Electronic Supplementary Information (ESI)

Sustainable Iron-catalyzed direct imine formation by acceptorless dehydrogenative coupling of alcohols with amines

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Contents

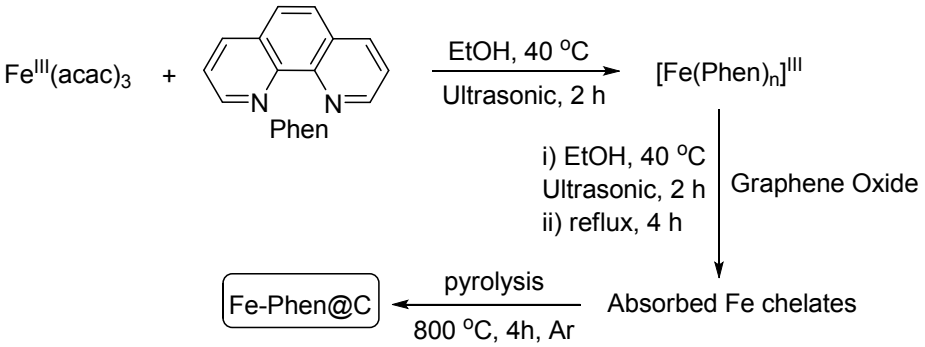
1. General Information

All catalytic experiments were carried out using standard Schlenk techniques. All solvents were reagent grade or better. Deuterated solvents were used as received without any additional purification. Most of the chemicals used in catalysis reactions were purified according to standard procedure (or by vacuum distillation/sublimation).[1] Thin layer chromatography (TLC) was performed using silica gel precoated glass plates, which were visualized with visualized with UV light at 254 nm or under iodine. Column chromatography was performed with SiO_2 (Silicycle Siliaflash F60 (230-400 mesh). ^{1}H NMR (400, 200 or 500 MHz), $^{13}C\{^{1}H\}$ NMR (100 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 relatives to the residual signals of this solvent [δ 7.27 for ^{1}H (chloroform-d), δ 77.0 for $^{13}C\{^{1}H\}$ (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 an 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) were obtained 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). Inductively couple plasma atomic emission spectroscopy (ICP-AES) were acquired for the elemental analysis of absolute iron content within the sample. Analysis performed by SPECTRO analytical instruments GmbH, model ARCOS simultaneous ICP spectrometer, Germany.

2. Catalyst Synthesis and Characterization

2.1 Synthesis of supported catalysts (Fe-Phen@SiO_2, Fe-Phen@TiO_2, and Fe-Phen@Al_2O_3 catalysts)

2.1a Synthesis of Fe-Phen@C catalyst††



Scheme 1. Synthesis of Fe-Phen@C catalyst

(a) Graphene oxide was prepared from graphite powder by Hummers method as reported in the literature.[2] Graphitic Oxide was heated at 160 °C for 12 h for exfoliation to get exfoliated graphene oxide (EGO).

(b) Fe (III) acetylacetonate 176 mg (0.5 mmol) and 1,10-phenanthroline 90 mg (0.5 mmol) were taken in a beaker containing 30 mL of ethanol and sonicated for 2 h to form Fe-Phenonthroline complex. In another beaker 560 mg of EGO†† was taken in 70 mL of ethanol and sonicated for 2 h. The EGO suspension and Fe-phenanthroline complex in ethanol were mixed together and further sonicated for 2 h. The suspension was subsequently refluxed for 4 h and ethanol was evaporated using rota-evaporator. After cooling to 30 °C, the ethanol was removed in vacuum and the solid sample obtained was dried at 80 °C for 14 h. Then, it was ground to a fine powder followed by calcination at 800 °C under a stream of argon with the flow rate of 30 mL/min and the heating rate: 25 °C/min for about 4 h to afford a catalyst Fe-

Phen@C. Iron present in the catalyst determined by ICP-AES analysis and was found to be 5.32%.

††In the case of other conventional support based catalysts such as Fe-Phen@SiO_2, Fe-Phen@TiO_2 and Fe-Phen@Al_2O_3 catalysts, 560 mg of the respective support (SiO_2, Al_2O_3, and TiO_2) was added and the other steps in the synthesis were identical as described in 2.1a.

2.2. Characterization of catalysts

a) XPS of Fe region of Fe-Phen@C

X-ray photoelectron spectroscopy (XPS) was done on a VG Microtech Multilab ESCA 3000 spectrometer that was equipped with a Mg K_α X-ray source ($h\upsilon$ = 1253.6 eV). The XPS peaks were fitted on XPSPEAK 4.1 having 70% Gaussian and 30% Lorentzian character, after performing a Shirley background subtraction. In the fitting procedure,[3-9] the full width at half-maximum (FWHM) values were fixed 1.5 eV for all the peaks.

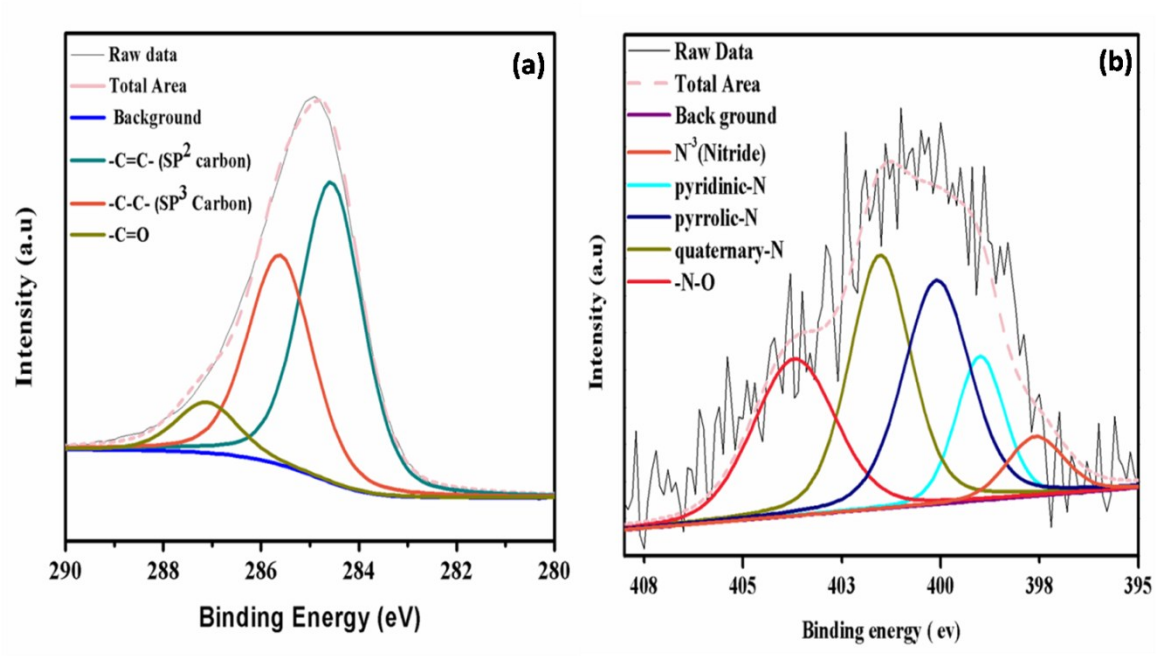


Fig. S1 Deconvoluted XPS spectra of Fe-Phen@C sample: **(a)** C1s region, **(b)** N1s region.

Table showing the peak positions in C1s and N1s XPS spectra and the corresponding chemical species.

C1s Spectra (Fig. S1a)	
Peak Position (eV)	**Inference**
284.5	sp^2 carbon (−C=C−)
285.8	sp^3 carbon such as −C−C− or −C−OH groups
287.3	Carbonyl functional group (C=O).
N1s Spectra (Fig. S1b)	
Peak Position (eV)	**Inference**
397.5	N of Fe_3N
399.1	pyridinic-N/N_{Pyri}
400.1	pyrrolic-N/N_{Pyrr}
401.4	quaternary-N/NR_4^+
403.6	–N–O

b. Raman spectra

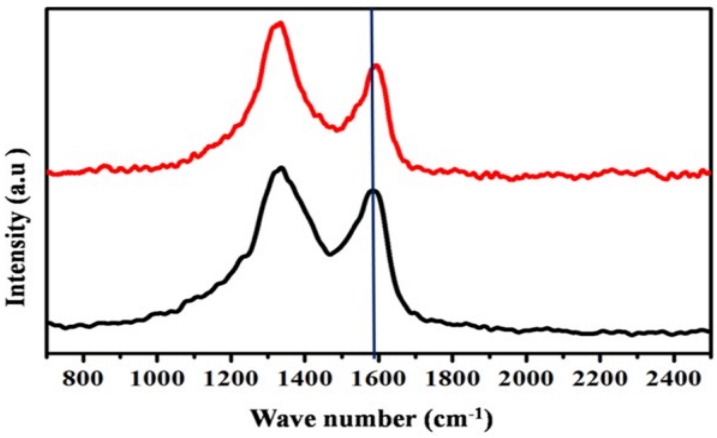


Fig. S2 Raman Spectra of reduced graphitic oxide support (black) and Fe-Phen@C (red).

Fig. S2 shows Raman spectra of Fe-Phen@C (red trace) and reduced graphitic oxide (black trace). The D band due to the vibration mode of A_{1g} symmetry of the sp^2 carbon of graphite lattice located at 1327 cm^{-1} for Fe-Phen@C and 1330 cm^{-1} for reduced graphitic oxide support. The D band mainly characterizes structural defects or edges that can break the symmetry and selection rule. The G band that arises due to the first-order scattering of the E_{2g} mode observed for sp^2 carbon domains was seen at 1595 cm^{-1} for Fe-Phen@C and at 1586 cm^{-1} for reduced graphitic oxide support. G band characterizes the highly ordered graphite

carbon materials. It was observed that deposition of iron in Fe-Phen@C resulted in an increased disorderliness of reduced graphitic oxide, as I_D/I_G increased to 1.36 in Fe-Phen@C compared to I_D/I_G=1.13 in reduced graphitic oxide support. G band showed a blue shift of 9 cm^{-1} in Fe-Phen@C as compared to reduced graphitic oxide support which was mainly due to charge transfer from graphene to iron nanoparticles.[10-11]

C. EDX analysis

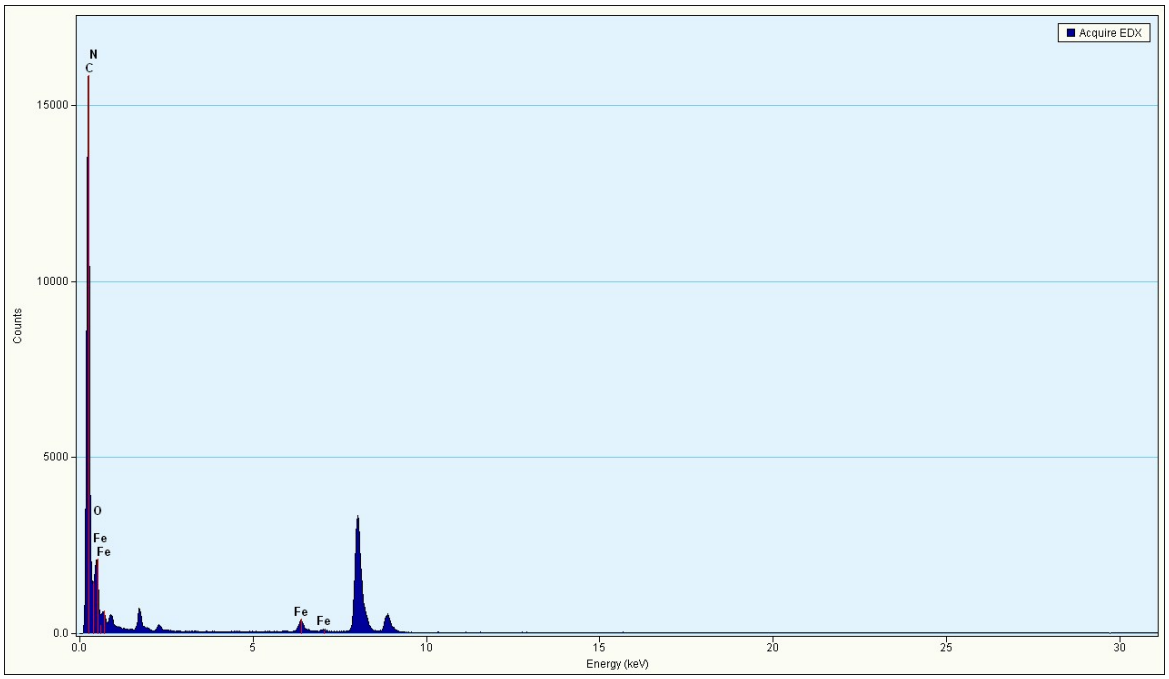


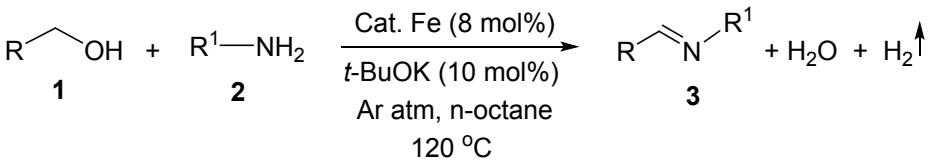
Fig. S3 EDX analysis of Fe-Phen@C.

Table showing the weight percent of different elements in the Fe-Phen@C catalyst.

Element	Weight %	Atomic %	Uncert. %	Correction	k-Factor
C(K)	76.36	83.29	0.41	0.26	3.940
N(K)	9.23	8.64	0.17	0.26	3.826
O(K)	8.02	6.56	0.09	0.49	1.974
Fe(K)	6.37	1.49	0.06	0.99	1.403

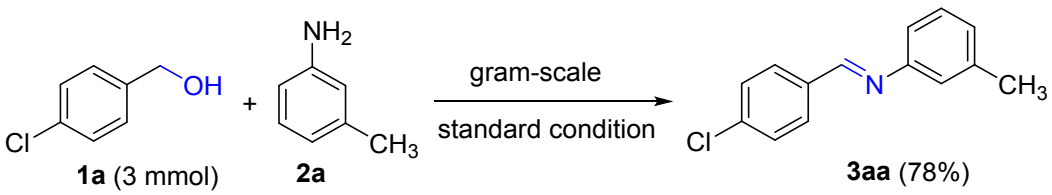
3. Experimental Section

3.1 General procedure for the iron-catalyzed direct imine formation



To a 25 mL oven dried schlenk tube, Fe-Phen@C catalyst (43 mg, 8 mol%), *t*-BuOK (10 mol%), alcohol (0.5 mmol), an amine (0.55 mmol), and n-octane (2 mL) were added under argon atmosphere. The schlenk tube was equipped with a reflux condenser, and the solution was heated at 120 °C (bath temperature) with stirring under open argon flow for 24 h. After cooling to 30 °C the catalyst was separated from the reaction mixture by an external permanent magnet and the reaction products were analyzed by GC and GC-MS. The supernatant was transferred into another flask, and the catalyst was washed with EtOAc (2 x 4 mL) and the washings were collected. The solvent was evaporated from the reaction mixture, and the crude product was subjected to deactivated silica gel column chromatography using EtOAc : petroleum ether to afford the imine derivatives.

3.2 Gram-scale synthesis of imine



To a 50 mL oven dried schlenk flask, Fe-Phen@C catalyst (258 mg, 8 mol%), *t*-BuOK (34 mg, 10 mol%,), (4-chlorophenyl)methanol (428 mg, 3 mmol), *m*-toluidine (374 mg, 3.5 mmol,), and n-octane (12 mL) were added under argon atmosphere. The schlenk flask was equipped with a reflux condenser, and the solution was heated at 120 °C (bath temperature)

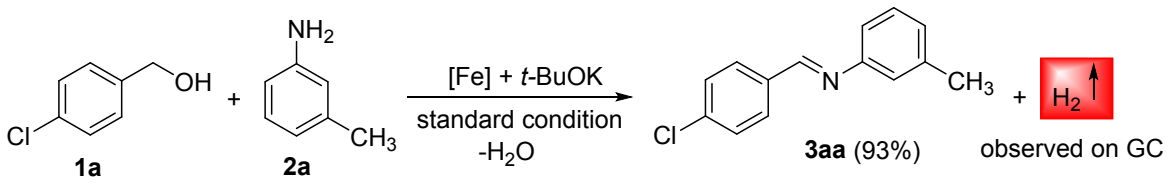
with stirring under open argon flow for 36 h. After cooling to 30 °C the reaction mixture was subjected to centrifugation and the supernatant was collected and the obtained solid was washed with EtOAc (3 x 5 mL) and the washings were collected. The collected reaction mixture was concentrated on rotavapor under reduce pressure. The crude product was purified through triethylamine (5 mL triethylamine in 100 ml pet ether/ethyl acetate) neutralized silica-gel column chromatography by using petroleum ether and ethyl acetate as an eluent.

3.3 Reusability procedure

To a 25 mL oven dried schlenk tube, Fe-Phen@C catalyst (86 mg, 8 mol%) *t*-BuOK (11 mg, 10 mol%), (4-chlorophenyl)methanol (143 mg, 1 mmol), *m*-toluidine (125 mg, 1.1 mmol), and n-octane (4 mL) were added under argon atmosphere. The schlenk tube was equipped with a reflux condenser, and the solution was heated at 120 °C (bath temperature) with stirring under open argon flow for 24 h. After cooling to 30 °C, the catalyst was separated from the reaction mixture by an external permanent magnet, washed with EtOAc several times and dried under vacuum at 60 °C for 4 h. Then the catalyst was reused for the next cycle. All yields are averages from at least 2 runs.

4. Mechanistic Investigation

4.1 Determination of hydrogen gas formation



To an oven dried 20 mL screw-capped septa vial, Fe-Phen@C catalyst (86 mg, 8 mol%), *t*-BuOK (11 mg, 10 mol%), (4-chlorophenyl)methanol **1a** (143 mg, 1 mmol), *m*-toluidine **2a** (125 mg, 1.1 mmol), and n-octane (4 mL) were added under argon atmosphere. The vial was heated at 120 °C for 4 h. After cooling to room temperature, the gaseous mixture (formation of hydrogen gas) was qualitatively analyzed by GC-TCD with a Carbon plot capillary column.

Area % Report

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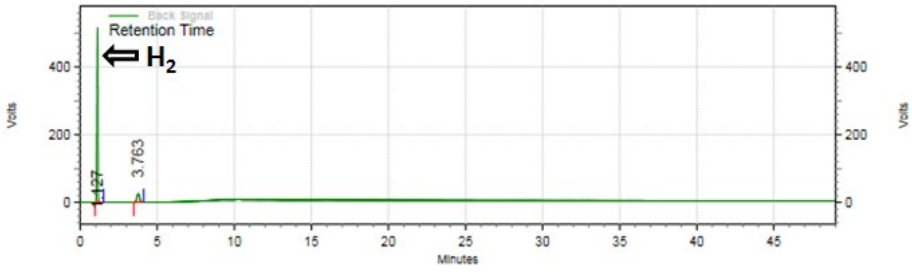
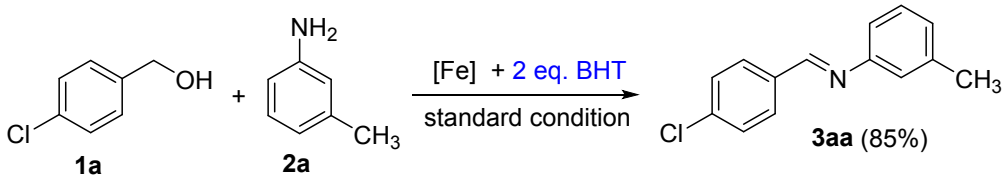


Back Signal
Results

Retention Time	Area	Area %	Height	Height %
1.127	16555386	87.39	3957450	95.22
3.763	2389762	12.61	198546	4.78
Totals	18945148	100.00	4155996	100.00

4.2 Reaction under presence of radical ($O^{\cdot-}_2$) scavenger



To a 25 mL oven dried schlenk tube, Fe-Phen@C catalyst (43 mg, 8 mol%), *t*-BuOK (6 mg, 10 mol%), (4-chlorophenyl)methanol (71 mg, 0.5 mmol), *m*-toluidine (62 mg, 0.55 mmol), 2,6-di-tert-butyl-4-methylphenol (BHT) (242 mg, 1.1 mmol), and n-octane (2 mL) were added under argon atmosphere. The schlenk tube was equipped with a reflux condenser and the solution was refluxed under argon atmosphere for 24 h. After cooling to 30 °C the

reaction mixture was subjected to centrifugation and the supernatant was collected and the obtained solid was washed with EtOAc (2 x 4 mL) and the washings were collected. The collected reaction mixture was concentrated on rotavapor under reduce pressure. The crude product was purified (deactivated silica gel column chromatography and the eluvent is a mixture of petroleum ether and ethyl acetate) and the yield of (*E*)-1-(4-chlorophenyl)-*N*-(*m*-tolyl)methanimine (**3aa**) is 85%.

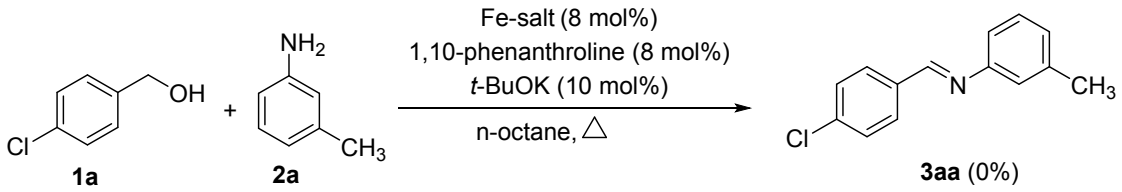
4.3. Hot Filtration Test

To a 25 mL oven dried schlenk tube, Fe-Phen@C catalyst (43 mg, 8 mol%), *t*-BuOK (6 mg, 10 mol%), (4-chlorophenyl)methanol **1a** (71 mg, 0.5 mmol), *m*-toluidine **2a** (62 mg, 0.55 mmol), and n-octane (2 mL) were added under argon atmosphere. The schlenk tube was equipped with a reflux condenser, and the solution was heated at 120 ^{o}C (bath temperature) with stirring under open argon flow for 8 h. After cooling to 30 ^{o}C the catalyst was separated from the reaction mixture by an external permanent magnet (at this stage the crude reaction mixture was analyzed by GC (67% of **3aa**)). Then, the reaction mixture was transferred into another 25 mL oven dried schlenk tube under an argon atmosphere and was equipped with a reflux condenser, and the solution was heated at 120 ^{o}C (bath temperature) with stirring under open argon flow for 24 h. After cooling to room temperature, the crude reaction mixture was quantitatively analyzed by GC and observed that no change in the yield of **3aa**.

4.4 Leaching Test

To crude sample (after removal the catalyst) were added sulfuric acid and aqua regia then the volume of the residue was adjusted to 50 mL using water to give a sample for Inductively coupled plasma (ICP) for the measurement of the leaching of Iron and the analyses confirmed that the iron concentration in the filtrate was less than 0.22 ppm.

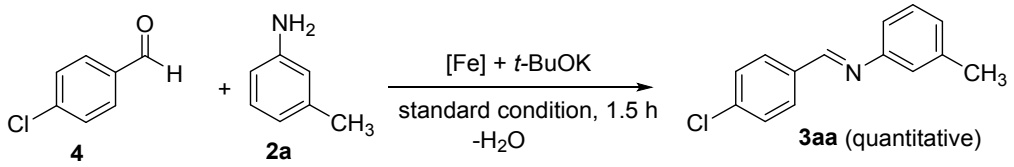
4.5 Reaction under homogeneous conditions



1a **2a** **3aa** (0%)

To a 25 mL oven dried schlenk tube, 8 mol% of Fe salt (iron(III) acetylacetonate or $Fe(CO)_5$) and 1,10-phenanthroline (7 mg, 8 mol%) and n-octane (2 mL) were added under argon atmosphere. The schlenk tube was equipped with a reflux condenser, and the solution was heated at 80 ^oC under argon atmosphere for 1 h. To the pre-formed Fe-complex, (4-chlorophenyl)methanol (71 mg, 0.5 mmol), *m*-toluidine (62 mg, 0.55 mmol), and *t*-BuOK (6 mg, 10 mol%) were added under argon atm and heated at 120 ^oC (bath temperature) for 24 h. After cooling to room temperature, the crude reaction mixture was analyzed by GC and observed no formation imine.

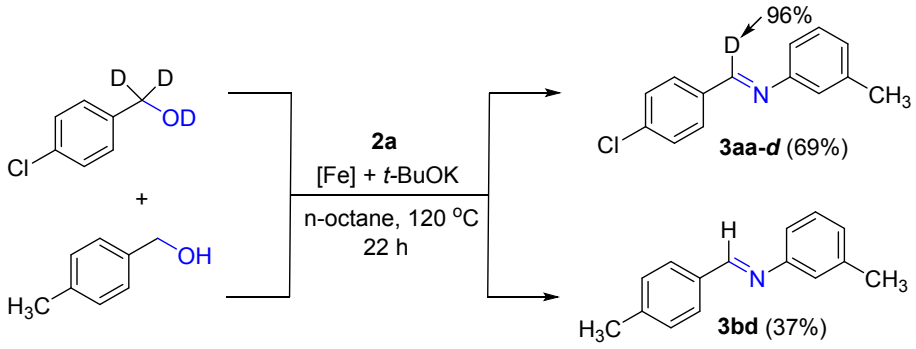
4.6 Presence of Lewis acid sites



4 **2a** **3aa** (quantitative)

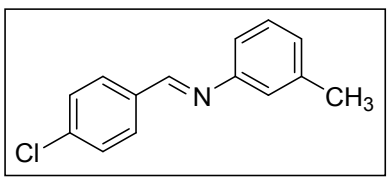
To a 25 mL oven dried schlenk tube, Fe-Phen@C catalyst (43 mg, 8 mol%), *t*-BuOK (6 mg, 10 mol%), 4-chlorobenzaldehyde **4** (71 mg, 0.5 mmol), *m*-toluidine **2a** (62 mg, 0.55 mmol), and n-octane (2 mL) were added under argon atmosphere. The schlenk tube was equipped with a reflux condenser and the solution was refluxed under argon atmosphere for 1.5 h. After cooling to 30 ^oC, the crude reaction mixture was analyzed by ^1H NMR and observed the quantitative formation of **3aa**. The same result was observed in the absence of *t*-BuOK.

4.7 Deuterium labelling studies



To a 25 mL oven dried schlenk tube, Fe-Phen@C catalyst (86 mg, 8 mol%), *t*-BuOK (11 mg, 10 mol%), *p*-tolylmethanol (62 mg, 0.5 mmol), (4-chlorophenyl)methan-d_2-ol-*d* (73 mg, 0.5 mmol),[12] and *m*-toluidine (138 mg, 1.1 mmol), and n-octane (4 mL) were added under argon atmosphere. The schlenk tube was equipped with a reflux condenser and the solution was refluxed under argon atmosphere for 22 h. After cooling to 30 °C the reaction mixture was subjected to centrifugation and the supernatant was collected and the obtained solid was washed with EtOAc (2 x 4 mL) and the washings were collected. The collected reaction mixture was concentrated under reduce pressure. The crude product was purified, and the yield of (*E*)-1-(4-chlorophenyl)-*N*-(*m*-tolyl)methanimine-*d* and (*E*)-*N*-*m*-tolyl-1-(*p*-tolyl)methanimine are 69% and 37% respectively.

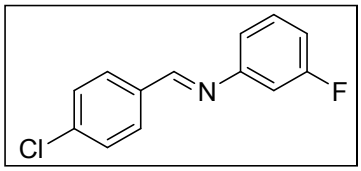
5. Characterization Data



(E)-N-(4-chlorobenzylidene)-3-methylaniline **(3aa)**

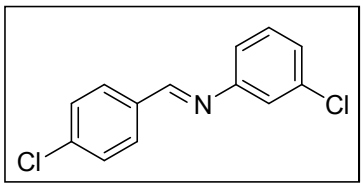
106 mg, 93% isolated yield. ^{1}H NMR ($CDCl_3$, 500 MHz) δ 8.43 (s, 1H), 7.85 (d, *J* = 8.4 Hz, 2H), 7.46 (d, *J* = 8.4 Hz, 2H), 7.30 (t, *J* = 7.5 Hz, 1H), 7.08 (d, *J* = 7.2 Hz, 1H), 7.04-7.02 (m,

2H), 2.41 (s, 3H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ 158.61, 151.62, 139.02, 137.25, 134.69, 129.89, 129.02(d, J = 4.8 Hz), 126.95, 121.58, 117.79, 21.38; HRMS Calcd for $C_{14}H_{12}NCl$ $[M+H]^+$: 230.0731; Found: 230.0734.



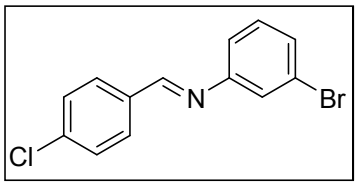
N-(4-chlorobenzylidene)-3-fluoroaniline **(3ab)**

100 mg, 86% isolated yield. ^{1}H NMR ($CDCl_3$, 200 MHz) δ 8.29 (s, 1H), 7.74 (d, *J* = 8.5 Hz, 2H), 7.36 (d, *J* = 8.4 Hz, 2H), 7.23-7.16 (m, 1H), 6.90-6.81 (m, 3H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ 164.23, 162.27, 159.58, 153.48, 153.40, 130.32, 130.05, 129.08, 116.66, 116.64, 112.88, 112.70, 108.09, 107.91; HRMS Calcd for $C_{13}H_9NClF$ $[M+H]^+$: 234.0480; Found: 234.0482.



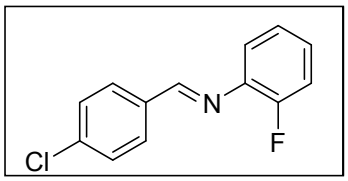
(E)-3-chloro-N-(4-chlorobenzylidene)aniline **(3ac)**

103 mg, 83% isolated yield. ^{1}H NMR ($CDCl_3$, 200 MHz) δ 8.29 (s, 1H), 7.74 (d, *J* = 8.6 Hz, 2H), 7.36 (d, *J* = 8.5 Hz, 2H), 7.23-7.10 (m, 3H), 6.98 (d, *J* = 7.91, 1H)**.** ^{13}C NMR ($CDCl_3$, 50 MHz) δ 159.76, 152.95, 137.81, 134.78, 134.31, 130.89, 130.18, 130.09, 129.46, 129.15, 126.05, 120.87, 119.36; HRMS Calcd for $C_{13}H_9NCl_2$ $[M+H]^+$: 250.0185; Found: 250.0187.



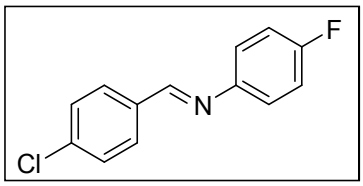
(E)-3-bromo-N-(4-chlorobenzylidene)aniline **(3ad)**

130 mg, 89% isolated yield. ^{1}H NMR ($CDCl_3$, 500 MHz) δ 8.31 (s, 1H), 7.76 (d, *J* = 8.3 Hz, 2H), 7.38 (d, *J* = 8.3 Hz, 2H), 7.31–7.14 (m, 3H), 7.06 (d, *J* = 7.8 Hz, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 159.76, 153.01, 137.77, 134.23, 130.85, 130.54, 130.44, 130.07, 129.41, 129.11, 128.92, 123.64, 119.90; HRMS Calcd for $C_{13}H_9NBrCl$ $[M+H]^+$: 293.9680; Found: 293.9684.



(E)-N-(4-chlorobenzylidene)-2-fluoroaniline **(3ae)**

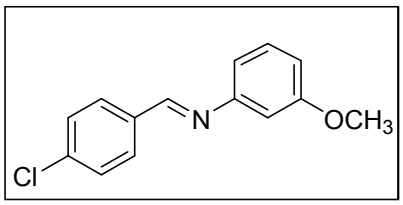
68 mg, 58% isolated yield. ^{1}H NMR ($CDCl_3$, 500 MHz) δ 8.50 (s, 1H), 7.87 (d, *J* = 8.6 Hz, 2H), 7.46 (d, *J* = 8.6 Hz, 2H), 7.27 - 7.15 (m, 4H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ 161.33, 156.15, 154.16, 139.61, 139.53, 137.77, 134.50, 130.08, 129.06, 126.94, 126.88, 124.50, 124.47, 122.02, 116.37, 116.21; HRMS Calcd for $C_{13}H_9NClF$ $[M+H]^+$: 234.0480; Found: 234.0482.



(E)-N-(4-chlorobenzylidene)-4-fluoroaniline **(3af)**

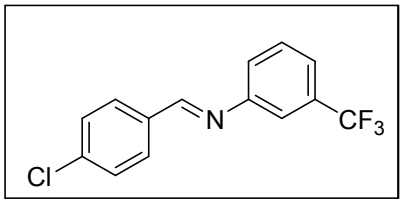
87 mg, 75% isolated yield. ^{1}H NMR ($CDCl_3$, 200 MHz) δ 8.41 (s, 1H), 7.85 (d, *J* = 8.7 Hz, 2H), 7.47 (d, *J* = 8.7 Hz, 2H), 7.37 (d, *J* = 8.5 Hz, 2H), 7.15 (d, *J* = 8.7 Hz, 2H). ^{13}C NMR

($CDCl_3$, 125 MHz) δ 159.12, 150.10, 137.65, 134.44, 131.75, 130.90, 130.01, 129.46, 129.29, 129.14, 122.17; HRMS Calcd for $C_{13}H_9NClF$ $[M+H]^+$: 234.0480; Found: 234.0482.



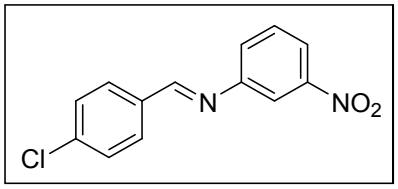
(E)-N-(4-chlorobenzylidene)-3-methoxyaniline **(3ag)**

68 mg, 55% isolated yield. ^1H NMR ($CDCl_3$, 500 MHz) δ 8.43 (s, 1H), 7.85 (d, J = 8.6 Hz, 2H), 7.46 (d, J = 8.2 Hz, 2H), 7.31 (t, J = 8.2 Hz, 1H), 6.82 - 6.78 (m, 3H), 3.85 (s, 3H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ 160.31, 159.01, 153.08, 137.42, 134.56, 129.97, 129.94, 129.08, 112.79, 112.02, 106.62, 55.33; HRMS Calcd for $C_{14}H_{12}NClO$ $[M+H]^+$: 246.0680; Found: 246.0683.



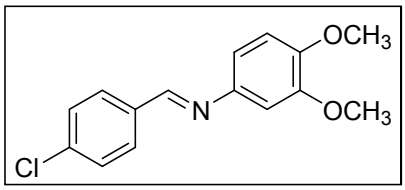
(E)-N-(4-chlorobenzylidene)-3-(trifluoromethyl)aniline **(3ah)**

134 mg. 95% isolated yield. ^1H NMR ($CDCl_3$, 500 MHz) δ 8.44 (s, 1H), 7.87 (d, J = 8.6 Hz, 2H), 7.53-7.45 (m, 4H), 7.39 - 7.37 (m, 2H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ 160.24, 152.12, 137.96, 134.19, 130.14, 129.73, 129.20, 128.32, 124.15, 122.66, 117.71; HRMS Calcd for $C_{14}H_9NClF_3$ $[M+H]^+$: 284.0448; Found: 284.0450.



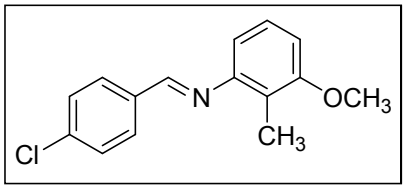
(E)-N-(4-chlorobenzylidene)-3-nitroaniline **(3ai)**

120 mg, 92% isolated yield. ^{1}H NMR ($CDCl_3$, 500 MHz) δ 8.47 (s,1H), 8.11 (dt, *J* = 8.2, 2.2 Hz, 1H), 8.05 (t, *J* = 2.2 Hz, 1H), 7.88 (d, *J* = 8.5 Hz, 2H), 7.58 (t, *J* = 7.7 Hz, 1H), 7.54 (dt, *J* = 8.5, 1.6 Hz, 1H), 7.50 (d, *J* = 8.5 Hz, 2H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ 161.08, 152.75, 138.33, 133.88, 130.29, 129.96, 129.27, 129.11, 127.62, 120.67, 115.31; HRMS Calcd for $C_{13}H_9N_2O_2$ $[M+H]^+$: 261.0425; Found: 261.0733.



