Supporting Information

Direct Access to *N*-Alkylated Amines and Imines *via*Acceptorless Dehydrogenative CouplingCatalyzed by Cobalt(II)-NNN Pincer Complex

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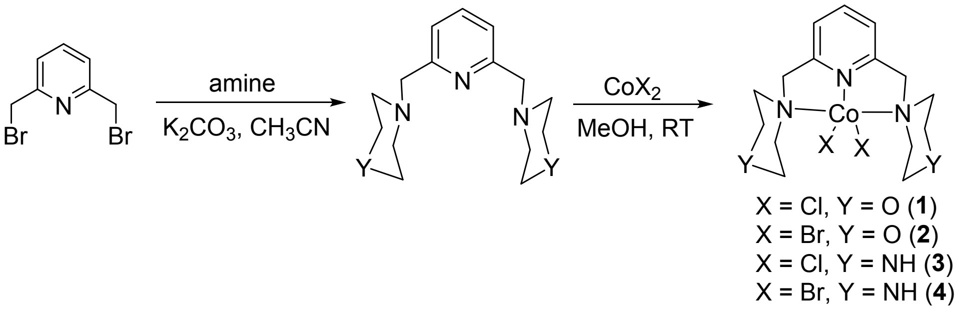
Contents

1. General Information

All catalytic experiments were carried out using standard Schlenk techniques. All solvents were reagent grade or better. Deuterated solvents were used as received. An *m*-xylene was refluxed over sodium/benzophenone and followed by distilled under argon atmosphere and stored over sodium. Cobalt salt precursors were used without additional purification. Most of the chemicals used in the catalytic reactions were purified according to standard procedure.[S1] Thin layer chromatography (TLC) was performed using silica gel precoated glass plates, which were visualized with UV light at 254 nm or under iodine. Column chromatography was performed with SiO_2 (SilicycleSilicaflash F60 (230-400 mesh). ^1H NMR (200, 400 or 500 MHz), ^{13}C NMR (50, 100 or 126 MHz) spectra were recorded on the NMR spectrometer. Deuterated chloroform was used as the solvent, and chemical shift values (δ) are reported in parts per million relative to the residual signals of this solvent [δ 7.27 for ^1H (chloroform-d), δ 77.0 for ^{13}C (chloroform-d). Abbreviations used in the NMR follow-up experiments: br, broad; s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet. GC analysis was carried out using a HP-5 column (30 m, 0.25 mm, 0.25μ). Mass spectra were obtained on a GCMS-QP 5000 instruments with ionization voltages of 70 eV. High resolution mass spectra (HRMS) were obtained on a High-resolution mass spectra (HRMS) by fast atom bombardment (FAB) using a double focusing magnetic sector mass spectrometer and electron impact (EI) ionization technique (magnetic sector-electric sector double focusing mass analyzer).Elemental analyses were performed on a Vario-EL cube elemental analyzer. Fourier transform infrared (FT-IR) FTIR analysis was carried out on a Perkin-Elmer Spectrometer. Optical absorption measurements were carried out by Shimadazu UV-vis-IR-3600 Plus spectrophotometer. Electron paramagnetic resonance spectra were recorded with a Bruker EMX-plus X-band spectrometer. The crystals were mounted on a Super Nova Dual source X-ray Diffractometer system (Agilent Technologies) equipped with a CCD area detector and operated at 250 W power (50 kV, 0.8 mA) to generate Mo Kα radiation (λ= 0.71073 Å) and Cu Kα radiation (λ= 1.54178 Å) at 298(2) K.

2. Experimental Section and Characterization of Products

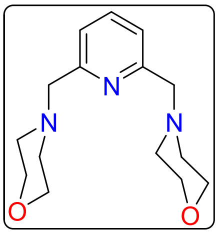
2.1 Synthesis of ligand and Cobalt-complexes



Scheme S1. Synthesis of Cobalt complexes (**1-4**)

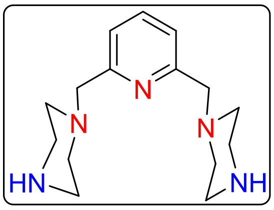
2.1.1 Synthesis of Ligand

2,6-bis(morpholinomethyl)pyridine (L_1)[S2]



To a solution of 2,6-Bis(bromomethyl)pyridine (0.3 g, 1.13 mmol) and K_2CO_3 (0.468 g, 3.39 mmol) in MeCN (30 mL), a solution of morpholine (0.197 g, 2.26 mmol) in MeCN (15 mL) were added under the nitrogen atmosphere. The resulting reaction mixture was allowed to stir for 14 h at 80 °C followed by cooled to room temperature. The mixture was diluted with water and extracted with Chloroform (3 x 10 mL). The organic fraction was collected, dried over anhydrous Na_2SO_4, and evaporated in vacuum under the reduced pressure afforded **Py-N³**. Yield (0.280 g, 89 %). IR (KBr): ν = 2800 (m), 1575 (m), 1454 (m), 1298 (m), 1111 (s), 906 (m). **^{1}H NMR** (200 MHz, CHLOROFORM-d) δ = 7.64 (t, *J* = 7.8 1H), 7.33 (d, *J* = 7.6 Hz, 2H), 3.76 - 3.72 (m, 8H), 3.67 (s, 4H), 2.54-2.50 (m, 8H). **HRMS (EI)**: *m/z* Calcd for $C_{15}H_{24}O_2N_3$: 278.1869; Found: 278.1863.

2,6-bis(piperazin-1-ylmethyl)pyridine (L_2)



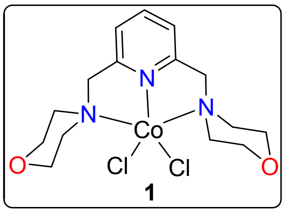
Step-1: Synthesis of ^{boc}NNN (L_2):

Solution of 2,6-bis(bromomethyl)pyridine (1 g, 3.77 mmol) in acetonitrile (40 mL) was added drop-wise to a solution of 1-boc-peprazine (1.4037 g, 7.54 mmol) and K_2CO_3 (1.56 g, 1.13 mmol) in CH_3CN (20 mL) and the resulting reaction mixture was allowed to stir for 14 hours at 85 °C. After cooled to room temperature, the solvent was evaporated under reduced pressure and the crude reaction mixture was extracted with chloroform (3 x 30 mL). The organic fraction were combined and dried over anhydrous Na_2CO_3 and evaporated under vacuum to afford *N*-boc protected NNN-L1 as a yellow liquid. Yield: 0.8 g; 80%. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.78 - 7.48 (m, 1H), 7.31 (dd, *J* = 13.3, 7.0Hz, 2H), 4.12 - 3.52 (m, 4H), 3.58 - 3.30 (m, 8H), 2.72 - 2.28 (m, 7H), 1.94 (s, 1H), 1.73 - 1.18 (m, 18H). **^{13}C NMR** (400 MHz, $CDCl_3$) δ 157.77, 154.81, 136.74, 121.43, 79.60, 64.45, 53.08, 28.43. **HRMS (ESI):** Calcd. For $C_{25}H_{41}N_5O_4$ $[M+H]^+$ 475.62; found 476.3244.

Step-2, Synthesis of NNN-L_2:

^{boc}NNN-L1 (0.8 g) was dissolved in MeOH (15 mL) followed by addition of 1N HCl (8 mL), then the mixture was allowed to stir for 6 hrs at 60 °C. After cooling the reaction mixture to room temperature, it was neutralized with aqueous solution of 5% $NaHCO_3$, then the solvent was evaporated under reduced pressure. The resulting product was further dissolved in ethanol and filtered. The filtrate was concentrated under vacuum and afforded NNN-L_2 (Yellow liquid). Yield (0.75 g, 75%). **^{1}H NMR** (500 MHz ,CHLOROFORM-d) δ = 7.62 (s, 1 H), 7.30 (d, *J* = 8.4 Hz, 2 H), 3.65 (s, 4 H), 2.92 (t, *J* = 4.8 Hz, 8 H), 2.49 (brs, 9 H), 2.07 (brs, 2 H). **^{13}C NMR** (126 MHz ,CHLOROFORM-d) δ = 157.8, 136.6, 121.4, 77.3, 76.7, 65.0, 54.6, 45.9. HRMS (ESI): calcd. For $C_{15}H_{25}N_5$ $[M+H]^+$ 275.39; found 276.21.

2.1.2 Synthesis of Cobalt-complexes



1

To a solution of **Py-N^3(L$_1$)** (0.1 g, 0.36 mmol) in MeOH (10 mL), a $CoCl_2$ (0.047 g, 0.36 mmol) was added and the resulted mixer was stirred at RT for 3 h. Diethyl ether was allowed to diffuse on to the resulting mixture for 2 days. The deep blue colour Co crystals were formed which was collected and washed with ether.

Yield (0.118 g, 81 %).

IR (KBr): 3403, 2960, 2871, 2839, 1613, 1453, 1292, 1112, 997, 868 cm^{-1}.

UV-Visible spectra of **1** recorded in acetonitrile show absorption centered at 588 and 652 nm.

HRMS (EI): *m/z* Calcd for $C_{15}H_{24}Cl_2N_3CoO_2$ $[M+H]^+$: 407.0499; Found: 407.0493.

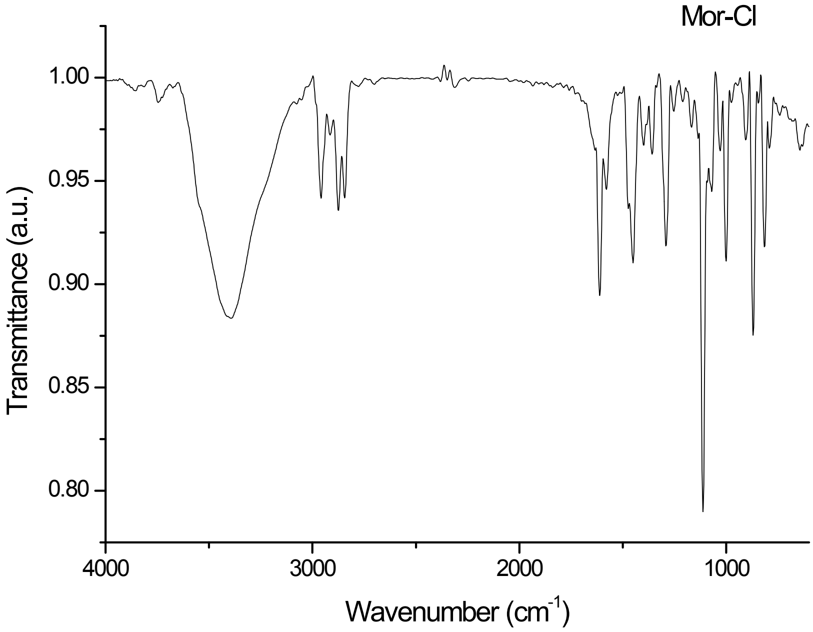


Figure S1. IR spectrum of **1**

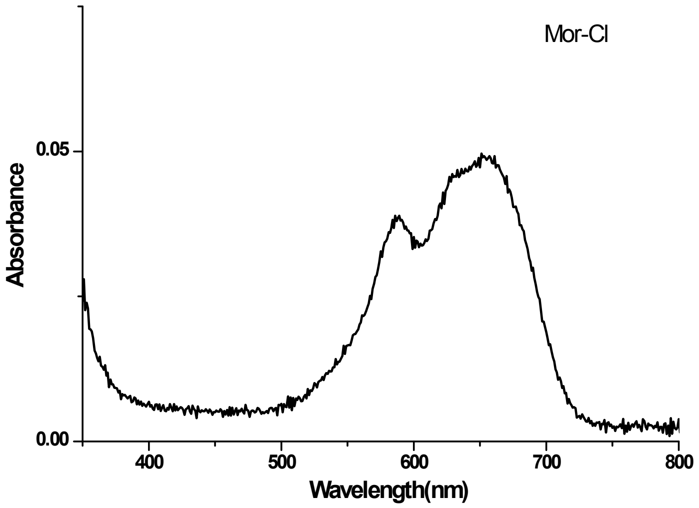
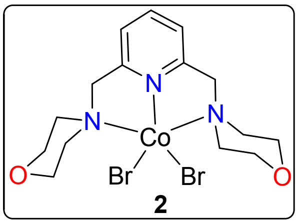


Figure S2. UV spectrum of **1**.



2

To a solution of **Py-N^3(L$_2$)** (0.1 g, 0.36 mmol) in MeOH (10 mL), a $CoBr_2$ (0.078 g, 0.36 mmol) was added and the resulting mixer was stirred at RT for 3 h. Diethyl ether was allowed to diffuse on to the resulting mixture for 2 days. The deep blue colour Co crystals were formed which was collected and washed with ether.

Yield (0.149 g, 84%).

IR (KBr): 3744, 2962, 2844, 2360, 1611, 1575, 1454, 1441, 1358, 1287, 1112, 1001, 871, 815, 787, 636 cm^{-1}.

UV-Visible spectra of **2** recorded in acetonitrile show absorption centered at 600 and 642 nm.

HRMS (EI): *m/z* Calcd for $C_{15}H_{24}Br_2N_3CoO_2$ $[M+H]^+$: 494.9567; Found: 494.9562.

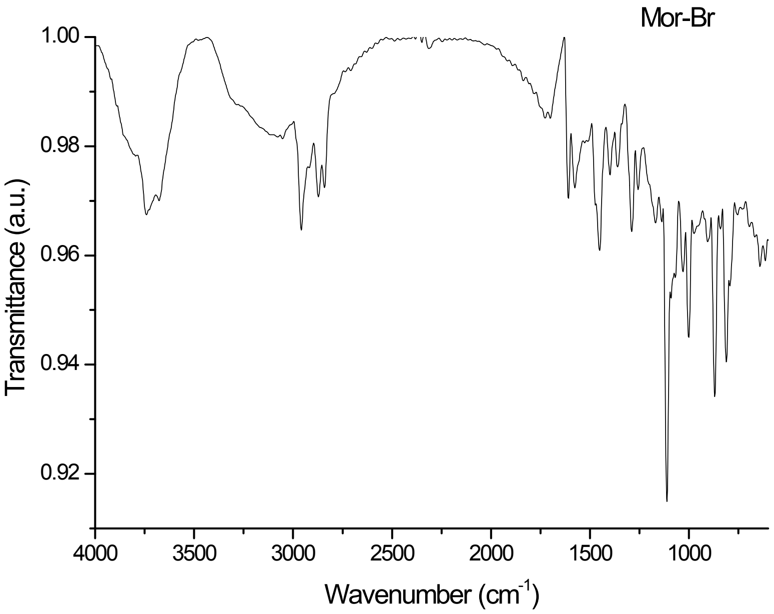


Figure S3. IR spectrum of **2**.

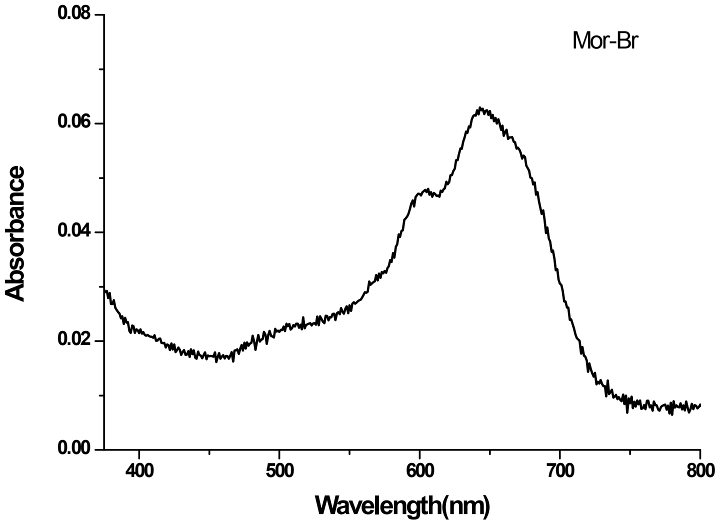
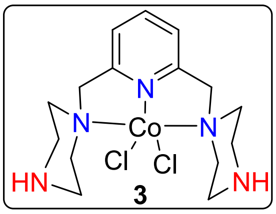


Figure S4. UV spectrum of **2**.



To a solution of **Py-N^3(L$_2$)** (0.1 g, 0.36 mmol) in MeOH (10 mL), a $CoCl_2.6H_2O$ (0.086 g, 0.36 mmol) was added and the resulting mixer was stirred at RT for 3 h. Then, the solvent was evaporated under reduced pressure. The deep blue colour powder of catalyst **3** was formed, which was collected and washed with ether and dried.

Yield (0.097 g, 68 %).

IR (KBr): 3446, 1633, 1460, 1165, 989, 613 cm^{-1}.

Elemental Analysis ($C_{15}H_{25}Cl_2CoN_5$) C, H, N: Calcd 44.46, 6.22, 17.28. Found: 44.33, 6.21, 17.30.

UV-Visible spectra of catalyst **3** recorded in acetonitrile show absorption centered at 615 and 687 nm.

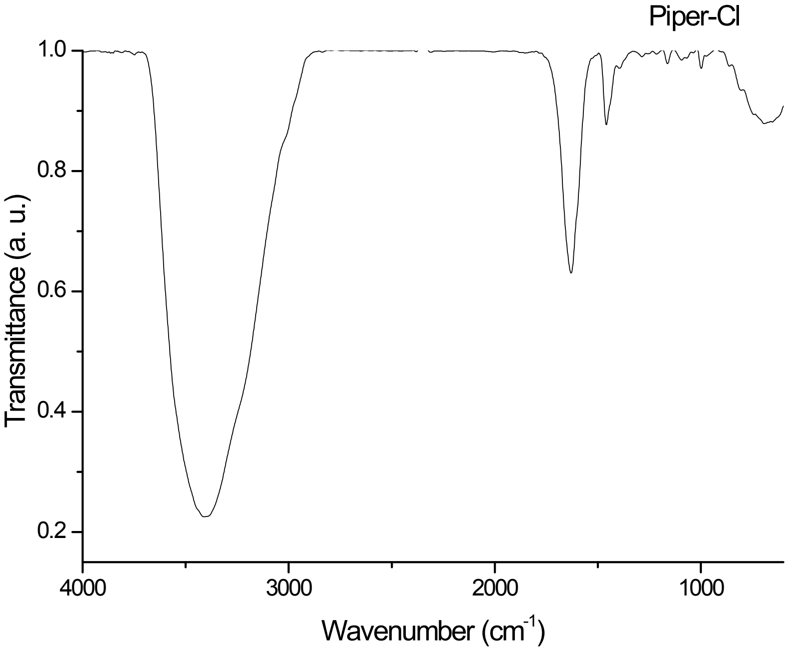


Figure S5. IR spectrum of **3**

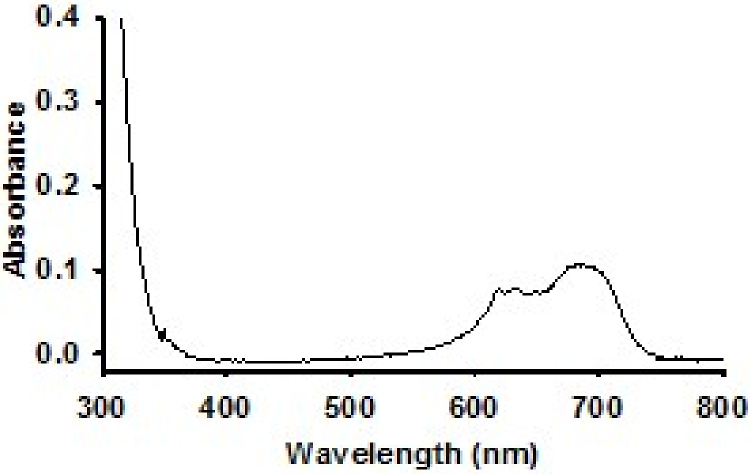
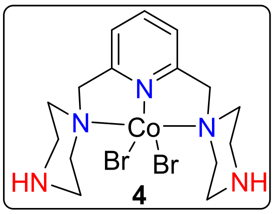


Figure S6. UV spectrum of **3**.

Crystallization procedure (3): The catalyst **3** (0.02 g, 0.048 mmol) was suspended in dry CH_3CN (5 mL), to this solution $NaBF_4$ (0.012 g, 0.11 mmol) was added followed by the reaction mixture was stirred for half an hour at RT; the resulting mixer was filtered. The compound was crystallized with diethyl ether diffusion into filtrate at room temperature. After 4 days blue color needle crystal was formed. The crystals were suitable for single crystal X-ray crystallography.

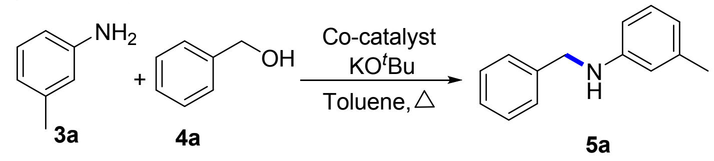


4

Synthesis of complex 4 (NNN^{pip}-$CoBr_2$): A solution of $CoBr_2$ (0.04 g, 0.18 mmol) in MeOH (2 mL) was added drop wise to a stirred solution of Py-NNN^{pip} (0.05 g, 0.18 mmol) in MeOH (3 mL). This reaction mixture stirred at room temperature for 3-4 h. Then the solvent was evaporated in vacuum under reduced pressure afforded blue powder as product, yield (0.079 g, 90 %).

2.2 Optimization conditions

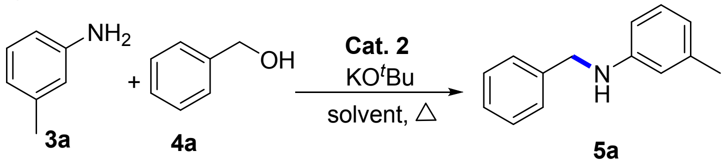
Table S1: Screening of catalyst[a]



Entry	Catalyst	Yield (%)[b]
1	Cat. 1	32
2	**Cat. 2**	**56**
3	Cat. 3	51
4	$CoBr_2$	12
5	$CoBr_2$/Py-N^3 (L_1)	24
6	-	4

[a]Reactions were performed using *m*-toluidine **3a** (0.25 mmol), benzyl alcohol **4a** (0.275 mmol), catalyst (2.5 mol%), KO*t*Bu (1.1 equiv.) using 1 mL of toluene as solvent at 130 °C. [b]Yield determined by GC using 1,4-dibromo butane as an internal standard.

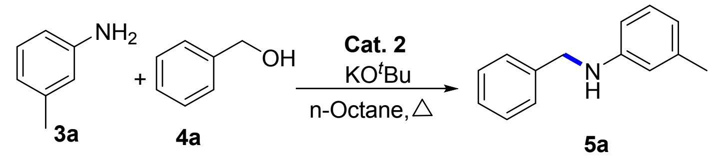
Table S2: Screening of solvent[a]



Entry	Solvent	Yield (%)[b]
1	Xylene	48
2	Mesitylene	33
3	DMF	Trace
4	THF	49
5	MeCN	NR
6	**n-Octane**	**72**
7	1,2 DCE	NR
8	1,4 Dioxane	58

*a*Reactions were performed using *m*-toluidine **3a** (0.25 mmol), benzyl alcohol **4a** (0.275 mmol), catalyst **2** (2.5 mol%), KO*t*Bu (1.1 equiv.) using 1 mL of solvent at 130 °C. *b*Yield determined by GC using 1,4-dibromo butane as an internal standard. NR = No reaction.

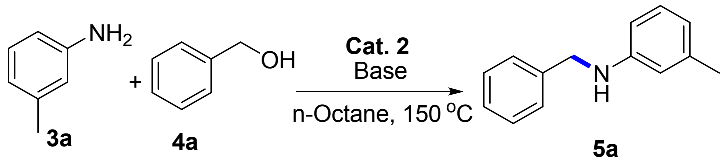
Table S3: Screening of temperature*a*



Entry	Temperature (°C)	Yield (%)^b
1	RT	NR
2	60 °C	NR
3	80 °C	8
4	100 °C	37
5	120 °C	66
6	**150 °C**	**84**

*a*Reactions were performed using *m*-toluidine **3a** (0.25 mmol), benzyl alcohol **4a** (0.275 mmol), catalyst **2** (2.5 mol%), KO*t*Bu (1.1 equiv.) using 1 mL of n-Octane at different temperature. *b*Yield determined by GC using 1,4-dibromo butane as an internal standard. NR = No reaction.

Table S4: Screening of base*a*

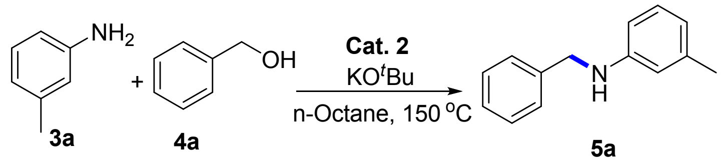


Entry	Base	Yield (%)^b
1	NaO*t*Bu	27
2	LiO*t*Bu	NR
3	KOH	68

4	NaOAc	4
5	KOAc	6
6	KO^{i}Pr	71
7	-	NR

[a]Reactions were performed using *m*-toluidine **3a** (0.25 mmol), benzyl alcohol **4a** (0.275mmol), catalyst **2** (2.5 mol%), Base (1.1 equiv.) using 1 mL of n-Octane at 150 °C. [b]Yield determined by GC using 1,4-dibromo butane as an internal standard. NR = No reaction.

Table S5: Screening of catalyst amount[a]



Entry	Catalyst **1** (mol%)	Yield (%)^b
1	1 mol%	63
2	2 mol%	78
3	3 mol%	89
4	**5 mol%**	**93**

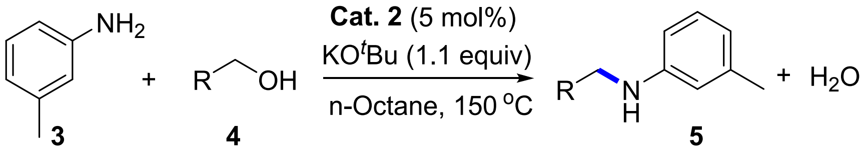
[a]Reactions were performed using amide **3a** (0.25 mmol), benzyl alcohol **4a** (0.275 mmol), catalyst **2** (mol%), KO^{t}Bu (1.1 equiv.) using 1 mL of n-Octane at 150 °C. [b]Yield determined by GC using 1,4-dibromo butane as an internal standard.

2.2.1 Homogenous test:

To an oven-dried 15 mL ace pressure tube, amine **3a** (0.25 mmol), alcohol **4a** (0.275 mmol), Co-complex **2** (5 mol%), 10 equiv. of mercury, and n-Octane (2 mL) were added under a gentle stream of argon. The mixture was of heated at reflux for 32 h followed by cooling to room temperature and 82% GC yield of the product **5a** observed.

2.3 Synthesis and characterization of alkylated amine derivatives

2.3.1 Alkylation of *m*-toluidine with various alcohols



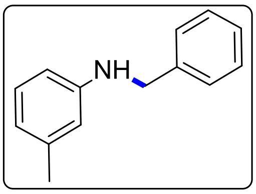
Scheme S2. Synthesis of alkylated *m*-toluidine (**5a-i**).

General procedure:

To an oven-dried 15 mL ace pressure tube, *m*-toluidine **3** (0.5 mmol), primary alcohol **4** (0.55 mmol), Co-complex **2** (5 mol%) and KO^{t}Bu (1.1 equiv.) in n-octane (1 mL) were added under a gentle stream of argon. The mixture was of heated at 150 °C for 32 h followed by cooling to room temperature. The reaction mixture was diluted with water (4 mL) and extracted with dichloromethane (3 x 5 mL). The resultant organic layer was dried over anhydrous Na_2SO_4 and the solvent was evaporated under reduced pressure. The crude mixture was purified by silica gel column chromatography (230-400 mesh size) using petroleum-ether/ethyl acetate as an eluting system.

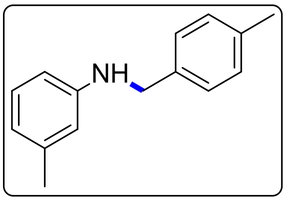
2.3.2 Characterization alkylated amine derivatives

***N*-benzyl-3-methylaniline (5a)**



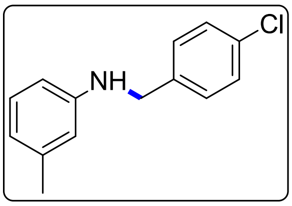
Colorless liquid. Yield: 90%. **^{1}H NMR** (200 MHz, CHLOROFORM-d) δ = 7.35 - 7.28 (m, 5H), 7.05 (t, *J* = 7.6Hz, 1H), 6.52 (d, *J* = 7.3Hz, 1H), 6.45 - 6.41 (m, 2H), 4.29 (s, 2H), 3.93 (s, br, 1H), 2.26 (s, 3H). **^{13}C NMR** (50 MHz, CHLOROFORM-d) δ = 148.17, 139.51, 138.98, 129.10, 128.56, 127.48, 127.14, 118.49, 113.60, 109.93, 48.31, 21.58.

3-methyl-*N*-(4-methylbenzyl)aniline (5b)



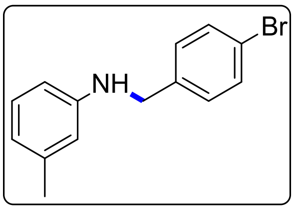
Colorless liquid. Yield: 92%. **^{1}H NMR** (500 MHz, CHLOROFORM-d) δ 7.28 (d, *J* = 8Hz, 2H), 7.17 (d, *J* = 8Hz, 2H), 7.08 (t, *J* = 8Hz, 1H), 6.56 (d, *J* = 7Hz, 1H), 6.50 - 6.44 (m, 2H), 4.29 (s, 2H), 3.93 (s, br, 1H), 2.36 (s, 3H), 2.29 (s, 3H). **^{13}C NMR** (126 MHz, CHLOROFORM-d) δ 148.27, 139.01, 136.82, 136.43, 129.26, 129.11, 127.52, 118.42, 113.57, 109.90, 48.08, 21.62, 21.09.

***N*-(4-chlorobenzyl)-3-methylaniline (5c)**



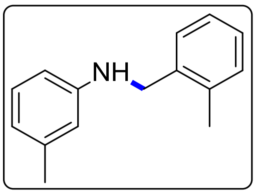
Colorless liquid. Yield: 77%. **^{1}H NMR** (200 MHz, CHLOROFORM-d) δ 7.31 (m, 4H), 7.07 (t, *J* = 8Hz, 1H), 6.57 (d, *J* = 7Hz, 1H), 6.49 - 6.36 (m, 2H), 4.31 (s, 2H), 4.01 (s, br, 1H), 2.28 (s, 3H). **^{13}C NMR** (50 MHz, CHLOROFORM-d) δ 147.88, 139.10, 138.10, 132.83, 129.17, 128.69, 118.77, 113.68, 109.98, 47.64, 21.60.

***N*-(4-bromobenzyl)-3-methylaniline (5d)**



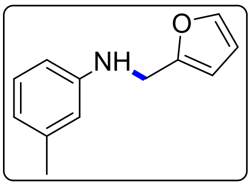
Colorless liquid. Yield: 65%. **^{1}H NMR** (200 MHz, CHLOROFORM-d) δ 7.54 - 7.42 (m, 2H), 7.29 (m, 2H), 7.11 - 7.01 (m, 1H), 6.66 - 6.51 (m, 1H), 6.50 - 6.37 (m, 2H), 4.30 (s, 1H), 4.01 (s, br, 1H), 2.27 (s, 3H). **^{13}C NMR** (50 MHz, CHLOROFORM-d) δ 147.86, 139.11, 138.66, 131.67, 129.17, 129.05, 118.80, 113.69, 110.00, 47.69, 21.60.

3-methyl-*N*-(2-methylbenzyl)aniline (5e)



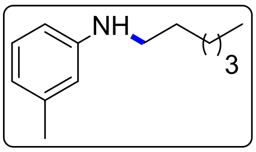
Colorless liquid. Yield: 47%. **^{1}H NMR** (200 MHz, CHLOROFORM-d) δ 7.43 - 7.35 (m, 1H), 7.31 - 7.23 (m, 3H), 7.20 - 7.09 (m, 1H), 6.66 - 6.48 (m, 3H), 4.32 (s, 2H), 3.84 (s, br, 1H), 2.44 (s, 3H), 2.35 (s, 3H). **^{13}C NMR** (50 MHz, CHLOROFORM-d) δ 148.36, 139.05, 137.11, 136.36, 130.37, 129.14, 128.31, 127.38, 126.13, 118.41, 113.43, 109.81, 46.42, 21.61, 18.89.

***N*-(furan-2-ylmethyl)-3-methylaniline (5f)**



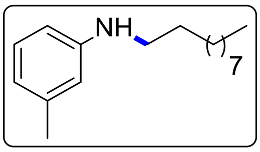
Colorless liquid. Yield: 63%. **^{1}H NMR** (500 MHz, CHLOROFORM-d) δ 7.38 (dd, $J = 2$, 1Hz, 1H), 7.18 - 7.05 (m, 1H), 6.58 (d, $J = 8$Hz, 1H), 6.53 - 6.46 (m, 2H), 6.33 (dd, $J = 3$, 2 Hz, 1H), 6.28 - 6.20 (m, 1H), 4.32 (s, 2H), 3.99 (s, br, 1H), 2.29 (s, 3H). **^{13}C NMR** (126 MHz, CHLOROFORM-d) δ 152.80, 147.65, 141.88, 139.01, 129.08, 118.96, 113.96, 110.31, 110.24, 106.91, 41.46, 21.61.

***N*-hexyl-3-methylaniline (5g)**



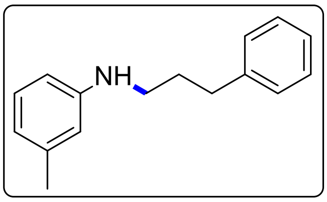
Colorless liquid. Yield: 69%. **^{1}H NMR** (500 MHz, CHLOROFORM-d) δ 7.09 (t, $J = 8$Hz, 1H), 6.55 (d, $J = 7$Hz, 1H), 6.50 - 6.43 (m, 2H), 3.62 (s, br, 1H), 3.12 (t, $J = 7$Hz, 2H), 2.31 (s, 3H), 1.59 - 1.70 (m, 2H), 1.39 - 1.48 (m, 2H), 1.26 - 1.39 (m, 4H), 0.87 - 0.98 (m, 3H). **^{13}C NMR** (126 MHz, CHLOROFORM-d) δ 148.51, 138.95, 129.05, 118.03, 113.46, 109.87, 44.03, 31.63, 29.54, 26.84, 22.61, 21.61, 14.03.

***N*-decyl-3-methylaniline (5h)**



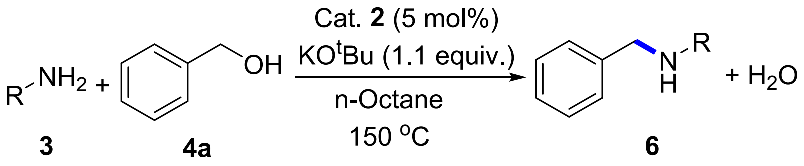
Colorless liquid. Yield: 71%. ^{1}**H NMR** (200 MHz, CHLOROFORM-d) δ 6.99 - 7.14 (m, 1H), 6.51 (d, *J* = 7Hz, 1H), 6.45 - 6.37 (m, 2H), 3.50 (s, br, 1H), 3.09 (t, *J* = 7Hz, 2H), 2.27 (s, 3H), 1.64 - 1.54 (m, 2H), 1.38 - 1.25 (m, 14H), 0.85 - 0.93 (m, 3H). ^{13}**C NMR** (50 MHz, CHLOROFORM-d) δ 148.60, 138.95, 129.07, 118.01, 113.46, 109.87, 44.02, 31.89, 29.61, 29.56, 29.44, 29.31, 27.18, 22.67, 21.61, 14.09.

3-methyl-*N*-(3-phenylpropyl)aniline (5i)



Colorless liquid. Yield: 40%. ^{1}**H NMR** (500 MHz, CHLOROFORM-d) δ 7.29 - 7.36 (m, 16 H), 7.26 - 7.22 (m, 3H), 7.11 - 7.07 (m, 3H), 6.55 (d, *J* = 7Hz, 1H), 6.46 - 6.38 (m, 2H), 3.17 (t, *J* = 7Hz, 2H), 2.77 (t, *J* = 8Hz, 2H), 2.30 (s, 3H), 2.02 - 1.95 (m, 2H). ^{13}**C NMR** (126 MHz, CHLOROFORM-d) δ 148.31, 141.67, 138.98, 129.42, 129.08, 128.40, 128.29, 128.04, 125.92, 118.18, 113.51, 109.94, 43.41, 33.36, 31.07, 21.61.

2.3.3 Alkylation of various anilines with benzyl alcohols



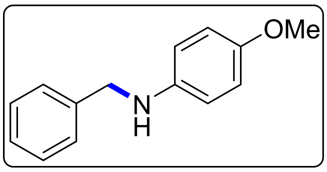
Scheme S3. Synthesis of alkylated amine derivatives of benzyl alcohol (**6a-k**)

General procedure:

To an oven-dried 15 mL ace pressure tube, amine **3** (0.5 mmol), benzyl alcohol **4** (0.55 mmol), Co-complex **2** (5 mol%) and KO^{t}Bu (1.1 equiv.) in n-octane (1 mL) were added under a gentle stream of argon. The mixture was of heated at 150 °C for 32 h followed by cooling to room temperature. The reaction mixture was diluted with water (4 mL) and extracted with dichloromethane (3 x 5 mL). The resultant organic layer was dried over anhydrous Na_2SO_4 and the solvent was evaporated under reduced pressure. The crude mixture was purified by silica gel column chromatography (230-400 mesh size) using petroleum-ether/ethyl acetate as an eluting system.

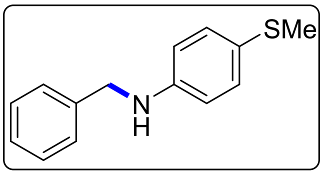
2.3.4 Characterization of benzylated amine products

***N*-benzyl-4-methoxyaniline (6a)**



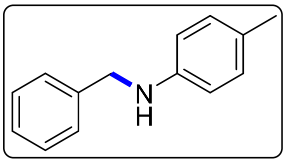
Colorless oil. Yield: 80%. ^{1}**H NMR** (500 MHz, CHLOROFORM-d) δ = 7.44 - 7. 32 (m, 4H), 7.29 (d, *J* = 7Hz, 1H), 6. 85 - 6.74 (m, 2H), 6.66 - 6.58 (m, 2H), 4.30 (s, 2H), 3.76 (s, 3H). ^{13}**C NMR** (126 MHz, CHLOROFORM-d) δ = 152.19, 142.44, 139.67, 128.57, 127.53, 127.15, 114.90, 114.09, 55.80, 49.24.

***N*-benzyl-4-(methylthio)aniline (6b)**



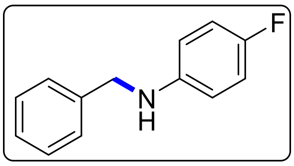
Colorless oil. Yield: 74%. ^{1}**H NMR** (200 MHz, CHLOROFORM-d) δ = 7.42 - 7.33 (m, 5H), 7.22 (d, *J* = 9Hz, 2H), 6.67 - 6.53 (m, 2H), 4.34 (s, 2H), 4.09 (s, br, 1H), 2.42 (s, 3H). ^{13}**C NMR** (50 MHz, CHLOROFORM-d) δ = 146.97, 131.48, 128.66, 127.43, 127.30, 113.45, 48.30, 19.12.

N-benzyl-4-methylaniline (6c)



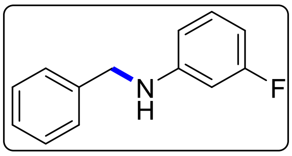
Colorless oil. Yield: 76%. **^{1}H NMR** (200 MHz, CHLOROFORM-d) δ = 7.37 - 7.29 (m, 5H), 7.00 - 6.92 (m, 2H), 6.54 (d, *J* = 9Hz, 2H), 4.27 (s, 2H), 3.86 (s, br, 1H), 2.22 (s, 3H). **^{13}C NMR** (50 MHz, CHLOROFORM-d) δ = 145.87, 139.62, 129.67, 128.52, 128.20, 127.42, 127.07, 112.93, 48.55, 20.33.

N-benzyl-4-fluoroaniline (6d)



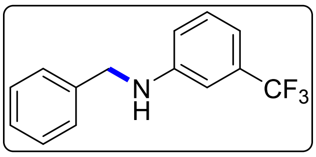
Colorless oil. Yield: 86%. **^{1}H NMR** (200 MHz, CHLOROFORM-d) δ = 7.42 - 7.27 (m, 5H), 6.88 (t, *J* = 9Hz, 2H), 6.56 (dd, *J* = 9, 4Hz, 2H), 4.29 (s, 2H), 3.95 (s, br, 1H). **^{13}C NMR** (50 MHz, CHLOROFORM-d) δ = 144.44, 139.21, 128.66, 127.48, 127.30, 115.87, 115.43, 113.72, 113.58, 48.95.

N-benzyl-3-fluoroaniline (6e)



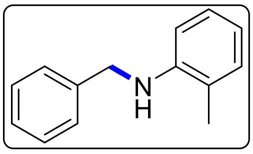
Colorless oil. Yield: 83%. **^{1}H NMR** (200 MHz, CHLOROFORM-d) δ = 7.47 - 7.28 (m, 5H), 7.19 - 7.02 (m, 1H), 6.51 - 6.28 (m, 3H), 4.33 (s, 2H), 4.19 (s, br, 1H). **^{13}C NMR** (50 MHz, CHLOROFORM-d) δ = 166.52, 161.70, 149.98, 149.77, 138.80, 130.37, 130.17, 128.71, 127.44, 127.40, 108.72, 108.67, 104.16, 103.73, 99.76, 99.26, 48.18.

N-benzyl-3-(trifluoromethyl)aniline (6f)



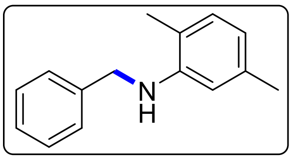
Colorless oil. Yield: 88%. **^{1}H NMR** (200 MHz, CHLOROFORM-d) δ = 7.41 - 7.24 (m, 5H), 7.24 - 7.12 (m, 1H), 6.99 - 6.84 (m, 1H), 6.84 - 6.75 (m, 1H), 6.75 - 6.65 (m, 1H), 4.29 (s, 2H), 4.15 (s, br, 1H). **^{13}C NMR** (50 MHz, CHLOROFORM-d) δ = 148.19, 138.55, 129.64, 128.74, 127.49, 115.66, 113.94, 113.86, 109.10, 109.02, 48.07.

***N*-benzyl-3-(trifluoromethyl)aniline (6g)**



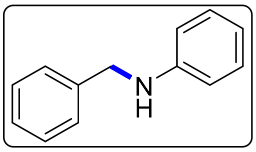
Colorless oil. Yield: 57%. **^{1}H NMR** (500 MHz, CHLOROFORM-d) δ = 7.42 - 7.34 (m, 4H), 7.34 - 7.28 (m, 1H), 7.14 - 7.06 (m, 2H), 6.69 (t, *J* = 7Hz, 1H), 6.63 (d, *J* = 8Hz, 1H), 4.39 (s, 2H), 3.89 (s, br, 1H), 2.18 (s, 3H). **^{13}C NMR** (126 MHz, CHLOROFORM-d) δ = 139.47, 130.06, 128.65, 127.54, 127.25, 127.14, 117.18, 109.97, 48.32, 17.54.

***N*-benzyl-2,5-dimethylaniline (6h)**



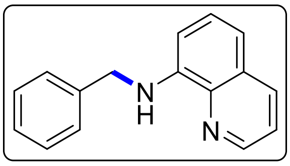
Colorless oil. Yield: 62%. **^{1}H NMR** (200 MHz, CHLOROFORM-d) δ = 7.47 - 7.31 (m, 5H), 6.99 (d, *J* = 7Hz, 1H), 6.58 - 6.45 (m, 2H), 4.38 (s, 2H), 3.80 (s, br, 1H), 2.29 (s, 3H), 2.15 (s, 3H). **^{13}C NMR** (50 MHz, CHLOROFORM-d) δ = 145.98, 139.58, 136.77, 129.91, 128.64, 127.62, 127.23, 118.94, 117.81, 110.83, 48.37, 21.53, 17.08.

***N*-benzylaniline (6i)**



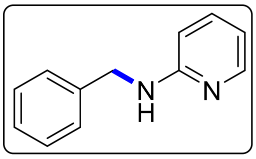
Colorless oil. Yield: 88%. **^{1}H NMR** (200 MHz, CHLOROFORM-d) δ = 7.42 - 7.24 (m, 5H), 7.21 - 7.10 (m, 2H), 6.73 (dt, *J* = 7, 1Hz, 1H), 6.67 - 6.57 (m, 2H), 4.32 (s, 2H), 4.01 (s, br, 1H). **^{13}C NMR** (50 MHz, CHLOROFORM-d) δ = 148.12, 139.41, 129.23, 128.60, 127.48, 127.19, 117.53, 112.81, 48.29.

N-benzylquinolin-8-amine (6j)



Colorless oil. Yield: 52%. ^{1}**H NMR** (500 MHz, CHLOROFORM-d) δ = 8.80 - 8.71 (m, 1H), 8.12 - 8.05 (m, 1H), 7.48 (d, *J* = 8Hz, 2H), 7.43 - 7.27 (m, 5H), 7.14 - 7.07 (m, 1H), 6.72 - 6.55 (m, 2H), 4.60 (s, 2H). ^{13}**C NMR** (126 MHz, CHLOROFORM-d) δ = 146.90, 144.53, 139.19, 138.18, 136.00, 128.59, 127.73, 127.38, 127.10, 121.39, 114.11, 105.09, 47.66.

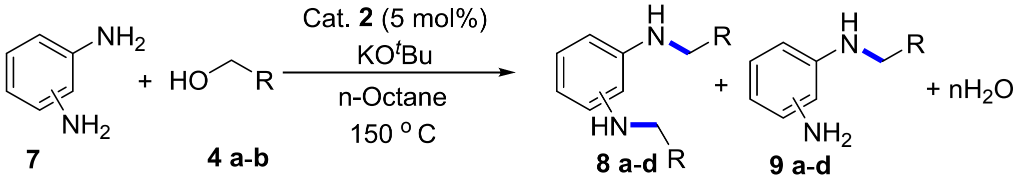
N-benzylpyridin-2-amine (6k)



Colorless oil. Yield: 63%. ^{1}**H NMR** (500 MHz, CHLOROFORM-d) δ = 8.15 - 8.01 (m, 1H), 7.42 - 7.18 (m, 6H), 6.62 - 6.52 (m, 1H), 6.40 - 6.31 (m, 1H), 4.93 (s, br, 1H), 4.50 (s, 3H). ^{13}**C NMR** (126 MHz, CHLOROFORM-d) δ = 158.62, 148.19, 139.15, 137.43, 128.61, 127.37, 127.20, 113.13, 106.76, 46.29.

2.4 Synthesis and characterization of alkylated phenylenediamines

2.4.1 Synthesis of alkylated phenylenediamine



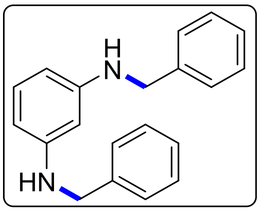
Scheme S4. Synthesis of mono- and bis- alkylated phenylenediamine

General procedure:

To an oven-dried 15 mL ace pressure tube, phenylenediamine **7** (0.5 mmol), primary alcohol **4** (1 mmol and 2 mmol respectively), Co-complex **2** (5 mol%) and KO^{t}Bu (1.1 equiv. and 2.2 equiv. respectively) in n-octane (1 mL) were added under a gentle stream of argon. The mixture was of heated at 150 °C for 32 h followed by cooling to room temperature. The reaction mixture was diluted with water (4 mL) and extracted with dichloromethane (3 x 5 mL). The resultant organic layer was dried over anhydrous Na_2SO_4 and the solvent was evaporated under reduced pressure. The crude mixture was purified by silica gel column chromatography (230-400 mesh size) using petroleum-ether/ethyl acetate as an eluting system.

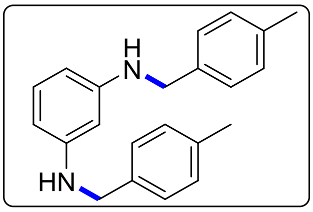
2.4.2 Characterization alkylated phenylenediamine derivatives

***N¹, N³*-dibenzylbenzene-1, 3-diamine (8a)**



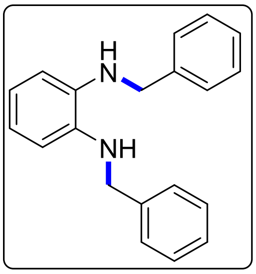
Light brown liquid. Yield: 49% and 62% respectively. **^{1}H NMR** (500 MHz, CHLOROFORM-d) δ = 7.40 - 7.32 (m, 7H), 7.31 - 7.29 (m, 3H), 7.01 (t, *J* = 8Hz, 1H), 6.10 (dd, *J* = 8, 2Hz, 2H), 5.98 (s, 1H), 4.30 (s, 4H). **^{13}C NMR** (126 MHz, CHLOROFORM-d) δ = 149.12, 139.40, 130.02, 128.57, 127.57, 127.16, 103.34, 48.45.

