Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information:

Metal-Free Radical Trifluoromethylation of β-Nitroalkenes through Visible-Light Photoredox Catalysis

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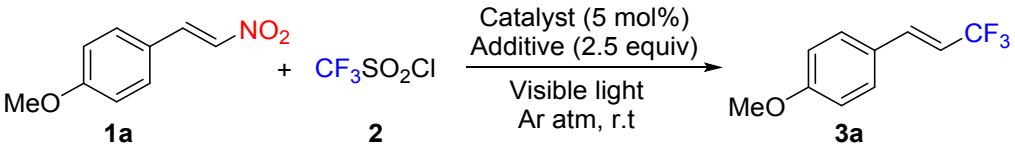
1. General Information

All catalytic experiments were carried out using standard Schlenk techniques. All solvents were reagent grade or better. Deuterated solvents were used as received. All non-deutrated solvents were dried according to standard procedure.[S1]All the reactions were performed in normal reaction tube received from the Fischer brand. Thin layer chromatography (TLC) was performed on Merck 1.05554 aluminum sheets precoated with silica gel 60 F254 and the spots visualized with UV light at 254 nm or under iodine. Column chromatography was performed with SiO_2 (SilicycleSiliaflash F60 (230-400 mesh)). ^{1}H and ^{13}C spectra were recorded on Bruker DRX-200 (200MHz), DRX-400 (400MHz) and DRX-500 (500MHz) spectrometers with tetramethylsilane or $CHCl_3$ as an internal standard. The peaks were internally referenced to TMS (0.00 ppm) or residual undeuterated solvent signal (7.27 ppm for ^{1}H NMR &77.0 ppm for ^{13}C NMR). ^{19}F NMR spectra were recorded onDRX-400.Abbreviations used in the NMR follow-up experiments: br, broad; s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet. GC analysis were carried out using a Carboxen 1000 column on a HP 690 series GC system or HP-5 cross linked 5% PH ME Siloxane column (30m × 0.32mm × 0.25 μm film thickness, FID) on a HP 6890 series GC system. GC-MS was carried out on HP 6890 (flame ionization detector and thermal conductivity detector) and HP 5973 (MS detector) instruments equipped with a 30 m column (Restek 5MS, 0.32 mm internal diameter) with a 5% phenylmethylsiliconecoating (0.25 mm) and helium as carrier gas. Emission intensities were recorded using a Perkin Elmer LS50 Luminescence spectrometer and cyclic voltammetry experiments were performed in CH 660D Electrochemical work station (CH Instruments, USA).

2. Experimental Section

2.1 Reaction Optimization

Table S1: Screening of photoredox catalyst[a]

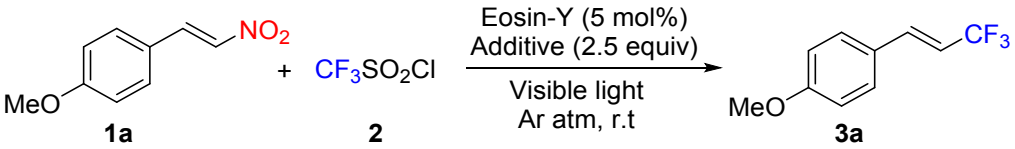


1a 2 3a

Entry	Catalyst	Yield (%)[b]
1	$Ru(bipy)_3Cl_2$	51
2	Eosin-Y	74
3	Rose Bengal	68
4	Rodamin-B	36
5	Alizarine-S	70
6	Fluorecene	12
7	Na salt of Eosin-Y	NR

[a] Reactions performed using **1a** (0.125 mmol), CF_3SO_2Cl (0.3 mmol), photoredox catalyst (5 mol%), additive K_2HPO_4 (0.3 mmol), and CH_3CN (0.5 mL) for 32 h under argon atm at room temperature (Light source: 32-W compact fluorescent light). [b] Yield determined by GC using *m*-xylene as an internal standard. NR = No reaction.

Table S2: Screening of additive[a]



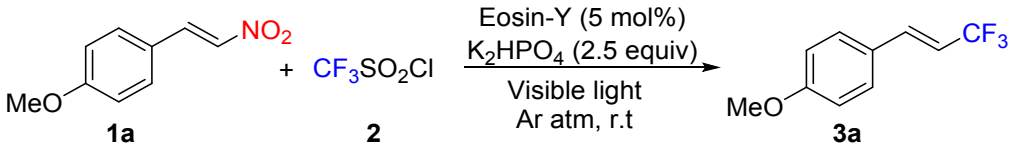
1a 2 3a

Entry	Additive	Yield (%)[b]
1	KH_2PO_4	42
2	Na_2HPO_4	trace
3	NaH_2PO_4	24
4	$KHSO_4$	31
5	$NaHSO_4$	21

6	K_3PO_4	NR
7	CsOAc	NR
8	K_2HPO_4	74

[a] Reactions performed using **1a** (0.125 mmol), CF_3SO_2Cl (0.3 mmol), Eosin-Y (5 mol%), additive (0.3 mmol), and CH_3CN (0.5 mL) for 32 h under argon atm at room temperature (Light source: 32-W compact fluorescent light). [b] Yield determined by GC using *m*-xylene as an internal standard. NR = No reaction.

Table S3: Screening of solvent[a]

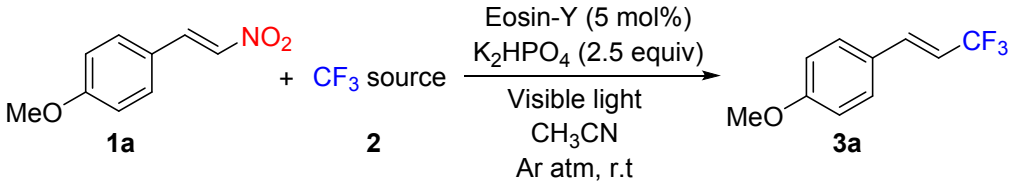


1a **2** **3a**

Entry	Solvent	Yield (%)[b]
1	CH_3CN	74
2	MeOH	31
3	DCE	27
4	THF	39
5	DMF	0
6	Toluene	NR
7	1,4-Dioxane	47
8	Water	NR
9	*o*-Xylene	NR
10	Et_2O	56
11	DMSO	NR

[a] Reactions performed using **1a** (0.125 mmol), CF_3SO_2Cl (0.3 mmol), Eosin-Y (5 mol%), K_2HPO_4(0.3 mmol), and solvent (0.5 mL) for 32 h under argon atm at room temperature (Light source: 32-W compact fluorescent light). [b] Yield determined by GC using *m*-xylene as an internal standard. NR = No reaction.

Table S4: Screening of CF_3source[a]



Entry	CF_3 source	Yield (%)[b]
1	CF_3COOH	NR
2	CF_3SO_2Cl	74
3	CF_3SO_2Na	NR
4	CF_3CO_2Na	NR
5	Togni's reagent	26
6	$(CF_3CO)_2O$	NR

[a] Reactions performed using **1a** (0.125 mmol), CF_3 source (0.3 mmol), Eosin-Y (5 mol%), K_2HPO_4(0.3 mmol), and CH_3CN (0.5 mL) for 32 h under argon atm at room temperature (Light source: 32-W compact fluorescent light). [b] Yield determined by GC using *m*-xylene as an internal standard. NR = No reaction.

Table S5: Reaction Kinetics[a,b]

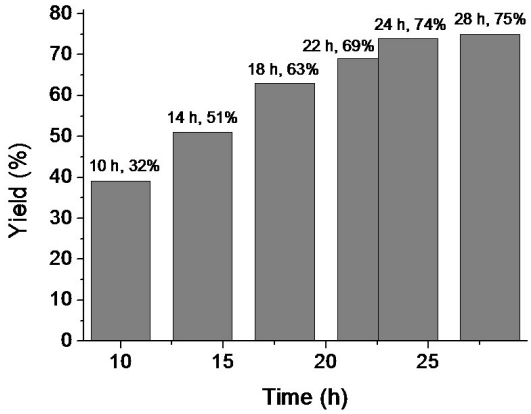
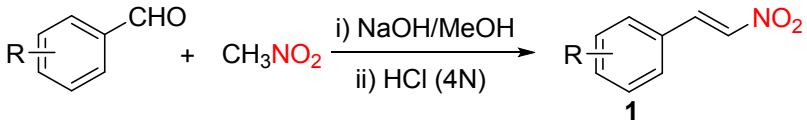


Figure S1. Reaction profile for the formation of **3a**.

[a] Reactions performed using **1a** (0.125 mmol), CF_3 source (0.3 mmol), Eosin-Y (5 mol%), K_2HPO_4 (0.3 mmol), and CH_3CN (0.5 mL) for 32 h under argon atm at room temperature (Light source: 32-W compact fluorescent light). [b] Yield determined by GC using *m*-xylene as an internal standard. NR = No reaction.

2.2 Synthesis and characterization of starting materials

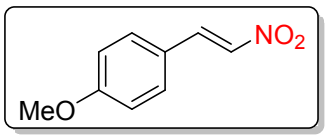
i) Method-A: synthesis of β-nitroalkene[S2]



Scheme S1. Synthesis of β-nitroalkene.

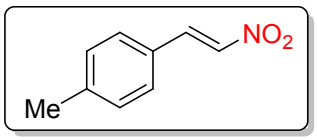
A mixture of aromatic aldehyde (10mmol) and nitromethane (11 mmol) were dissolved 25 mL of methanol in a 100 mL round bottle flask and then the mixture was cooled to 0°C. Then, NaOH(11 mmol) was added into the reaction mixture and kept it stirring for 2 h. After the completion of the reaction, the mixture was neutralised by 4N HCl, which afforded yellow coloured solid. This was filtered by a sintered funnel and washed with cold methanol to get a crude yellow, amorphous solid. Recrystallization in methanol (after 1 day) then gave analytically pure sample of β-nitro alkene derivative.

(*E*)-1-methoxy-4-(2-nitrovinyl)benzene (1a)[S2]



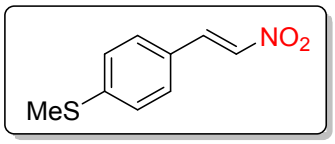
Compound **1a**was prepared according to the general procedure as described above (Method A) using 4-methoxy benzaldehyde. Yellow solid. Yield: 88%. **^{1}H NMR** (500 MHz, Chloroform-d) δ 7.93 (d, *J* = 13.7 Hz, 1H), 7.51-7.47 (m, 3H), 6.91 (d, *J* = 7.6 Hz, 2H), 3.84 (s, 3H). **^{13}C NMR** (125.8 MHz, Chloroform-d) δ 162.80, 138.96, 134.76, 131.07, 122.32, 114.74, 55.36.

(*E*)-1-methyl-4-(2-nitrovinyl)benzene (1b)[S2]



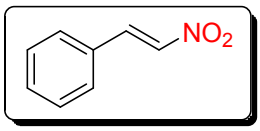
Compound **1b** was prepared according to the general procedure as described above (Method A) using 4-methyl benzaldehyde. Yellow solid. Yield: 82%.**^{1}H NMR** (500 MHz, Chloroform-d) δ 8.0 (d, *J* = 13.7 Hz, 1H), 7.59 (d, *J* = 13.7 Hz, 1H), 7.46 (d, *J* = 7.6 Hz, 2H), 7.28 (d, *J* = 7.6 Hz, 2H), 2.43 (s, 3H). **^{13}C NMR** (125.8 MHz, Chloroform-d) δ 143.07, 139.13, 136.24, 130.10, 129.15, 127.23, 21.60.