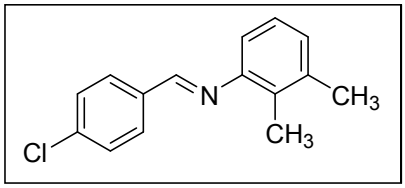
(E)-N-(4-chlorobenzylidene)-3,4-dimethoxyaniline (**3aj)**

71 mg, 51% isolated yield. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.44 (s, 1H), 7.81 (d, *J* = 8.6 Hz, 2H), 7.42 (d, *J* = 8.6 Hz, 2H), 6.89-6.87 (m, 2H), 6.82 (dd, *J* = 8.2, 2.3 Hz, 1H), 3.92 (s, 3H), 3.90 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 156.80, 149.26, 147.83, 144.74, 136.92, 134.73, 129.64, 128.93, 112.12, 111.30, 105.51, 55.99, 55.80; HRMS Calcd for $C_{15}H_{15}NO_2Cl$ $[M+H]^+$: 276.0786; Found: 276.0787.



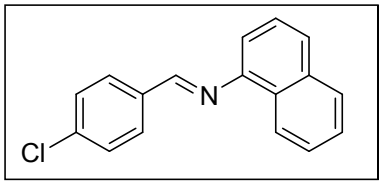
(E)-N-(4-chlorobenzylidene)-3-methoxy-2-methylaniline **(3ak)**

91 mg, 70% isolated yield. ^{1}H NMR ($CDCl_3$, 500 MHz) δ 8.33 (s, 1H), 7.87 (d, *J* = 7.4 Hz, 2H), 7.46 (d, *J* = 8.1 Hz, 2H), 7.18 (t, *J* = 7.5 Hz, 1H), 6.77 (d, *J* = 7.3 Hz, 1H), 6.60 (d, *J* = 7.7 Hz), 3.88 (s, 3H), 2.25 (s, 3H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ 158.13, 151.62, 137.20, 134.98, 129.86, 129.01, 126.56, 120.40, 110.50, 107.79, 55.68, 10.32; HRMS Calcd for $C_{15}H_{14}ONCl$ $[M+H]^+$: 260.0764; Found: 260.0837.



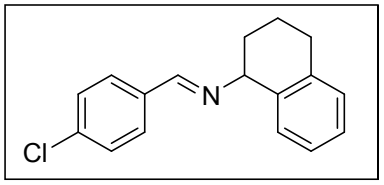
(*E*)-*N*-(4-chlorobenzylidene)-2,3-dimethylaniline **(3al)**

97 mg, 81% isolated yield. ^{1}H NMR ($CDCl_3$, 200 MHz) δ 8.32 (s, 1H), 7.87 (d, *J* = 8.7 Hz, 2H), 7.46 (d, *J*= 8.2 Hz, 2H), 7.17 - 7.04 (m, 2H), 6.79 (d, *J* = 7.2 Hz, 1H), 2.33 (s, 3H), 2.30 (s, 3H). ^{13}C NMR ($CDCl_3$, 50 MHz) δ 157.69, 150.67, 137.51, 137.05, 135.01, 130.47, 129.80, 128.98, 127.46, 126.02, 115.33, 20.09, 13.79; HRMS Calcd for $C_{15}H_{14}NCl$ $[M+H]^+$: 244.0888; Found: 244.0890.



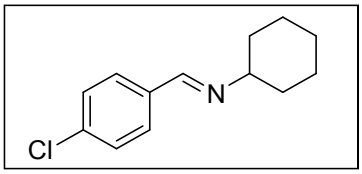
(E)-N-(4-chlorobenzylidene) naphthalen-1-amine **(3am)**

121 mg, 91% isolated yield. ^{1}H NMR ($CDCl_3$, 500 MHz) δ 8.6 (s, 1H), 7.91-7.86 (m, 5H), 7.62 (s, 1H), 7.53 - 7.45 (m, 5H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ 158.92, 149.16, 137.38, 134.66, 134.00, 132.05, 129.97, 129.08, 129.00, 127.92, 127.71, 126.45, 125.47, 120.89, 117.93; HRMS Calcd for $C_{17}H_{12}NCl$ $[M+H]^+$: 266.0731; Found: 266.0733.



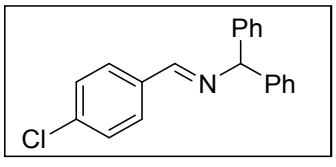
(E)-N-(4-chlorobenzylidene)-1,2,3,4-tetrahydronaphthalen-1-amine **(3an)**

109 mg, 81% isolated yield. ^{1}H NMR ($CDCl_3$, 500 MHz) δ 8.4 (s, 1H), 7.74 (d, *J* = 8.2 Hz, 2H), 7.40 (d, *J* = 8.9 Hz, 2H), 7.19 - 7.14 (m, 3H), 7.02 (2, *J* = 8.2 Hz, 1H), 4.54 (t, *J* = 7 Hz, 1H), 2.96 – 2.84 (m, 2H), 2.13 - 2.02 (m, 3H), 1.91 - 1.84 (m, 1H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ 159.15 137.15, 136.96, 136.56, 134.80, 129.56, 129.25, 128.84, 128.58, 127.01, 125.83, 68.52, 31.52, 29.49, 20.10; HRMS Calcd for $C_{17}H_{16}NCl$ $[M+H]^+$: 270.1044; Found: 270.1042.



(E)-N-(4-chlorobenzylidene)cyclohexanamine **(3ao)**

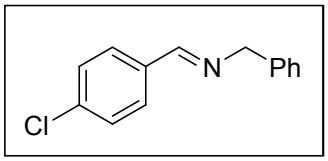
82 mg, 74% isolated yield. ^{1}H NMR ($CDCl_3$, 500 MHz) δ 8.27 (s, 1H), 7.67 (d, *J* = 7.7 Hz, 2H), 7.37 (d, *J* = 7.7 Hz, 2H), 3.19 (s, 1H), 1.85 - 1.82 (m, 2H), 1.74 - 1.67 (m, 3H), 1.62 - 1.55 (m, 2H), 1.40 - 1.33 (m, 2H), 1.30 - 1.25 (m, 1H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ 157.25, 136.16, 135.01, 129.20, 128.72, 69.92, 34.25, 25.55, 24.71; HRMS Calcd for $C_{13}H_{16}NCl$ $[M+H]^+$: 222.1044; Found: 222.1042.



(E)-N-(4-chlorobenzylidene)-1,1-diphenylmethanamine **(3aq)**

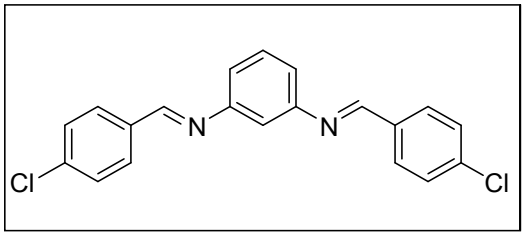
94 mg, 62% isolated yield. ^{1}H NMR ($CDCl_3$, 500 MHz) δ 8.40 (s, 1H), 7.80 (d, *J* = 8.5 Hz, 2H), 7.42 – 7.30 (m, 11H), 7.26 – 7.20 (m, 1H), 5.62 (s, 1H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ

159.44, 143.65, 136.70, 134.74, 129.62, 128.79, 128.46, 127.60, 127.05, 77.84; HRMS Calcd for $C_{20}H_{16}NCl$ $[M+H]^+$: 306.1044; Found: 306.1042.



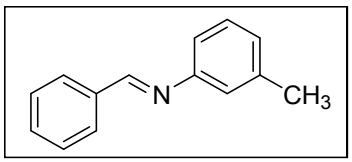
(E)-N-(4-chlorobenzylidene)-1-phenylmethanamine **(3ar)**

46 mg, 40% isolated yield. ^{1}H NMR ($CDCl_3$, 200 MHz) δ 8.25 (s, 1H), 7.63 (d, *J* = 8.5 Hz, 2H), 7.31 – 7.21 (m, 7H), 4.73 (d, *J* = 1.1 Hz, 1H). ^{13}C NMR ($CDCl_3$, 50 MHz) δ 160.47, 139.01, 136.66, 134.60, 129.41, 128.83, 128.50, 127.95, 127.04, 64.94; HRMS Calcd for $C_{14}H_{12}NCl$ $[M+H]^+$: 230.0731; Found: 230.0730.



(E,E)-N^1,N^3-bis(4-chlorobenzylidene)benzene-1,3-diamine **(3as)**

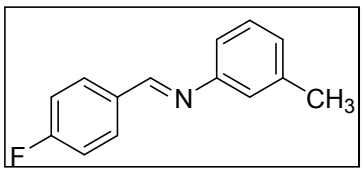
132 mg, 75% isolated yield. ^{1}H NMR ($CDCl_3$, 500 MHz) δ 8.48 (s, 2H), 7.86 (d, *J* = 8.5 Hz, 4H), 7.47 (d, *J* = 8.5 Hz, 4H), 7.42 (t, *J* = 8.1 Hz, 1H), 7.11 (dd, *J* = 7.6, 1.8 Hz, 2H), 7.06 (s, 1H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ 159.25, 152.64, 137.52, 134.53, 129.99, 129.86, 129.10, 129.01, 118.77, 113.04; HRMS Calcd for $C_{20}H_{14}N_2Cl_2$ $[M+H]^+$: 353.0607; Found: 353.0603.



(E)-N-benzylidene-3-methylaniline **(3ba)**

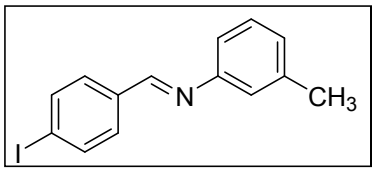
70 mg, 72% isolated yield. ^{1}H NMR ($CDCl_3$, 200 MHz) δ 8.47 (s, 1H), 7.94 – 7.89 (m, 2H), 7.50–7.47 (m, 3H), 7.33 – 7.29 (m, 1H), 7.09 – 7.01 (m, 3H), 2.41 (s, 3H). ^{13}C NMR ($CDCl_3$,

50 MHz) δ ppm 160.25, 131.35, 129.79, 129.01, 128.80, 126.75, 121.66, 117.87, 21.45; HRMS Calcd for $C_{14}H_{13}N$ $[M+H]^+$: 196.1121; Found: 196.1121.



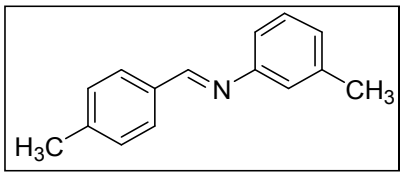
(E)-N-(4-fluorobenzylidene)-3-methylaniline **(3bb)**

92 mg, 86% isolated yield. ^1H NMR ($CDCl_3$, 200 MHz) δ 8.31 (s, 1H), 7.79 (d, *J* = 8.1 Hz, 2H), 7.23 - 6.90 (m, 6H), 2.30 (s, 3H). ^{13}C NMR ($CDCl_3$, 50 MHz) δ 167.12, 162.12, 158.52, 151.81, 138.96, 132.58, 130.77, 130.60, 128.95, 126.75, 121.55, 117.76, 116.07, 115.63, 21.34; HRMS Calcd for $C_{14}H_{12}NF$ $[M+H]^+$: 214.1027; Found: 214.1027.



(E)-N-(4-iodobenzylidene)-3-methylaniline **(3bc)**

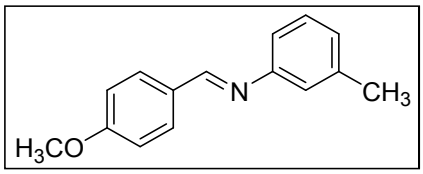
125 mg, 78% isolated yield. ^1H NMR ($CDCl_3$, 400 MHz) δ 8.37 (s, 1H), 7.81 (d, *J* = 8.2 Hz, 2H), 7.61 (d, *J* = 8.2 Hz, 2H), 7.26 (s, 1H), 7.06-6.99 (m, 1H), 2.38 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 158.91, 151.62, 139.04, 137.97, 135.70, 130.14, 129.01, 127.00, 121.57, 117.79, 98.09, 21.38; HRMS Calcd for $C_{14}H_{12}NI$ $[M+H]^+$: 322.0087; Found: 322.0086.



(E)-3-methyl-N-(4-methylbenzylidene)aniline **(3bd)**

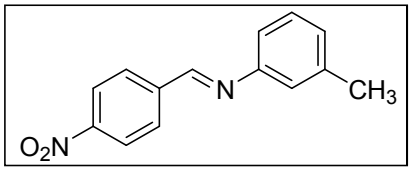
53 mg, 51% isolated yield. ^1H NMR ($CDCl_3$, 200 MHz) δ 8.32 (s, 1H), 7.70 (d, *J* = 8.8 Hz, 2H), 7.20-7.15 (m, 3H), 6.97-6.91 (m, 3H), 2.33 (s, 3H), 2.30 (s, 3H). ^{13}C NMR ($CDCl_3$, 50

MHz) δ 160.07, 152.22, 141.72, 138.87, 133.71, 129.45, 128.90, 128.74, 126.47, 121.60, 117.81, 21.56, 21.36; HRMS Calcd for $C_{15}H_{15}N$ $[M+H]^+$: 210.1277; Found: 210.1277.



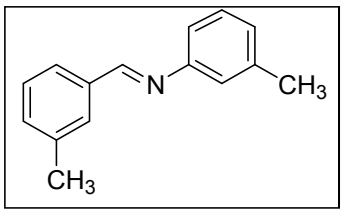
(*E)-N-(4-methoxybenzylidene)-3-methylaniline* **(3be)**

70 mg, 62% isolated yield. ^{1}H NMR ($CDCl_3$, 200 MHz) δ 8.38 (s, 1H), 7.84 (d, *J* = 8.9 Hz, 2H), 7.31-7.23 (m, 1H), 7.04 - 6.96 (m, 5H), 3.87 (s, 3H), 2.38 (s, 3H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ 162.15, 159.53, 152.30, 138.90, 130.44, 129.25, 128.91, 126.31, 121.61, 117.81, 114.13, 55.41, 21.40.



(E)-3-methyl-N-(4-nitrobenzylidene)aniline **(3bf)**

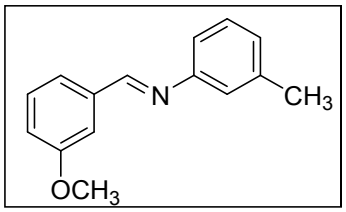
96 mg, 80% isolated yield. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.56 (s, 1H), 8.34 (d, *J* = 8.7 Hz, 2H), 8.08 (d, *J* = 8.7 Hz, 2H), 7.33 (t, *J* = 7.3 Hz, 1H), 7.14-7.07 (m, 3H), 2.42 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz)) δ 157.19, 151.01, 149.34, 141.74, 139.32, 129.43, 129.23, 127.93, 124.09, 121.78, 118.00, 77.08, 21.47; HRMS Calcd for $C_{14}H_{12}O_2N_2$ $[M+H]^+$: 241.0972; Found: 241.0972.



(E)-3-methyl-N-(3-methylbenzylidene)aniline **(3bg)**

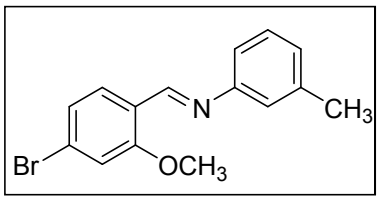
95 mg, 91% isolated yield. ^{1}H NMR ($CDCl_3$, 200 MHz) δ 8.33 (s, 1H), 7.67 (s, 1H), 7.56 (d, *J* = 7.8 Hz, 1H), 7.22-7.15 (m, 3H), 6.97-6.90 (m, 3H), 2.33 (s, 3H), 2.30 (s, 3H). ^{13}C NMR

($CDCl_3$, 50 MHz) δ 160.42, 152.16, 138.94, 138.52, 136.23, 132.15, 128.93, 128.62, 126.62, 126.37, 121.61, 117.81, 21.38, 21.28; HRMS Calcd for $C_{15}H_{15}N$ $[M+H]^+$: 210.1277; Found: 210.1279.



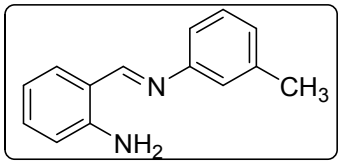
(E)-N-(3-methoxybenzylidene)-3-methylaniline **(3bh)**

67 mg, 60% isolated yield. ^1H NMR ($CDCl_3$, 200 MHz) δ 8.37 (s, 1H), 7.47-7.31 (m, 3H), 7.23-7.19 (dd, J = 7.3, 2.6 Hz, 1H), 7.02-6.69 (m, 4H), 3.84 (s, 3H), 2.34 (s, 3H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ 162.15, 159.53, 152.30, 138.90, 130.44, 129.25, 128.91, 126.31, 121.61, 117.81, 114.13, 55.41, 21.40; HRMS Calcd for $C_{15}H_{15}NO$ $[M+H]^+$: 226.1226; Found: 226.1227.



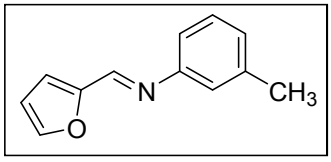
(E)-N-(4-bromo-2-methoxybenzylidene)-3-methylaniline **(3bi)**

70 mg, 46% isolated yield. ^1H NMR ($CDCl_3$, 500 MHz) δ 8.78 (s, 1H), 7.97 (d, J = 8.2 Hz, 1H), 7.23-6.96 (m, 6H), 3.86 (s, 3H), 2.35 (s, 3H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ 159.66, 155.14, 152.33, 138.90, 128.89, 128.65, 126.67, 126.46, 124.15, 123.79, 121.71, 118.01, 115.33, 114.69, 55.83, 21.38; HRMS Calcd for $C_{15}H_{14}ONBr$ $[M+H]^+$: 304.0332; Found: 304.0333.



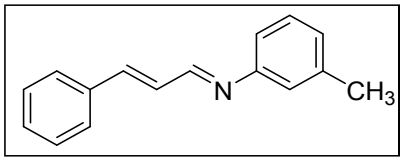
(E)-N-(2-aminobenzylidene)-3-methylaniline **(3bj)**

70 mg, 67% isolated yield. ^{1}H NMR ($CDCl_3$, 500 MHz) δ 8.53 (s, 1H), 7.35 (d, *J* = 8.0 Hz, 1H), 7.20 (d, *J* = 8.0 Hz, 1 H), 7.06-6.99 (m, 3H), 6.77-6.70 (m, 3H), 6.53(s, 1H), 2.40 (s, 3H). HRMS Calcd for $C_{14}H_{14}N_2$ $[M+H]^+$: 211.1230; Found: 211.1230.



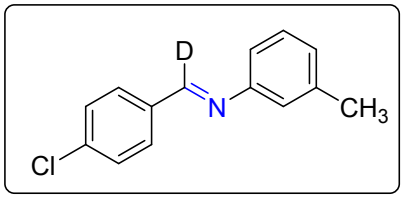
(E)-N-(furan-2-ylmethylene)-3-methylaniline **(3bk)**

70 mg, 76% isolated yield. ^{1}H NMR ($CDCl_3$, 200 MHz) δ 8.24 (s, 1H), 7.57 (s, 1H), 7.24-7.19 (m, 1H), 7.03-6.99 (m, 3H), 6.90 (d, *J* = 3.5 Hz, 1H), 6.52-6.50 (m, 1H), 2.34 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 152.10, 151.32, 147.49, 145.52, 138.94, 128.93, 126.97, 121.65, 118.02, 116.04, 112.08, 21.35; HRMS Calcd for $C_{12}H_{11}ON$ $[M+H]^+$: 186.0913; Found: 186.0914.



(E)-3-methyl-N-((E)-3-phenylallylidene)aniline **(3bl)**

50 mg, 45% Isolated yield. ^{1}H NMR ($CDCl_3$, 500 MHz) δ 8.26 (d, *J* = 7.5 Hz, 1H), 7.53 (d, *J* = 7.5 Hz, 1H), 7.40-7.34 (m, 3H), 7.25 (d, *J* = 6.5Hz, 1H), 7.16-6.97 (m, 3H), 2.37 (s, 3H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ 161.44, 151.71, 143.83, 138.99, 135.62, 129.54, 128.98, 128.91, 128.65, 127.47, 126.89, 121.61, 117.95, 21.39; HRMS Calcd for $C_{16}H_{15}N$ $[M+H]^+$: 222.1277; Found: 222.1277.



(E)-1-(4-chlorophenyl)-N-(m-tolyl)methanimine-d **(3aa-*d*)**

^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.85 (d, *J* = 8.4 Hz, 2H), 7.46 (d, *J* = 8.4 Hz, 2H), 7.29 (t, *J* = 7.2 Hz, 1H), 7.08-7.02 (m, 3H), 2.40 (s, 3H); HRMS Calcd for $C_{14}H_{11}NClD$ $[M+H]^+$: 231.0794; Found: 231.0794.

6. References

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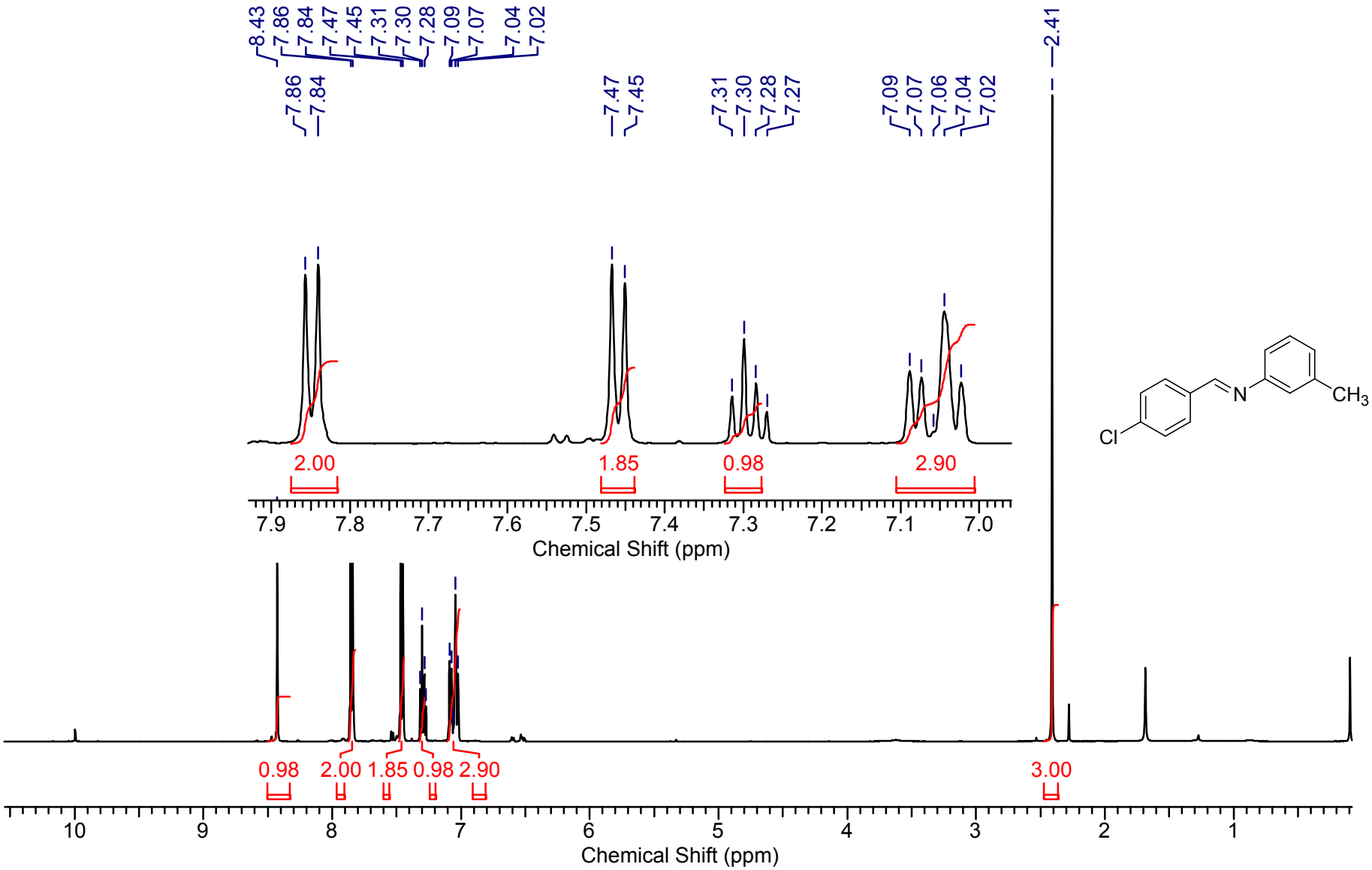
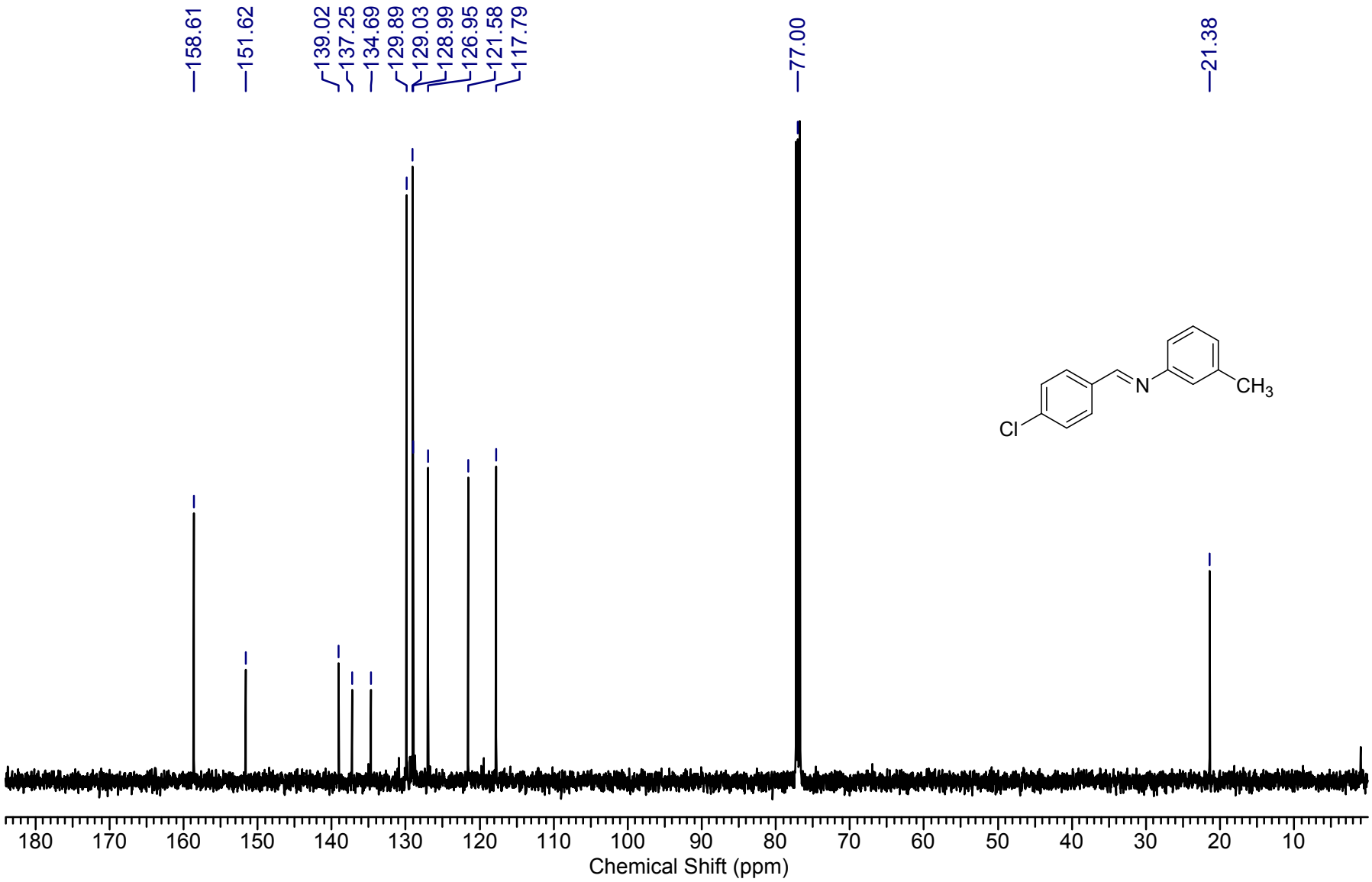
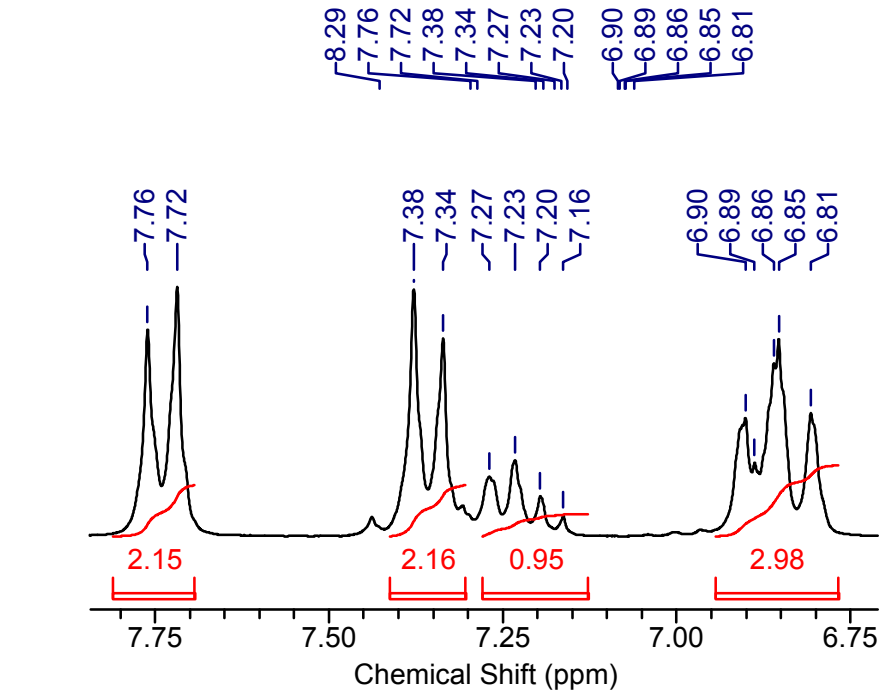
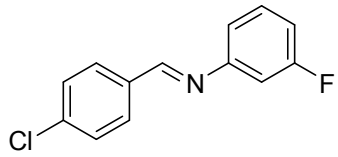
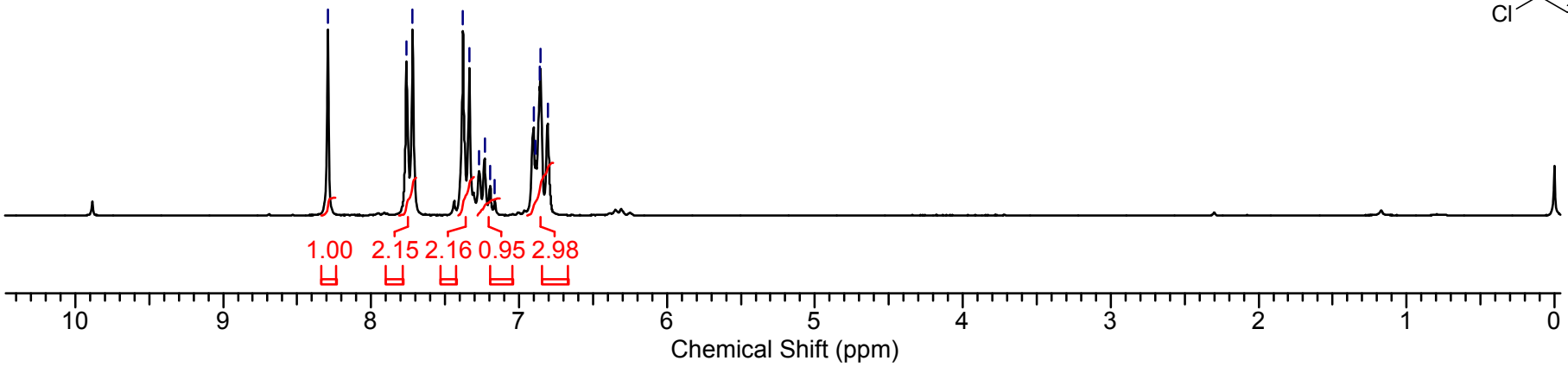


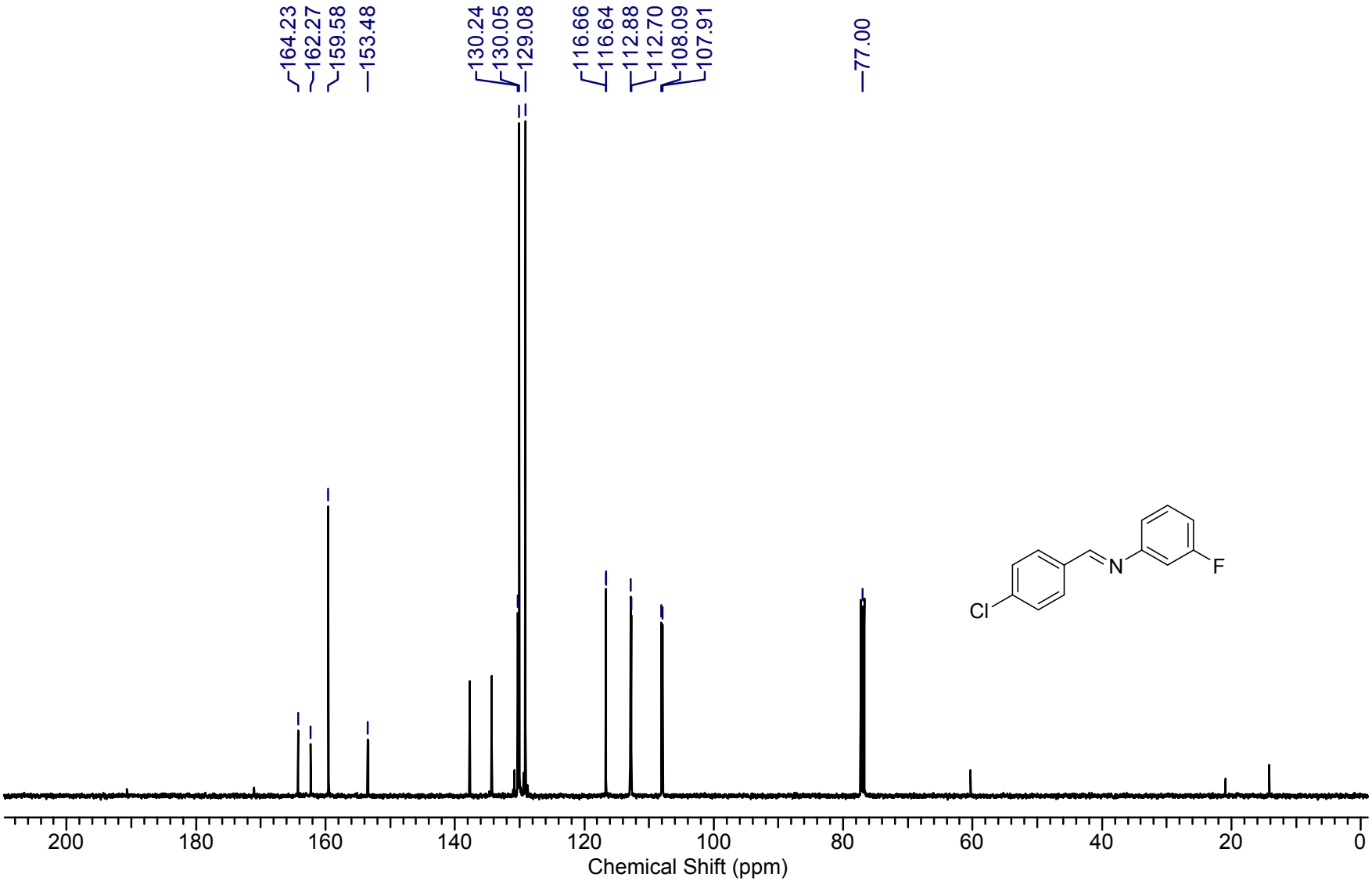
Supplementary Figure 1. ^{1}H NMR of **3aa**


158.61
151.62
139.02
137.25
134.69
129.89
129.03
128.99
126.95
121.58
117.79
77.00
21.38
Cl
N
CH3
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
Chemical Shift (ppm)