***N¹, N³*-bis(4-methylbenzyl)benzene-1, 3-diamine (8b)**



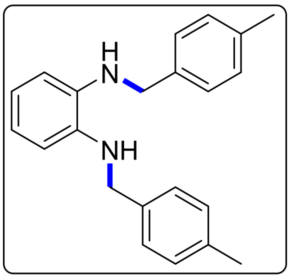
Light brown liquid. Yield: 42% and 50% respectively. **^{1}H NMR** (200 MHz, CHLOROFORM-d) δ = 7.31 - 7.23 (m, 4H), 7.20 - 7.10 (m, 4H), 6.99 (t, *J* = 8Hz, 1H), 6.06 (dd, *J* = 8, 2Hz, 2H), 5.94 (s, 1H), 4.24 (s, 4H), 3.91 (s, br, 2H), 2.35 (s, 6H). **^{13}C NMR** (50 MHz, CHLOROFORM-d) δ = 149.37, 136.74, 136.52, 129.98, 129.23, 127.54, 103.05, 97.27, 48.13, 21.08.

N¹,*N²*-dibenzylbenzene-1,2-diamine (8c)



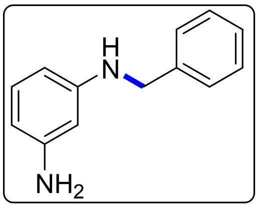
Light brown liquid. Yield: 31% and 53% respectively. **^{1}H NMR** (200 MHz, CHLOROFORM-d) δ = 7.38 - 7.29 (m, 10H), 6.86 - 6.64 (m, 4H), 4.30 (s, 4H), 3.49 (s, br, 2H). **^{13}C NMR** (50 MHz, CHLOROFORM-d) δ = 139.40, 137.12, 128.55, 128.21, 127.78, 127.20, 119.41, 112.00, 48.77.

N¹,*N²*-bis(4-methylbenzyl)benzene-1,2-diamine (8d)



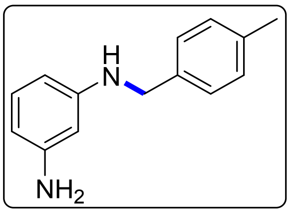
Light brown liquid. Yield: 25% and 48% respectively. **^{1}H NMR** (200 MHz, CHLOROFORM-d) δ = 7.32 - 7.26 (m, 4H), 7.20 - 7.14 (m, 4H), 6.89 - 6.64 (m, 4H), 4.27 (s, 4H), 3.53 (s, br, 2H), 2.36 (s, 6H). **^{13}C NMR** (50 MHz, CHLOROFORM-d) δ = 137.15, 136.81, 136.34, 129.22, 128.39, 127.79, 119.30, 111.84, 48.51, 21.06.

N¹-benzylbenzene-1,3-diamine (9a)



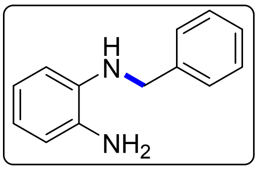
Light brown liquid. Yield: 25% and 29% respectively. **^{1}H NMR** (200 MHz, CHLOROFORM-d) δ = 7.43 - 7.26 (m, 5H), 6.98 (t, *J* = 8Hz, 1H), 6.15 - 6.05 (m, 2H), 6.05-5.93 (m, 1H), 4.31 (s, 2H), 3.70 (s, br, 3H). **^{13}C NMR** (50 MHz, CHLOROFORM-d) δ = 149.35, 147.50, 139.56, 130.08, 128.58, 127.46, 127.14, 105.05, 104.04, 99.45, 48.25.

N^1-(4-methylbenzyl)benzene-1,3-diamine (9b)



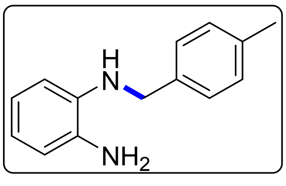
Light brown liquid. Yield: 10% and 15% respectively. **^{1}H NMR** (200 MHz, CHLOROFORM-d) δ = 7.29 - 7.20 (m, 2H), 7.20 - 7.08 (m, 2H), 6.95 (t, J = 8Hz, 1H), 6.13 - 6.02 (m, 2H), 5.02 - 6.92 (m, 1H), 4.23 (s, 2H), 3.46 (s, br, 3H), 2.33 (s, 3H). **^{13}C NMR** (50 MHz, CHLOROFORM-d) δ = 149.39, 147.45, 136.76, 136.45, 130.05, 129.23, 127.46, 105.00, 104.05, 99.46, 48.01, 21.05.

N^1-benzylbenzene-1,2-diamine (9c)



Light brown liquid. Yield: 43% and 13% respectively. **^{1}H NMR** (500 MHz, CHLOROFORM-d) δ = 7.47 - 7.28 (m, 5H), 6.87 - 6.79 (m, 1H), 6.79 - 6.66 (m, 3H), 4.34 (s, 2H), 3.38 (s, br, 3H). **^{13}C NMR** (126 MHz, CHLOROFORM-d) δ = 139.37, 137.70, 134.13, 128.59, 127.78, 127.25, 120.72, 118.79, 116.50, 111.94, 48.62.

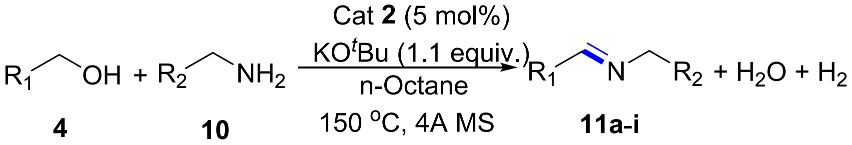
N^1-(4-methylbenzyl)benzene-1,2-diamine (9d)



Light brown liquid. Yield: 38% and 12% respectively. **^{1}H NMR** (200 MHz, CHLOROFORM-d) δ = 7.33 - 7.20 (m, 2H), 7.19 - 7.10 (m, 2H), 6.84 - 6.75 (m, 1H), 6.74 - 6.63 (m, 3H), 4.25 (s, 2H), 3.38 (s, br, 3H), 2.34 (s, 3H). **^{13}C NMR** (50 MHz, CHLOROFORM-d) δ = 137.74, 136.84, 136.33, 134.12, 129.23, 127.75, 127.05, 120.67, 118.72, 116.44, 111.94, 77.63, 76.36, 48.36, 21.07.

2.5 Synthesis and characterization of dehydrogenative coupling product of various amines with alcohols

2.5.1 Synthesis of alkylated imine derivatives



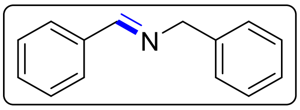
Scheme S5. Synthesis of dehydrogenative coupling product of various amines with alcohols

General procedure:

To an oven-dried 15 mL ace pressure tube, primary amine **10** (0.5 mmol), primary alcohol **4** (0.55 mmol), Co-complex **2** (5 mol%) and KO^{t}Bu (1.1 equiv.) in n-octane (1 mL) were added under a gentle stream of argon. The mixture was of heated at 150 °C for 32 h with 4Å MS followed by cooling to room temperature. The reaction mixture was diluted with dichloromethane (5 mL) and the solvent was evaporated under reduced pressure. The crude mixture was purified by basic alumina (Al_2O_3) column chromatography (activity I-II according to Brockmann) using petroleum-ether/ethyl acetate as an eluting system.

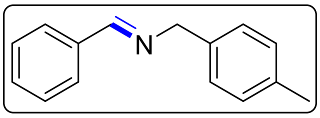
2.5.2 Characterization alkylated imine derivatives

***(E)*-*N*-benzyl-1-phenylmethanimine (11a)**



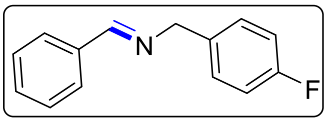
Light yellow liquid. Yield: 84%. **^{1}H NMR** (200 MHz, CHLOROFORM-d) δ = 8.37 (s, 1H), 7.83 - 7.68 (m, 2H), 7.46 - 7.36 (m, 3H), 7.36 - 7.14 (m, 5H), 4.80 (s, 2H). **^{13}C NMR** (50 MHz, CHLOROFORM-d) δ = 161.97, 139.25, 136.12, 130.74, 128.57, 128.46, 128.24, 127.94, 126.95, 65.02.

***(E)*-*N*-(4-methylbenzyl)-1-phenylmethanimine (11b)**



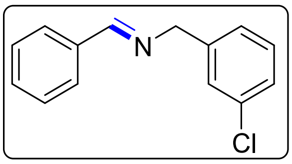
Light yellow liquid. Yield: 80%. ^{1}**H NMR** (200 MHz, CHLOROFORM-d) δ = 8.33 (s, 1H), 7.66 (d, *J* = 8Hz, 2H), 7.44 - 7.30 (m, 1H), 7.27 - 7.06 (m, 6H), 4.76 (s, 2H), 2.37 (s, 3H). ^{13}**C NMR** (50 MHz, CHLOROFORM-d) δ = 161.65, 140.92, 136.46, 136.31, 133.58, 129.26, 129.11, 128.53, 128.42, 128.20, 127.91, 64.76, 21.47.

***(E)*-*N*-(4-fluorobenzyl)-1-phenylmethanimine (11c)**



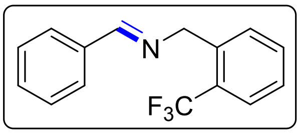
Light yellow liquid. Yield: 77%. ^{1}**H NMR** (500 MHz, CHLOROFORM-d) δ = 8.43 (s, 1H), 7.81 (d, *J* = 8Hz, 2H), 7.50 - 7.43 (m, 3H), 7.38 - 7.34 (m, 4H), 4.86 (s, 2H). ^{13}**C NMR** (126 MHz, CHLOROFORM-d) δ = 161.99, 139.28, 136.15, 130.75, 129.88, 128.59, 128.48, 128.26, 127.97, 126.97, 65.04.

***(E)*-*N*-(3-chlorobenzyl)-1-phenylmethanimine (11d)**



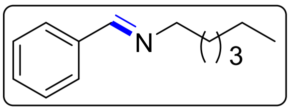
Light yellow liquid. Yield: 79%. ^{1}**H NMR** (200 MHz, CHLOROFORM-d) δ = 8.33 (t, *J* = 2Hz, 1H), 7.84 - 7.75 (m, 1H), 7.67 - 7.57 (m, 1H), 7.45 - 7.29 (m, 4H), 7.27 - 7.18 (m, 3H), 4.78 (s, 2H). ^{13}**C NMR** (50 MHz, CHLOROFORM-d) δ = 160.89, 141.00, 137.66, 134.84, 134.37, 130.88, 129.88, 129.76, 129.69, 128.63, 128.53, 128.30, 128.00, 127.94, 127.24, 127.09, 126.63, 126.01, 64.24.

***(E)*-1-phenyl-N-(2-(trifluoromethyl)benzyl)methanimine (11e)**



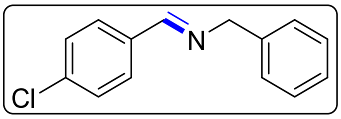
Light yellow liquid. Yield: 72%. ^{1}**H NMR** (200 MHz, CHLOROFORM-d) δ = 8.77 (s., 1H), 8.29 (d, *J* = 7Hz, 1H), 7.72 - 7.63 (m, 2H), 7.62 - 7.52 (m, 4H), 7.48 - 7.33 (m, 2H), 5.05 (s, 2H). ^{13}**C NMR** (50 MHz, CHLOROFORM-d) δ = 159.13, 132.01, 130.95, 130.32, 129.97, 129.74, 128.66, 128.39, 128.29, 127.18, 127.05, 126.79, 125.94, 125.82, 125.66, 125.54, 61.08.

(E)-N-hexyl-1-phenylmethanimine (11f)



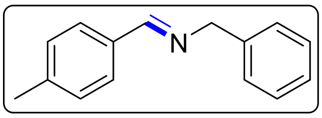
Light yellow liquid. Yield: 73%. ^{1}**H NMR** (200 MHz, CHLOROFORM-d) δ = 8.32 - 8.22 (m, 1H), 7.74 (dt, *J* = 4, 3Hz, 2H), 7.51 - 7.33 (m, 3H), 3.69 - 3.53 (m, 2H), 1.79 - 1.64 (m, 2H), 1.42 - 1.26 (m, 6H), 0.95 - 0.85 (m, 3H). ^{13}**C NMR** (50 MHz, CHLOROFORM-d) δ = 160.69, 136.34, 130.39, 128.53, 127.98, 77.63, 76.36, 61.81, 31.65, 30.87, 27.02, 22.60, 14.05.

(E)-N-benzyl-1-(4-chlorophenyl)methanimine (11g)



Light yellow liquid. Yield: 82%. ^{1}**H NMR** (200 MHz, CHLOROFORM-d) δ = 8.39 (d, *J* = 10Hz, 1H), 7.84 - 7.69 (m, 2H), 7.47 - 7.41 (m, 2H), 7.39 - 7.28 (m, 6H), 4.84 (s, 2H).

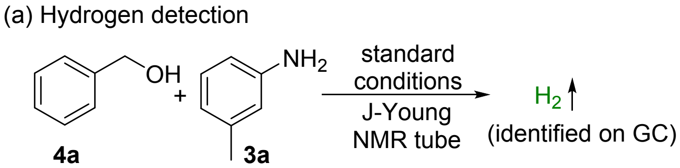
(E)-N-benzyl-1-(p-tolyl)methanimine (11h)



Light yellow liquid. Yield: 75%. ^{1}**H NMR** (200 MHz, CHLOROFORM-d) δ = 8.40 - 8.35 (m, 1H), 7.80 - 7.76 (m, 1H), 7.69 -7.65 (m, 1H), 7.43 - 7.39 (m, 2H), 7.37 – 7.31 (m, 3H), 7.24 - 7.16 (m, 2H), 4.85 - 4.79 (m, 2H), 2.37 -2.33 (m, 3H). ^{13}**C NMR** (50 MHz, CHLOROFORM-d) δ = 161.95, 161.90, 161.70, 139.24, 136.15, 130.72, 130.65, 129.28, 129.13, 128.55, 128.45, 128.23, 127.93, 126.94, 126.88, 64.99, 64.77, 21.47, 21.07.

3. Mechanistic studies

3.1.1 Hydrogen gas detection



Procedure: we have performed our standard reaction in a J-Young NMR tube under the optimal reaction conditions. After 4 hrs of reaction, we have analyzed the gas phase of reaction using gas chromatography and molecular hydrogen was identified.

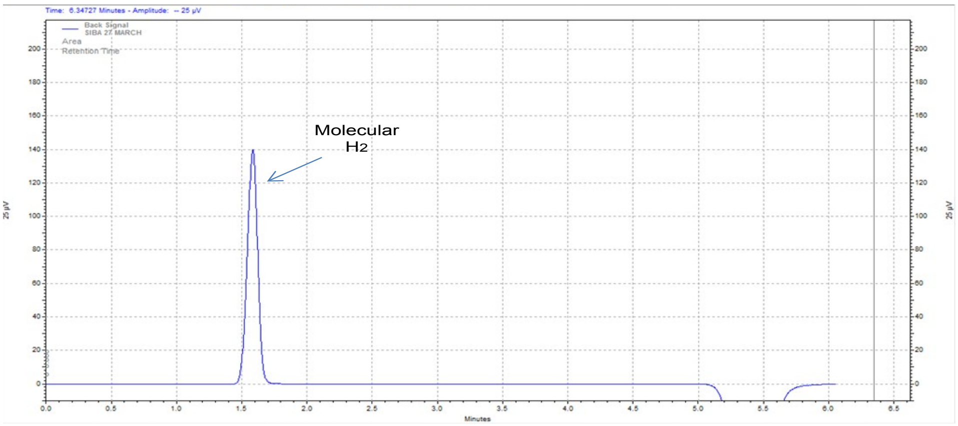
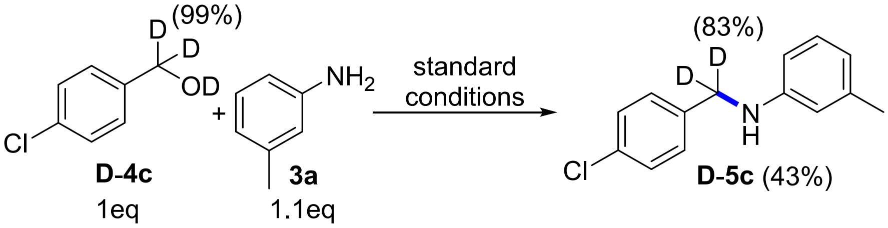


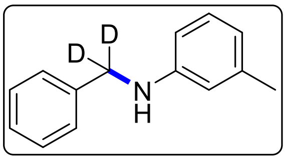
Figure S7. Gas phase GC for the identification of molecular hydrogen.

3.1.2 Deuterium labeling experiment



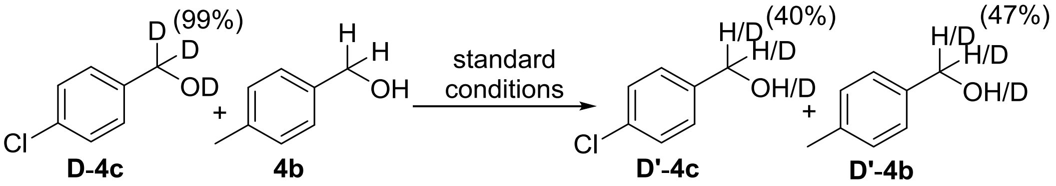
Procedure: To a 15 mL clean, oven-dried screw cap reaction tube, **D-4c** (0.275 mmol) and **3a** (0.25 mmol) was added under argon atmosphere. Then the reaction was performed under standard condition for 4 h at reduced temperature of 90 °C. After cooling to room temperature, the product was extracted with EtOAc (3 x 10 mL) and the combined organic layer was dried over anhydrous Na_2SO_4 and concentrated under vacuum. Then the crude product was purified through silica gel column chromatography (230-400 mesh size) by using petroleum-ether/ethyl acetate as an eluting system and yielded 43% of deuterated alkylated amine product (**D-5c**), supporting borrowing hydrogenative alkylation process.

3-methyl-*N*-(phenylmethyl-d_2)aniline (D-5c)



Colorless liquid. Yield 43%. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.45 - 7.36 (m, 1H), 7.36 - 7.30 (m, 3H), 7.15 - 7.04 (m, 1H), 6.60 (d, *J* = 8Hz, 1H), 6.55 - 6.40 (m, 2H), 4.32 (s, 0.34H), 4.02 (s, br, 1H), 2.31 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 147.90, 139.08, 139.02, 138.08, 138.02, 132.84, 130.87, 129.45, 129.16, 128.70, 128.60, 128.48, 127.53, 127.19, 118.75, 118.53, 113.69, 113.64, 109.99, 47.32 (very less intense), 21.59.

3.1.3 Reversibility test: alcohol to aldehyde step



To a 15 mL clean, oven-dried screw cap reaction tube, **D-4c** (0.2 mmol, 99%-D) and **4b** (0.2 mmol) was added under argon atmosphere. Then the reaction was performed under standard condition for 24 h. The yield of the product **D'-4c** and **D'-4b** calculated by isolation. The percentage of deuterium incorporation in the product was calculated by ^{1}H NMR analysis.

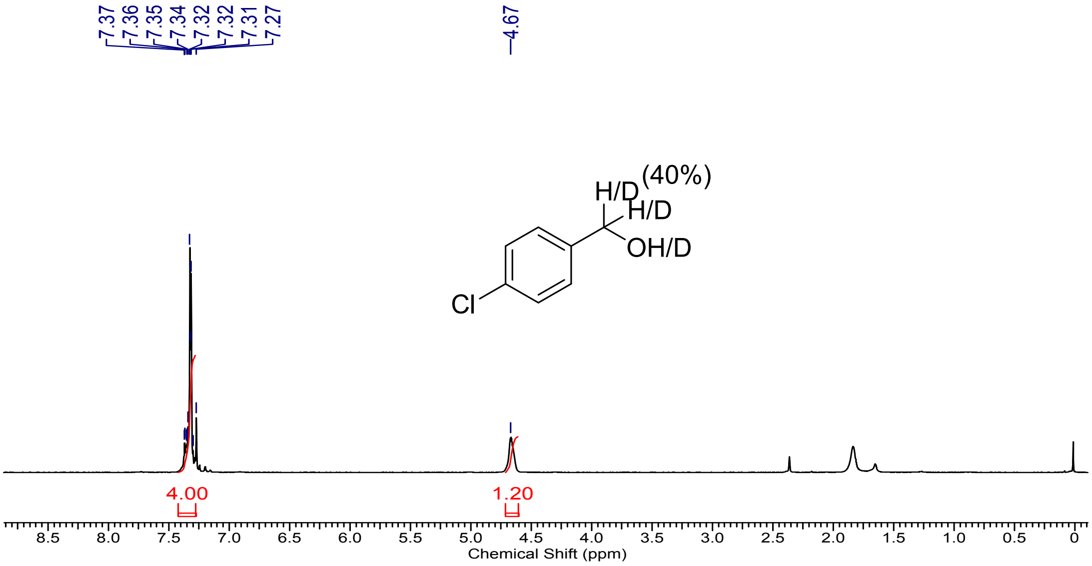


Figure S8. ^{1}H of **D'-4c**

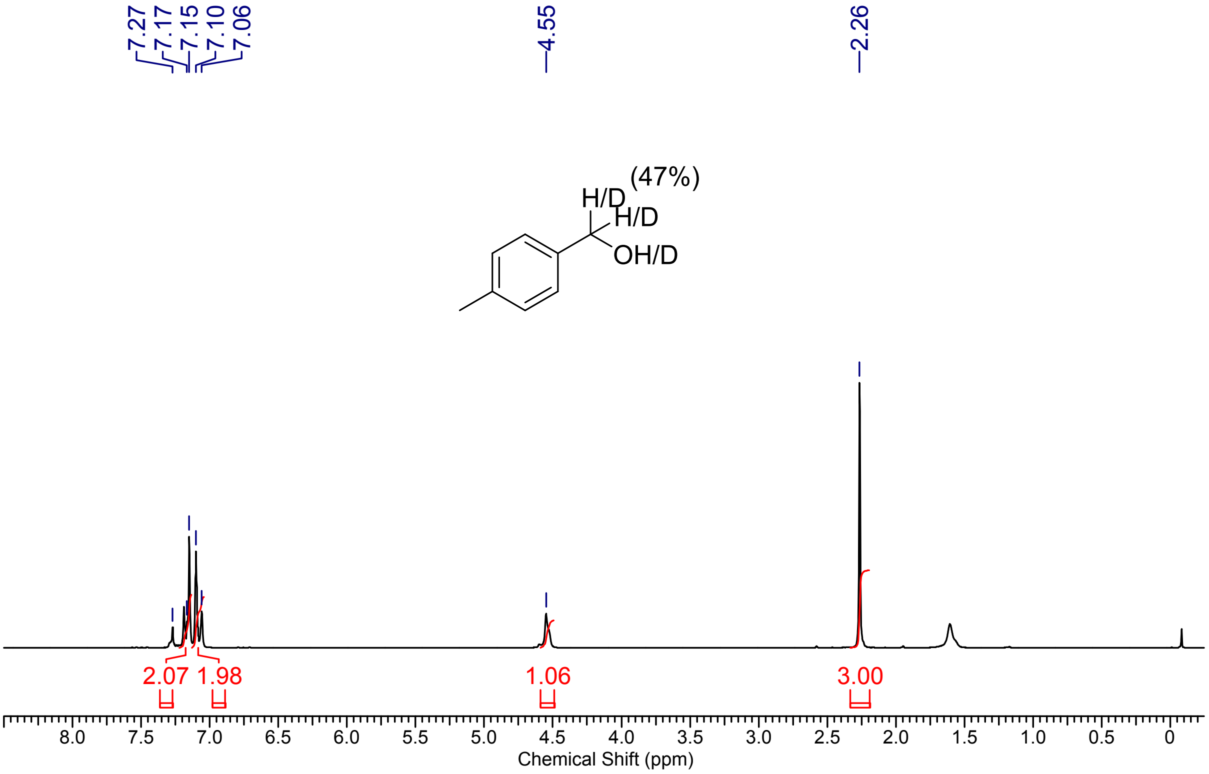


Figure S9. ^{1}H of **D'-4b**

5. X-ray Crystal Structure Determination of 1 and 3

Crystallographic data

Crystal structure determination of 1 (CCDC 1557308)

CoMorCl

Table S6 Crystal data and structure refinement for CoMorCl

Identification code	CoMorCl
Empirical formula	$C_{15}H_{23}Cl_2CoN_3O_2$
Formula weight	407.19
Temperature/K	473(2)
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	10.2125(9)
b/Å	13.9736(12)
c/Å	12.5470(10)
α/°	90
β/°	92.0530(10)
γ/°	90
Volume/Å^3	1789.4(3)
Z	4
ρ_{calc}mg/mm^3	1.511
m/mm^{-1}	1.269
F(000)	844
Crystal size/mm^3	0.420 × 0.320 × 0.270
Theta range for data collection	4.364 to 49.986°
Index ranges	$-12 \leq h \leq 12$, $-16 \leq k \leq 16$, $-14 \leq l \leq 14$
Reflections collected	16414
Independent reflections	3151[R(int) = 0.0336]
Data/restraints/parameters	3151/0/208
Goodness-of-fit on F^2	1.063
Final R indexes [I>2σ (I)]	$R_1 = 0.0297$, $wR_2 = 0.0623$
Final R indexes [all data]	$R_1 = 0.0355$, $wR_2 = 0.0648$
Largest diff. peak/hole / e Å^{-3}	0.230/-0.317

Table S7 Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for CoMorCl. U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{IJ} tensor.

Atom	***x***	***y***	***Z***	**U(eq)**
Co1	9108.2(3)	7924.2(2)	9059.7(2)	22.22(10)
Cl1	9319.0(5)	8055.7(4)	10852.0(4)	29.14(14)

Cl2	7912.8(6)	6643.1(4)	8509.1(5)	36.80(16)
O1	4983.5(15)	8895.2(12)	9164.2(13)	33.0(4)
O2	12656.8(15)	6282.8(12)	10436.1(13)	34.2(4)
N1	9946.3(16)	8660.9(12)	7871.4(14)	22.0(4)
N2	7724.5(16)	9229.8(12)	8814.7(14)	21.2(4)
N3	11140.8(16)	7077.9(12)	8671.5(14)	21.8(4)
C1	9576(2)	9568.0(15)	7688.0(18)	24.1(5)
C2	10023(2)	10071.6(17)	6826.5(19)	31.0(5)
C3	10869(2)	9623.1(18)	6153.2(19)	33.2(6)
C4	11267(2)	8693.1(17)	6350.1(18)	29.3(5)
C5	10778(2)	8224.9(16)	7221.9(17)	24.3(5)
C6	8685(2)	9962.2(15)	8499.0(19)	27.2(5)
C7	7052(2)	9586.1(16)	9762.9(18)	26.1(5)
C8	5934(2)	8938.5(17)	10014.5(19)	31.6(6)
C9	5584(2)	8510.5(17)	8248.8(19)	31.4(5)
C10	6729(2)	9116.4(17)	7927.7(17)	26.5(5)
C11	11060(2)	7201.8(16)	7506.3(17)	25.8(5)
C12	12380(2)	7515.0(17)	9088.5(19)	29.2(5)
C13	12628(2)	7290.9(17)	10258.2(19)	32.5(6)
C14	11433(2)	5873.3(17)	10083.2(19)	32.7(6)
C15	11174(2)	6042.8(15)	8910.4(18)	28.1(5)

Table S8 Anisotropic Displacement Parameters (Å^2×10^3) for CoMorCl. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+...+2hka\times b\times U_{12}]$

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Co1	28.87(17)	20.09(16)	17.86(16)	-0.10(12)	2.97(12)	-6.58(12)
Cl1	31.1(3)	36.5(3)	19.8(3)	-1.3(2)	1.6(2)	3.7(2)
Cl2	30.2(3)	22.9(3)	56.8(4)	-10.0(3)	-5.8(3)	-3.4(2)
O1	23.9(8)	39.3(10)	36.2(10)	-1.3(8)	8.5(7)	3.1(7)
O2	31.6(9)	39.1(10)	31.8(10)	7.2(8)	0.6(7)	9.2(7)
N1	20.6(9)	23.2(10)	22.1(10)	1.9(8)	1.6(7)	-0.5(7)
N2	22.6(9)	21.2(9)	19.9(10)	0.0(8)	2.6(7)	-0.2(7)
N3	23.5(9)	21.8(9)	20.3(10)	1.0(8)	1.7(7)	0.7(7)
C1	18.6(11)	24.2(12)	29.1(13)	5.7(10)	-3.1(9)	-3.7(9)
C2	25.0(12)	29.5(13)	38.4(14)	11.7(11)	-1.7(10)	-5(1)
C3	26.5(12)	45.9(15)	27.1(13)	15.8(11)	-2.2(10)	-13.0(11)
C4	25.4(12)	38.6(14)	24.2(13)	1.0(11)	4.4(10)	-4.6(10)
C5	21.8(11)	31.3(12)	19.6(12)	0.6(10)	0.6(9)	-2.4(9)
C6	28.1(12)	18.8(11)	34.7(14)	4.2(10)	0.9(10)	-0.2(9)
C7	29.2(12)	24.9(12)	24.4(12)	-2.7(10)	2.9(10)	8.1(10)
C8	34.9(13)	34.7(14)	25.8(13)	3.2(11)	9.9(10)	8.6(11)
C9	24.3(12)	34.8(14)	35.1(14)	-6.5(11)	1.3(10)	-0.9(10)
C10	26.3(12)	32.1(13)	21.0(12)	1.2(10)	-0.4(9)	2.7(10)
C11	27.2(12)	29.6(13)	20.8(12)	-2.4(10)	4.9(9)	2.2(10)
C12	26.1(12)	30.9(13)	30.8(13)	3.9(11)	0.7(10)	-2.3(10)
C13	27.9(12)	38.1(14)	31.2(14)	0.8(11)	-2.8(10)	1.4(10)

C14	31.9(13)	31.3(13)	35.4(14)	6.5(11)	6.0(11)	4.7(10)
C15	30.2(12)	22.2(12)	32.2(13)	0.1(10)	4.6(10)	4(1)

Table S9 Bond Lengths for CoMorCl.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Co1	Cl1	2.2589(6)	N3	C11	1.472(3)
Co1	Cl2	2.2609(6)	N3	C12	1.484(3)
Co1	N1	2.0265(18)	N3	C15	1.477(3)
Co1	N2	2.3215(17)	C1	C2	1.381(3)
Co1	N3	2.4530(17)	C1	C6	1.495(3)
O1	C8	1.418(3)	C2	C3	1.380(3)
O1	C9	1.426(3)	C3	C4	1.381(3)
O2	C13	1.426(3)	C4	C5	1.383(3)
O2	C14	1.431(3)	C5	C11	1.499(3)
N1	C1	1.340(3)	C7	C8	1.500(3)
N1	C5	1.344(3)	C9	C10	1.510(3)
N2	C6	1.481(3)	C12	C13	1.513(3)
N2	C7	1.481(3)	C14	C15	1.505(3)
N2	C10	1.489(3)			

Table S10 Bond Angles for CoMorCl.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
Cl1	Co1	Cl2	113.56(3)	C11	N3	C15	108.47(17)
Cl1	Co1	N2	95.95(5)	C12	N3	Co1	116.66(13)
Cl1	Co1	N3	100.71(4)	C15	N3	Co1	116.41(13)
Cl2	Co1	N2	105.21(5)	C15	N3	C12	108.59(17)
Cl2	Co1	N3	90.52(4)	N1	C1	C2	121.1(2)
N1	Co1	Cl1	131.56(5)	N1	C1	C6	113.99(18)
N1	Co1	Cl2	114.52(5)	C2	C1	C6	124.9(2)
N1	Co1	N2	76.97(6)	C3	C2	C1	118.7(2)
N1	Co1	N3	73.51(6)	C2	C3	C4	120.3(2)
N2	Co1	N3	150.23(6)	C3	C4	C5	118.3(2)
C8	O1	C9	108.63(16)	N1	C5	C4	121.3(2)
C13	O2	C14	109.51(17)	N1	C5	C11	114.10(18)
C1	N1	Co1	118.87(14)	C4	C5	C11	124.6(2)
C1	N1	C5	120.34(19)	N2	C6	C1	110.65(17)
C5	N1	Co1	120.57(14)	N2	C7	C8	110.16(18)
C6	N2	Co1	99.95(12)	O1	C8	C7	111.93(19)
C6	N2	C10	108.33(17)	O1	C9	C10	111.28(19)
C7	N2	Co1	117.08(13)	N2	C10	C9	112.01(18)
C7	N2	C6	108.24(16)	N3	C11	C5	110.62(17)
C7	N2	C10	108.22(16)	N3	C12	C13	111.59(18)
C10	N2	Co1	114.30(13)	O2	C13	C12	110.97(19)
C11	N3	Co1	97.05(12)	O2	C14	C15	111.15(19)
C11	N3	C12	108.58(17)	N3	C15	C14	110.76(18)

Table S11 Torsion Angles for CoMorCl.

A	B	C	D	Angle/°

Co1	N1	C1	C2	-173.82(16)
Co1	N1	C1	C6	7.3(2)
Co1	N1	C5	C4	174.16(16)
Co1	N1	C5	C11	-3.4(2)
Co1	N2	C6	C1	45.75(18)
Co1	N2	C7	C8	-76.56(19)
Co1	N2	C10	C9	79.31(19)
Co1	N3	C11	C5	48.73(17)
Co1	N3	C12	C13	80.0(2)
Co1	N3	C15	C14	-79.29(19)
O1	C9	C10	N2	56.5(2)
O2	C14	C15	N3	-59.4(2)
N1	C1	C2	C3	-0.2(3)
N1	C1	C6	N2	-39.7(3)
N1	C5	C11	N3	-37.4(3)
N2	C7	C8	O1	-60.9(2)
N3	C12	C13	O2	57.2(2)
C1	N1	C5	C4	-0.3(3)
C1	N1	C5	C11	-177.85(19)
C1	C2	C3	C4	-0.7(3)
C2	C1	C6	N2	141.5(2)
C2	C3	C4	C5	1.1(3)
C3	C4	C5	N1	-0.6(3)
C3	C4	C5	C11	176.6(2)
C4	C5	C11	N3	145.2(2)
C5	N1	C1	C2	0.8(3)
C5	N1	C1	C6	-178.10(19)
C6	N2	C7	C8	171.56(18)
C6	N2	C10	C9	-170.24(18)
C6	C1	C2	C3	178.5(2)
C7	N2	C6	C1	168.73(17)
C7	N2	C10	C9	-53.1(2)
C8	O1	C9	C10	-59.0(2)
C9	O1	C8	C7	61.9(2)
C10	N2	C6	C1	-74.1(2)
C10	N2	C7	C8	54.4(2)
C11	N3	C12	C13	-171.72(18)
C11	N3	C15	C14	172.62(18)
C12	N3	C11	C5	-72.5(2)
C12	N3	C15	C14	54.8(2)
C13	O2	C14	C15	60.7(2)
C14	O2	C13	C12	-59.2(2)
C15	N3	C11	C5	169.66(17)
C15	N3	C12	C13	-54.0(2)

Table S12 Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters

(Å^2×10^3) for CoMorCl.

Atom	***x***	***y***	***Z***	**U(eq)**
H2	9754	10714	6700	37
H3	11179	9955	5552	40
H4	11861	8383	5898	35
H6A	9208	10173	9135	33
H6B	8214	10526	8199	33
H7A	6720	10241	9624	31
H7B	7682	9613	10381	31
H8A	6275	8287	10163	38
H8B	5515	9172	10664	38
H9A	4929	8477	7649	38
H9B	5891	7852	8406	38
H10A	7145	8816	7311	32
H10B	6406	9756	7702	32
H11A	10358	6787	7197	31
H11B	11899	7005	7200	31
H12A	12337	8217	8991	35
H12B	13119	7271	8677	35
H13A	13476	7574	10503	39
H13B	11929	7582	10679	39
H14A	10717	6160	10489	39
H14B	11445	5177	10226	39
H15A	11869	5734	8502	34
H15B	10325	5750	8687	34

Experimental

A suitable crystal of $C_{15}H_{23}Cl_2CoN_3O_2$ **[CoMorCl]** was selected and mounted on a diffractometer. The crystal was kept at 473(2) K. Using Olex2 [1], the structure was solved with the XS [2] structure solution program using Direct Methods and refined with the XL [3] refinement package using Least Squares minimisation.

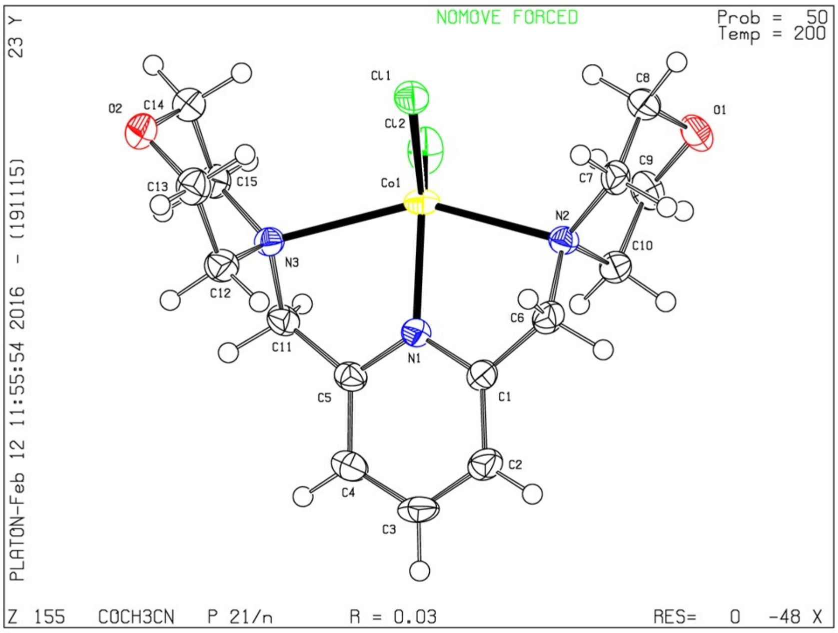
[1] O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard and H. Puschmann, OLEX2: a complete structure solution, refinement and analysis program. J. Appl. Cryst. (2009). 42, 339-341.

[2] SHELXS-97 (Sheldrick, 2008)

[3] XL, G.M. Sheldrick, Acta Cryst. (2008). A64, 112-122.

Crystal structure determination of [CoMorCl]

Crystal Data. $C_{15}H_{23}Cl_2CoN_3O_2$, *M* =407.19, monoclinic, *a* = 10.2125(9) Å, *b* = 13.9736(12) Å, *c* = 12.5470(10) Å, *β* = 92.0530(10), *U* = 1789.4(3) Å^3, *T* = 473(2), space group $P2_1/n$ (no. 14), *Z* = 4, μ(MoKα) = 1.269, 16414 reflections measured, 3151 unique (R_{int} = 0.0336) which were used in all calculations. The final $wR(F_2)$ was 0.0648 (all data).



Crystal structure determination of 3 (CCDC 1836378)

NNNCoBF$_4$

Table S13 Crystal data and structure refinement for NNNCoBF$_4$

Identification code	NNNCoBF$_4$
Empirical formula	$C_{15}H_{29}B_2Cl_2CoF_8N_5O$
Formula weight	598.88
Temperature/K	373(2)
Crystal system	Triclinic
Space group	P-1
a/Å	6.8380(14)
b/Å	13.077(3)
c/Å	13.377(3)
α/°	89.44(3)
β/°	78.44(3)
γ/°	82.78(3)
Volume/Å^3	1162.5(4)
Z	2

ρ_{calc}mg/mm^3	1.711
m/mm^{-1}	0.752
F(000)	610
Crystal size/mm^3	0.121 × 0.105 × 0.055
Theta range for data collection	2.754 to 51.998°
Index ranges	$-9 \le h \le 9$, $-18 \le k \le 18$, $-18 \le l \le 18$
Reflections collected	11996
Independent reflections	6106[R(int) = 0.0298]
Data/restraints/parameters	6106/3/313
Goodness-of-fit on F^2	0.970
Final R indexes [I>2σ (I)]	R_1 = 0.0460, wR_2 = 0.1219
Final R indexes [all data]	R_1 = 0.0660, wR_2 = 0.1304
Largest diff. peak/hole / e Å^{-3}	0.568/-1.159

Table S14 Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for NNNCoBF$_4$. U$_{eq}$ is defined as 1/3 of of the trace of the orthogonalised U$_{IJ}$ tensor.

Atom	***x***	***y***	***Z***	**U(eq)**
Co1	2667.1(5)	5840.2(3)	8083.1(3)	15.09(10)
Cl1	-321.0(9)	5874.6(5)	7593.4(5)	22.40(15)
Cl2	2512.9(9)	6443.4(5)	9699.2(5)	19.08(14)
N1	5015(3)	5340.1(16)	6966.8(16)	15.4(4)
N2	3223(3)	4117.0(16)	8440.6(16)	16.5(4)
N3	1650(3)	2249.4(17)	9327.0(17)	20.8(4)
N4	3536(3)	7325.5(16)	7310.1(16)	16.4(4)
N5	4030(4)	9498.8(18)	7550.2(19)	25.1(5)
C1	5933(3)	4372(2)	6988(2)	18.5(5)
C2	7342(4)	3955(2)	6151(2)	22.8(6)
C3	7825(4)	4565(2)	5315(2)	23.8(6)
C4	6923(4)	5577(2)	5321(2)	22.4(5)
C5	5482(4)	5945(2)	6162(2)	19.5(5)
C6	5394(4)	3833(2)	7983(2)	21.0(5)
C7	1923(4)	3524(2)	7956(2)	19.2(5)
C8	2110(4)	2384(2)	8196(2)	23.3(5)
C9	2953(4)	2807(2)	9845(2)	22.2(5)
C10	2766(4)	3932(2)	9555.4(19)	18.3(5)
C11	4272(4)	7006(2)	6236(2)	21.0(5)
C12	1828(4)	8165(2)	7445(2)	21.2(5)
C13	2415(4)	9192(2)	7047(2)	26.3(6)
C14	5806(4)	8687(2)	7390(2)	23.4(5)
C15	5151(4)	7668(2)	7776(2)	19.1(5)
B1	7648(5)	409(3)	9298(2)	24.7(6)
F1	9459(3)	736.4(18)	8828.4(16)	50.3(6)
F2	7908(3)	-666.7(13)	9289.8(14)	32.7(4)

F3	6121(3)	755.8(15)	8781.1(15)	42.9(5)
F4	7140(3)	783.6(16)	10296.7(14)	42.2(5)
B2	1094(5)	1539(3)	5416(2)	25.5(6)
F5	1584(4)	2369.8(19)	5920(2)	68.7(8)
F6	2880(3)	883.0(16)	5095.9(14)	38.7(5)
F7	293(4)	1917(2)	4620.0(16)	61.9(7)
F8	-234(3)	1080(2)	6117(2)	77.5(10)
O1W	5589(3)	1138.5(18)	6453.9(17)	30.6(5)

Table S15 Anisotropic Displacement Parameters (Å^2×10^3) for NNNCoBF$_4$. The Anisotropic displacement factor exponent takes the form: -2π^2[h^{2}a*^{2}U$_{11}$+...+2hka×b×U$_{12}$]

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Co1	9.29(15)	22.14(18)	14.72(18)	-2.94(12)	-4.92(12)	-1.12(12)
Cl1	12.5(3)	28.4(3)	29.3(4)	-2.3(3)	-11.8(2)	-1.4(2)
Cl2	15.9(3)	26.4(3)	16.2(3)	-3.3(2)	-5.9(2)	-3.0(2)
N1	9.6(8)	23.1(10)	13.6(10)	-4.4(8)	-1.9(8)	-2.6(7)
N2	12.4(9)	22(1)	16.2(11)	-2.0(8)	-6.0(8)	-1.5(8)
N3	20.7(10)	22.2(11)	20.7(12)	0.4(8)	-6.3(9)	-4.2(8)
N4	11.8(9)	23.1(11)	15.3(10)	-1.5(8)	-5.4(8)	-1.7(8)
N5	30.2(12)	21.4(11)	24.4(13)	-0.2(9)	-6.1(10)	-4.9(9)
C1	10.1(10)	24.0(12)	23.1(13)	-5.4(10)	-5.7(10)	-4.0(9)
C2	10.8(10)	27.1(14)	30.4(15)	-10.5(11)	-3.7(10)	-1.4(9)
C3	11.6(10)	37.1(15)	22.7(14)	-13.5(11)	0.2(10)	-7.8(10)
C4	16.6(11)	35.9(15)	15.9(13)	-5(1)	-2.2(10)	-9.5(11)
C5	15.6(11)	27.9(13)	17.2(13)	-3.9(10)	-4.9(10)	-8.1(10)
C6	11.8(10)	24.7(13)	26.2(14)	-2.2(10)	-5(1)	1.0(9)
C7	17.3(11)	23.8(12)	19.1(13)	-1.7(10)	-7.9(10)	-5.0(9)
C8	25.3(13)	25.5(13)	20.6(14)	-3.1(10)	-5.9(11)	-6.6(10)
C9	21.8(12)	24.5(13)	22.9(14)	-1.5(10)	-11.5(11)	-1.4(10)
C10	17.0(11)	22.9(12)	15.9(12)	-1.8(9)	-5.9(10)	-2.0(9)
C11	20.9(12)	26.8(13)	17.9(13)	0.4(10)	-7.8(10)	-6.1(10)
C12	15.0(11)	25.2(13)	23.9(14)	2.6(10)	-6.5(10)	-0.5(9)
C13	24.0(13)	26.5(14)	28.9(16)	3.8(11)	-9.7(12)	1.2(11)
C14	19.7(12)	28.6(14)	23.8(14)	-3.2(11)	-6.6(11)	-6.5(10)
C15	13.8(10)	26.1(13)	19.7(13)	-3(1)	-8(1)	-3.6(9)
B1	29.8(15)	25.1(15)	22.2(16)	-0.6(12)	-10.1(13)	-6.9(12)
F1	57.9(13)	59.6(14)	39.5(12)	3.3(10)	-4.7(10)	-39.4(12)
F2	34.9(9)	25.9(9)	41.4(11)	-0.1(7)	-16.7(8)	-4.4(7)
F3	59.5(13)	33.1(10)	41.9(11)	-2.1(8)	-30.7(10)	5.8(9)
F4	52.9(12)	48.9(12)	25.6(10)	-8.7(8)	-10.4(9)	-4.4(10)
B2	24.4(14)	31.7(16)	19.7(16)	1.3(12)	-6.6(13)	2.3(12)
F5	81.4(19)	53.1(15)	79.6(18)	-22.2(13)	-43.4(15)	6.2(13)
F6	33.5(10)	46.9(12)	31.7(11)	-1.7(8)	-6.9(8)	10.9(8)
F7	63.4(15)	83.7(18)	34.0(12)	-4.1(11)	-24.4(11)	32.3(13)
F8	26.5(11)	84(2)	110(2)	55.8(18)	6.5(13)	-1.5(12)

O1W	23.6(10)	39.1(12)	28.5(12)	0.8(9)	-3.6(9)	-4.0(9)

Table S16 Bond Lengths for NNNCoBF$_4$.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Co1	Cl1	2.2625(8)	C1	C6	1.501(4)
Co1	Cl2	2.2865(9)	C2	C3	1.378(4)
Co1	N1	2.007(2)	C3	C4	1.387(4)
Co1	N2	2.299(2)	C4	C5	1.384(4)
Co1	N4	2.280(2)	C5	C11	1.518(4)
N1	C1	1.343(3)	C7	C8	1.516(4)
N1	C5	1.340(3)	C9	C10	1.514(4)
N2	C6	1.489(3)	C12	C13	1.511(4)
N2	C7	1.492(3)	C14	C15	1.512(4)
N2	C10	1.485(3)	B1	F1	1.389(4)
N3	C8	1.496(3)	B1	F2	1.395(4)
N3	C9	1.492(3)	B1	F3	1.392(4)
N4	C11	1.470(3)	B1	F4	1.389(4)
N4	C12	1.483(3)	B2	F5	1.394(4)
N4	C15	1.487(3)	B2	F6	1.394(4)
N5	C13	1.499(4)	B2	F7	1.354(4)
N5	C14	1.492(4)	B2	F8	1.360(4)
C1	C2	1.388(4)			

Table S17 Bond Angles for NNNCoBF$_4$.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
Cl1	Co1	Cl2	115.71(4)	C2	C1	C6	124.5(2)
Cl1	Co1	N2	99.30(6)	C3	C2	C1	118.7(3)
Cl1	Co1	N4	96.82(6)	C2	C3	C4	120.2(2)
Cl2	Co1	N2	96.62(6)	C5	C4	C3	118.8(3)
N1	Co1	Cl1	112.67(6)	N1	C5	C4	120.3(3)
N1	Co1	Cl2	131.55(6)	N1	C5	C11	115.3(2)
N1	Co1	N2	78.08(9)	C4	C5	C11	124.3(3)
N1	Co1	N4	76.88(9)	N2	C6	C1	110.3(2)
N4	Co1	Cl2	94.63(6)	N2	C7	C8	114.0(2)
N4	Co1	N2	153.96(8)	N3	C8	C7	109.6(2)
C1	N1	Co1	119.43(18)	N3	C9	C10	109.7(2)
C5	N1	Co1	118.67(17)	N2	C10	C9	114.7(2)
C5	N1	C1	121.5(2)	N4	C11	C5	110.5(2)
C6	N2	Co1	103.12(15)	N4	C12	C13	113.8(2)
C6	N2	C7	111.5(2)	N5	C13	C12	109.9(2)
C7	N2	Co1	110.33(15)	N5	C14	C15	109.6(2)
C10	N2	Co1	111.77(15)	N4	C15	C14	114.4(2)
C10	N2	C6	112.31(19)	F1	B1	F2	108.1(3)
C10	N2	C7	107.82(19)	F1	B1	F3	111.1(3)
C9	N3	C8	111.8(2)	F1	B1	F4	108.9(2)
C11	N4	Co1	103.23(15)	F3	B1	F2	109.1(2)
C11	N4	C12	112.5(2)	F4	B1	F2	110.0(3)

C11	N4	C15	112.0(2)	F4	B1	F3	109.7(3)
C12	N4	Co1	112.71(16)	F5	B2	F6	106.6(3)
C12	N4	C15	108.4(2)	F7	B2	F5	107.6(3)
C15	N4	Co1	107.82(15)	F7	B2	F6	112.0(3)
C14	N5	C13	110.8(2)	F7	B2	F8	112.7(3)
N1	C1	C2	120.4(3)	F8	B2	F5	106.1(3)
N1	C1	C6	115.0(2)	F8	B2	F6	111.3(3)

Table S18 Hydrogen Bonds for NNNCoBF$_4$.