(*E*)-methyl(4-(2-nitrovinyl)phenyl)sulfane (1c)[S3]



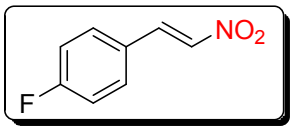
Compound **1c**was prepared according to the general procedure as described above (Method A) using 4-thiomethyl benzaldehyde. Yellow solid. Yield: 79%.**^{1}H NMR** (200 MHz, Chloroform-d) δ 7.97 (d, *J* = 13.6 Hz, 1H), 7.57 (d, *J* = 13.6 Hz, 1H), 7.46 (d, *J* = 8.5 Hz, 2H), 7.26 (d, *J* = 8.6 Hz, 2H). **^{13}C NMR** (50.3 MHz, Chloroform-d) δ 145.08, 138.68, 135.96, 129.39, 126.07, 125.81, 14.74.

(*E*)-(2-nitrovinyl)benzene (1d)[S2]



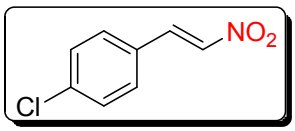
Compound **1e**was prepared according to the general procedure as described above (Method A) using benzaldehyde. Yellow solid. Yield: 82%.**^{1}H NMR** (200 MHz, Chloroform-d) δ 8.02 (d, *J* = 13.6 Hz, 1H), 7.60 (d, *J* = 13.6 Hz, 1H), 7.59 - 7.52 (m, 2H), 7.51 - 7.41 (m, 3H). **^{13}C NMR** (50.3 MHz, Chloroform-d) δ 139.00, 137.05, 132.08, 130.01, 129.33, 129.09.

(*E*)-1-fluoro-4-(2-nitrovinyl)benzene (1e)



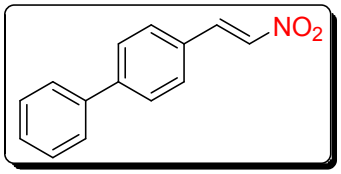
Compound **1f**was prepared according to the general procedure as described above (Method A) using 4-fluoro benzaldehyde. Yellow solid. Yield: 83%.**^{1}H NMR** (500 MHz, Chloroform-d) δ 7.99 (d, *J* = 13.7 Hz, 1H), 7.59-7.56 (m, 2H), 7.54 (d, *J* = 13.4 Hz, 1H), 7.16 (t, *J* = 8.2 Hz, 2H).**^{13}C NMR** (125.8 MHz, Chloroform-d) δ 164.82 (d, $J_{C\text{-}F}$ = 254.6 Hz), 137.80, 136.79, 131.25 (d, $J_{C\text{-}F}$ = 8.6 Hz), 126.28, 116.71 (d, $J_{C\text{-}F}$ = 22.9 Hz).

(*E*)-1-chloro-4-(2-nitrovinyl)benzene (1f)[S2]



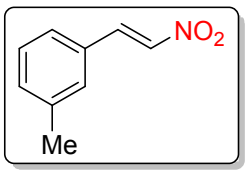
Compound **1g**was prepared according to the general procedure as described above (Method A) using 4-chloro benzaldehyde. Yellow solid. Yield: 76%.**^{1}H NMR** (500 MHz, Chloroform-d) δ 7.97 (d, *J* = 13.7 Hz, 1H), 7.57 (d, *J* = 13.4 Hz, 1H), 7.50 (d, *J* = 8.5 Hz, 2H), 7.44 (d, *J* = 8.2 Hz, 2H). **^{13}C NMR** (125.8 MHz, Chloroform-d) δ 138.32, 137.66, 137.39, 130.24, 129.75, 128.50.

(*E*)-4-(2-nitrovinyl)biphenyl (1g)



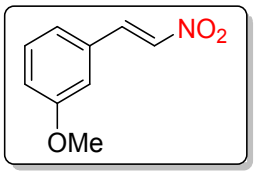
Compound **1h** was prepared according to the general procedure as described above (Method A) using 4-phenyl benzaldehyde. Yellow solid. Yield: 63%. **^{1}H NMR** (500 MHz, Chloroform-d) δ 8.06 (d, *J* = 13.3 Hz, 1H), 7.71 - 7.69 (m, 2H), 7.66 - 7.63 (m, 5H), 7.49 (t, *J* = 7.6 Hz, 2H), 7.42 (t, *J* = 7.6 Hz, 1H). **^{13}C NMR** (125.8 MHz, Chloroform-d) δ 144.96, 139.54, 138.67, 136.86, 129.67, 129.01, 128.91, 128.35, 127.95, 127.08.

(*E*)-1-methyl-3-(2-nitrovinyl)benzene (1i)



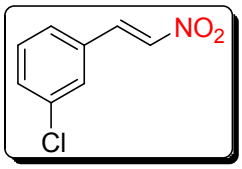
Compound **1j** was prepared according to the general procedure as described above (Method A) using 3-methyl benzaldehyde. Yellow solid. Yield: 74%.**^{1}H NMR** (500 MHz, Chloroform-d) δ 7.98 (d, *J* = 13.7 Hz, 1H), 7.58 (d, *J* = 13.7 Hz, 1H), 7.37 - 7.35 (m, 2H), 7.35 (s, 1H), 7.33 - 7.31 (m, 1H), 2.40 (s, 3H). **^{13}C NMR** (125.8 MHz, Chloroform-d) δ 139.21, 139.17, 136.86, 132.97, 129.94, 129.66, 129.20, 126.32, 21.19.

(*E*)-1-methoxy-3-(2-nitrovinyl)benzene (1j)



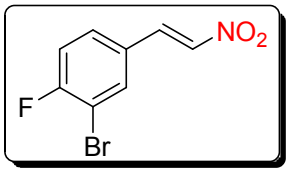
Compound **1k** was prepared according to the general procedure as described above (Method A) using 3-methoxy benzaldehyde. Yellow solid. Yield: 87%.**^{1}H NMR** (500 MHz, Chloroform-d) δ 7.95 (d, *J* = 13.4 Hz, 1H), 7.56 (d, *J* = 13.4 Hz, 1H), 7.36 (t, *J* = 7.6 Hz, 1H), 7.14 (d, *J* = 7.3 Hz, 1H), 7.06 - 7.02 (m, 2H), 3.85 (s, 3H). **^{13}C NMR** (125.8 MHz, Chloroform-d) δ 160.4, 138.96, 137.24, 131.24, 130.34, 121.67, 117.87, 113.92, 55.33.

(*E*)-1-chloro-3-(2-nitrovinyl)benzene (1k)



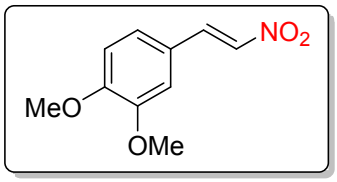
Compound **1l** was prepared according to the general procedure as described above (Method A) using 3-chloro benzaldehyde. Yellow solid. Yield: 86%. **^{1}H NMR** (500 MHz, Chloroform-d) δ 7.93 (d, *J* = 13.7 Hz, 1H), 7.57 (d, *J* = 13.7 Hz, 1H), 7.46 (t, *J* = 7.6 Hz, 1H), 7.43 - 7.39 (m, 2H). **^{13}C NMR** (125.8 MHz, Chloroform-d) δ 138.05, 137.37, 135.38, 131.78, 130.59, 128.69, 127.19.

(*E*)-2-bromo-1-fluoro-4-(2-nitrovinyl)benzene (1l)



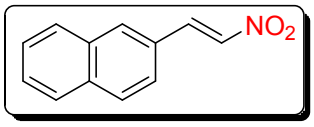
Compound **1m** was prepared according to the general procedure as described above (Method A) using 3-bromo 4-fluoro benzaldehyde. Light yellow solid. Yield: 70%.**^{1}H NMR** (500 MHz, Chloroform-d) δ 7.91 (d, *J* = 13.7 Hz, 1H), 7.78 (dd, *J* = 6.4, 1.8 Hz, 1H), 7.53 (d, *J* = 13.7 Hz, 1H), 7.53 - 7.50 (m, 1H), 7.22 (t, *J* = 8.2 Hz, 1H). **^{13}C NMR** (125.8 MHz, Chloroform-d) δ 160.94 (d, $J_{C\text{-}F}$ = 255.6 Hz), 137.65, 136.36, 134.10, 129.91 (d, $J_{C\text{-}F}$ = 7.6 Hz), 127.73, 117.54 (d, $J_{C\text{-}F}$ = 22.9 Hz), 110.34 (d, $J_{C\text{-}F}$ = 21.9 Hz).

(*E*)-1,2-dimethoxy-4-(2-nitrovinyl)benzene (1m)



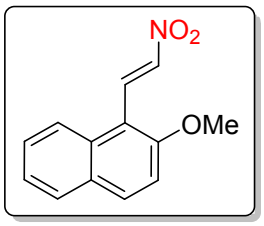
Compound **1n** was prepared according to the general procedure as described above (Method A) using 3,4-dimethoxy benzaldehyde. Yellow solid. Yield: 88%.**^{1}H NMR** (500 MHz, Chloroform-d) δ 7.94 (d, *J* = 13.4 Hz, 1H), 7.52 (d, *J* = 13.4 Hz, 1H), 7.16 (d, *J* = 8.2 Hz, 1H), 7.00 (s, 1H), 6.90 (d, *J* = 8.2 Hz, 1H), 3.92 (s, 3H), 3.91 (s, 1H).**^{13}C NMR** (125.8 MHz, Chloroform-d) δ 152.71, 149.45, 139.24, 135.05, 124.56, 122.70, 111.25, 110.18, 55.97, 55.90.

(*E*)-2-(2-nitrovinyl)naphthalene (1n)



Compound **1o** was prepared according to the general procedure as described above (Method A) using 2-napthaldehyde. Yellow solid. Yield: 68%.**^{1}H NMR** (500 MHz, Chloroform-d) δ 8.16 (d, *J* = 13.4 Hz, 1H), 8.02 (s, 1H), 7.91 - 7.87 (m, 3H), 7.70 (d, *J* = 13.7 Hz, 1H), 7.62 - 7.56 (m, 3H). **^{13}C NMR** (125.8 MHz, Chloroform-d) δ 139.20, 137.10, 134.87, 133.10, 132.25, 129.33, 128.80, 128.35, 127.91, 127.50, 127.25, 123.28.

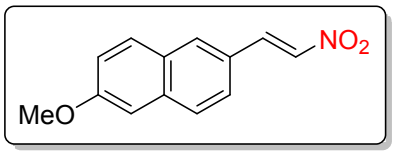
(*E*)-2-methoxy-1-(2-nitrovinyl)naphthalene (1o)



Compound **1p** was prepared according to the general procedure as described above (Method A) using 2-methoxy 1-napthaldehyde. Yellow solid. Yield: 55%.**^{1}H NMR** (500 MHz, Chloroform-d) δ 8.83 (d, *J* = 13.3 Hz, 1H), 8.16 (d, *J* = 8.8 Hz, 1H), 8.14 (d, *J* = 13.3 Hz,

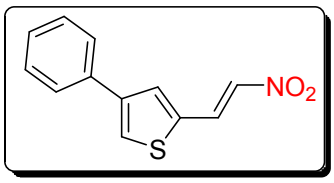
1H), 7.98 (d, *J* = 9.2 Hz, 1H), 7.83 (d, *J* = 8.0 Hz, 1H), 7.61 (t, *J* = 7.6 Hz, 1H), 7.44 (d, *J* = 7.6 Hz, 1H), 7.31 (d, J = 9.2 Hz, 1H), 4.09 (s, 3H). **^{13}C NMR** (125.8 MHz, Chloroform-d) δ 158.90, 140.07, 134.35, 133.29, 130.78, 128.99, 128.42, 124.40, 122.10, 112.16, 111.50, 56.21.

