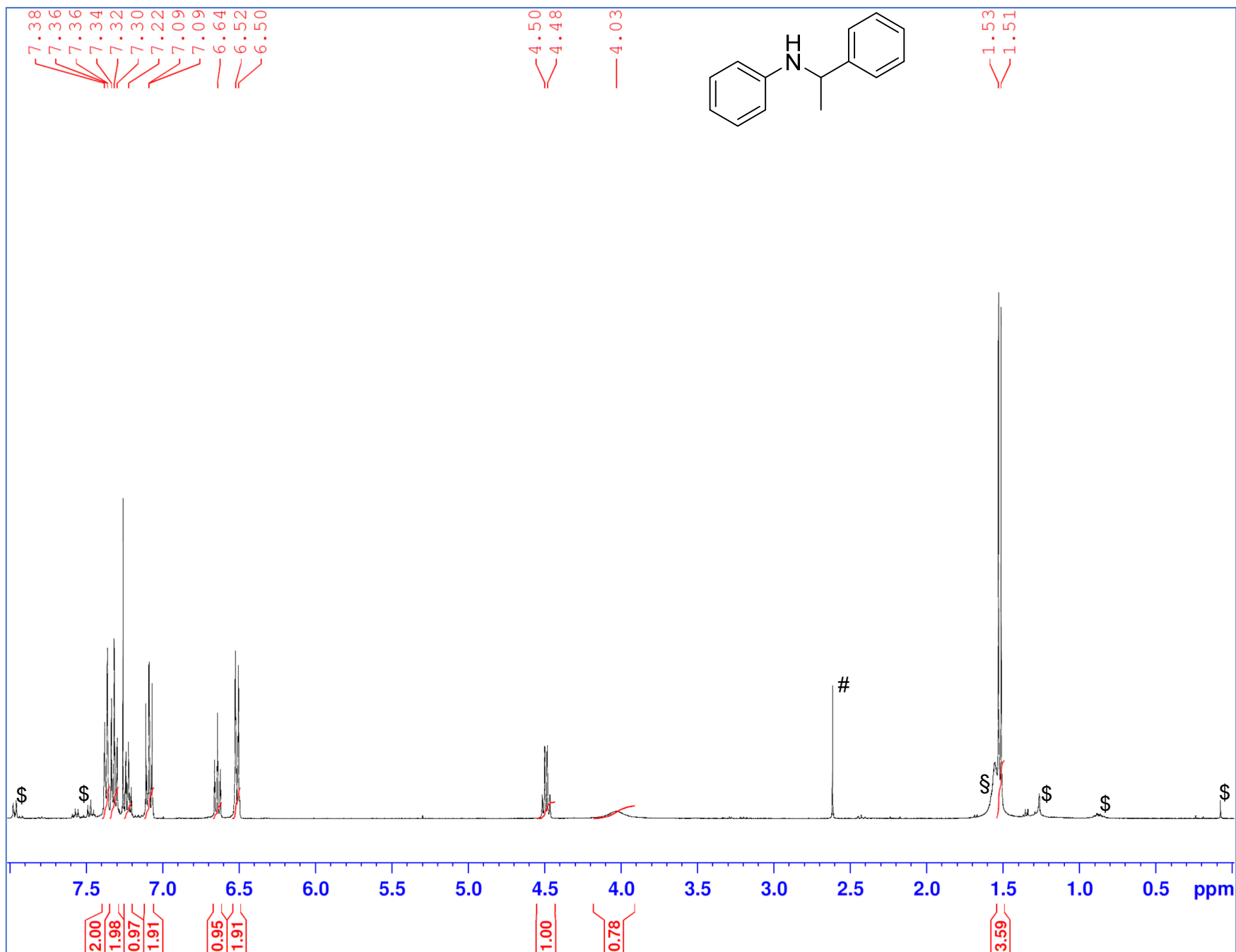
Supplementary Figure S82. $^{13}\text{C}\{^1\text{H}\}$ -NMR spectrum of **3r** in CDCl_3 ; * \equiv deuterated solvent.