D	H	A	d(D-H)/Å	d(H-A)/Å	d(D-A)/Å	D-H-A/°
N3	H3A	Cl2[1]	0.91	2.29	3.171(3)	161.5
N3	H3B	F2[2]	0.91	2.05	2.791(3)	137.8
N5	H5A	O1W[3]	0.91	1.90	2.788(3)	165.2
N5	H5B	F4[4]	0.91	2.00	2.864(3)	156.9
O1W	H1OW	F8[5]	0.829(10)	1.964(10)	2.792(3)	177(3)
O1W	H2OW	F6	0.835(10)	2.113(15)	2.891(3)	155(3)

[1]-X,1-Y,2-Z; [2]1-X,-Y,2-Z; [3]+X,1+Y,+Z; [4]1-X,1-Y,2-Z; [5]1+X,+Y,+Z

Table S19 Torsion Angles for NNNCoBF$_4$.

A	B	C	D	Angle/°
Co1	N1	C1	C2	169.79(17)
Co1	N1	C1	C6	-13.4(3)
Co1	N1	C5	C4	-171.95(17)
Co1	N1	C5	C11	5.6(3)
Co1	N2	C6	C1	-38.7(2)
Co1	N2	C7	C8	-177.07(17)
Co1	N2	C10	C9	175.79(16)
Co1	N4	C11	C5	-39.0(2)
Co1	N4	C12	C13	173.28(18)
Co1	N4	C15	C14	-176.30(18)
N1	C1	C2	C3	2.1(4)
N1	C1	C6	N2	37.5(3)
N1	C5	C11	N4	26.0(3)
N2	C7	C8	N3	56.6(3)
N3	C9	C10	N2	-55.7(3)
N4	C12	C13	N5	-56.7(3)
N5	C14	C15	N4	56.2(3)
C1	N1	C5	C4	0.6(3)
C1	N1	C5	C11	178.2(2)
C1	C2	C3	C4	0.5(4)
C2	C1	C6	N2	-145.8(2)
C2	C3	C4	C5	-2.5(4)
C3	C4	C5	N1	2.0(4)
C3	C4	C5	C11	-175.3(2)
C4	C5	C11	N4	-156.5(2)
C5	N1	C1	C2	-2.7(3)

C5	N1	C1	C6	174.1(2)
C6	N2	C7	C8	69.0(3)
C6	N2	C10	C9	-68.9(3)
C6	C1	C2	C3	-174.4(2)
C7	N2	C6	C1	79.6(3)
C7	N2	C10	C9	54.4(3)
C8	N3	C9	C10	55.0(3)
C9	N3	C8	C7	-55.6(3)
C10	N2	C6	C1	-159.2(2)
C10	N2	C7	C8	-54.8(3)
C11	N4	C12	C13	-70.5(3)
C11	N4	C15	C14	70.8(3)
C12	N4	C11	C5	-160.8(2)
C12	N4	C15	C14	-54.0(3)
C13	N5	C14	C15	-56.1(3)
C14	N5	C13	C12	56.7(3)
C15	N4	C11	C5	76.7(3)
C15	N4	C12	C13	54.0(3)

Table S20 Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for NNNCoBF4.

Atom	*x*	*y*	*Z*	U(eq)
H3A	336	2490	9576	25
H3B	1836	1566	9468	25
H5A	4415	10103	7287	30
H5B	3536	9599	8231	30
H2	7960	3263	6155	27
H3	8778	4292	4732	29
H4	7289	6010	4758	27
H6A	5679	3078	7867	25
H6B	6224	4029	8459	25
H7A	2275	3602	7207	23
H7B	502	3825	8187	23
H8A	1162	2046	7880	28
H8B	3493	2057	7909	28
H9A	4372	2493	9640	27
H9B	2540	2748	10594	27
H10A	1377	4253	9838	22
H10B	3687	4282	9879	22
H11A	5126	7511	5882	25
H11B	3116	6994	5896	25
H12A	1215	8245	8180	25
H12B	794	7965	7088	25
H13A	2910	9142	6299	32
H13B	1225	9724	7188	32
H14A	6824	8882	7760	28

H14B	6425	8622	6654	28
H15A	6335	7132	7640	23
H15B	4670	7725	8524	23
H1OW	6830(16)	1120(30)	6330(20)	37
H2OW	5090(40)	1140(30)	5932(16)	37

Experimental

A suitable crystal of $C_{15}H_{29}B_2Cl_2CoF_8N_5O$ **[NNNCoBF$_4$]** was selected and mounted on a diffractometer. The crystal was kept at 373(2) K. Using Olex2 [1], the structure was solved with the XS [2] structure solution program using Direct Methods and refined with the XL [3] refinement package using Least Squares minimisation.

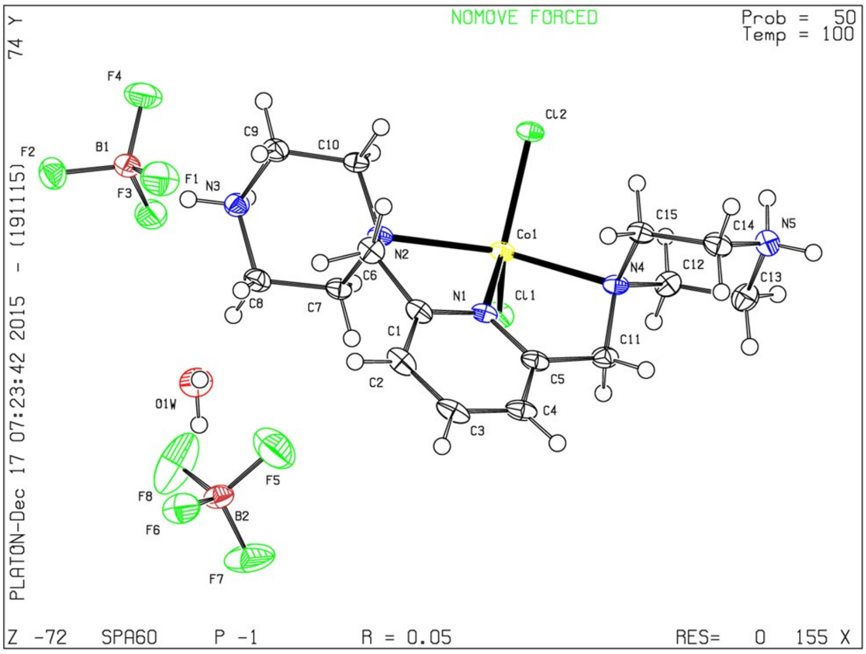
[1] O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard and H. Puschmann, OLEX2: a complete structure solution, refinement and analysis program. J. Appl. Cryst. (2009). 42, 339-341.

[2] *SHELXT-2014/5*(Sheldrick, 2015a).

[3] XL, G.M. Sheldrick, Acta Cryst. (2008). A64, 112-122.

Crystal structure determination of[NNNCoBF4]

Crystal Data. $C_{15}H_{29}B_2Cl_2CoF_8N_5O$, M =598.88, triclinic, a = 6.8380(14) Å, b = 13.077(3) Å, c = 13.377(3) Å, α = 89.44(3), β = 78.44(3), γ = 82.78(3), U = 1162.5(4)Å^3, T = 373(2), space group P-1 (no. 2), Z = 2, μ(synchrotron) = 0.752, 11996 reflections measured, 6106 unique (R_{int} = 0.0298) which were used in all calculations. The final $wR(F_2)$ was 0.1304 (all data).



6. References:

S1. W. L. F. Armarego and Perrin, D. D. *Purification of Laboratory Chemicals* (Pergamon Press, Oxford, 1988) ed 3.

S2. V. G. Landge, J. Pitchaimani, S. P. Midya, M. Subramanian, V. Madhu, E. Balaraman, *Catal. Sci. Technol.*, **2018**, *8*, 428-433.

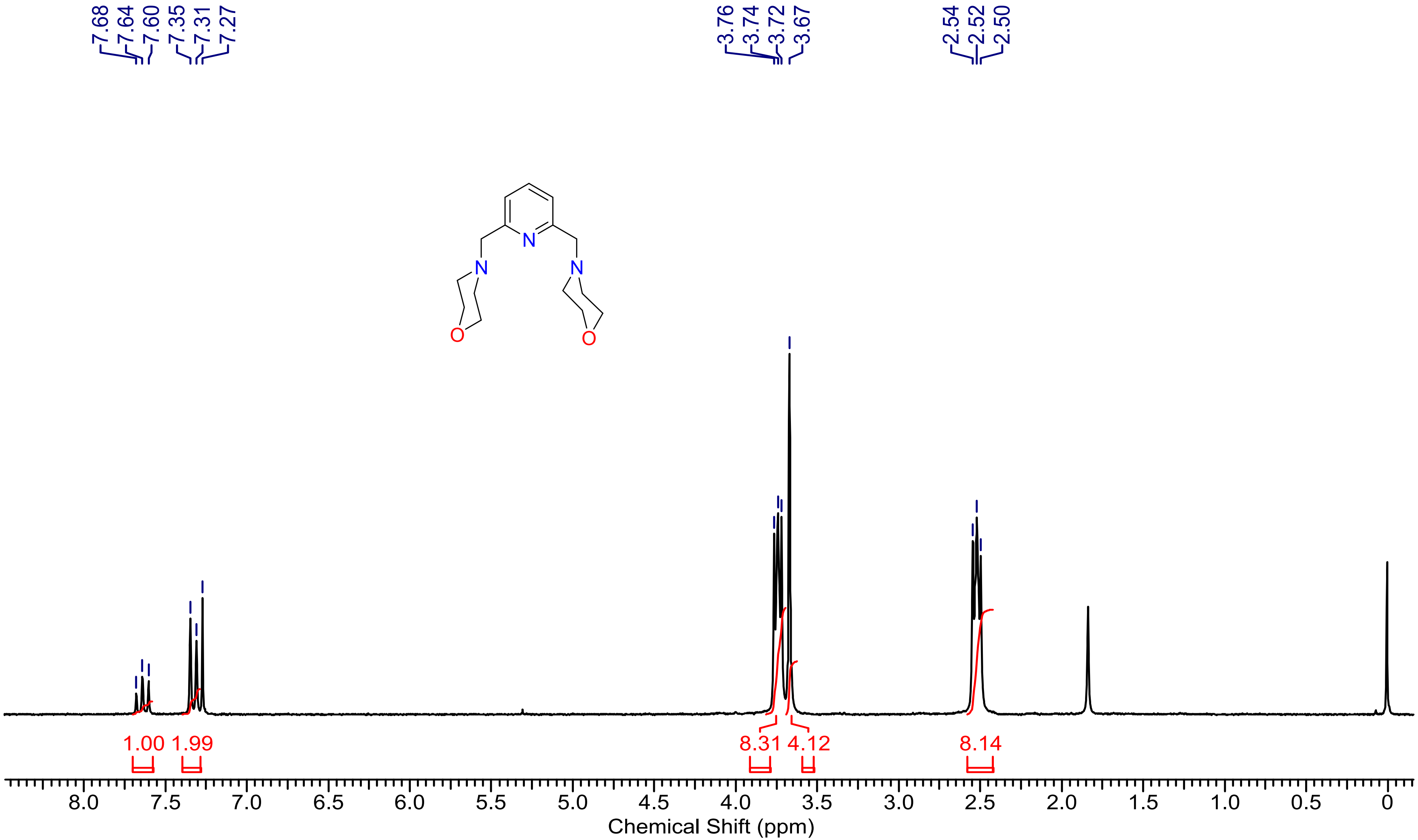


Figure S10. ^{1}H of Py-N^{3} (**L$_{1}$**)