(*E*)-2-methoxy-6-(2-nitrovinyl)naphthalene (1p)



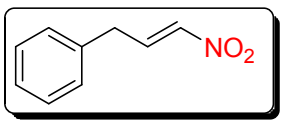
Compound **1q** was prepared according to the general procedure as described above (Method A) using 6-methoxy 2-napthaldehyde. Yellow solid. Yield: 78%.**^{1}H NMR** (200 MHz, Chloroform-d) δ 8.14 (d, *J* = 13.6 Hz, 1H), 7.93 (s, 1H), 7.78 (dd, *J* = 8.8, 4.7 Hz, 2H), 7.67 (d, *J* = 13.6 Hz, 1H), 7.56 (dd, *J* = 8.6, 1.6 Hz, 1H), 7.22 (dd, *J* = 8.8, 2.5 Hz, 1H), 7.16 (s, 1H), 3.96 (s, 3H). **^{13}C NMR** (50.3 MHz, Chloroform-d) δ. 159.71, 139.56, 136.61, 136.13, 132.14, 130.42, 128.50, 128.06, 125.25, 124.04, 120.04, 106.10, 55.45.

(*E*)-2-(2-nitrovinyl)-4-phenylthiophene (1r)



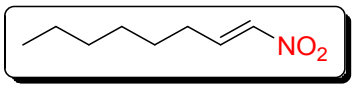
Compound **1s** was prepared according to the general procedure as described above (Method A) using 4-phenyl thiophene aldehyde. Yellow solid. Yield: 59%.**^{1}H NMR** (400 MHz, Chloroform-d) δ 8.17 (d, *J*=13.8 Hz, 1H), 7.69 (s, 1H), 7.65 (s, 1H), 7.55 - 7.60 (m, 2H), 7.51 (d, *J*=13.3 Hz, 1H), 7.42 - 7.48 (m, 2H), 7.34 - 7.40 (m, 1H).**^{13}C NMR** (100.5 MHz, Chloroform-d) δ 144.06, 135.49, 134.26, 134.13, 133.14, 131.99, 129.04, 128.07, 126.25, 126.06.

(*E*)-(3-nitroallyl)benzene (1s)



Compound **1u** was prepared according to the general procedure as described above (Method A) using phenylacetaldehyde. Yellow liquid. Yield: 76%.**^{1}H NMR** (500 MHz, Chloroform-d) δ 7.40 - 7.48 (m, 1 H), 7.37 (t, *J*=7.4 Hz, 2H), 7.31 (t, *J*=7.2 Hz, 1H), 7.20 (d, *J*= 7.3 Hz, 2H), 6.93 (d, *J*=13.3 Hz, 1H), 3.60 (d, *J* = 6.0 Hz, 2H). **^{13}C NMR** (125.8 MHz, Chloroform-d) δ 141.03, 140.32, 135.66, 129.01, 128.70, 127.35, 34.57.

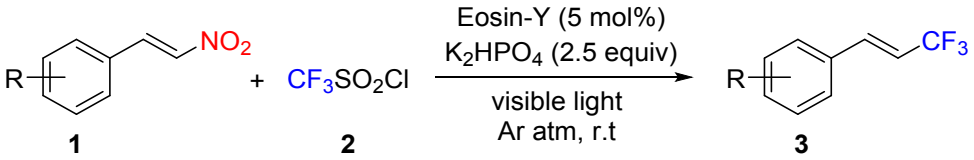
(*E*)-1-nitrooct-1-ene (1t)



Compound **1v** was prepared according to the general procedure as described above (Method A) using heptaldehyde. Light yellow liquid. Yield: 72%. **^{1}H NMR** (200 MHz, Chloroform-d) δ 4.21 - 4.52 (m, 2H), 1.46 - 1.64 (m, 2H), 1.29 (br. s., 8H), 0.79 - 0.98 (m, 3H).**^{13}C NMR** (50.3 MHz, Chloroform-d) δ 80.64, 68.67, 33.68, 31.58, 28.93, 25.09, 22.49, 13.99.

2.3 Synthesis and Characterization of Products

Synthesis of1-trifluoromethylalkenes: Visible-light metal-free photoredox catalysis



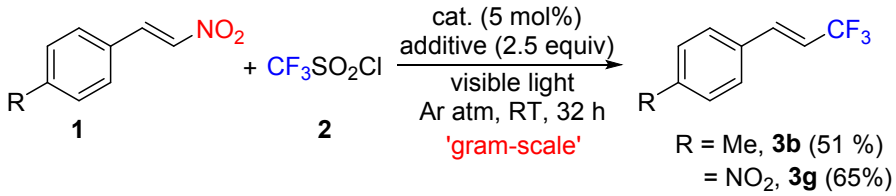
Scheme S2. Synthesis of 1-trifluoromethylalkenes**3.**

(a) Experimental procedure:

To a 10 mL clean, oven-dried screw cap reaction tube was added eosin-Y (0.0125 mmol, 5 mol%), K_2HPO_4 (0.625 mmol, 2.5 equiv), β-nitroalkene **1** (0.25 mmol), CF_3SO_2Cl (0.625 mmol, 2.5 equiv), and CH_3CN (1mL) under inert atm. The reaction mixture was kept for stirring at room temperature with 32W compact fluorescent light bulb for 32 h. Then, the reaction mixture was diluted with water (4 mL) and extracted with diethyl ether (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.

(b) Gram-scale synthesis:

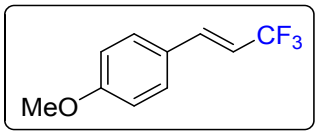
To a 25 mL clean, oven-dried screw cap reaction tube was added eosin-Y (0.185 mmol, 5 mol%), K_2HPO_4 (2.5 equiv), β-nitroalkene **1b** or **1g** (3.7 mmol), CF_3SO_2Cl (9.24 mmol, 2.5 equiv), and CH_3CN (5 mL) under inert atm. The reaction mixture was kept for stirring at room temperature with 32-W compact fluorescent light bulb for 32 h. Then, the reaction mixture was diluted with water (4 mL) and extracted with diethyl ether (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 and gave the desired product (product **3b** in 51% and product **3g** in 65%).



- If starting material is remaining, add additional quantities of CF_3 source and continue the visible-light irradiation.
- Solvent dilution is the most important factor.
- Sometimes higher yields were observed when recrystallized eosin-Y (thrice from ethanol) was used.
- Reaction should be conducted strictly under an inert atmosphere of argon for better performance.

(c) Characterization of Products:

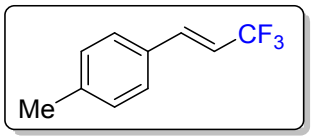
(*E*)-1-methoxy-4-(3,3,3-trifluoroprop-1-enyl)benzene (3a)



Colorless oil. Yield: 74%. **^{1}H NMR** (500 MHz, Chloroform-d) δ 7.41 (d, *J* = 8.5 Hz, 2H), 7.10 (qd, *J* = 16.2, 1.8 Hz, 1H), 6.92 (d, *J* = 8.8 Hz, 2H), 6.07 (qd, *J* = 16.0, 6.6 Hz, 1H), 3.85 (s, 3H). **^{13}C NMR** (125.8 MHz, Chloroform-d) δ 161.02, 137.08 (q, *J* = 6.8 Hz), 129.01, 126.06, 123.89 (q, *J* = 268.4 Hz), 114.30, 113.44 (q, *J* = 33.7 Hz), 55.36. **^{19}F NMR** (376.5

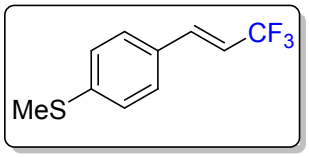
MHz, Chloroform-d) δ -62.84. (Known compound: Iqbal, N.; Jung, J.; Park, S.; Cho, E. J. *Angew. Chem. Int. Ed.***2014**, *53*, 539).

(*E*)-1-methyl-4-(3,3,3-trifluoroprop-1-enyl)benzene (3b)



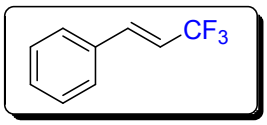
Colorless oil. Yield: 71%. **^{1}H NMR** (400 MHz, Chloroform-d) δ 7.36 (d, *J* = 7.9 Hz, 2H), 7.21 (d, *J* = 8.1 Hz, 2H), 7.13 (qd, *J* = 16.1, 2.2 Hz, 1H), 6.16 (qd, *J* = 16.1, 6.6 Hz, 1H), 2.39 (s, 3H). **^{13}C NMR** (100.6 MHz, Chloroform-d) δ 140.28, 137.53 (q, *J* = 6.9 Hz), 130.65, 129.61, 127.46, 123.64 (q, *J* = 268.9 Hz), 114.76 (q, *J* = 33.9 Hz), 21.35. **^{19}F NMR** (376.5 MHz, Chloroform-d) δ -62.84. (Known compound: Iqbal, N.; Jung, J.; Park, S.; Cho, E. J. *Angew. Chem. Int. Ed.* **2014**, *53*, 539).

(*E*)-methyl(4-(3,3,3-trifluoroprop-1-enyl)phenyl)sulfane (3c)



Colorless oil. Yield: 73%. **^{1}H NMR** (500 MHz, Chloroform-d) δ 7.37 (d, *J* = 8.5 Hz, 2H), 7.25 (d, *J* = 8.5 Hz, 2H), 7.10 (qd, *J* = 16.2, 2.1 Hz, 1H), 6.16 (qd, *J* = 16.2, 6.4 Hz, 1H), 2.51 (s, 3H). **^{13}C NMR** (125.8 MHz, Chloroform-d) δ 141.44, 137.01 (q, *J* = 7.6 Hz), 129.95, 127.86, 126.16, 123.68 (q, *J* = 265.2 Hz), 114.89 (q, *J* = 33.4), 15.25. **^{19}F NMR** (376.5 MHz, Chloroform-d) δ -63.09. (Known compound: Omote, M.; Tanaka, M.; Ikeda, A.; Nomura, S.; Tarui, A.; Sato, K.; Ando, A. *Org. Lett*., **2012**, *14*, 9).

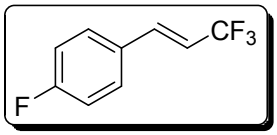
(*E*)-(3,3,3-trifluoroprop-1-enyl)benzene (3d)



Colorless oil. Yield: 68%. **^{1}H NMR** (400 MHz, Chloroform-d) δ 7.48 - 7.36 (m, 5H), 7.17 (qd, *J* = 16.2, 2.1 Hz, 1H), 6.22 (qd, *J* = 16.0, 6.6 Hz, 1H). **^{19}F NMR** (376.5 MHz,

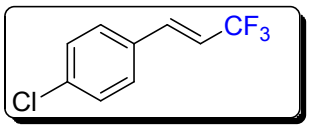
Chloroform-d) δ -63.34. (Known compound: Ma, J. -J.; Yi, W. -B.; Lu, G. -P.; Cai, C. *Adv. Synth. Catal.* **2015**, *357*, 3447).