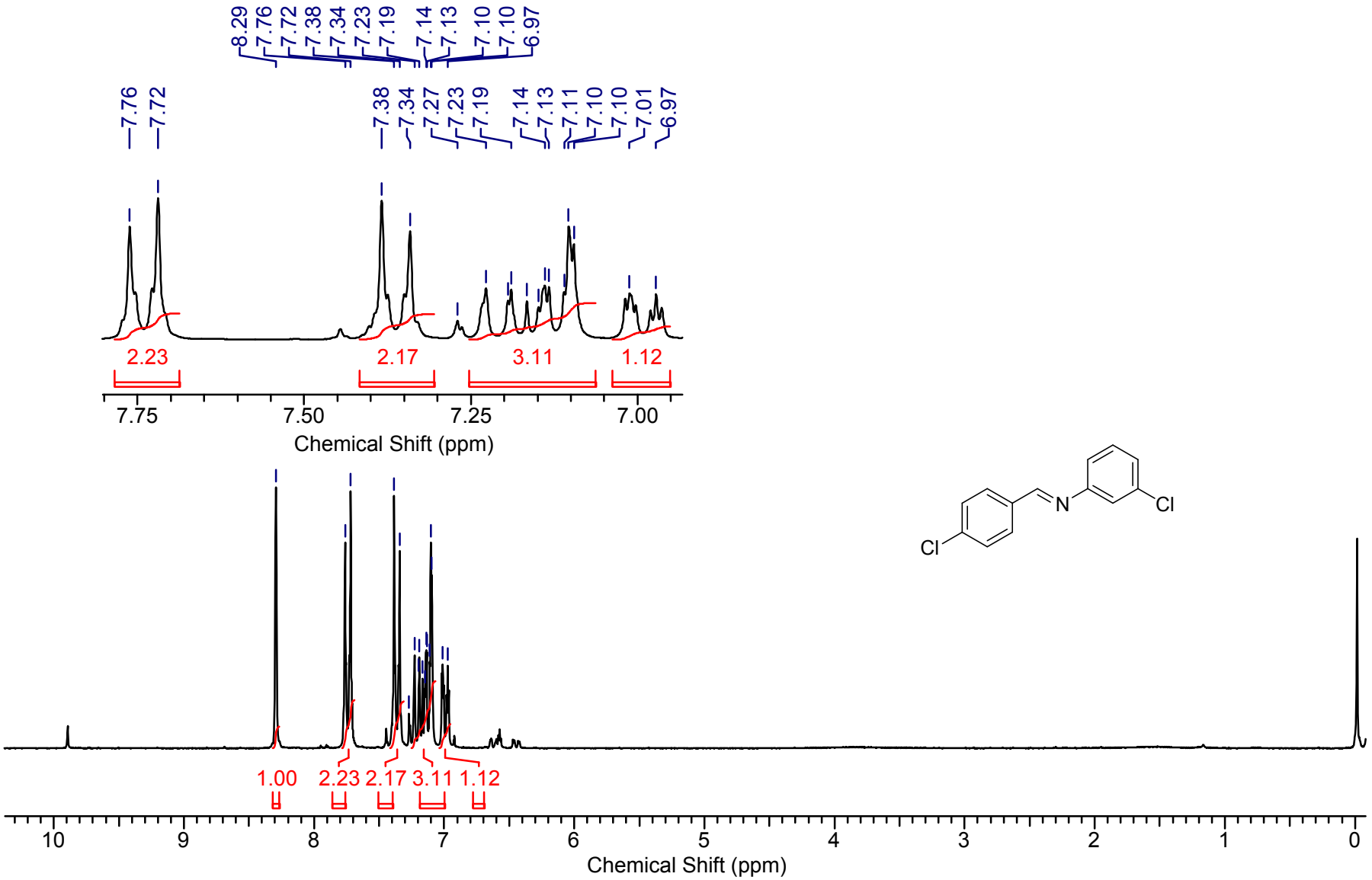

8.29
7.76
7.72
7.38
7.34
7.27
7.23
7.20
6.90
6.89
6.86
6.85
6.81
7.76
7.72
7.38
7.34
7.27
7.23
7.20
7.16
6.90
6.89
6.86
6.85
6.81
2.15
2.16
0.95
2.98
7.75
7.50
7.25
7.00
6.75
Chemical Shift (ppm)

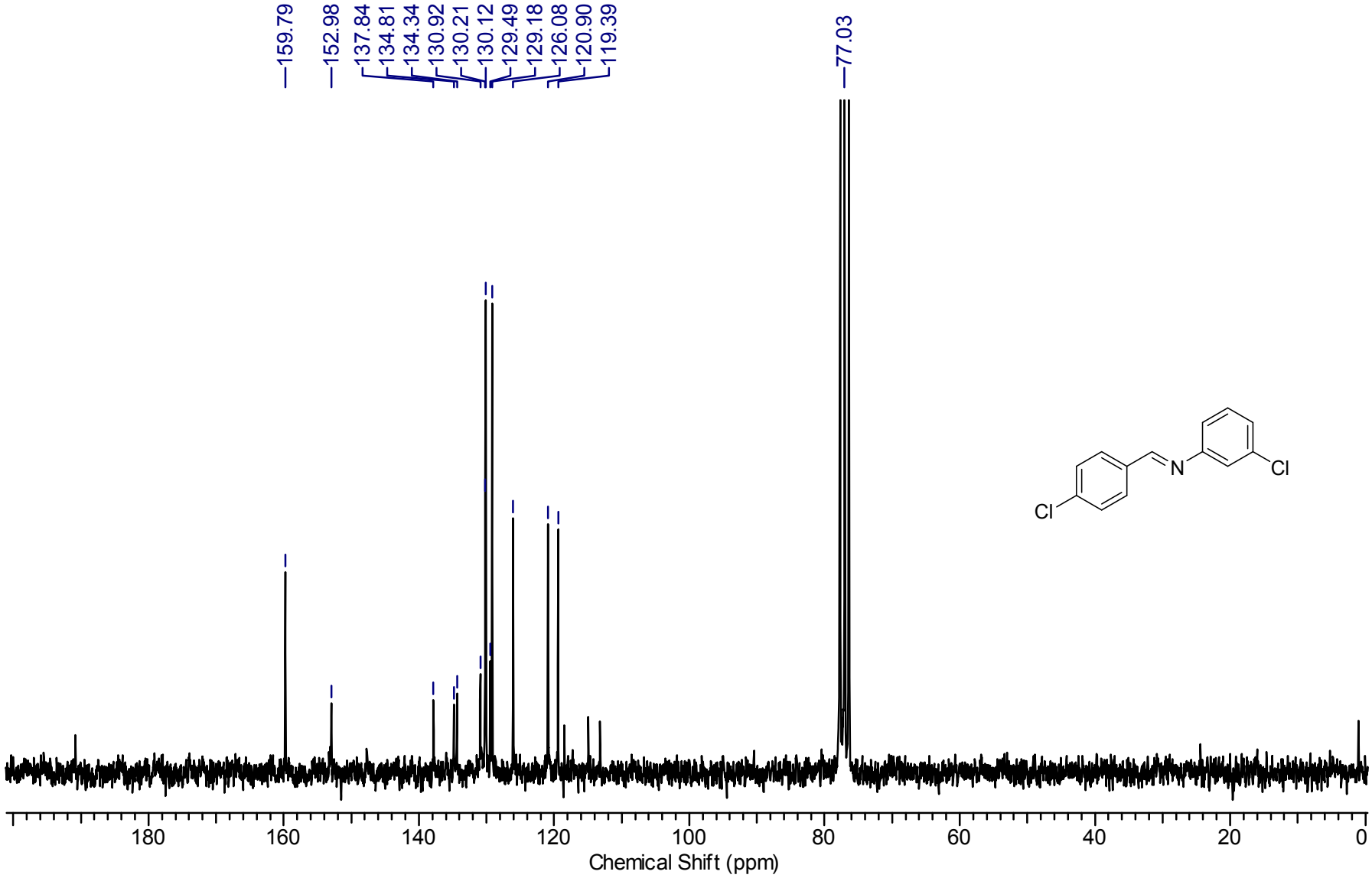

N
F
Cl

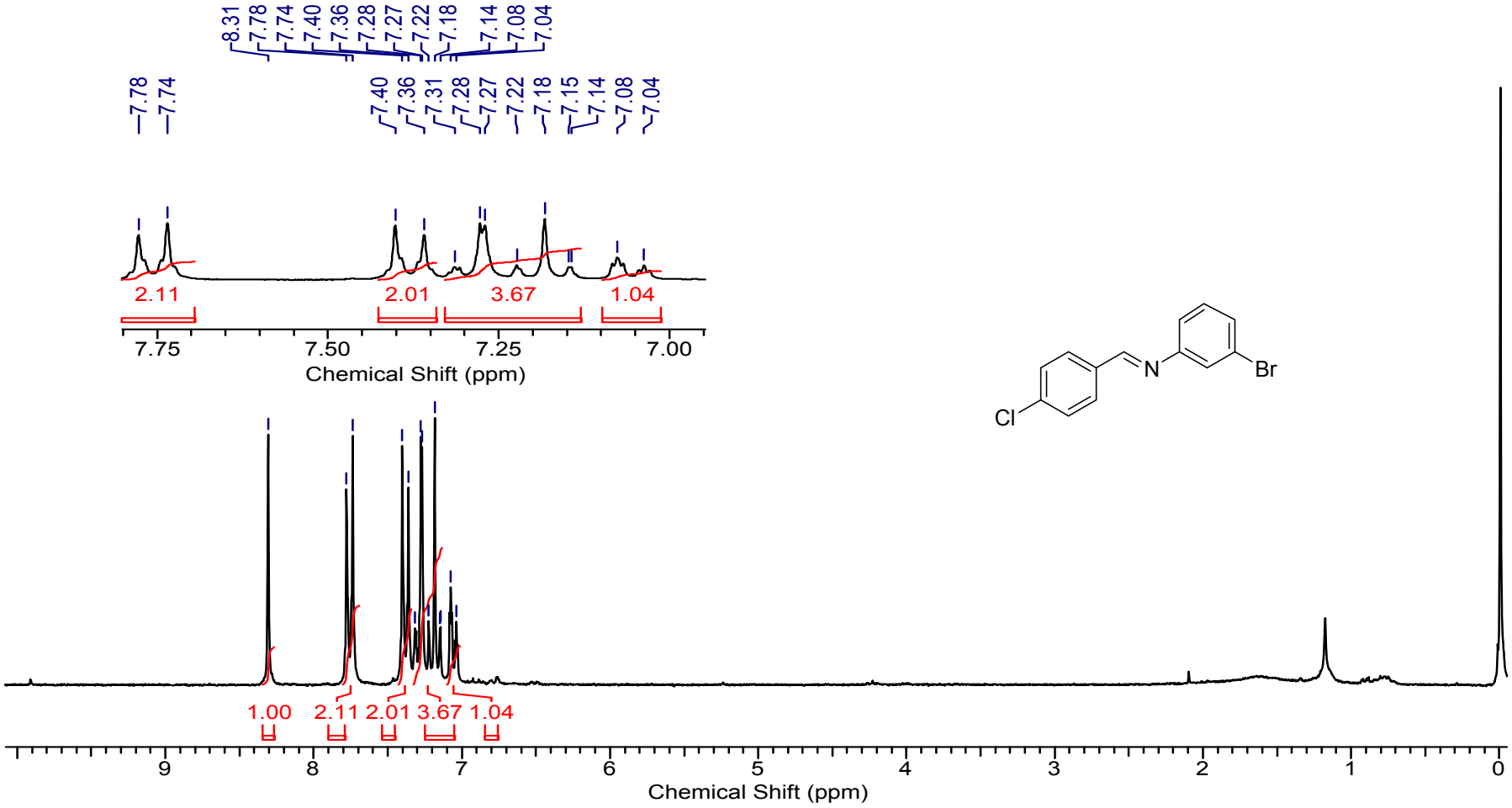

1.00
2.15
2.16
0.95
2.98
10
9
8
7
6
5
4
3
2
1
0
Chemical Shift (ppm)



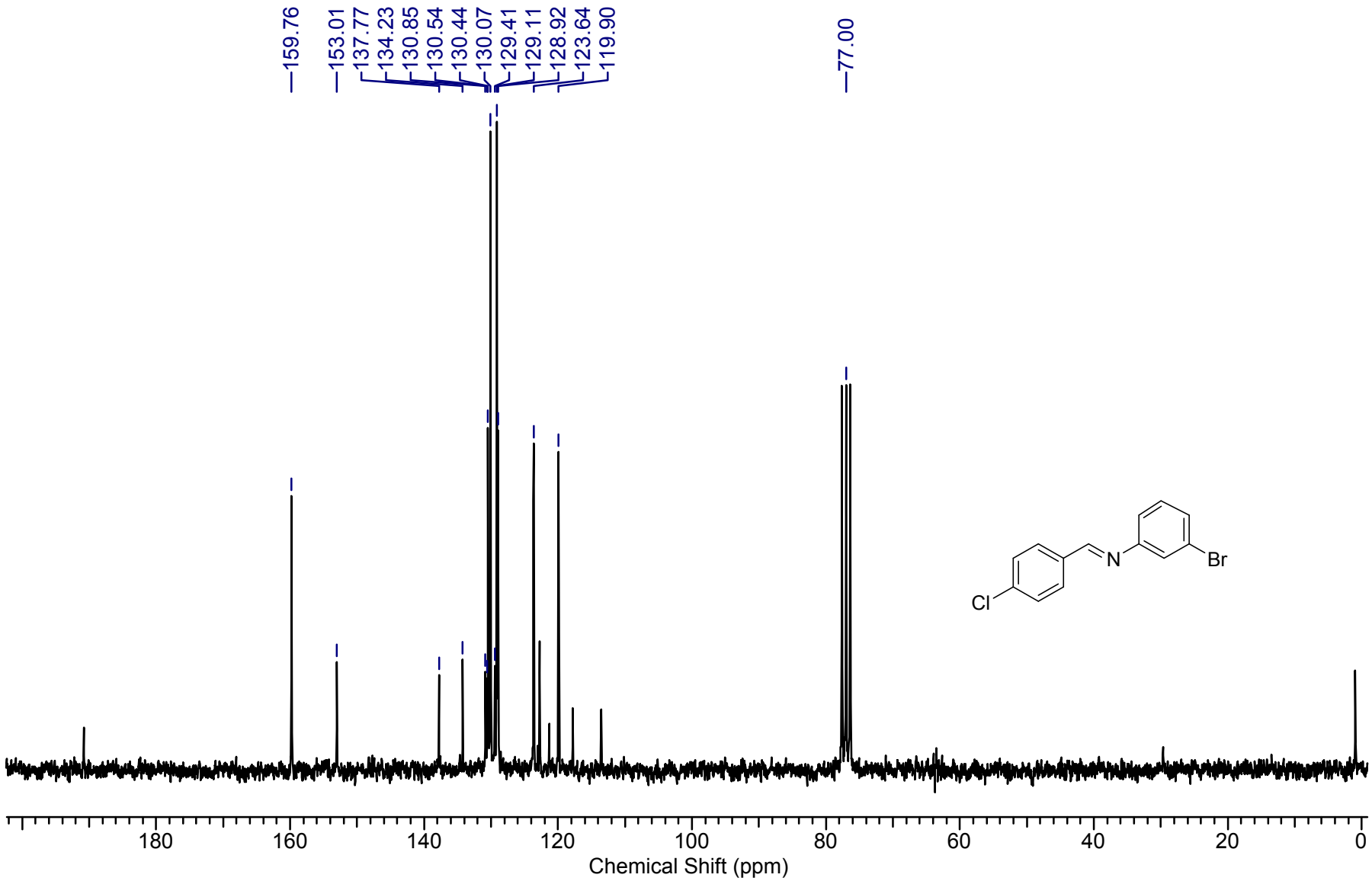
Supplementary Figure 4. ^{13}C NMR of **3ab**


8.29
7.76
7.72
7.38
7.34
7.23
7.19
7.14
7.13
7.10
7.10
6.97
7.76
7.72
7.38
7.34
7.27
7.23
7.19
7.14
7.13
7.11
7.10
7.10
7.01
6.97
2.23
2.17
3.11
1.12
7.75
7.50
7.25
7.00
Chemical Shift (ppm)
N
Cl
Cl
1.00
2.23
2.17
3.11
1.12
10
9
8
7
6
5
4
3
2
1
0
Chemical Shift (ppm)

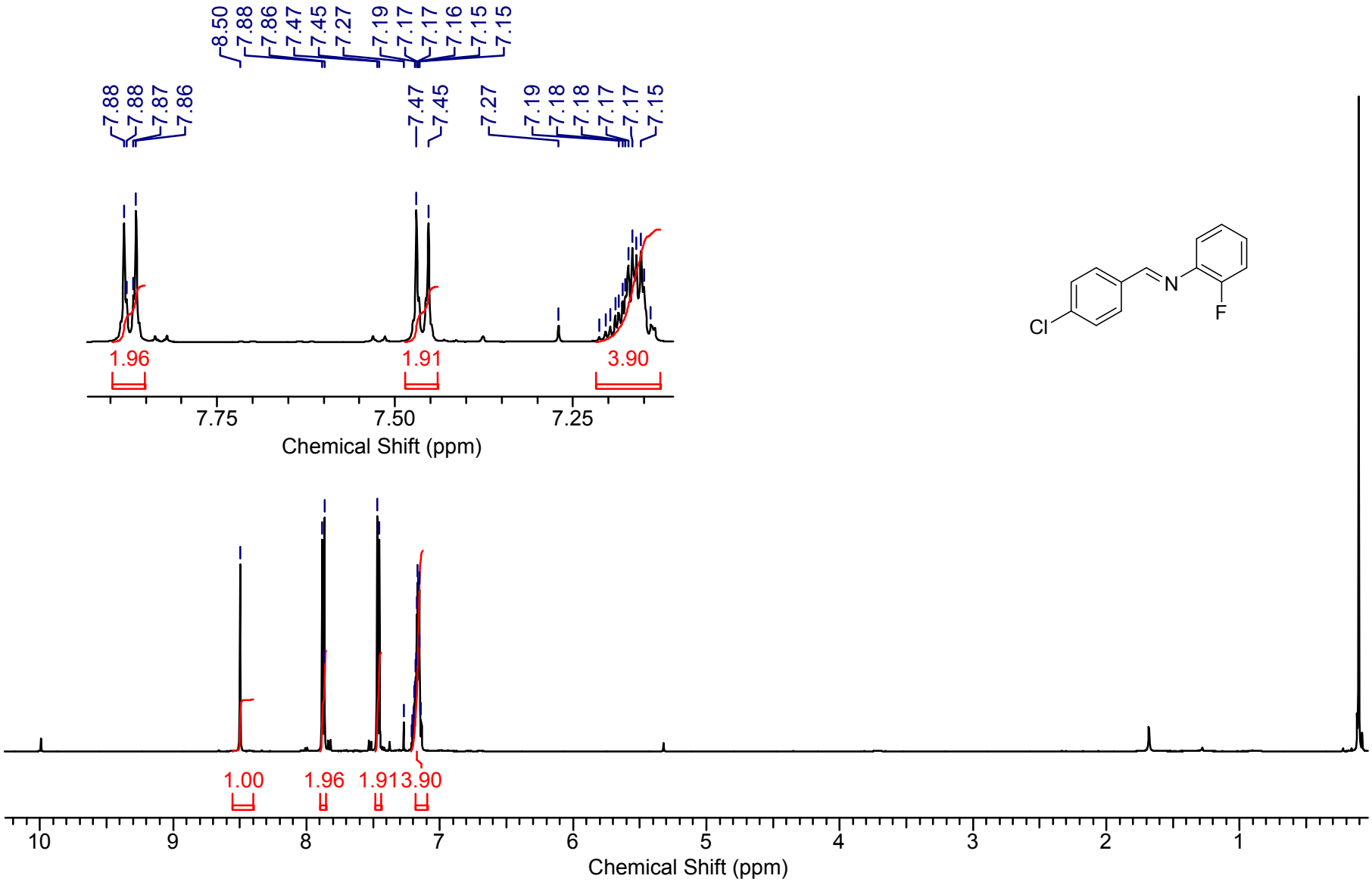

159.79
152.98
137.84
134.81
134.34
130.92
130.21
130.12
129.49
129.18
126.08
120.90
119.39
77.03
Cl
N
Cl
180
160
140
120
100
80
60
40
20
0
Chemical Shift (ppm)



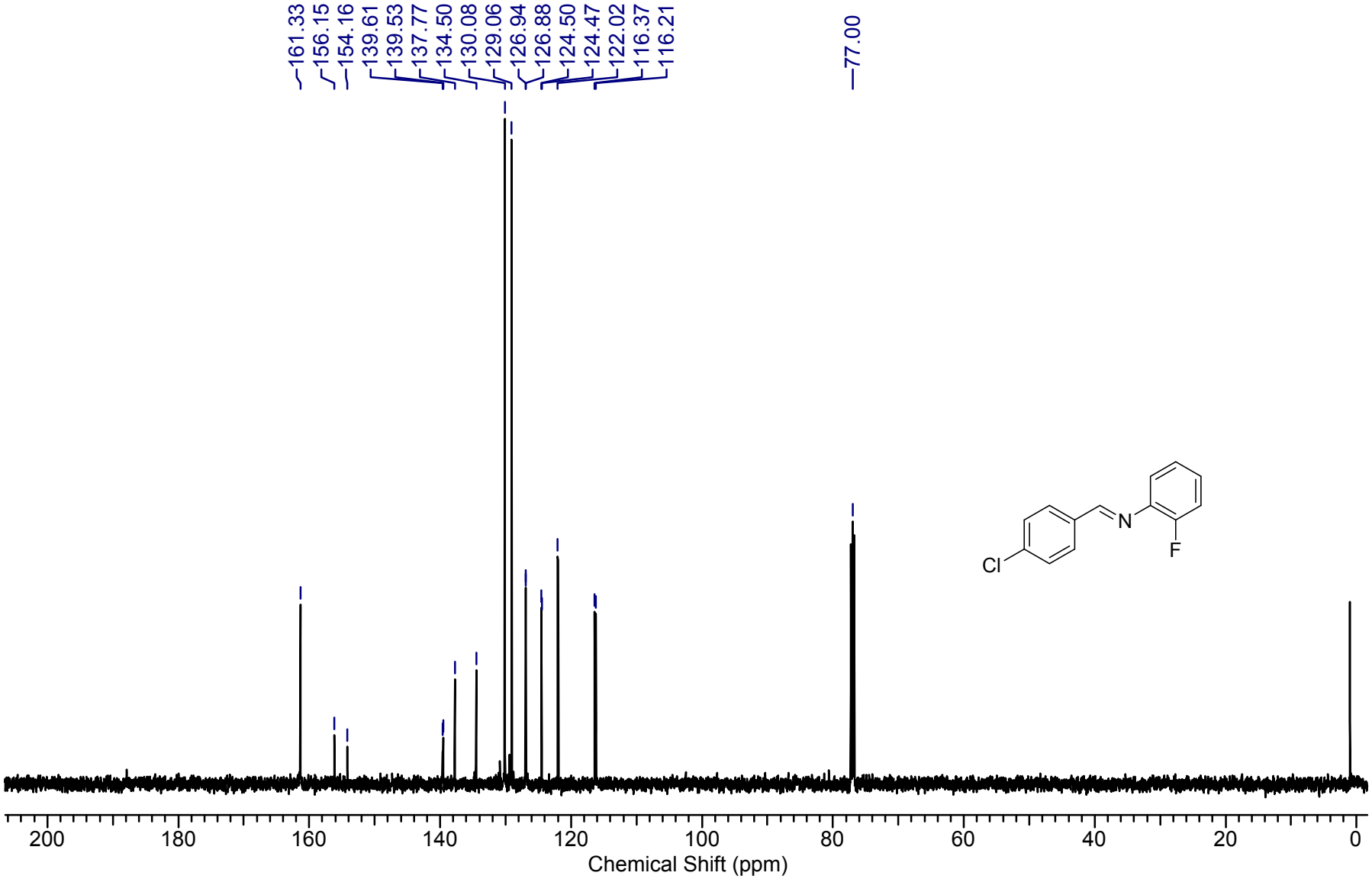
Supplementary Figure 7. ^{1}H NMR of **3ad**



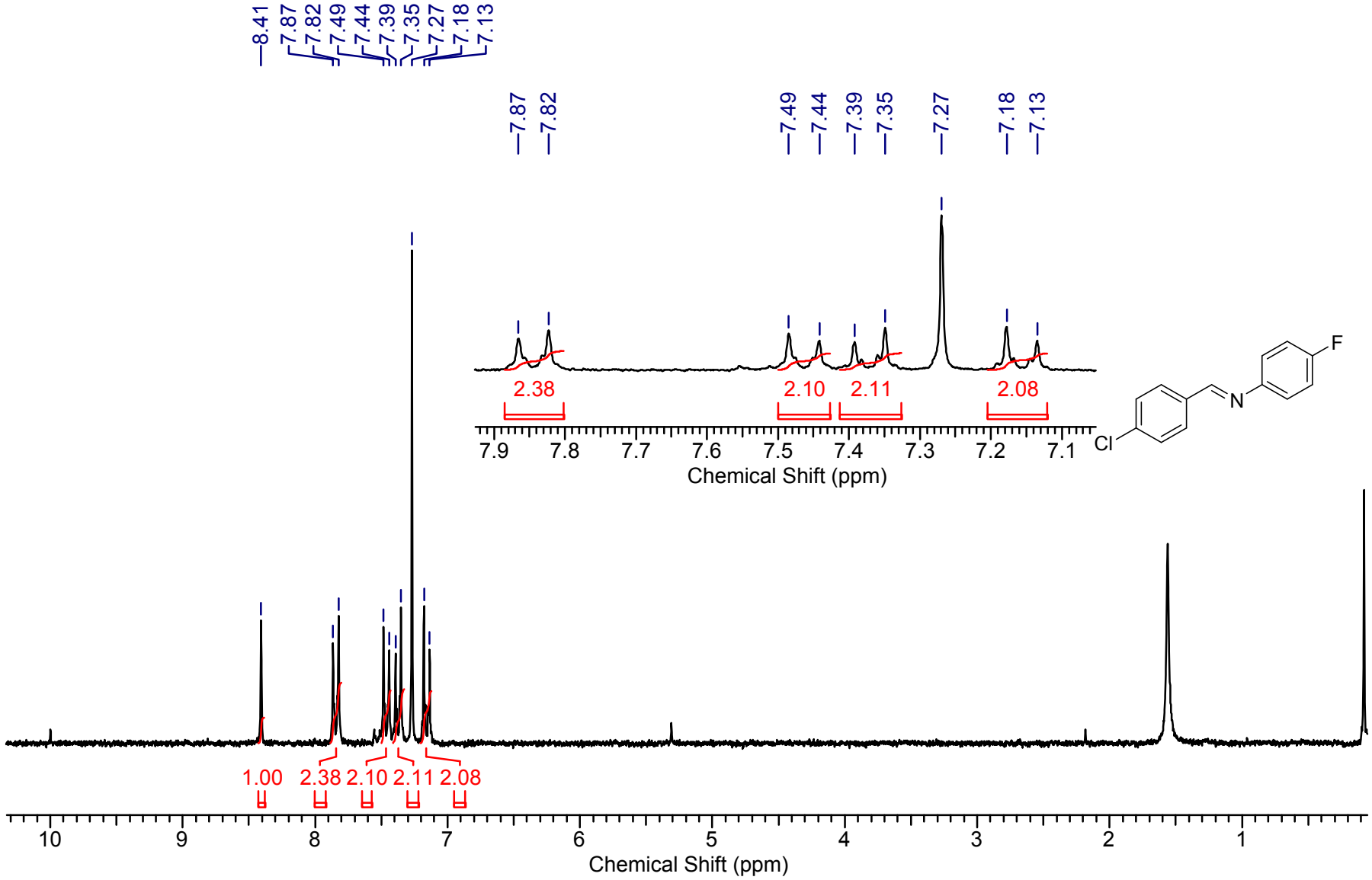
Supplementary Figure 8. ^{13}C NMR of **3ad**



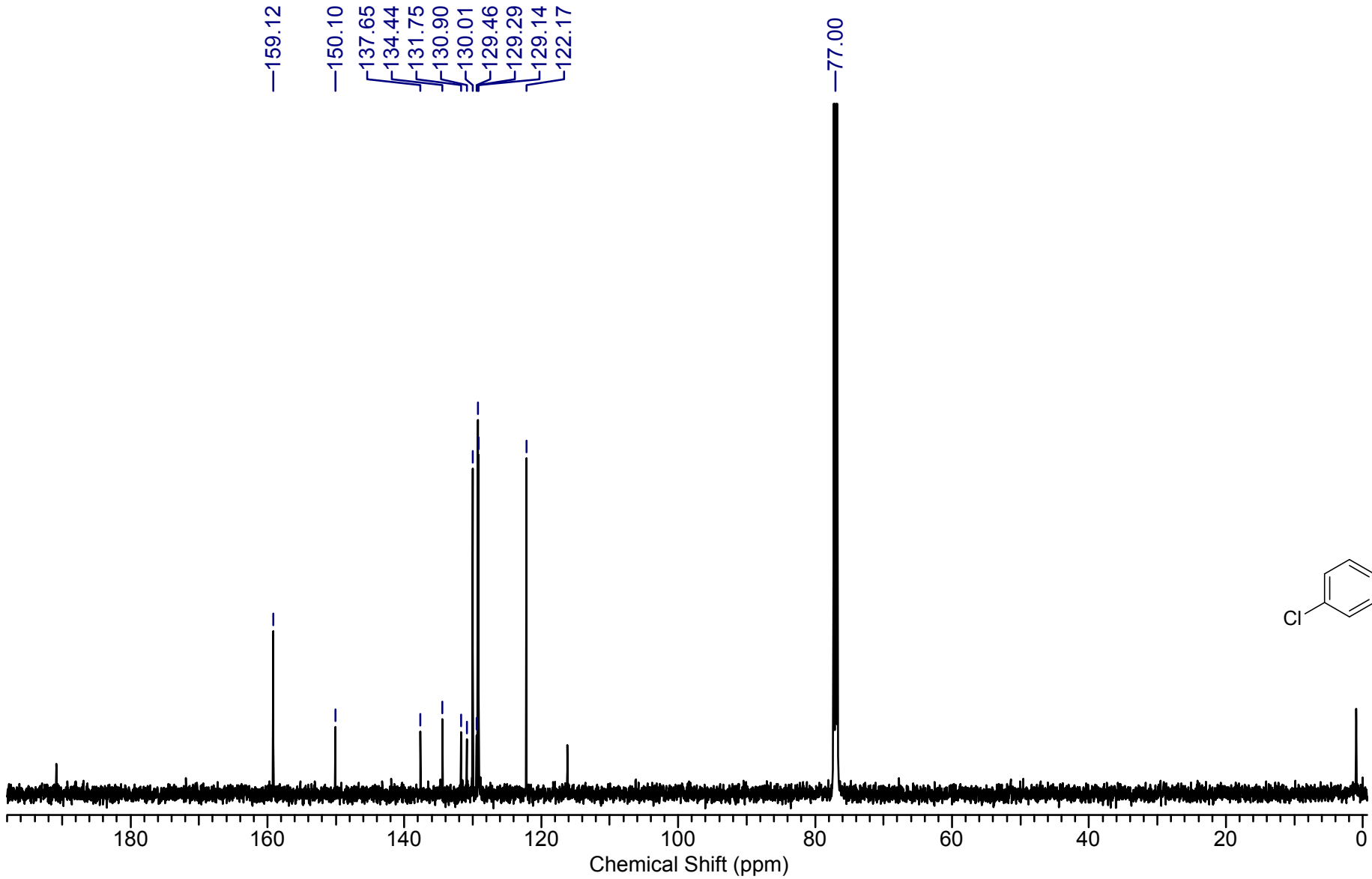
Supplementary Figure 9. ^{1}H NMR of **3ae**