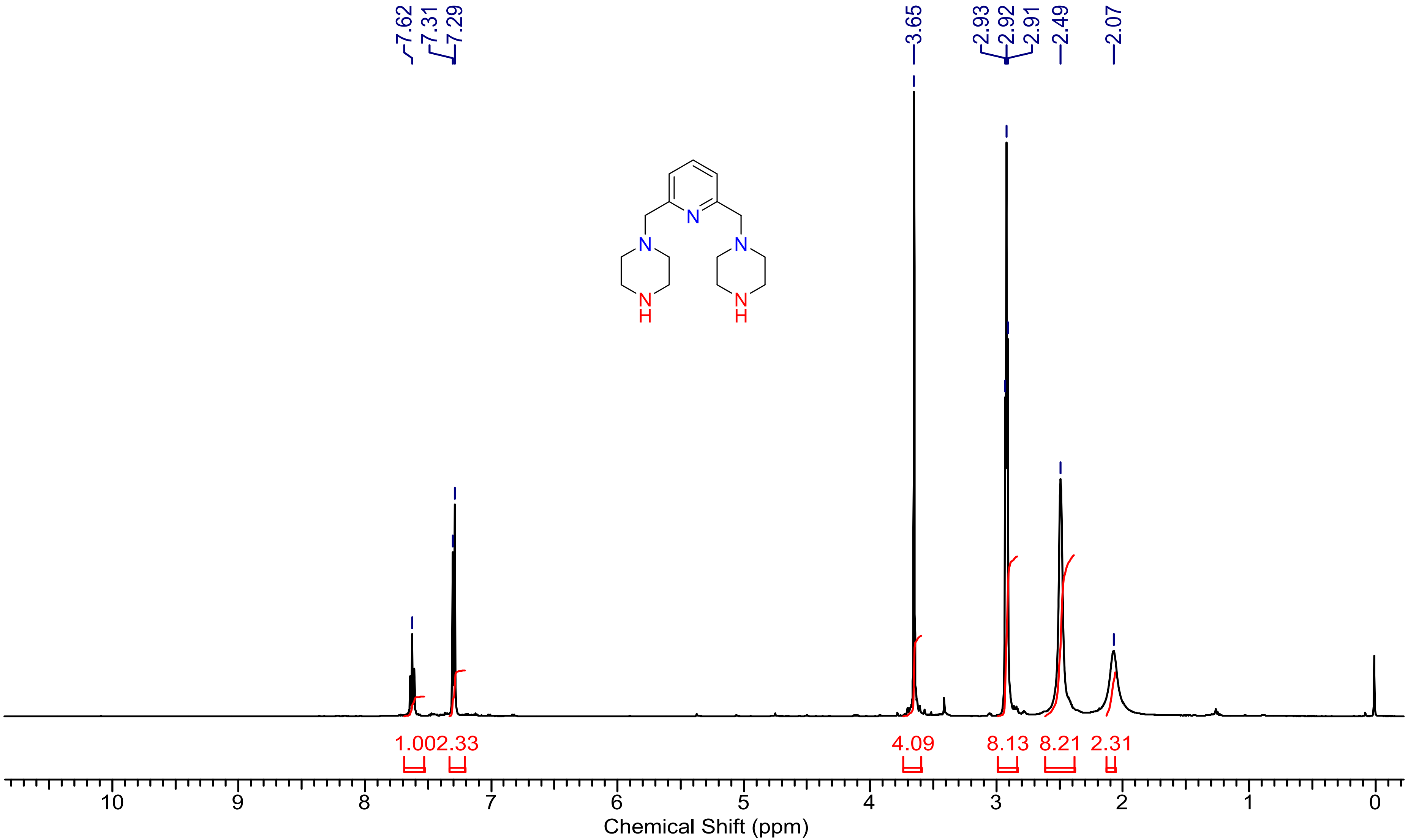


Figure S11. ^{1}H of $\mathbf{L_2}$

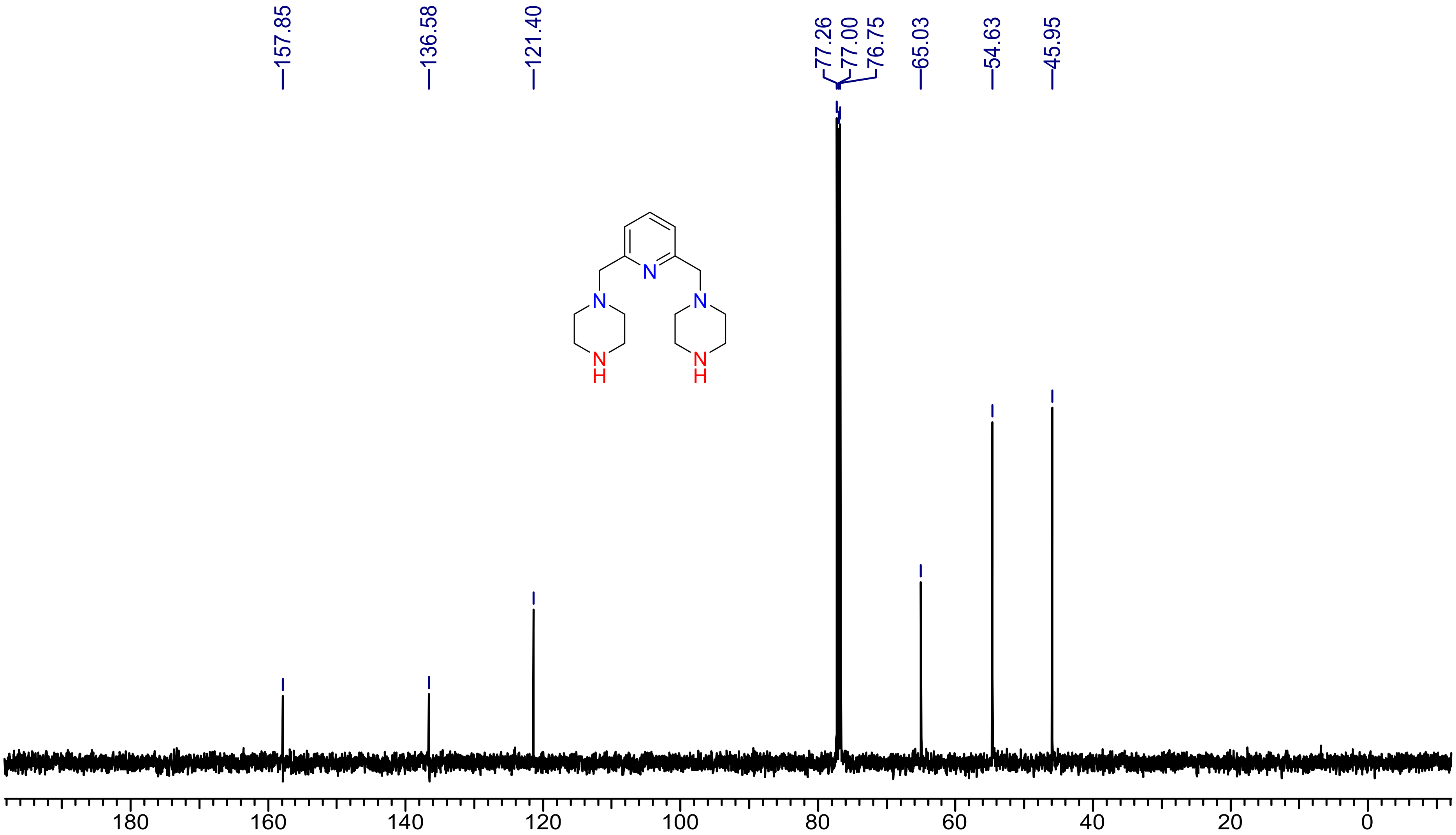


Figure S12. ^{13}C of $\mathbf{L_2}$

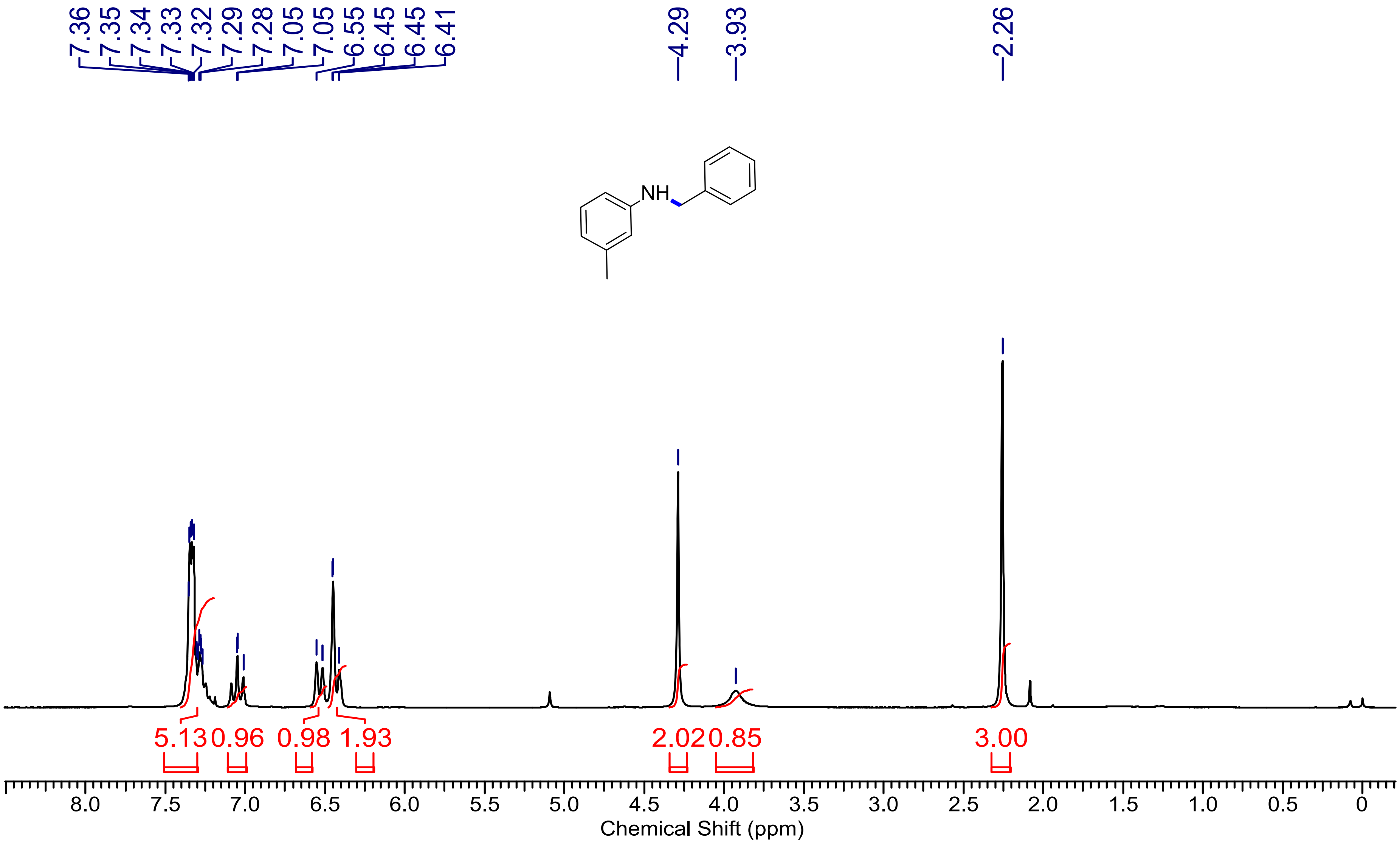


Figure S13. ^{1}H of **5a**

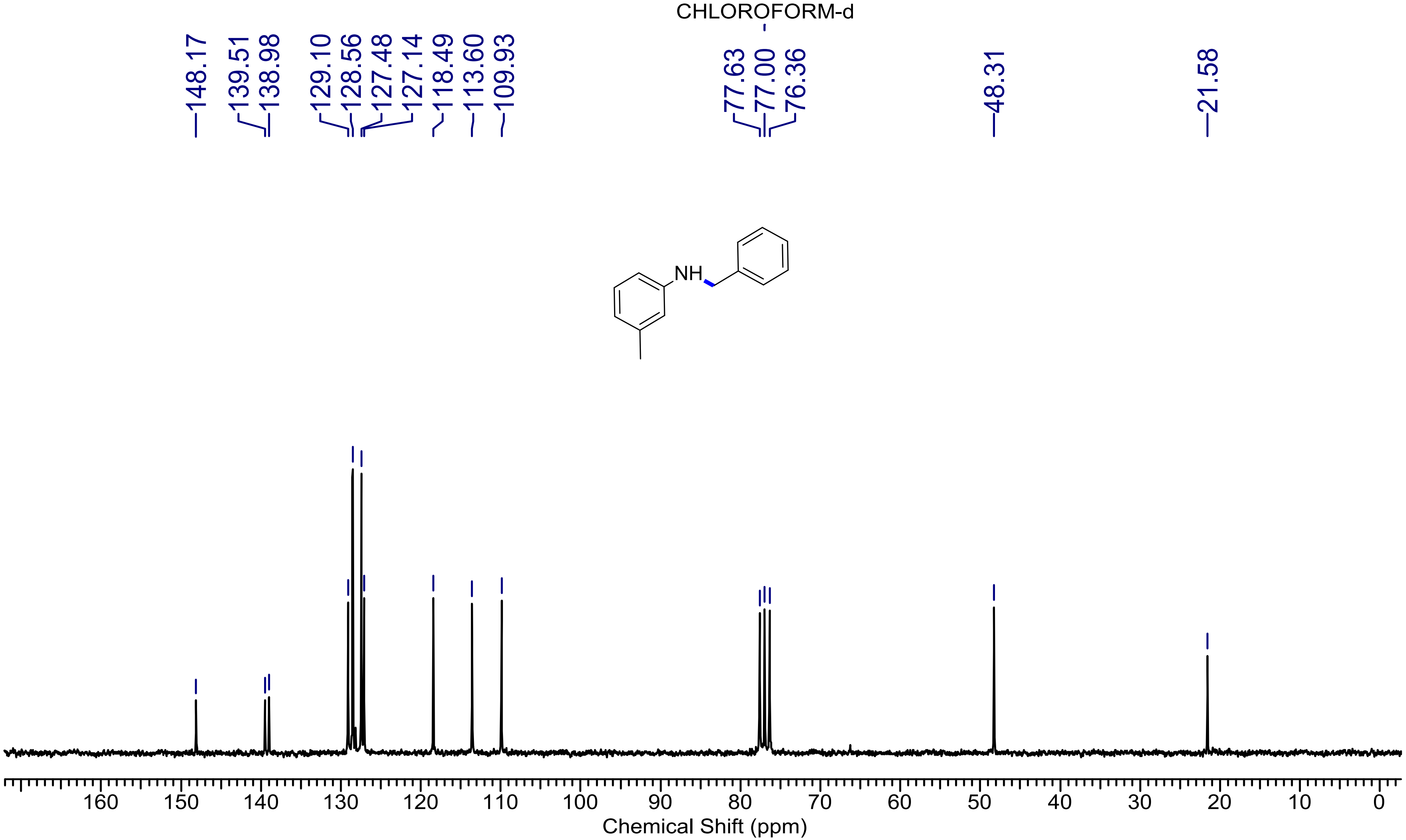


Figure S14. ^{13}C of **5a**

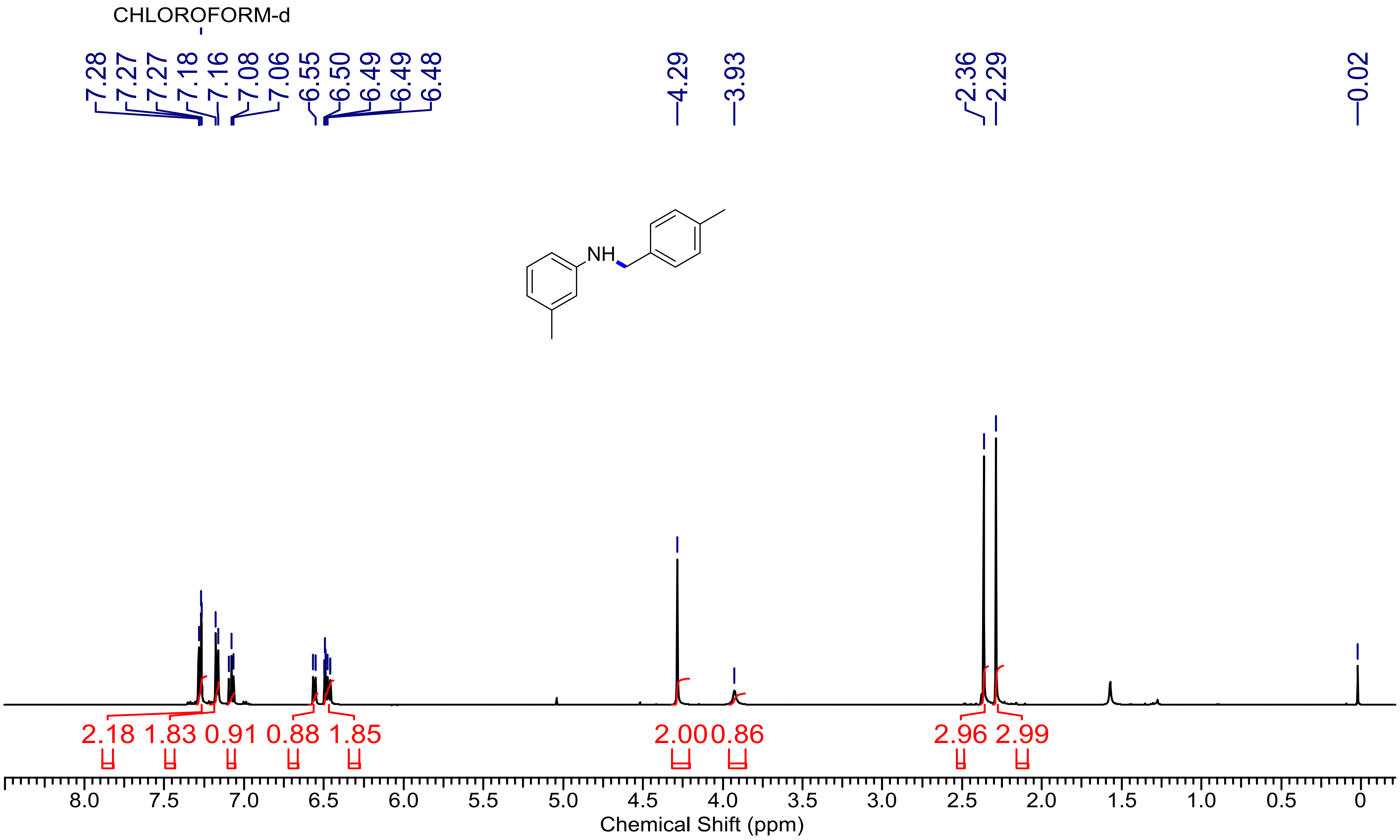


Figure S15. ^{1}H of **5b**

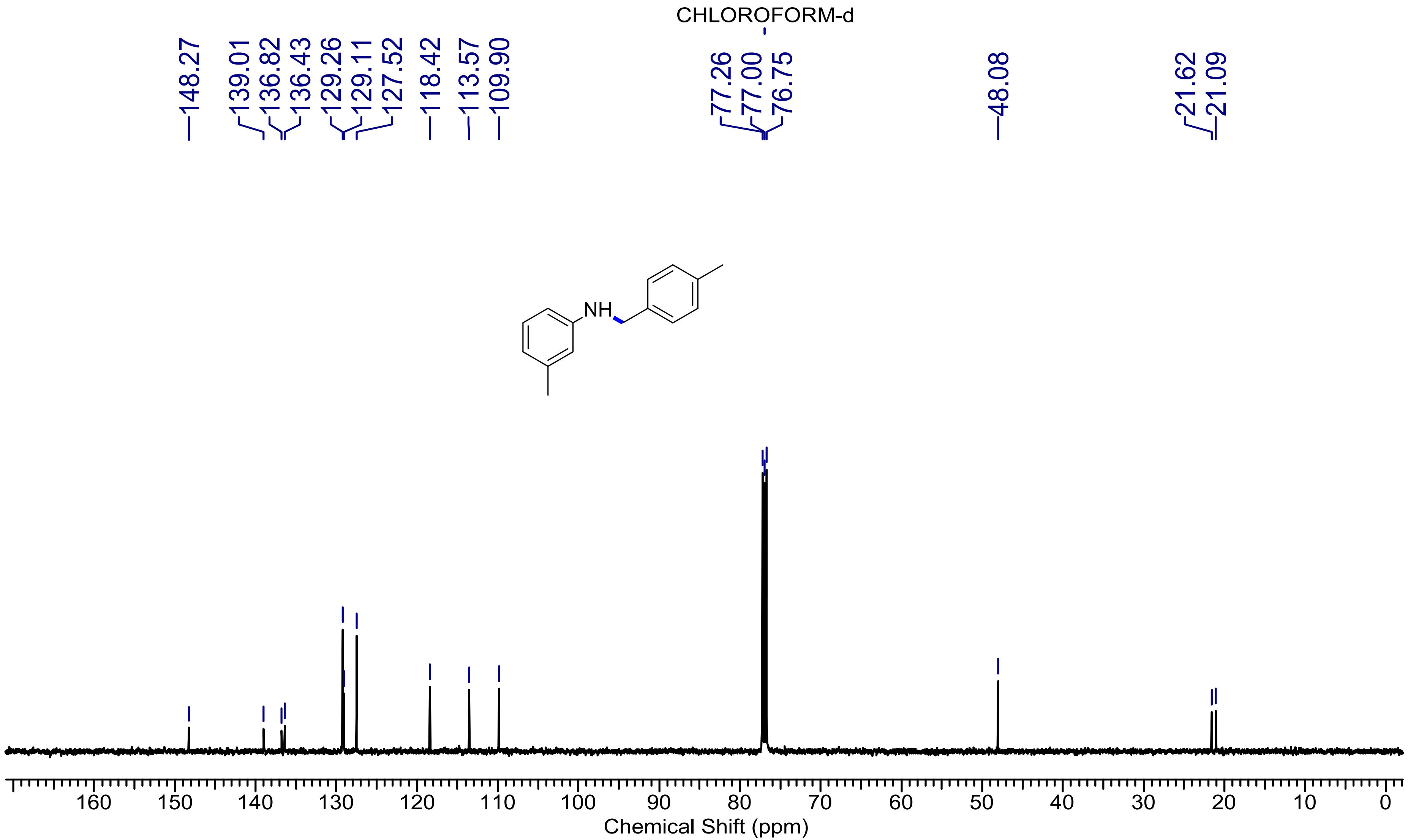


Figure S16. ^{13}C of **5b**

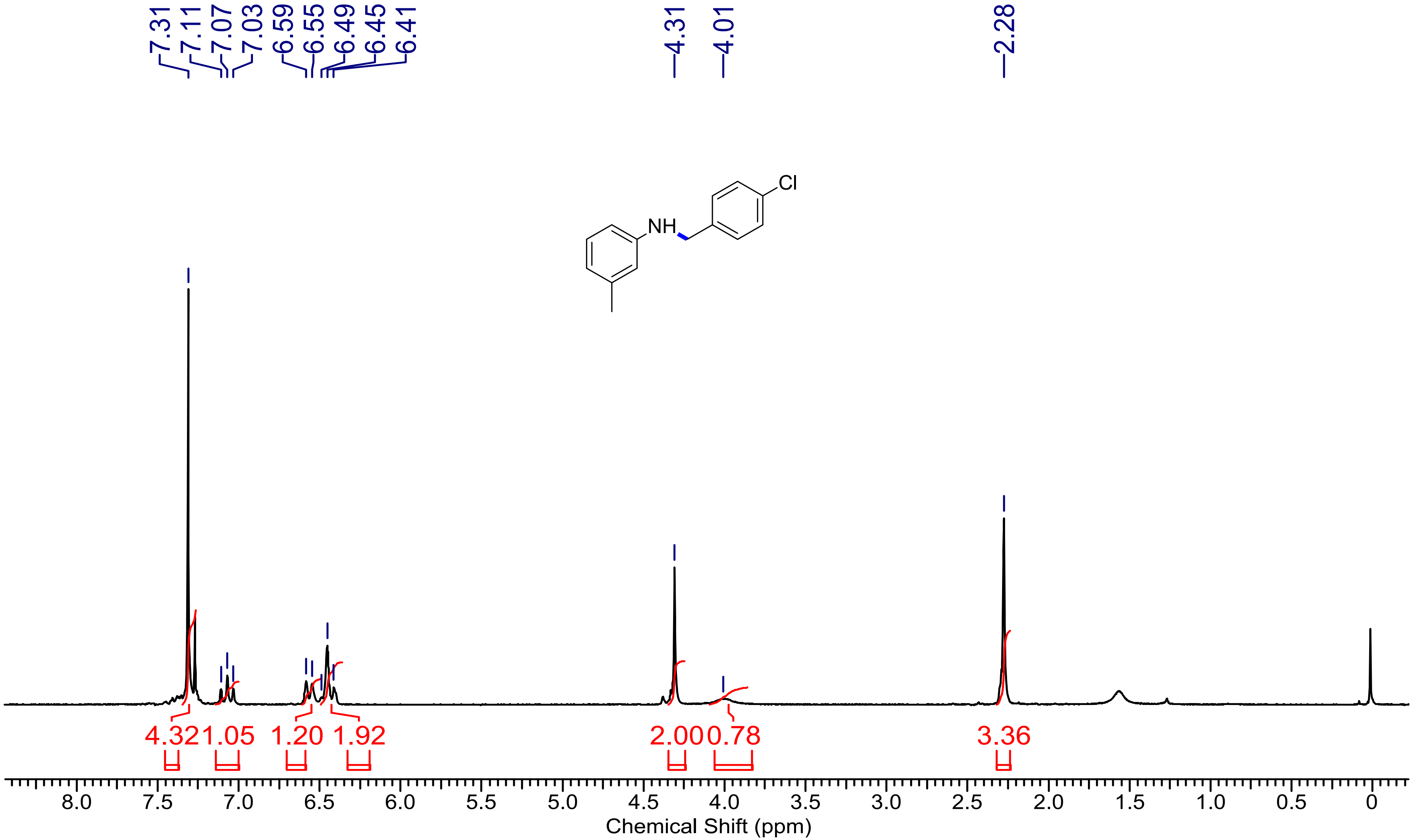


Figure S17. ^{1}H of **5c**

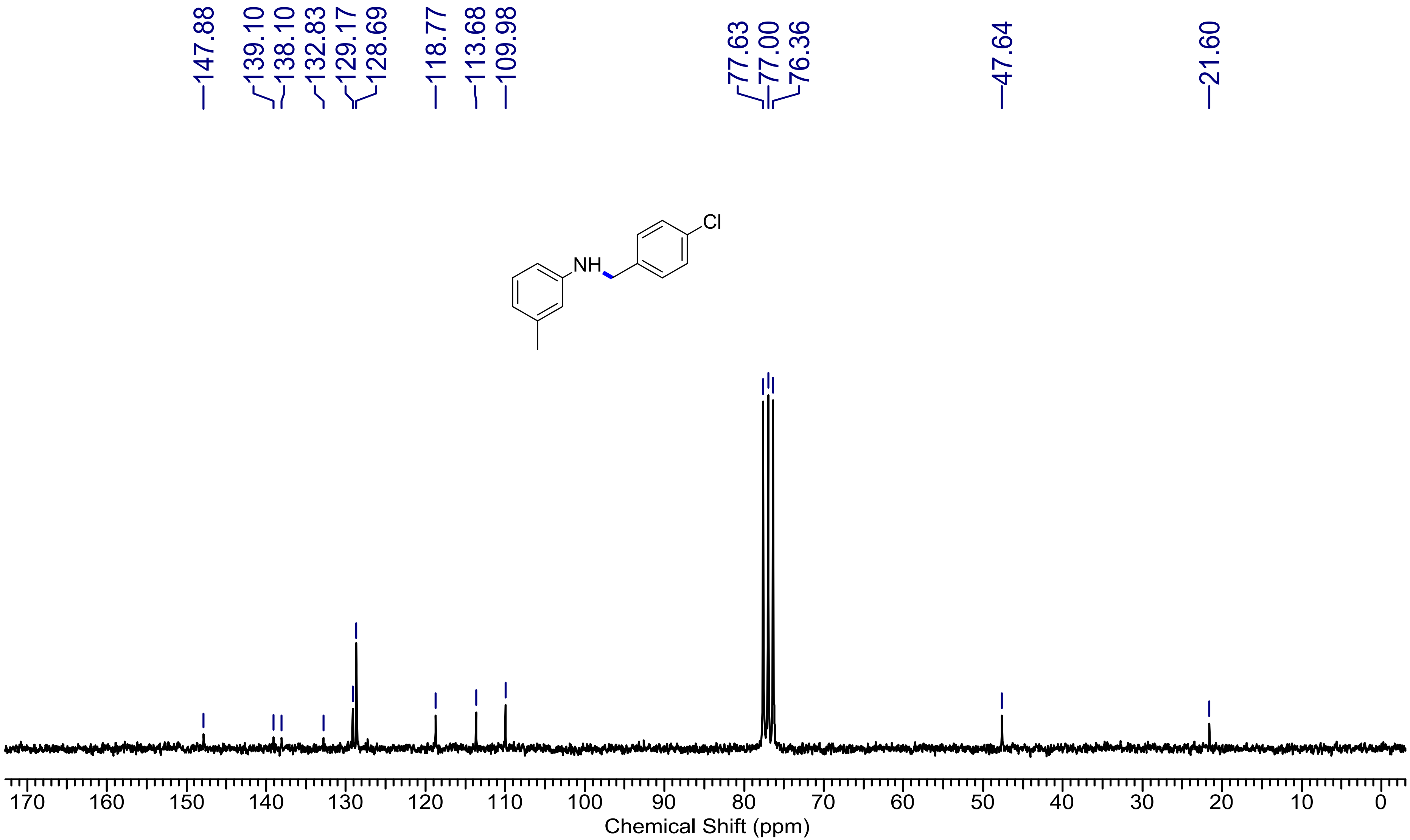


Figure S18. ^{13}C of **5c**

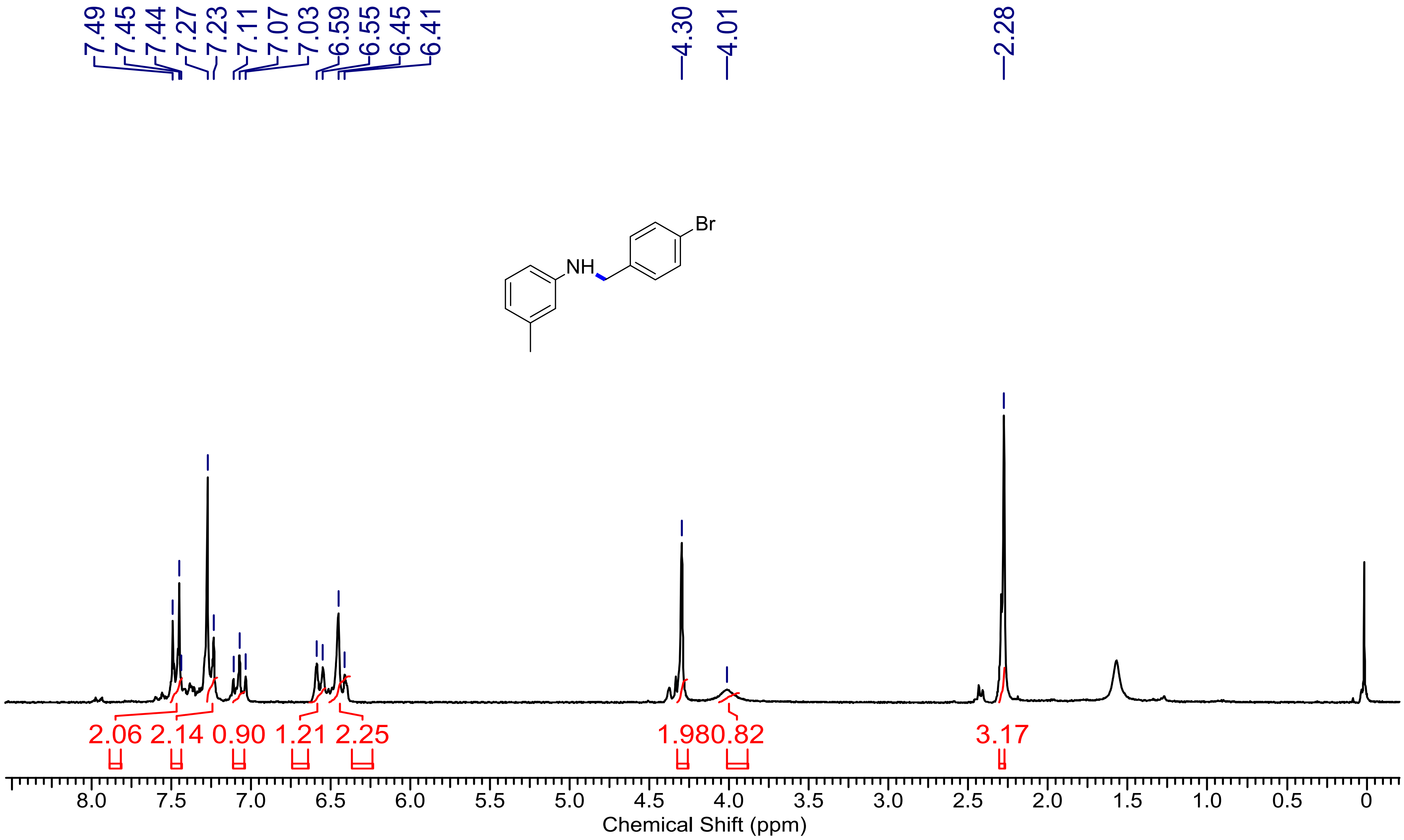


Figure S19. ^{1}H of **5d**

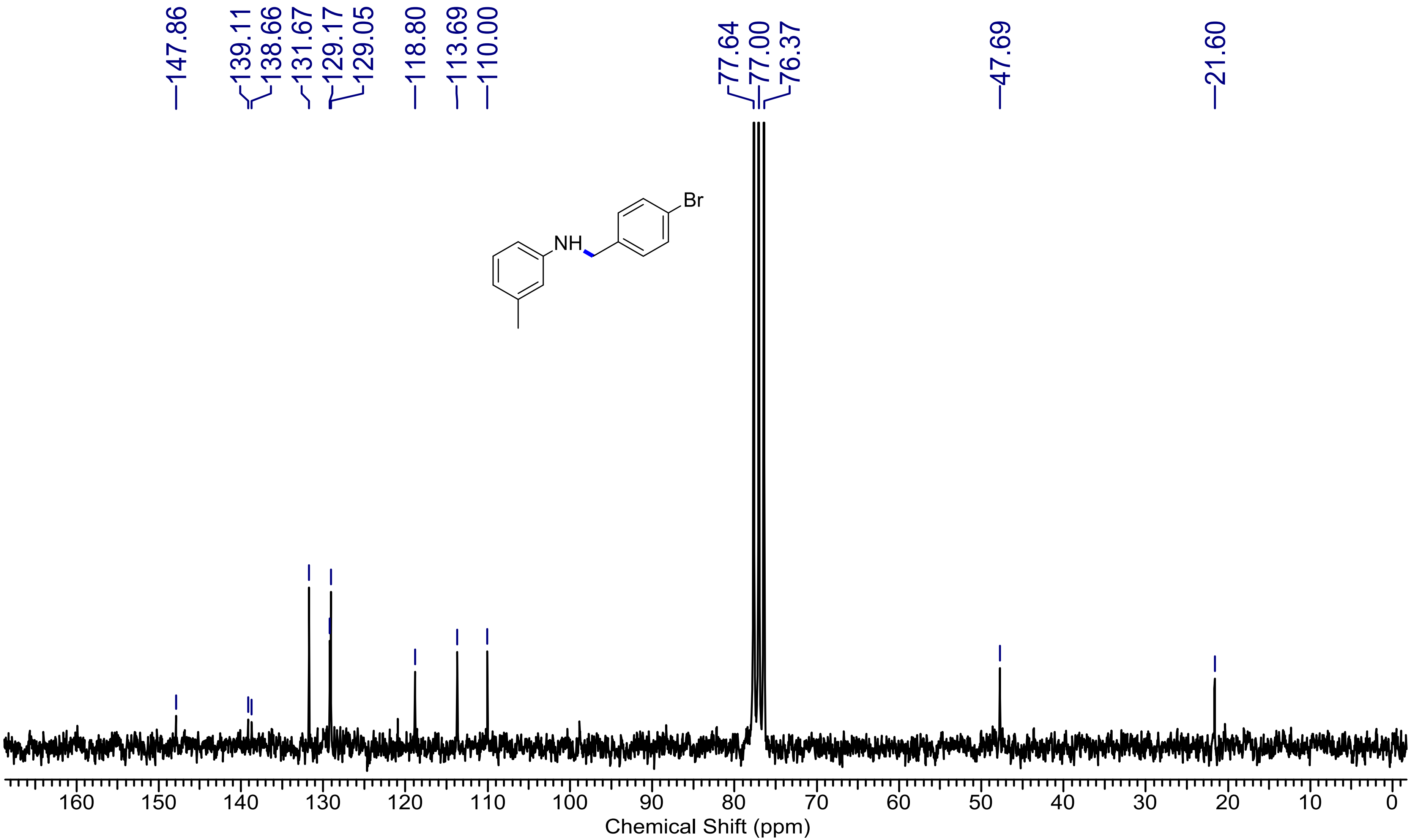


Figure S20. ^{13}C of **5d**

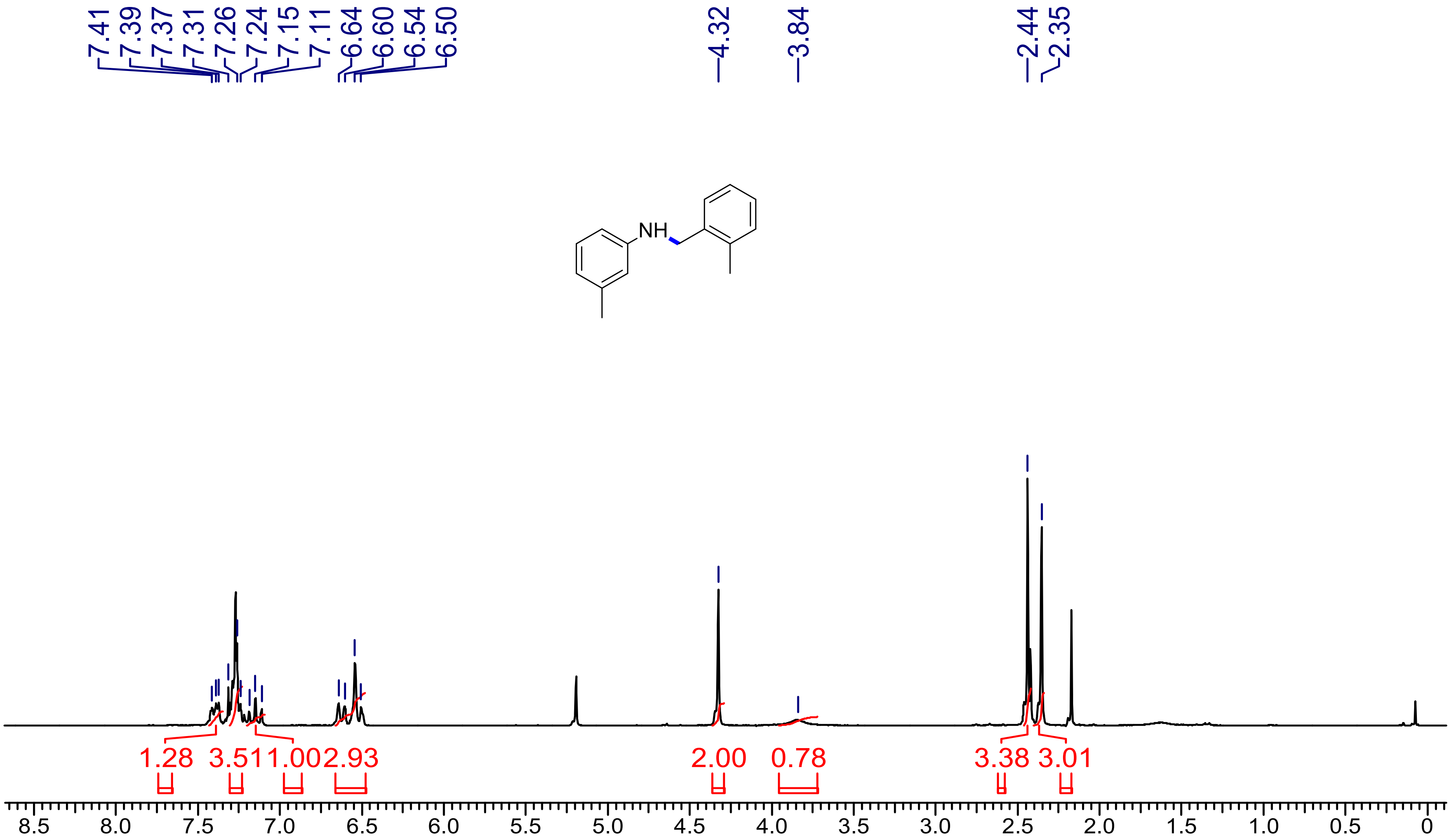


Figure S21. ^{1}H of **5e**

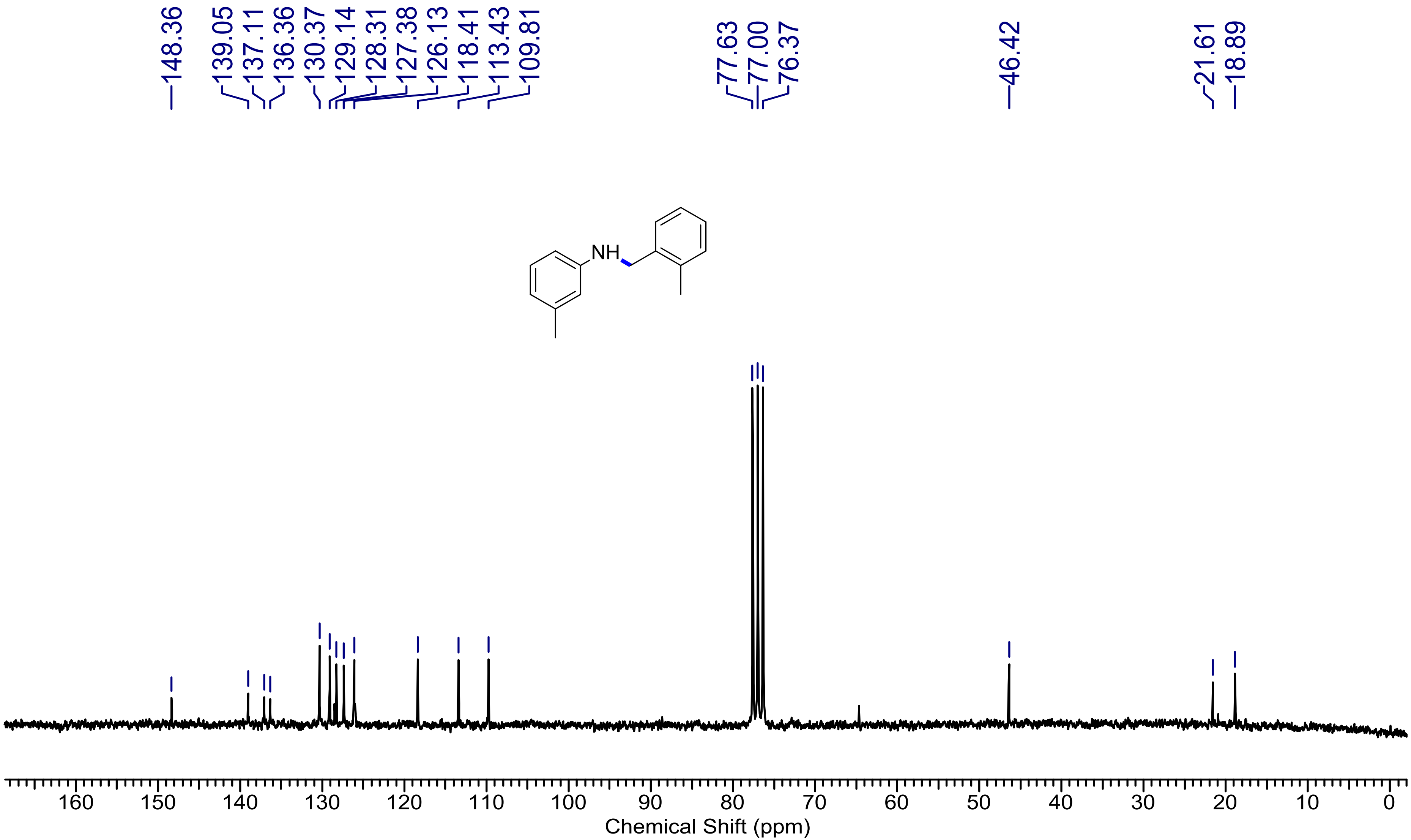


Figure S22. ^{13}C of **5e**

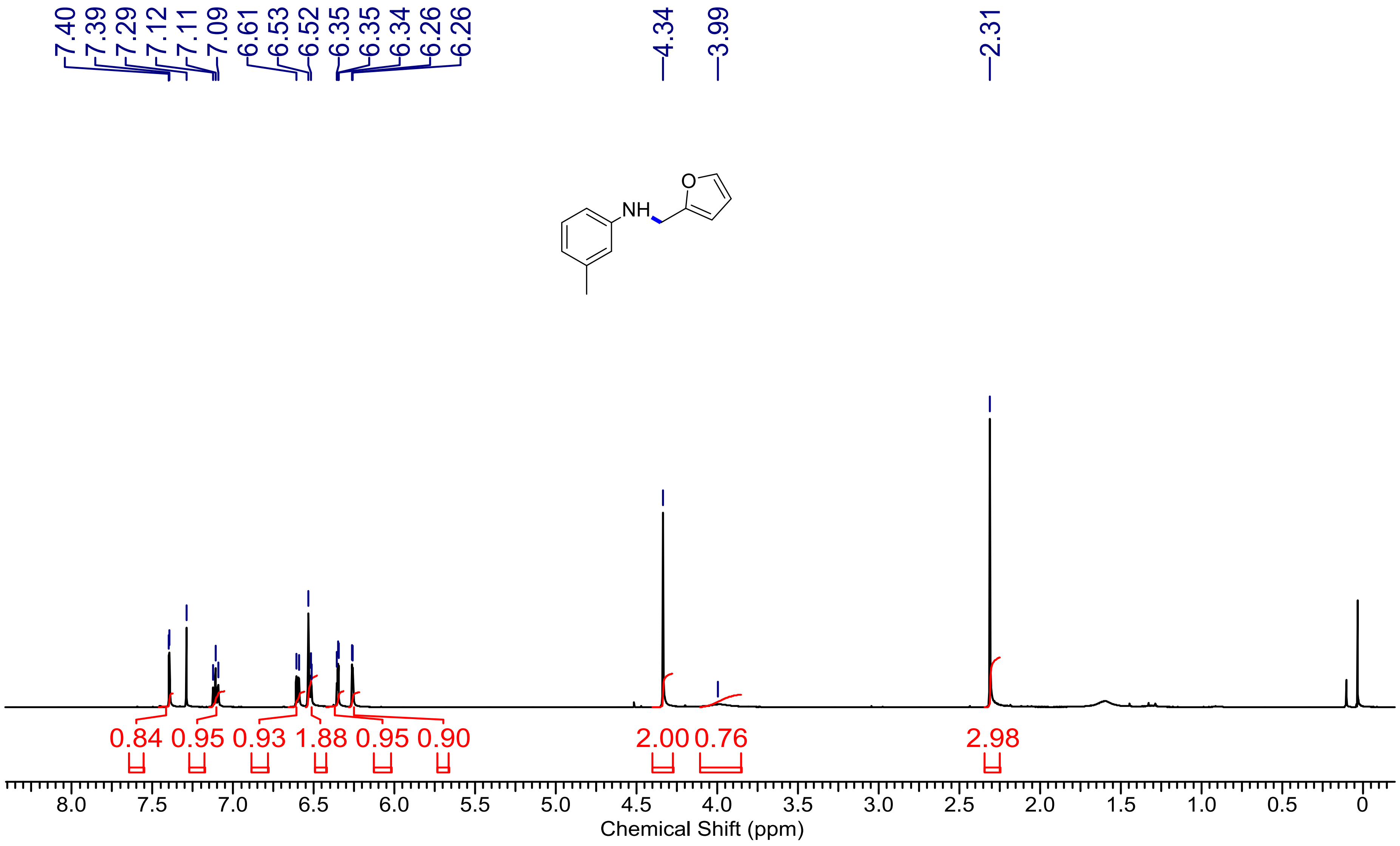


Figure S23. ^{1}H of **5f**

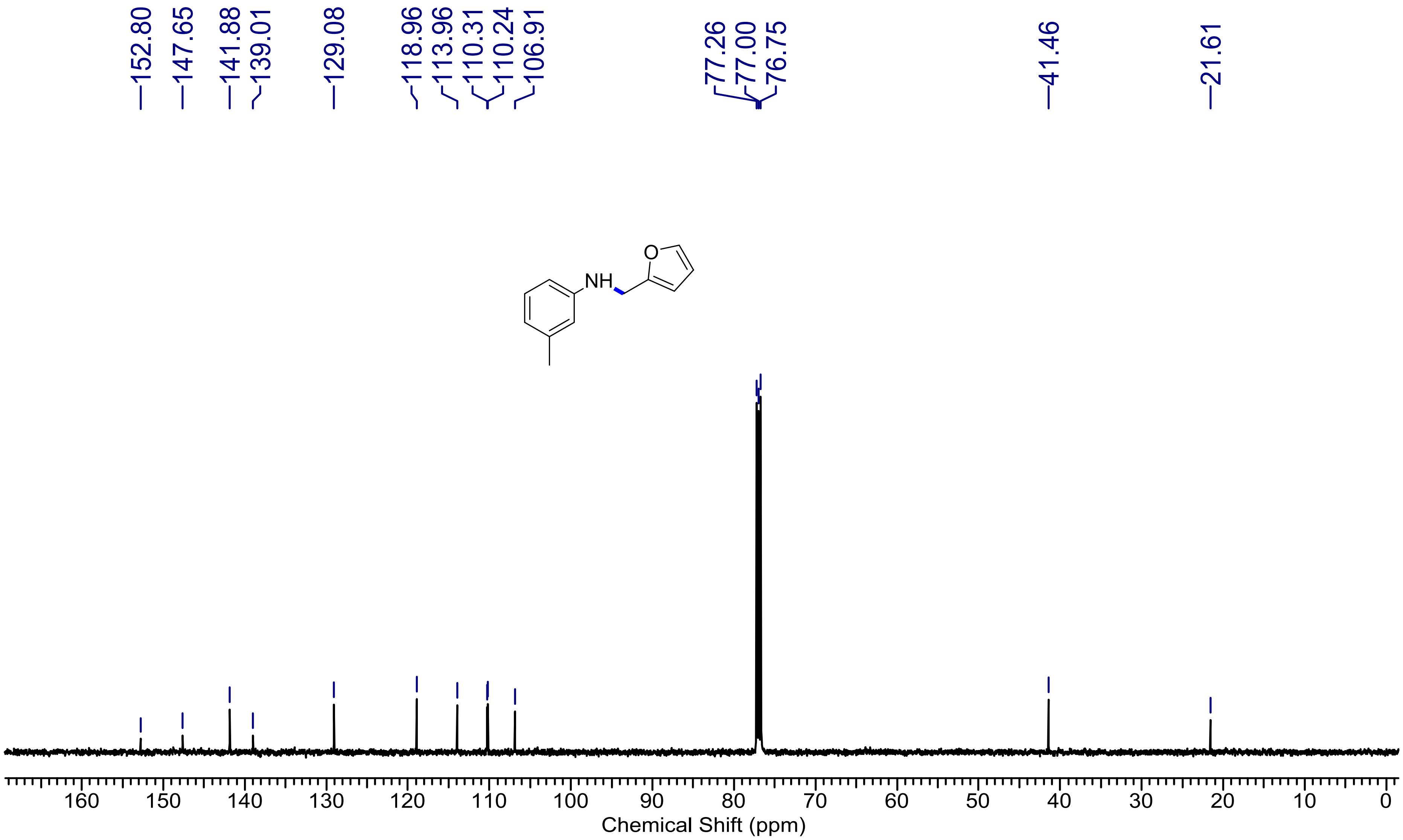

152.80
147.65
141.88
139.01
129.08
118.96
113.96
110.31
110.24
106.91
77.26
77.00
76.75
41.46
21.61
NH
O
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
Chemical Shift (ppm)