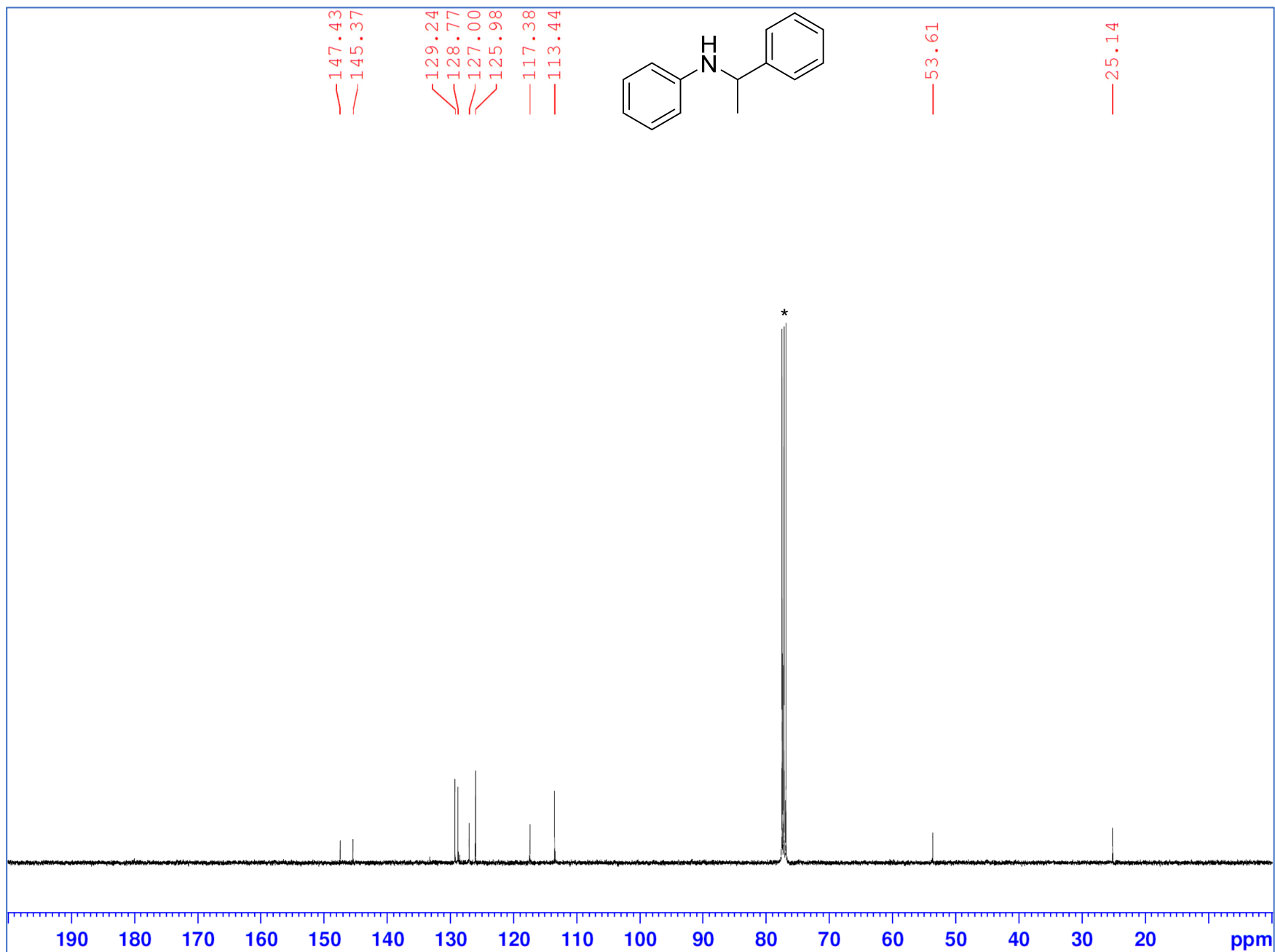
Supplementary Figure S83. ¹H-NMR spectrum of **3s** in CDCl₃; * ≡ deuterated solvent, \$ ≡ residual petrol ether.