(*E*)-1-fluoro-4-(3,3,3-trifluoroprop-1-enyl)benzene (3e)



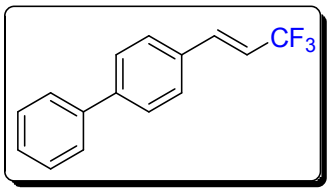
Colorless oil. Yield: 70%. **^{1}H NMR** (200 MHz, Chloroform-d) δ 7.46 - 7.38 (m, 4H), 7.17 (qd, *J* = 16.2, 2.1 Hz, 1H), 6.22 (qd, *J* = 16.2, 6.6 Hz, 1H). **^{19}F NMR** (376.5 MHz, Chloroform-d) δ -63.32, -110.25. (Known compound: Ma, J. -J.; Yi, W. -B.; Lu, G. -P.; Cai, C. *Adv. Synth. Catal.* **2015**, *357*, 3447).

(*E*)-1-chloro-4-(3,3,3-trifluoroprop-1-enyl)benzene (3f)



Colorless oil. Yield: 63%. **^{1}H NMR** (200 MHz, Chloroform-d) δ 7.43 - 7.34 (m, 4H), 7.12 (qd, *J* = 16.2, 2.1 Hz, 1H), 6.19 (qd, J = 16.2, 6.4 Hz, 1H). **^{19}F NMR** (376.5 MHz, Chloroform-d) δ -63.44. (Known compound: Ma, J. -J.; Yi, W. -B.; Lu, G. -P.; Cai, C. *Adv. Synth. Catal.* **2015**, *357*, 3447).

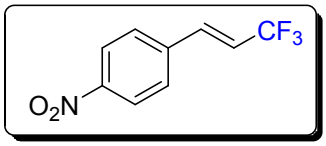
(*E*)-4-(3,3,3-trifluoroprop-1-enyl)biphenyl (3g)



White solid. Yield: 69%. **^{1}H NMR** (500 MHz, Chloroform-d) δ7.64 (t, *J*=8.8 Hz, 4H), 7.54 (d, *J*=8.0 Hz, 2H), 7.48 (t, *J*=7.6 Hz, 2H), 7.36 - 7.43 (m, 1H) 7.21 (dd, *J*=16.0, 1.9 Hz, 1H) 6.26 (dq, *J*= 16.16, 6.56 Hz, 1H). **^{13}C NMR** (125.8 MHz, Chloroform-d) δ142.82, 140.10, 137.21 (q, *J* = 6.7 Hz), 132.34, 128.90, 128.00, 127.84, 127.57, 127.04, 124.73, 122.59, 115.73 (q, *J* = 33.4 Hz). **^{19}F NMR** (376.5 MHz, Chloroform-d) δ -63.19. (Known compound:

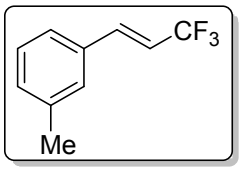
Omote, M.; Tanaka, M.; Ikeda, A.; Nomura, S.; Tarui, A.; Sato, K.; Ando, A. *Org. Lett*., **2012**, *14*, 9)

(*E*)-1-nitro-4-(3,3,3-trifluoroprop-1-enyl)benzene (3h)



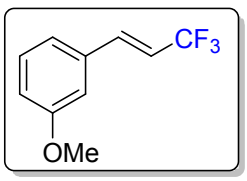
Yellow solid. Yield: 81%. **^{1}H NMR** (400 MHz, Chloroform-d) δ 8.82 (d, *J* = 8.7 Hz, 2H), 7.64 (d, *J* = 8.7 Hz, 2H), 7.24 (qd, *J* = 16.5, 1.8 Hz, 1H), 6.37 (qd, *J* = 16.0, 6.4 Hz, 1H). **^{19}F NMR** (376.5 MHz, Chloroform-d) δ -63.97. (Known compound: Ma, J. -J.; Yi, W. -B.; Lu, G. -P.; Cai, C. *Adv. Synth. Catal.* **2015**, *357*, 3447).

(*E*)-1-methyl-3-(3,3,3-trifluoroprop-1-enyl)benzene (3i)



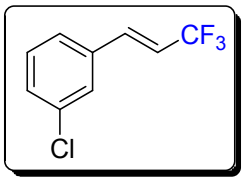
Colorless oil. Yield: 60%. **^{1}H NMR** (200 MHz, Chloroform-d) δ 7.26 - 7.22 (m, 3H), 7.17 (d, *J* = 6.2 Hz, 1H), 7.11 (qd, *J* = 16.2, 2.2 Hz, 1H), 6.20 (qd, *J* = 16.1, 6.4 Hz, 1H), 2.38 (s, 3H). **^{19}F NMR** (376.5 MHz, Chloroform-d) δ -63.27. (Known compound: Ma, J. -J.; Yi, W. -B.; Lu, G. -P.; Cai, C. *Adv. Synth. Catal.* **2015**, *357*, 3447).

(*E*)-1-methoxy-3-(3,3,3-trifluoroprop-1-enyl)benzene (3j)



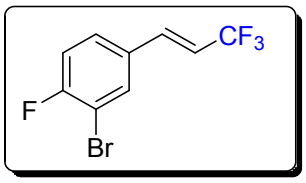
Colorless oil. Yield: 63%. **^{1}H NMR** (200 MHz, Chloroform-d) δ 7.32 (t, *J* = 7.4 Hz, 1H), 7.14 (qd, *J* = 16.0, 1.2 Hz, 1H), 7.06 (d, *J* = 7.5 Hz, 1H), 6.98 (s, 1H), 6.95 (d, *J*= 8.2 Hz, 1H), 6.21 (qd, *J* = 16.1, 6.4 Hz, 1H), 3.85 (s, 3H). **^{19}F NMR** (376.5 MHz, Chloroform-d) δ -63.33. (Known compound: Ma, J. -J.; Yi, W. -B.; Lu, G. -P.; Cai, C. *Adv. Synth. Catal.* **2015**, *357*, 3447).

(*E*)-1-chloro-3-(3,3,3-trifluoroprop-1-enyl)benzene (3k)



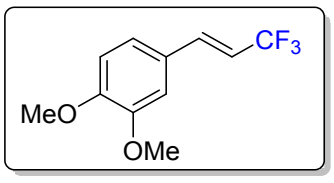
Colorless oil. Yield: 67%. **^{1}H NMR** (200 MHz, Chloroform-d) δ 7.48 (s, 1H), 7.39 - 7.32 (m, 3H), 7.11 (dq, *J* = 16.4, 2.1 Hz, 1H), 6.22 (dq, *J*= 16.0, 6.4 Hz, 1H). **^{19}F NMR** (376.5 MHz, Chloroform-d) δ -63.61. (Known compound: Ma, J. -J.; Yi, W. -B.; Lu, G. -P.; Cai, C. *Adv. Synth. Catal.* **2015**, *357,* 3447 - 3452)

(*E*)-2-bromo-1-fluoro-4-(3,3,3-trifluoroprop-1-enyl)benzene (3l)



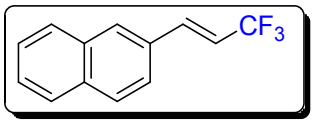
Colorless oil. Yield: 66%. **^{1}H NMR** (500 MHz, Chloroform-d) δ 7.68 (dd, *J* = 6.4, 2.1 Hz, 1H), 7.40 - 7.37 (m, 1H), 7.16 (t, *J* = 8.5 Hz, 1H), 7.07 (qd, *J* = 16.2, 2.1 Hz, 1H), 6.16 (qd, *J* = 16.2, 6.4 Hz, 1H). **^{13}C NMR** (125.8 MHz, Chloroform-d) δ 159.87 (d, *J* = 251.8 Hz), 135.23 (q, *J* = 6.7 Hz), 132.55, 131.00, 128.21 (d, *J* = 7.6 Hz), 122.10, 117.01 (q, *J* = 22.9 Hz), 109.84 (d, *J* = 21.94 Hz). **^{19}F NMR** (376.5 MHz, Chloroform-d) δ -63.56, -104.55.

(*E*)-1,2-dimethoxy-4-(3,3,3-trifluoroprop-1-enyl)benzene (3m)



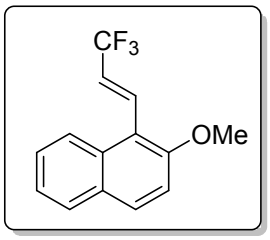
Colorless oil. Yield: 69%. **^{1}H NMR** (500 MHz, Chloroform-d) δ 7.09 (d, *J* = 15.9 Hz, 1H), 7.03 (d, *J* = 7.9 Hz, 1H), 6.97 (s, 1H), 6.88 (d, *J* = 8.2 Hz, 1H), 6.08 (qd, *J* = 16.2, 7.9 Hz, 1H), 3.93 (s, 3H), 3.92 (s, 3H). **^{13}C NMR** (125.8 MHz, Chloroform-d) δ 150.76, 149.27, 137.40 (q, *J* = 6.7 Hz), 126.35, 121.62, 113.68 (q, *J* = 33.3 Hz), 111.09, 109.36, 55.97, 55.94. **^{19}F NMR** (376.5 MHz, Chloroform-d) δ -62.82.(Known compound: Xu, P.; Abdukader, A.; Hu, K.; Cheng, Y.; Zhu, C. *Chem. Commun.*, **2014**, *50*, 2308-2310).

(*E*)-2-(3,3,3-trifluoroprop-1-enyl)naphthalene (3n)



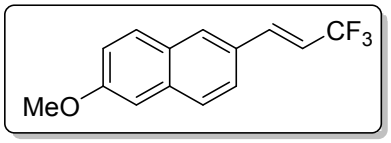
Colorless oil. Yield: 60%. **^{1}H NMR** (500 MHz, Chloroform-d) δ 7.88 - 7.84 (m, 4H), 7.61 (dd, *J* = 8.5, 1.8 Hz, 1H), 7.55 - 7.52 (m, 2H), 7.33 (qd, *J* = 16.2, 2.1 Hz, 1H), 6.33 (qd, *J* = 16.2, 6.4 Hz, 1H). **^{13}C NMR** (125.8 MHz, Chloroform-d) δ 137.73 (q, *J* = 6.7 Hz), 134.02, 133.25, 130.84, 129.10, 128.80, 128.41, 127.80, 127.17, 126.80, 124.79, 123.13, 115.95 (q, *J* = 33.4 Hz). **^{19}F NMR** (376.5 MHz, Chloroform-d) δ -62.82. (Known compound: Kathiravan, S.; Nicholls, I. A. *Org. Lett.,* **2015**, *17*, 1874 - 1877).