Figure S24. ^{13}C of **5f**

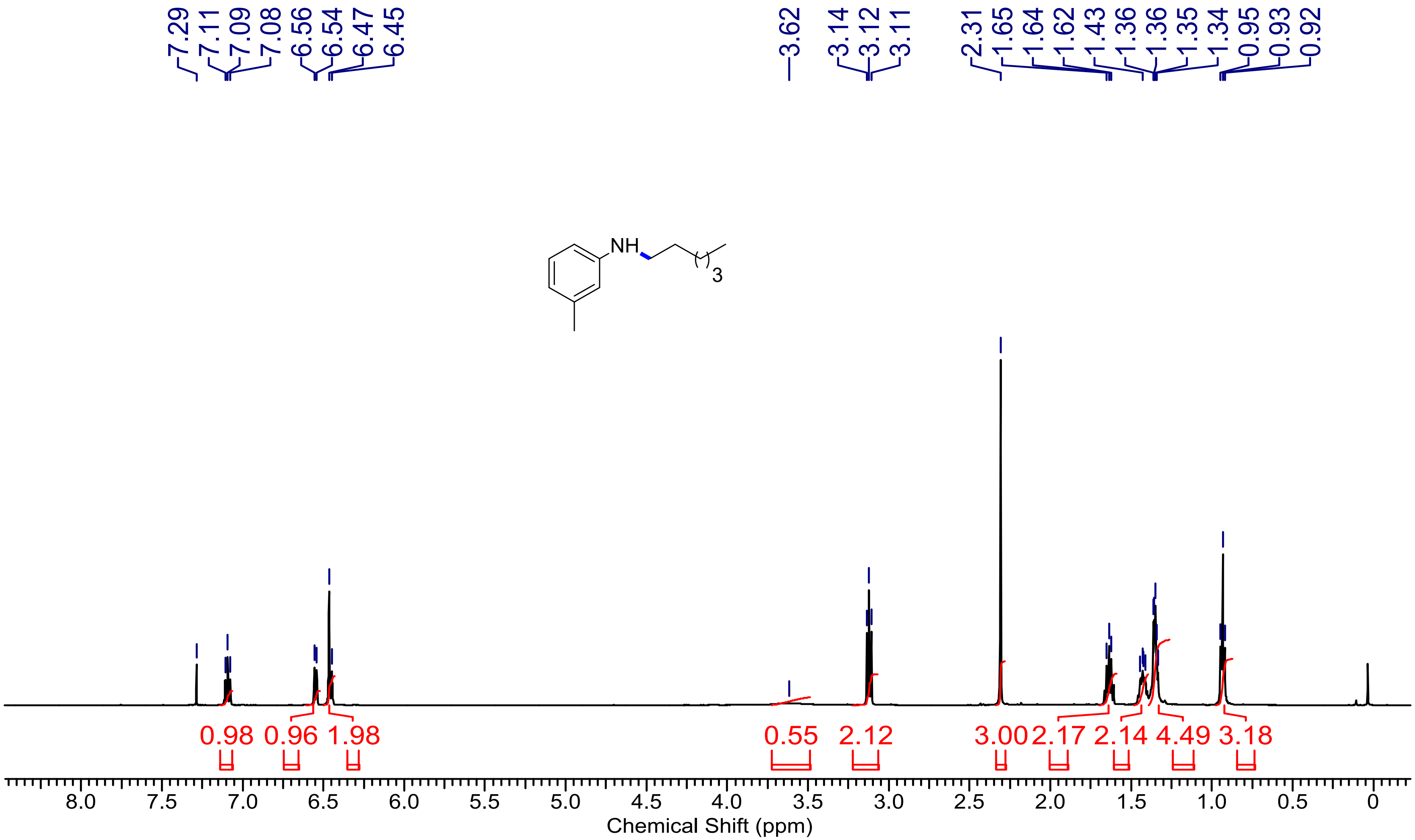


Figure S25. ^{1}H of **5g**

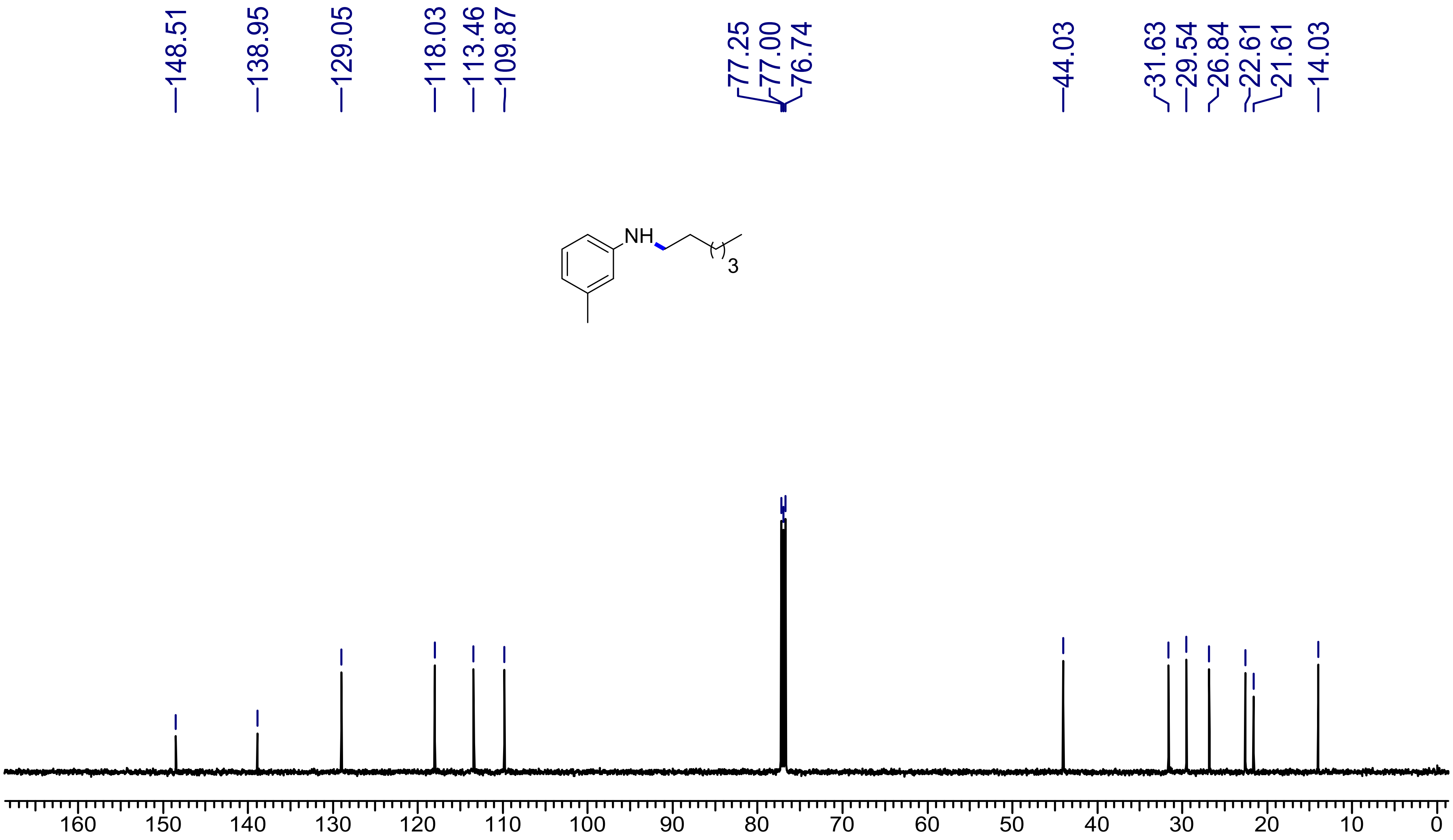


Figure S26. ^{13}C of **5g**

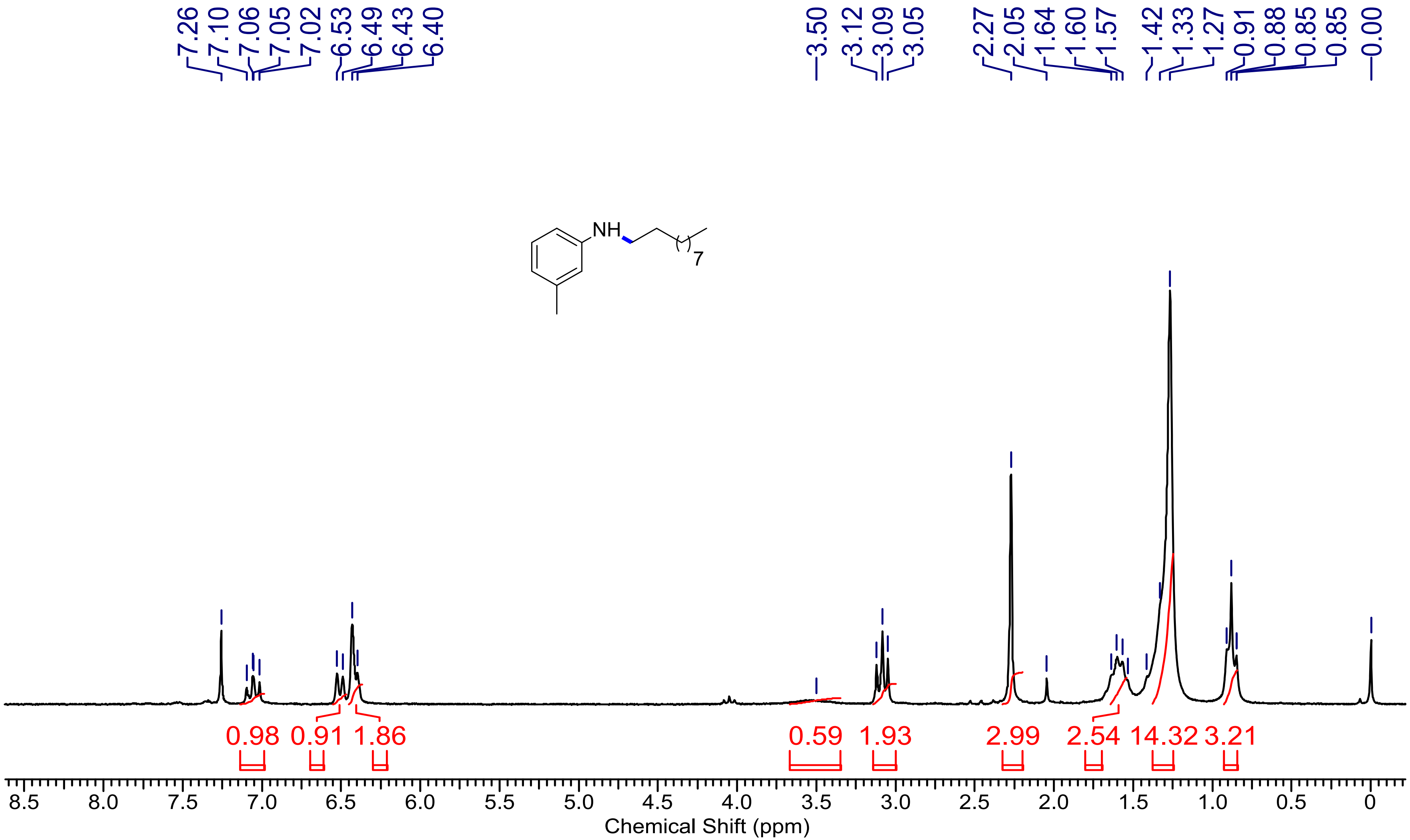


Figure S27. ^{1}H of **5h**

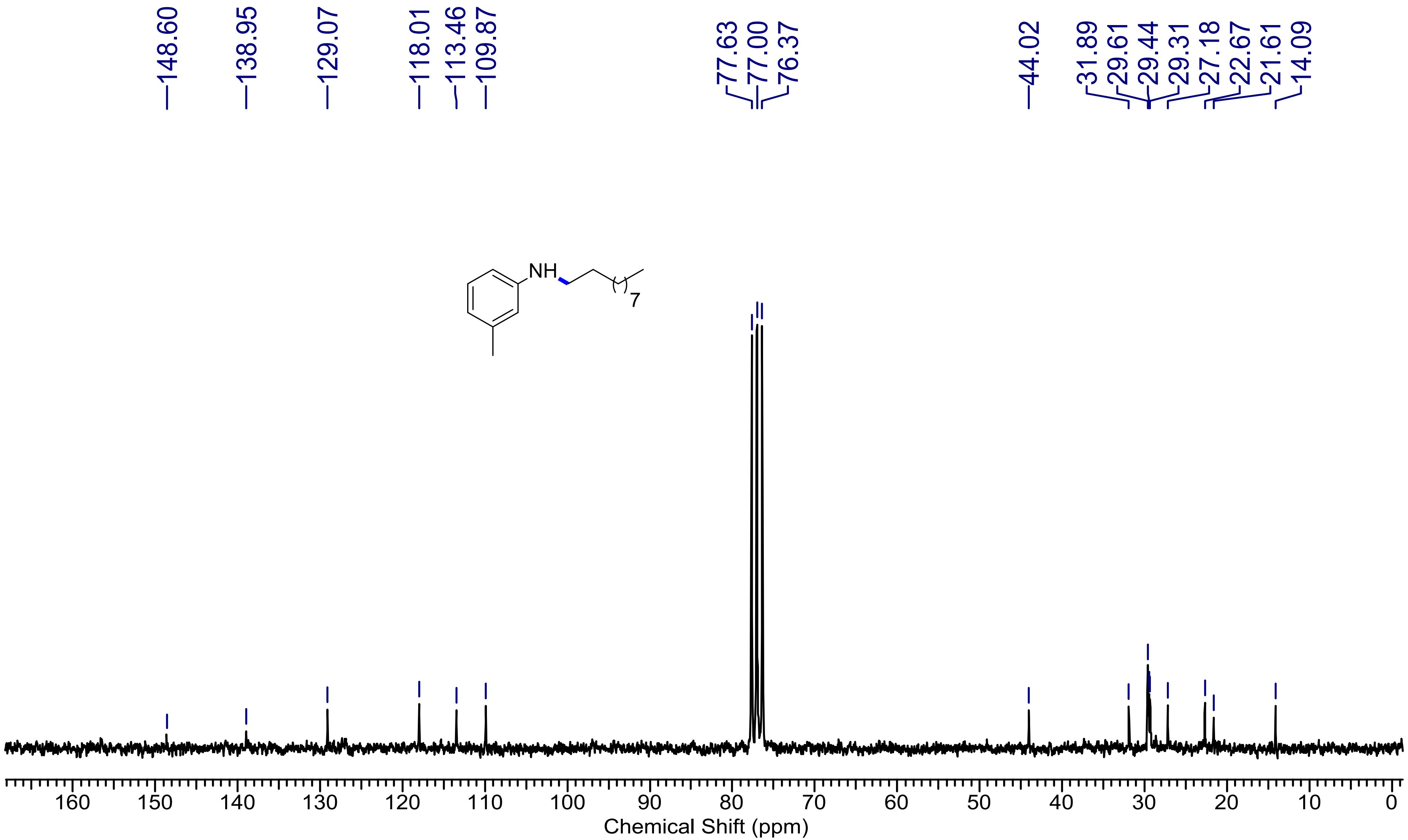


Figure S28. ^{13}C of **5h**

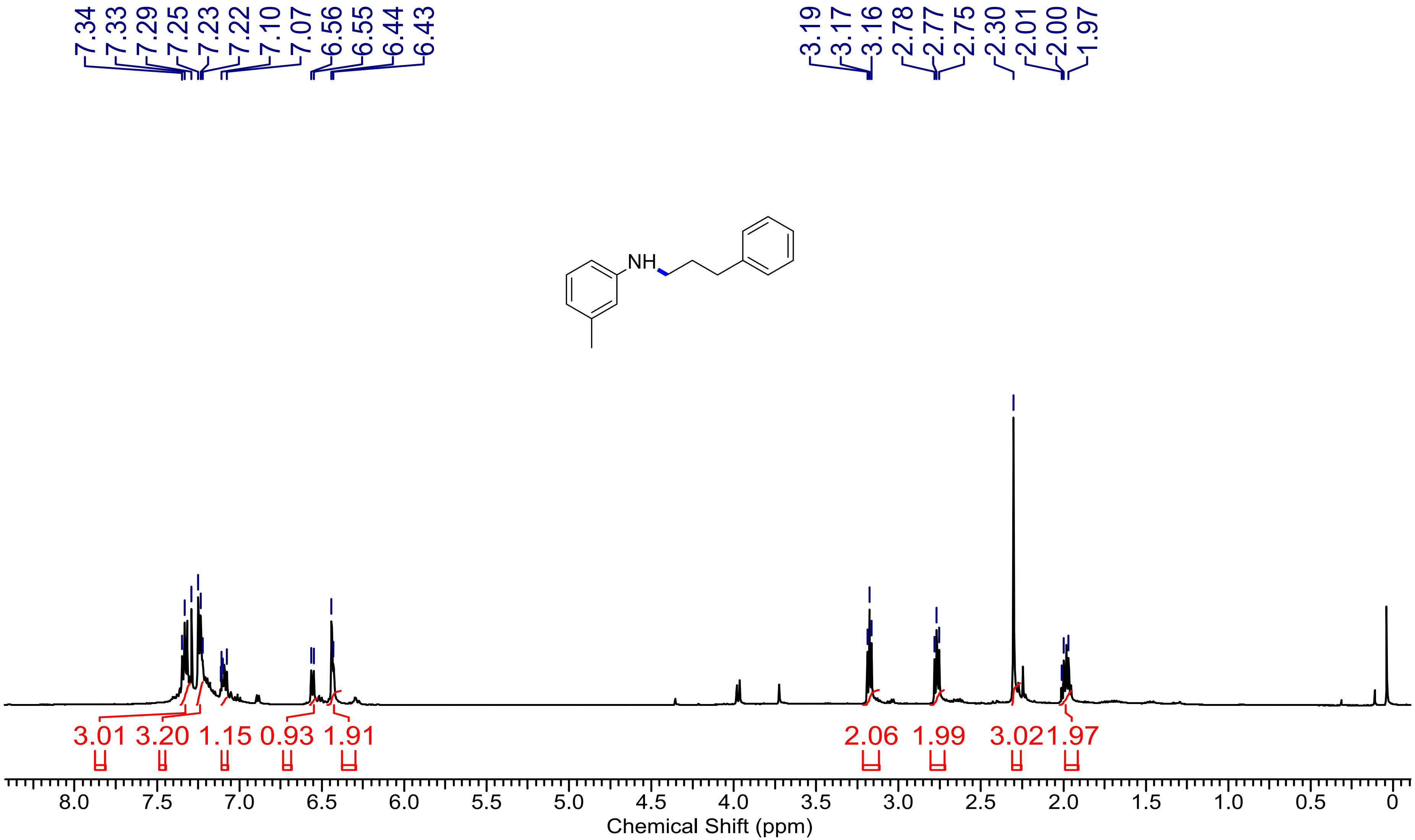


Figure S29. ^{1}H of **5i**

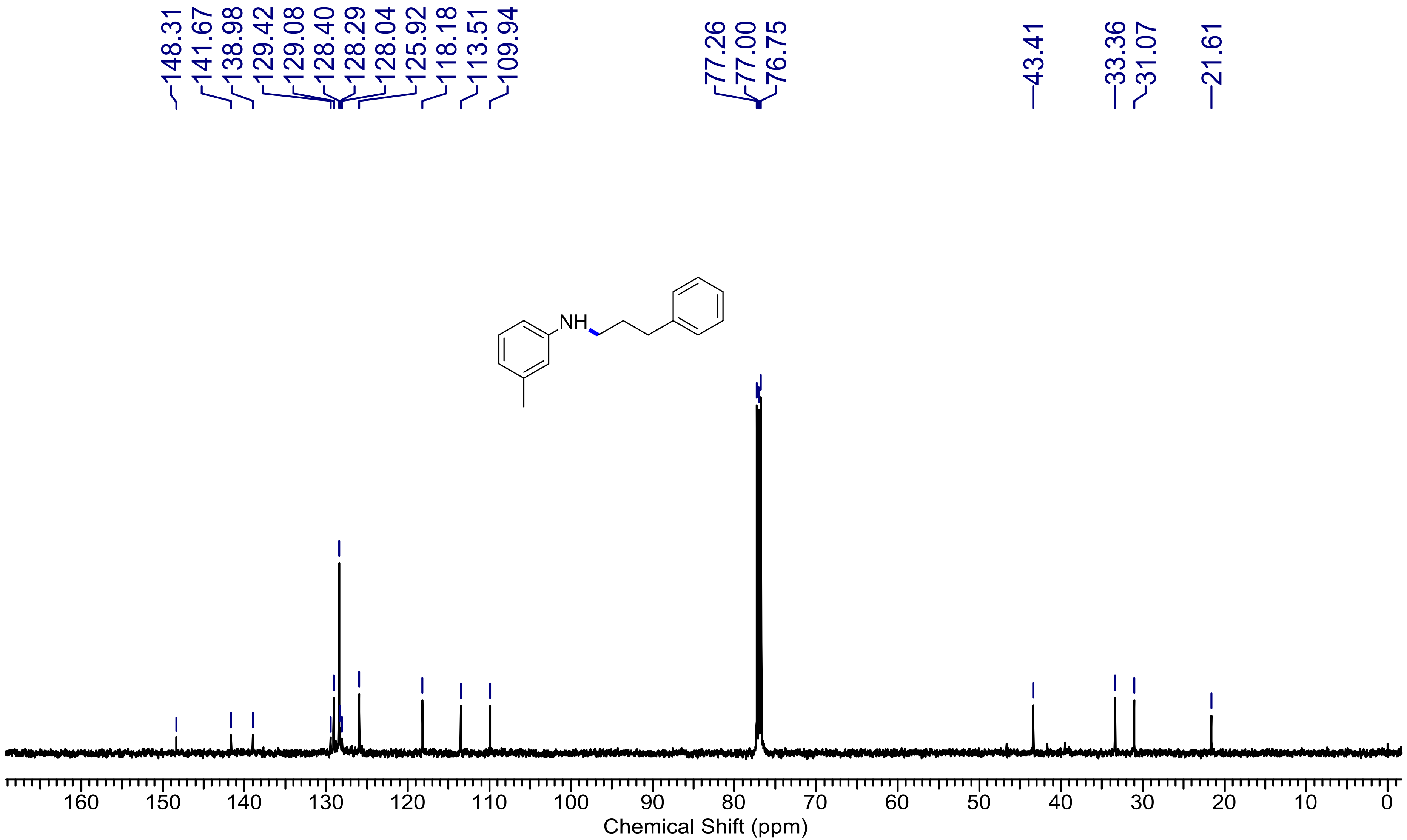


Figure S30. ^{13}C of **5i**

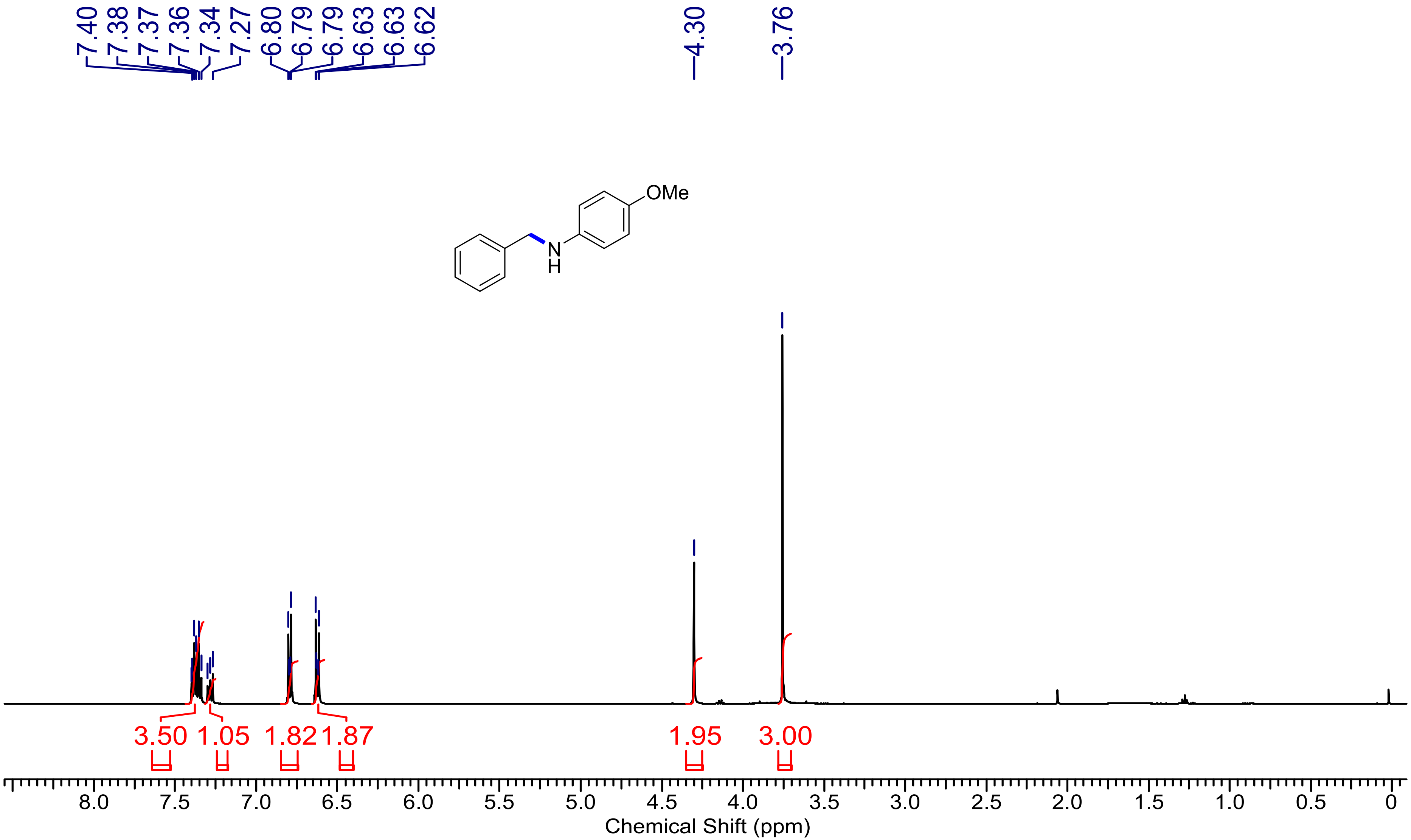


Figure S31. ^{1}H of **6a**

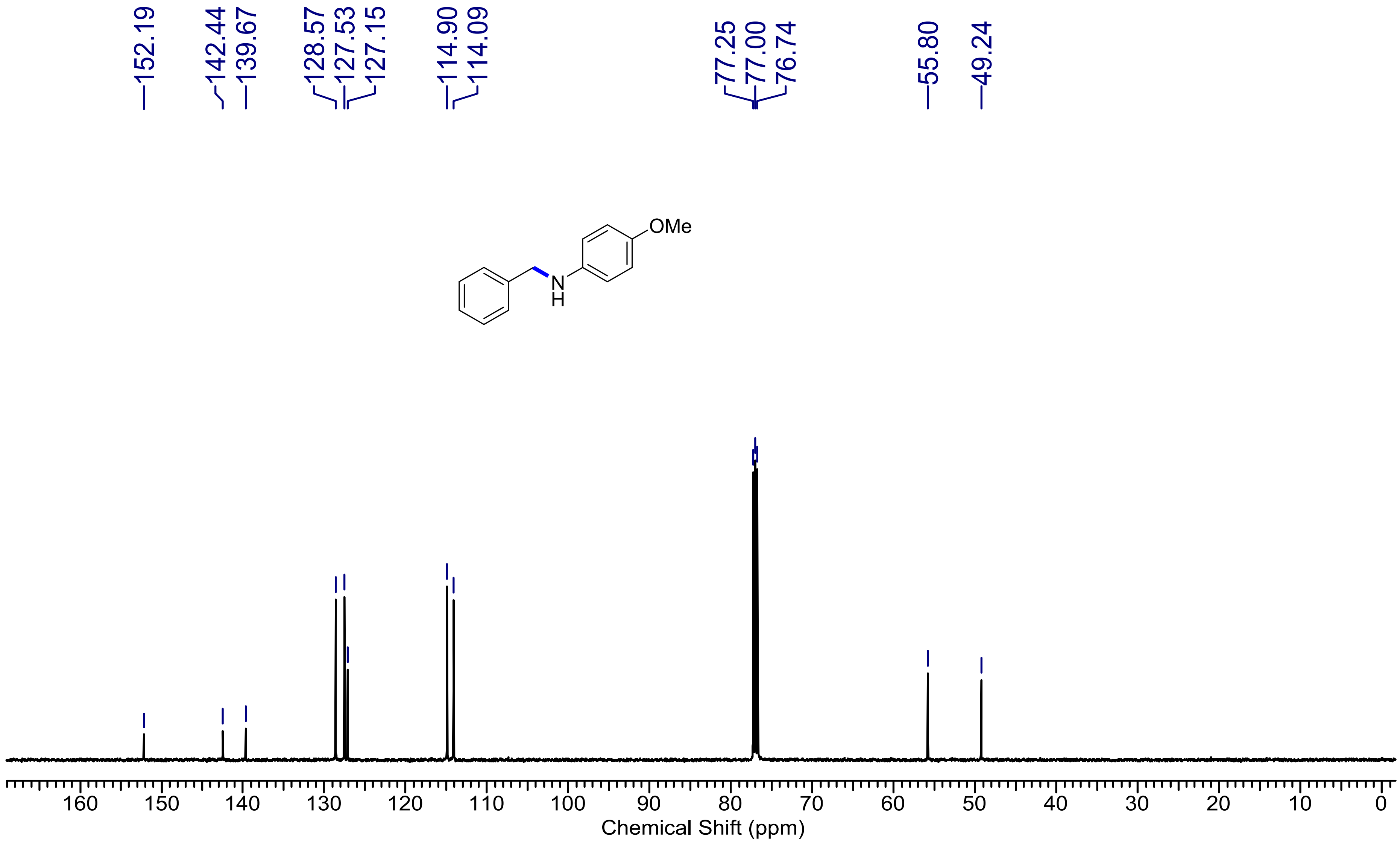


Figure S32. ^{13}C of **6a**

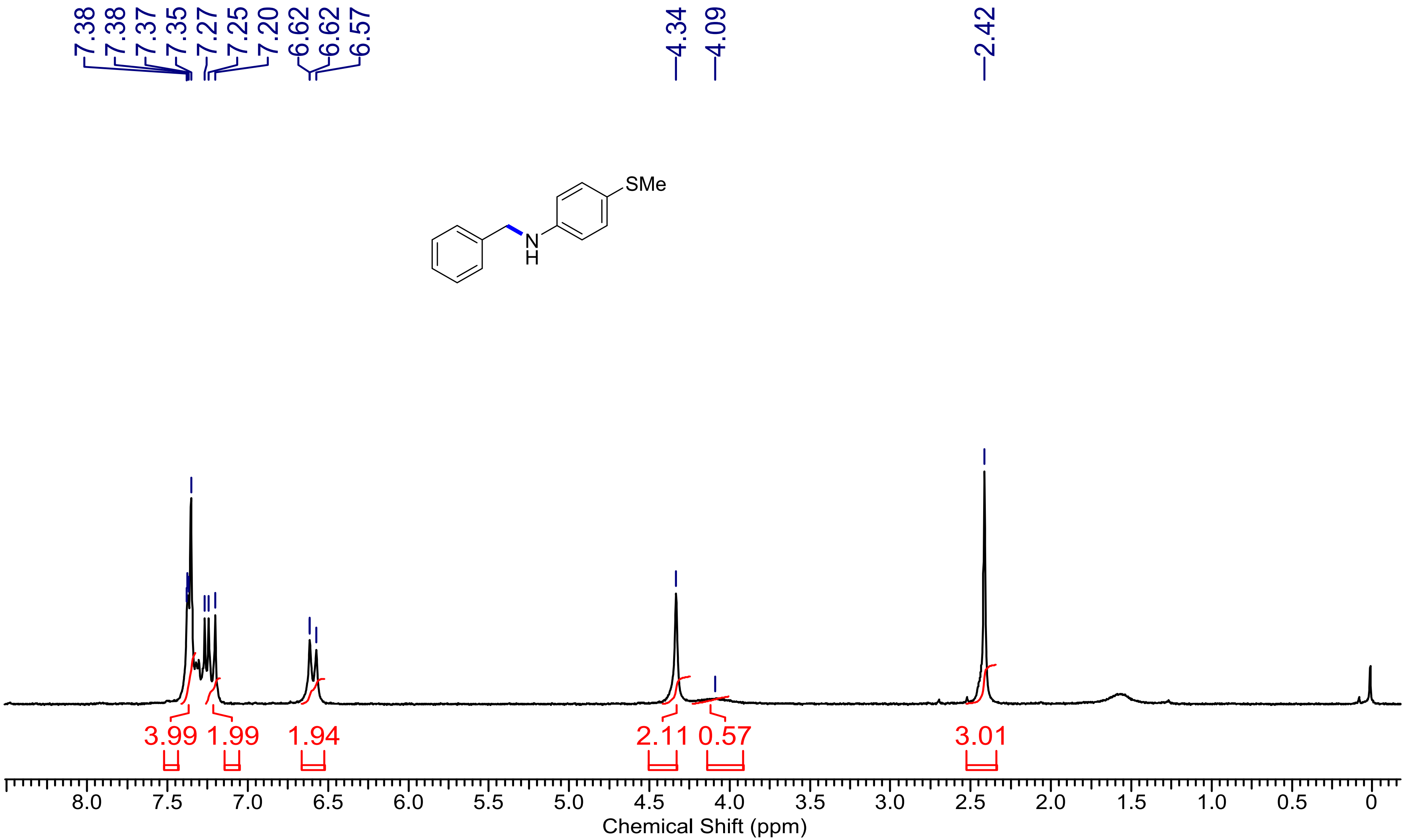


Figure S33. ^{1}H of **6b**

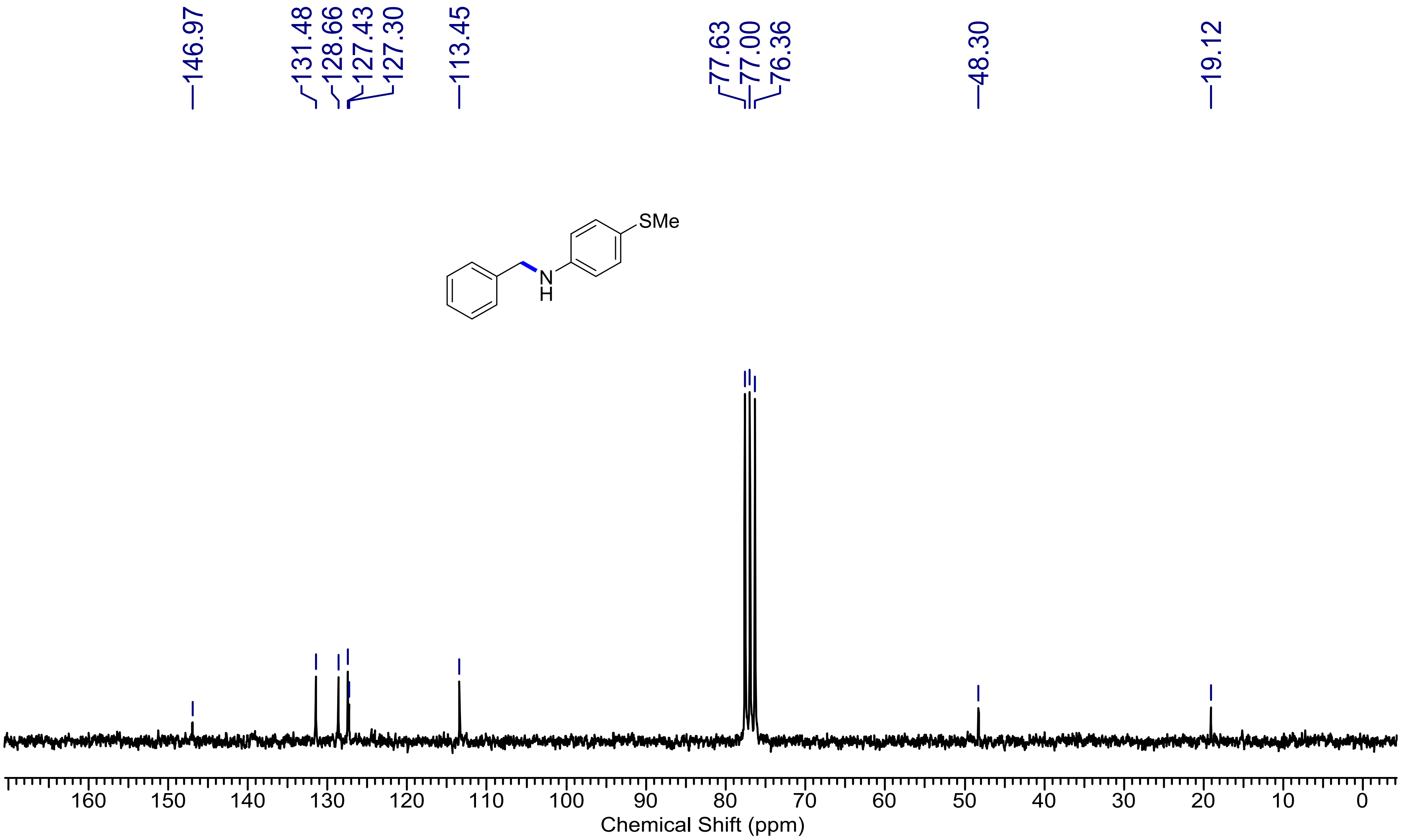


Figure S34. ^{13}C of **6b**

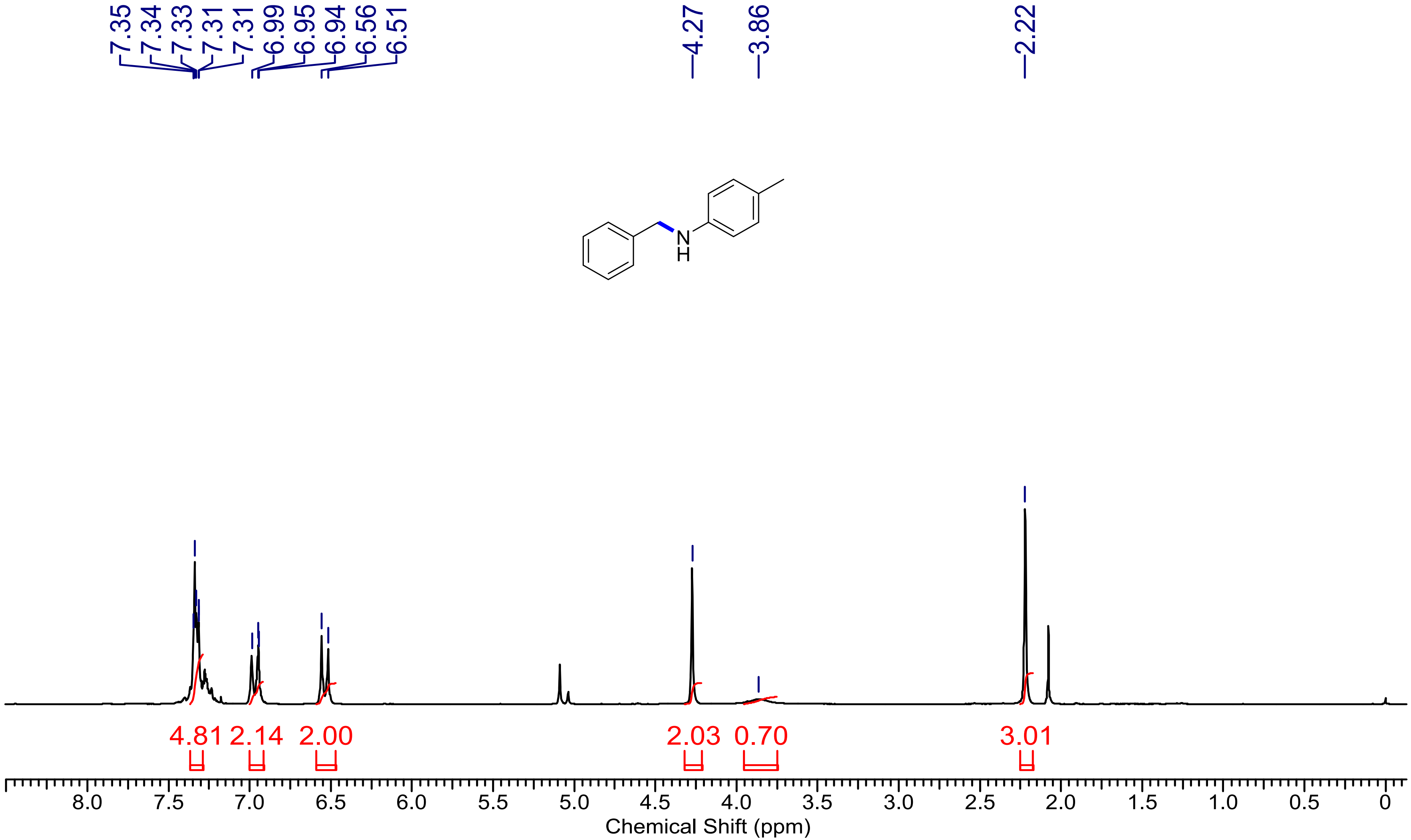


Figure S35. ^{1}H of **6c**

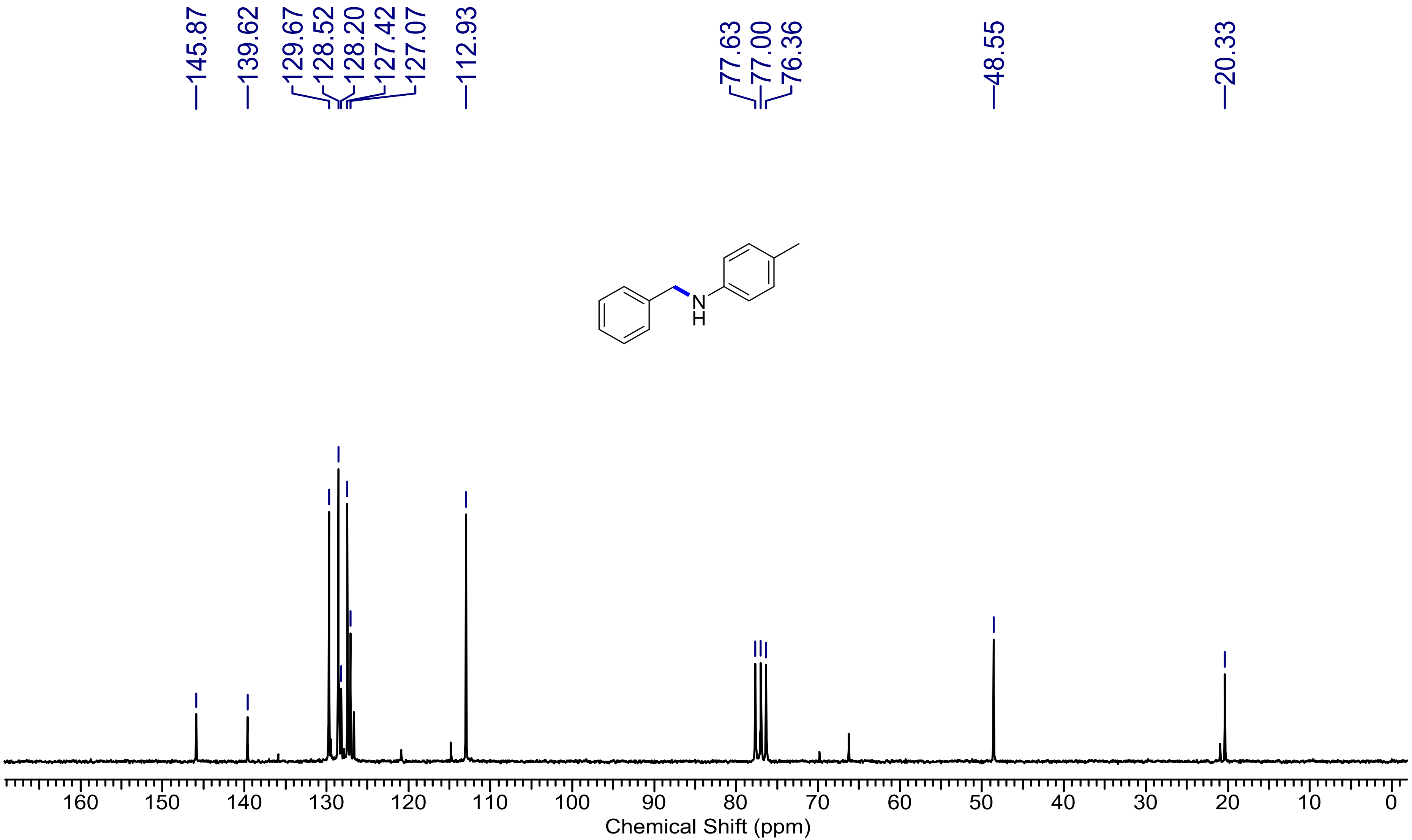


Figure S36. ^{13}C of **6c**

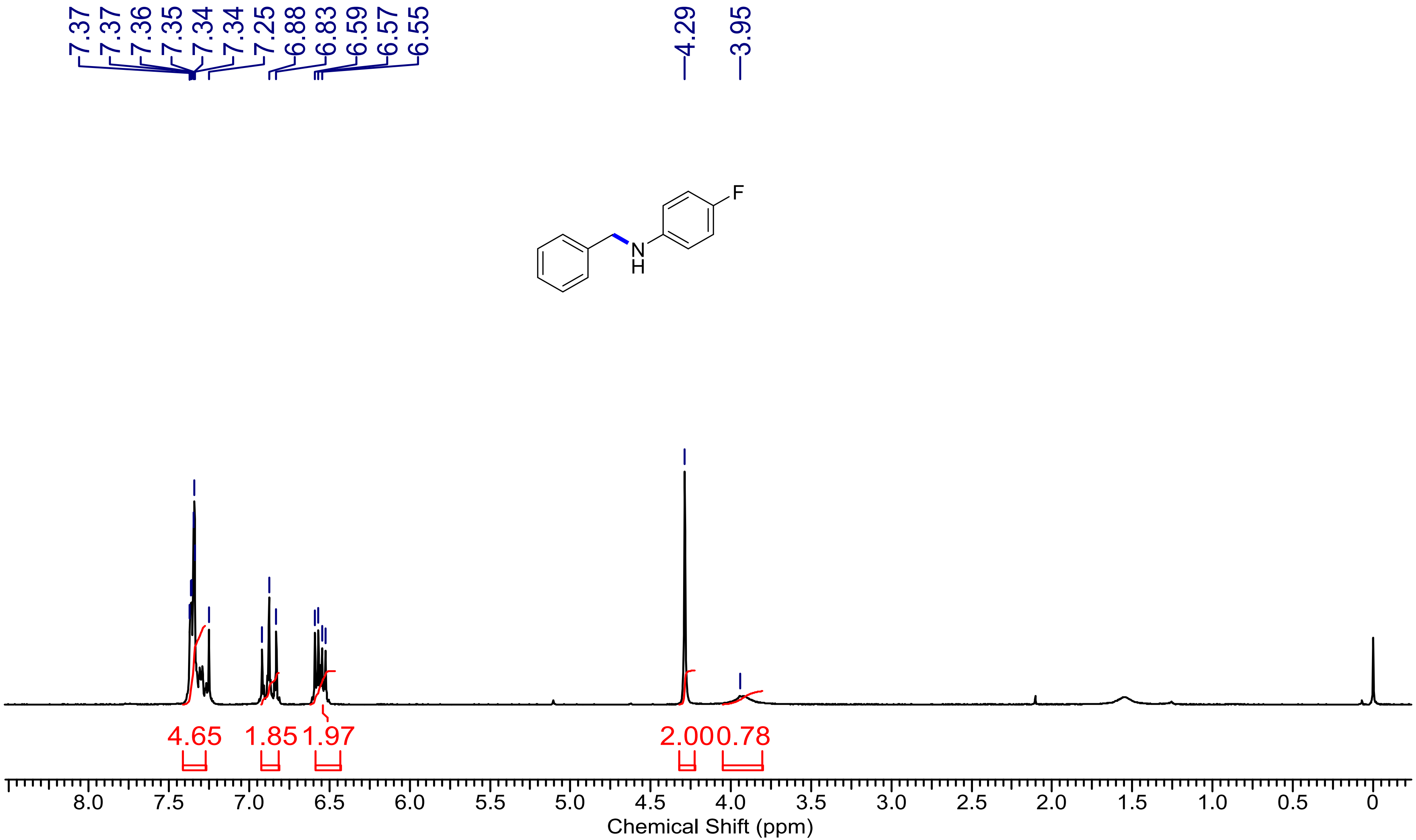


Figure S37. ^{1}H of **6d**

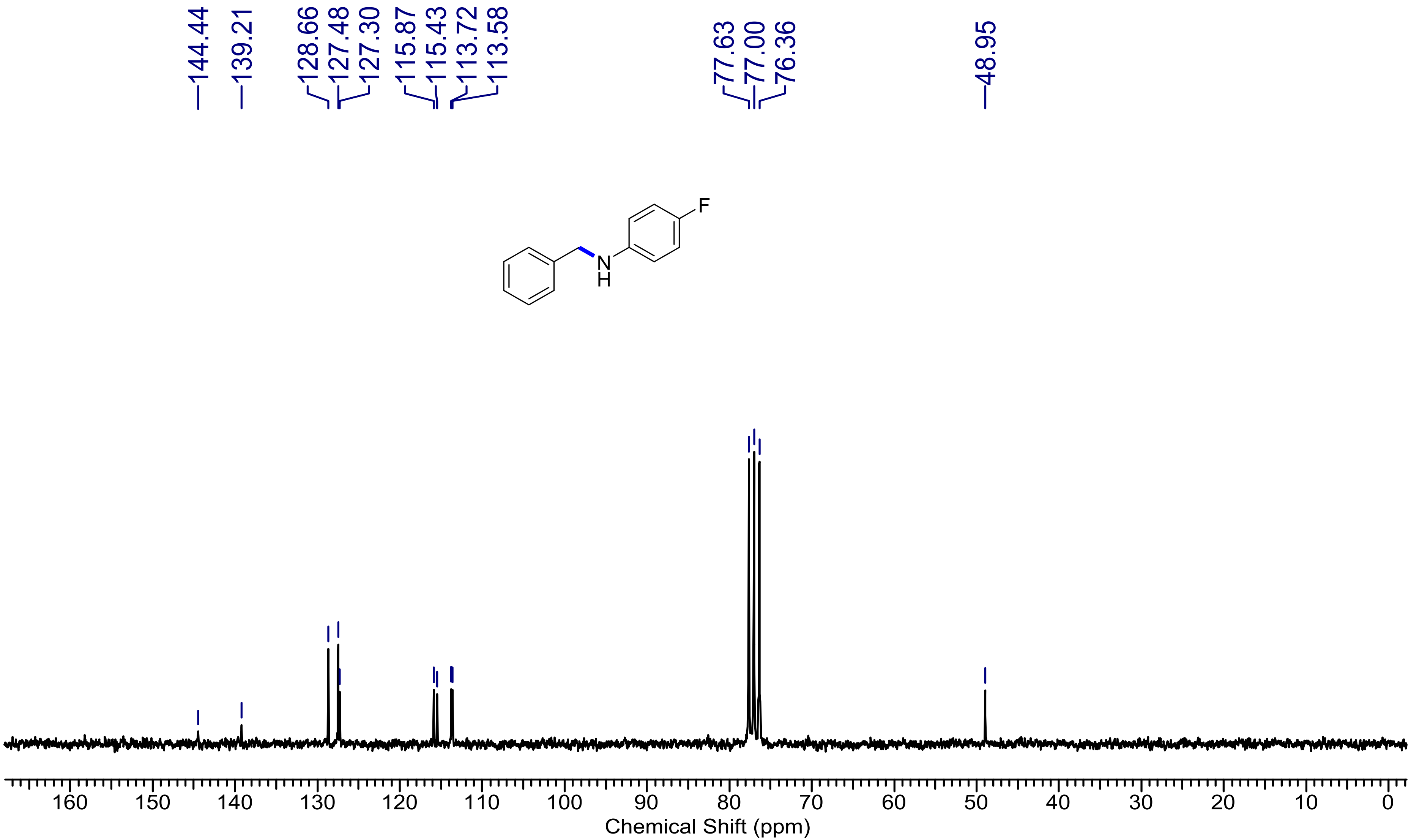


Figure S38. ^{13}C of **6d**

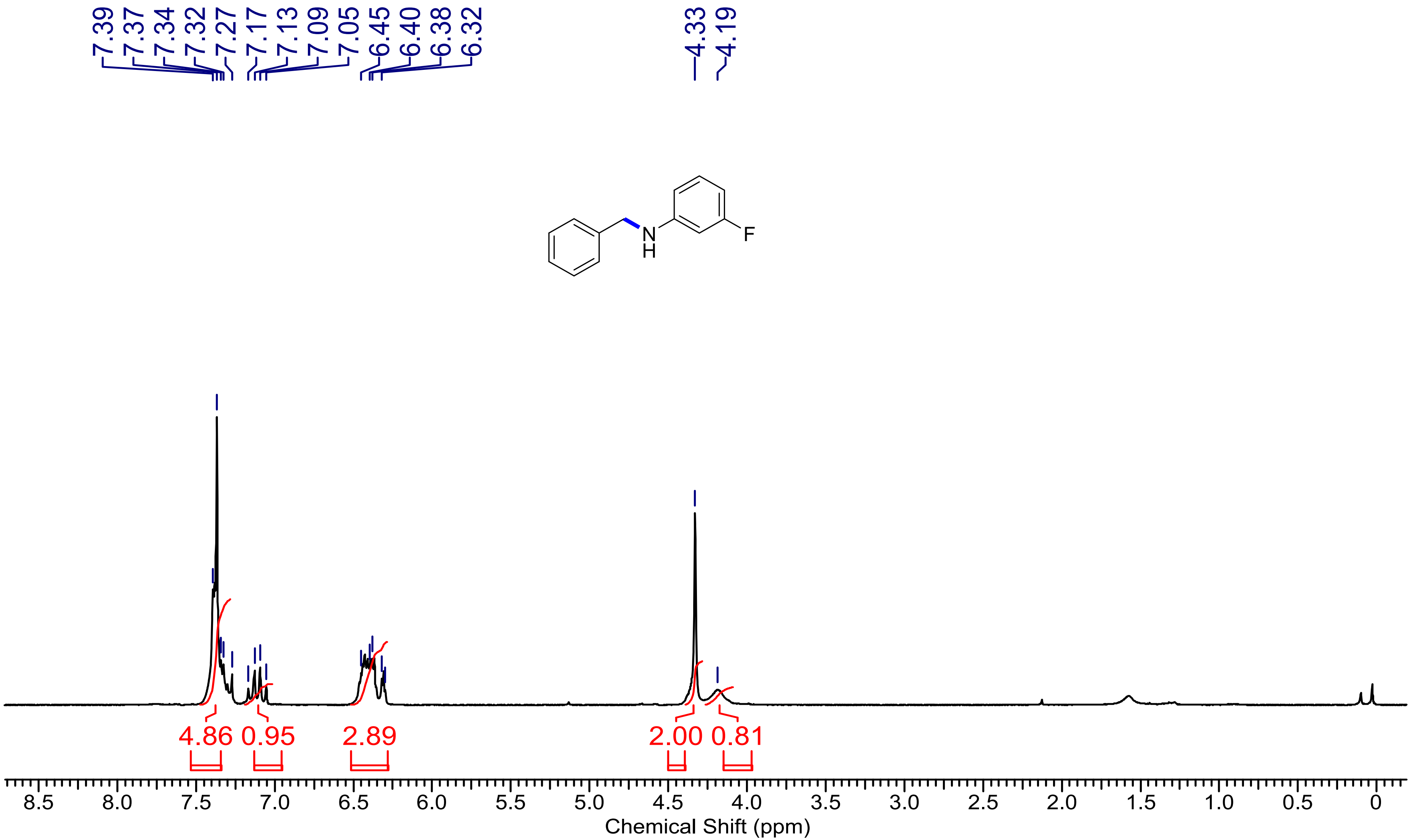


Figure S39. ^{1}H of **6e**