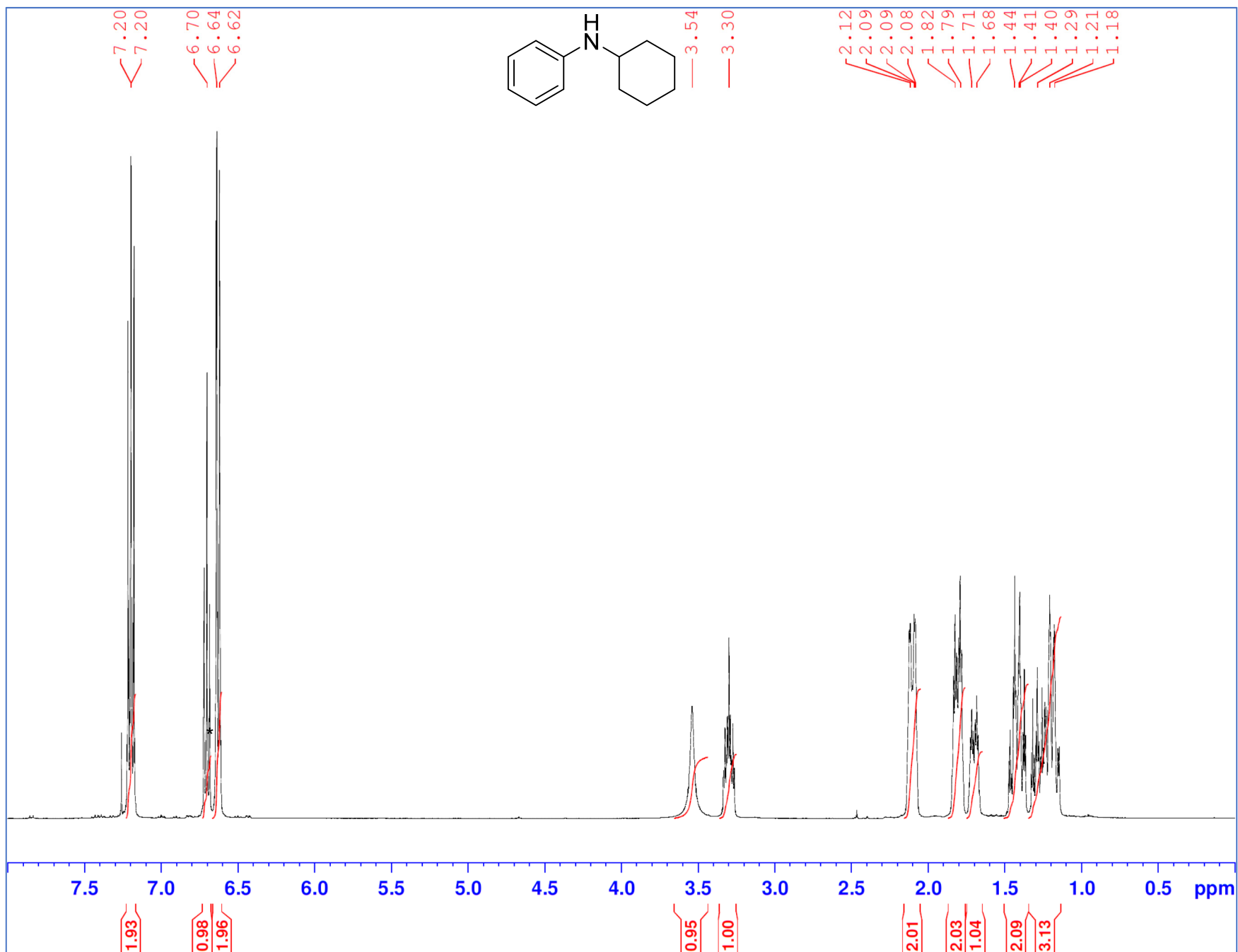
Supplementary Figure S84. $^{13}\text{C}\{^1\text{H}\}$ -NMR spectrum of **3s** in CDCl_3 ; * \equiv deuterated solvent.