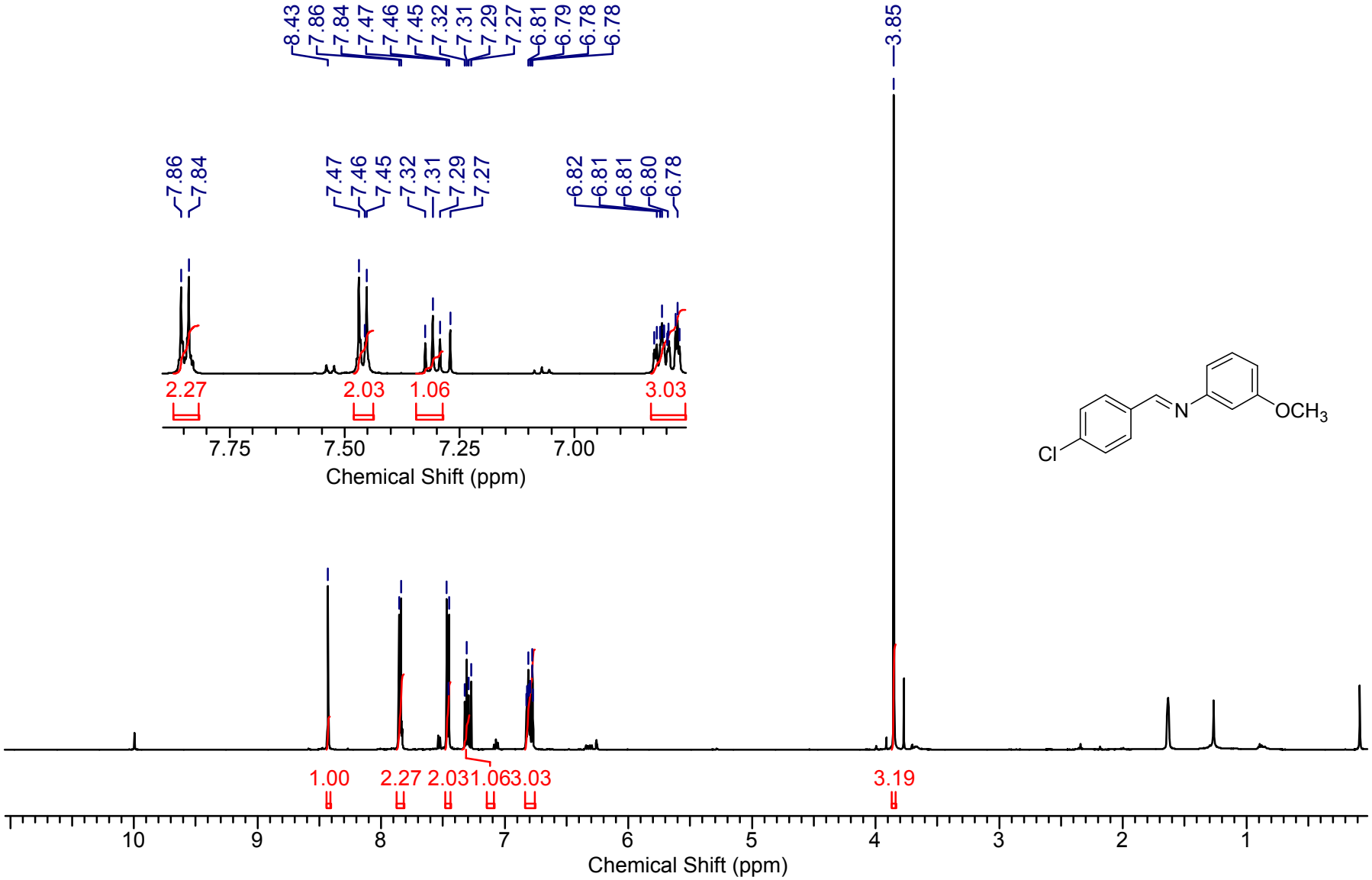


Supplementary Figure 10. ^{13}C NMR of **3ae**

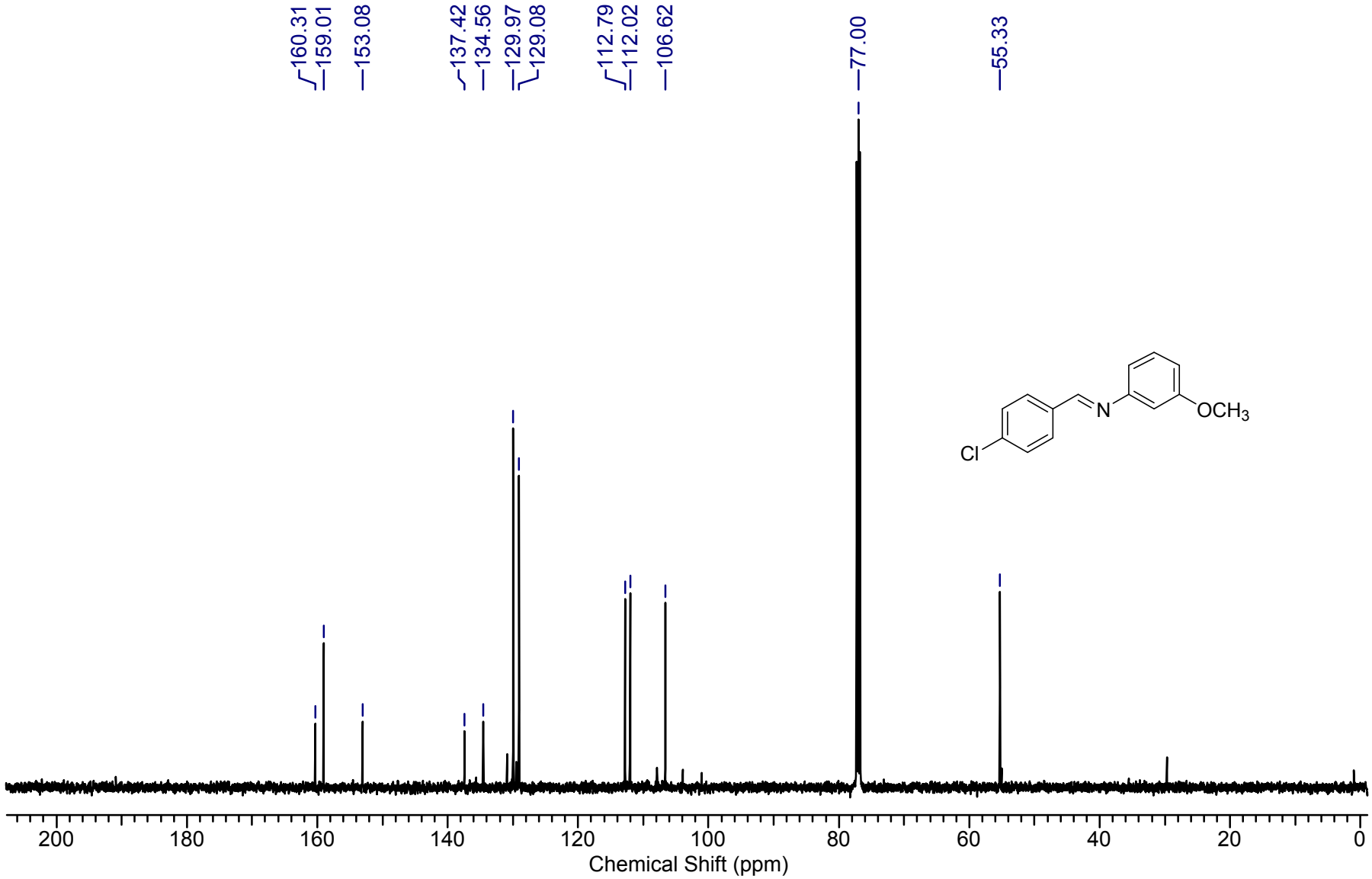


Supplementary Figure 11. ^{1}H NMR of **3af**

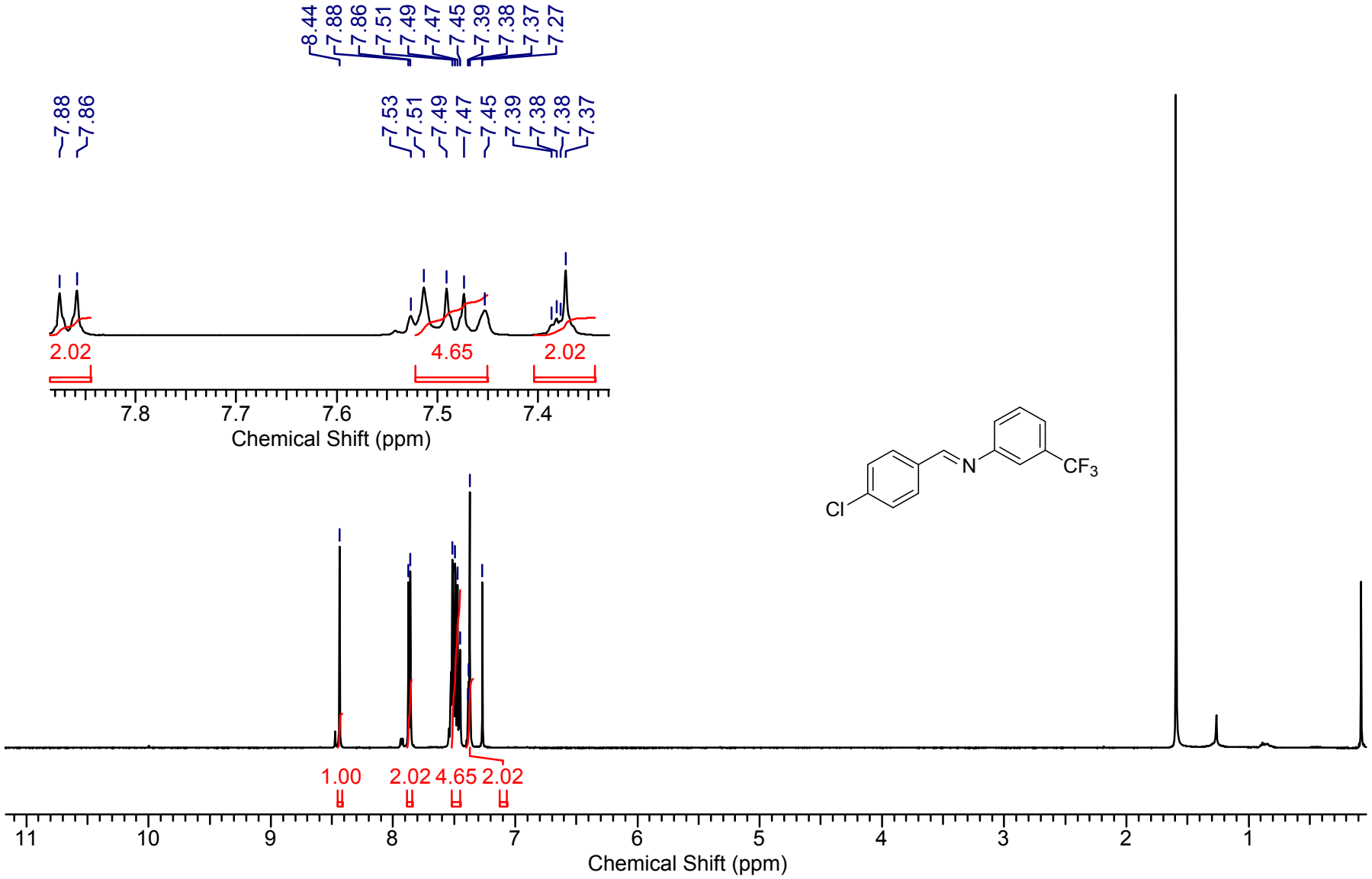

159.12
150.10
137.65
134.44
131.75
130.90
130.01
129.46
129.29
129.14
122.17
77.00
180
160
140
120
100
80
60
40
20
0
Chemical Shift (ppm)
F
N
Cl



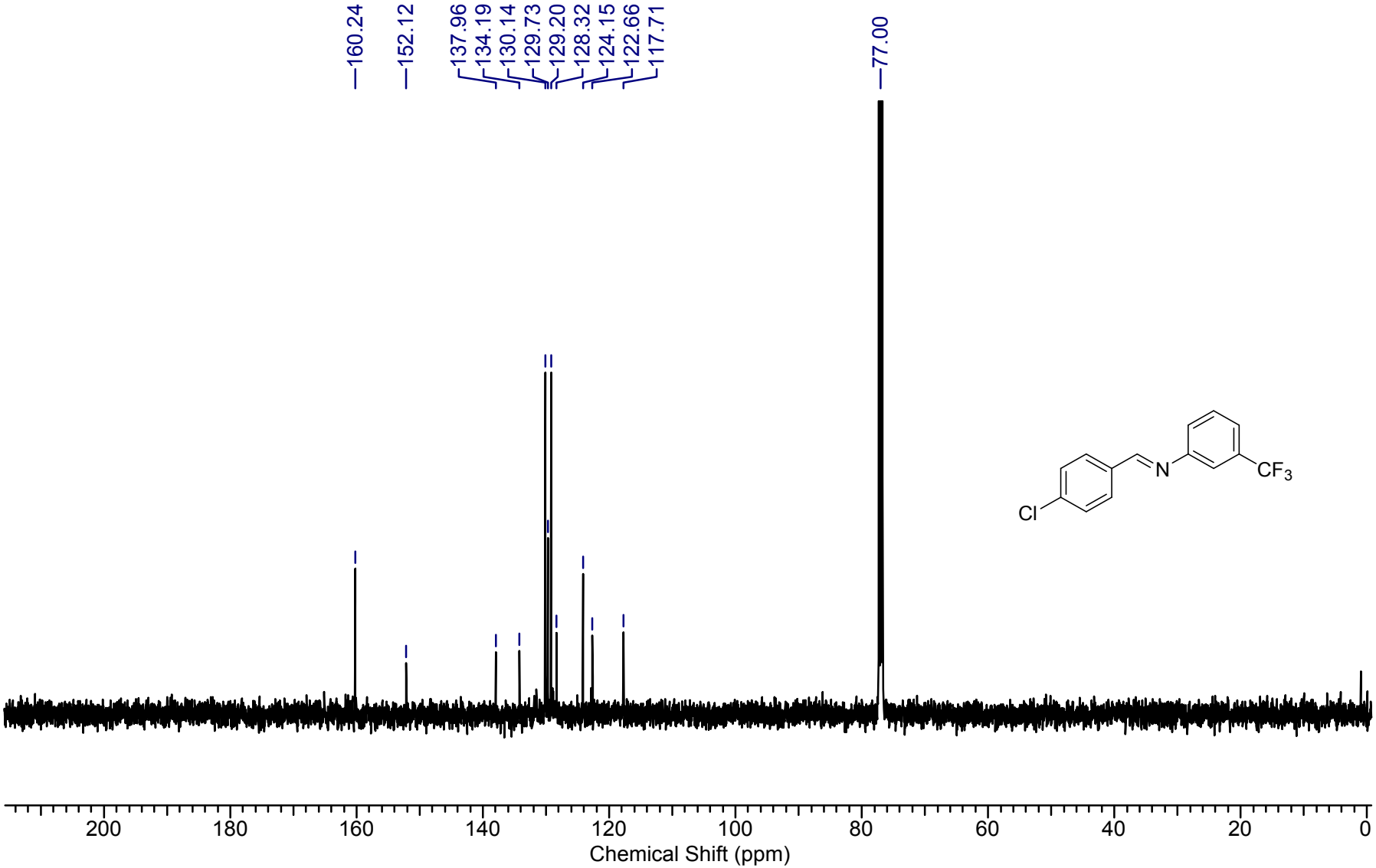
Supplementary Figure 13. ^{1}H NMR of **3ag**



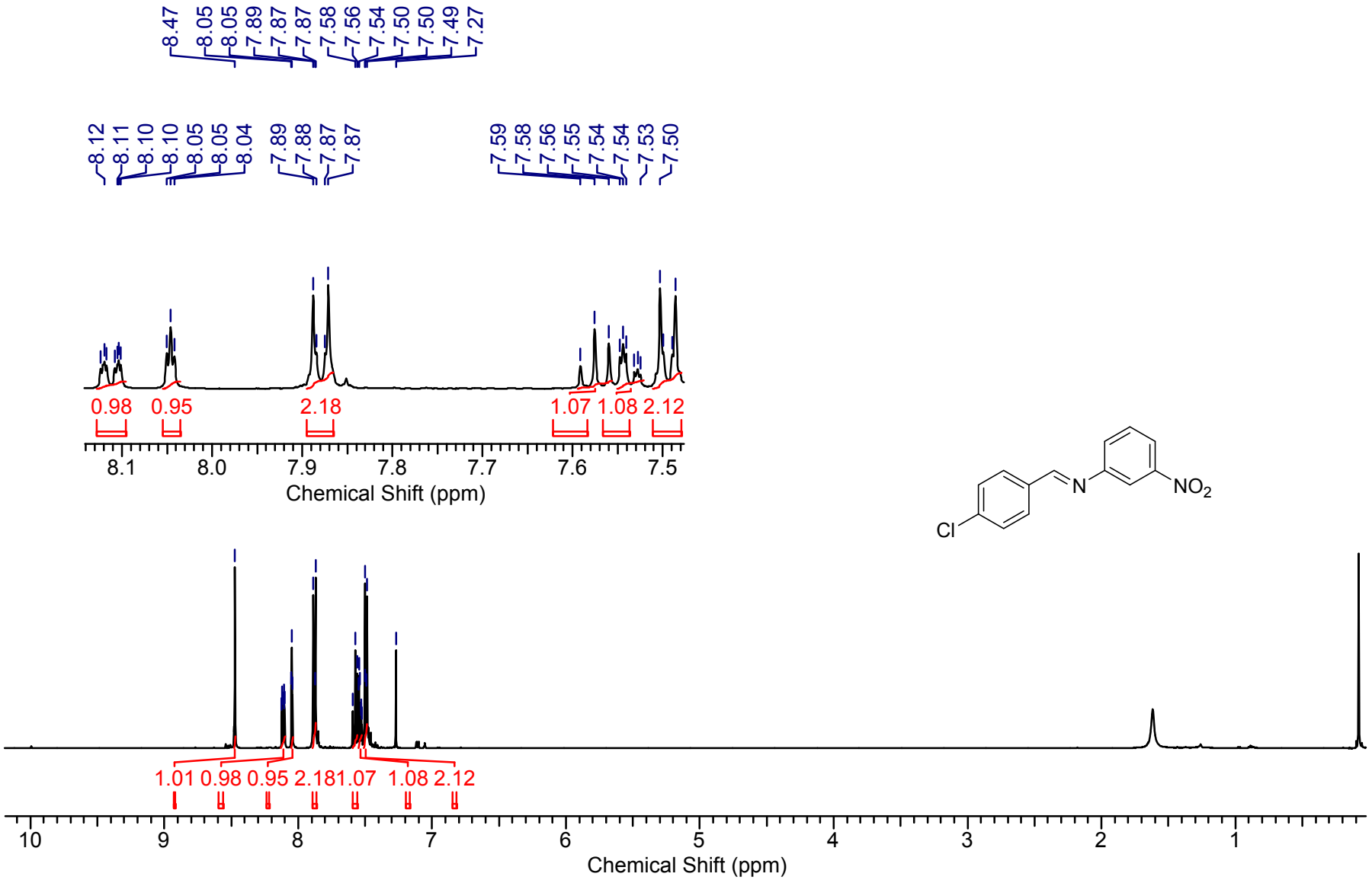
Supplementary Figure 14. ^{13}C NMR of **3ag**



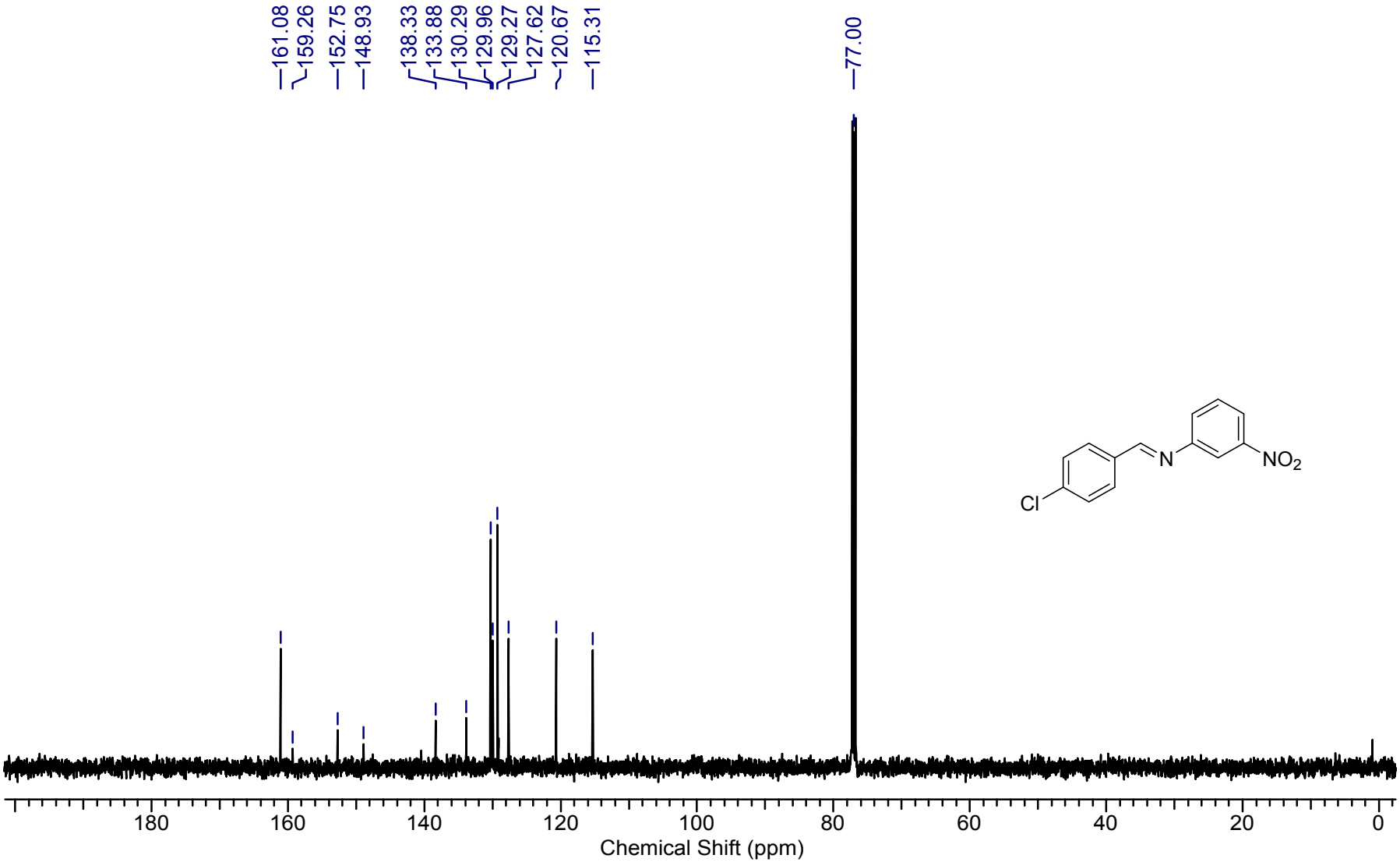
Supplementary Figure 15. ^{1}H NMR of **3ah**



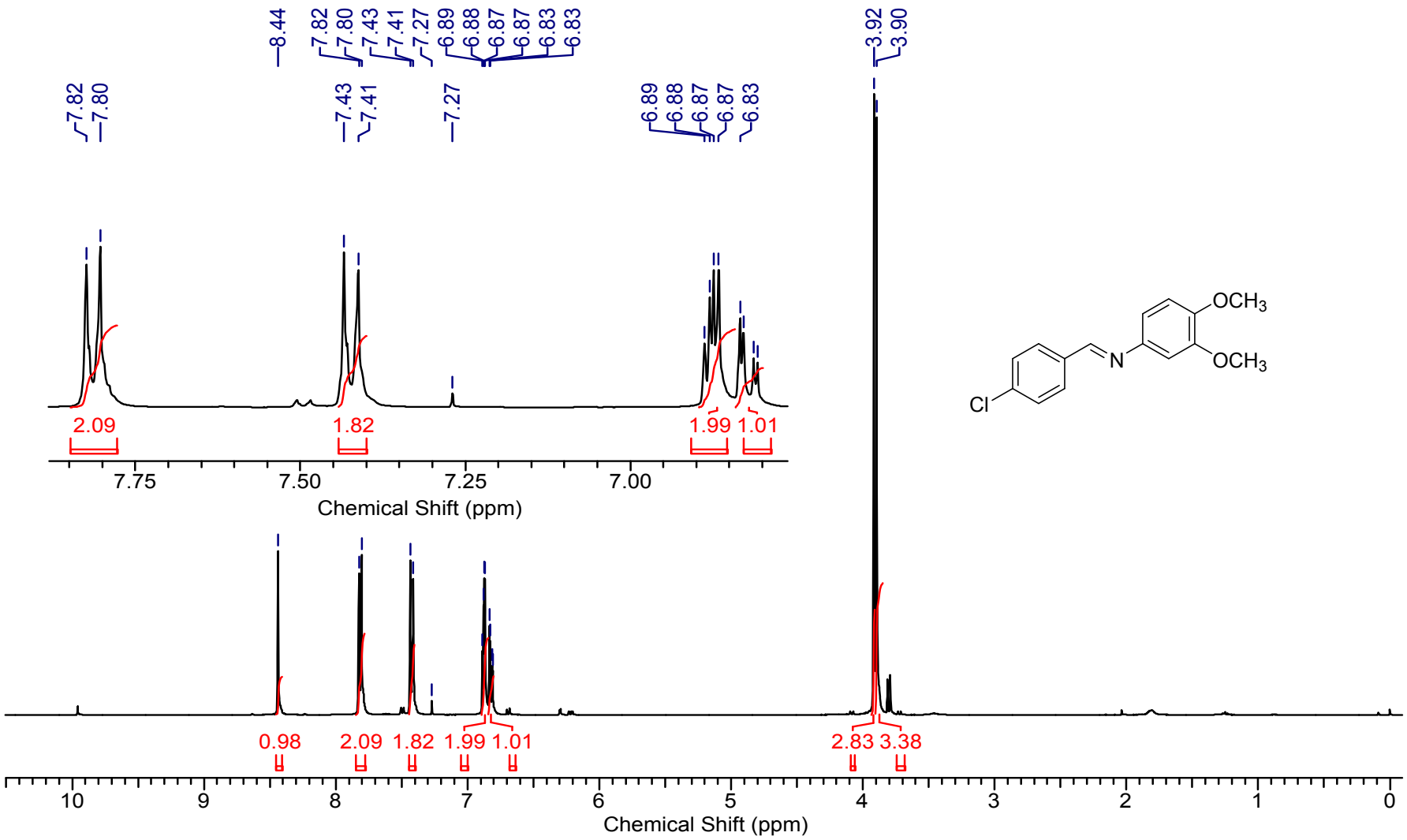
Supplementary Figure 16. ^{13}C NMR of **3ah**



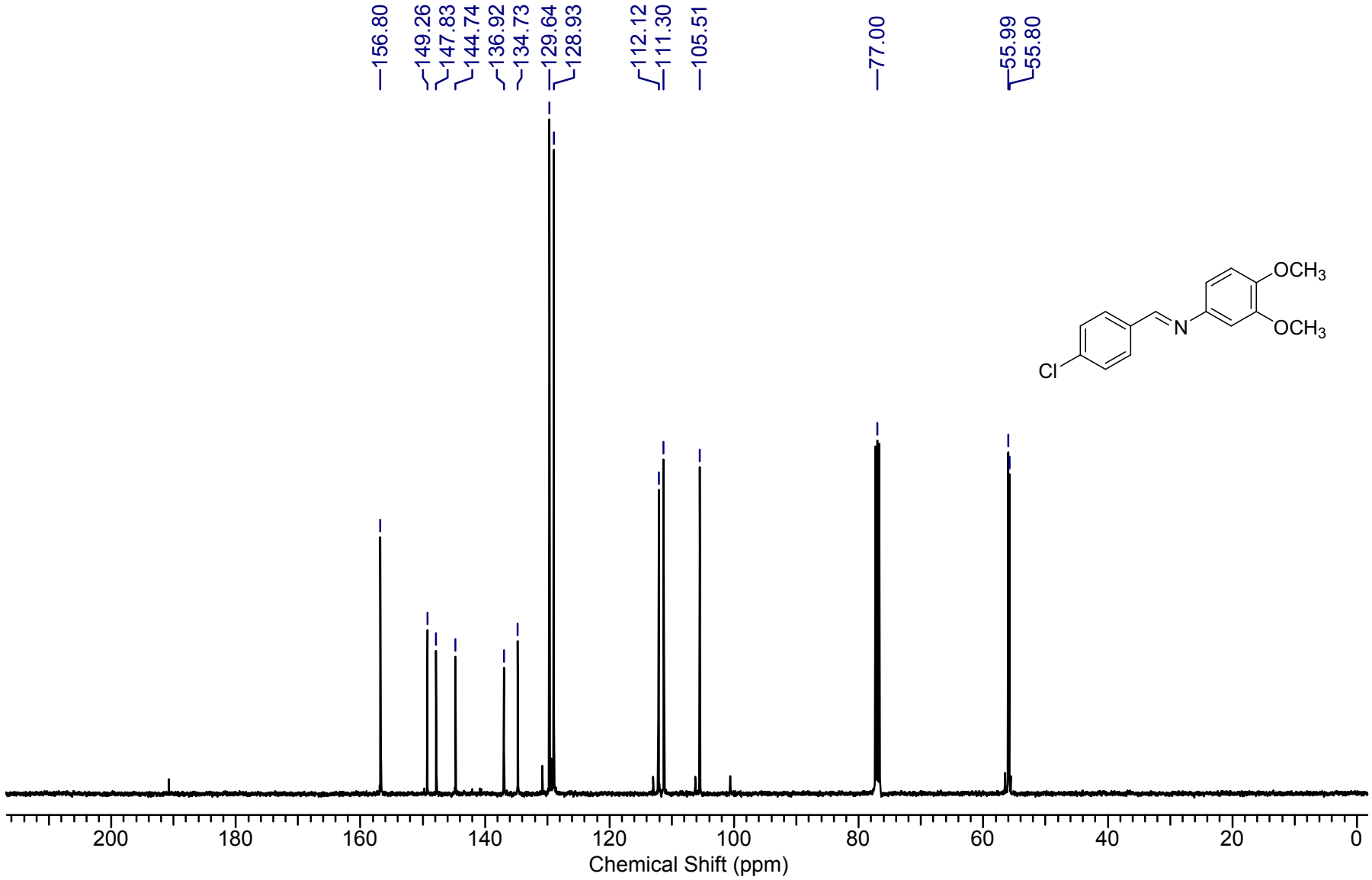
Supplementary Figure 17. ^{1}H NMR of **3ai**



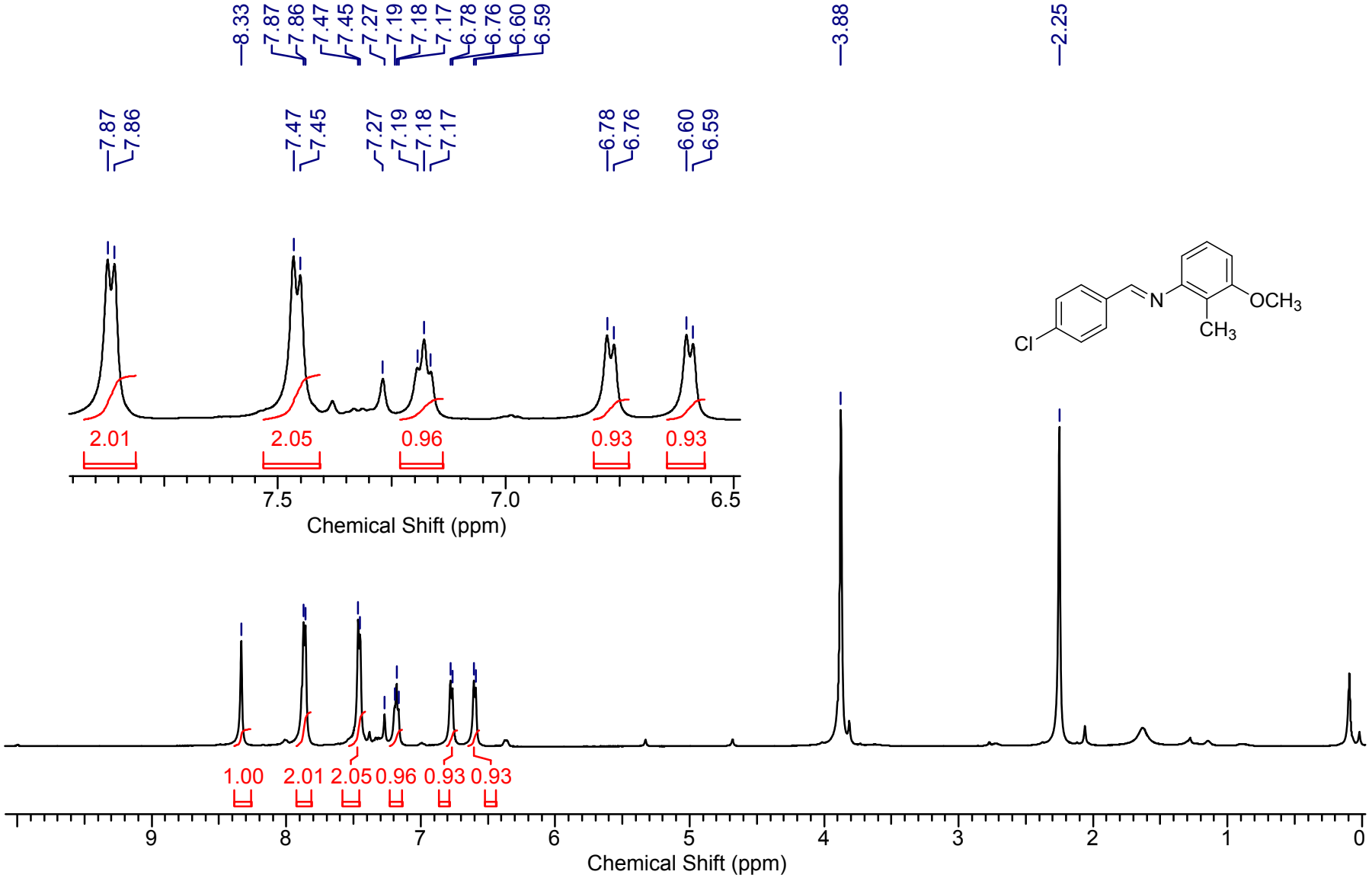
Supplementary Figure 18. ^{13}C NMR of **3ai**

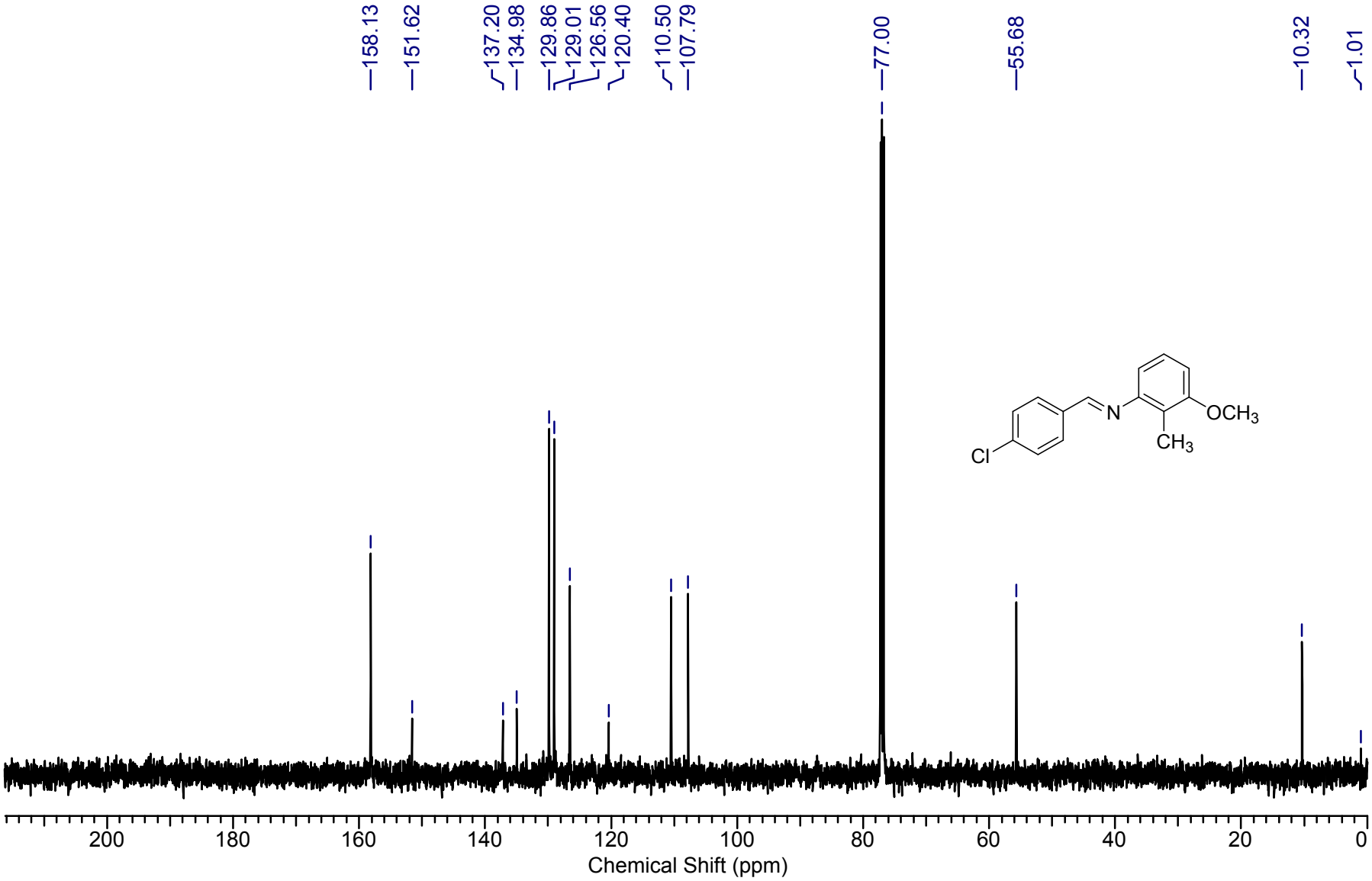


Supplementary Figure 19. ^{1}H NMR of **3aj**

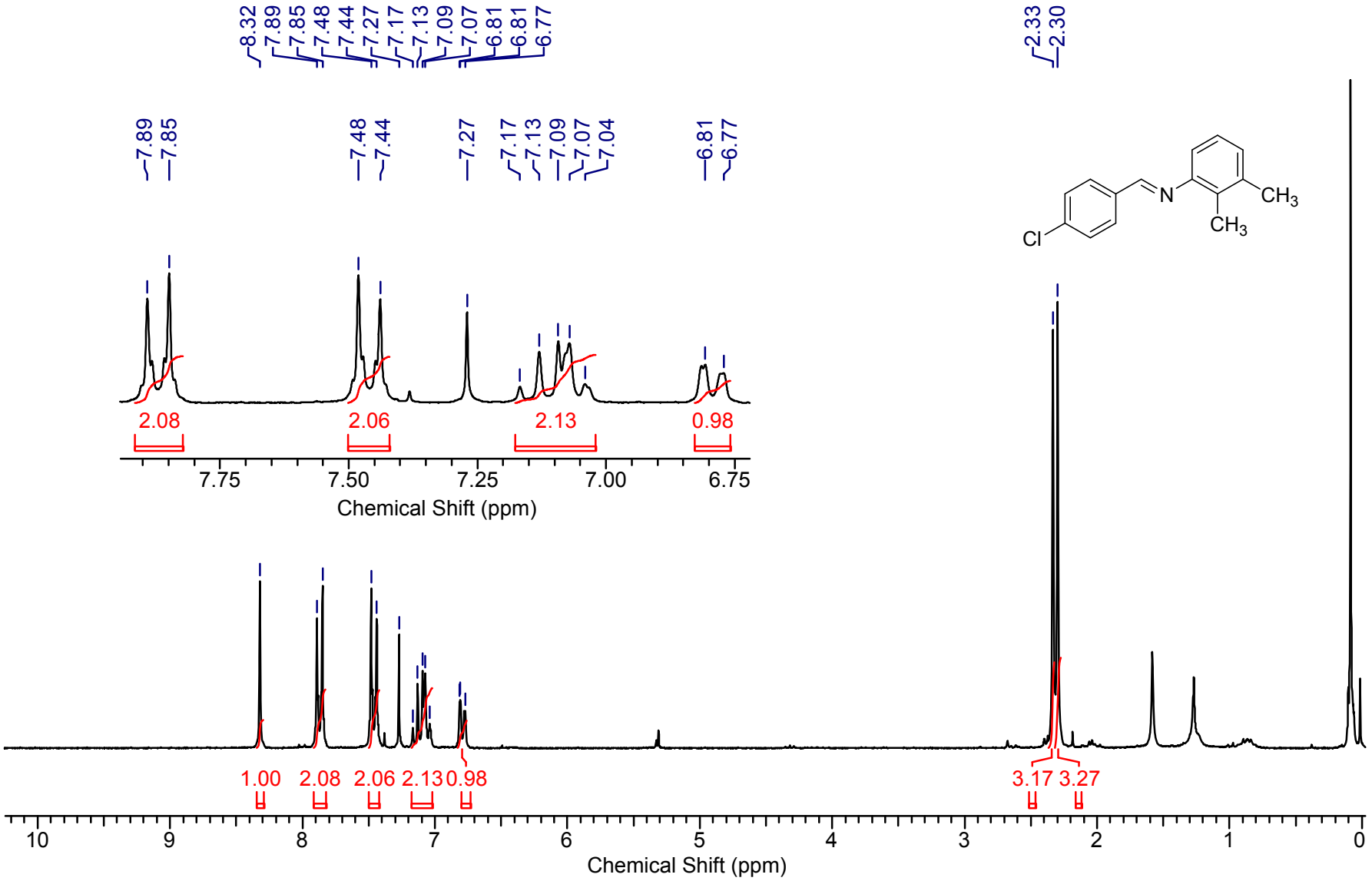


Supplementary Figure 20. ^{13}C NMR of **3ai**

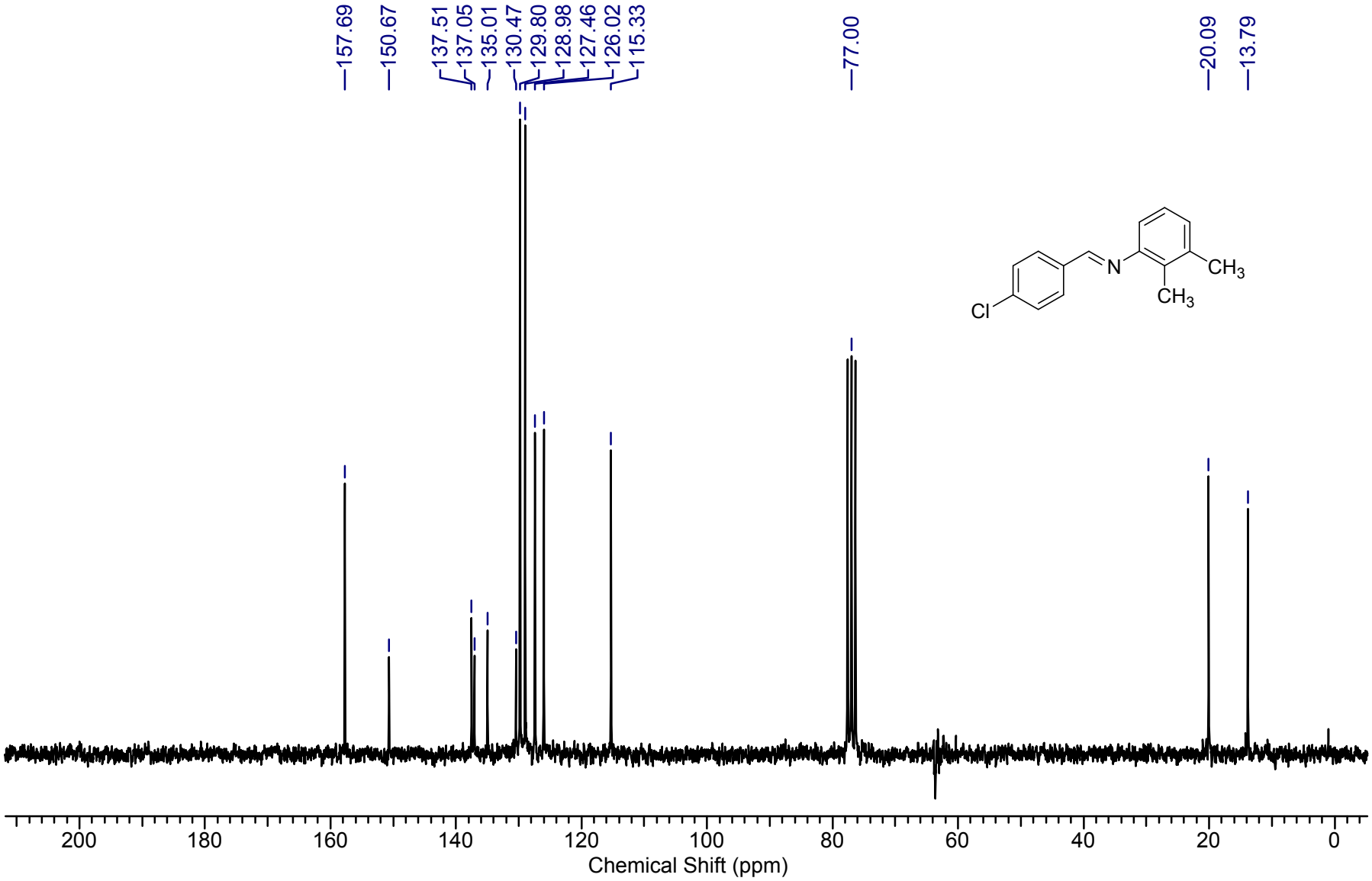

8.33
7.87
7.86
7.47
7.45
7.27
7.19
7.18
7.17
6.78
6.76
6.60
6.59
3.88
2.25
2.01
2.05
0.96
0.93
0.93
7.5
7.0
6.5
Chemical Shift (ppm)
Cl
N
OCH3
CH3
1.00
2.01
2.05
0.96
0.93
0.93
9
8
7
6
5
4
3
2
1
0
Chemical Shift (ppm)