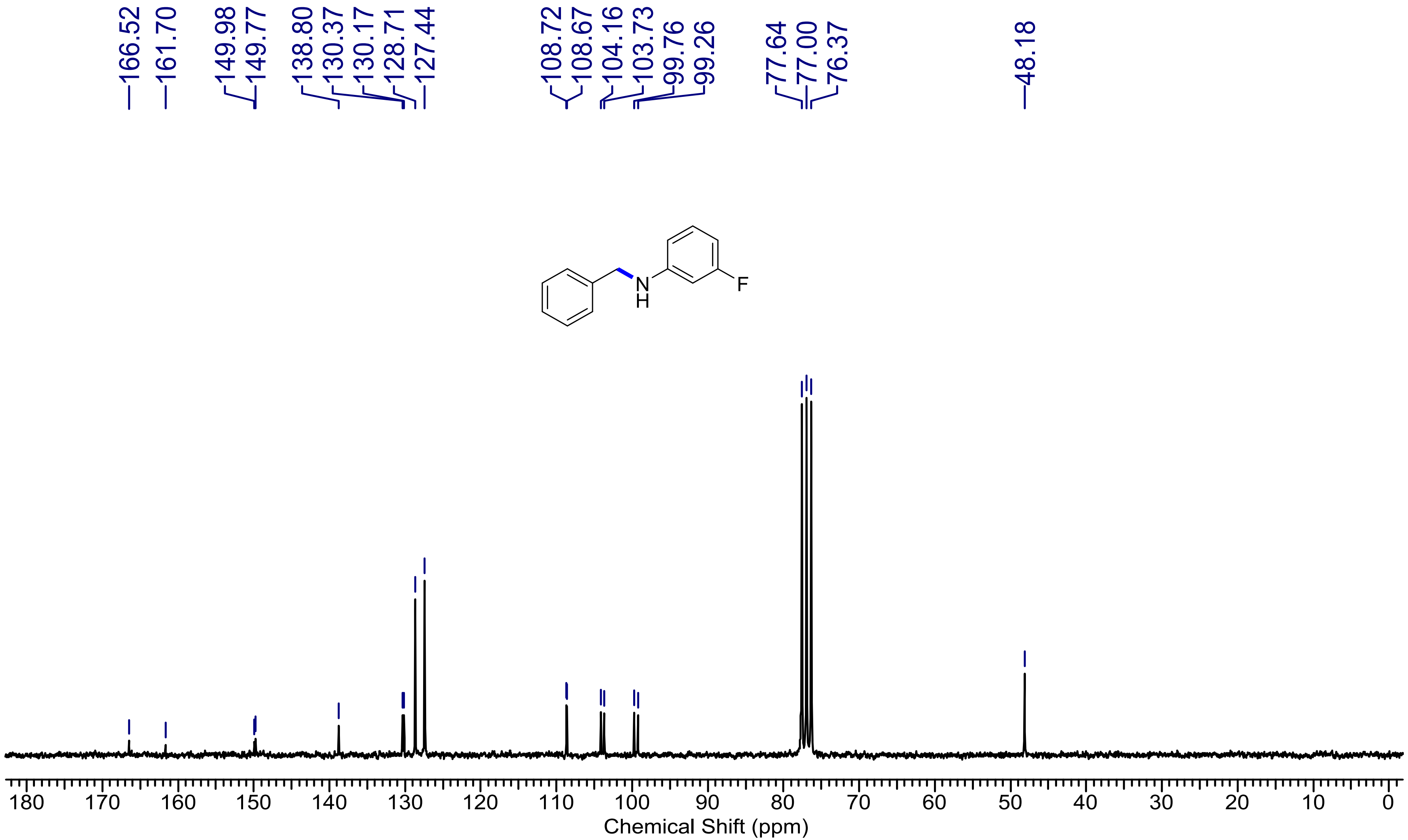


Figure S40. ^{13}C of **6e**

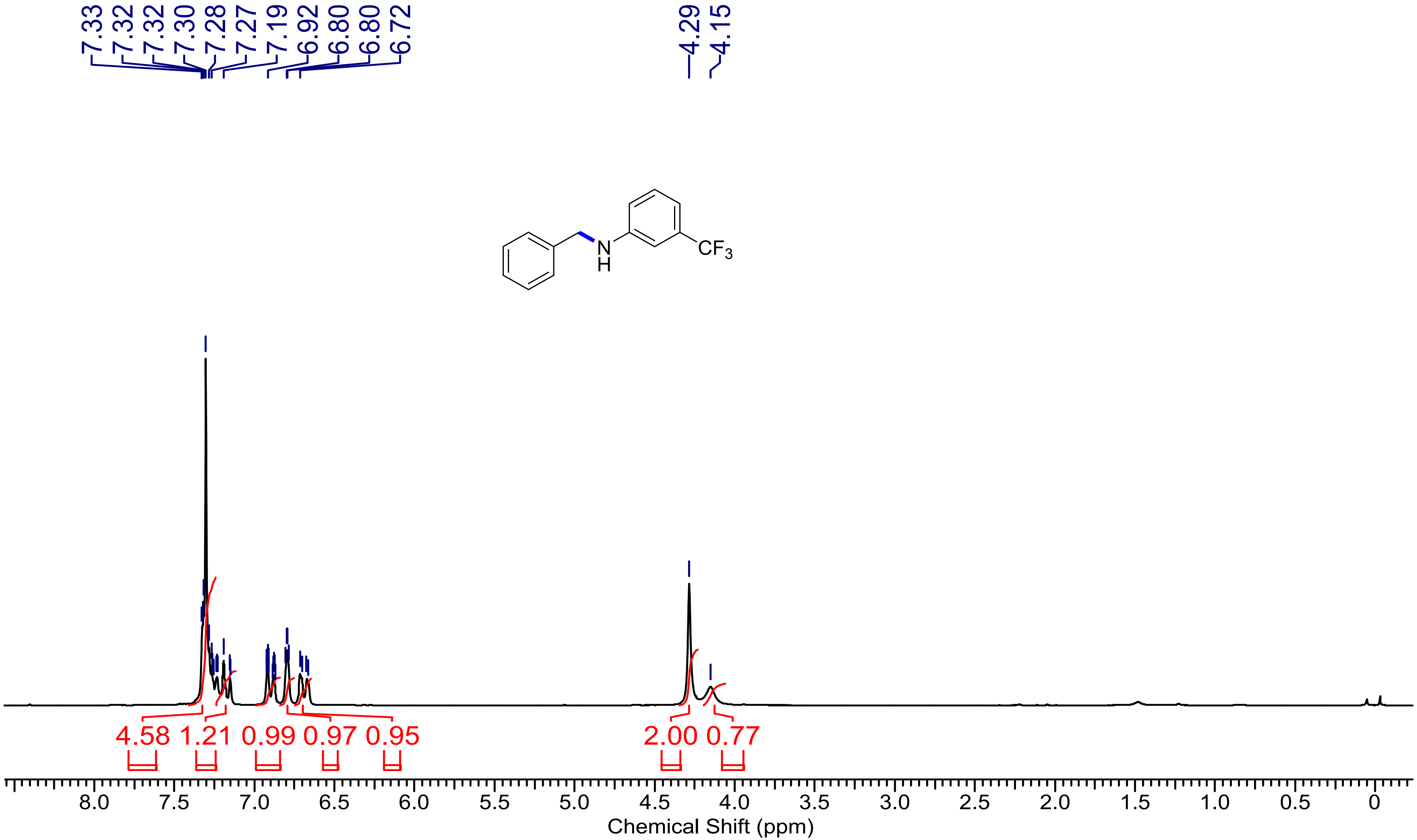


Figure S41. ^{1}H of **6f**

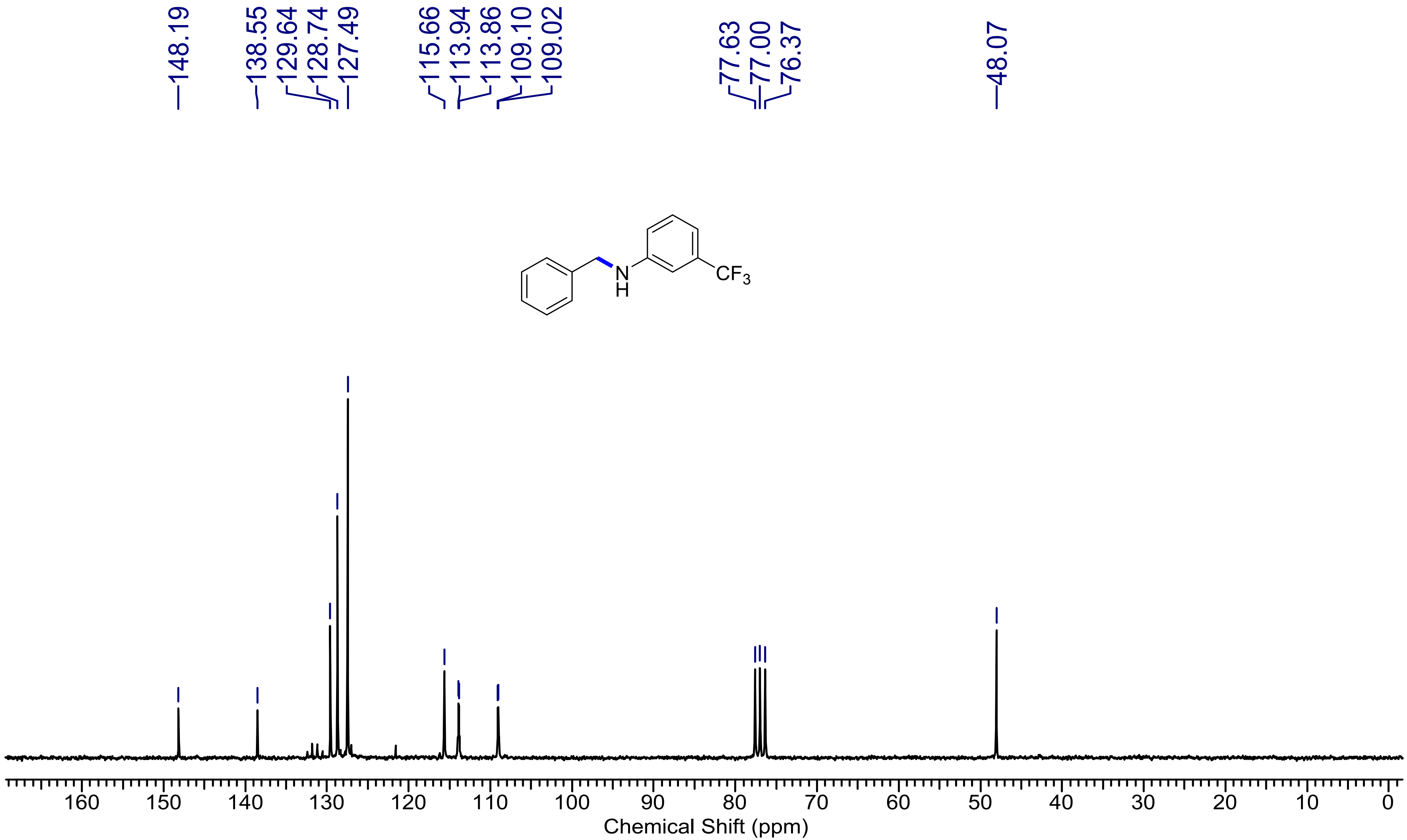


Figure S42. ^{13}C of **6f**

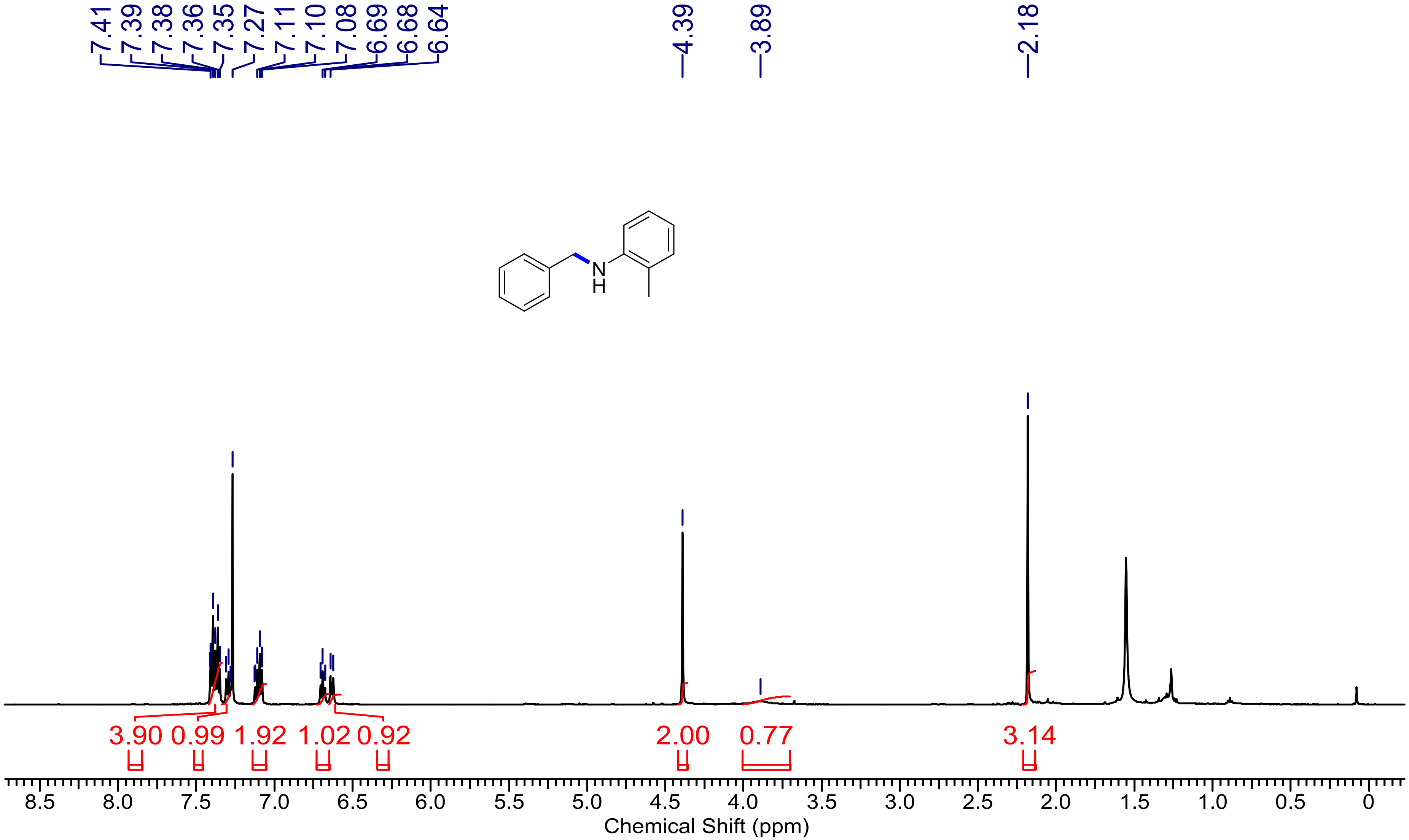


Figure S43. ^{1}H of **6g**

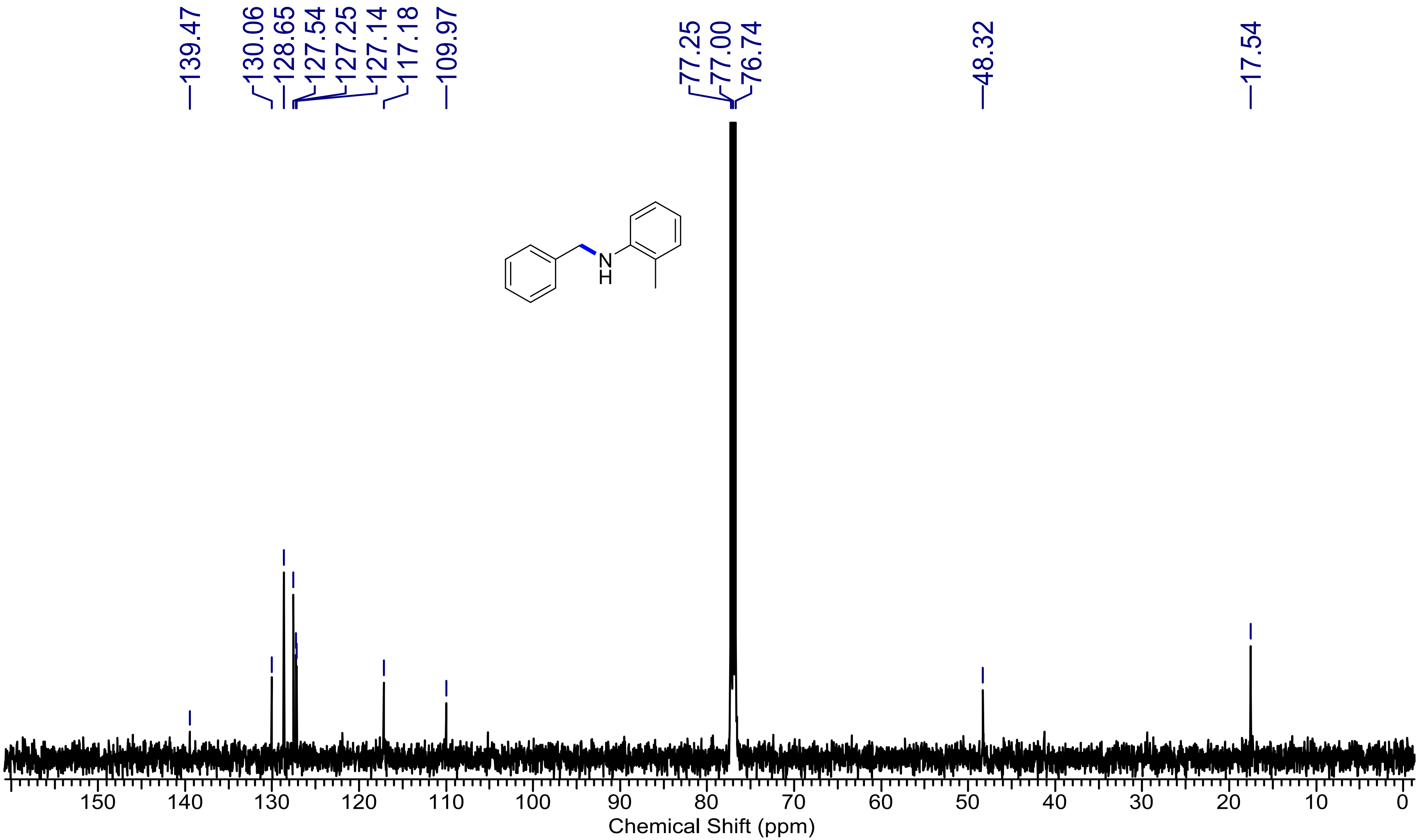


Figure S44. ^{13}C of **6g**

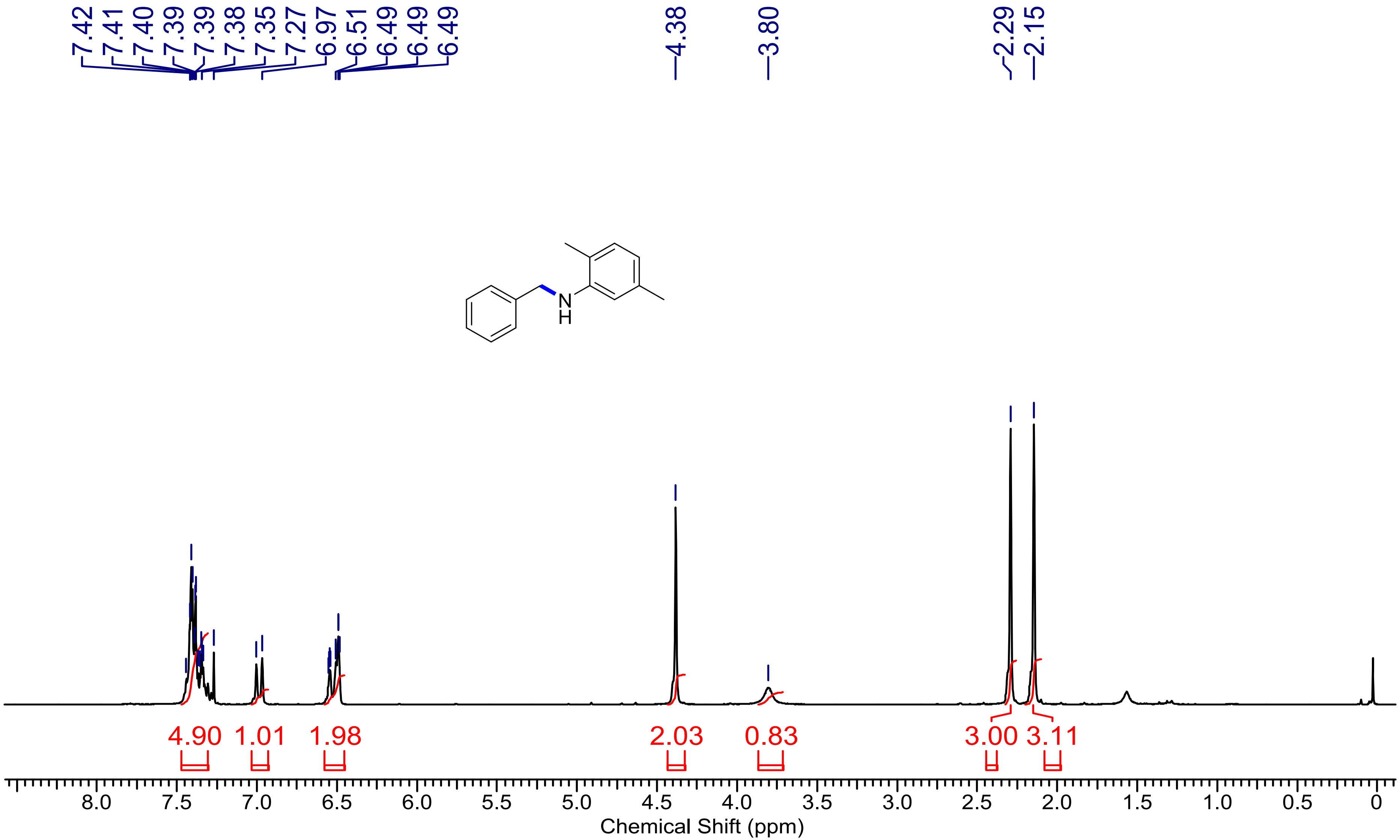


Figure S45. ^{1}H of **6h**

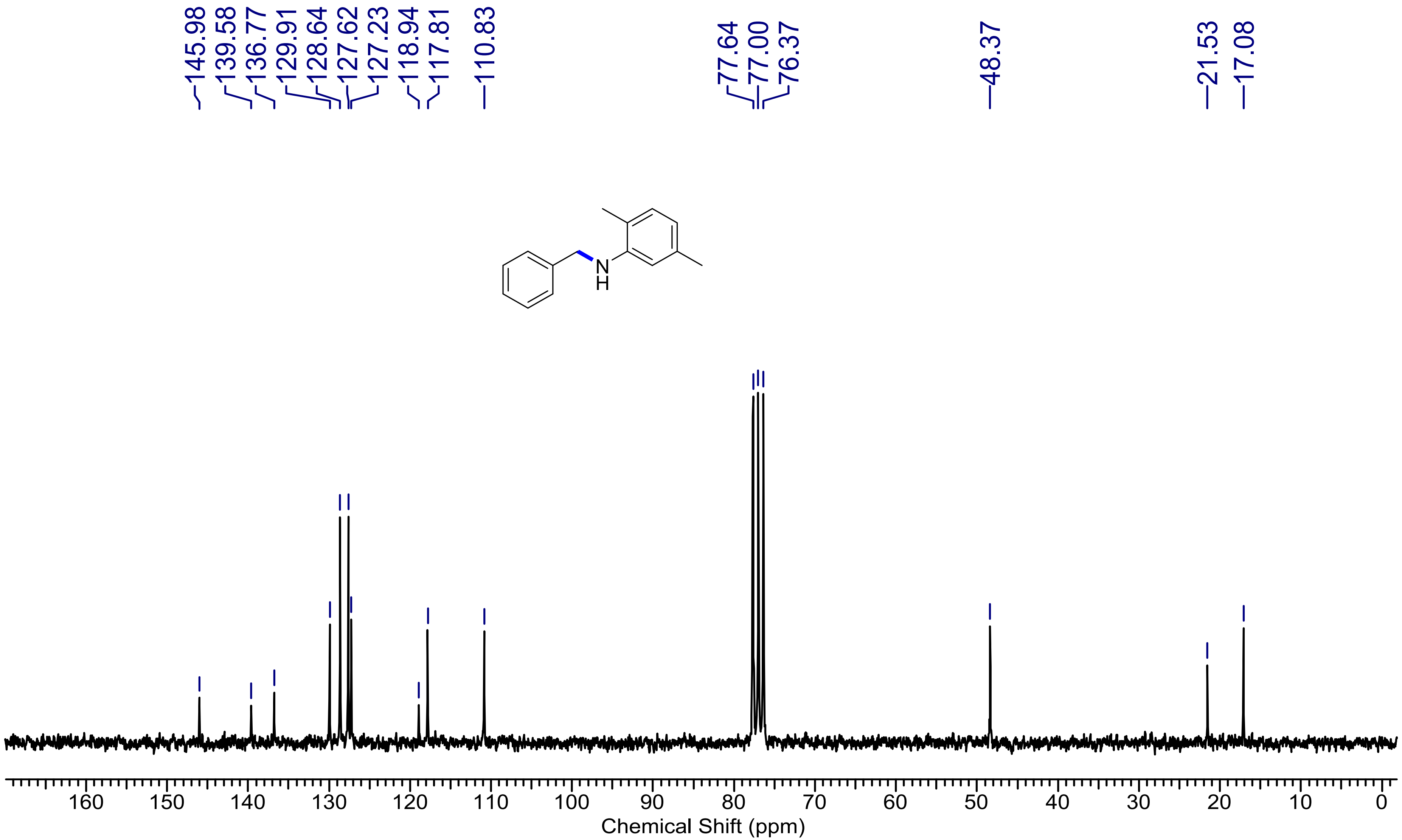


Figure S46. ^{13}C of **6h**

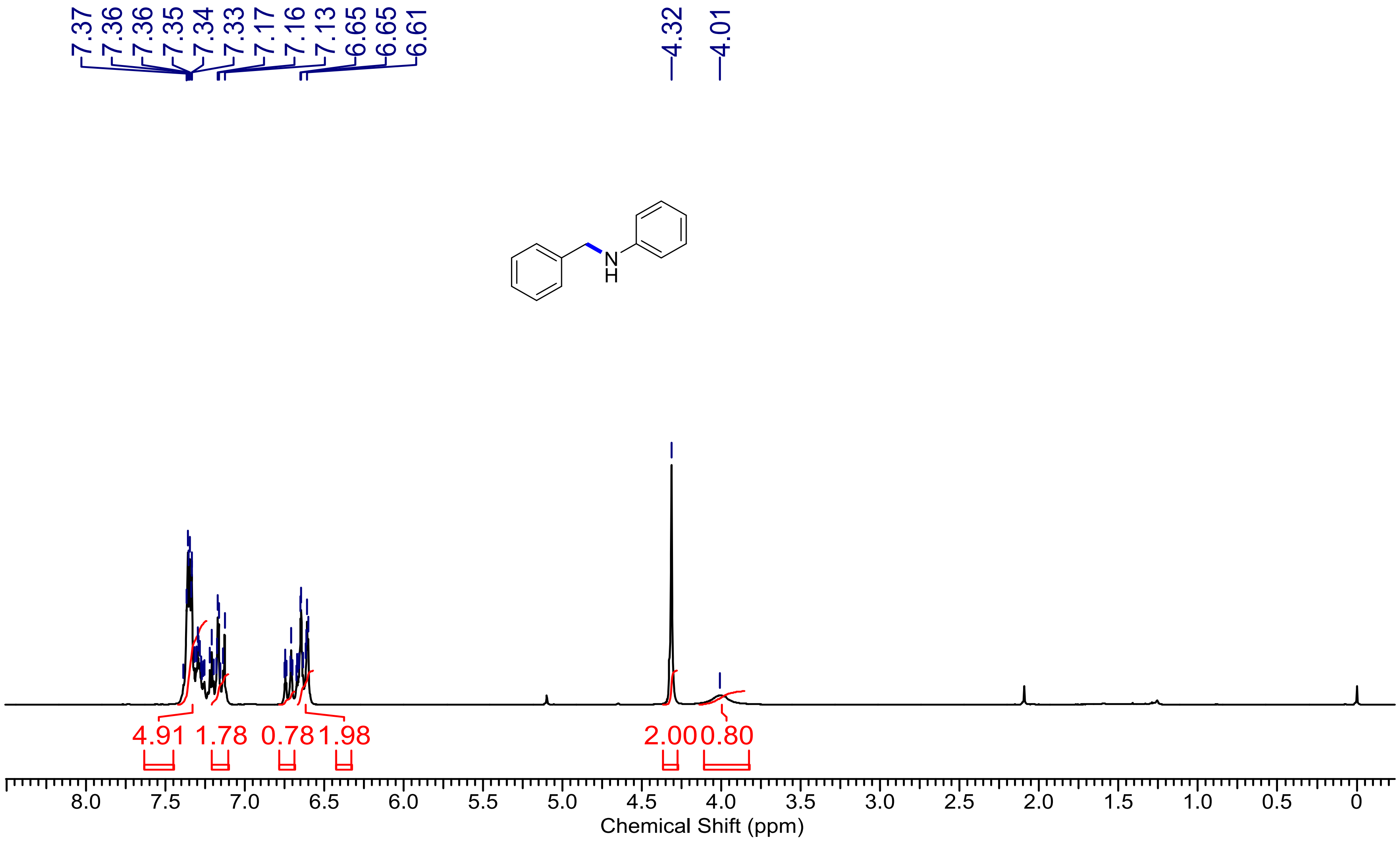


Figure S47. ^{1}H of **6i**

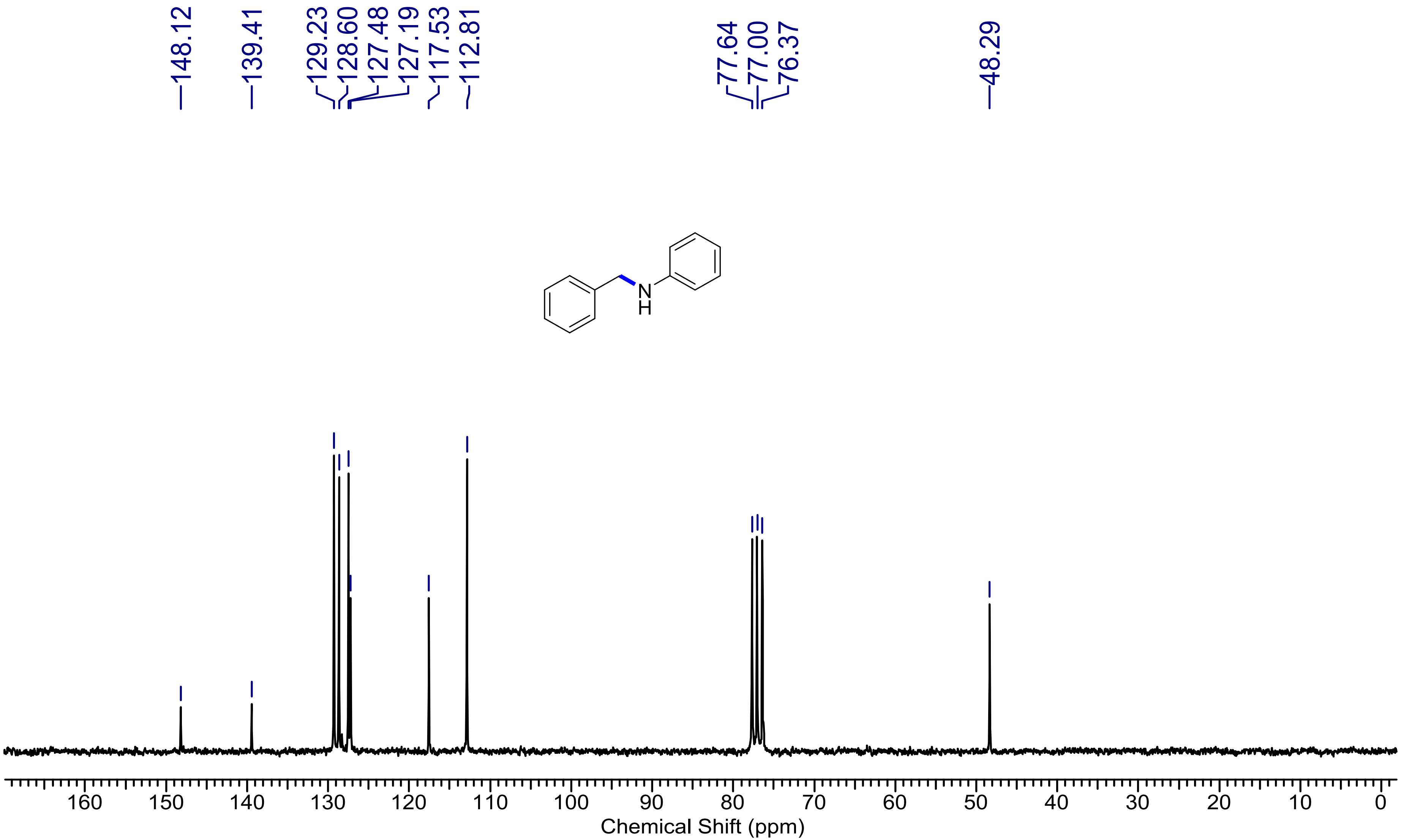


Figure S48. ^{13}C of **6i**

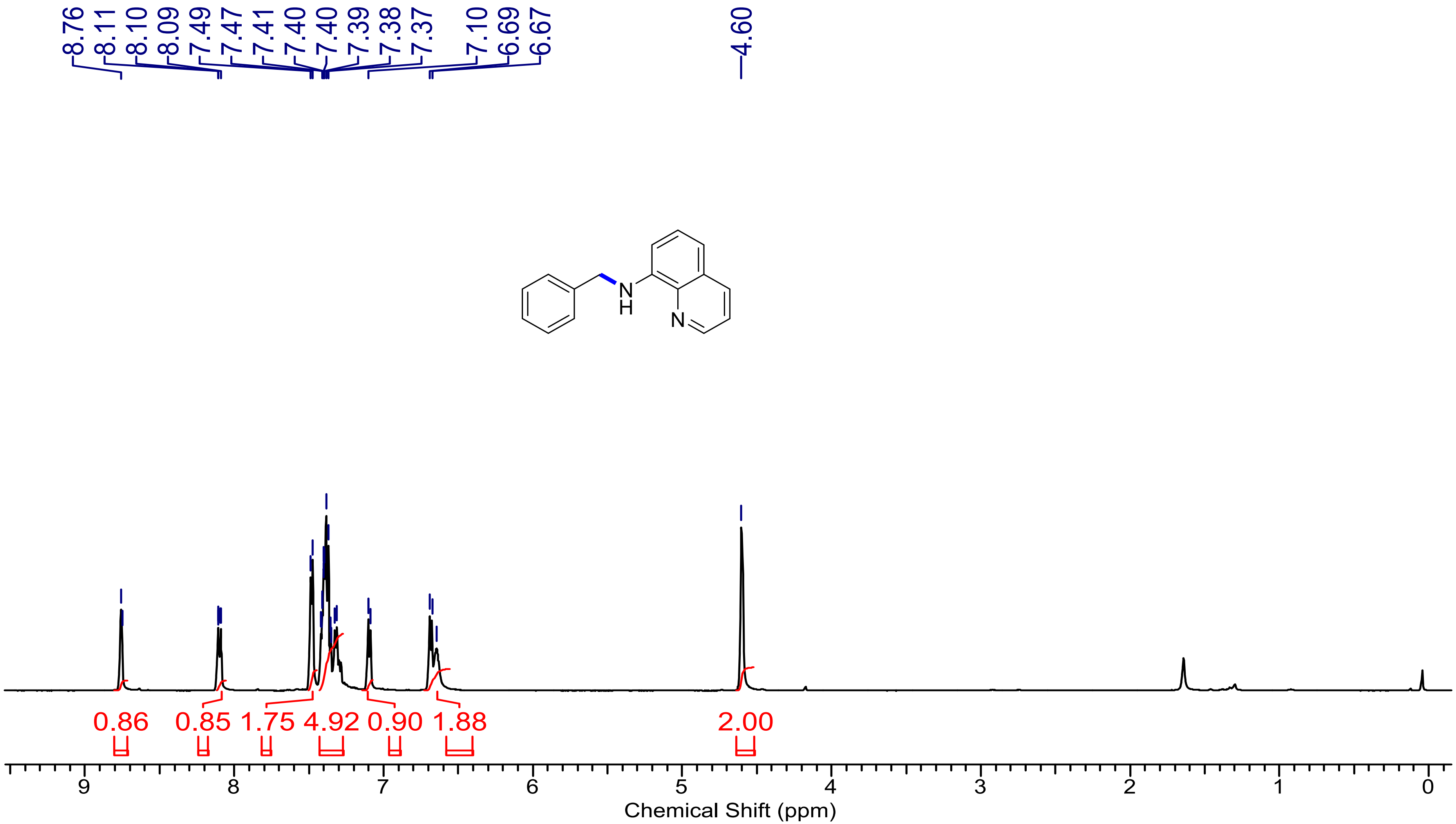


Figure S49. ^{1}H of **6j**

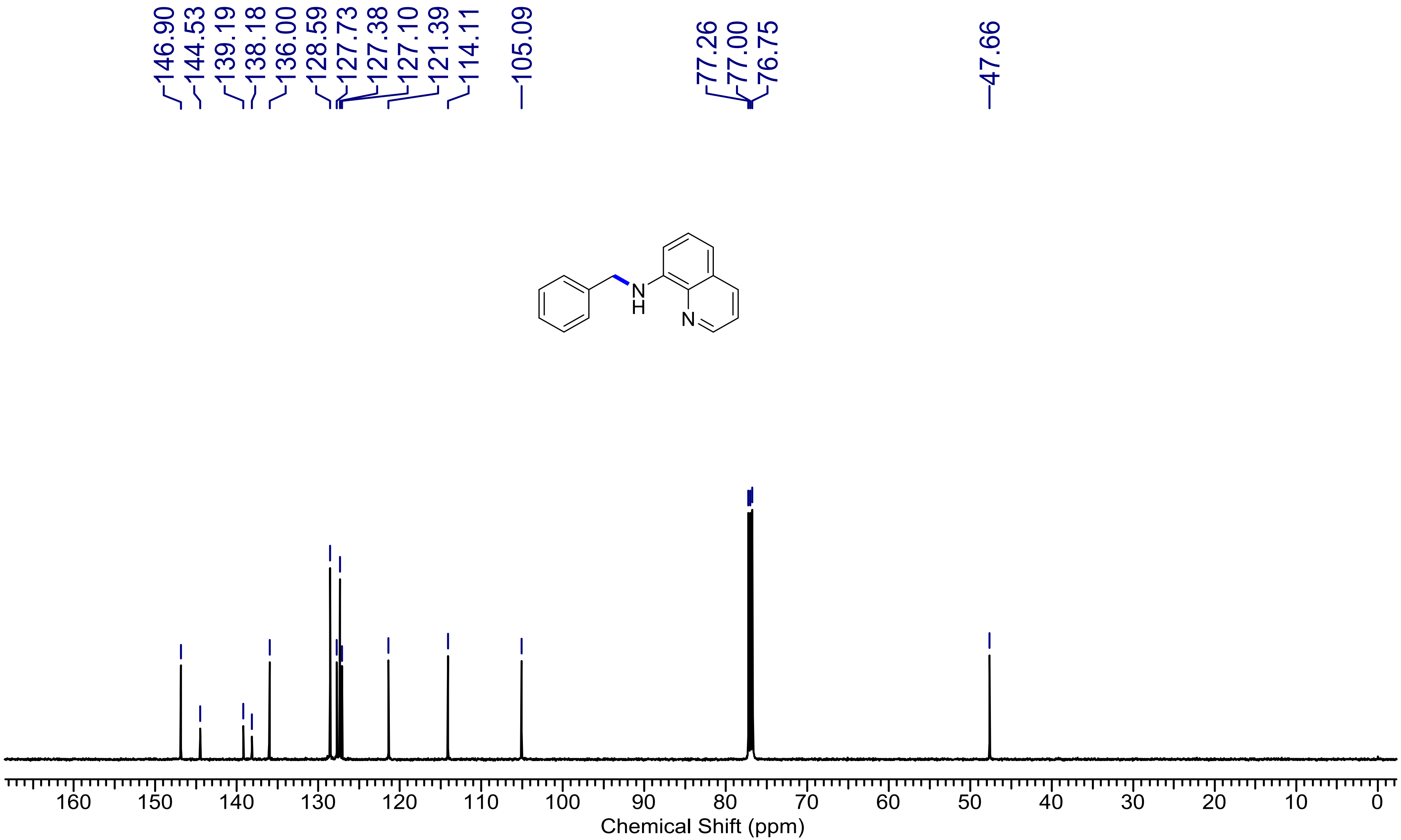


Figure S50. ^{13}C of **6j**

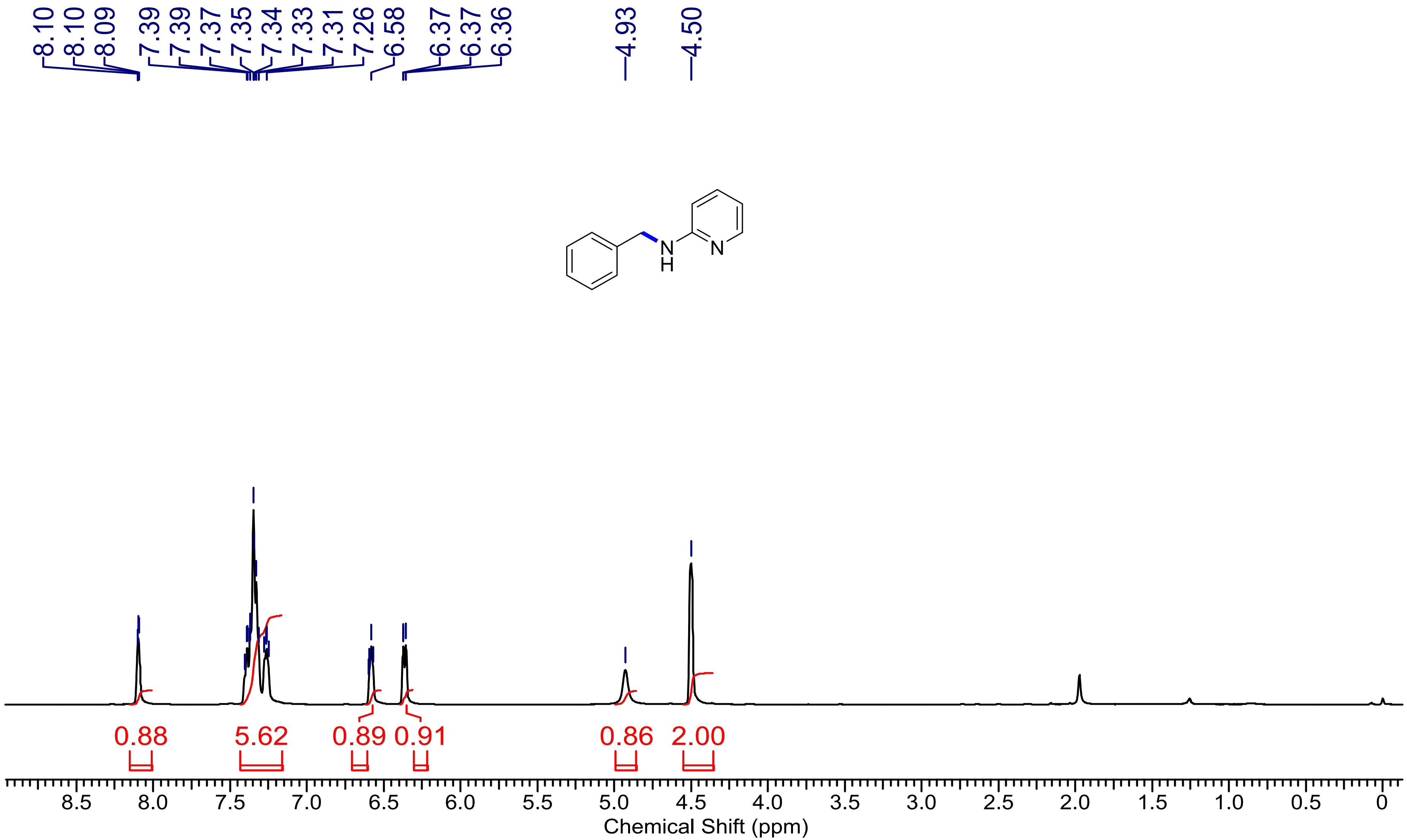


Figure S51. ^{1}H of **6k**

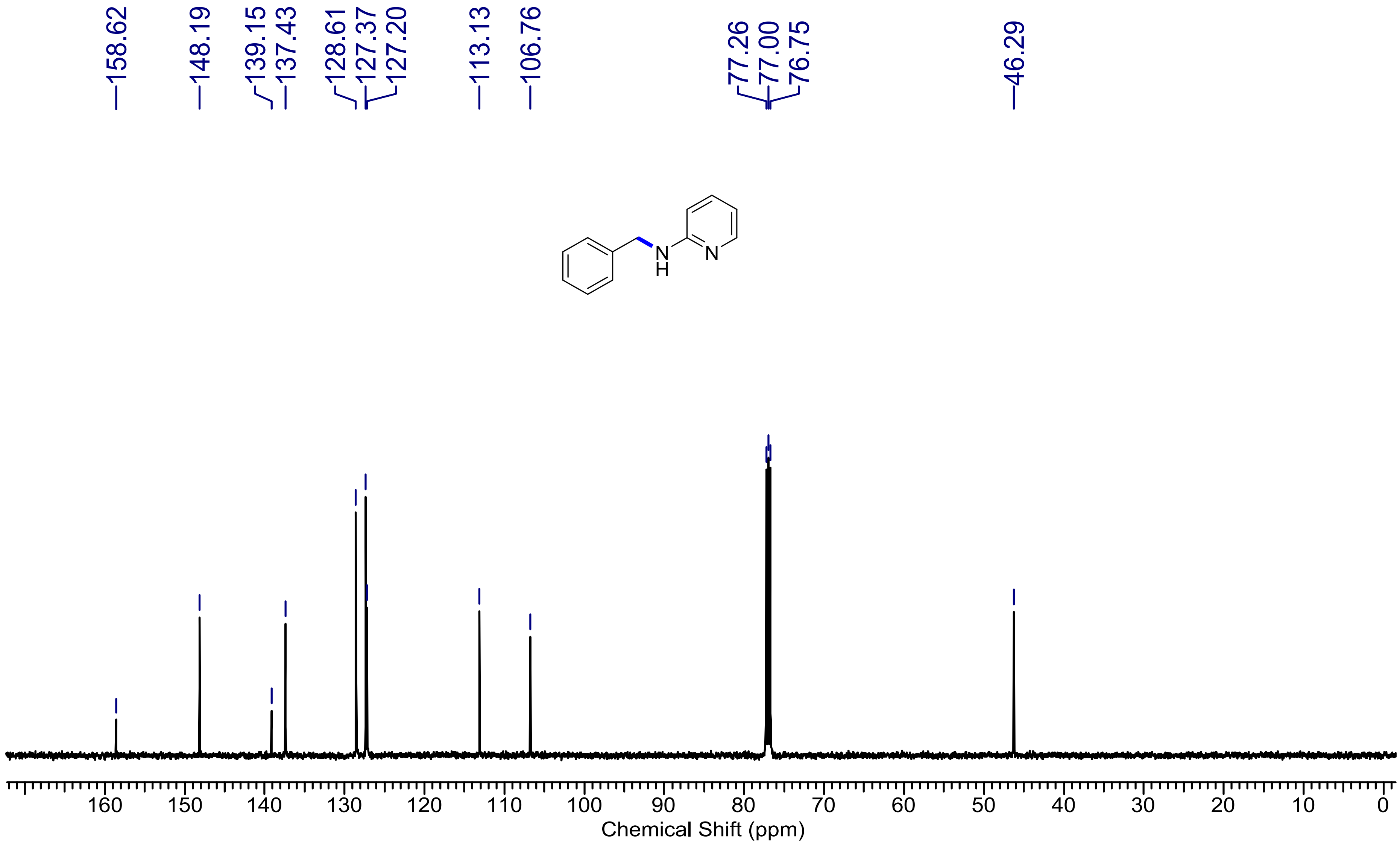


Figure S52. ^{13}C of **6k**

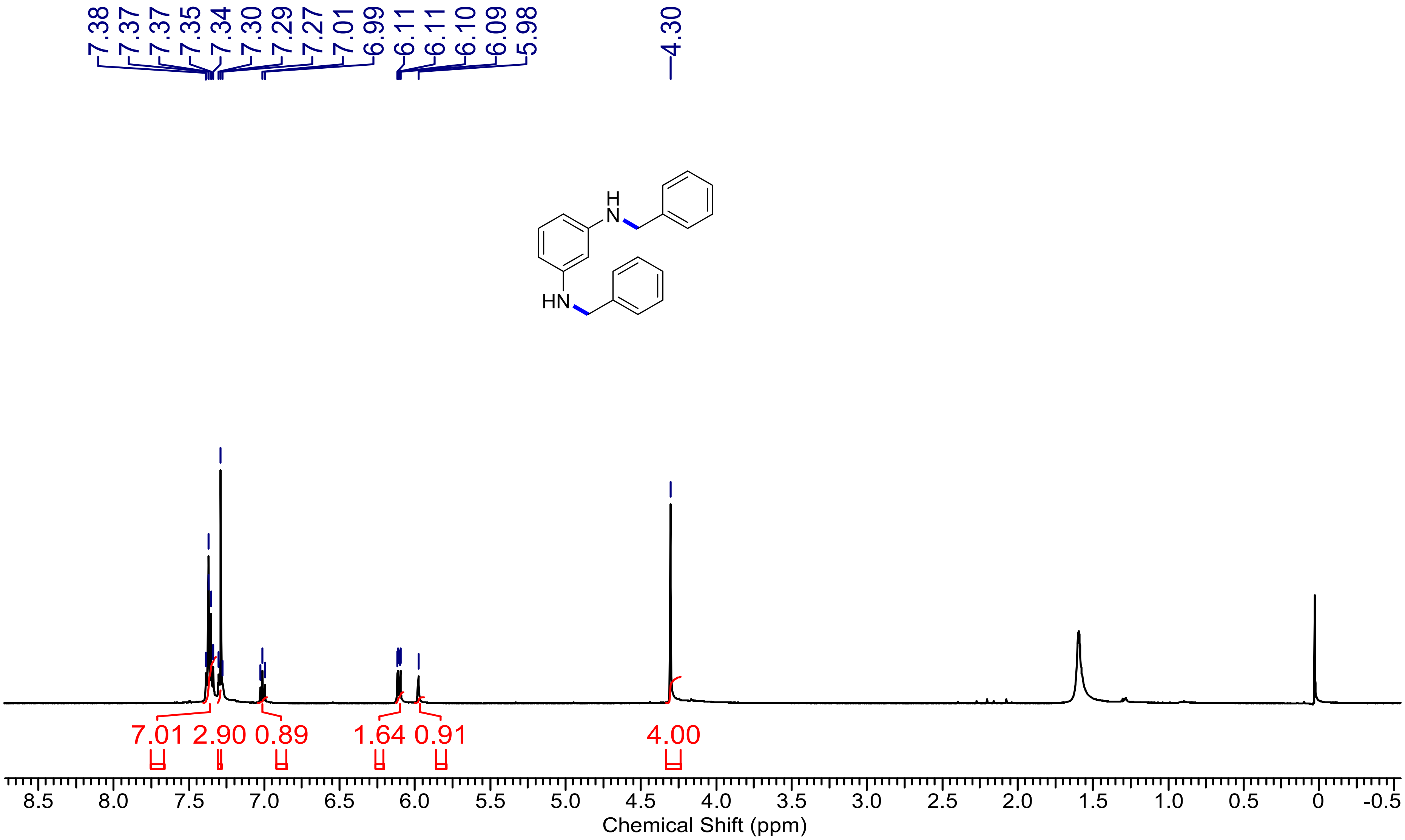


Figure S53. ^{1}H of **8a**

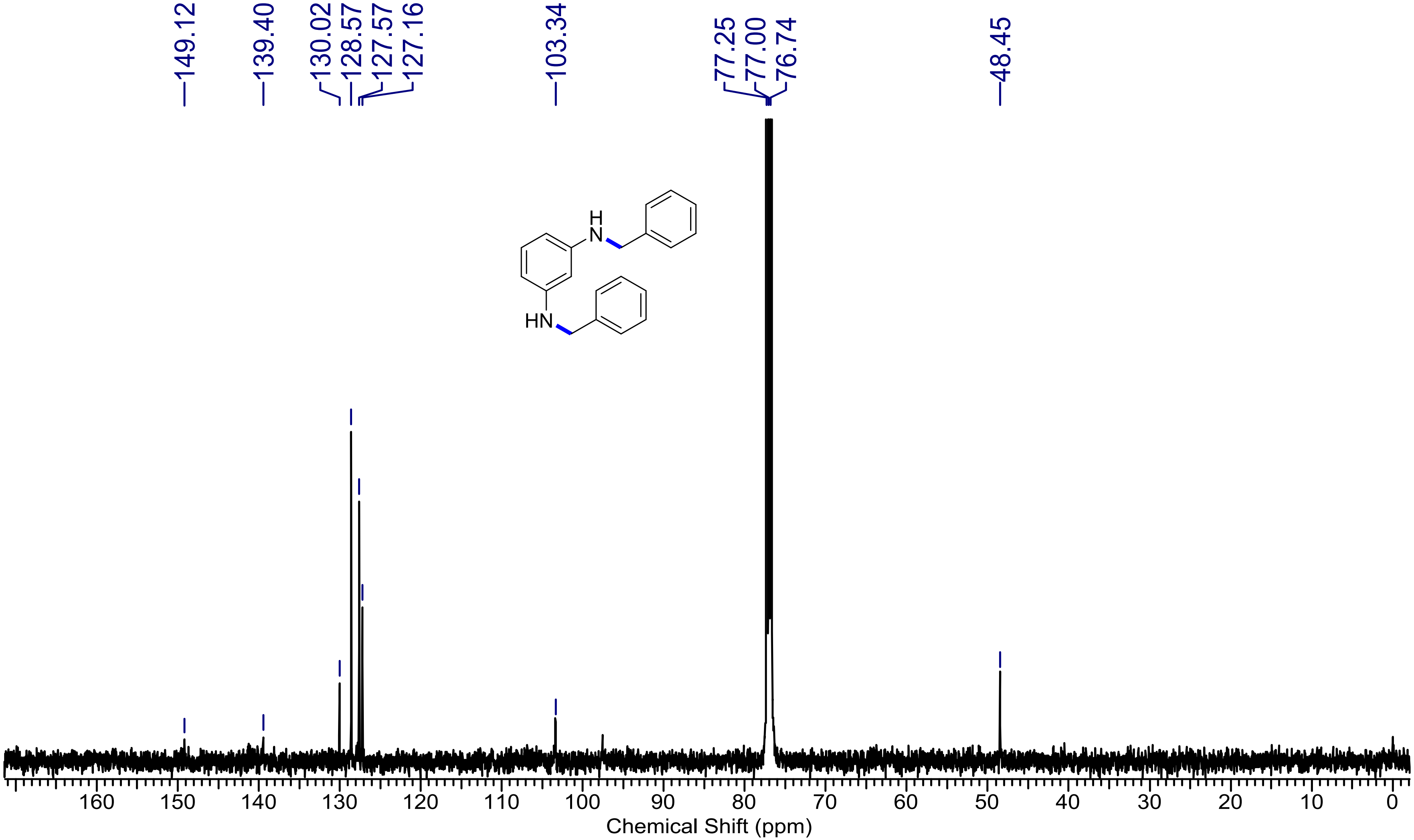


Figure S54. ^{13}C of **8a**

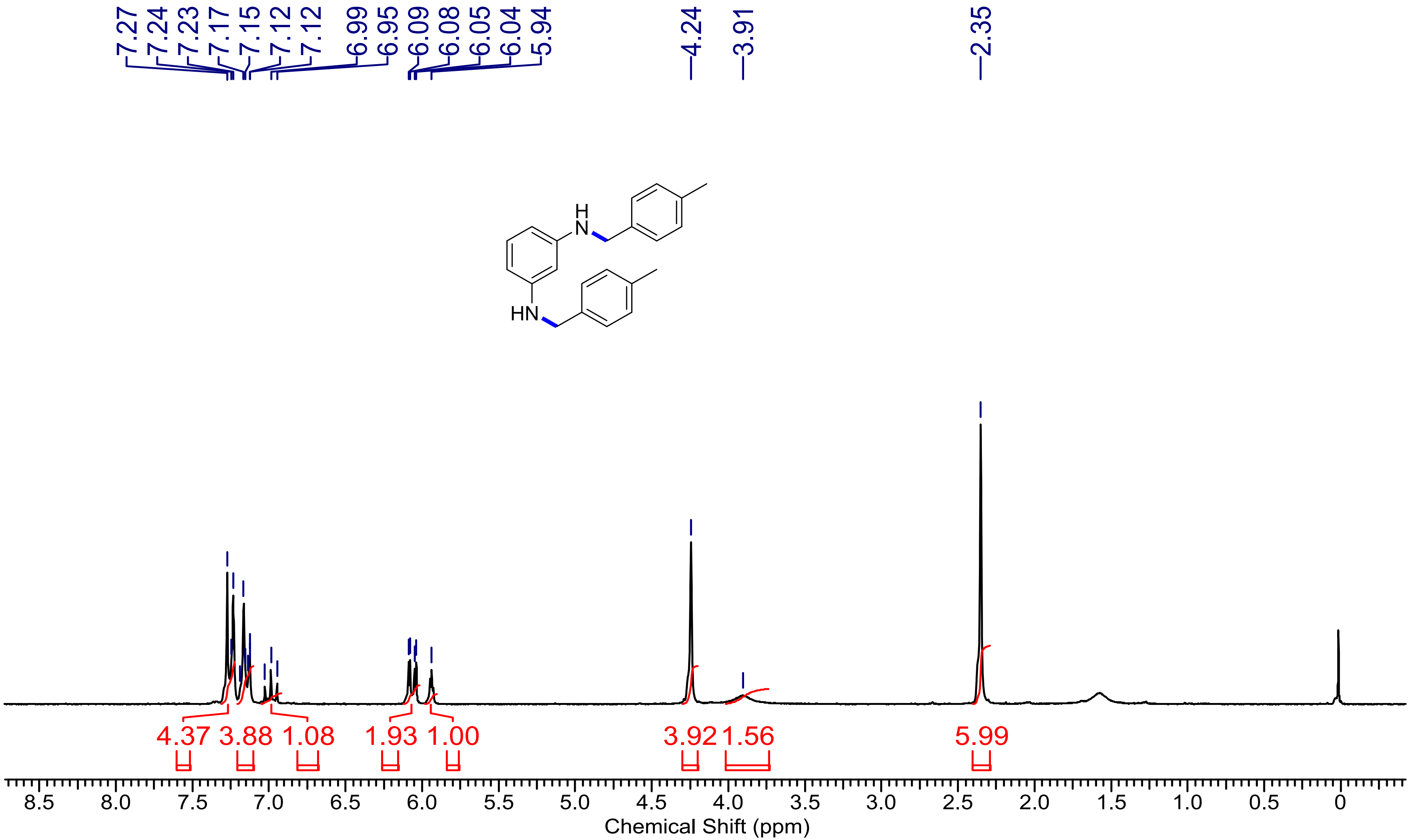


Figure S55. ^{1}H of **8b**