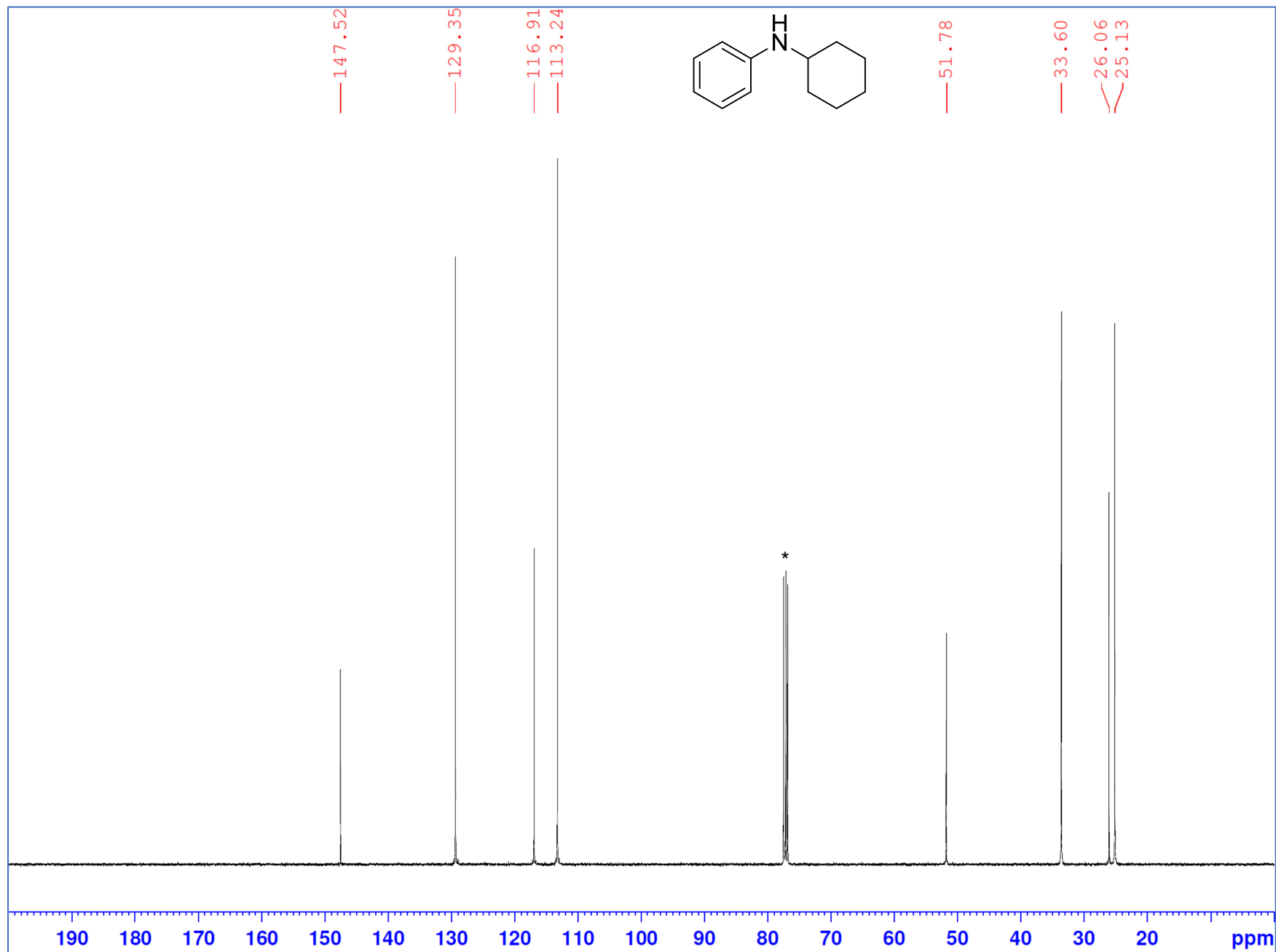
Supplementary Figure S85. ¹H-NMR spectrum of **3t** in CDCl₃; § ≡ residual water; § ≡ *N*,1-diphenylethan-1-imine, residual heptanes and silicon grease; # ≡ non-identified impurity.