(*E*)-2-methoxy-1-(3,3,3-trifluoroprop-1-enyl)naphthalene (3o)



Pale yellow oil. Yield: 59%. **^{1}H NMR** (500 MHz, Chloroform-d) δ 8.08 (d, *J* = 8.5 Hz, 1H), 7.88 (d, *J* = 9.2 Hz, 1H), 7.82 (d, *J* = 8.2 Hz, 1H), 7.72 (qd, *J* = 16.2, 2.1 Hz, 1H), 7.54 (t, *J* = 7.6 Hz, 1H), 7.40 (t, *J*= 7.3 Hz, 1H), 7.32 (d, *J* = 8.8 Hz, 1H), 6.56 (qd, *J* = 16.5, 6.7 Hz, 1H), 4.02 (s, 3H). **^{13}C NMR** (125.8 MHz, Chloroform-d) δ 156.97, 132.43, 131.21, 130.32 (q, *J* = 7.6 Hz), 128.92, 128.64, 127.43, 123.87, 122.82, 121.20 (q, *J* = 33.38 Hz), 112.76, 56.23. **^{19}F NMR** (376.5 MHz, Chloroform-d) δ -63.53.

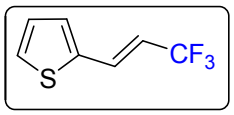
(*E*)-2-methoxy-6-(3,3,3-trifluoroprop-1-enyl)naphthalene (3p)



Light yellow oil. Yield: 64%.**^{1}H NMR** (500 MHz, Chloroform-d) δ 7.80 (s, 1H), 7.77 - 7.74 (m, 2H), 7.57 (d, *J* = 8.8 Hz, 1H), 7.29 (qd, *J* = 15.64, 1.9 Hz, 1H), 7.19 (d, *J* = 9.2 Hz, 1H), 7.15 (s, 1H), 6.28 (qd, *J* = 16.0, 6.5 Hz, 1H), 3.95 (s, 3H). **^{19}F NMR** (376.5 MHz,

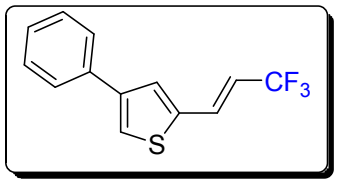
Chloroform-d) δ -62.96. (Known compound: Lin, H.; Dong, X.; Li, X.; Shen, Q.; Lu, L. *Eur. J. Org. Chem.* **2012**, 4675 - 4679).

(*E*)-2-(3,3,3-trifluoroprop-1-en-1-yl)thiophene (3q)



Colorless oil. Yield: 66%. **^{1}H NMR** (300 MHz, Chloroform-d): δ 7.34 (d, J = 5.1 Hz, 1H), 7.26 (dq, J = 2.1, 15.9 Hz, 1H) 7.19 (d, J = 3.6 Hz, 1H), 7.03(dd, J = 3.8, 5.0Hz, 1H), 6.01 (dq, J = 6.6, 15.9 Hz, 1H); **^{19}F NMR** (282 MHz, Chloroform-d): δ -64.6. (Known compound: Ramachandran, P. V.; Otoo, B. *Chem. Commun.*, **2015**, *51*, 12388-12390).

(*E*)-4-phenyl-2-(3,3,3-trifluoroprop-1-enyl)thiophene (3r)

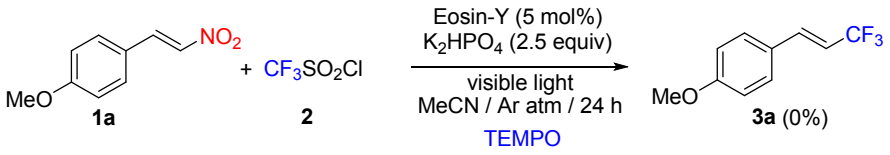


White solid. Yield: 65%. **^{1}H NMR** (400 MHz, Chloroform-d) δ 7.57 - 7.59 (m, 1H), 7.55 - 7.57 (m, 1H), 7.47 (d, *J* = 2.7 Hz, 2H), 7.40 - 7.45 (m, 2H), 7.33 - 7.36 (m, 1H), 7.29 - 7.32 (m, 1H), 6.07 (dq, *J*= 15.7, 6.5 Hz, 1H).**^{19}F NMR** (376.5 MHz, Chloroform-d) δ -63.12.**HRMS (ESI)** calcd.for $C_{13}H_9F_3S$ $[M+Na]^+$: 277.0269, found: 277.0274.

2.4 Mechanistic Studies

(i) Radical trapping experiment

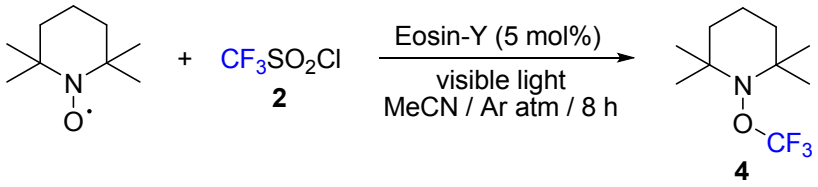
To a 10 mL clean, oven-dried screw cap reaction tube was added eosin-Y (5 mol%), K_2HPO_4 (2.5 equiv), β-nitroalkene**1a** (1 equiv), CF_3SO_2Cl (2.5 equiv), TEMPO (4 equiv), and CH_3CN (2 mL) under argon atm. The reaction mixture was kept for stirring at room temperature with 32W compact fluorescent light bulb for 24 h. After usual work-up procedure, 96% of starting material (**1a**) was recovered.



Scheme S3. Radical trapping experiment by TEMPO.

(ii) TEMPO:CF_3 adduct

To a 10 mL clean, oven-dried screw cap reaction tube was added eosin-Y (5 mol%), CF_3SO_2Cl (1 equiv), TEMPO (1.1 equiv), and CH_3CN (1mL) under argon atm. The reaction mixture was kept for stirring at room temperature with 32W compact fluorescent light bulb. After 8h of irradiation, a CF_3-TEMPO adduct **4** was observed, which was identified through GC-MS analysis of the reaction mixture.



Scheme S4. Identification of TEMPO:CF_3 adduct**4**.

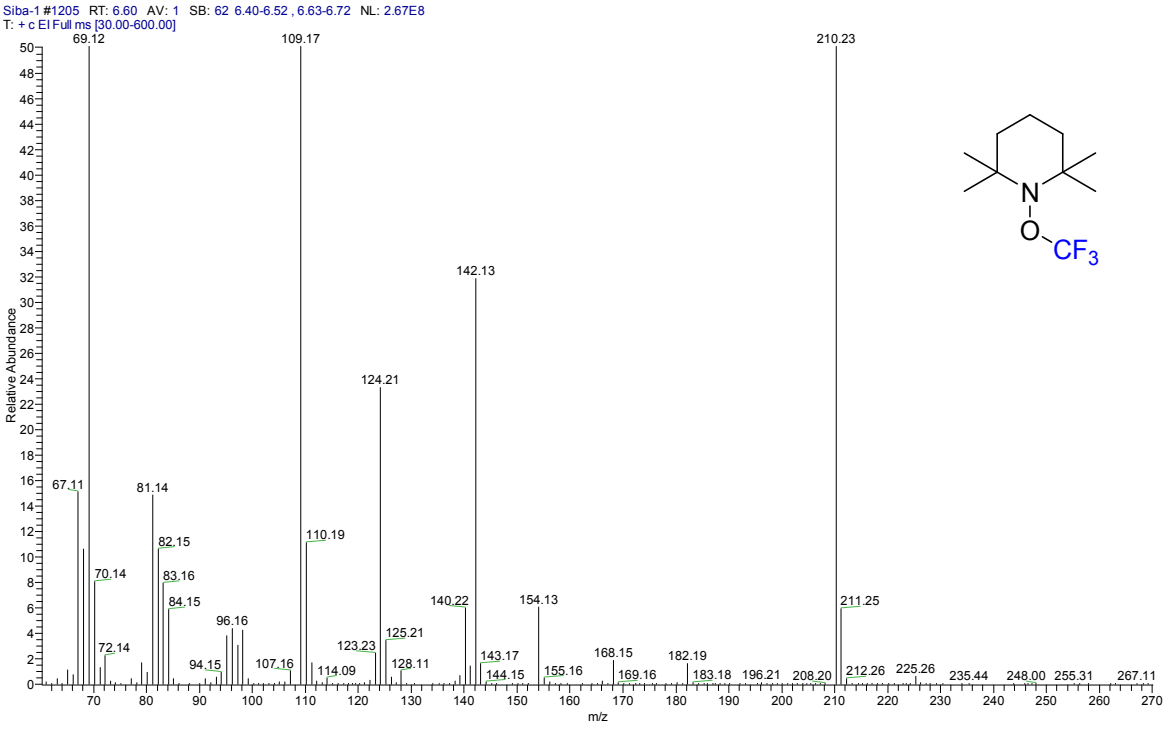
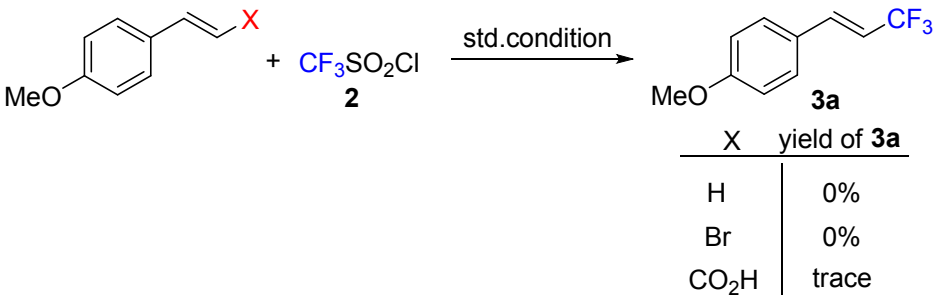


Figure S2. GC-MS data of compound **4**.

(iii) Experimental procedure for other olefinic compounds

Initially, three 10 mL clean, oven-dried screw cap reaction tube were taken. To these reaction tubes, eosin-Y (5 mol%), K_2HPO_4 (2.5 equiv), CF_3SO_2Cl (2.5 equiv), and CH_3CN (1 mL) under argon atm were added separately. To this solution, 0.125 mmol of each 4-methoxy styrene, 4-methoxy β-bromostyrene and 4-methoxy cinnamic acid was added respectively. Then all three reaction mixtures were kept for stirring at room temperature with 32W

compact fluorescent light bulb for 24 h. After usual work-up procedure, trifluoromethylated product was not observed for all the three cases.



X	yield of **3a**
H	0%
Br	0%
CO_2H	trace

Scheme S5. Trifluoromethylationfor other olefinic compounds.

(iv) Emission Quenching Experiments

For the emission quenching experiment we used 2.06 x 10^{-3} (M) solution of eosin-Y in acetonitrile (2 mg in 1.5 mL). An appropriate amount of quencher was added for several times to that eosin-Y solution in a screw-top 3.0 cm quartz cuvette. All eosin-Y solution with or without quencher were excited at 460 nm and the emission intensity at 555 nm was observed and the emission spectrum of the sample was collected.