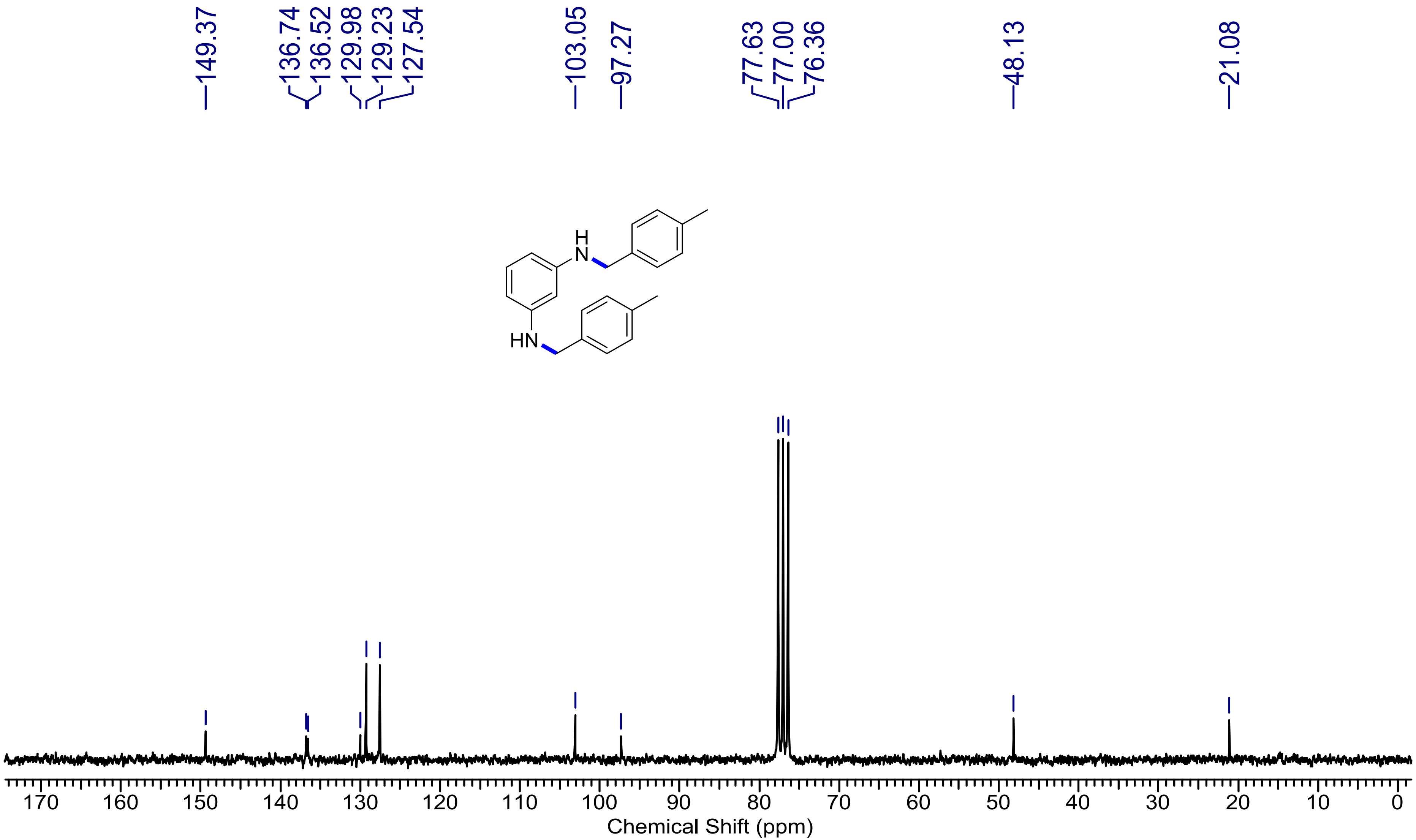


Figure S56. ^{13}C of **8b**

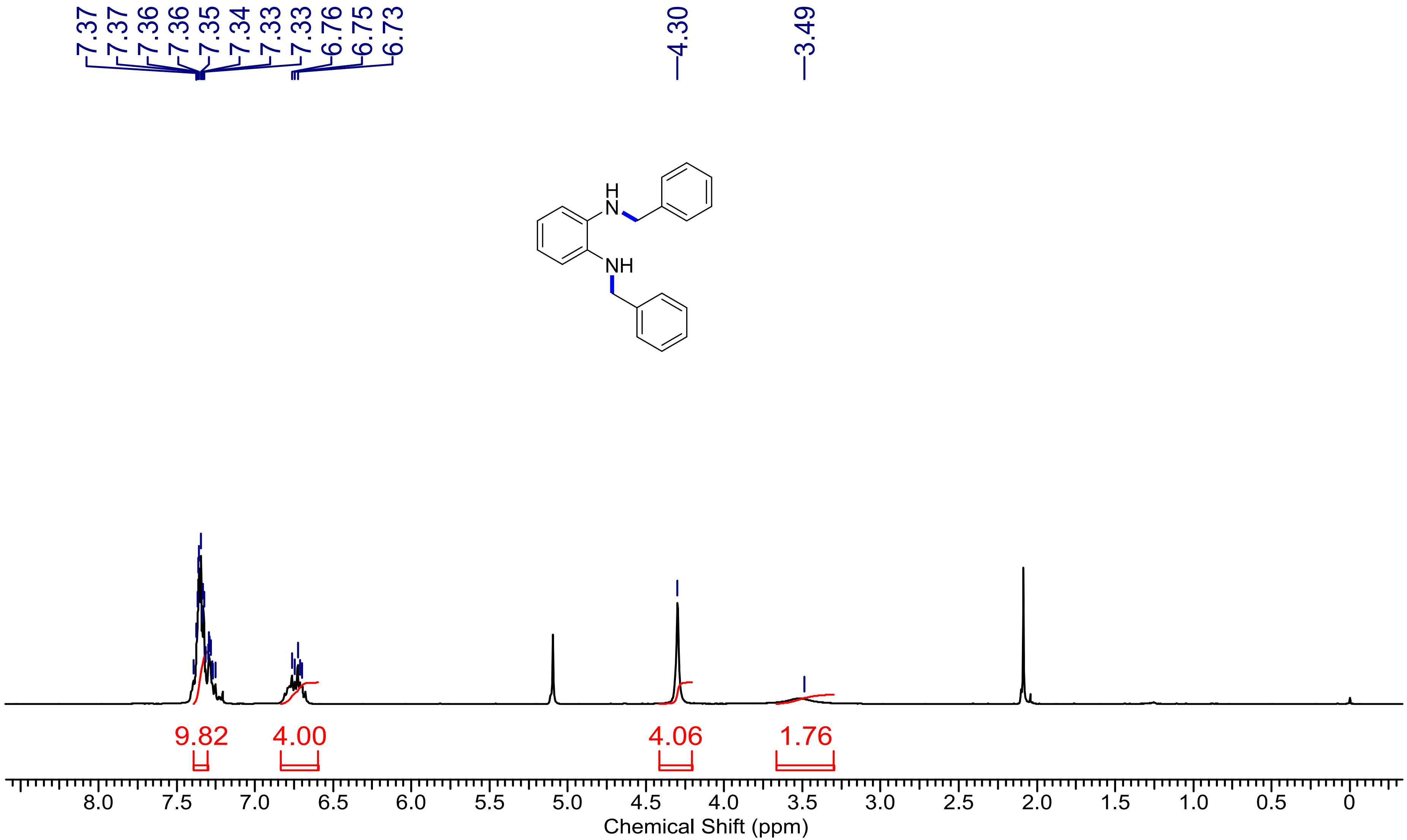


Figure S57. ^{1}H of **8c**

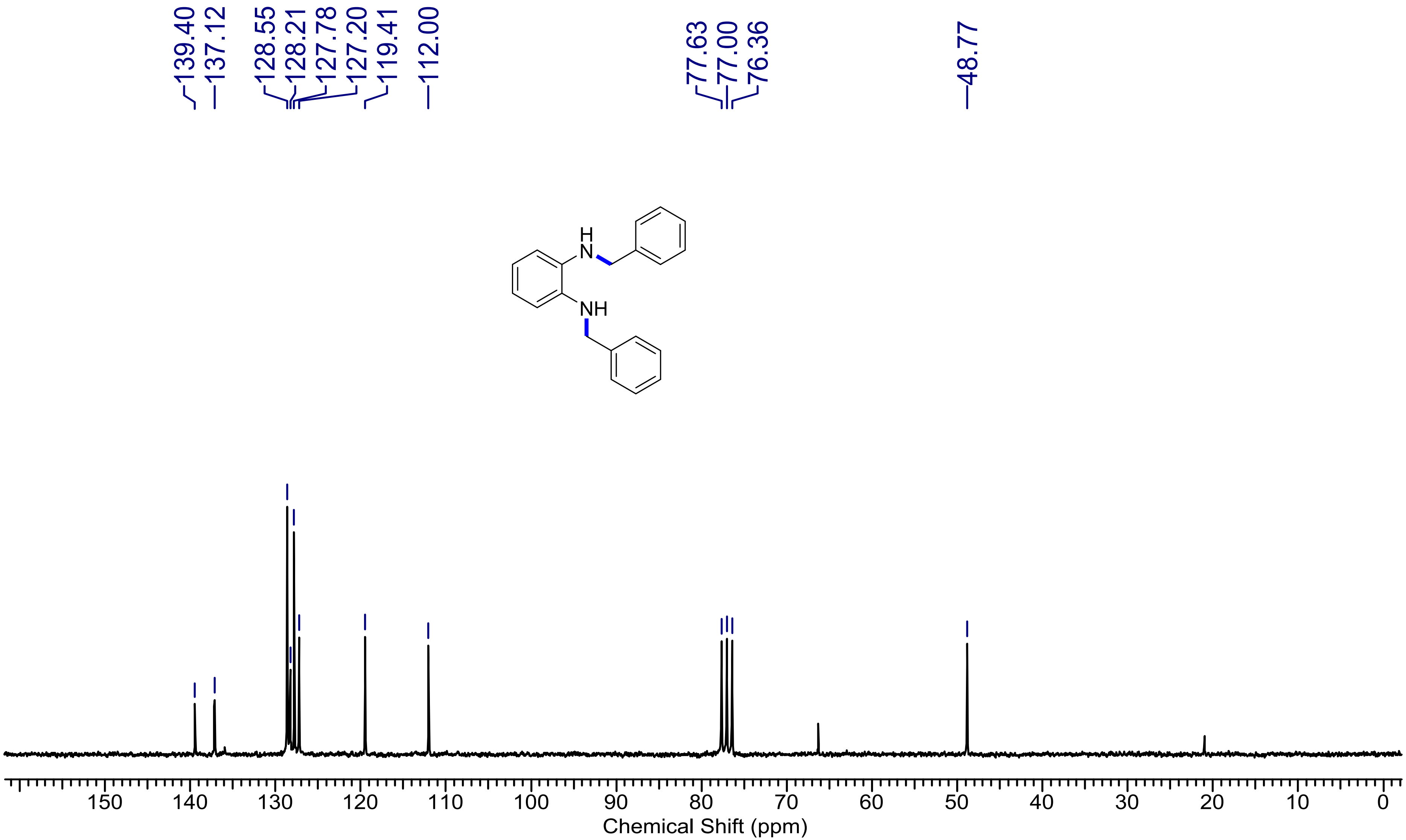


Figure S58. ^{13}C of **8c**

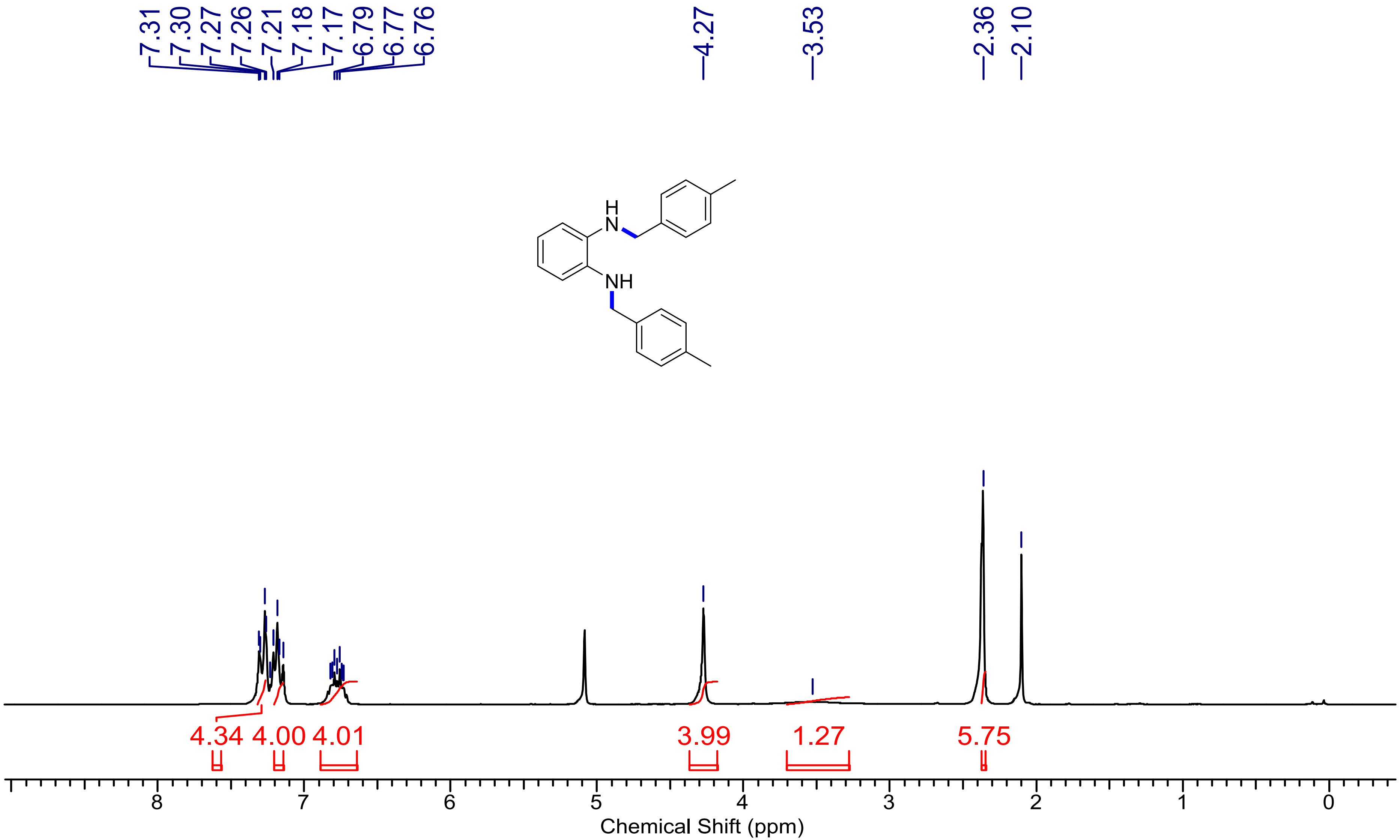


Figure S59. ^{1}H of **8d**

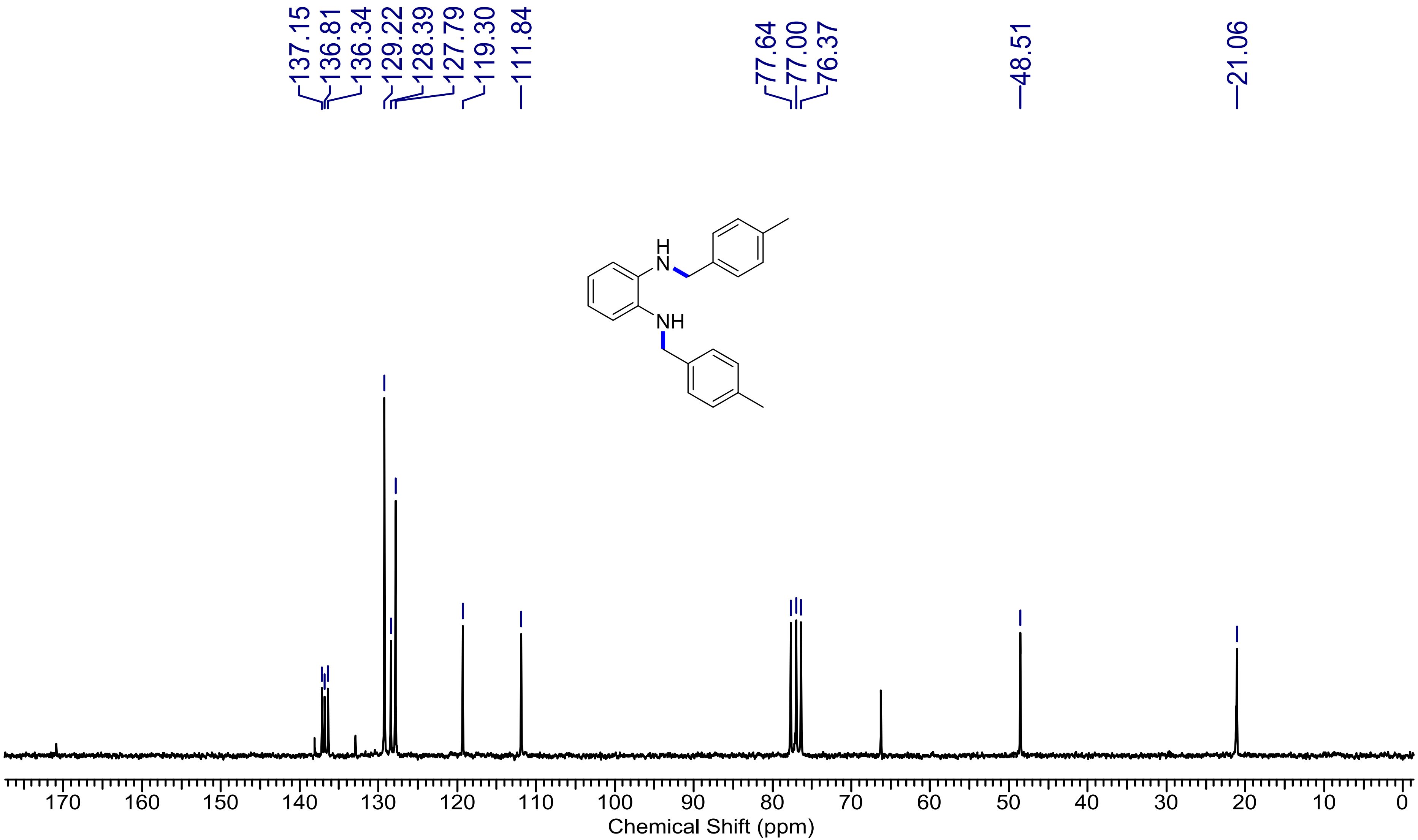


Figure S60. ^{13}C of **8d**

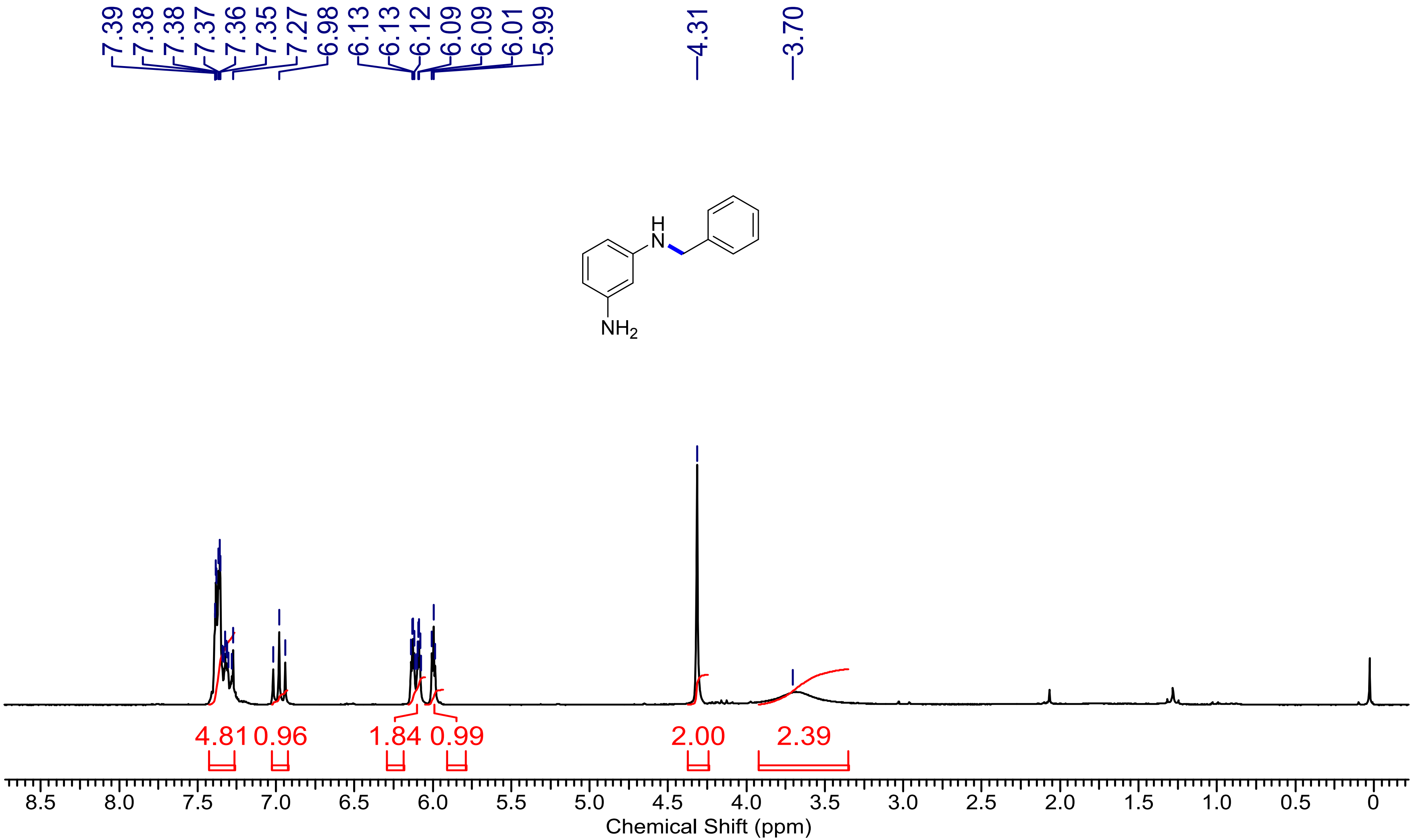


Figure S61. ^{1}H of **9a**

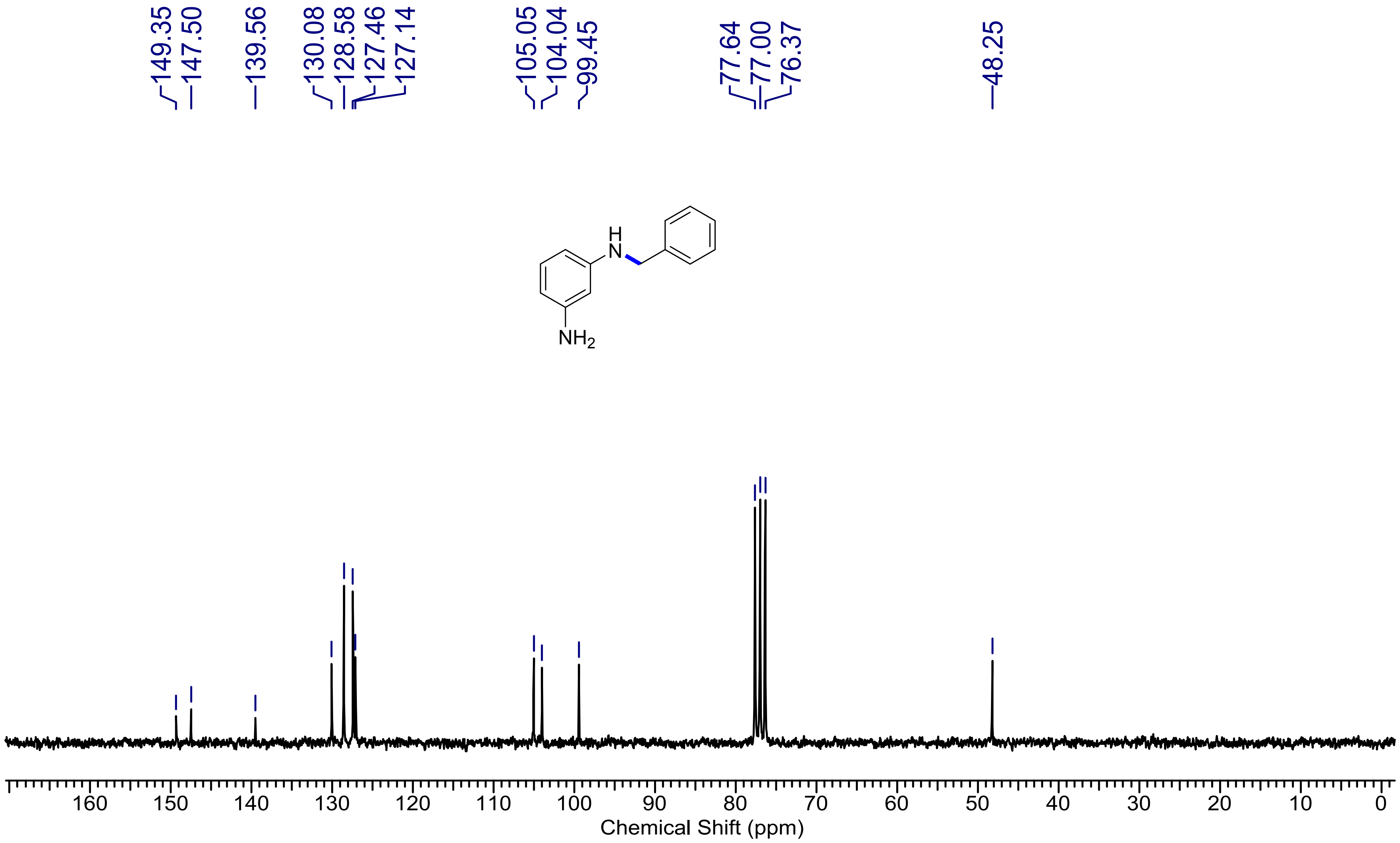


Figure S62. ^{13}C of **9a**

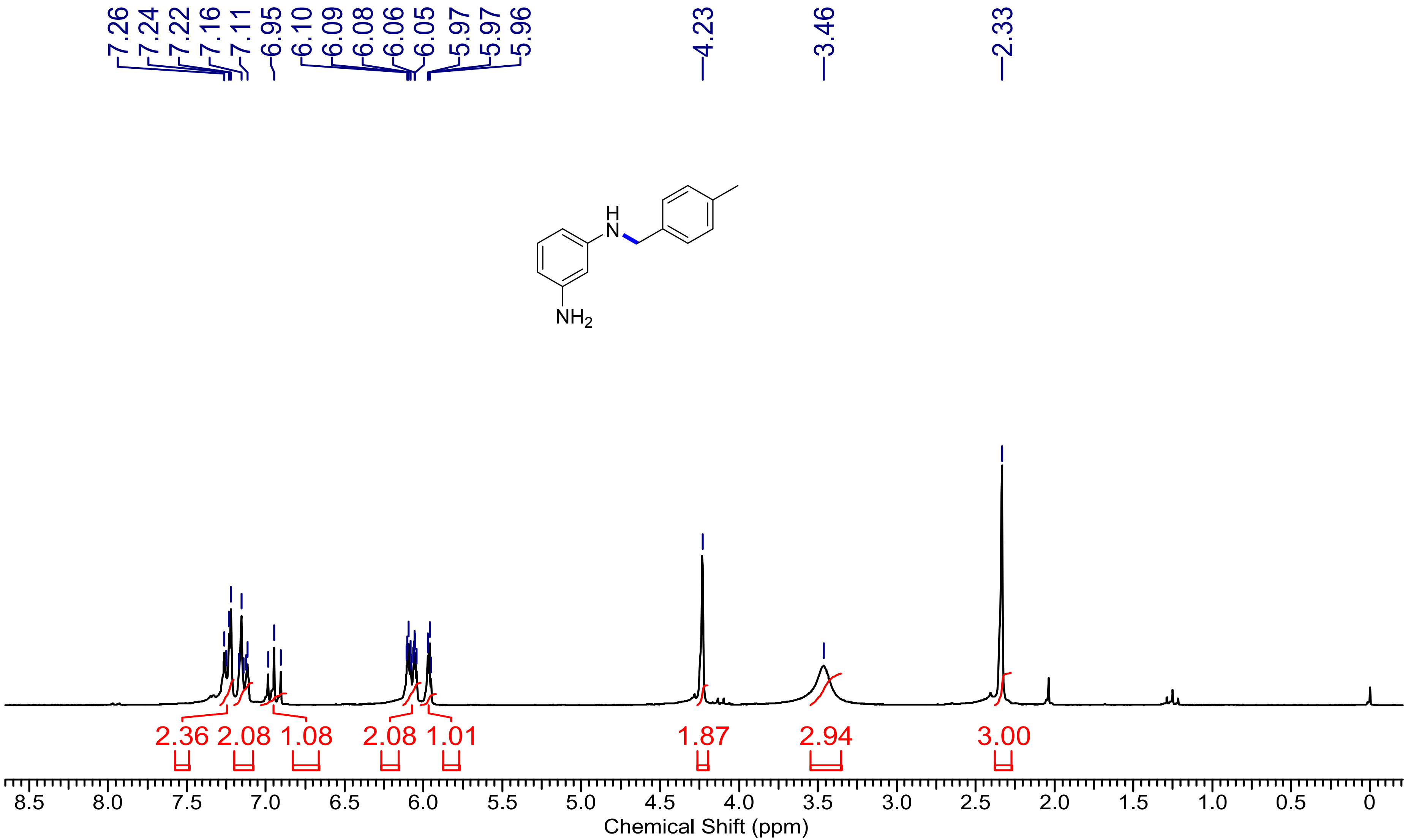


Figure S63. ^{1}H of **9b**

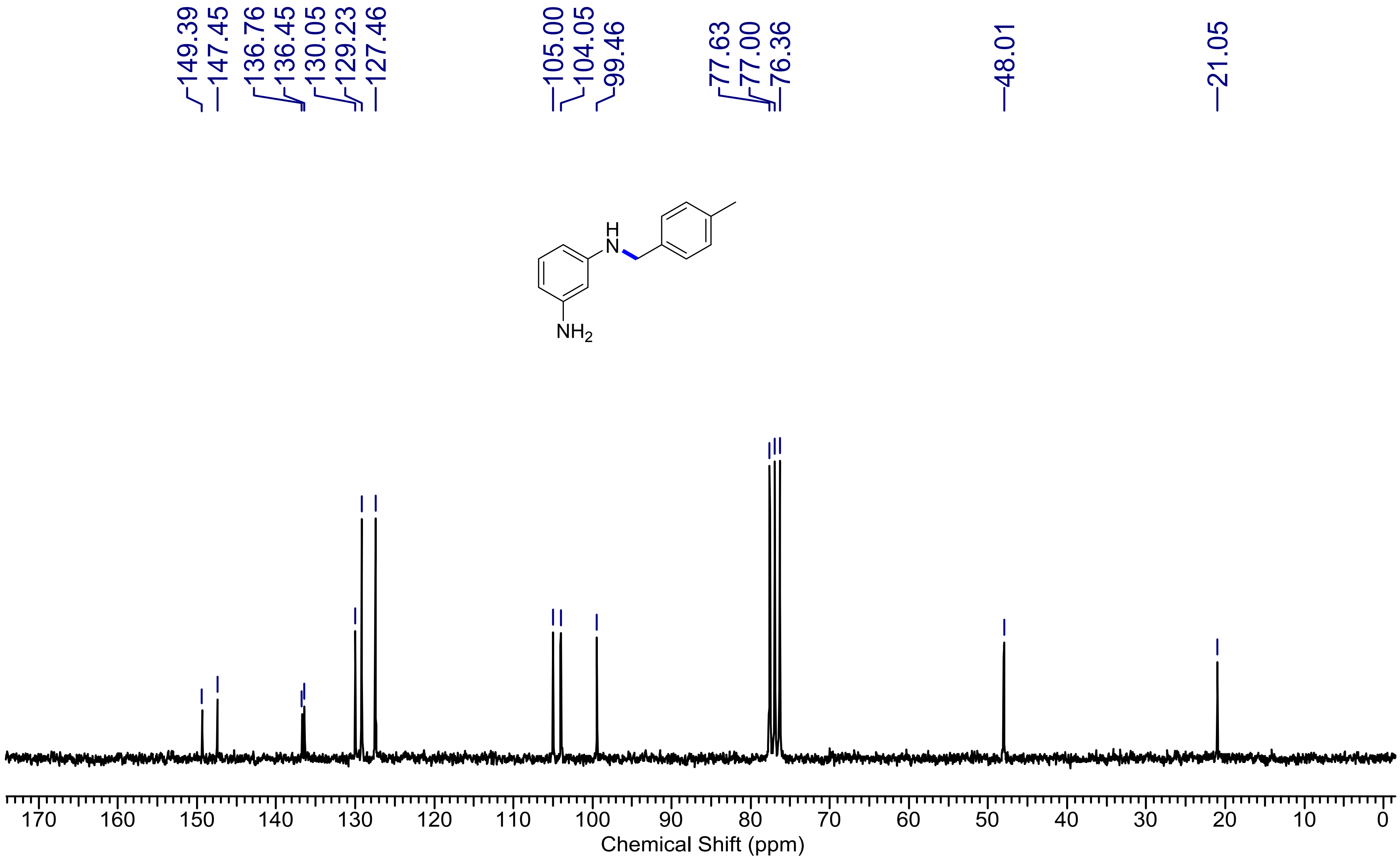


Figure S64. ^{13}C of **9b**

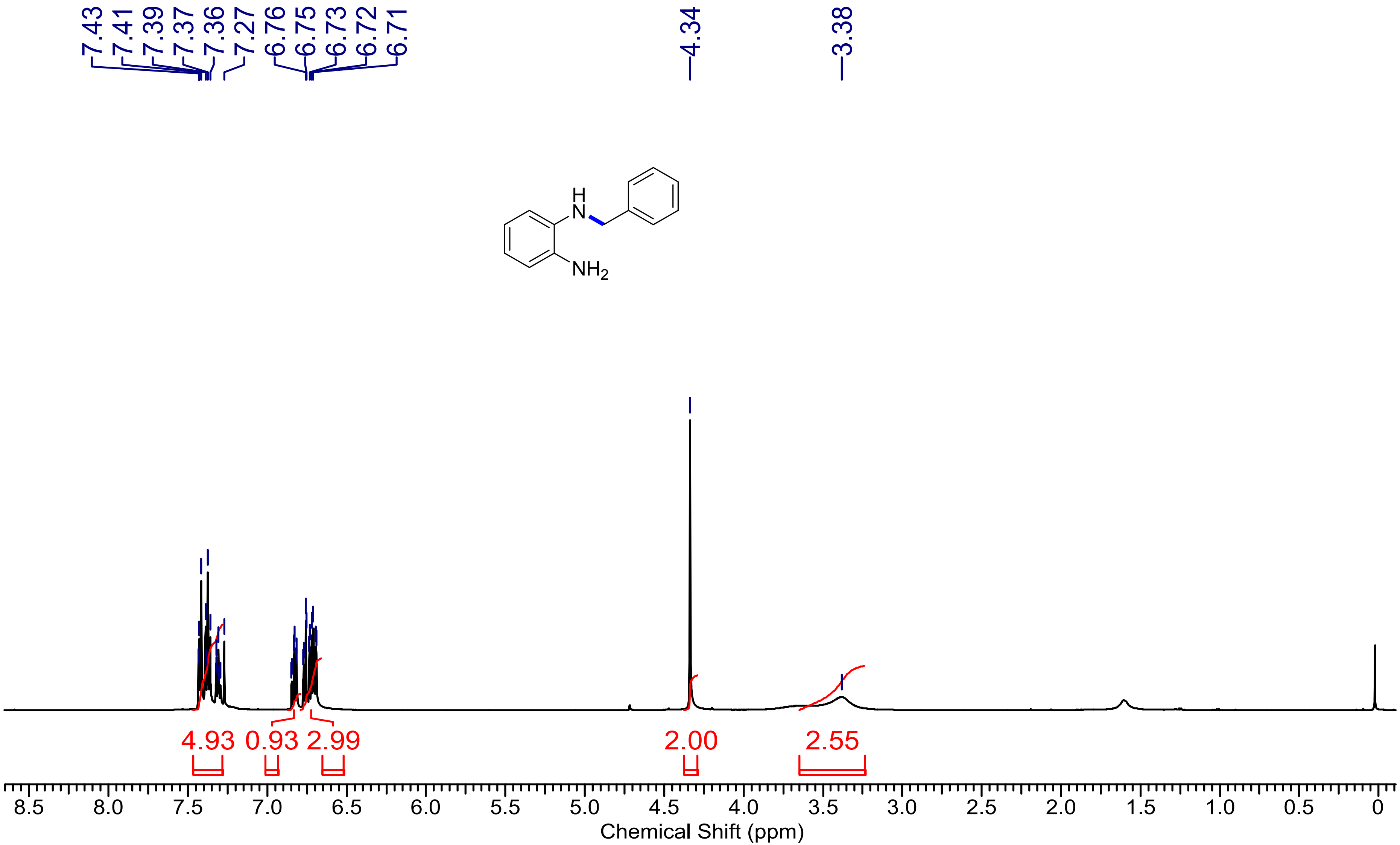


Figure S65. ^{1}H of **9c**

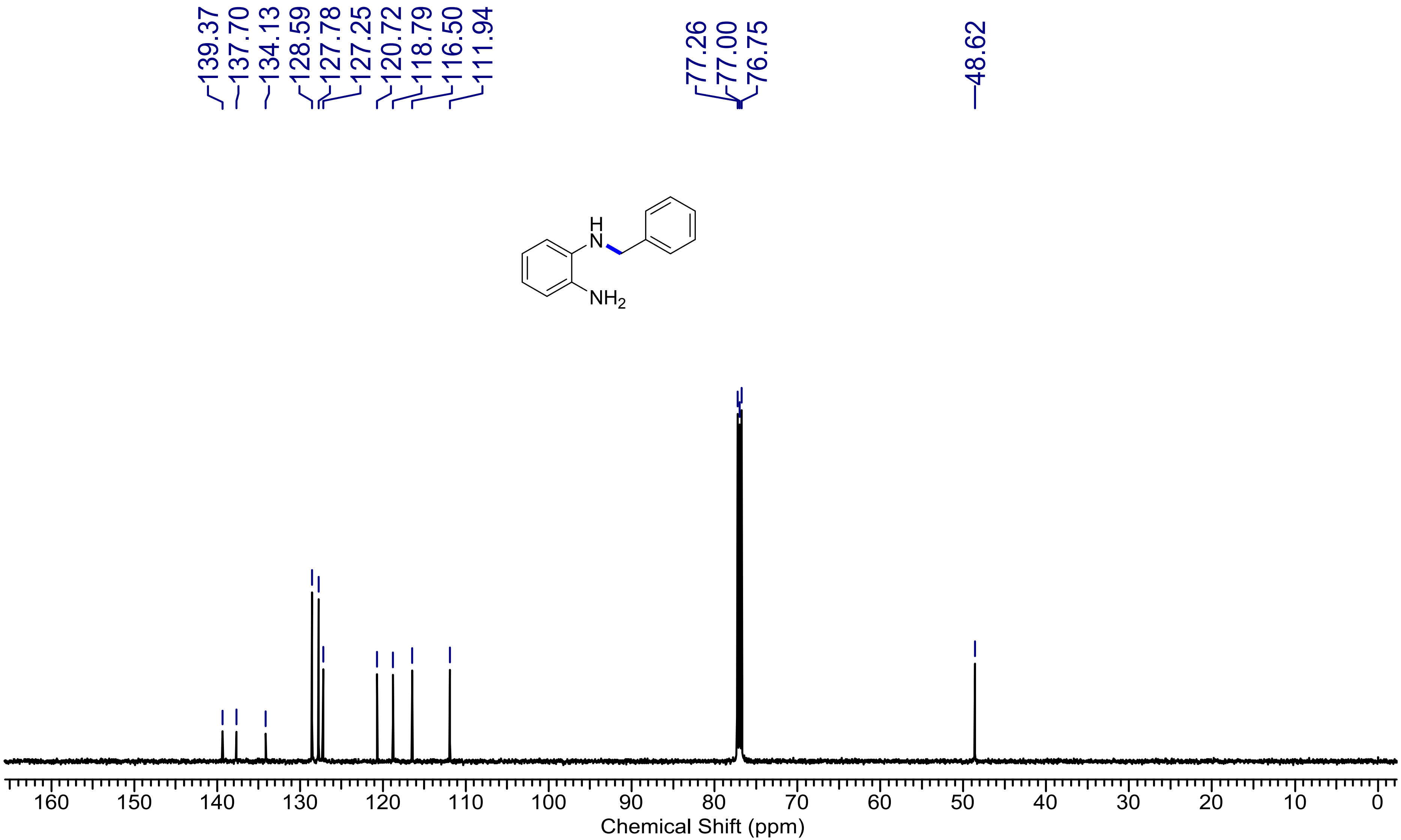


Figure S66. ^{13}C of **9c**

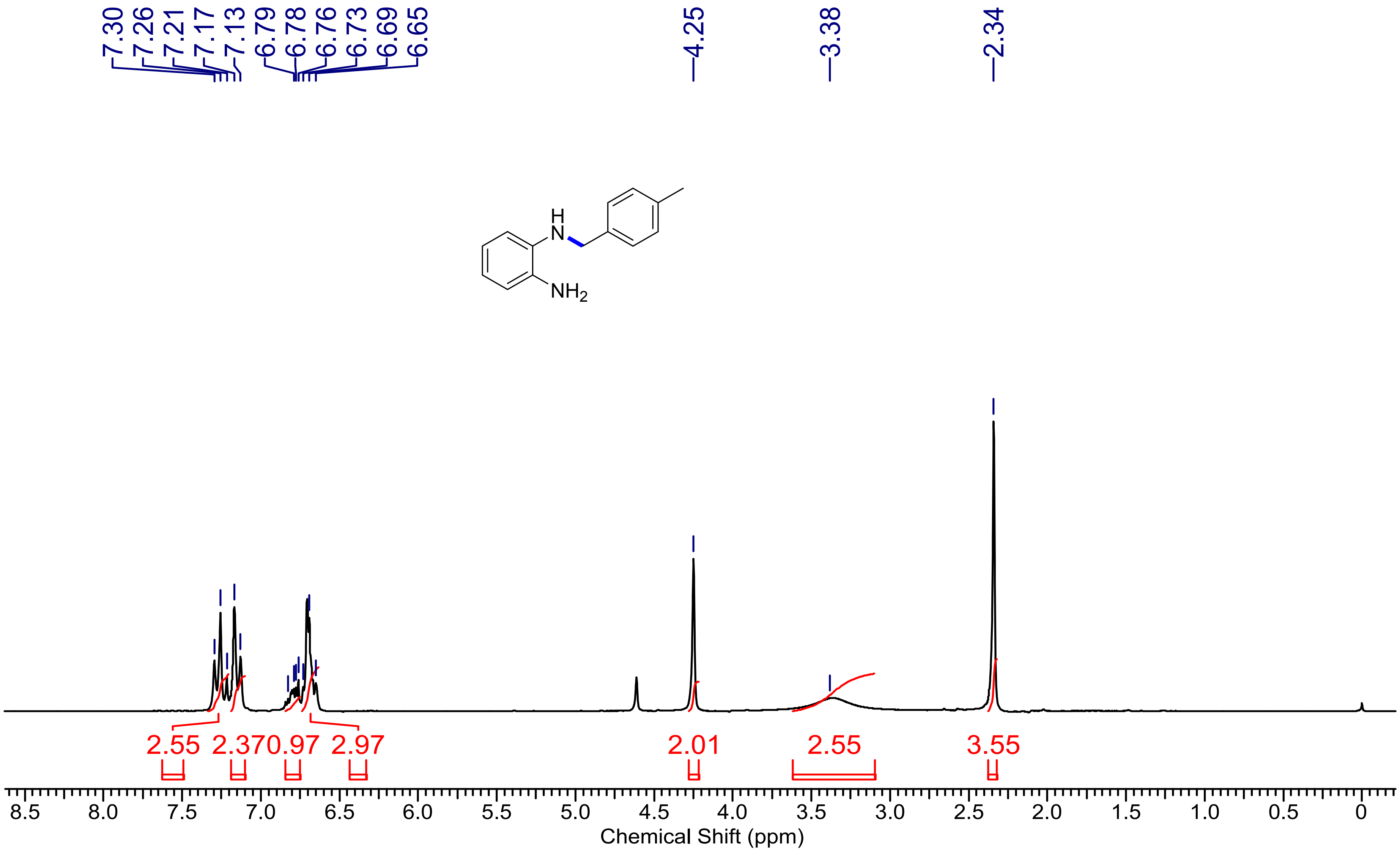


Figure S67. ^{1}H of **9d**

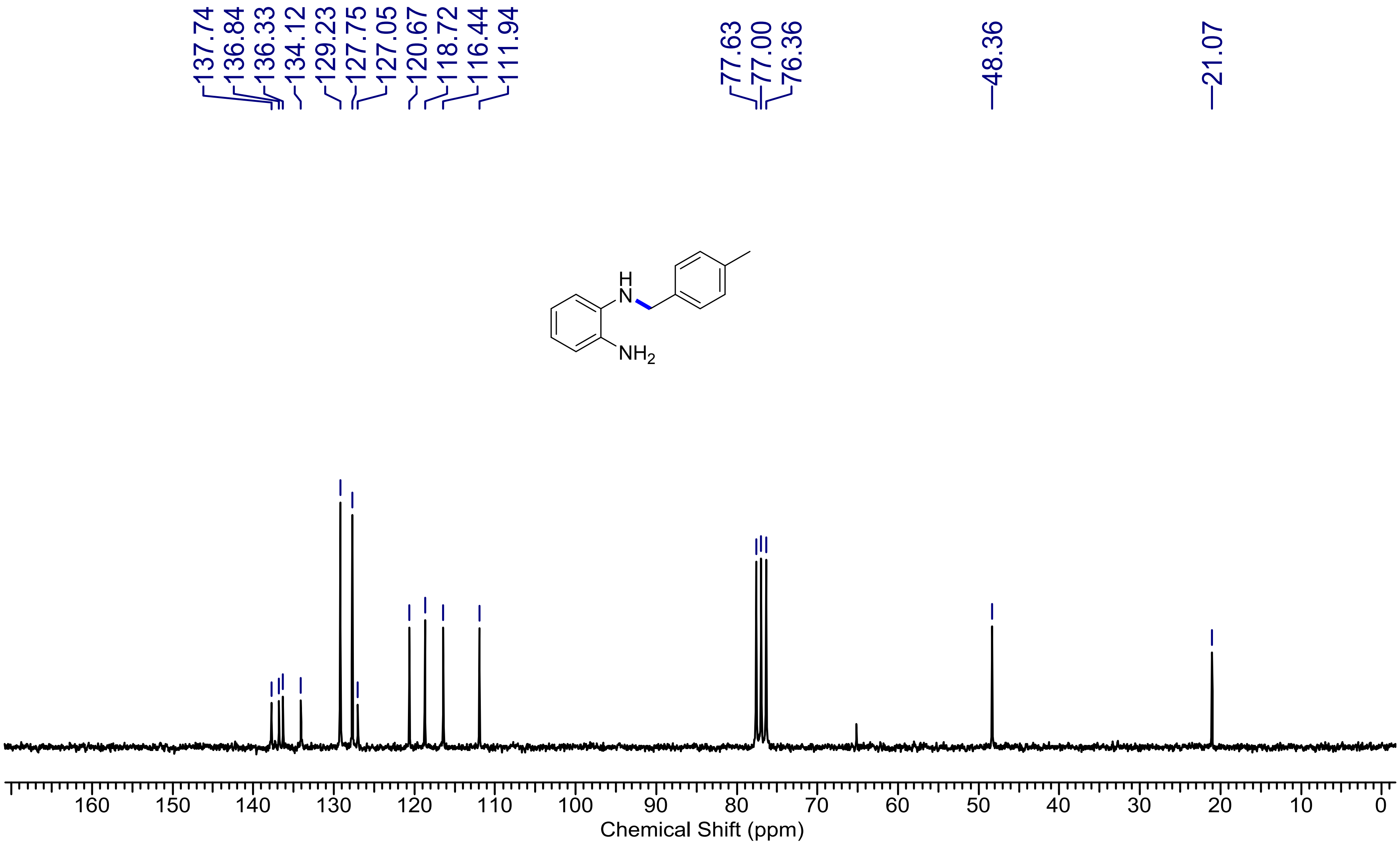


Figure S68. ^{13}C of **9d**

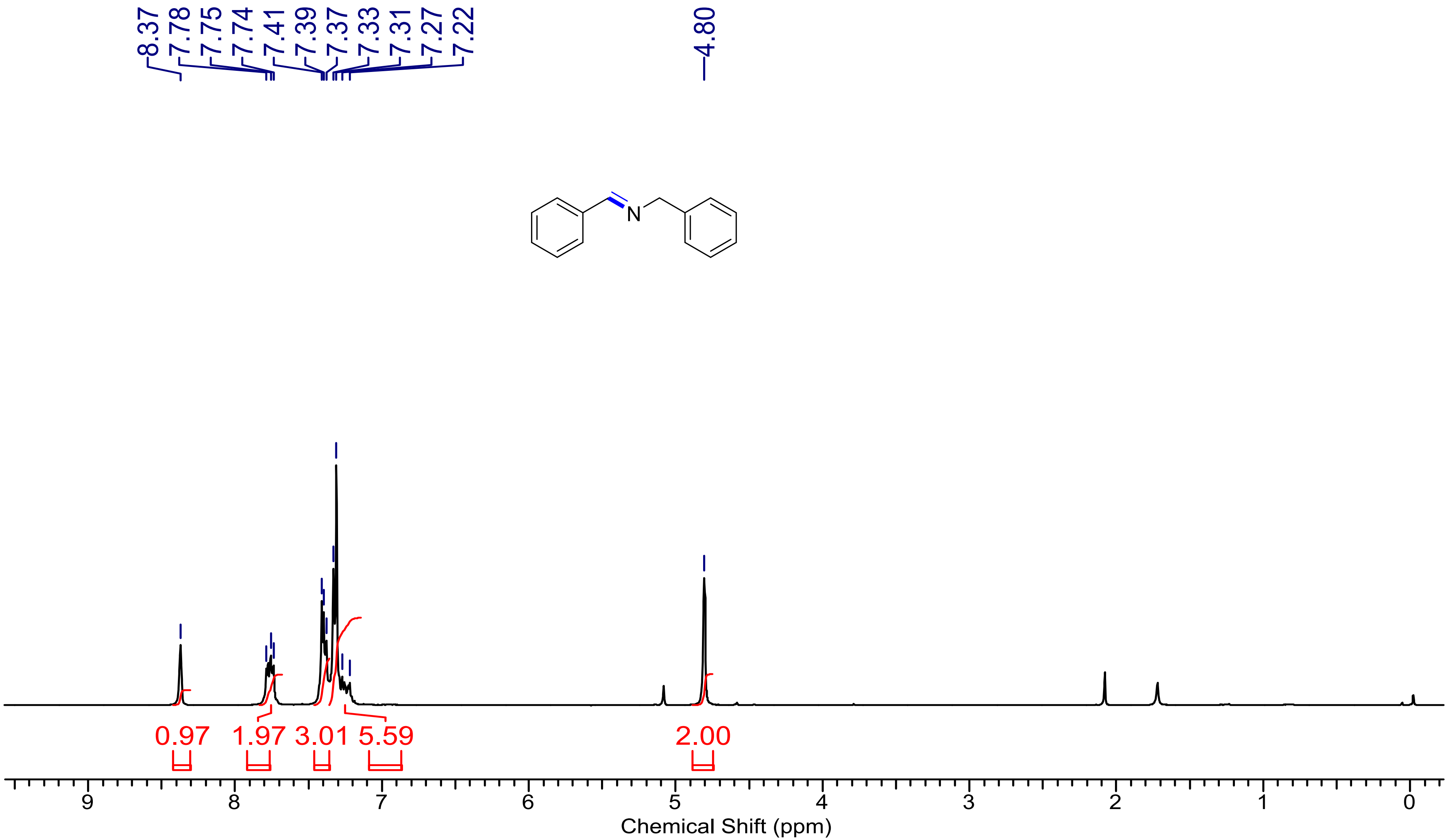


Figure S69. ^{1}H of **11a**

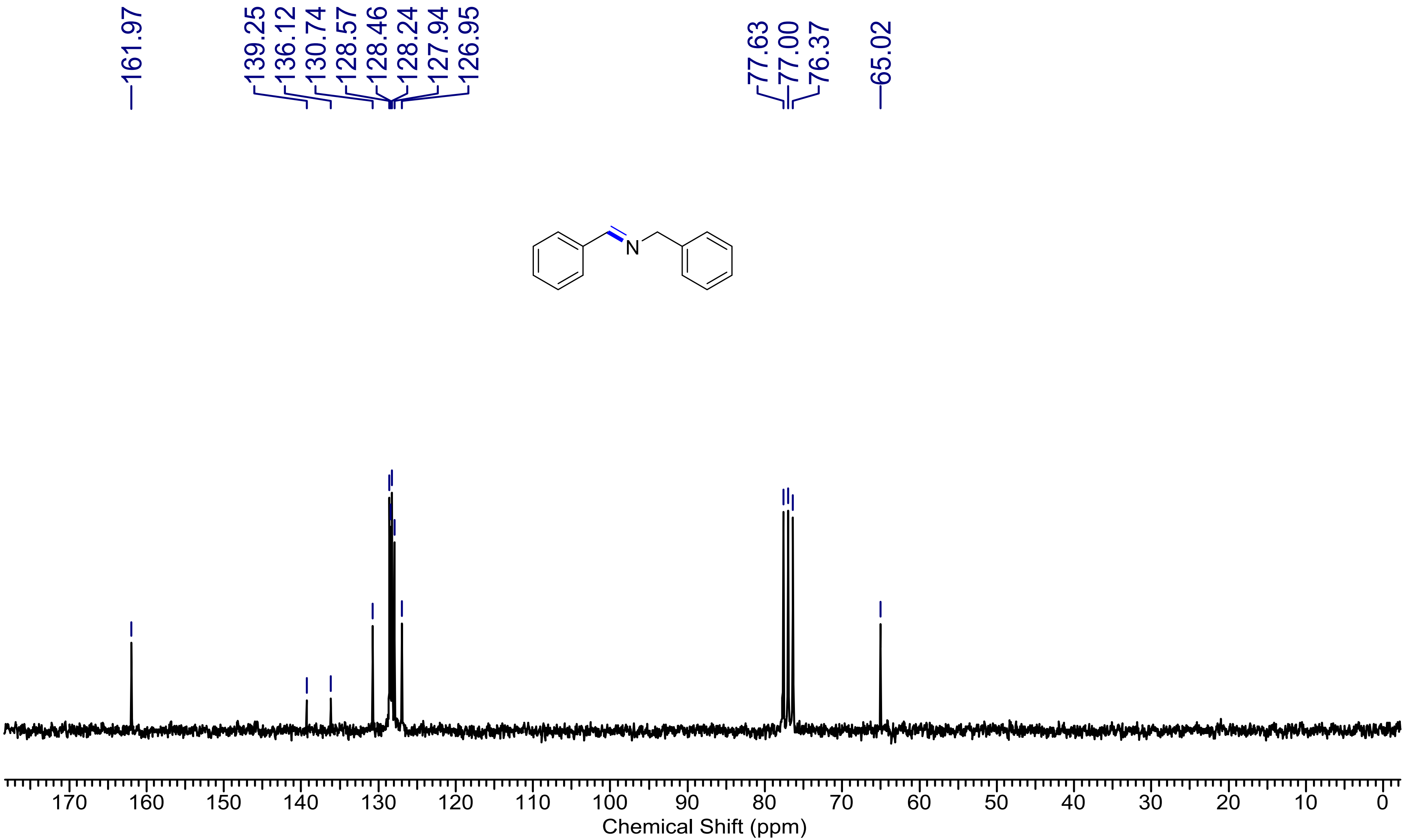


Figure S70. ^{13}C of **11a**

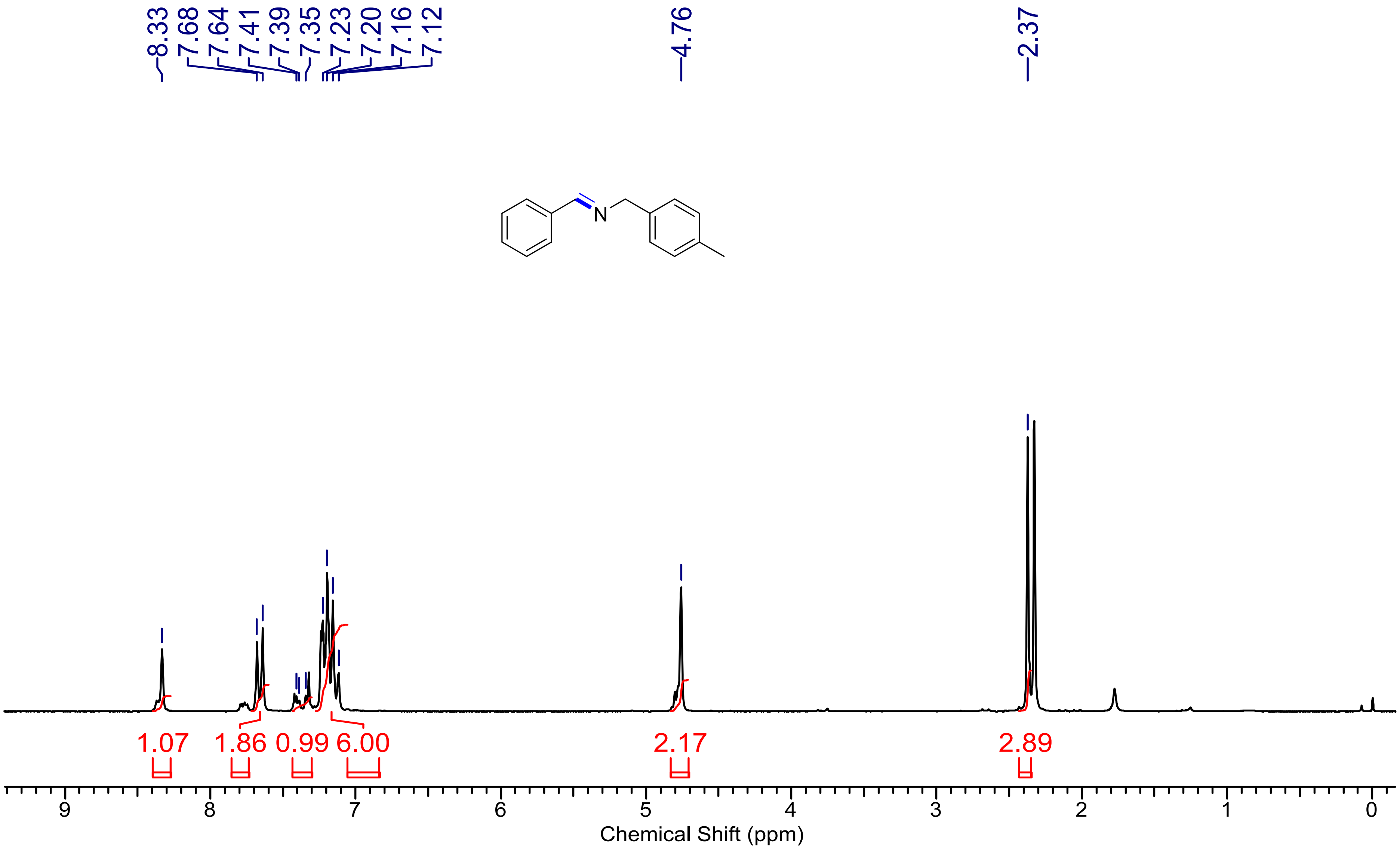