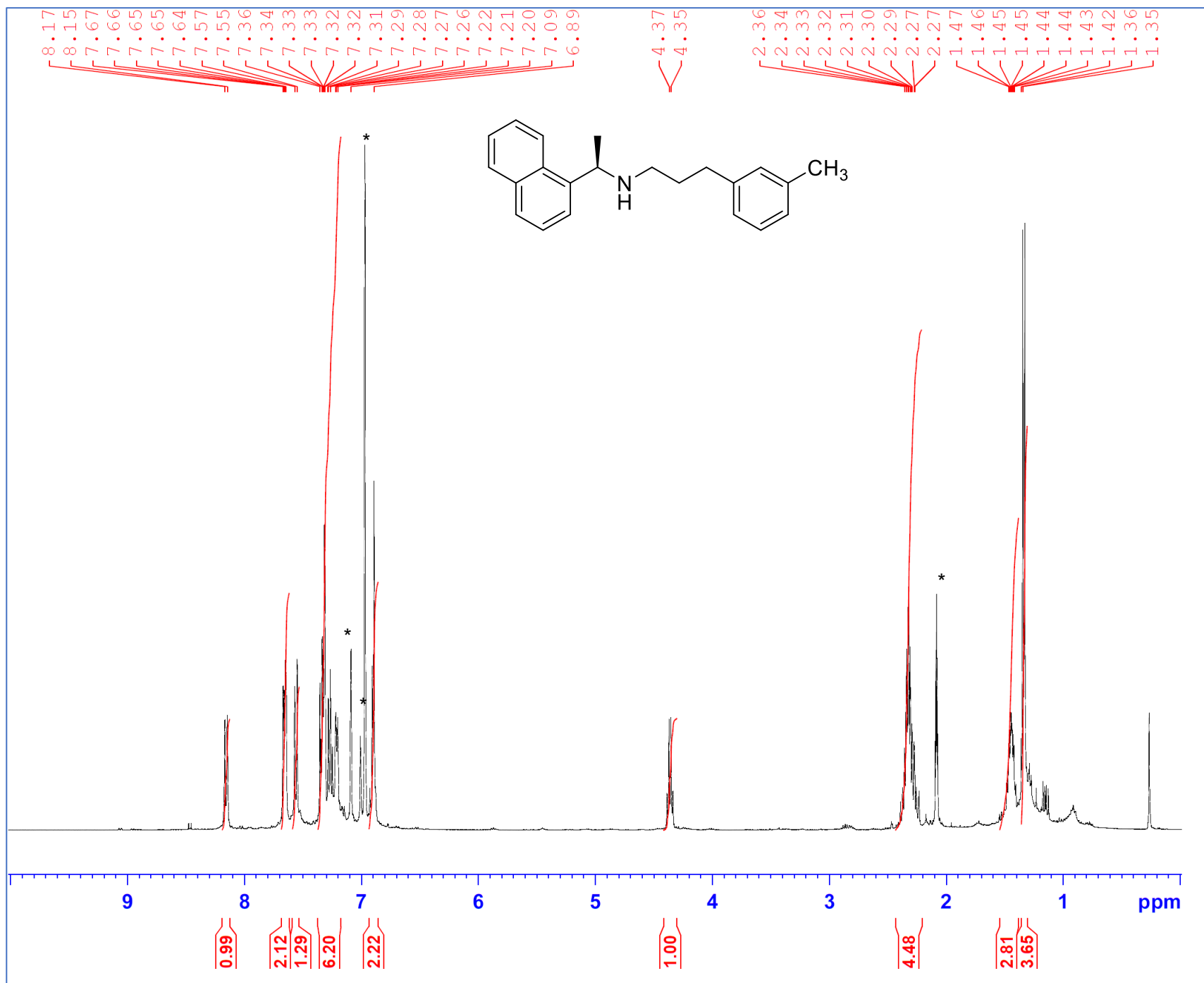
Supplementary Figure S86. $^{13}\text{C}\{^1\text{H}\}$ -NMR spectrum of **3t** in CDCl_3 ; * \equiv deuterated solvent.