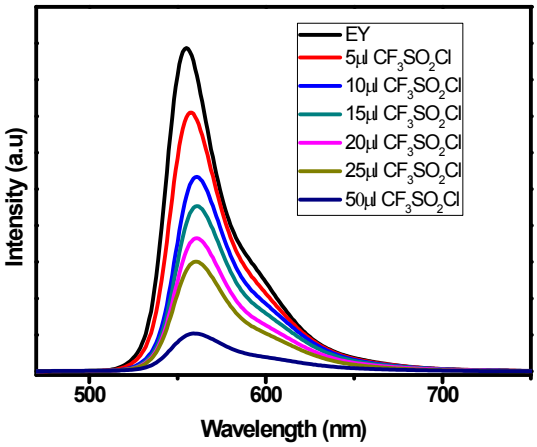


Figure S4. Fluorescence spectroscopy of eosin-Y in presence different concentration of quencher CF_3SO_2Cl.

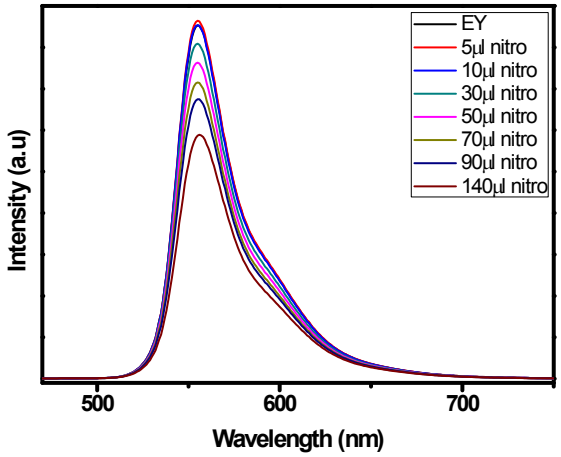


Figure S5. Fluorescence spectroscopy of eosin-Y in presence different concentration of quencher 4-fluoro nitroalkene.

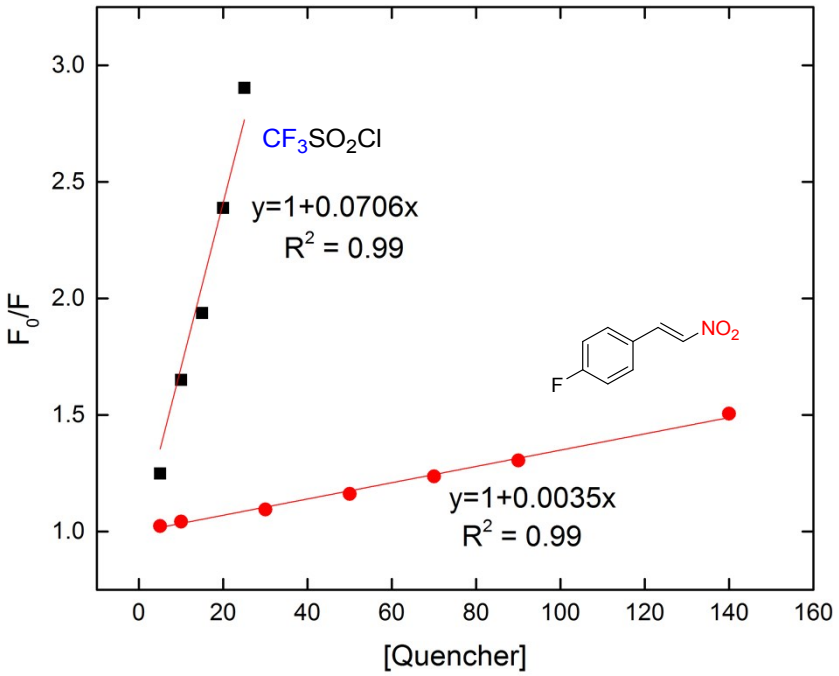


Figure S6. Eosin-Y emission quenchingusing CF_3SO_2Cl and 4-fluoro-nitroalkene as quenchers.

Summary of emission quenchingexperiment:

Quencher	Stern-Volmer constant ($K_{sv}x10^{-3}$)
CF_3SO_2Cl	71
4-fluoro nitroalkene	3.4

(v) Cyclic voltammetry (CV) study

Cyclic Voltammetry measured at 10mVS-1 scan rate using Ag/AgCl as reference electrode and Pt wire counter electrode in anhydrous acetonitrile with 0.1M Tetra butyl ammoniumperchlorate (TBAP) as supporting electrolyte. Nitrobenzene undergoes 2e reduction, thus we have observed two reduction peaks.

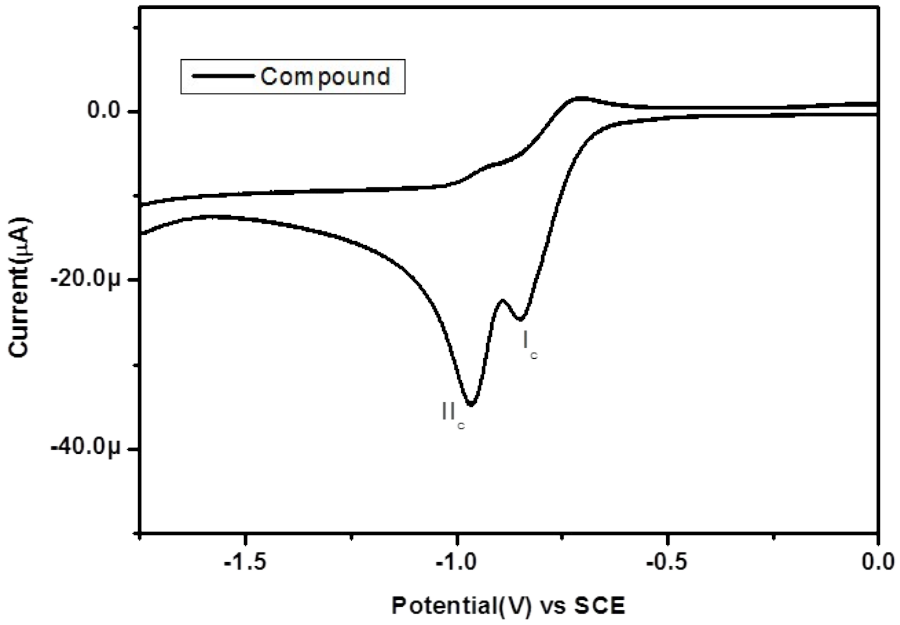


Figure S7. Cyclic voltammetry of 4-methoxy nitroalkene**1a**.

3. References

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

S2. V. Ashokkumar and A. Siva, *Org. Biomol. Chem.*, 2015, **13**, 10216-10225.

S3 J. G. Greger, S. J. P. Yoon-Miller, N. R. Bechtold, S. A. Flewelling, J. P. MacDonald, C. R. Downey, E. A. Cohen and E. T. Pelkey, *J. Org. Chem.,* 2011, **76**, 8203-8214.