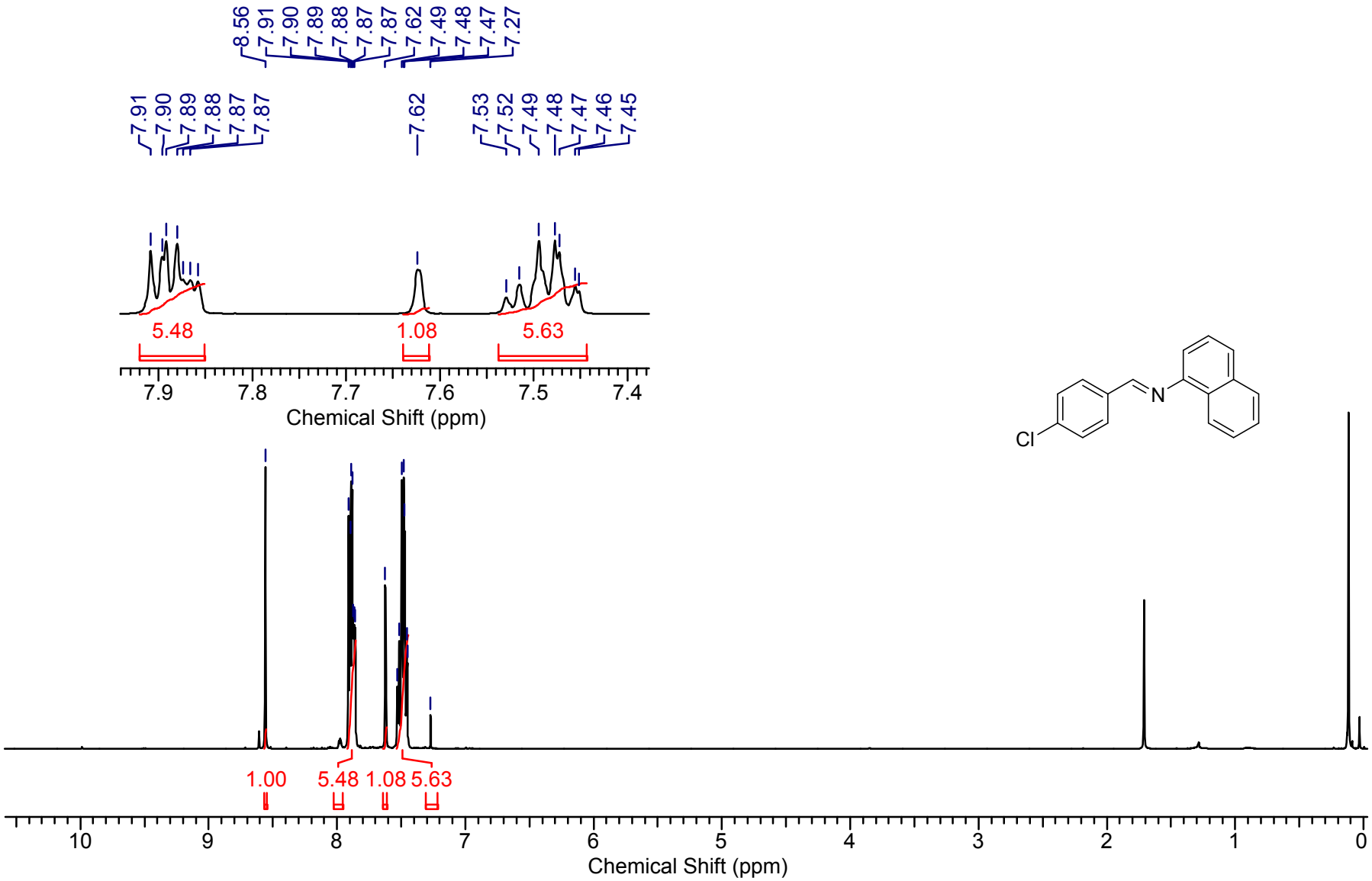
Supplementary Figure 22. ^{13}C NMR of **3ak**



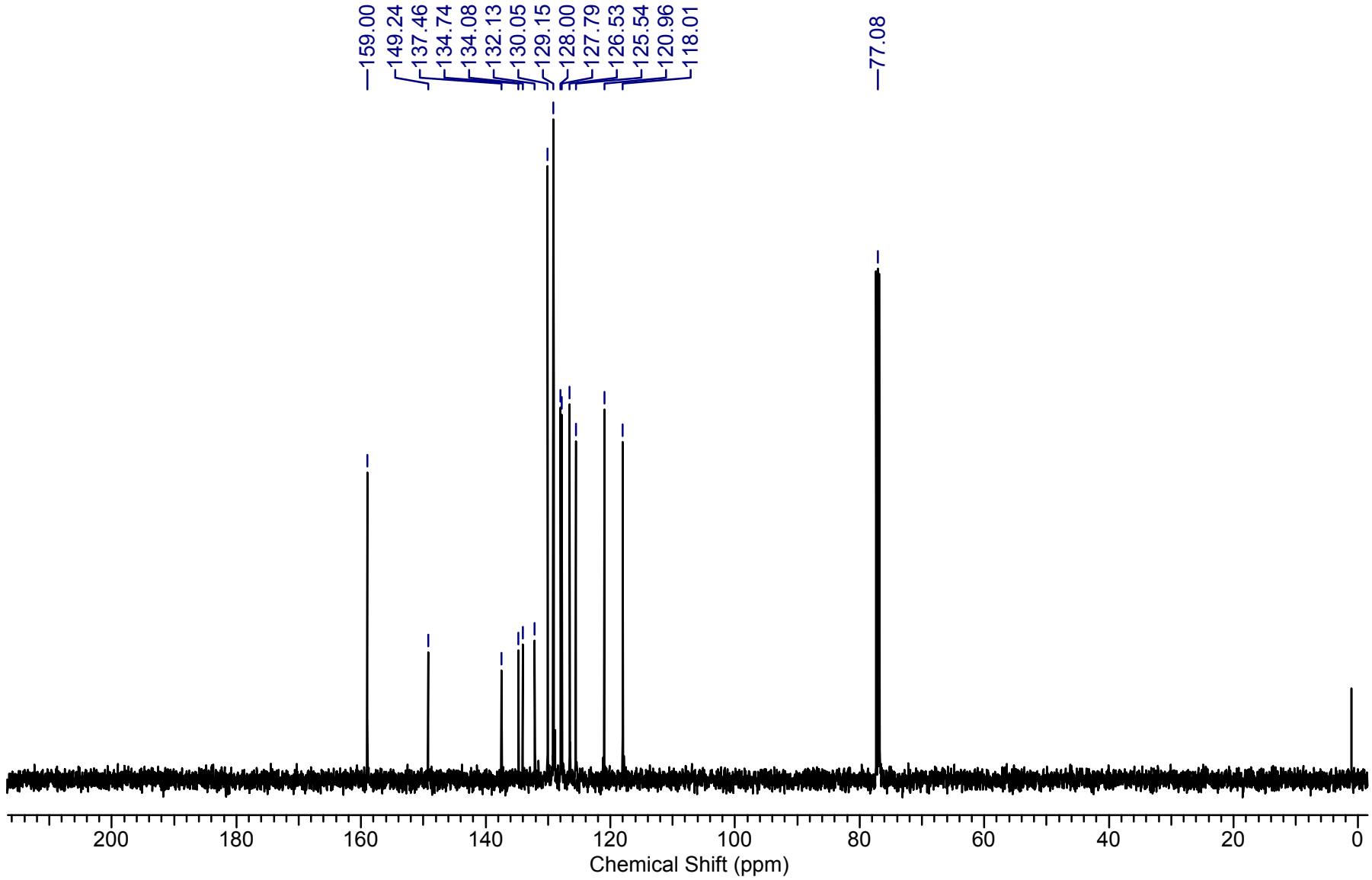
Supplementary Figure 23. ^{1}H NMR of **3al**

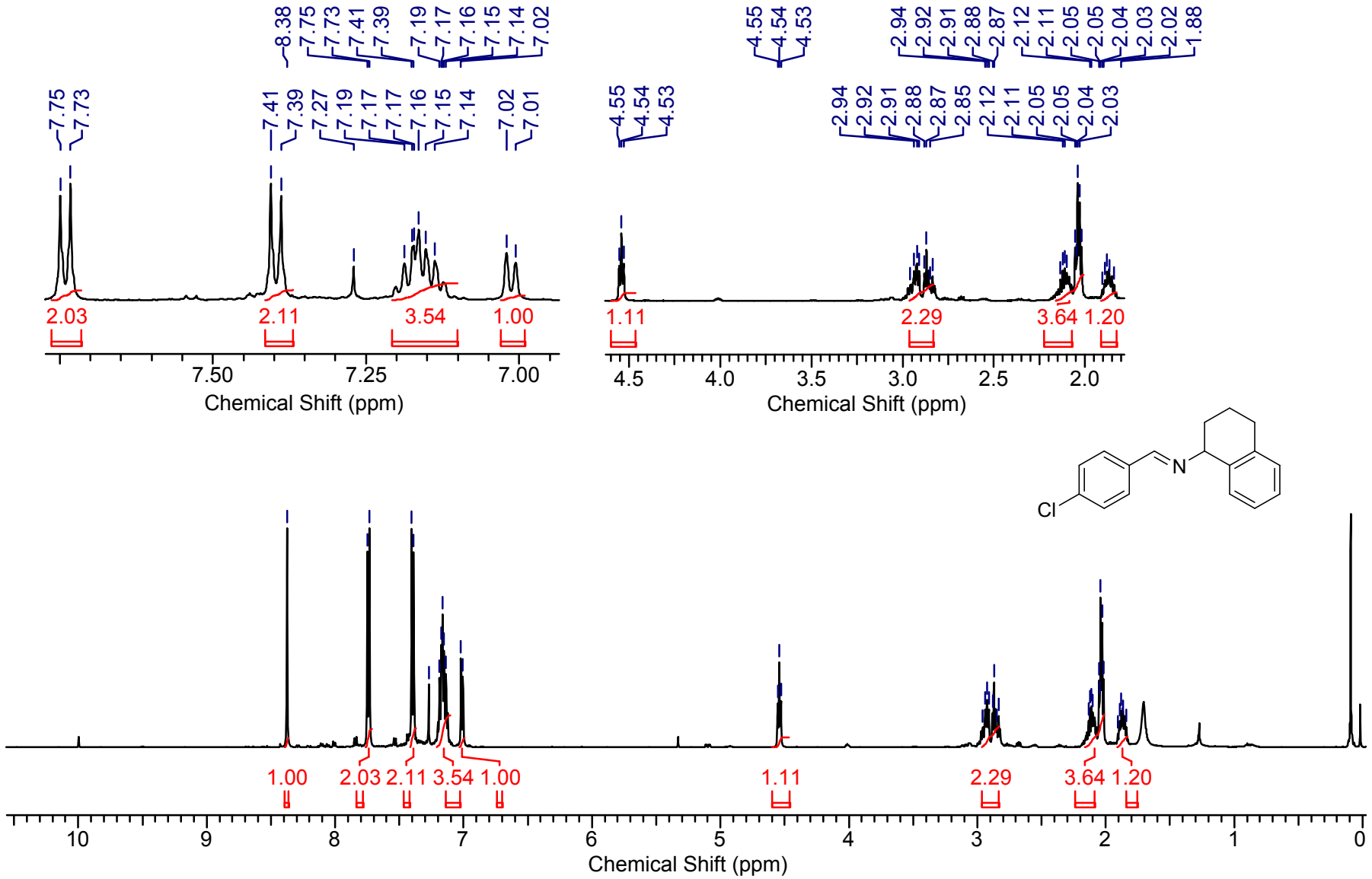


Supplementary Figure 24. ^{13}C NMR of **3al**

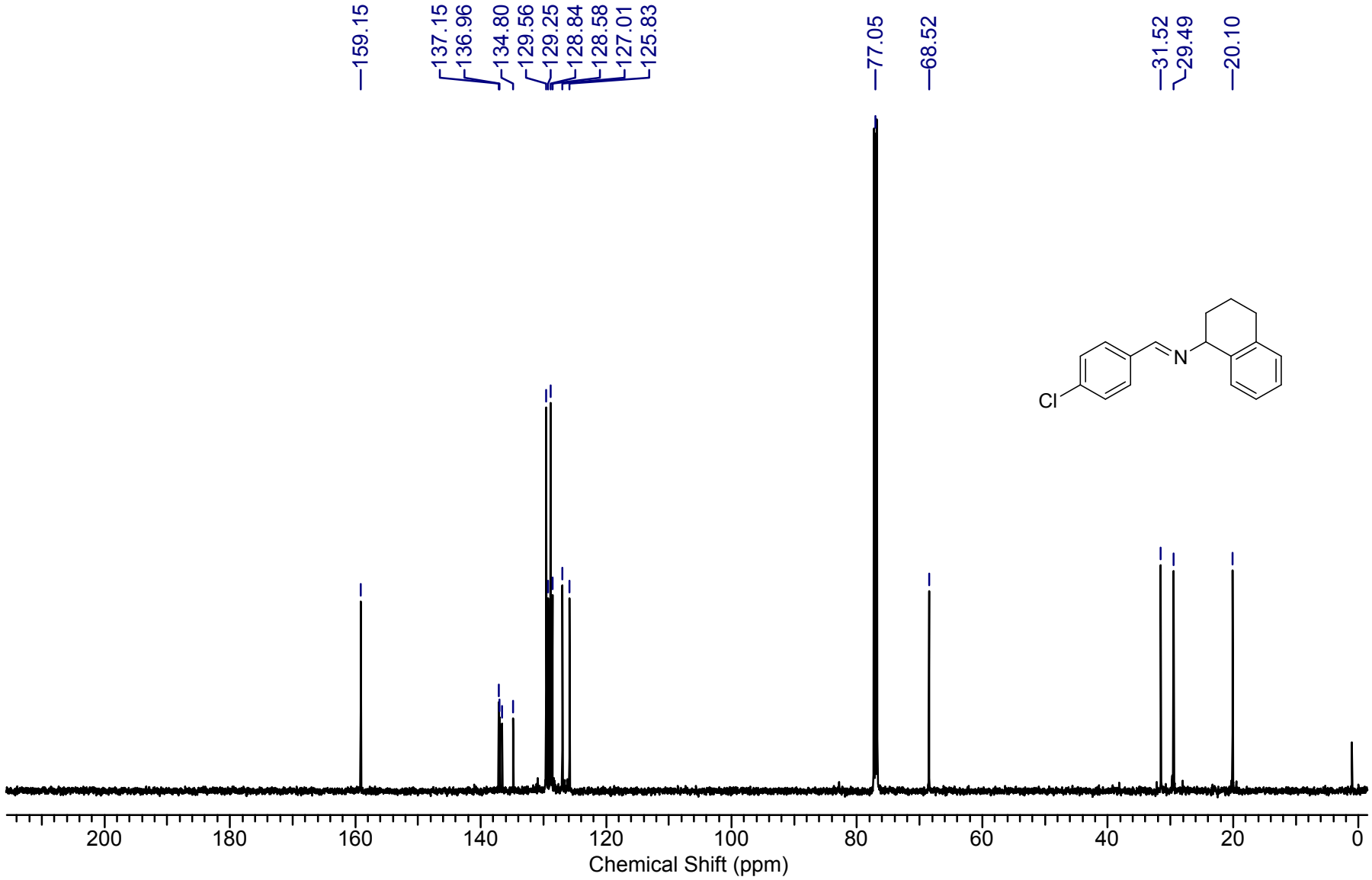


Supplementary Figure 25. ^{1}H NMR of **3am**

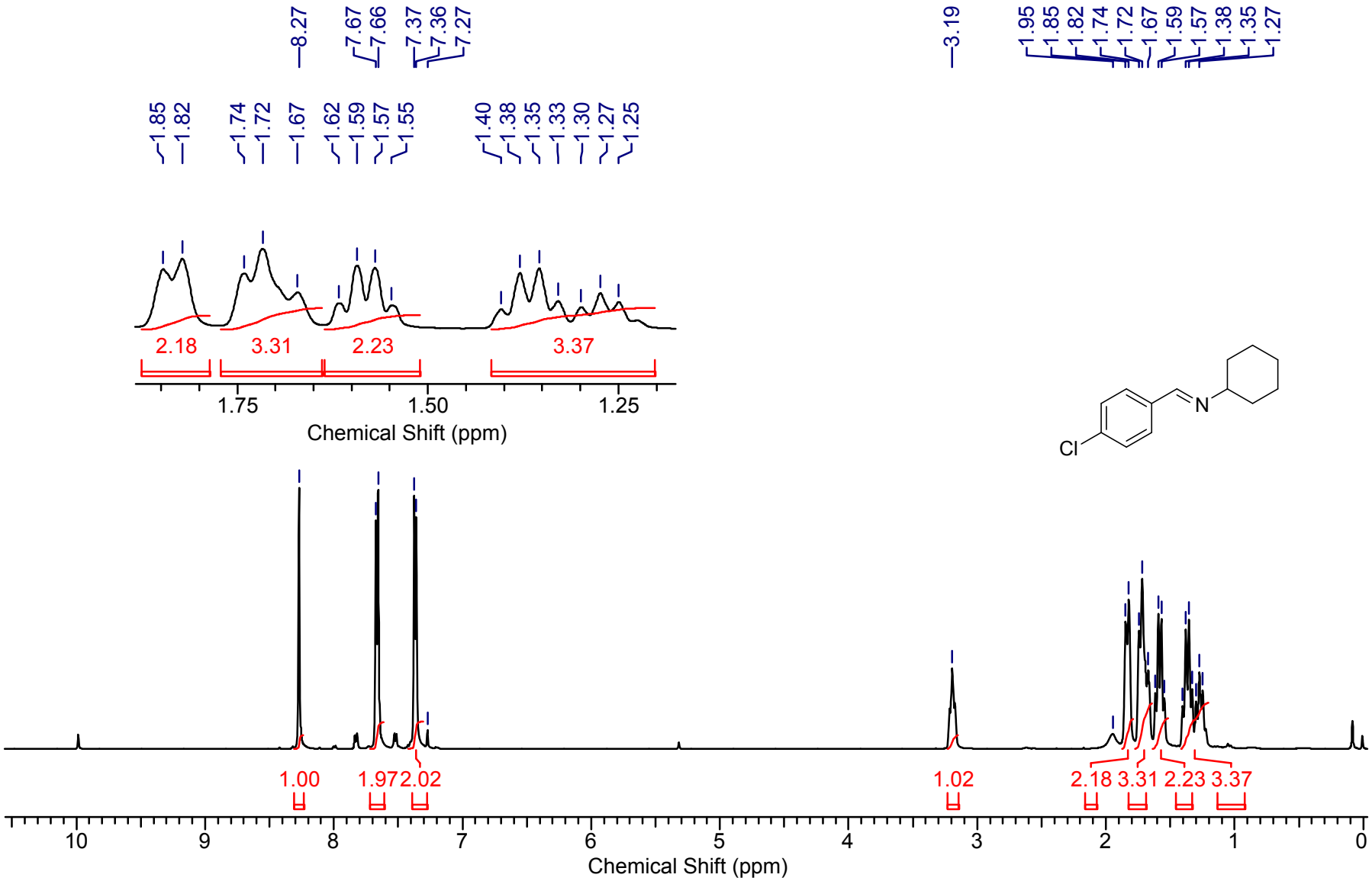

159.00
149.24
137.46
134.74
134.08
132.13
130.05
129.15
128.00
127.79
126.53
125.54
120.96
118.01
77.08
200
180
160
140
120
100
80
60
40
20
0
Chemical Shift (ppm)



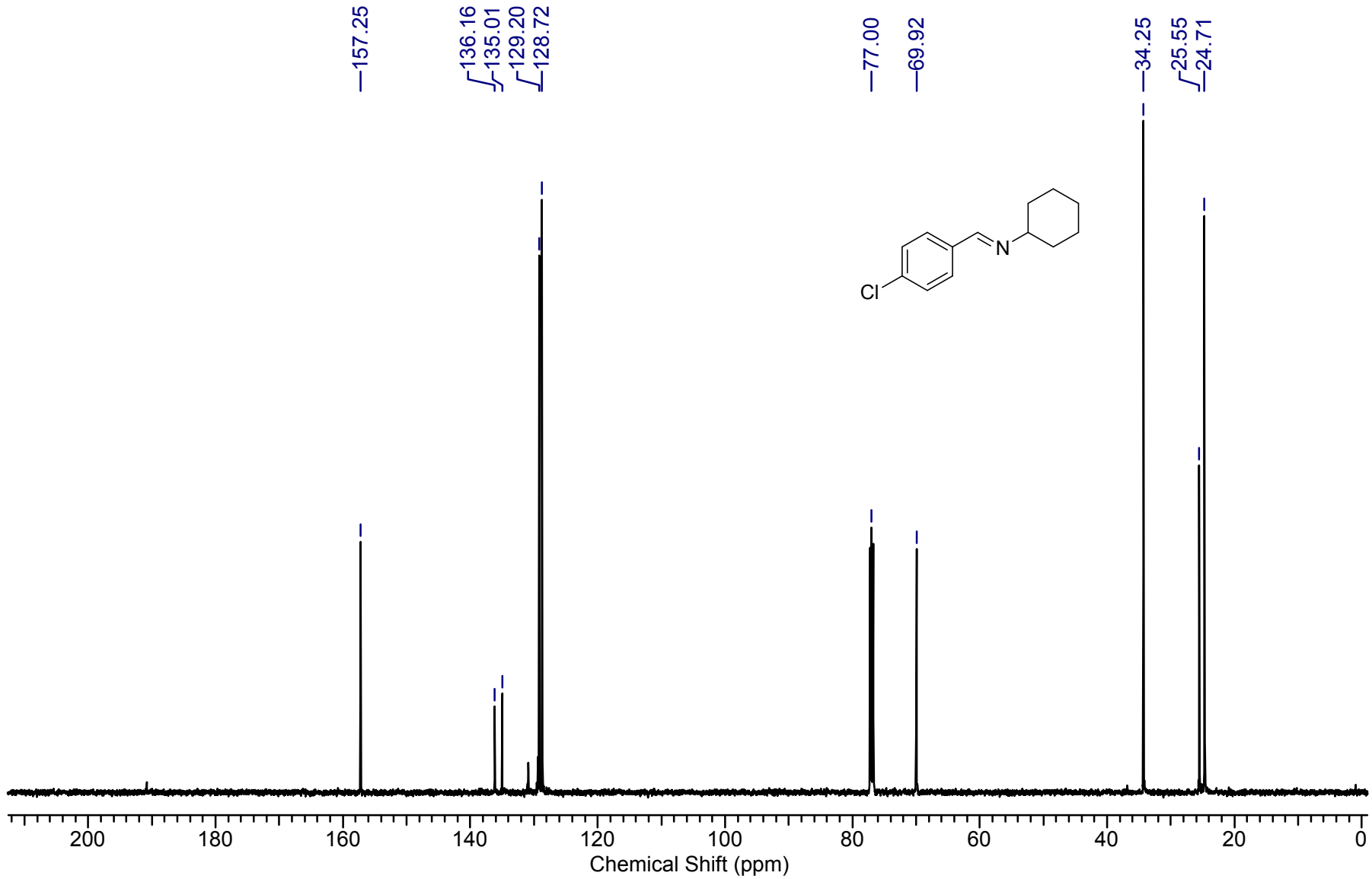
Supplementary Figure 27. ^{1}H NMR of **3an**



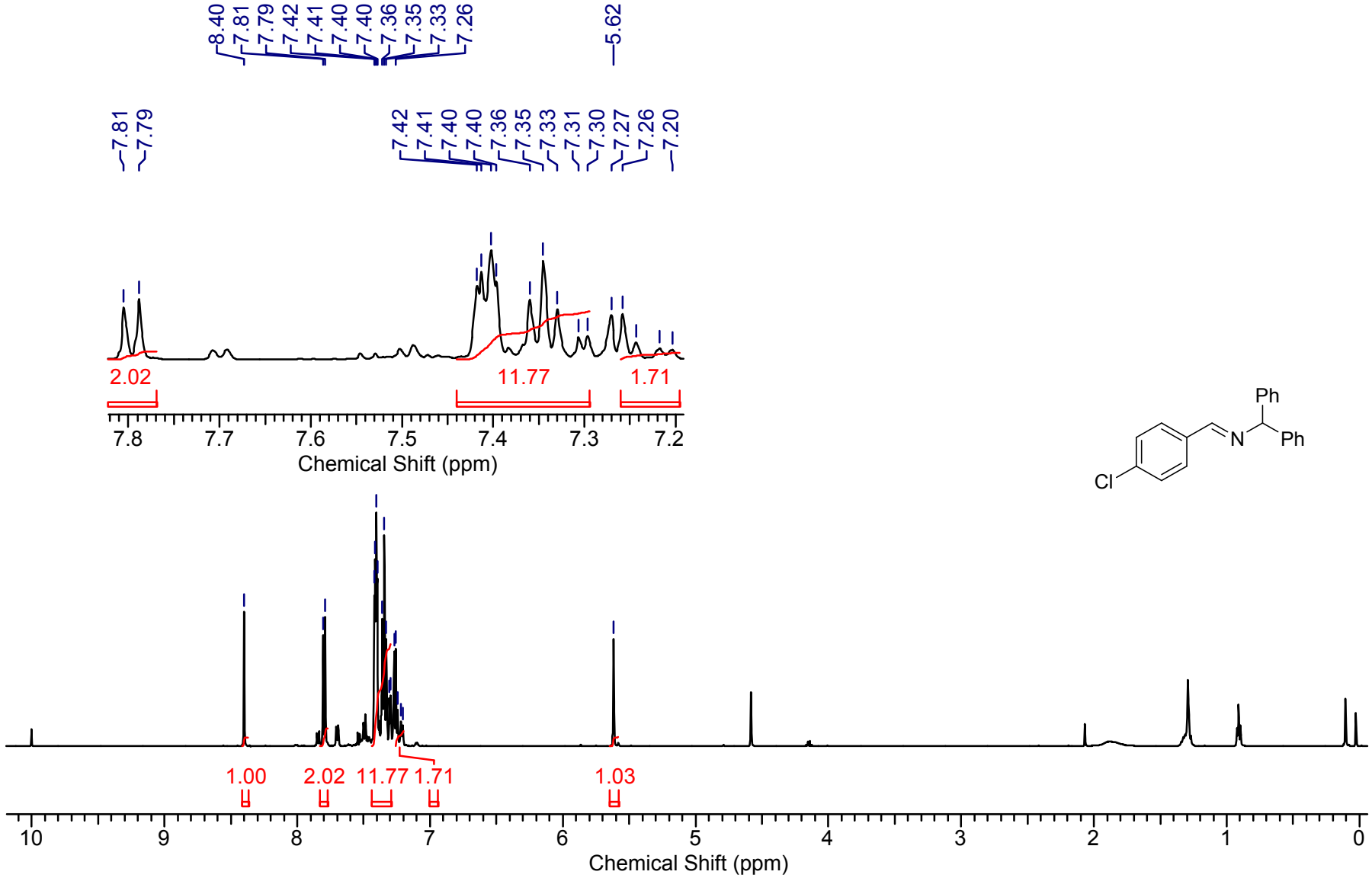
Supplementary Figure 28. ^{13}C NMR of **3an**



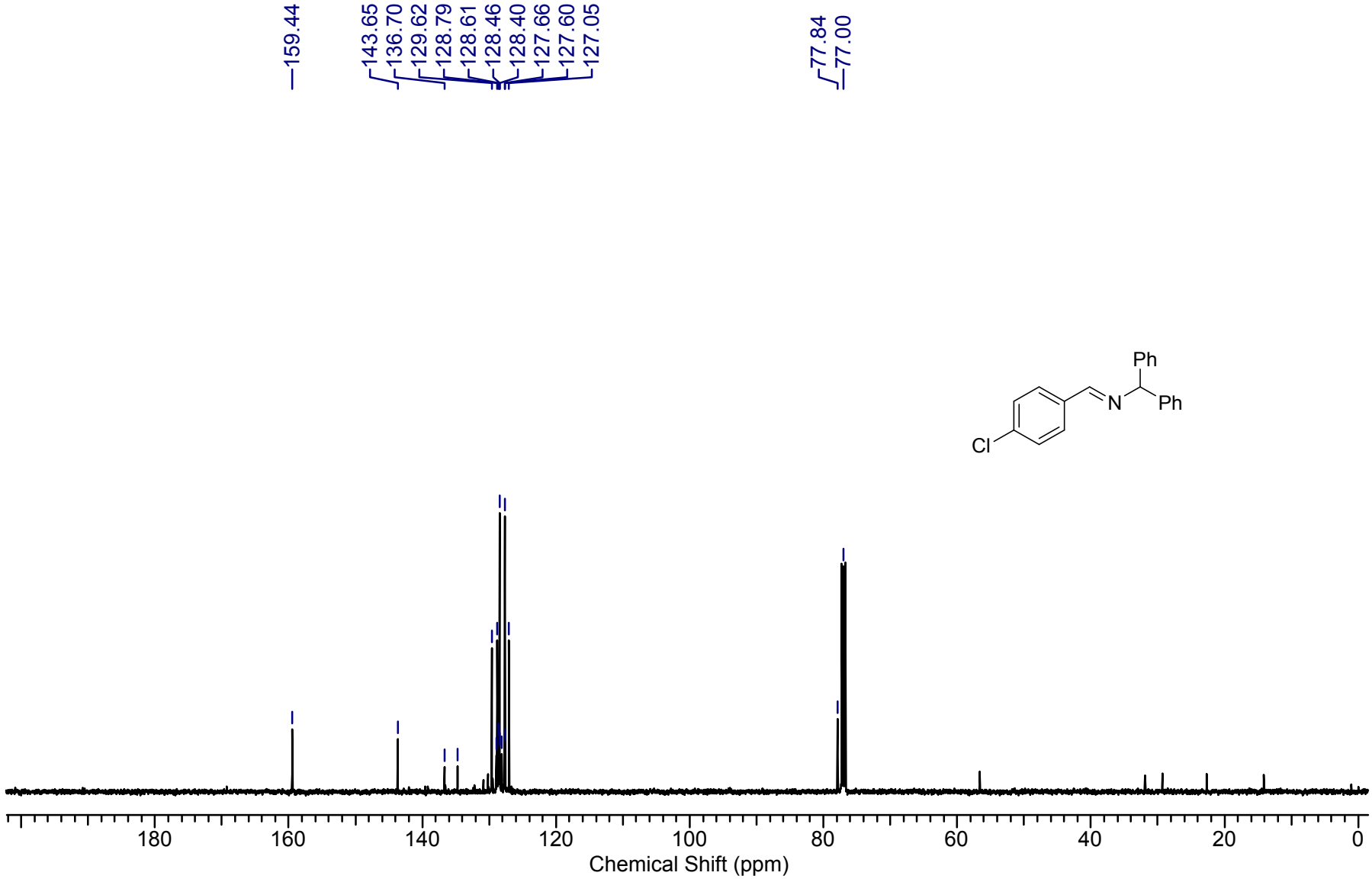
Supplementary Figure 29. ^{1}H NMR of **3ao**