Figure S71. ^{1}H of **11b**

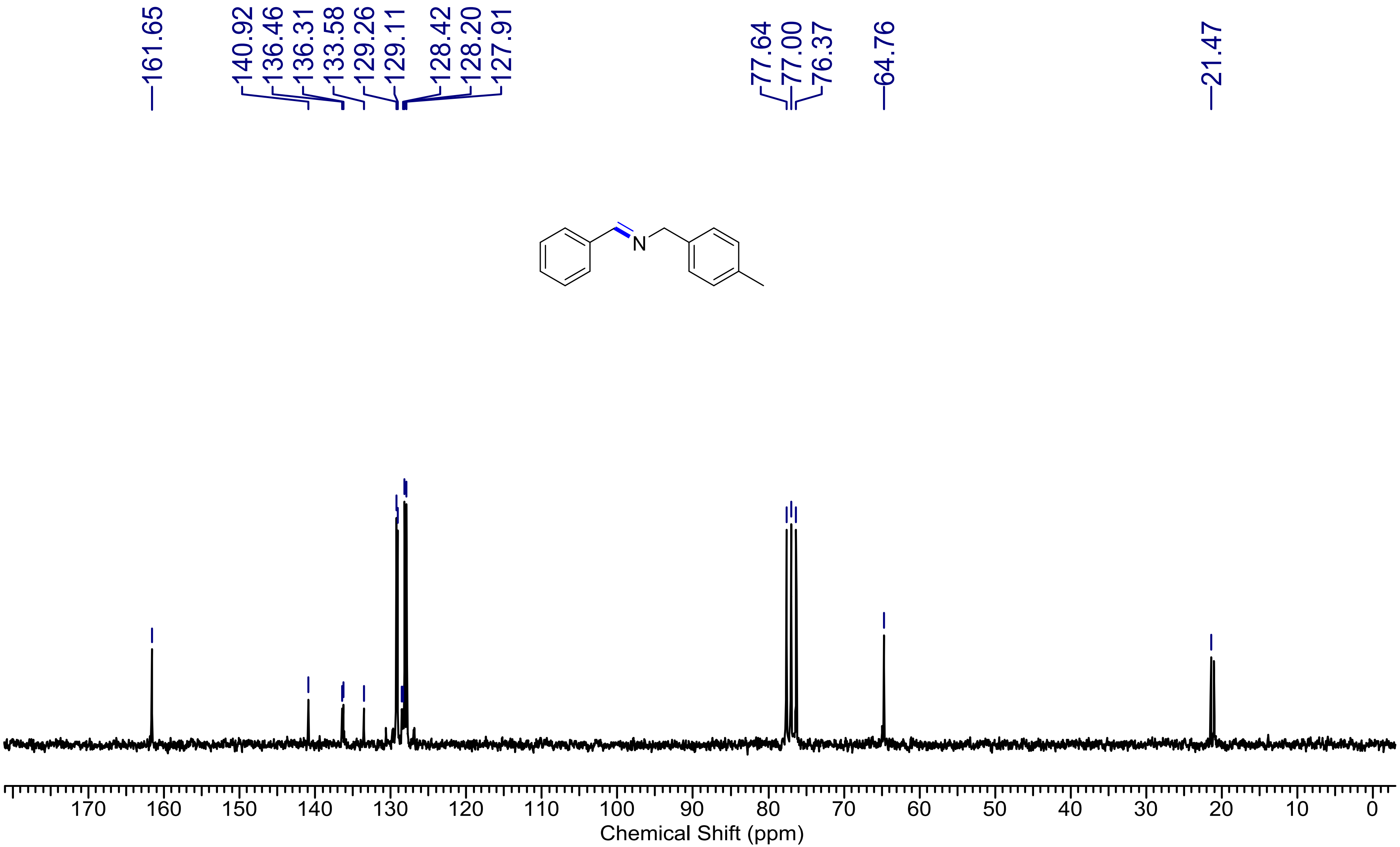


Figure S72. ^{13}C of **11b**

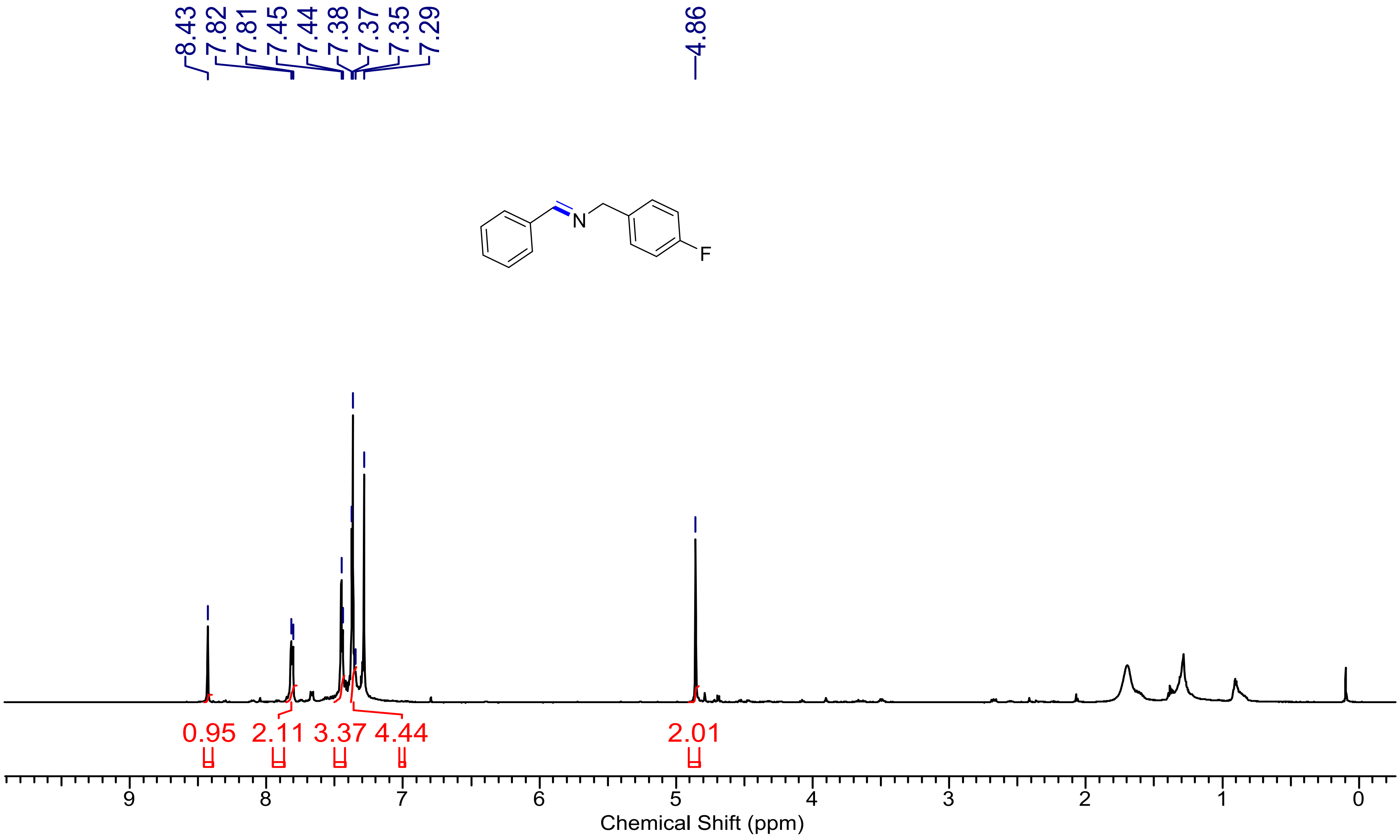


Figure S73. ^{1}H of **11c**

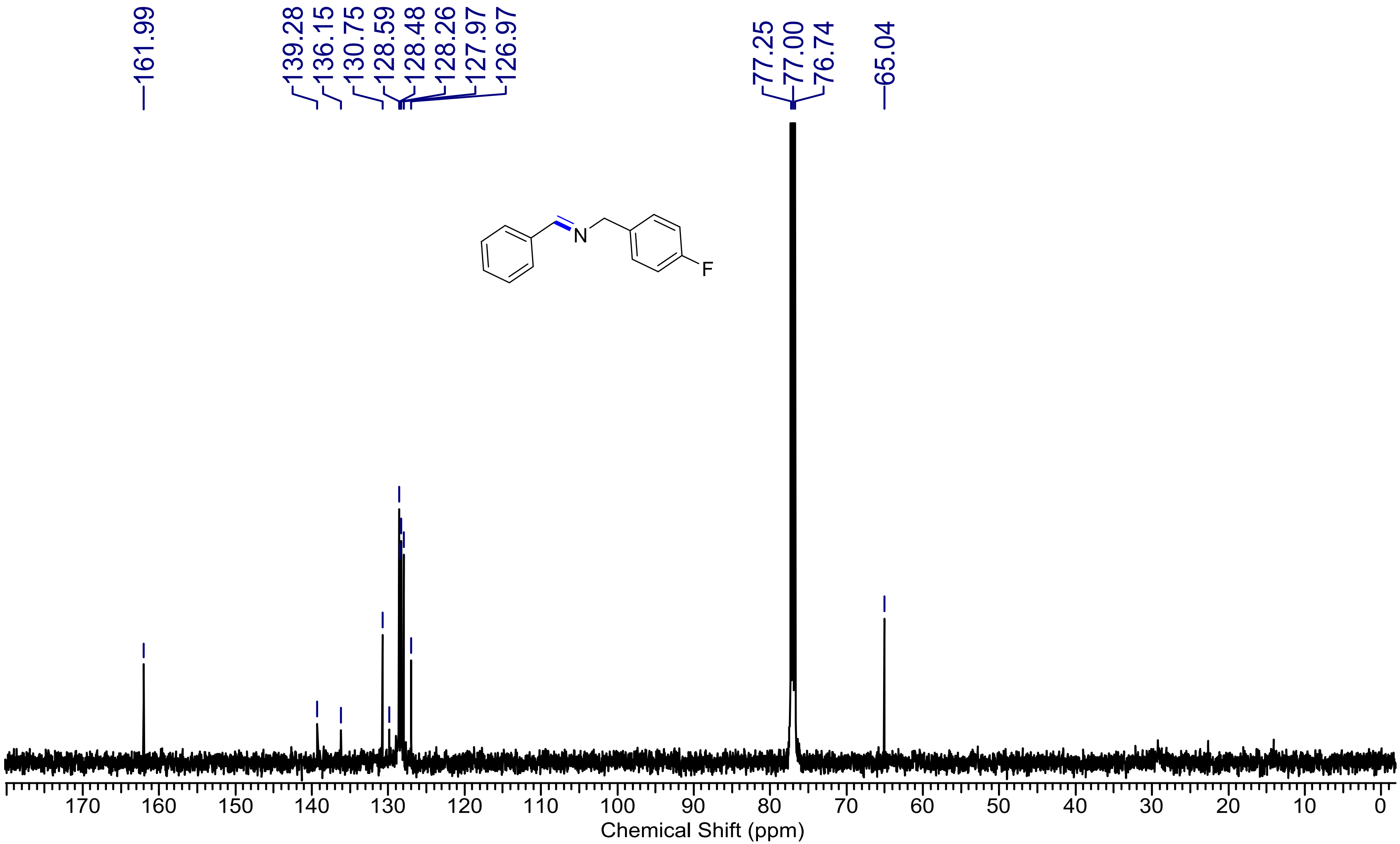


Figure S74. ^{13}C of **11c**

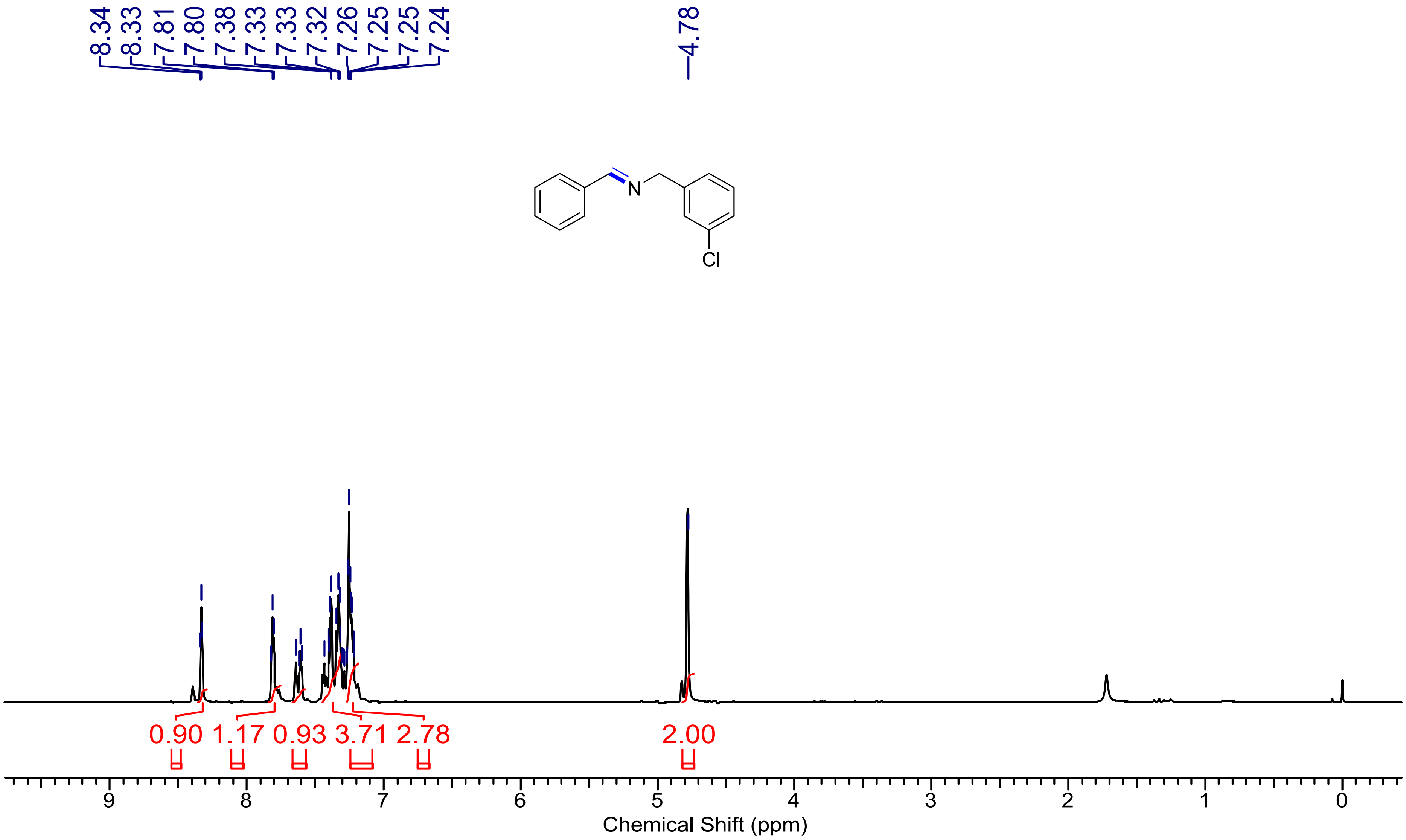


Figure S75. ^{1}H of **11d**

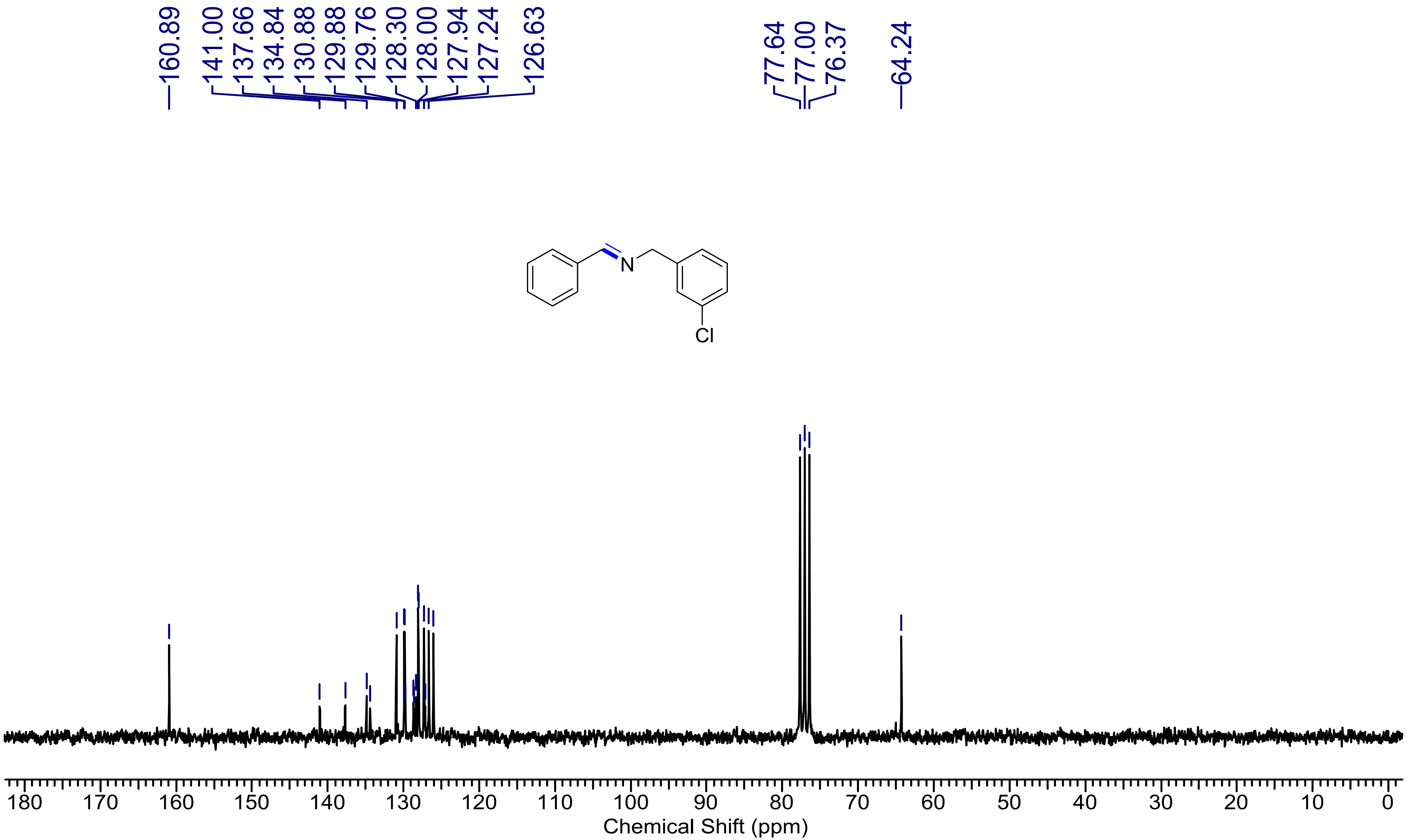


Figure S76. ^{13}C of **11d**

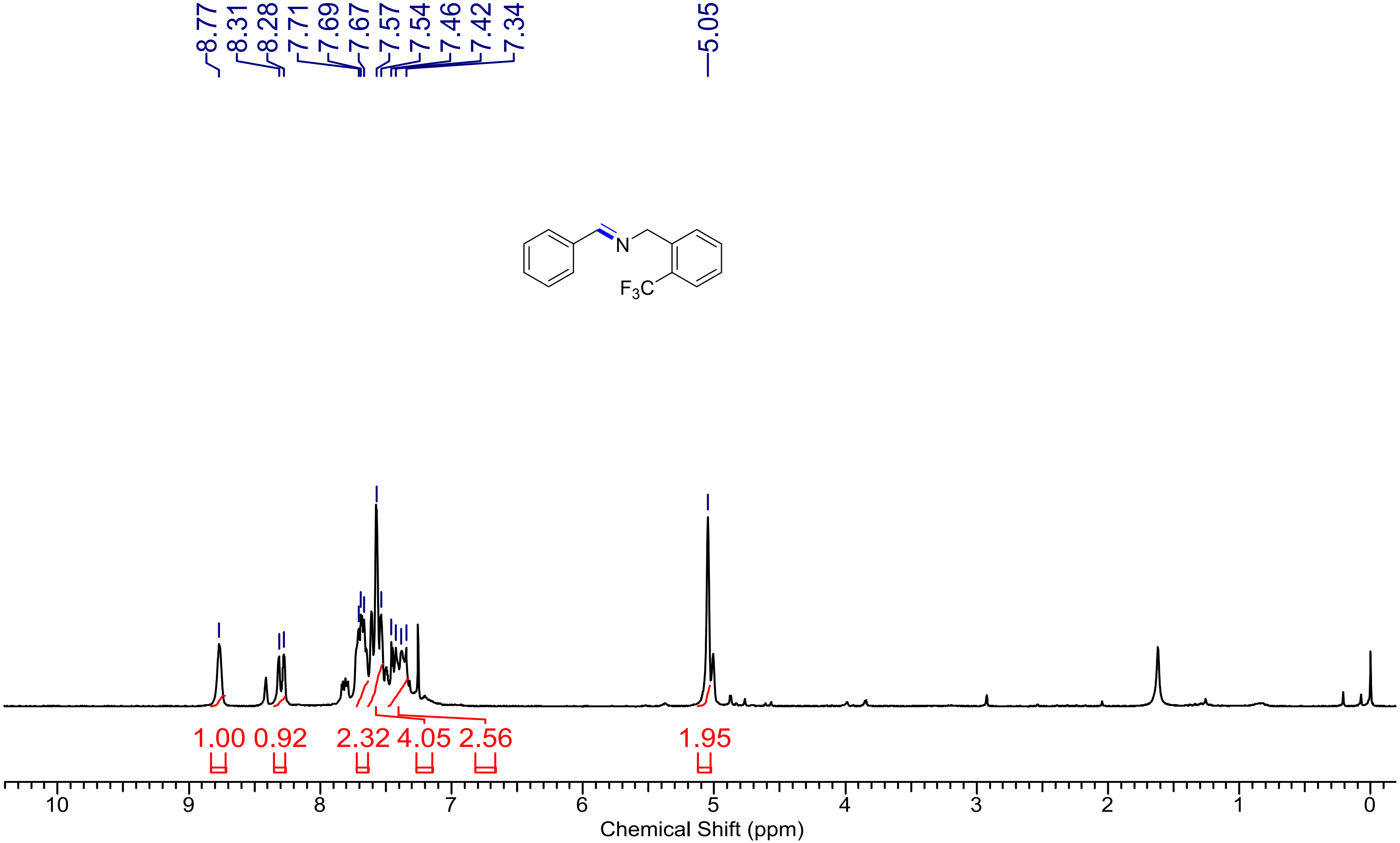


Figure S77. ^{1}H of **11e**

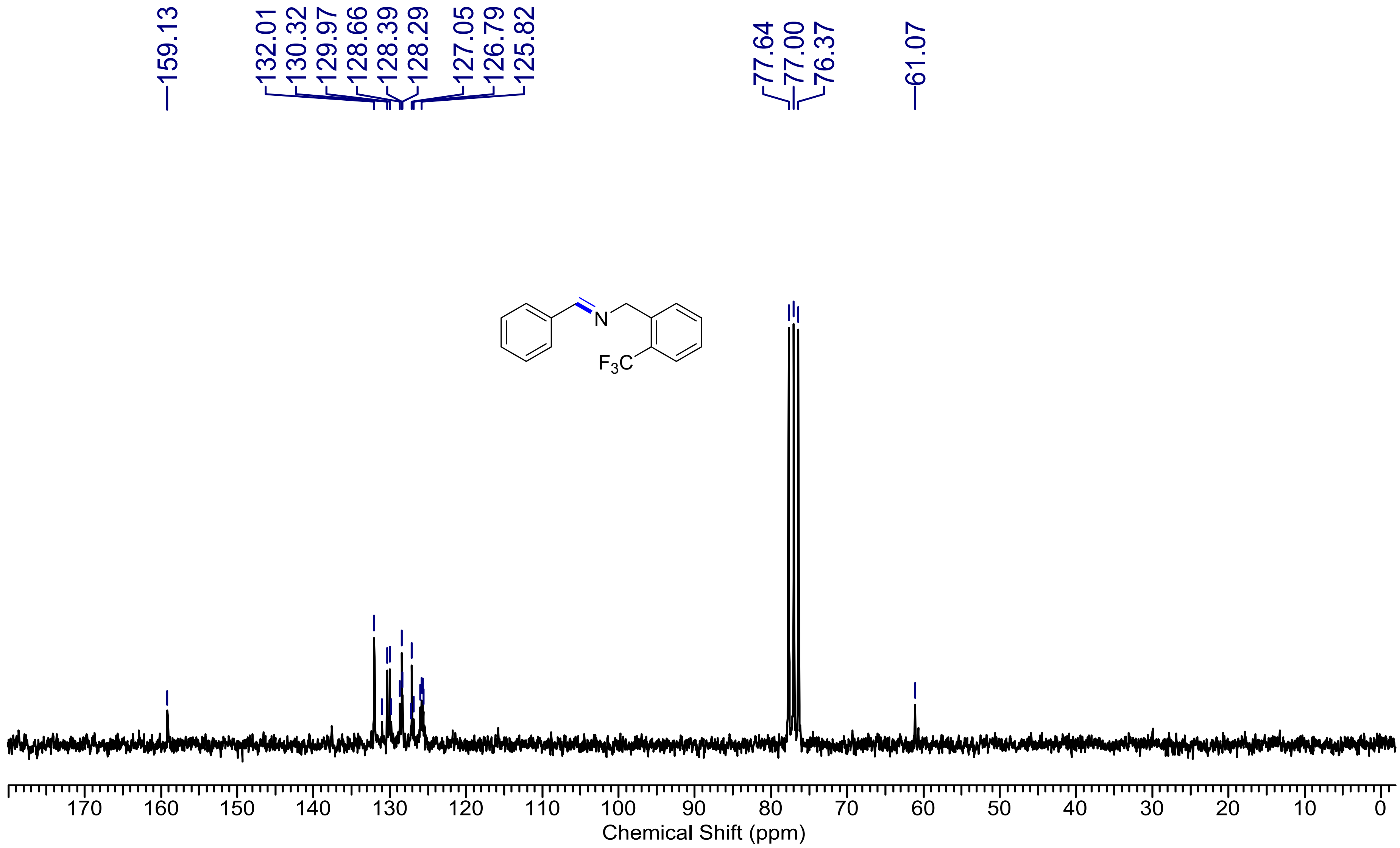


Figure S78. ^{13}C of **11e**

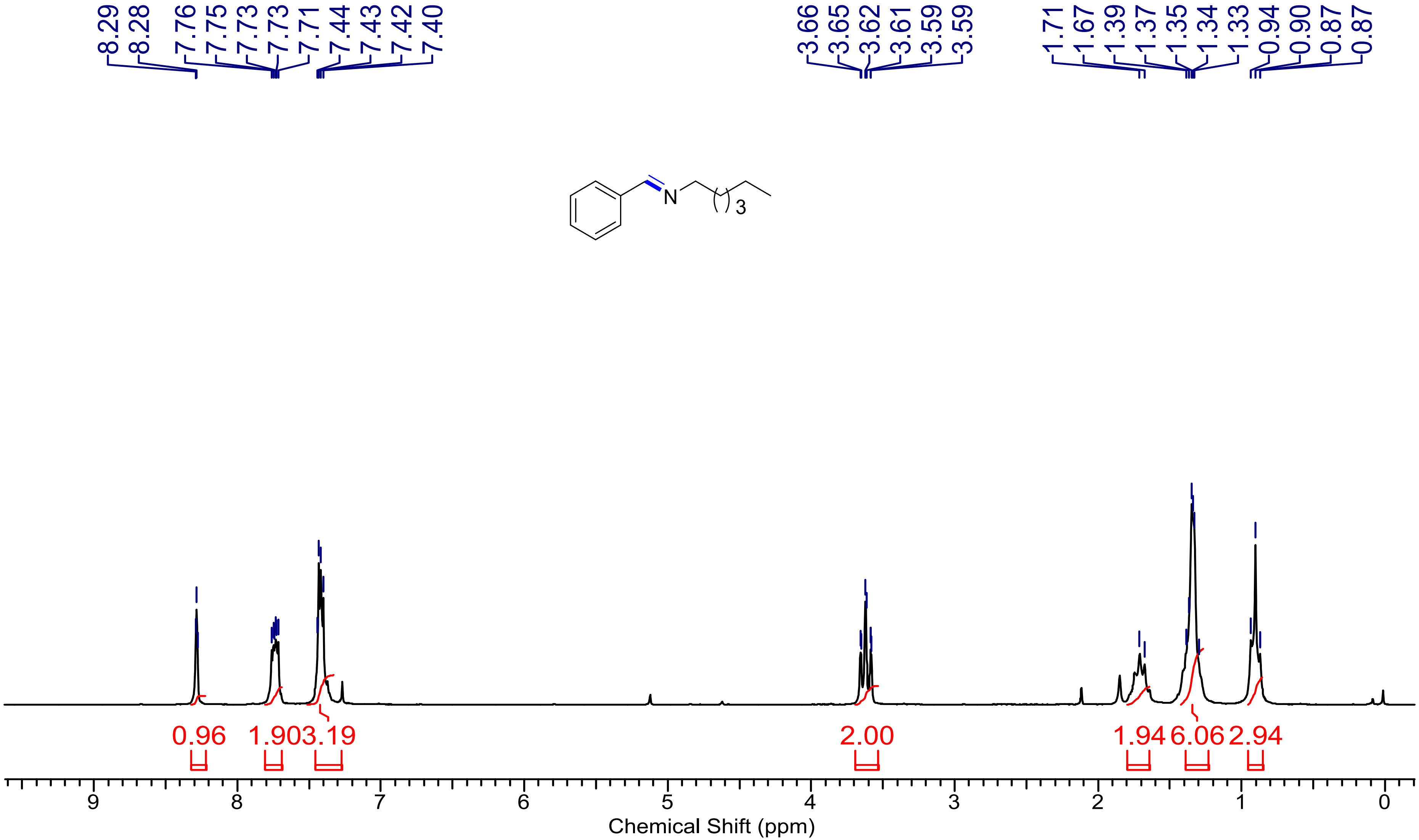


Figure S79. ^{1}H of **11f**

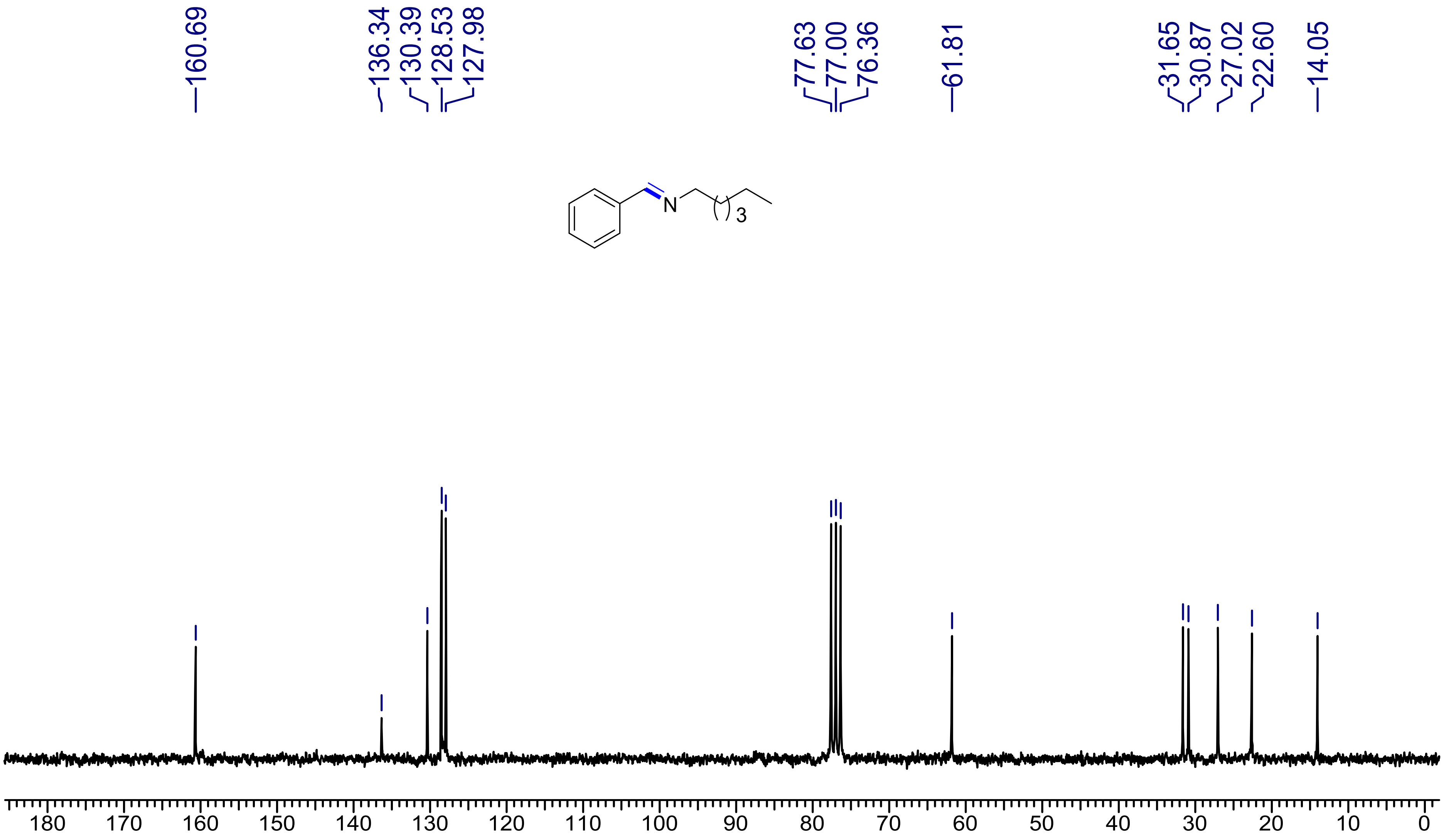


Figure S80. ^{13}C of **11f**

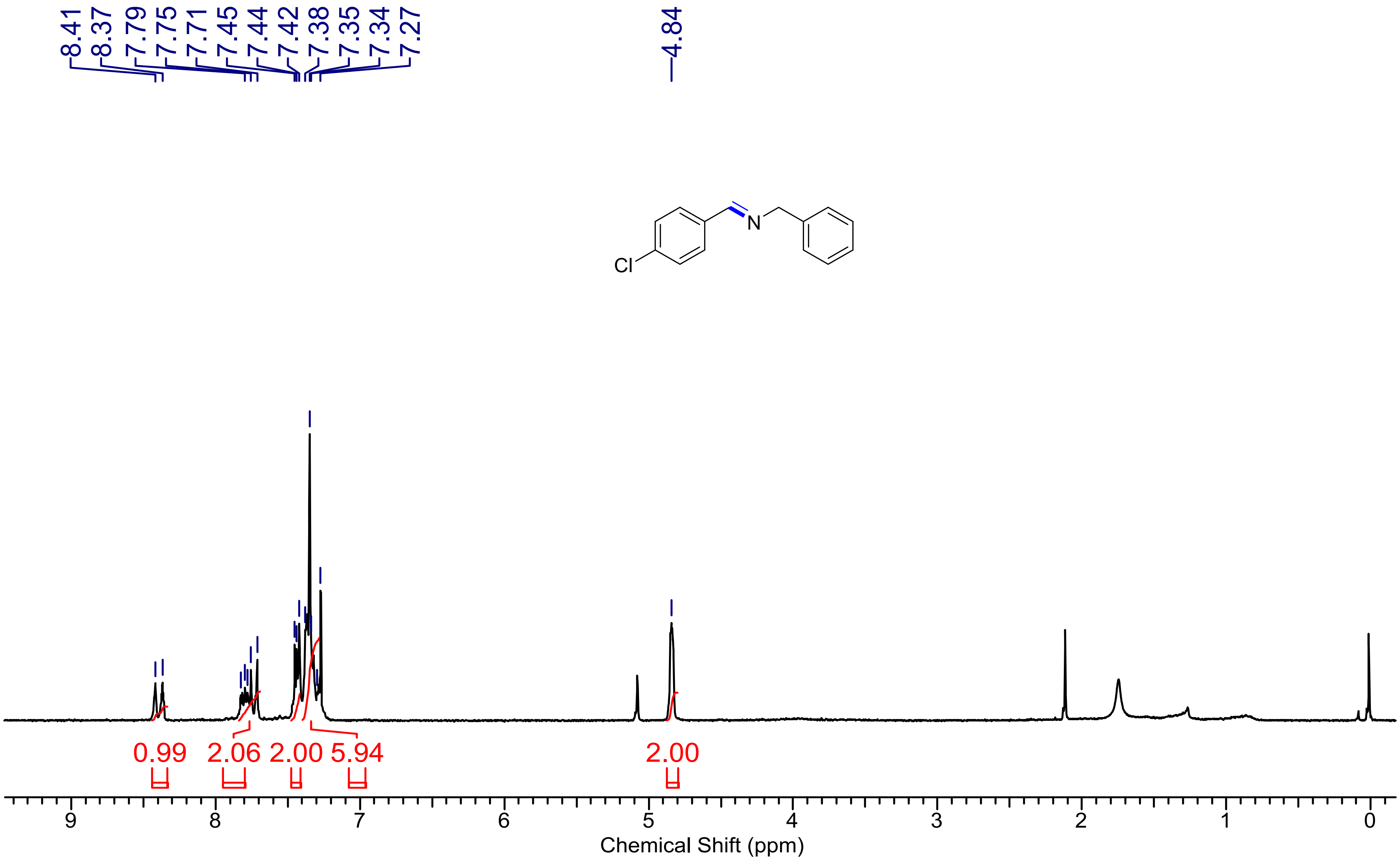


Figure S81. ^{1}H of **11g**

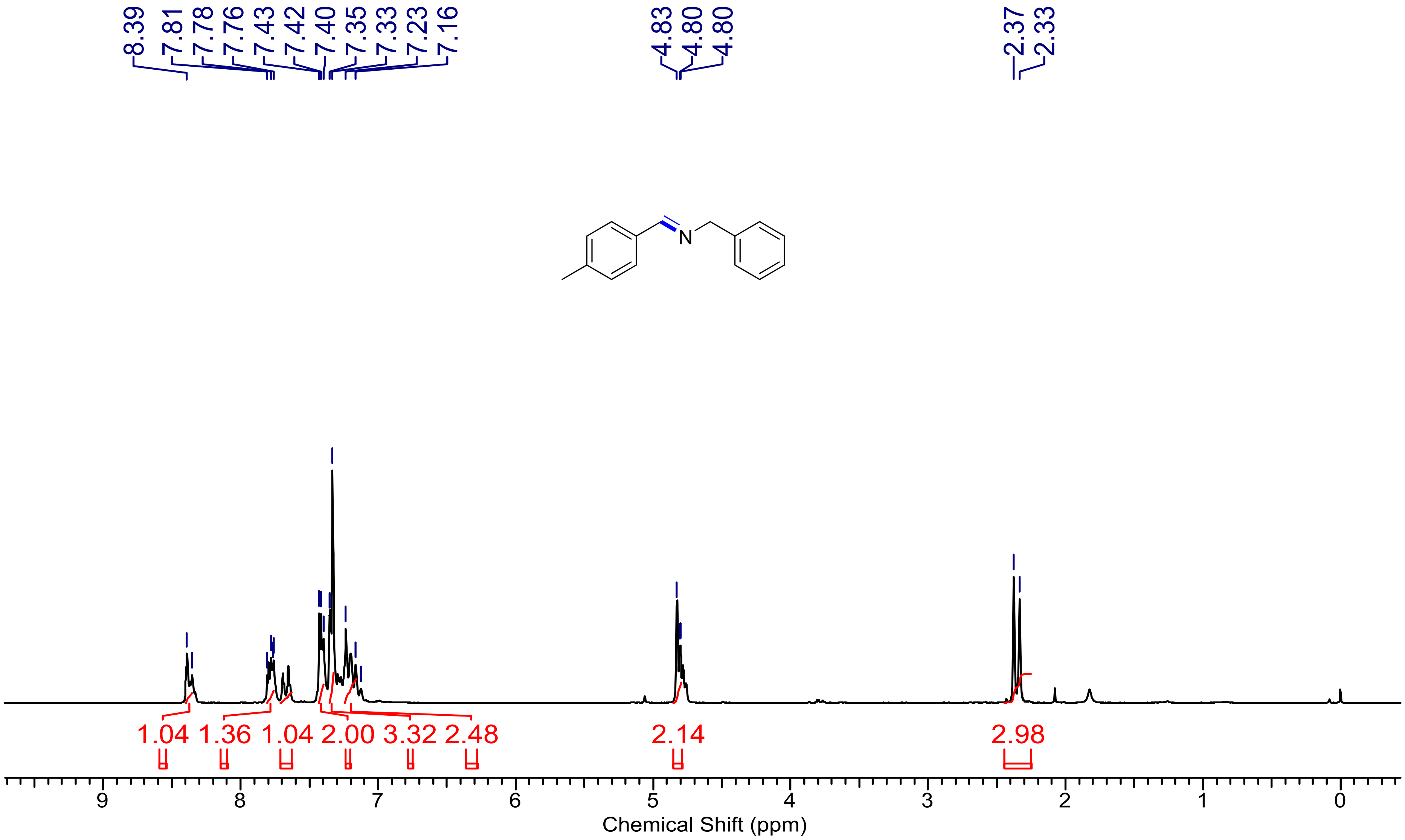


Figure S82. ^{1}H of **11h** (mixture of cis and trans imine product)

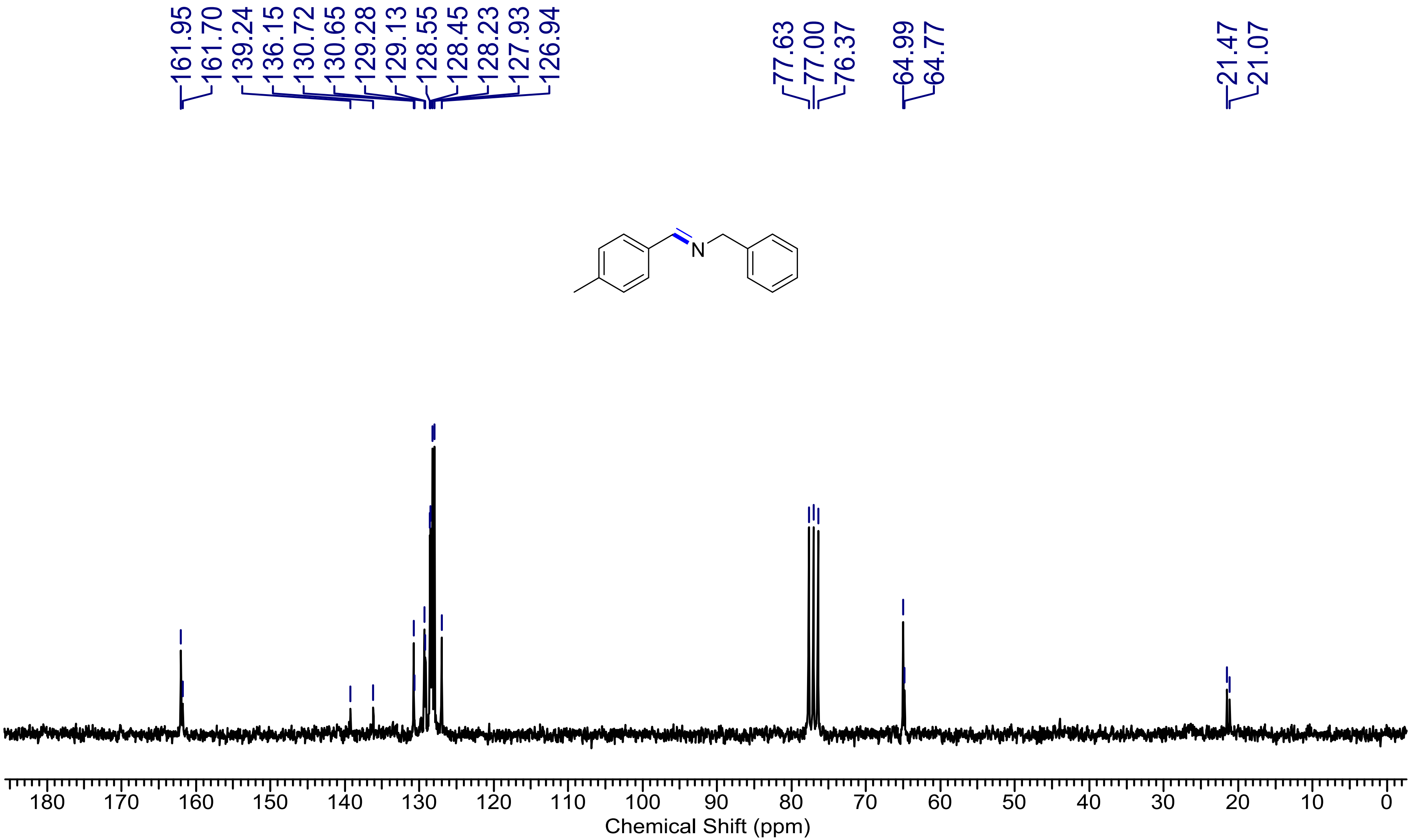


Figure S83. ^{13}C of **11h** (mixture of cis and trans imine product)

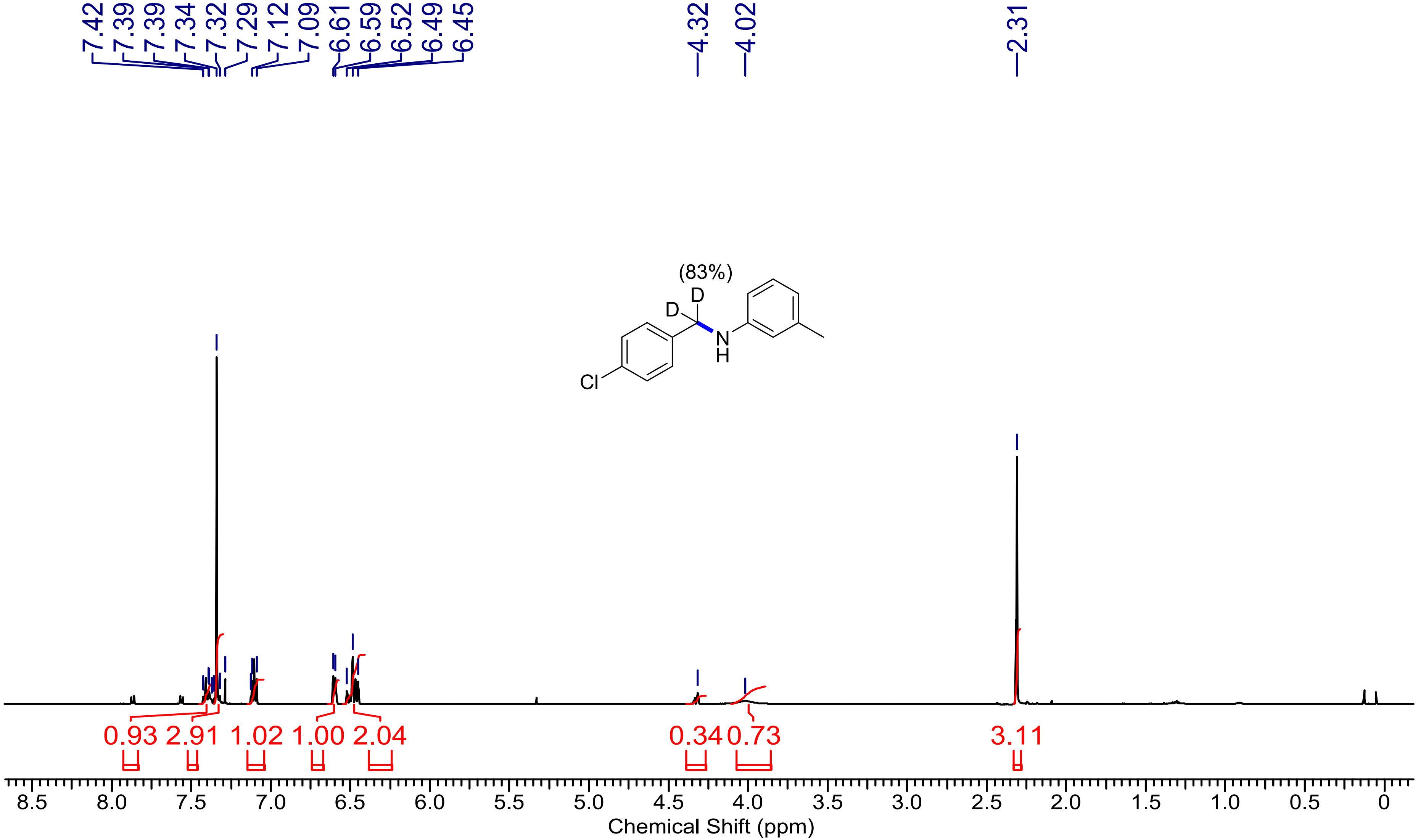


Figure S84. ^{1}H of **D-5c**

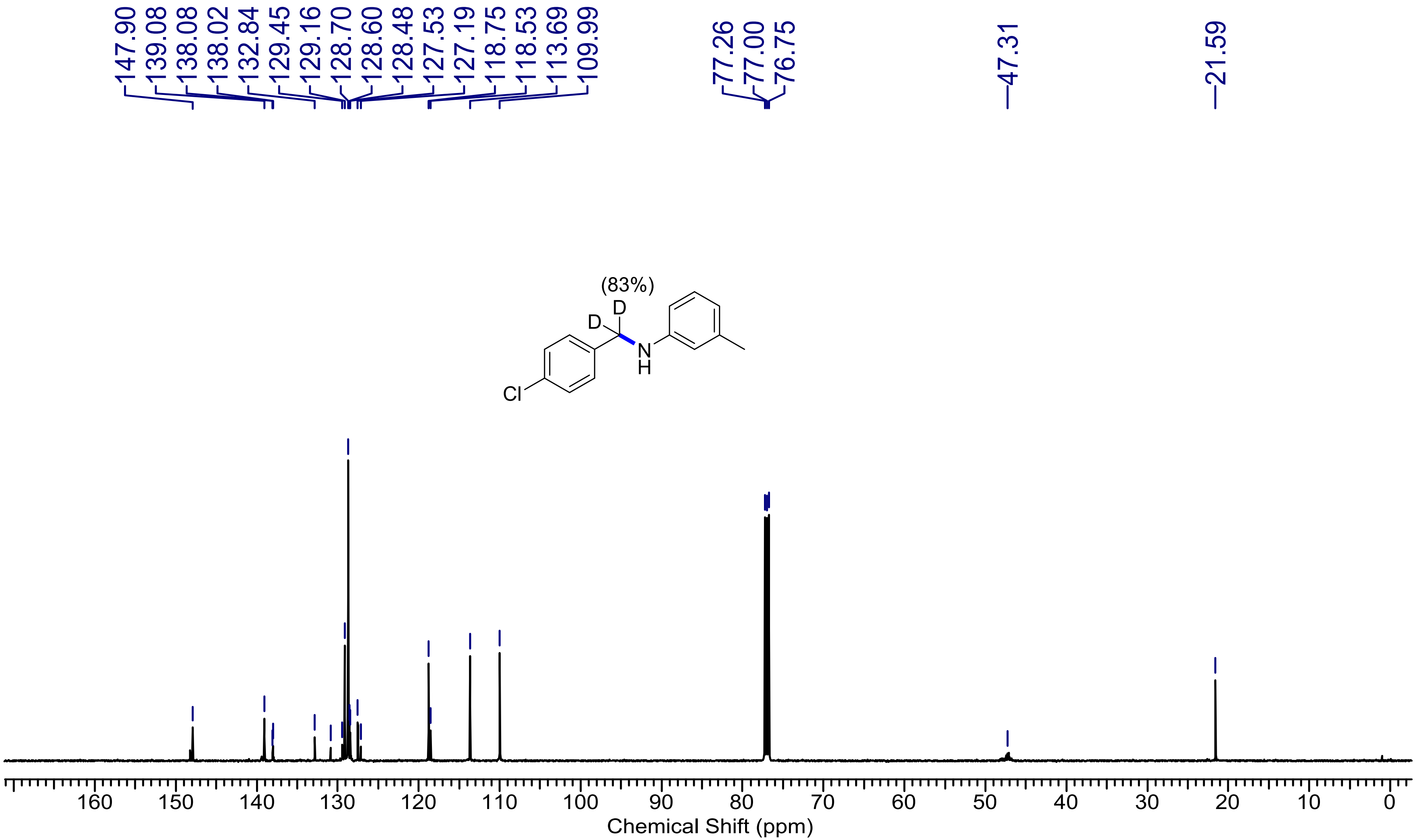


Figure S85. ^{13}C of **D-5c**