4. NMR Spectra

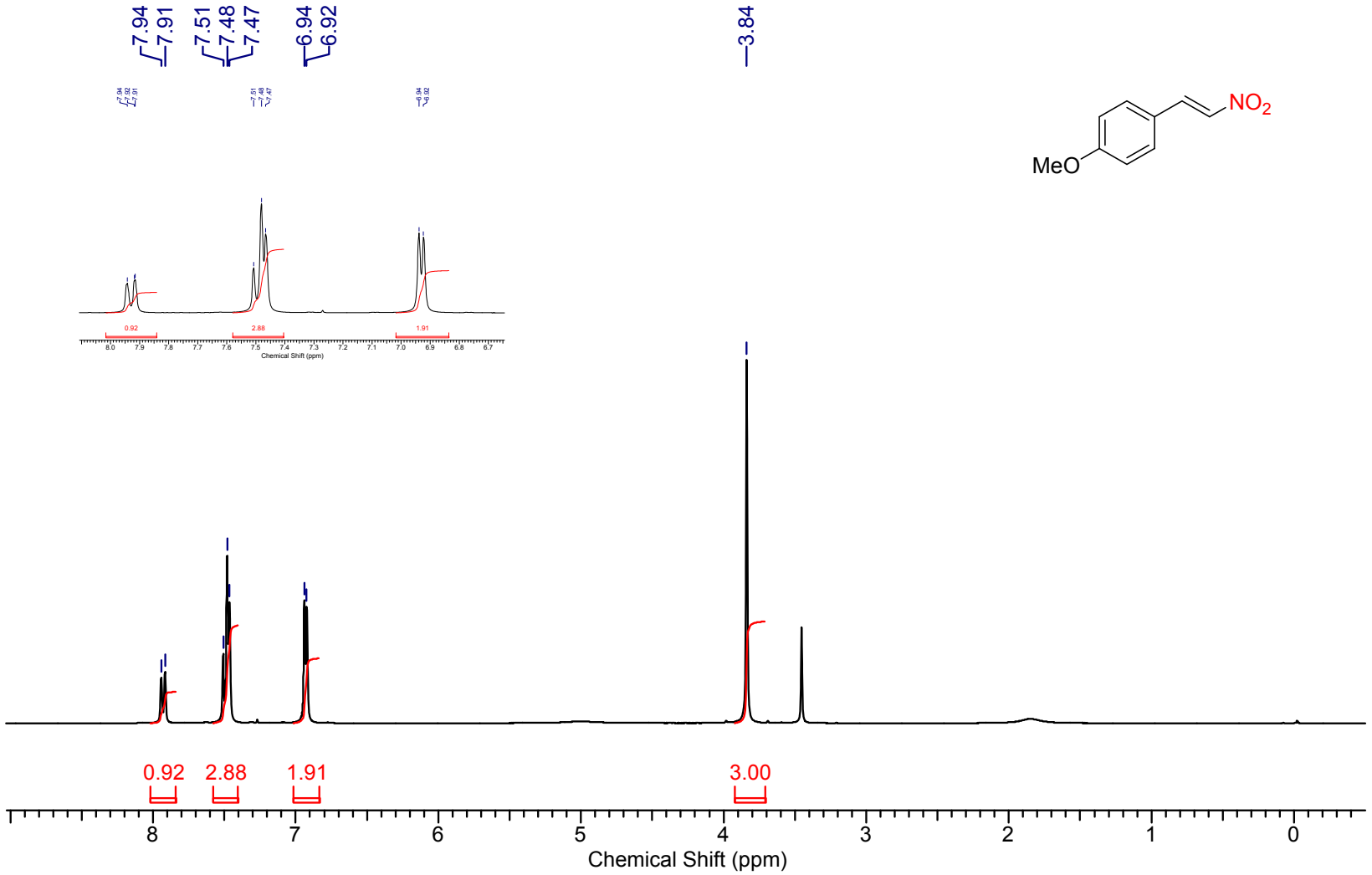


Figure S7a. ^{1}H NMR of **1a**

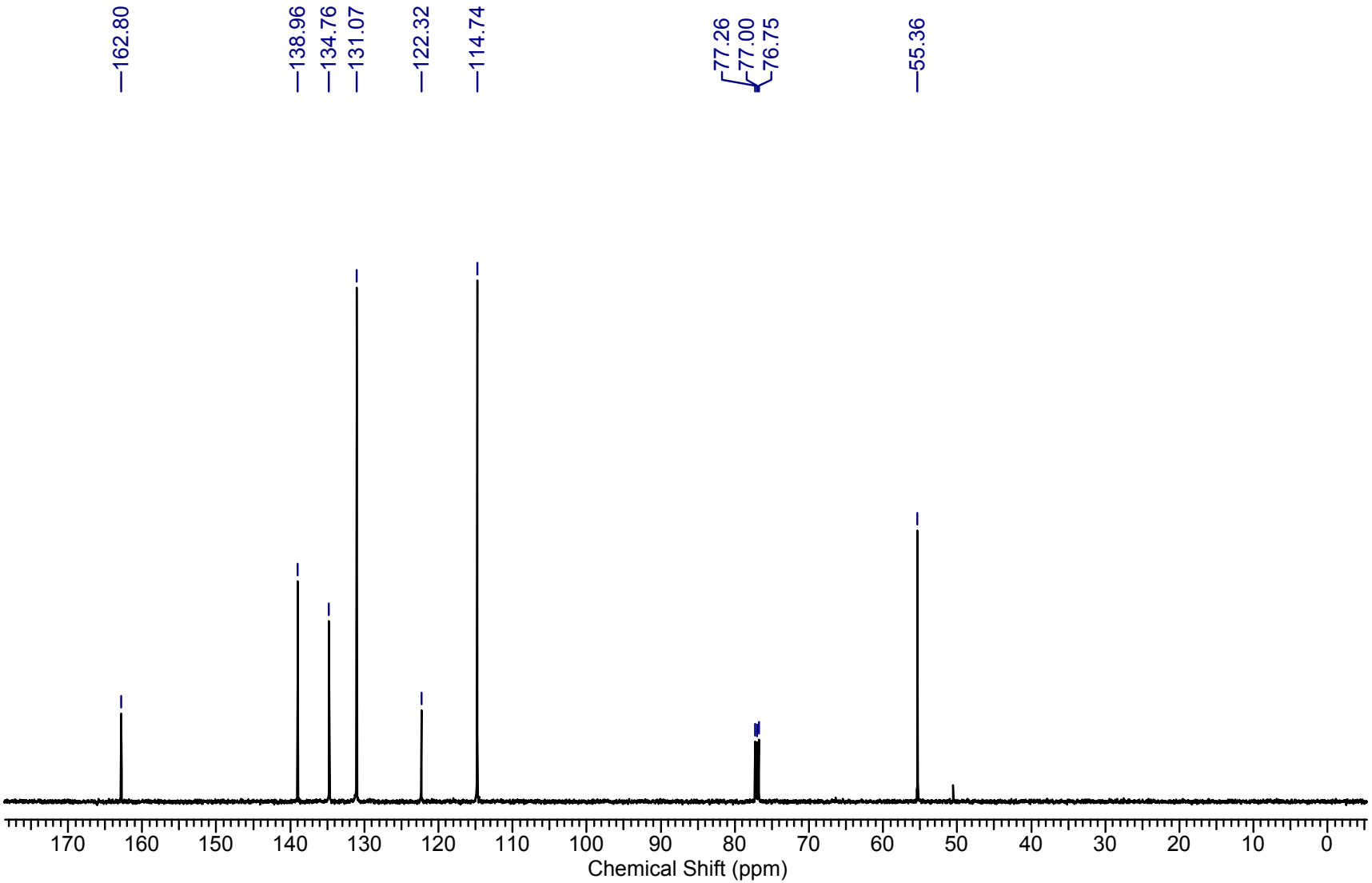


Figure S7b. ^{13}C NMR of **1a**

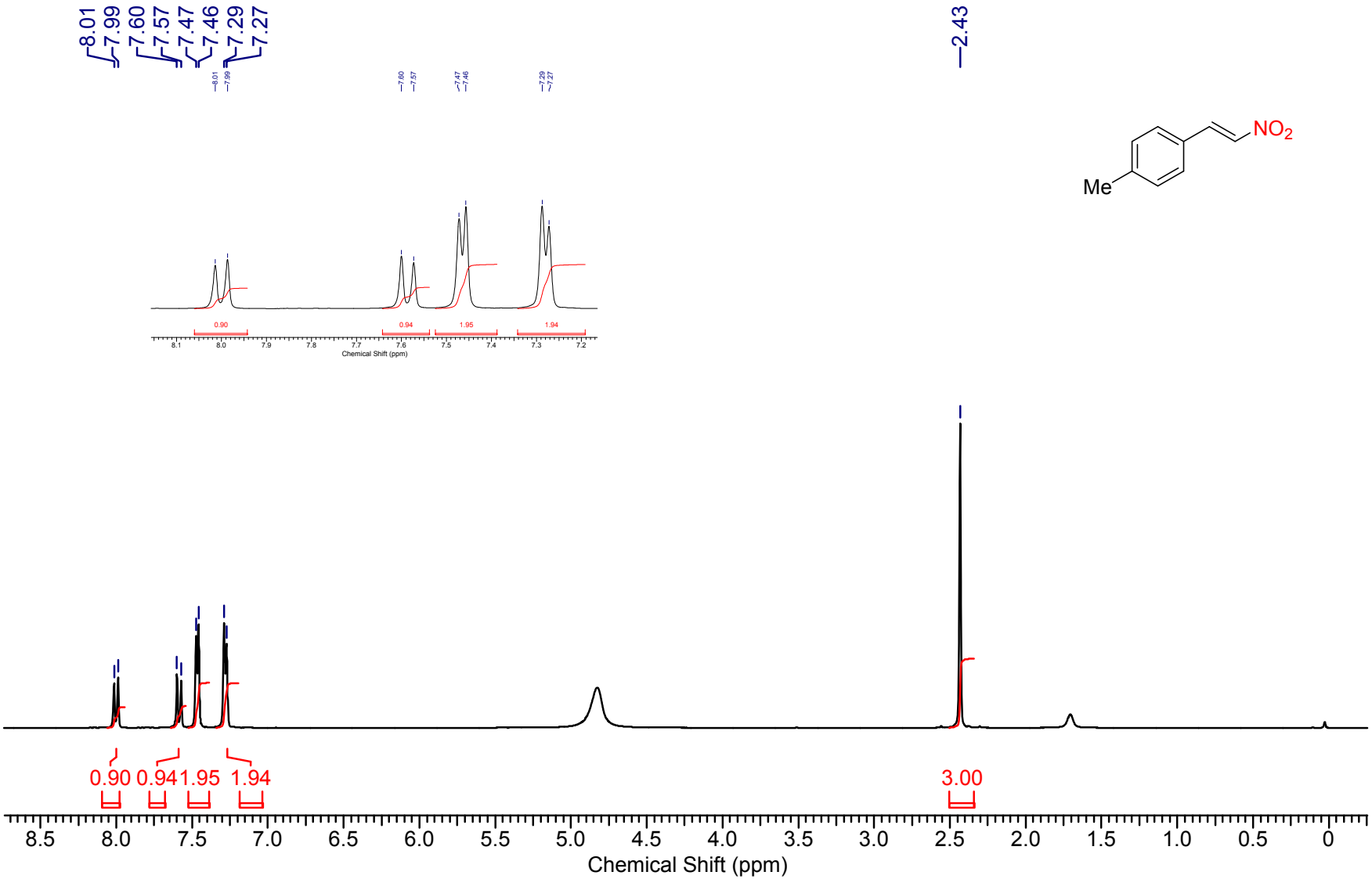


Figure S8a. ^{1}H NMR of **1b**

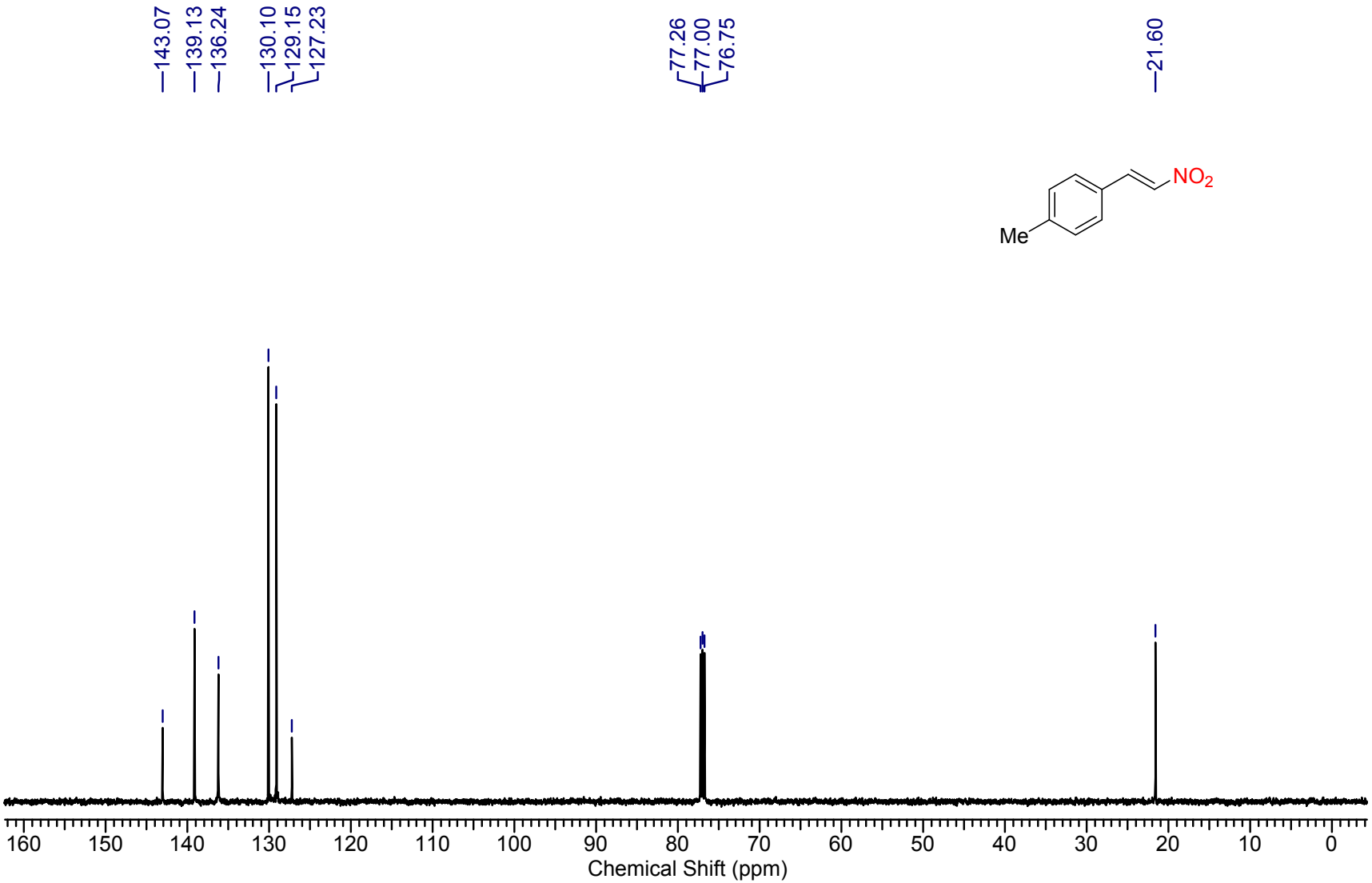