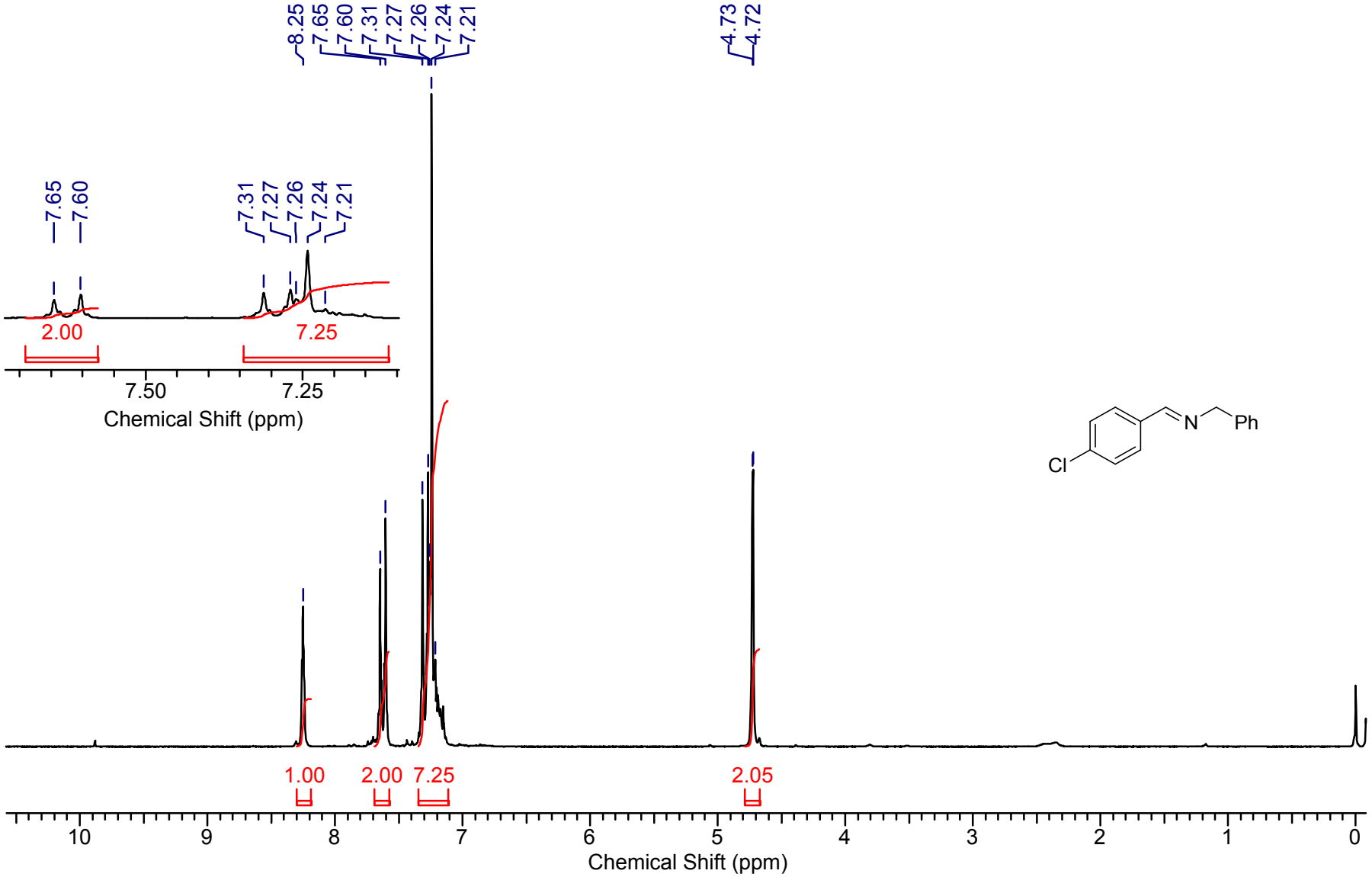
Supplementary Figure 30. ^{13}C NMR of **3ao**



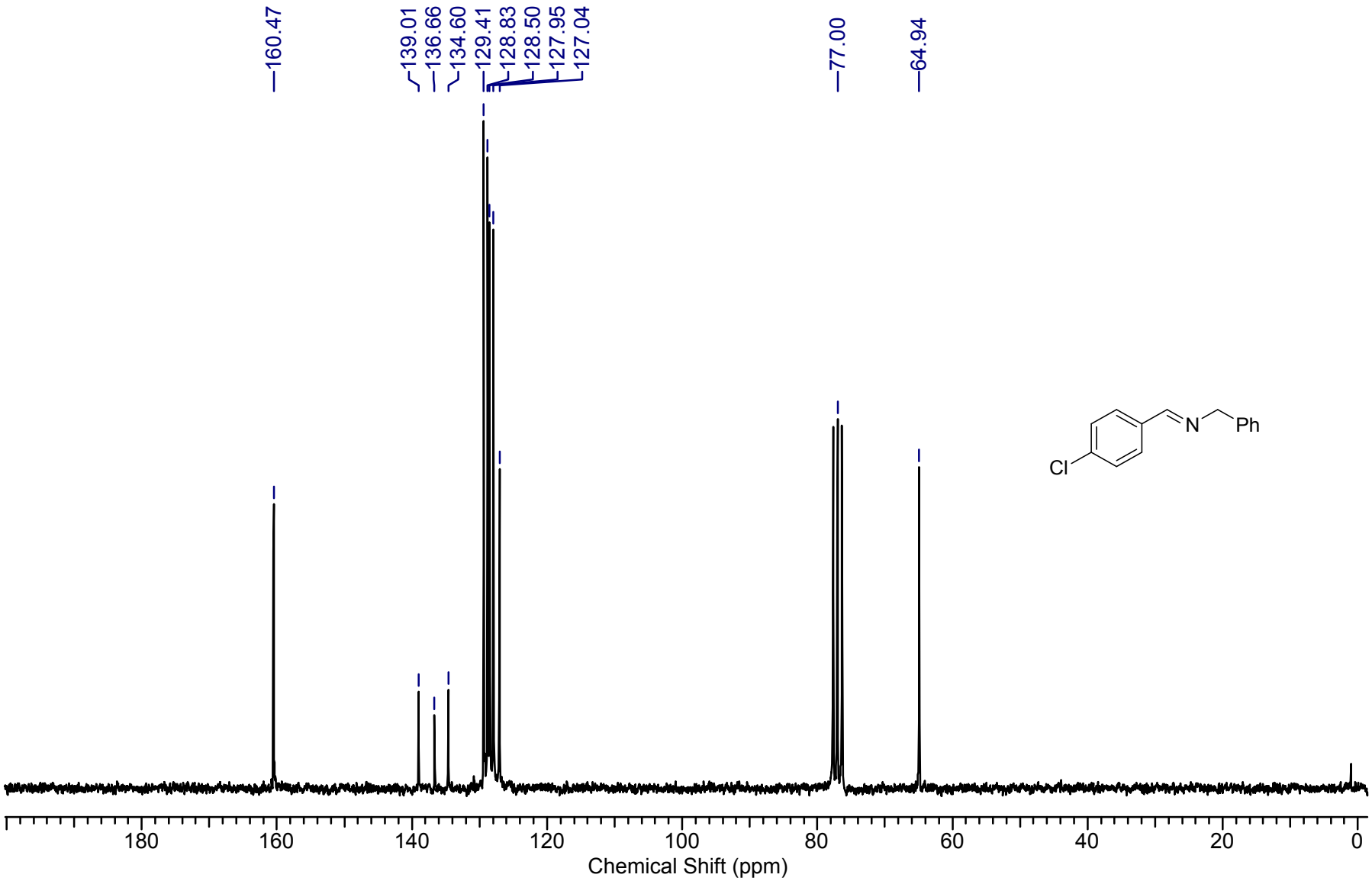
Supplementary Figure 31. ^{1}H NMR of **3aq**



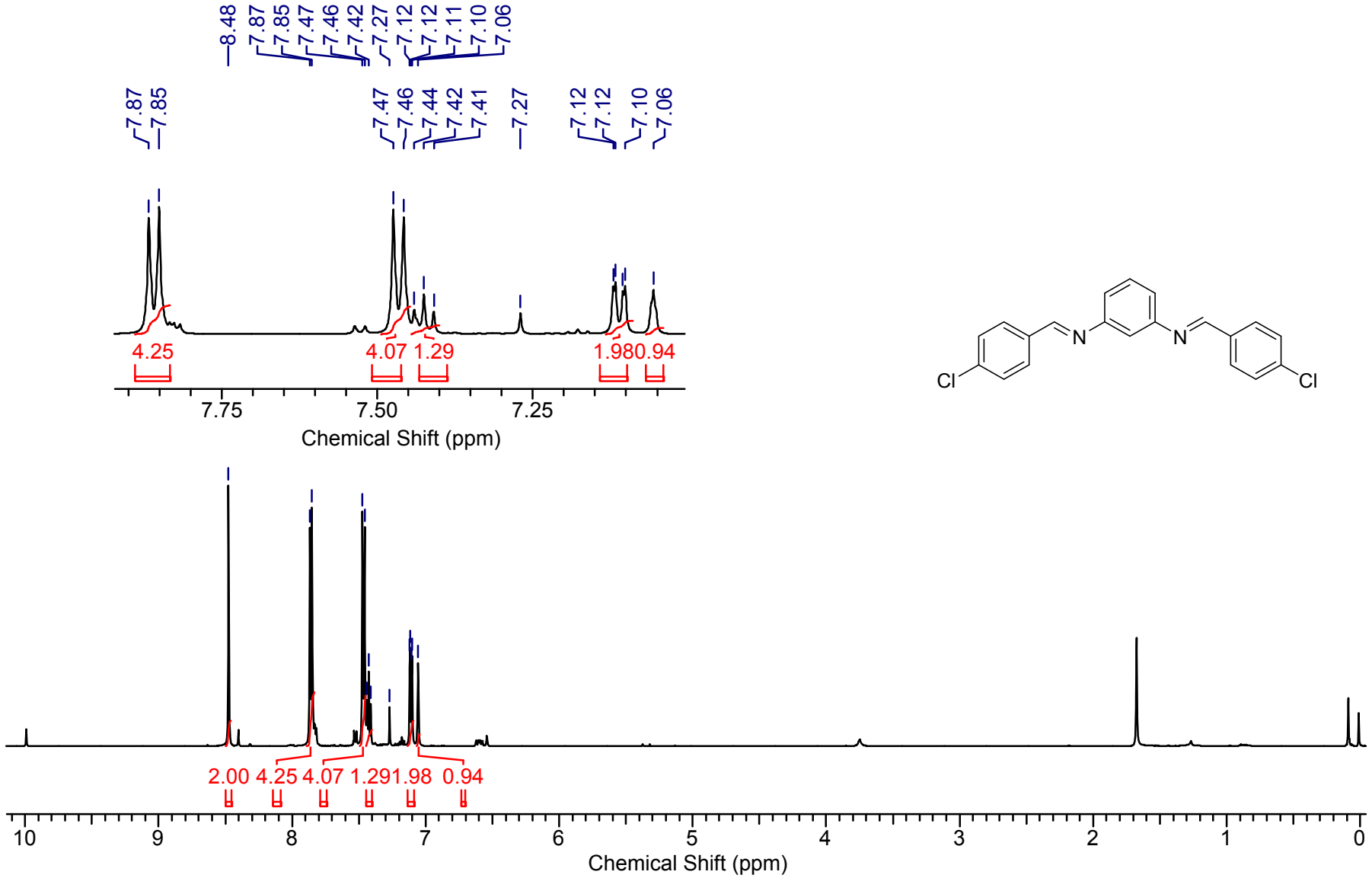
Supplementary Figure 32. ^{13}C NMR of **3aq**



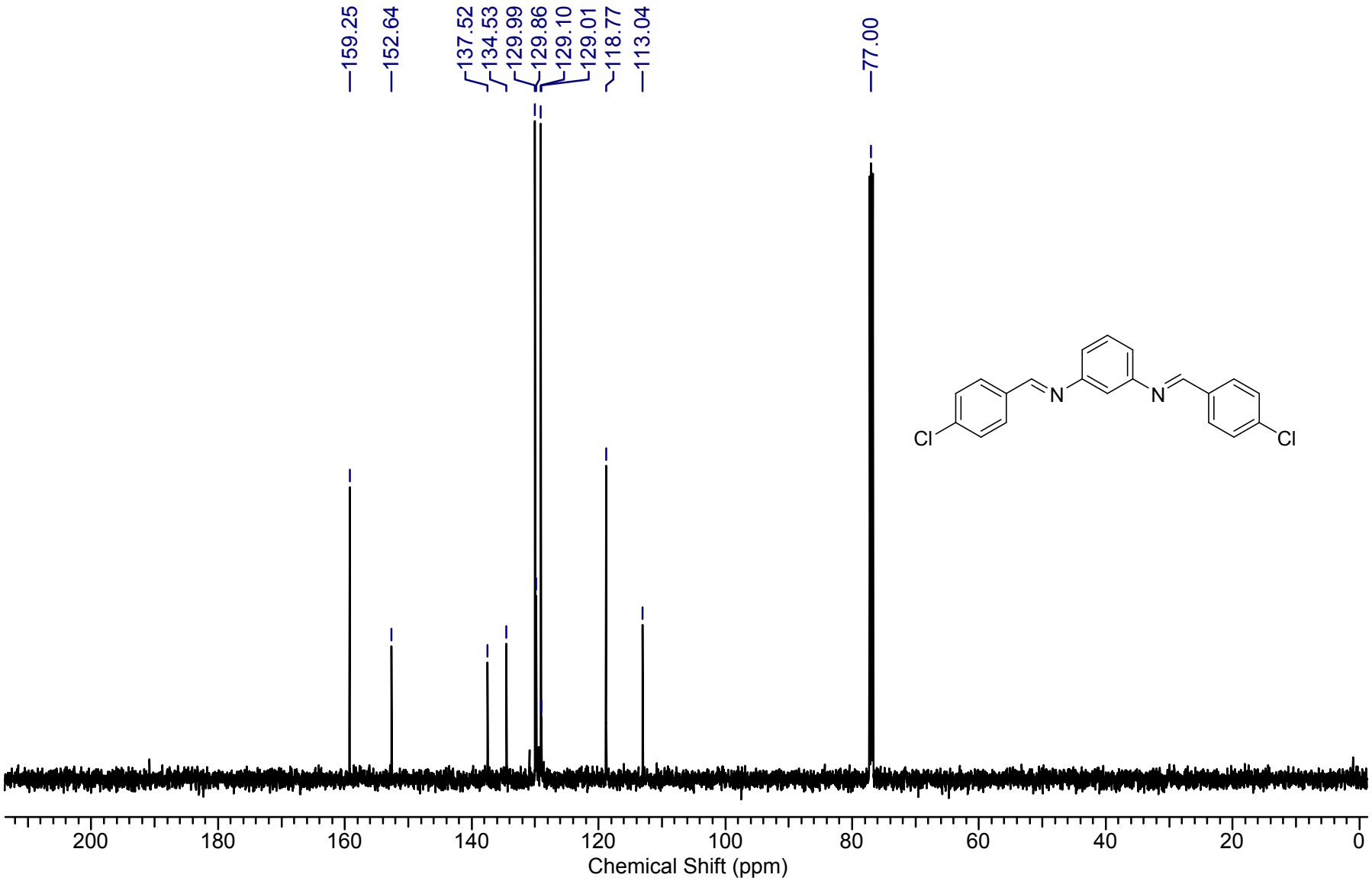
Supplementary Figure 33. ^{1}H NMR of **3ar**



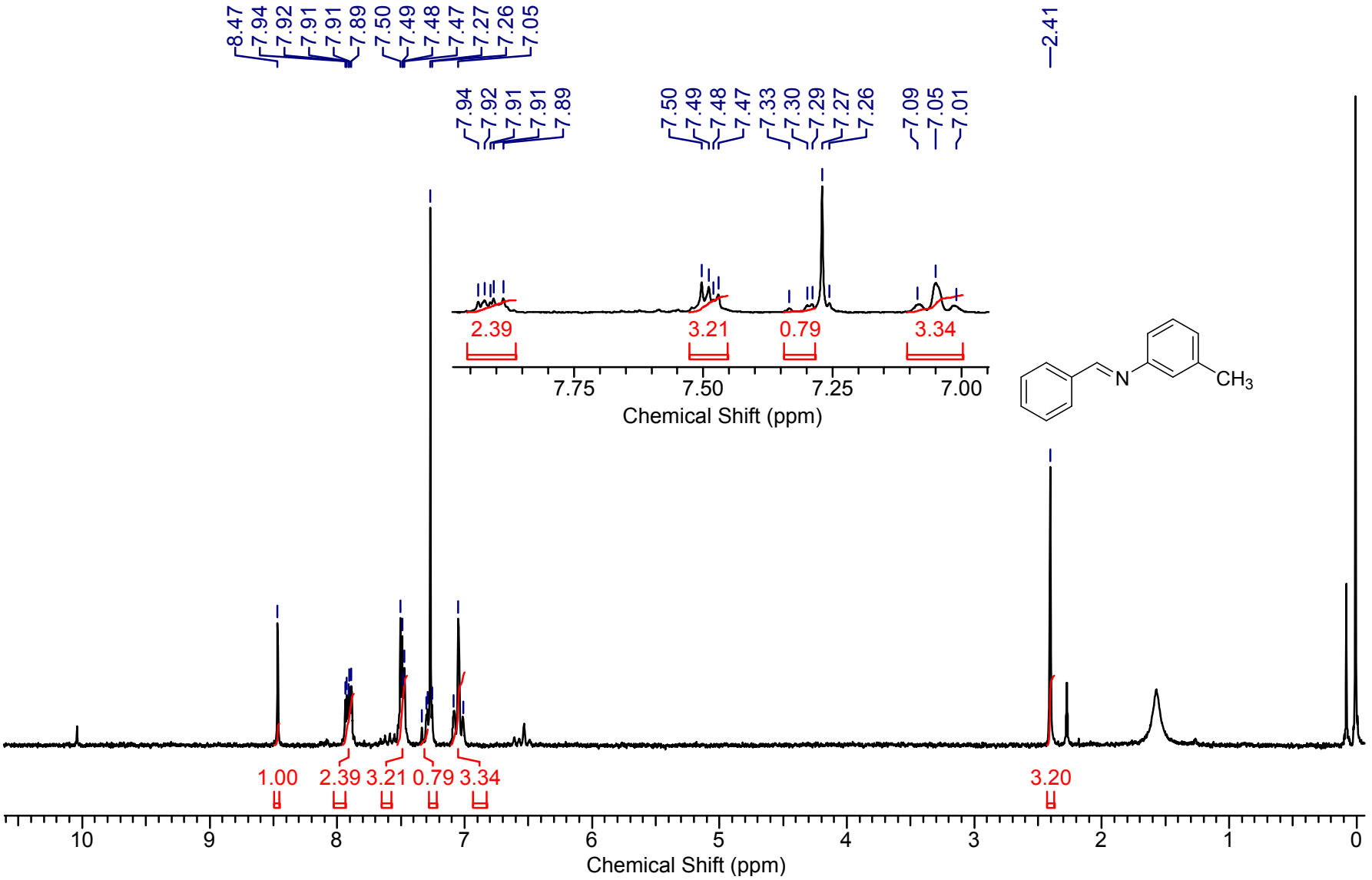
Supplementary Figure 34. ^{13}C NMR of **3ar**



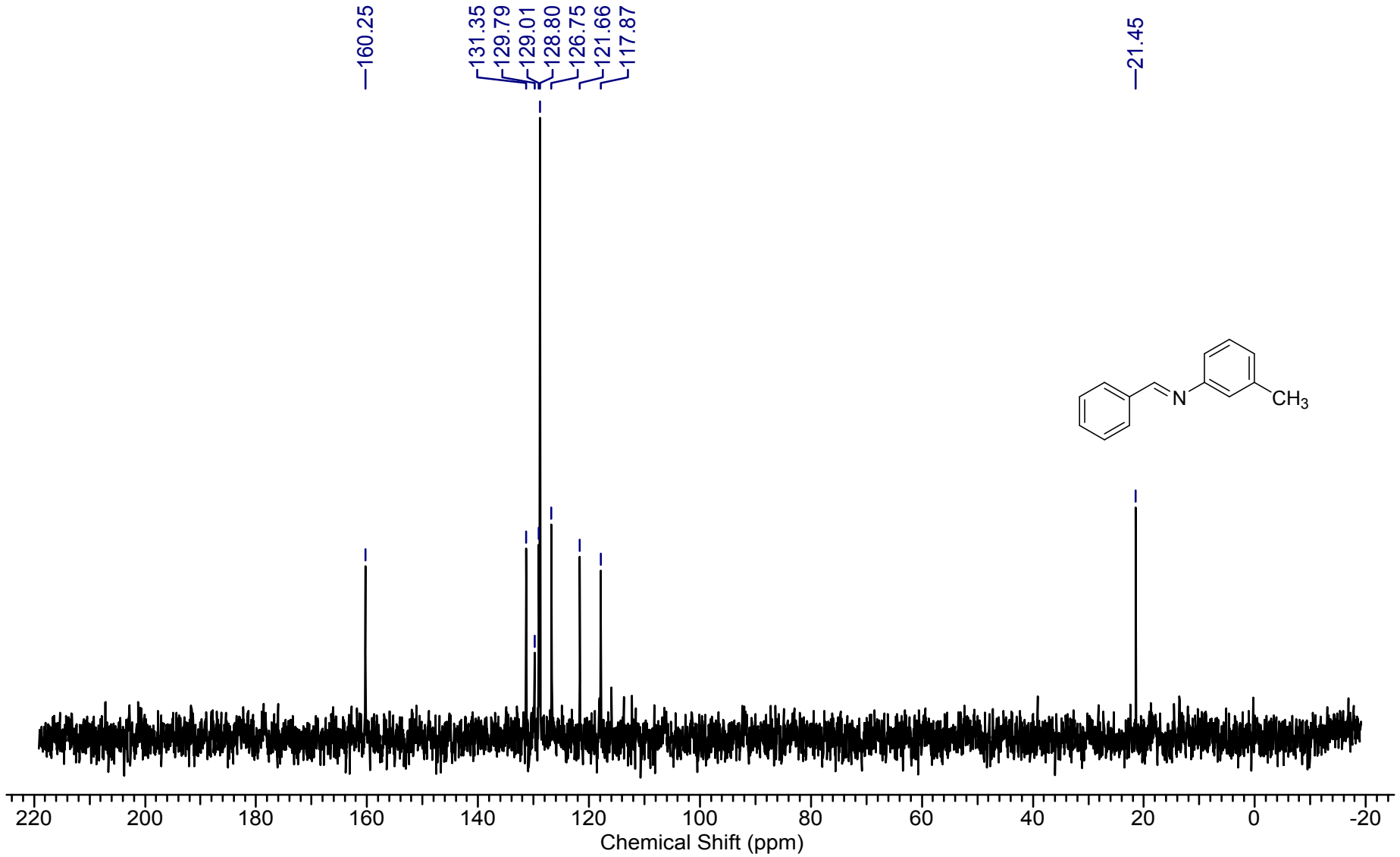
Supplementary Figure 35. ^{1}H NMR of **3as**



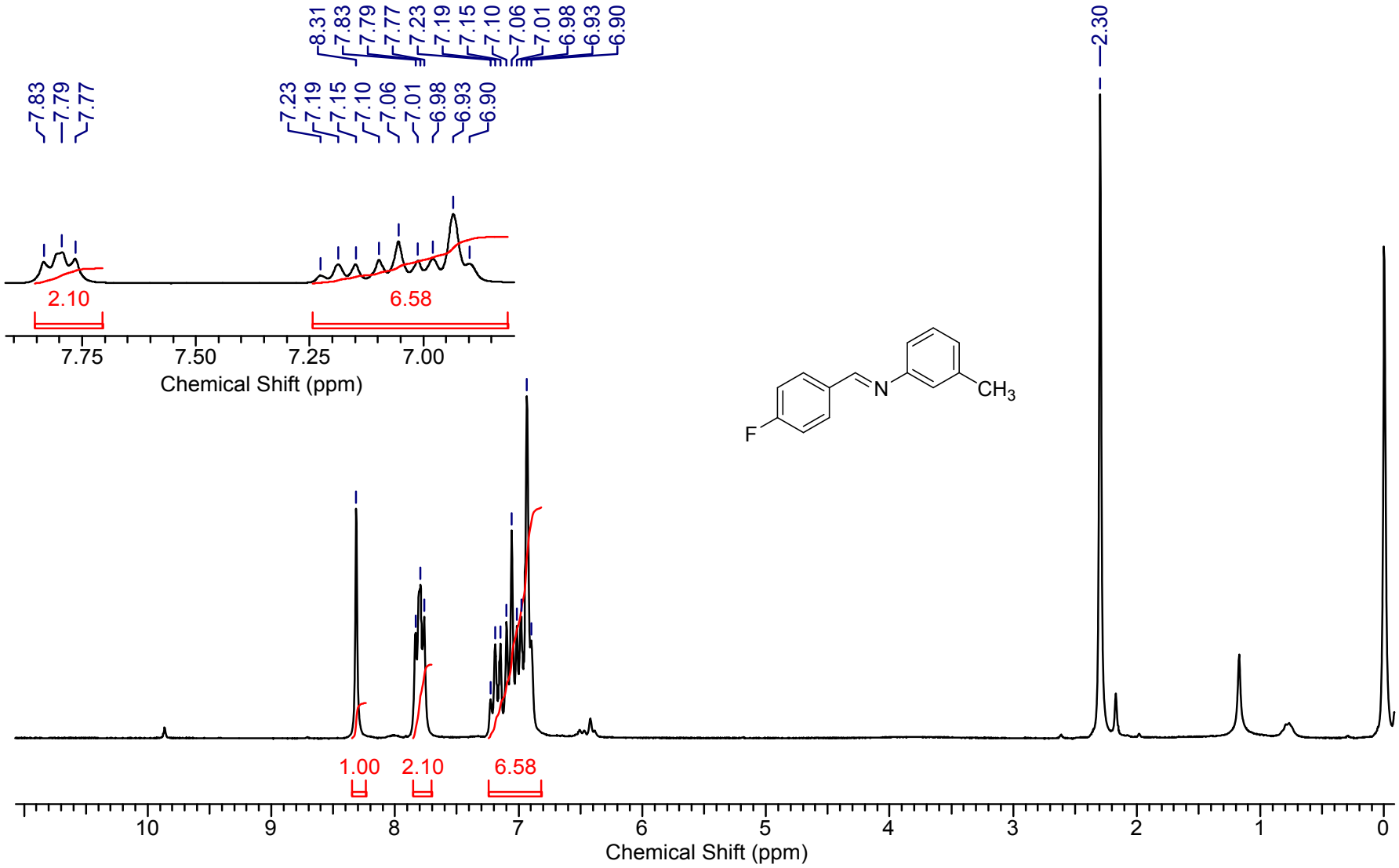
Supplementary Figure 36. ^{13}C NMR of **3as**



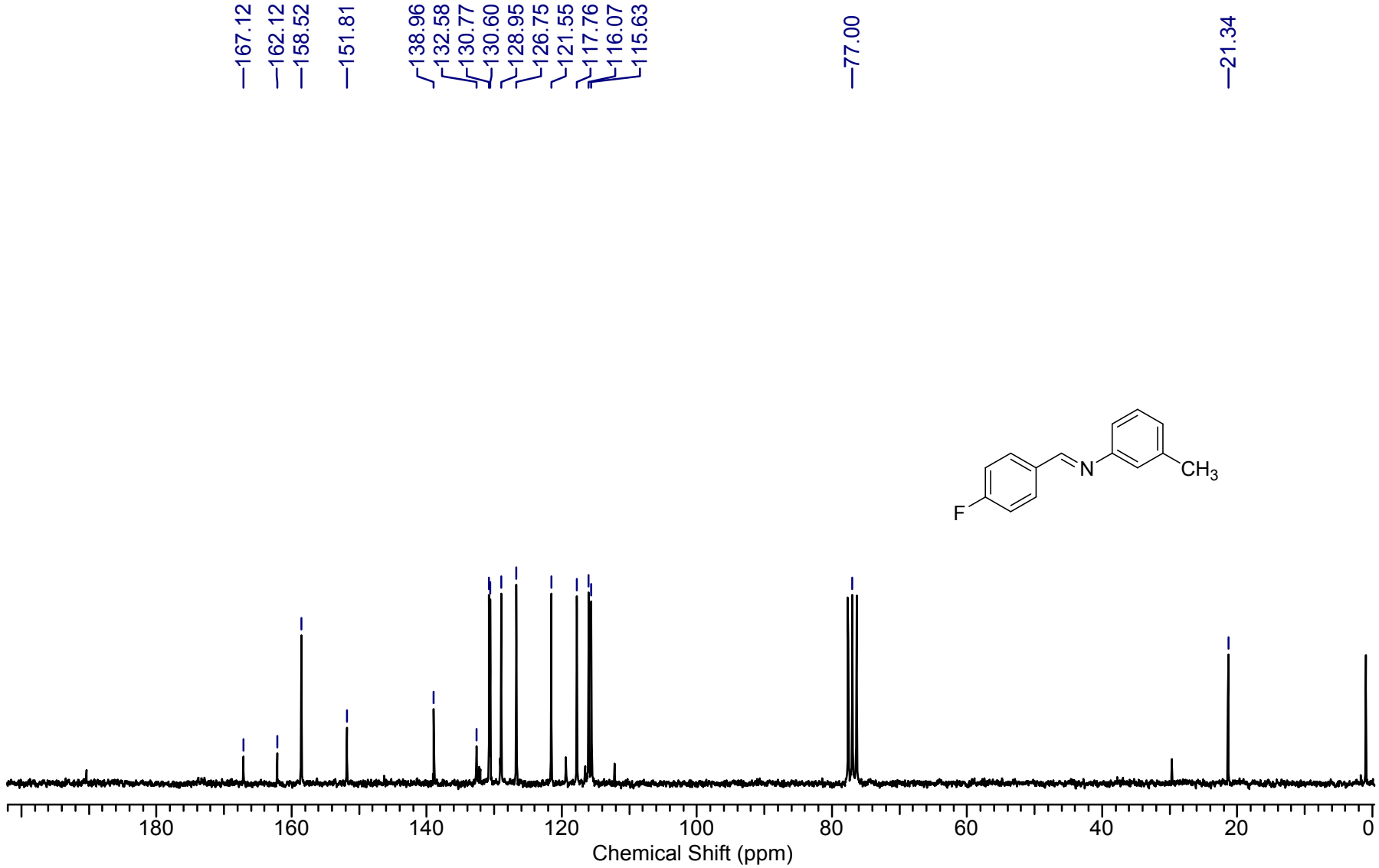
Supplementary Figure 37. ^{1}H NMR of **3ba**



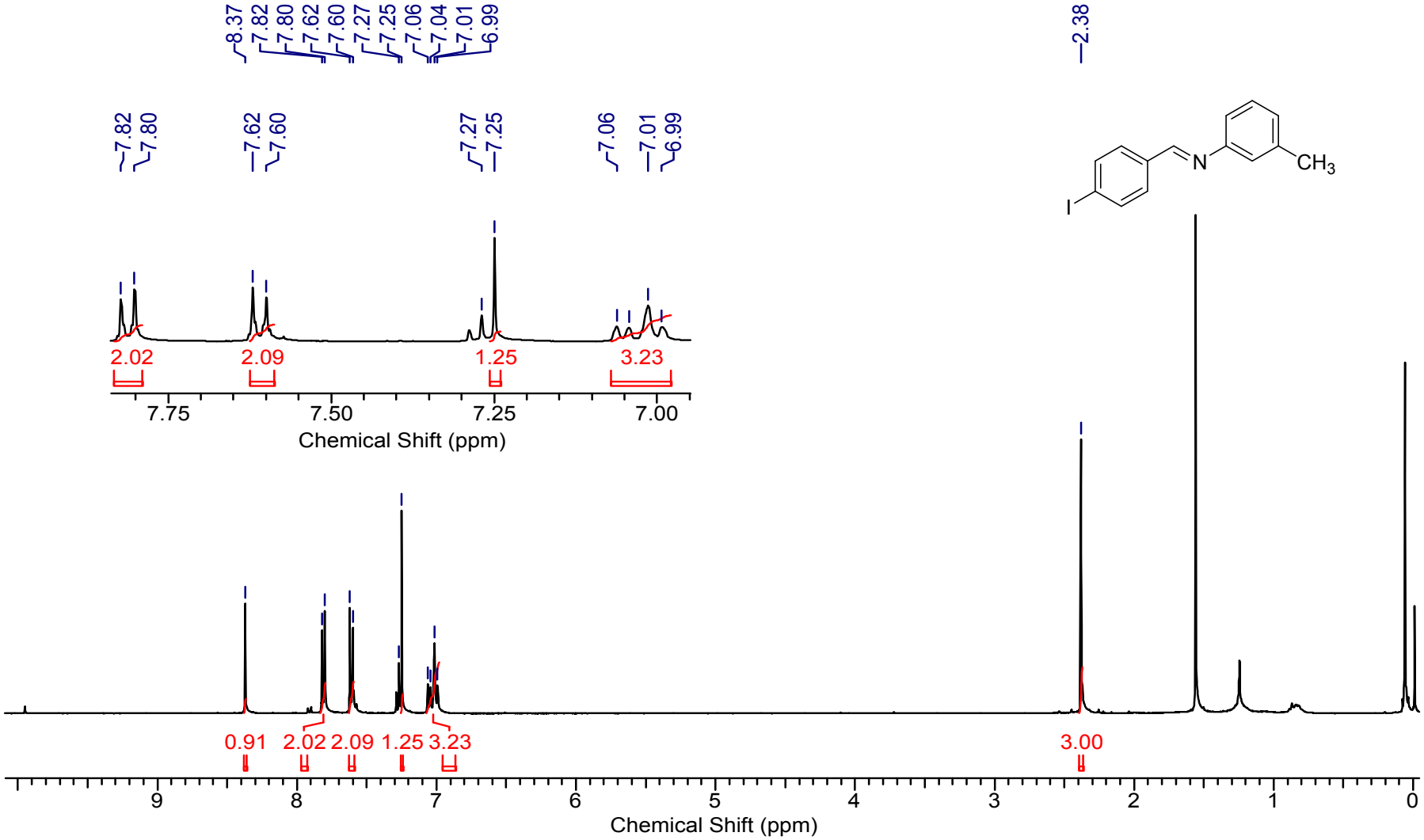
Supplementary Figure 38. ^{13}C NMR of **3ba**



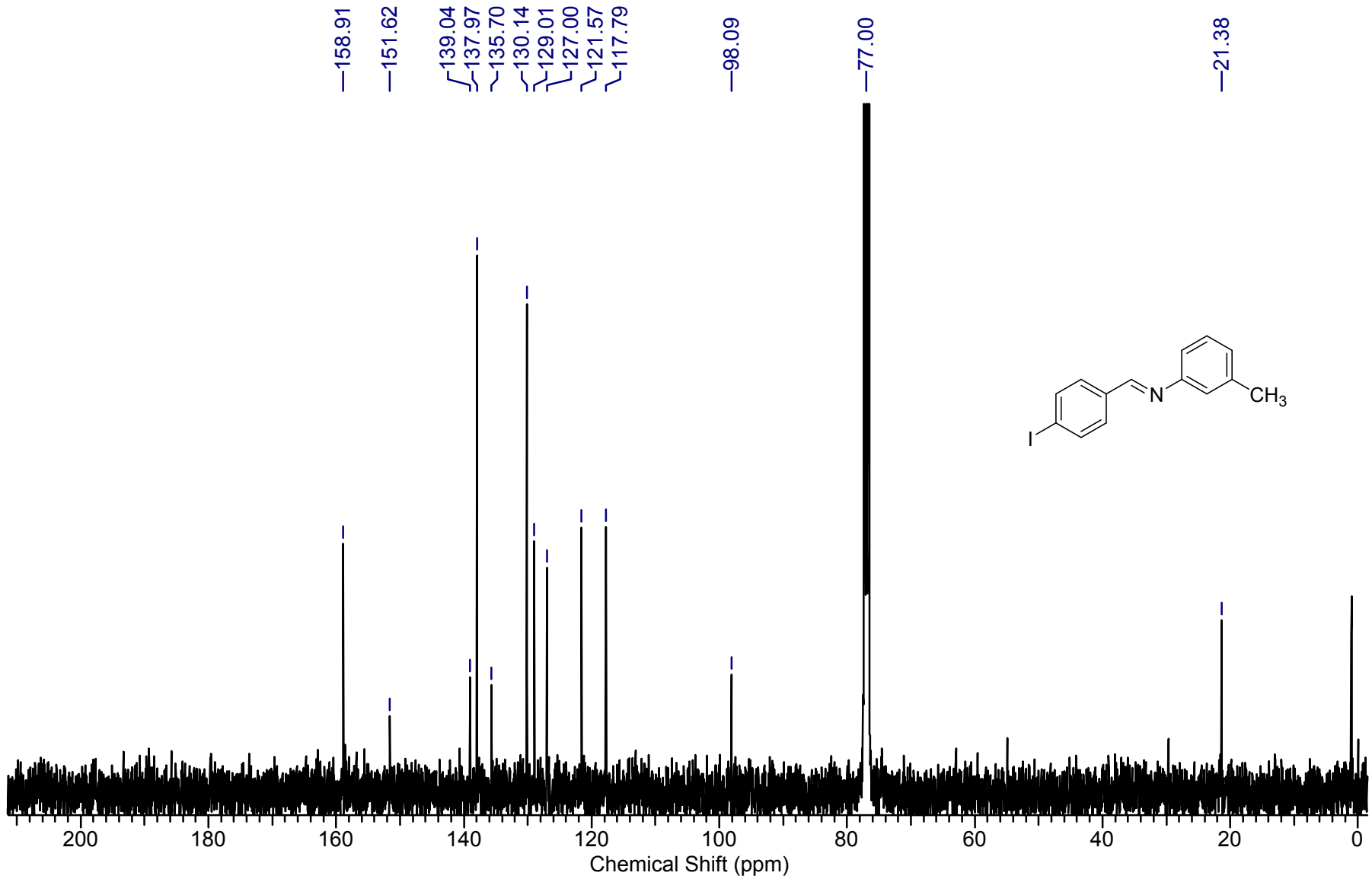
Supplementary Figure 39. ^{1}H NMR of **3bb**