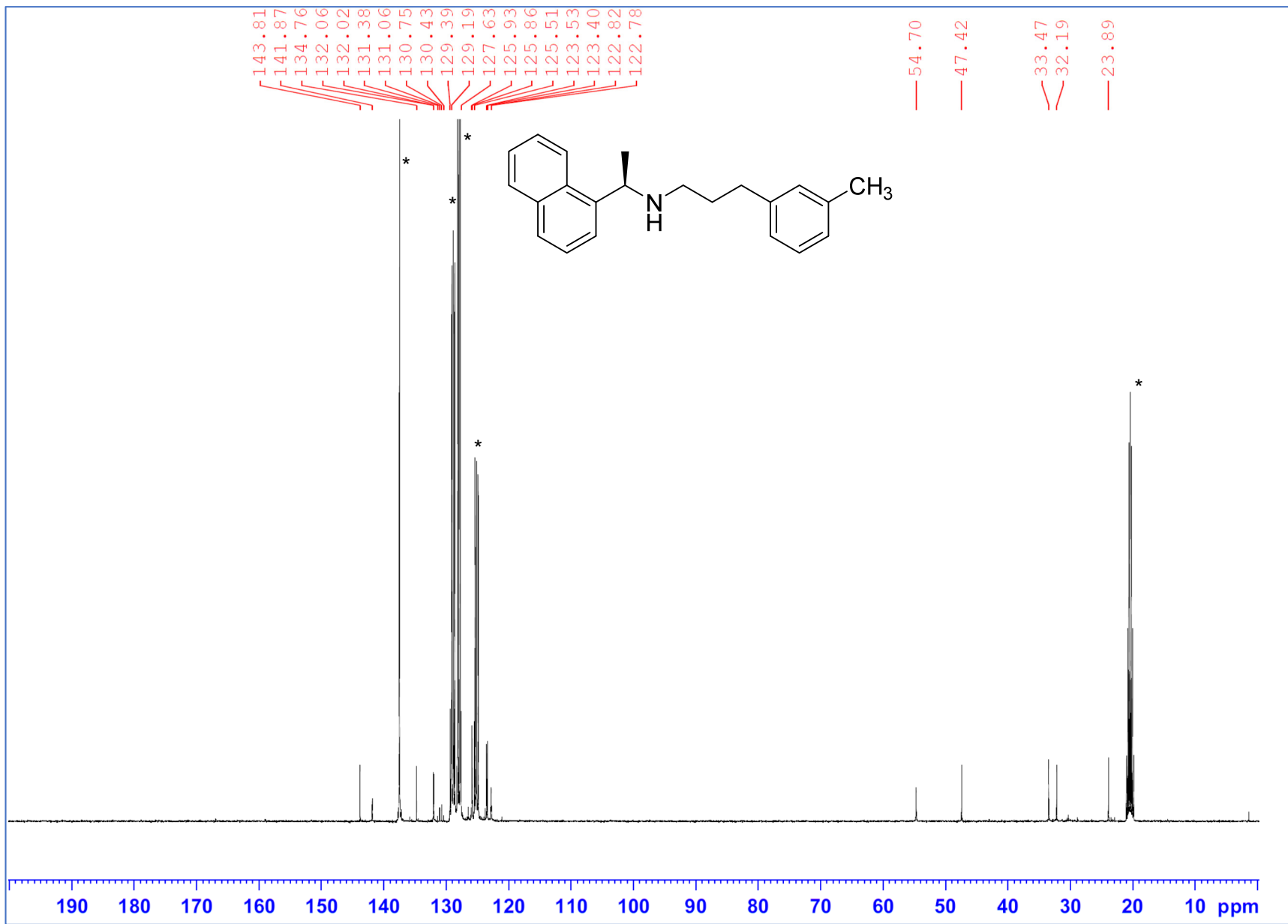
Supplementary Figure S87. ¹H-NMR spectrum of **3u** in CDCl₃; * ≡ deuterated solvent.



Supplementary Figure S88. $^{13}\text{C}\{^1\text{H}\}$ -NMR spectrum of **3u** in CDCl_3 ; * \equiv deuterated solvent.



Supplementary Figure S89. ¹H-NMR spectrum of **4** in toluene-*d*₈; * ≡ deuterated solvent.



Supplementary Figure S90. $^{13}\text{C}\{^1\text{H}\}$ -NMR spectrum of **4** in toluene- d_8 ; * \equiv deuterated solvent.