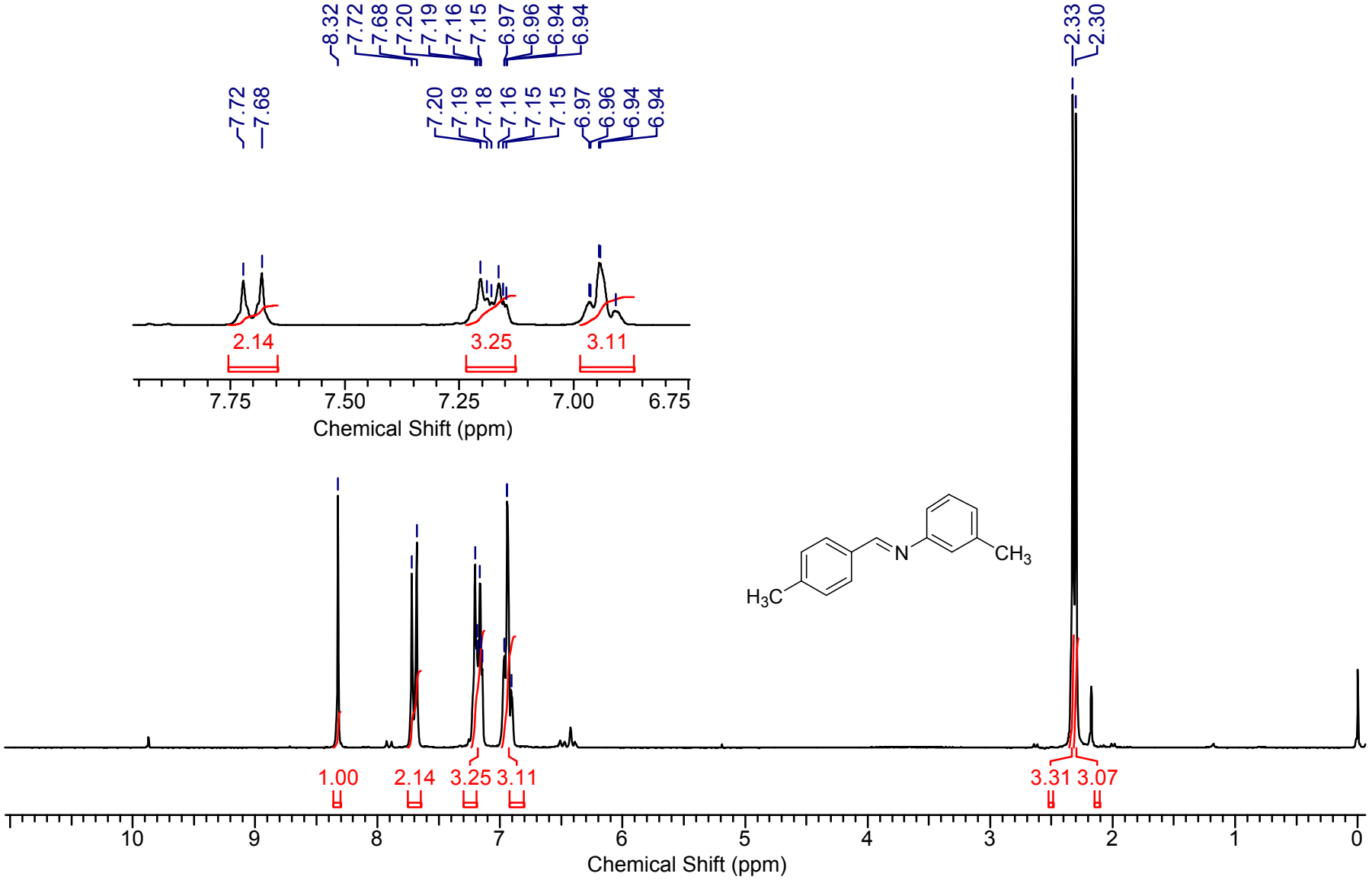
Supplementary Figure 40. ^{13}C NMR of **3bb**

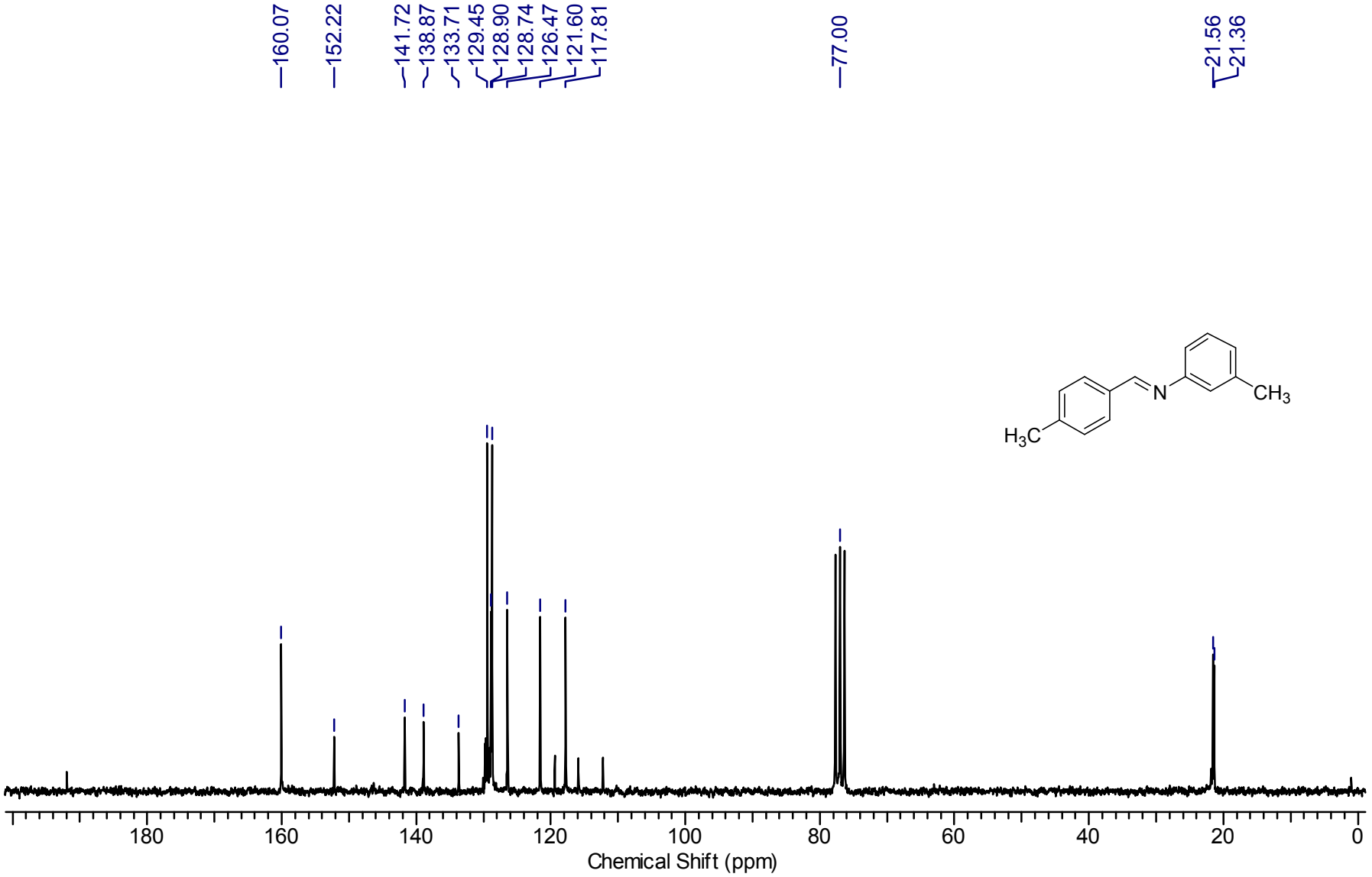


Supplementary Figure 41. ^{1}H NMR of **3bc**

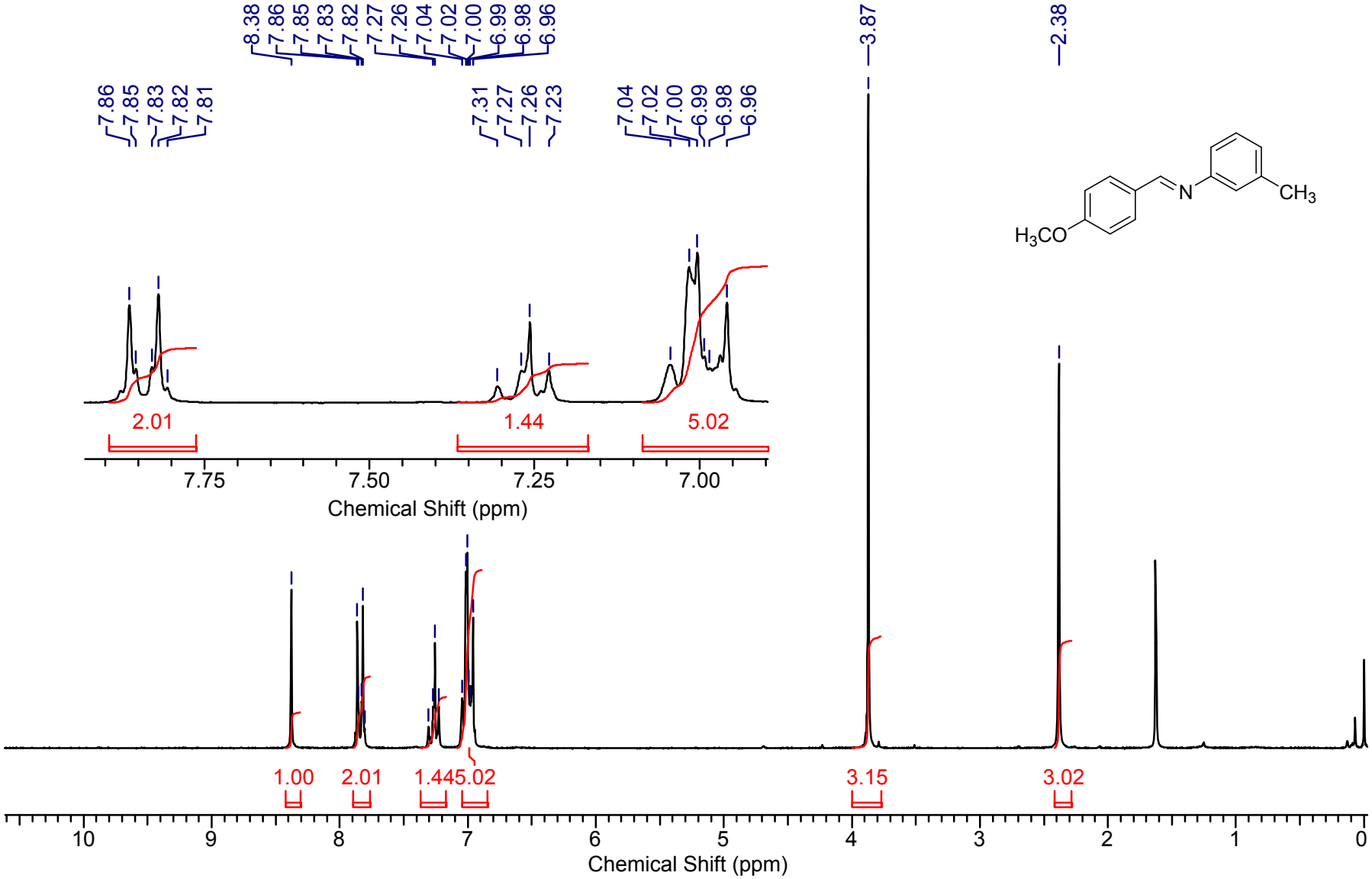


Supplementary Figure 42. ^{13}C NMR of **3bc**

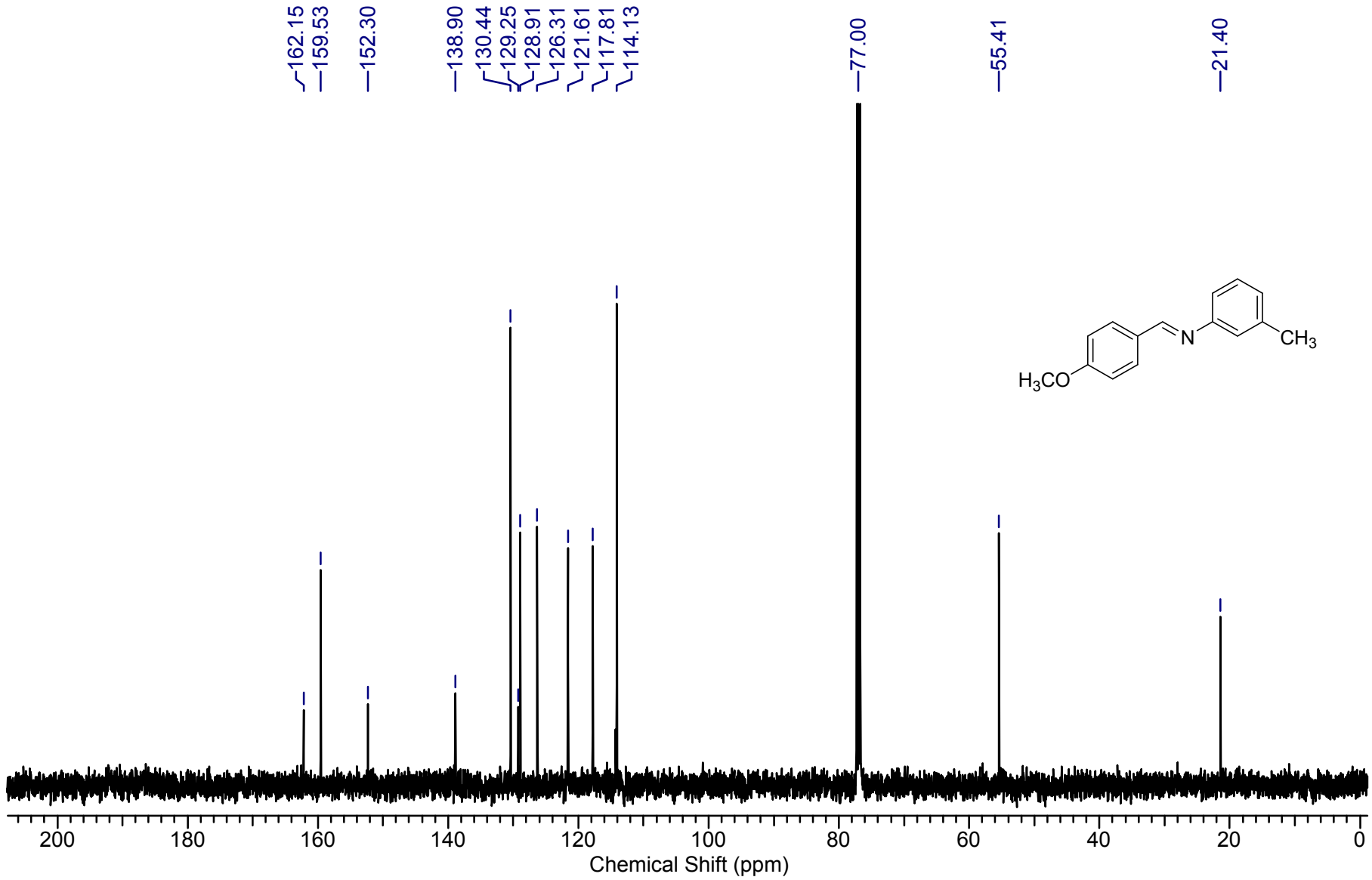

8.32
7.72
7.68
7.20
7.19
7.16
7.15
6.97
6.96
6.94
6.94
2.33
2.30
7.72
7.68
7.20
7.19
7.18
7.16
7.15
7.15
6.97
6.96
6.94
6.94
2.14
3.25
3.11
7.75
7.50
7.25
7.00
6.75
Chemical Shift (ppm)
N
CH3
H3C
1.00
2.14
3.25
3.11
3.31
3.07
10
9
8
7
6
5
4
3
2
1
0
Chemical Shift (ppm)

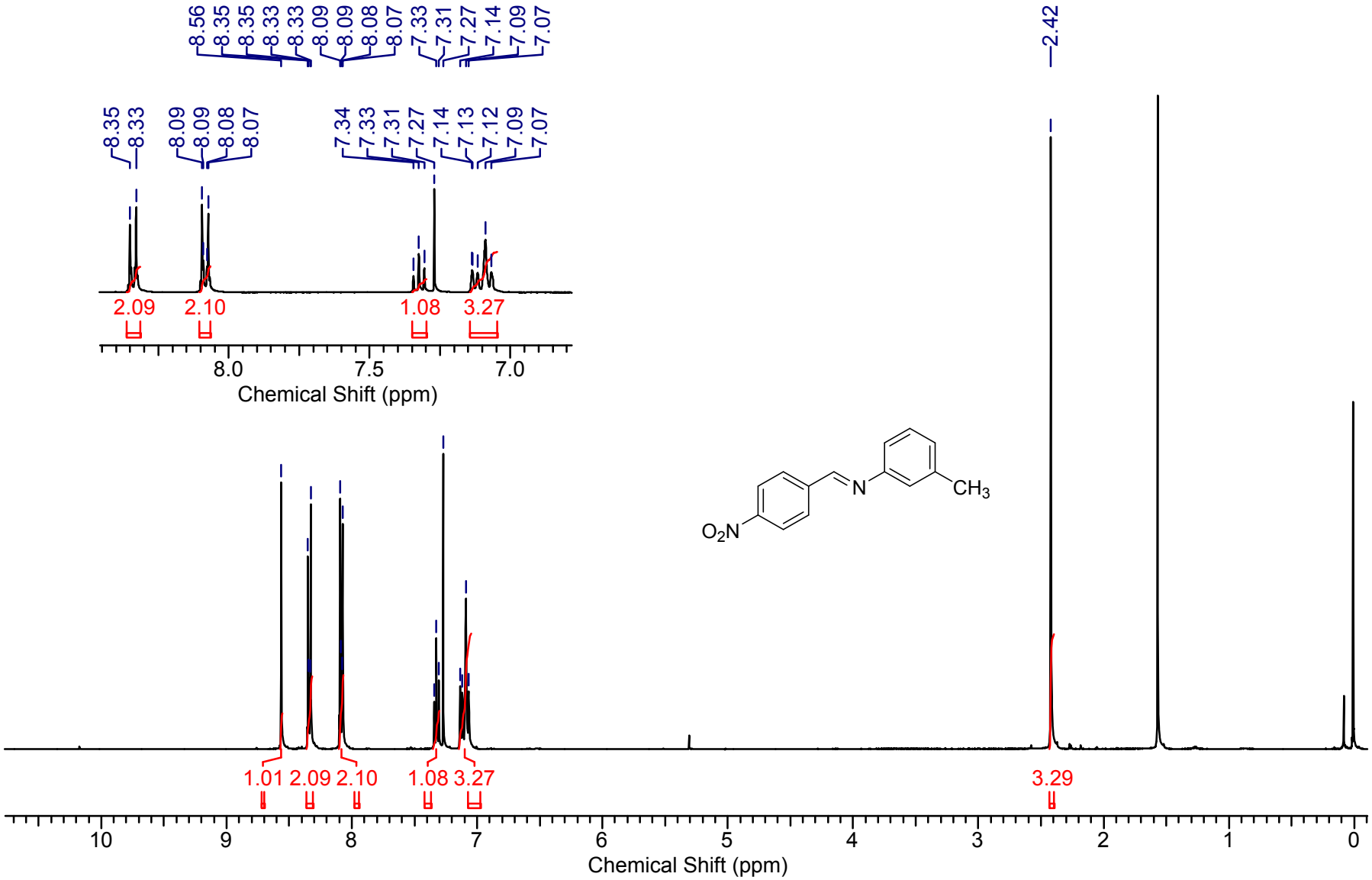


Supplementary Figure 44. ^{13}C NMR of **3bd**

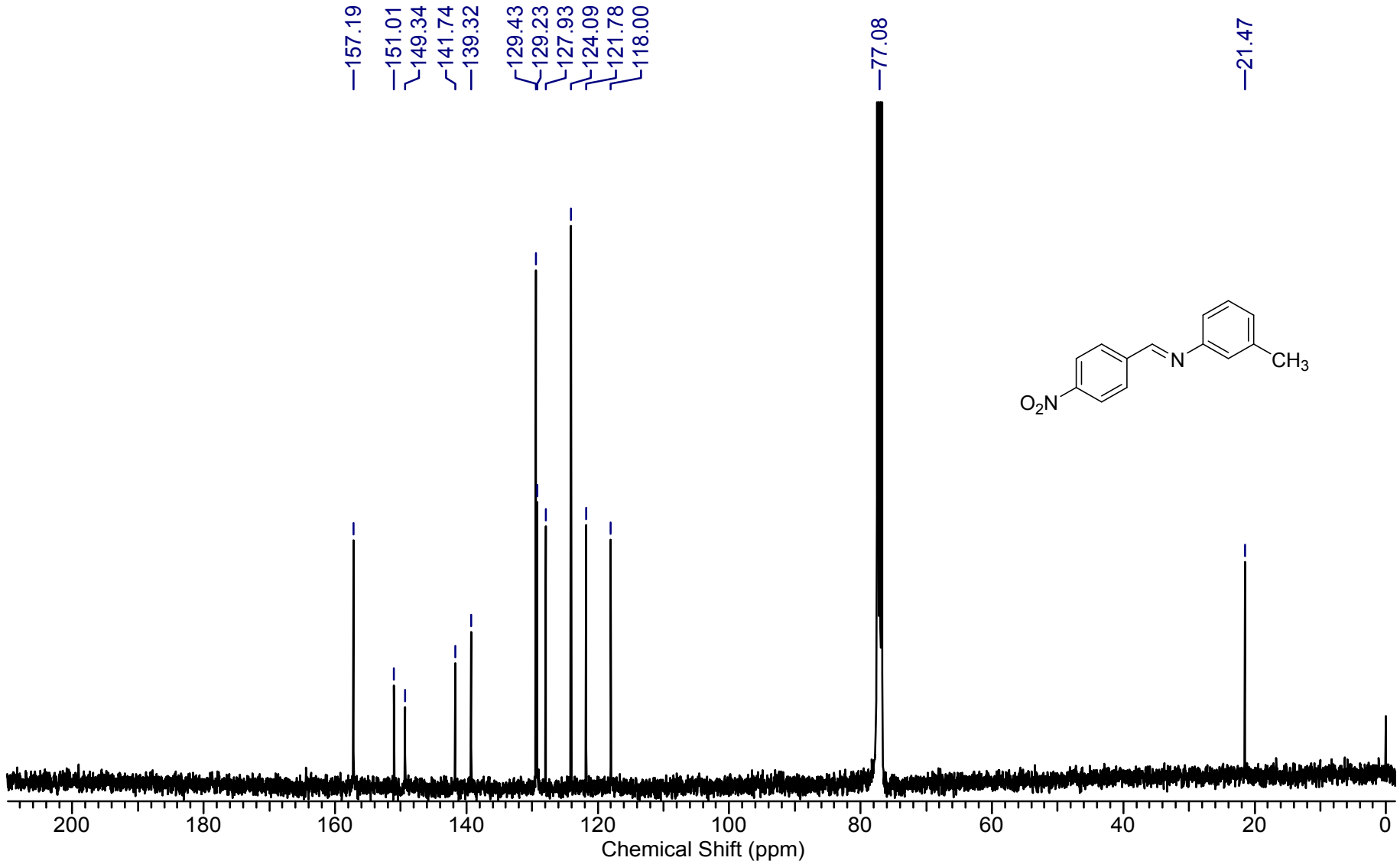


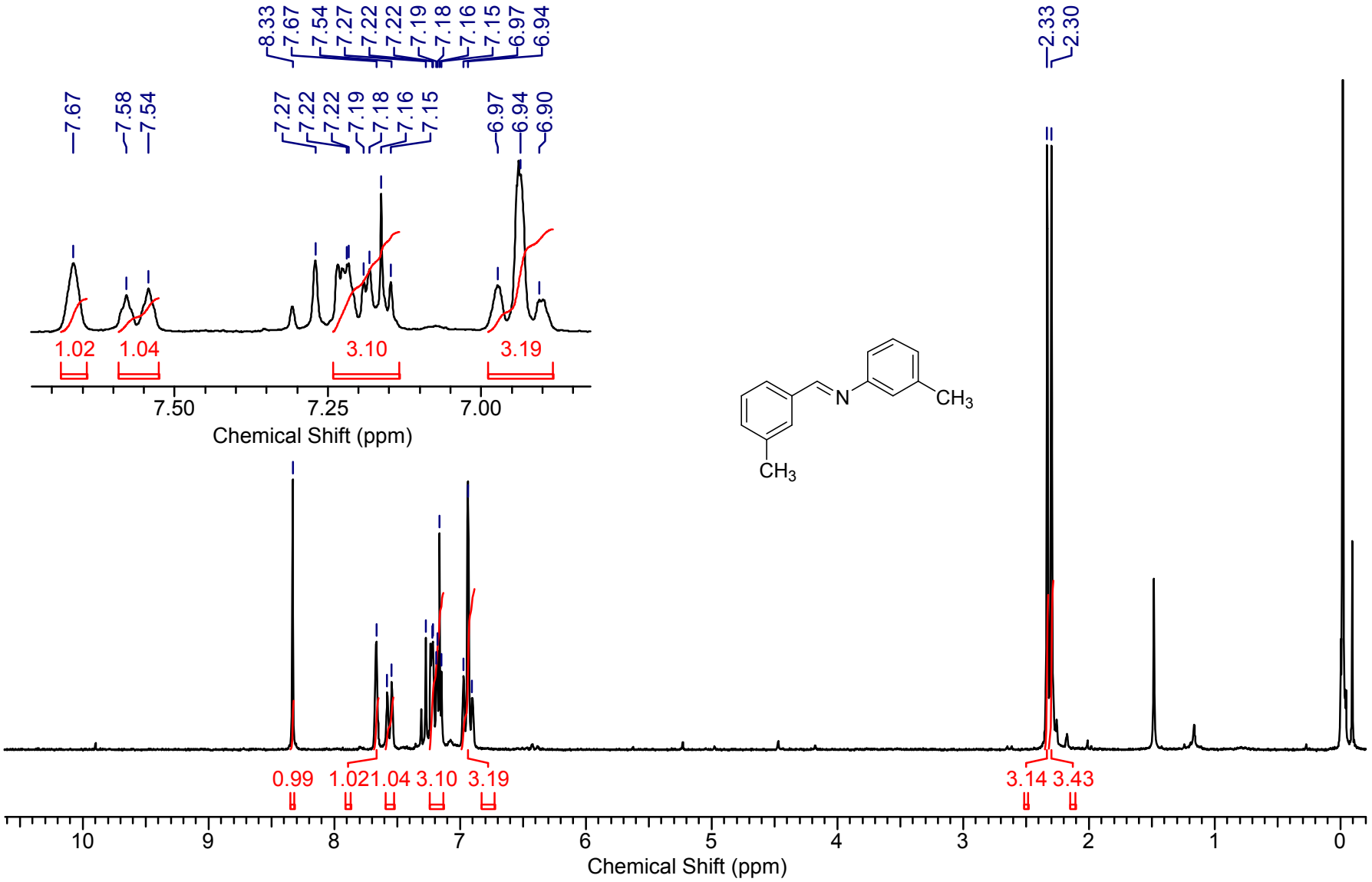
Supplementary Figure 45. ^{1}H NMR of **3be**


162.15
159.53
152.30
138.90
130.44
129.25
128.91
126.31
121.61
117.81
114.13
77.00
55.41
21.40
H3CO
N
CH3
200
180
160
140
120
100
80
60
40
20
0
Chemical Shift (ppm)

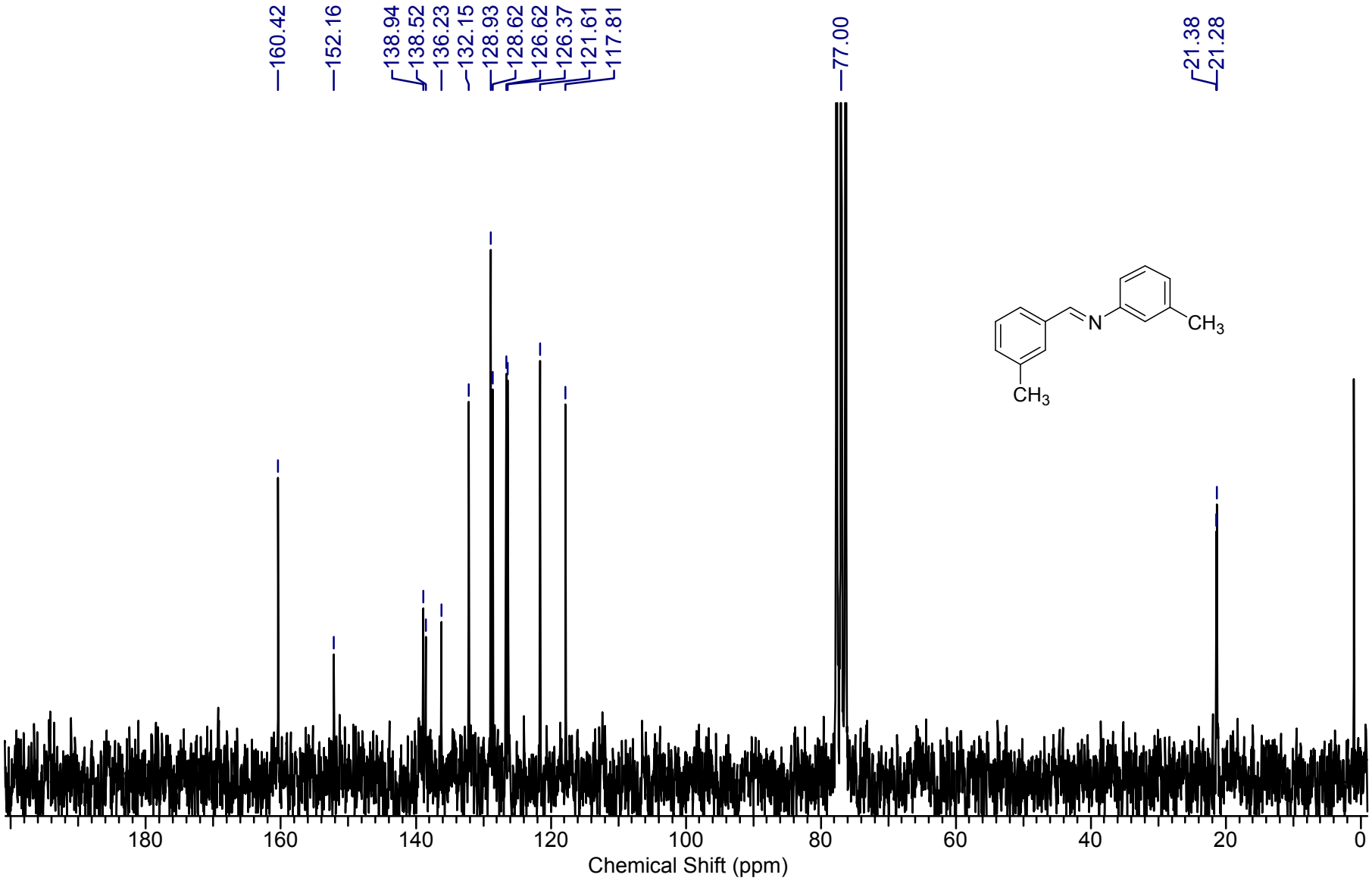


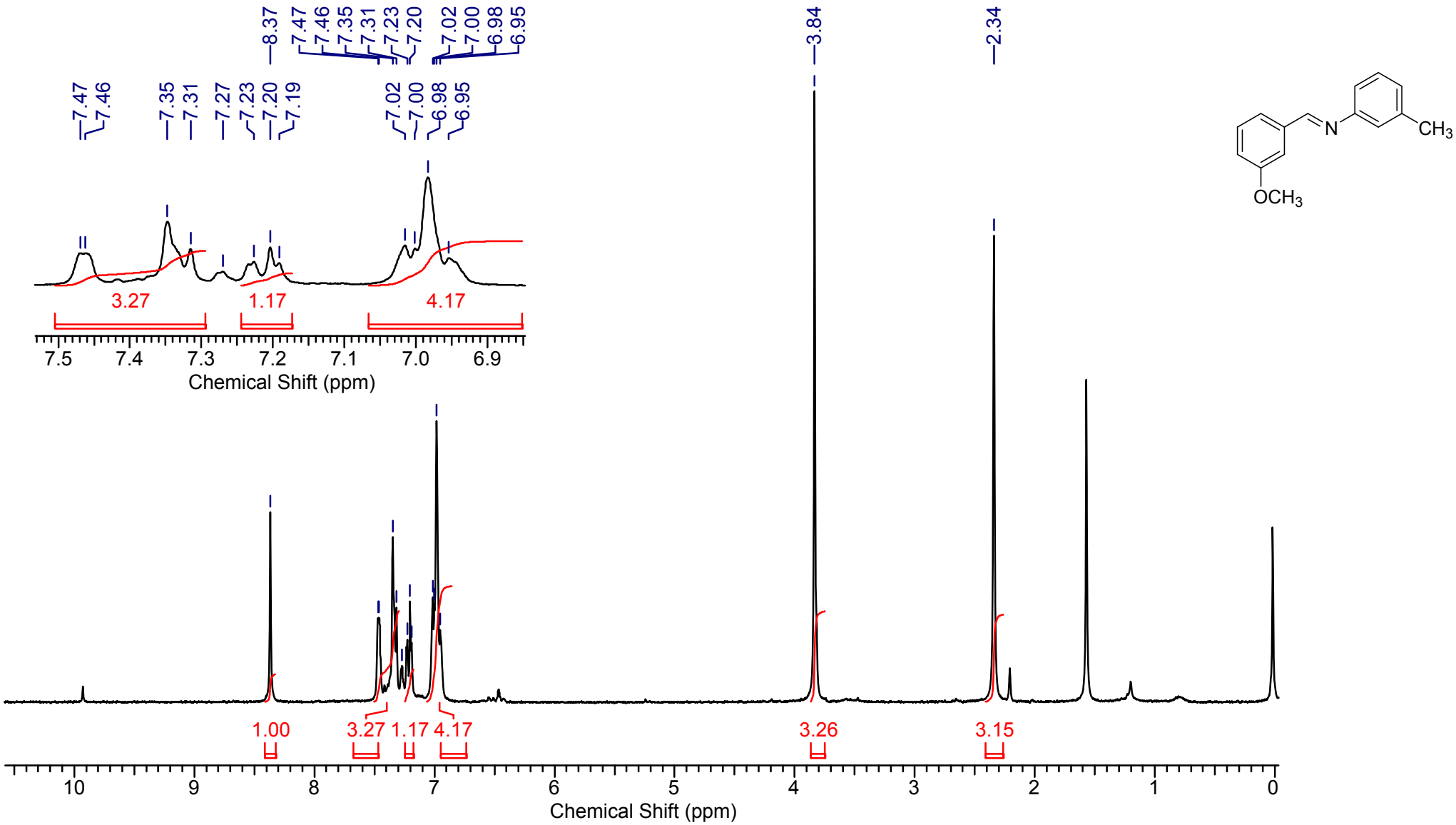
Supplementary Figure 47. ^{1}H NMR of **3bf**

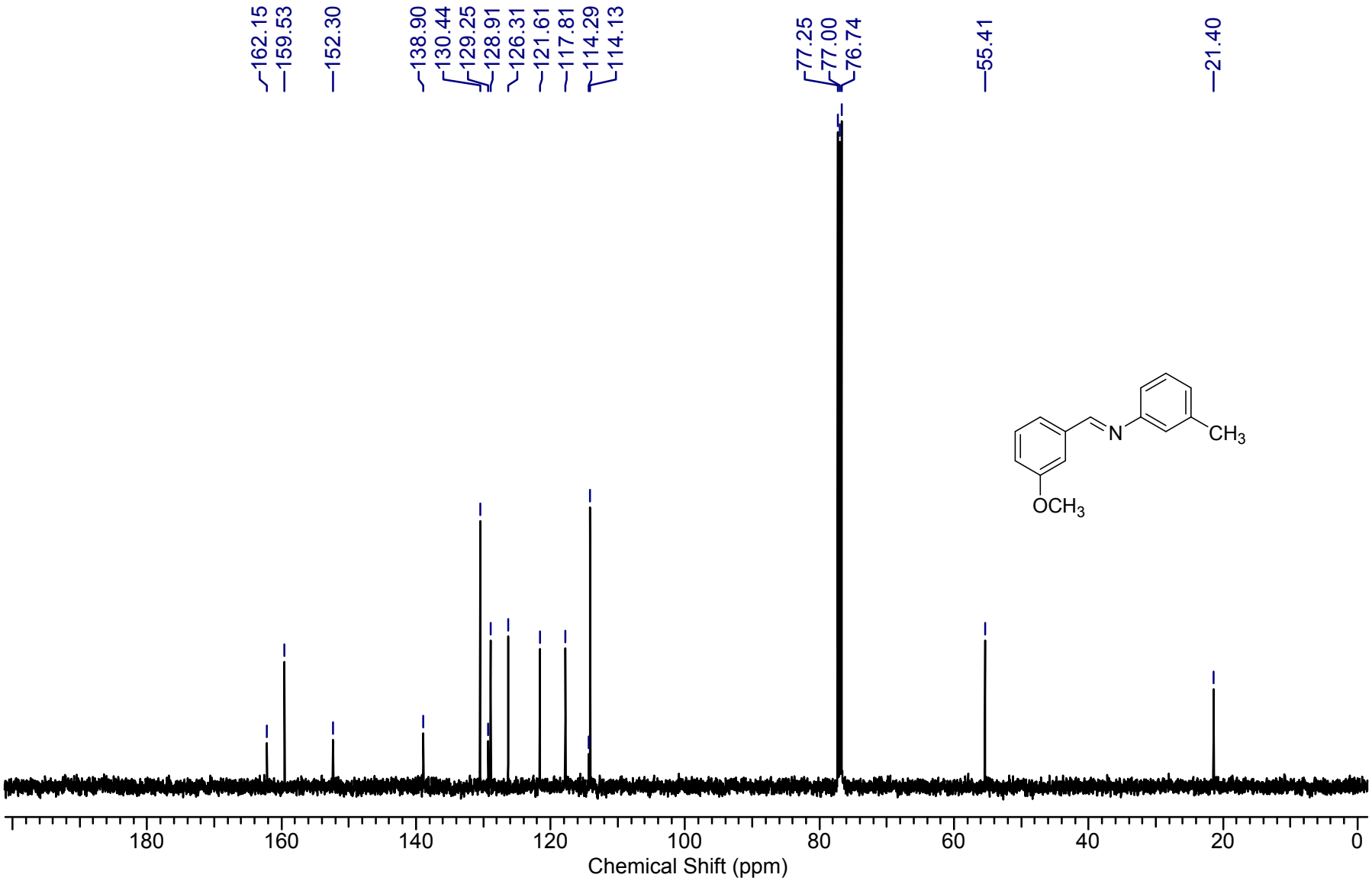

157.19
151.01
149.34
141.74
139.32
129.43
129.23
127.93
124.09
121.78
118.00
77.08
21.47
N
CH3
O2N
200
180
160
140
120
100
80
60
40
20
0
Chemical Shift (ppm)



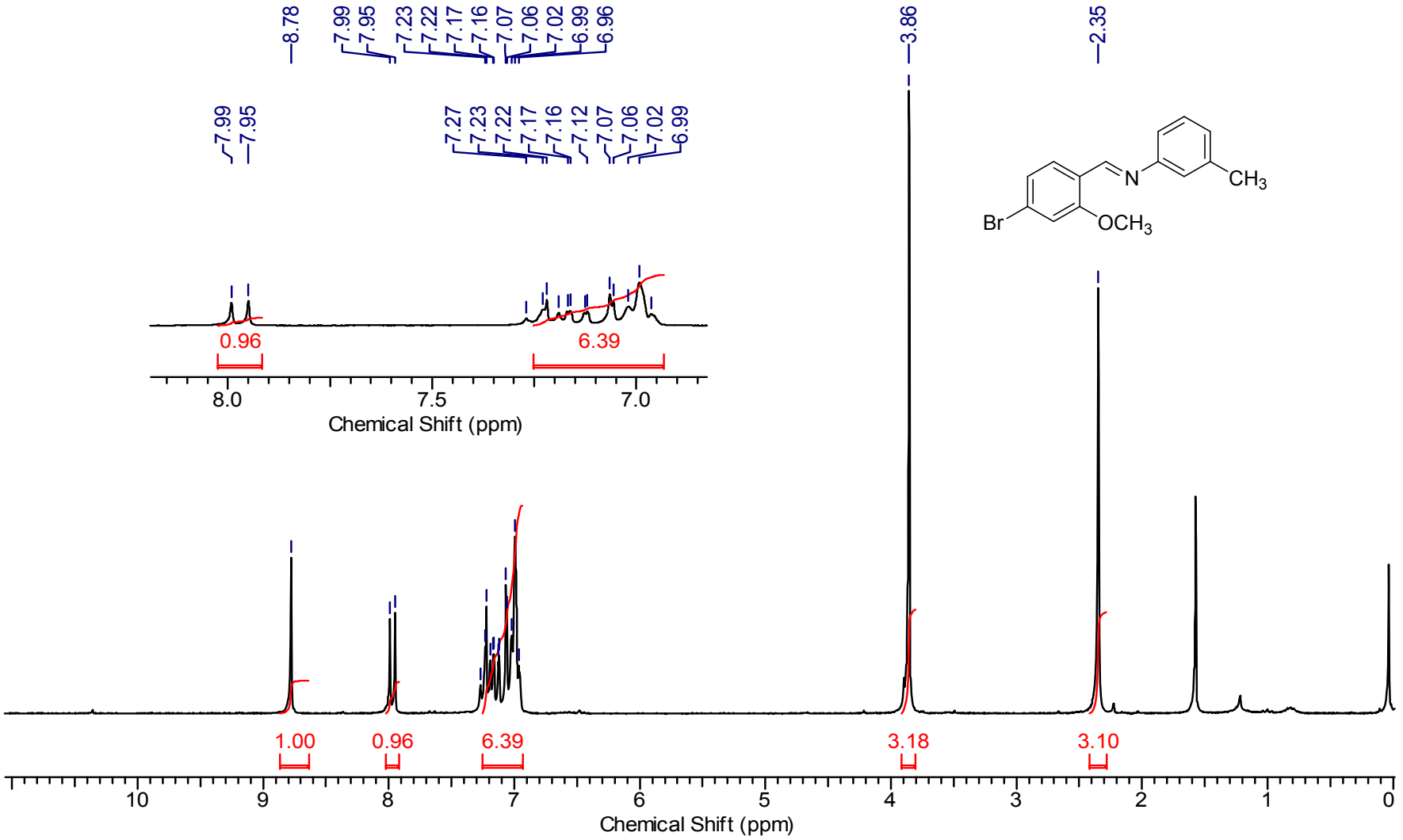
Supplementary Figure 49. ^{1}H NMR of **3bg**


160.42
152.16
138.94
138.52
136.23
132.15
128.93
128.62
126.62
126.37
121.61
117.81
77.00
21.38
21.28
N
CH3
CH3
180
160
140
120
100
80
60
40
20
0
Chemical Shift (ppm)

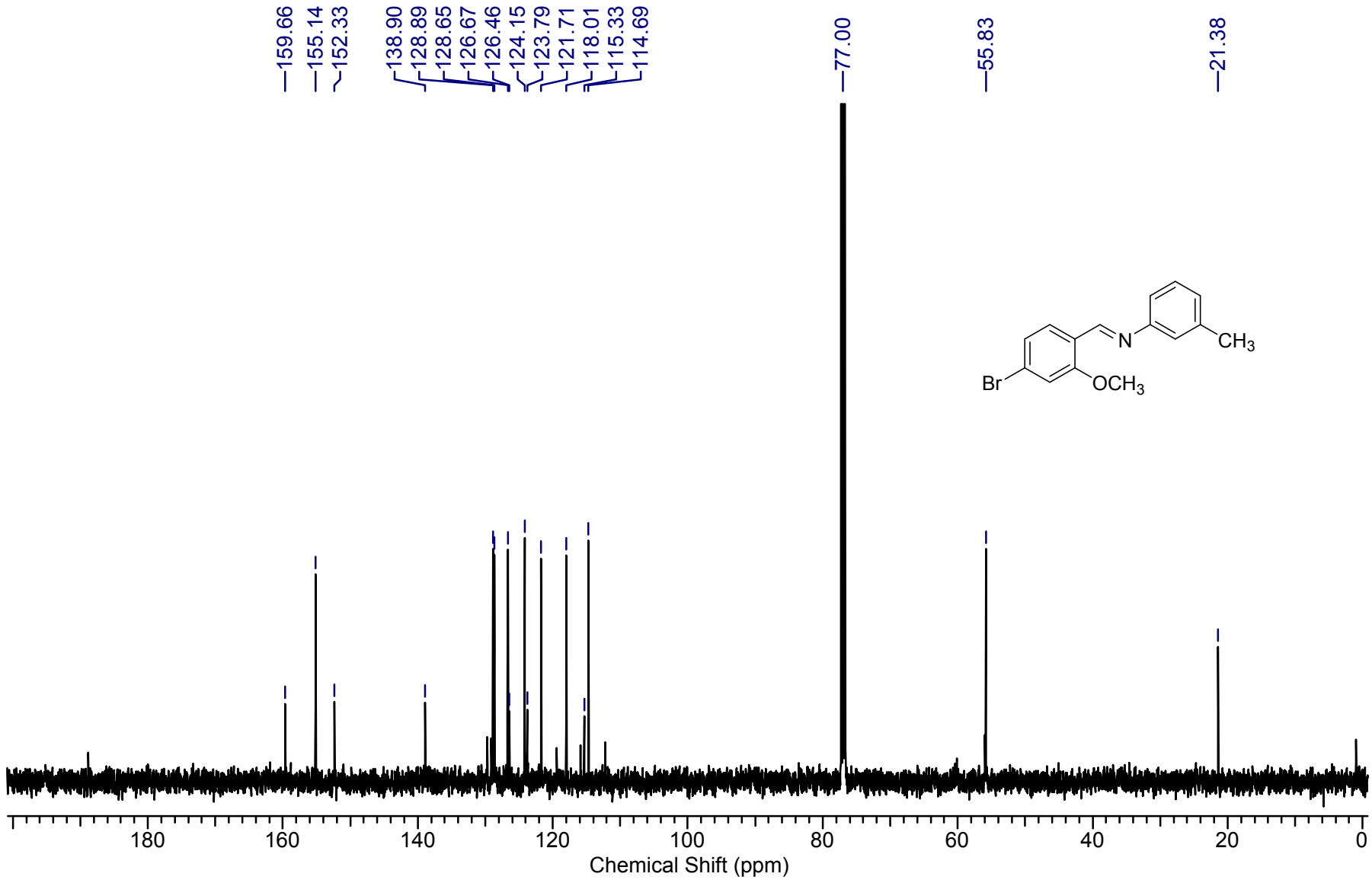

8.37
7.47
7.46
7.35
7.31
7.23
7.20
7.02
7.00
6.98
6.95
3.84
2.34
7.47
7.46
7.35
7.31
7.27
7.23
7.20
7.19
7.02
7.00
6.98
6.95
3.27
1.17
4.17
7.5
7.4
7.3
7.2
7.1
7.0
6.9
Chemical Shift (ppm)
1.00
3.27
1.17
4.17
3.26
3.15
10
9
8
7
6
5
4
3
2
1
0
Chemical Shift (ppm)
N
CH3
OCH3

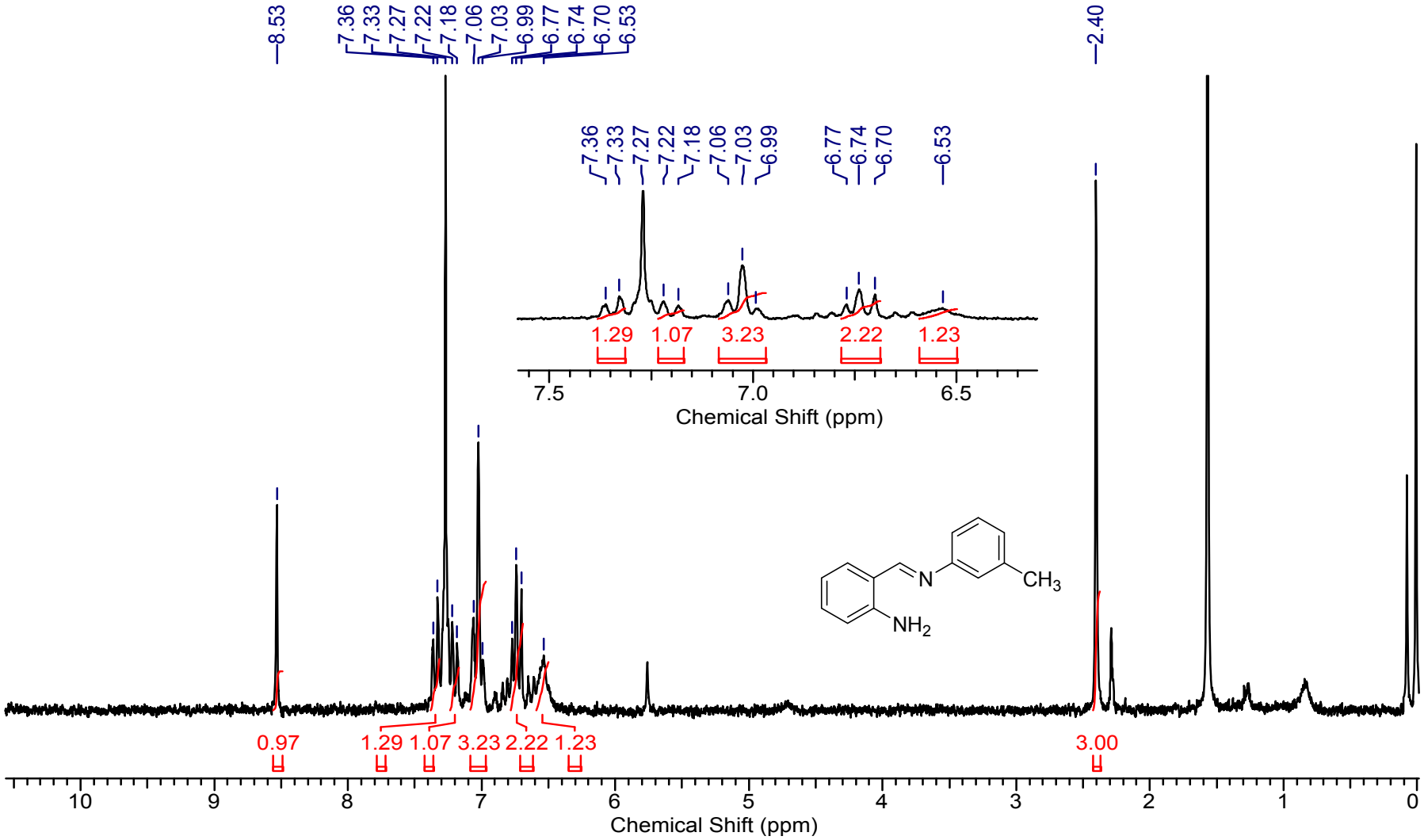


Supplementary Figure 52. ^{13}C NMR of **3bh**

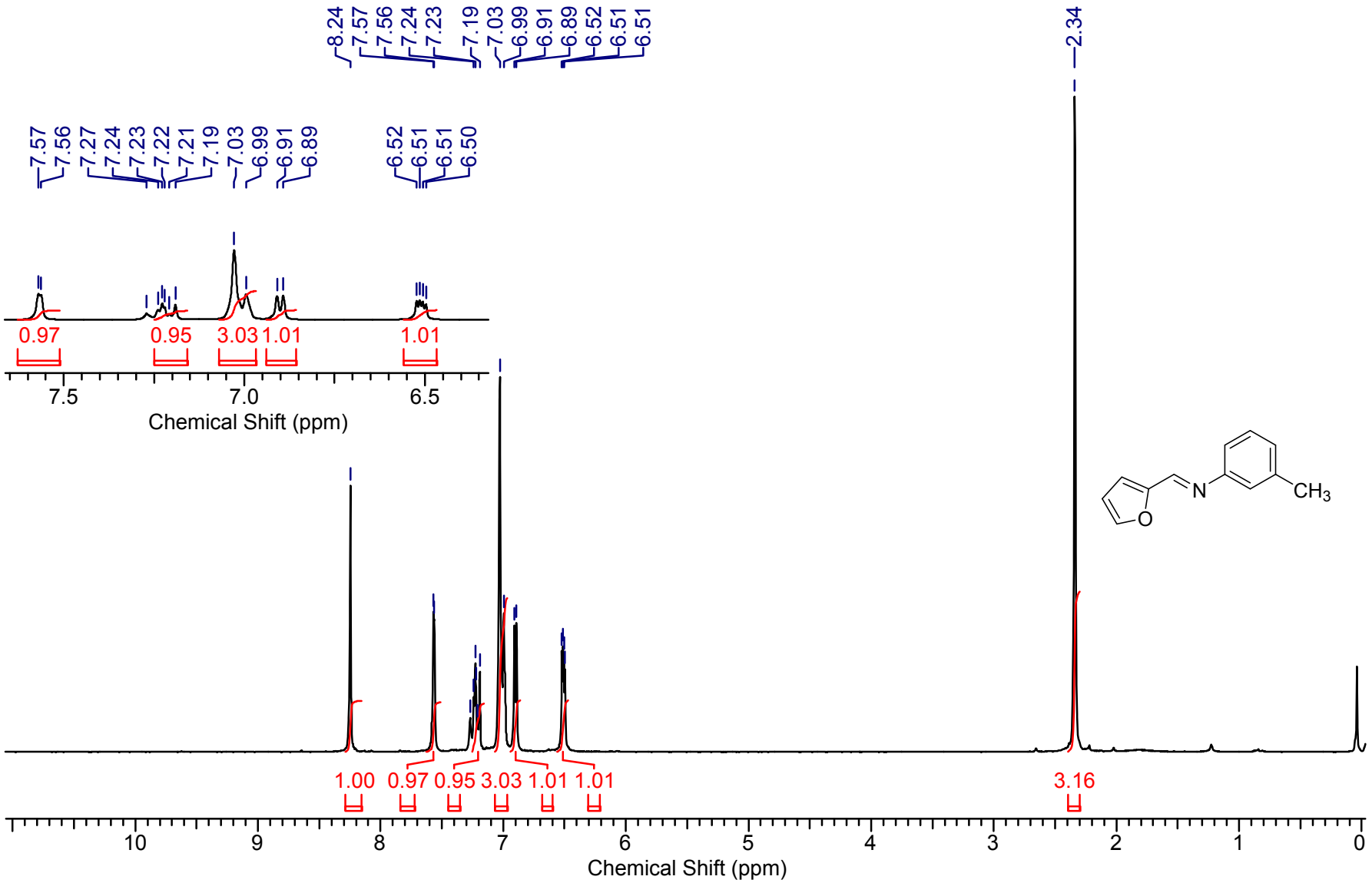


Supplementary Figure 53. ^{1}H NMR of **3bi**

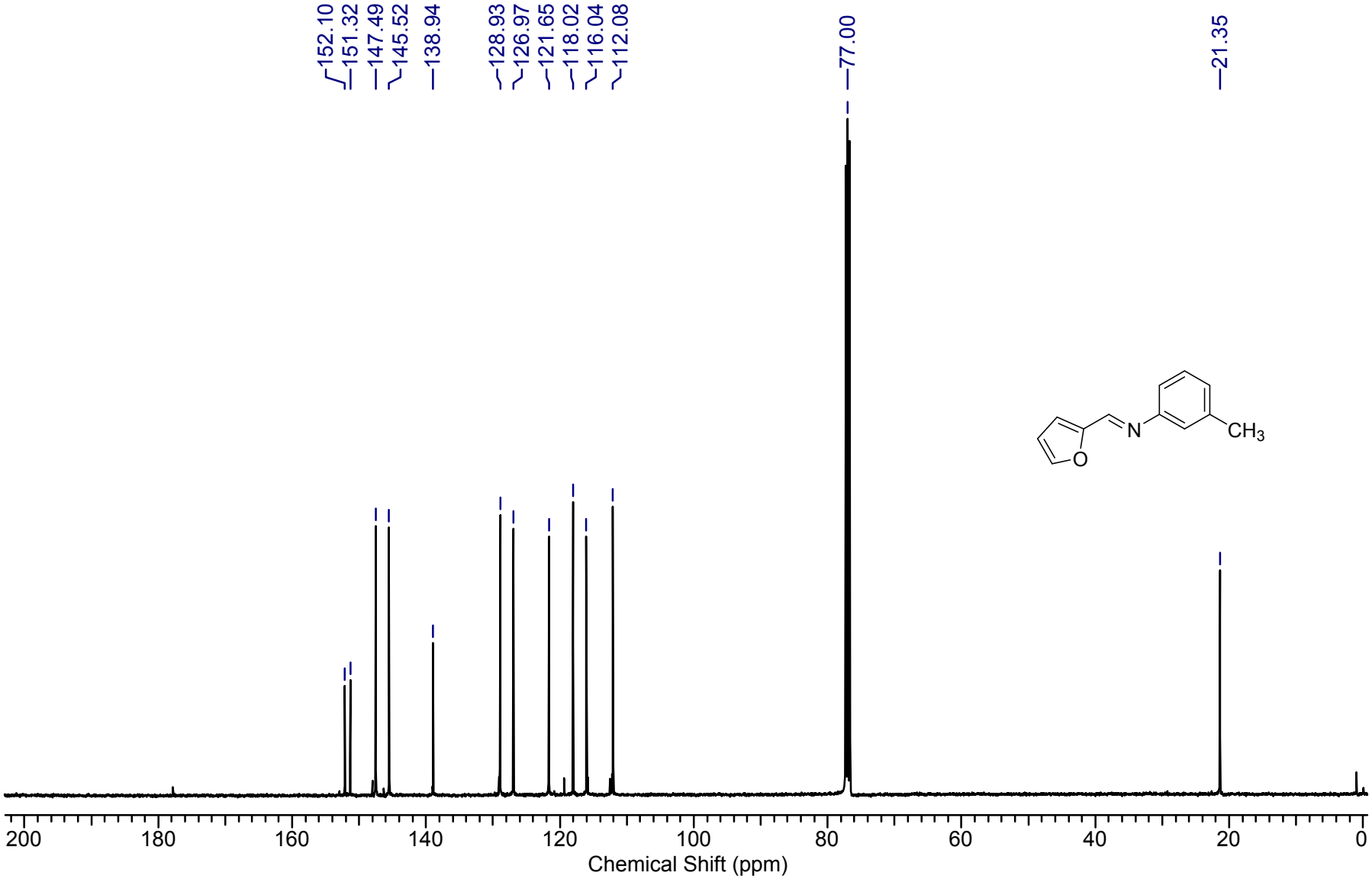

159.66
155.14
152.33
138.90
128.89
128.65
126.67
126.46
124.15
123.79
121.71
118.01
115.33
114.69
77.00
55.83
21.38
N
CH3
Br
OCH3
180
160
140
120
100
80
60
40
20
0
Chemical Shift (ppm)



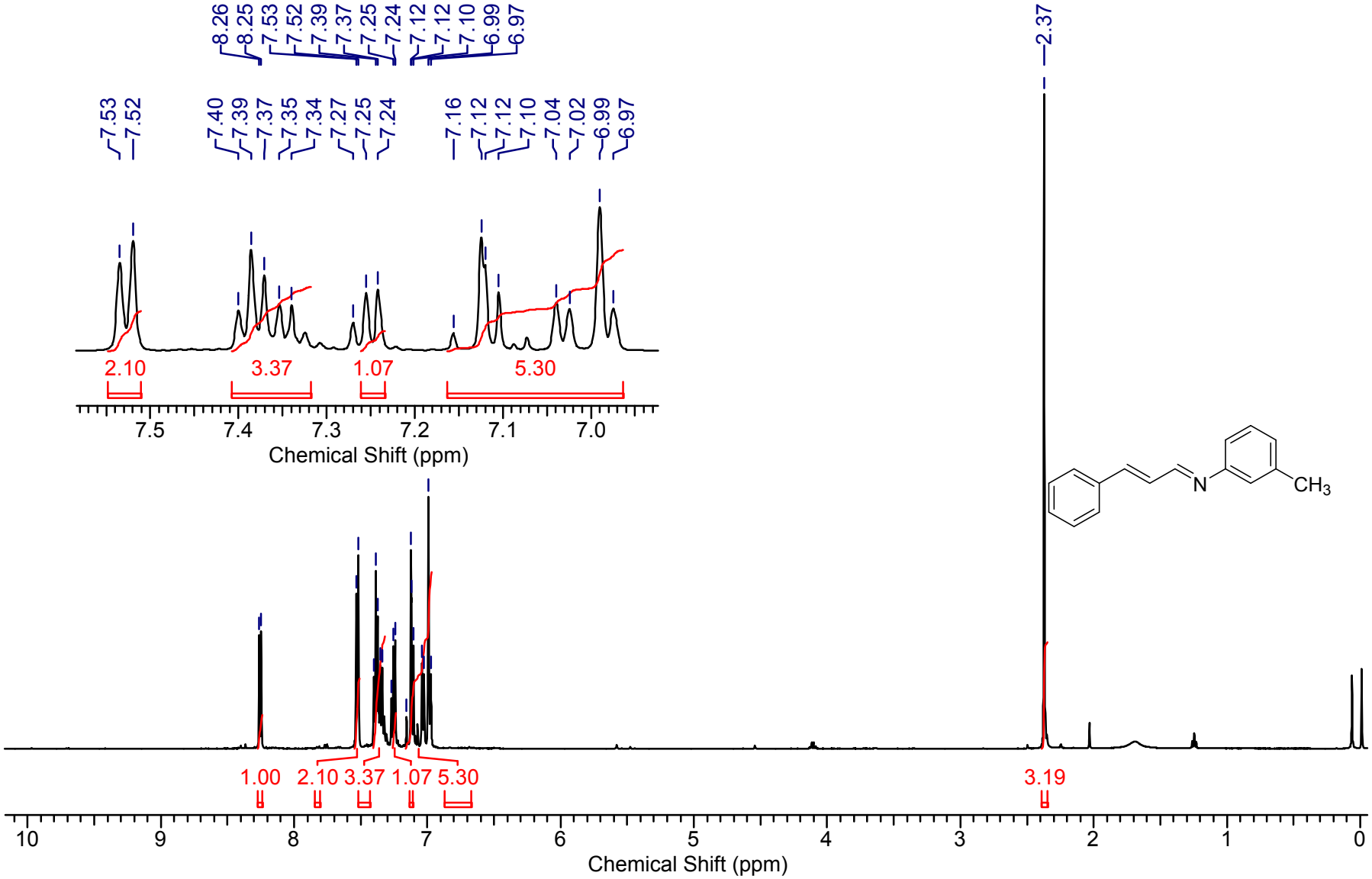
Supplementary Figure 55. ^{1}H NMR of



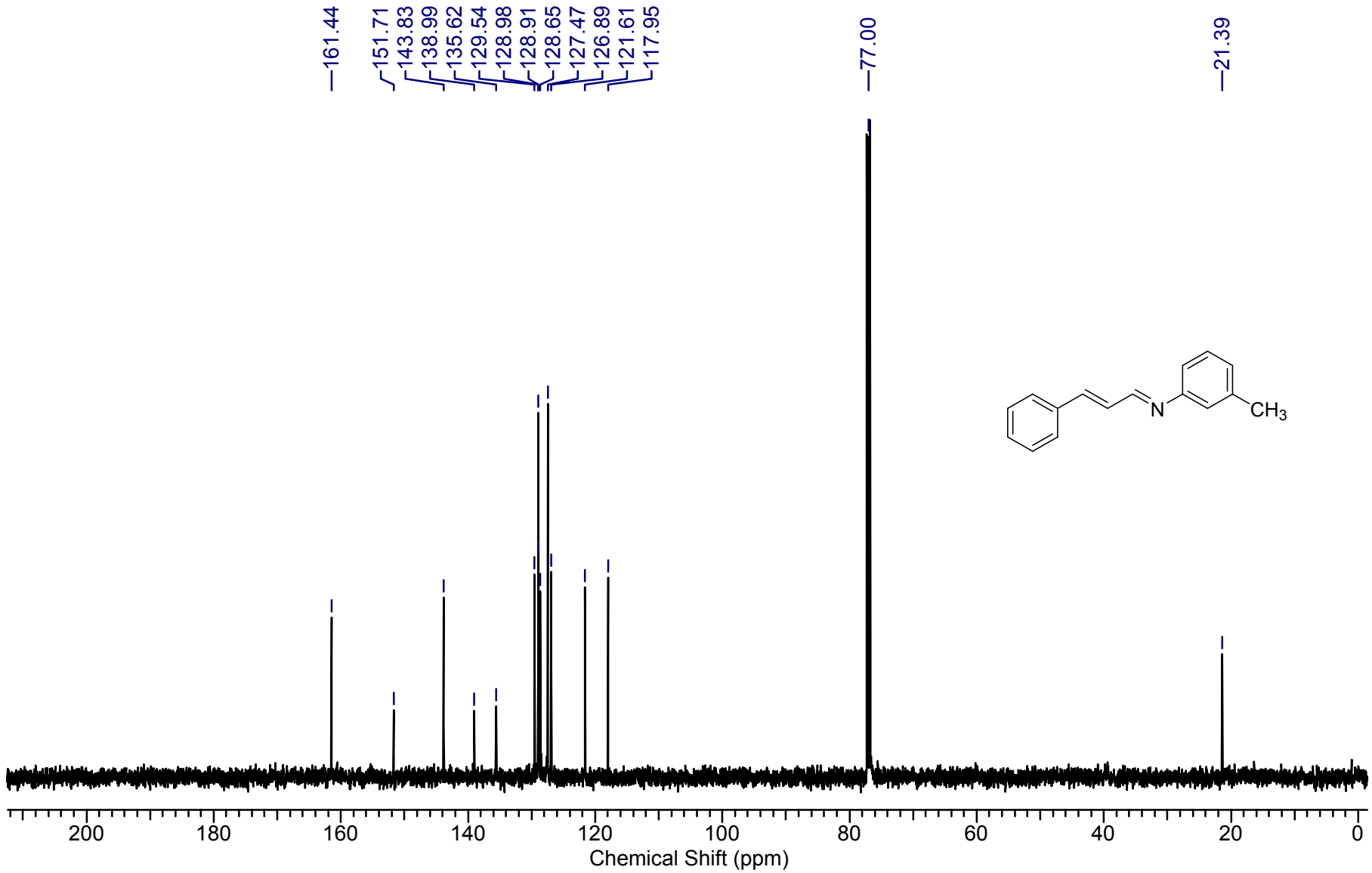
Supplementary Figure 56. ^{1}H NMR of **3bk**

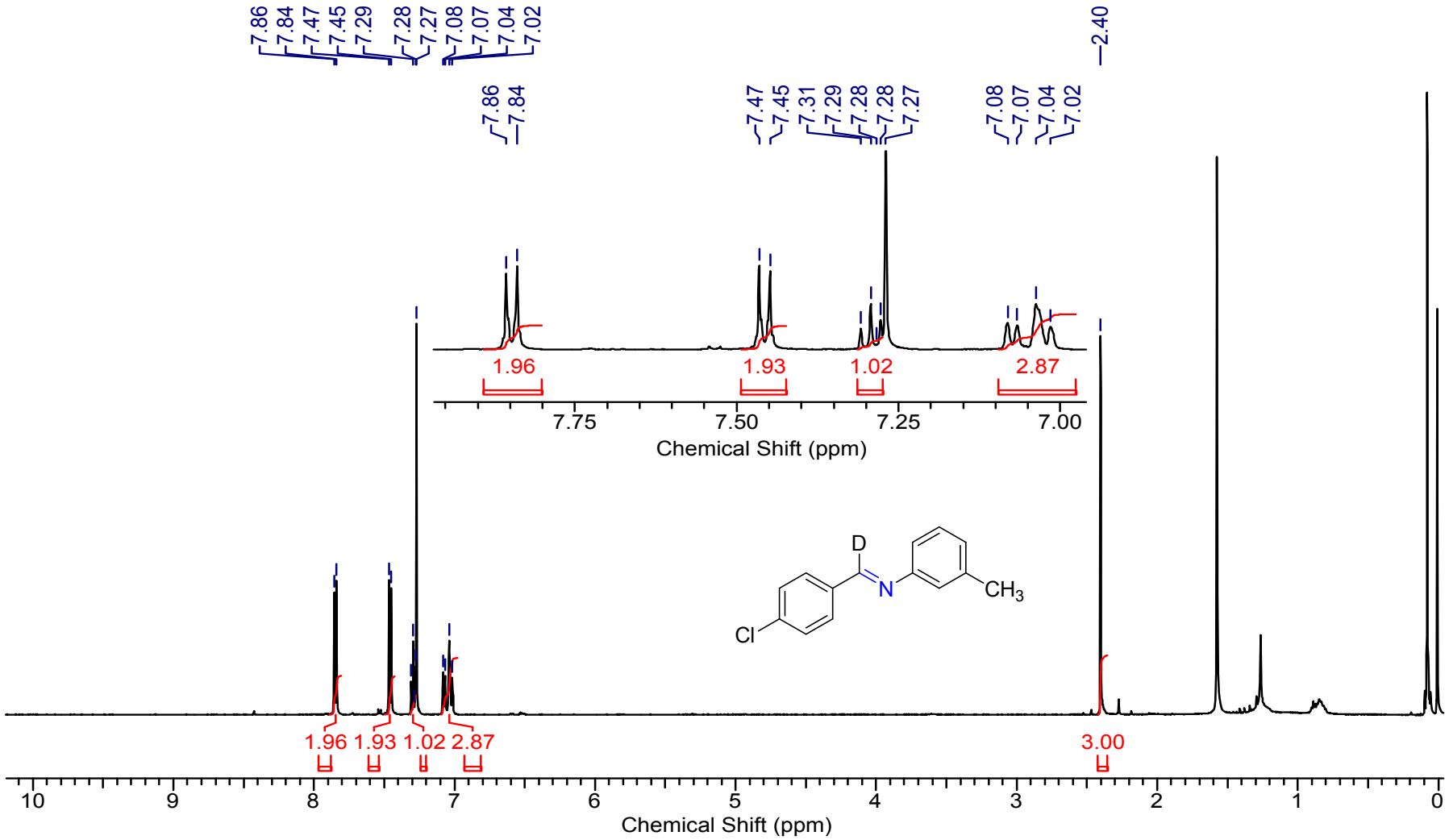


Supplementary Figure 57. ^{13}C NMR of **3bk**



Supplementary Figure 58. ^{1}H NMR of **3bl**


161.44
151.71
143.83
138.99
135.62
129.54
128.98
128.91
128.65
127.47
126.89
121.61
117.95
77.00
21.39
N
CH3
200
180
160
140
120
100
80
60
40
20
0
Chemical Shift (ppm)



Supplementary Figure 60. ^{1}H NMR of **3aa-*d***