Figure S8b. ^{13}C NMR of **1b**

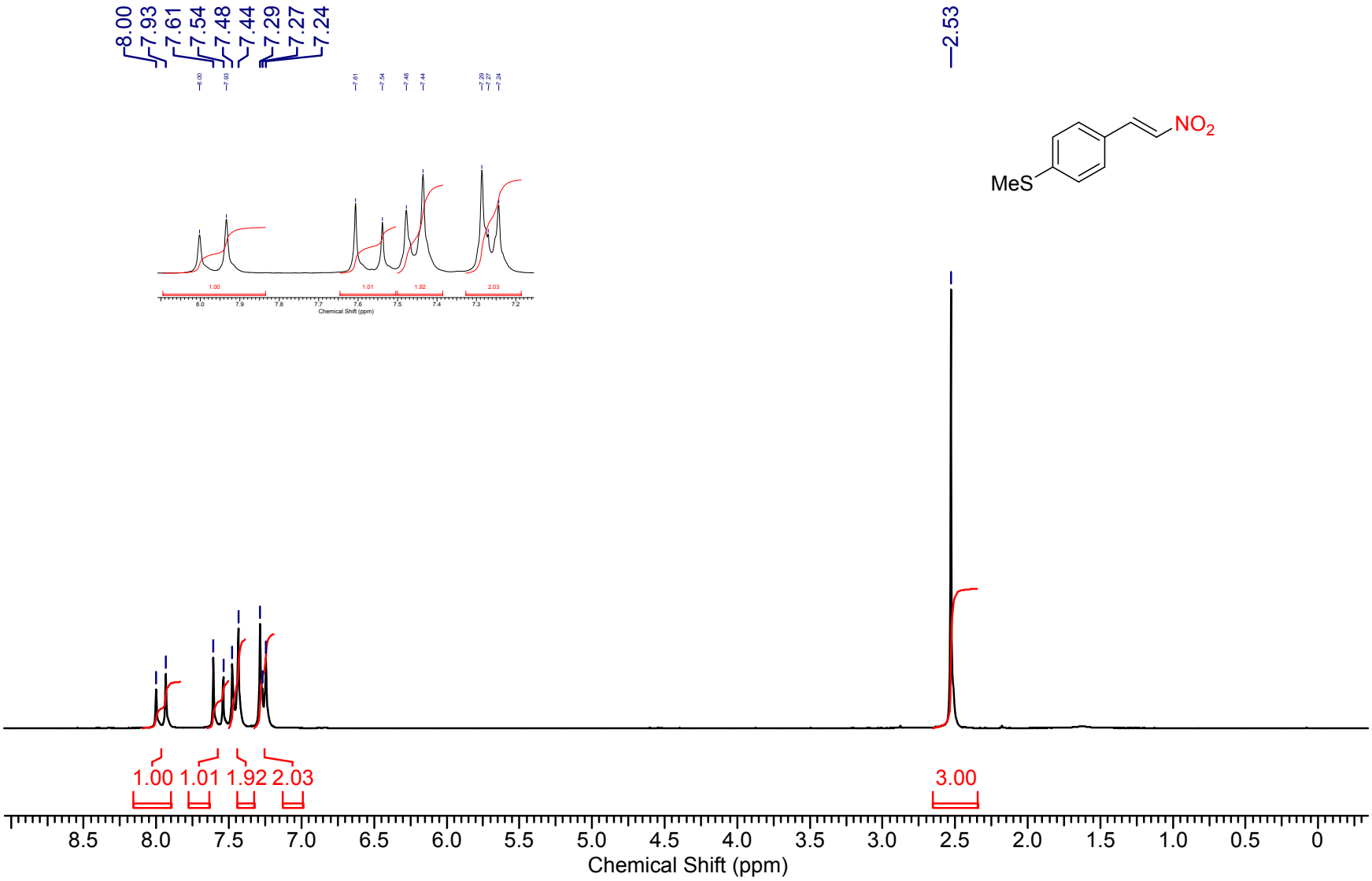


Figure S9a. ^{1}H NMR of **1c**

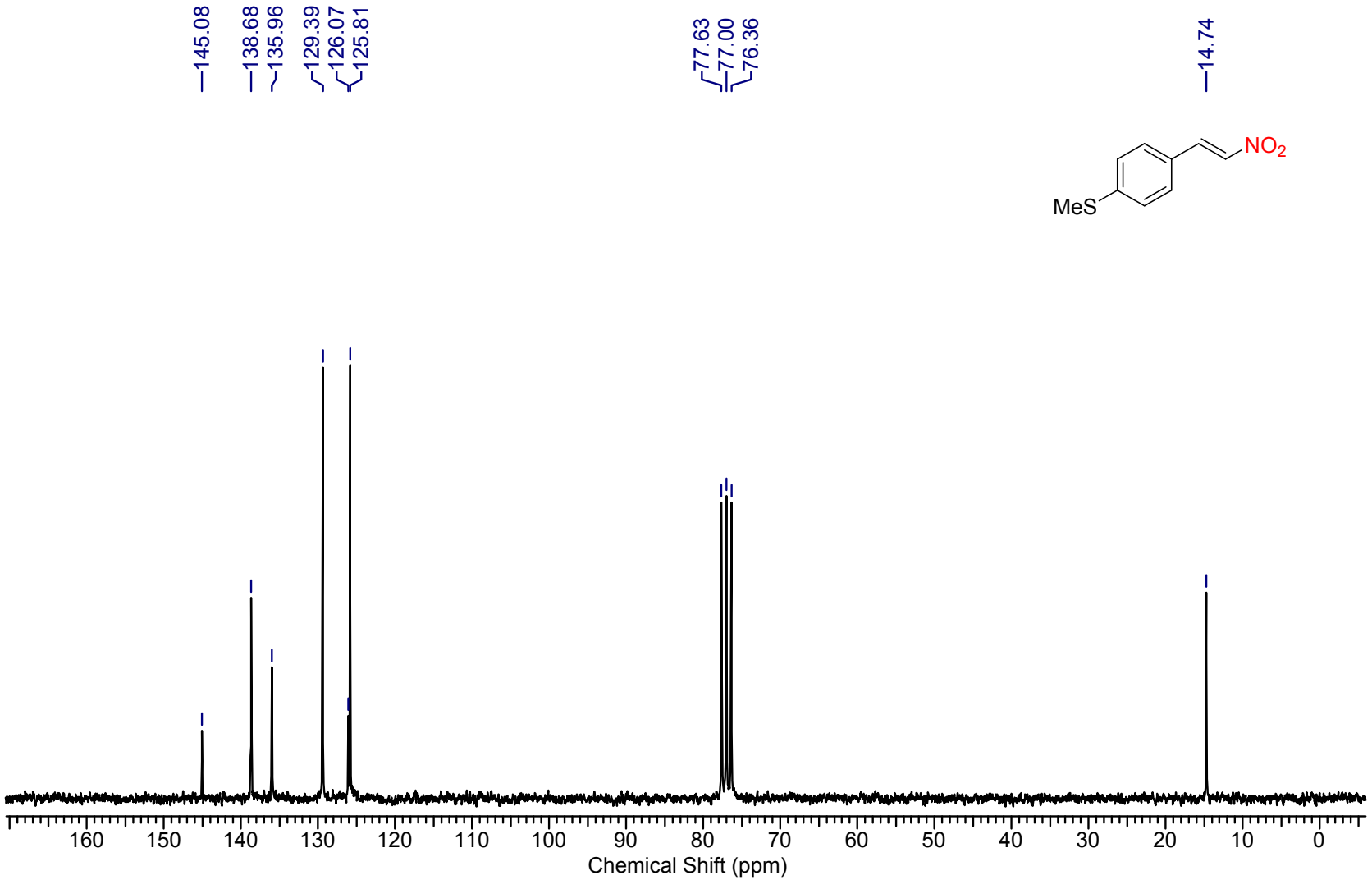


Figure S9b. ^{13}C NMR of **1c**

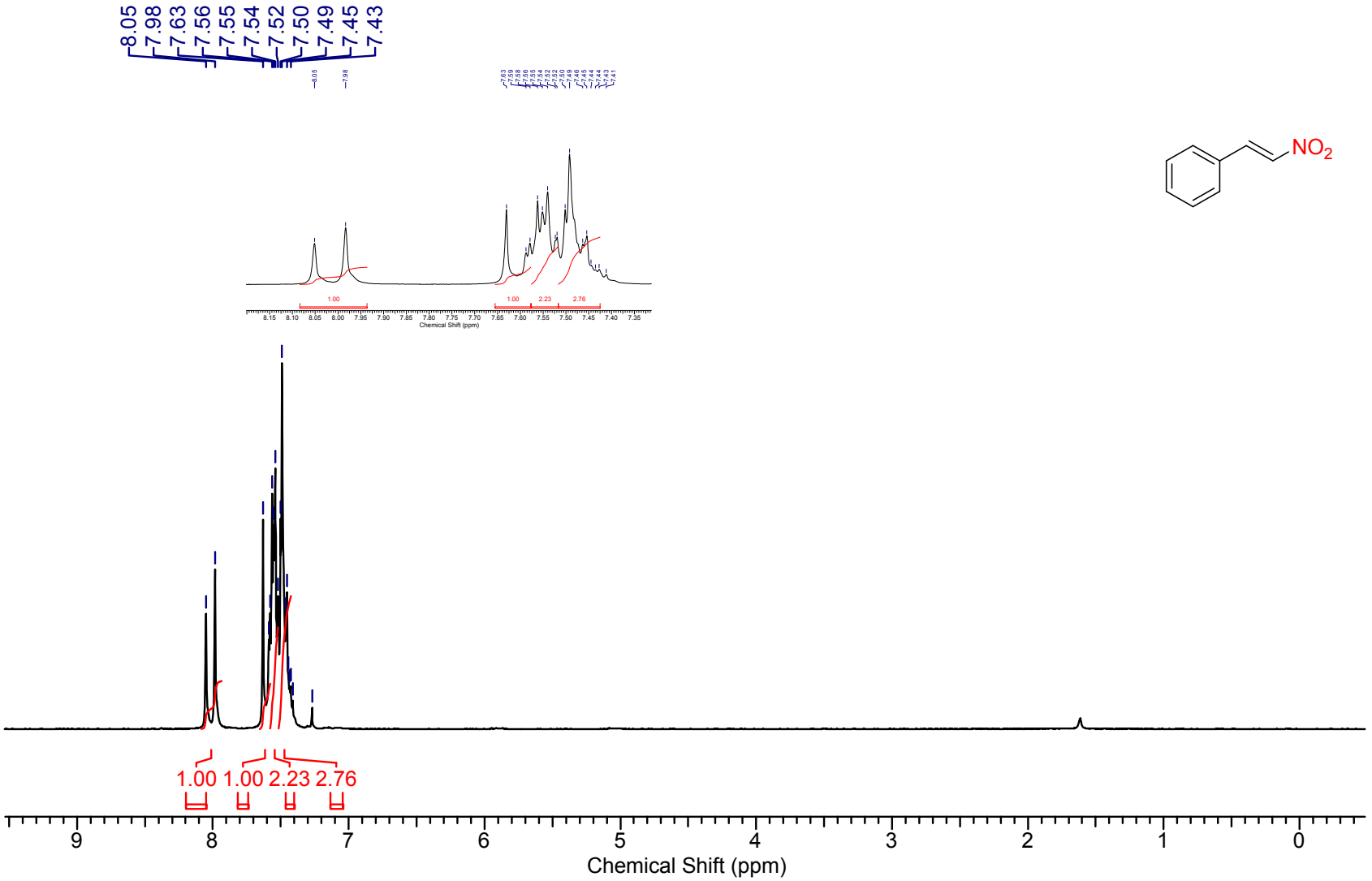


Figure S10a. ^{1}H NMR of **1d**

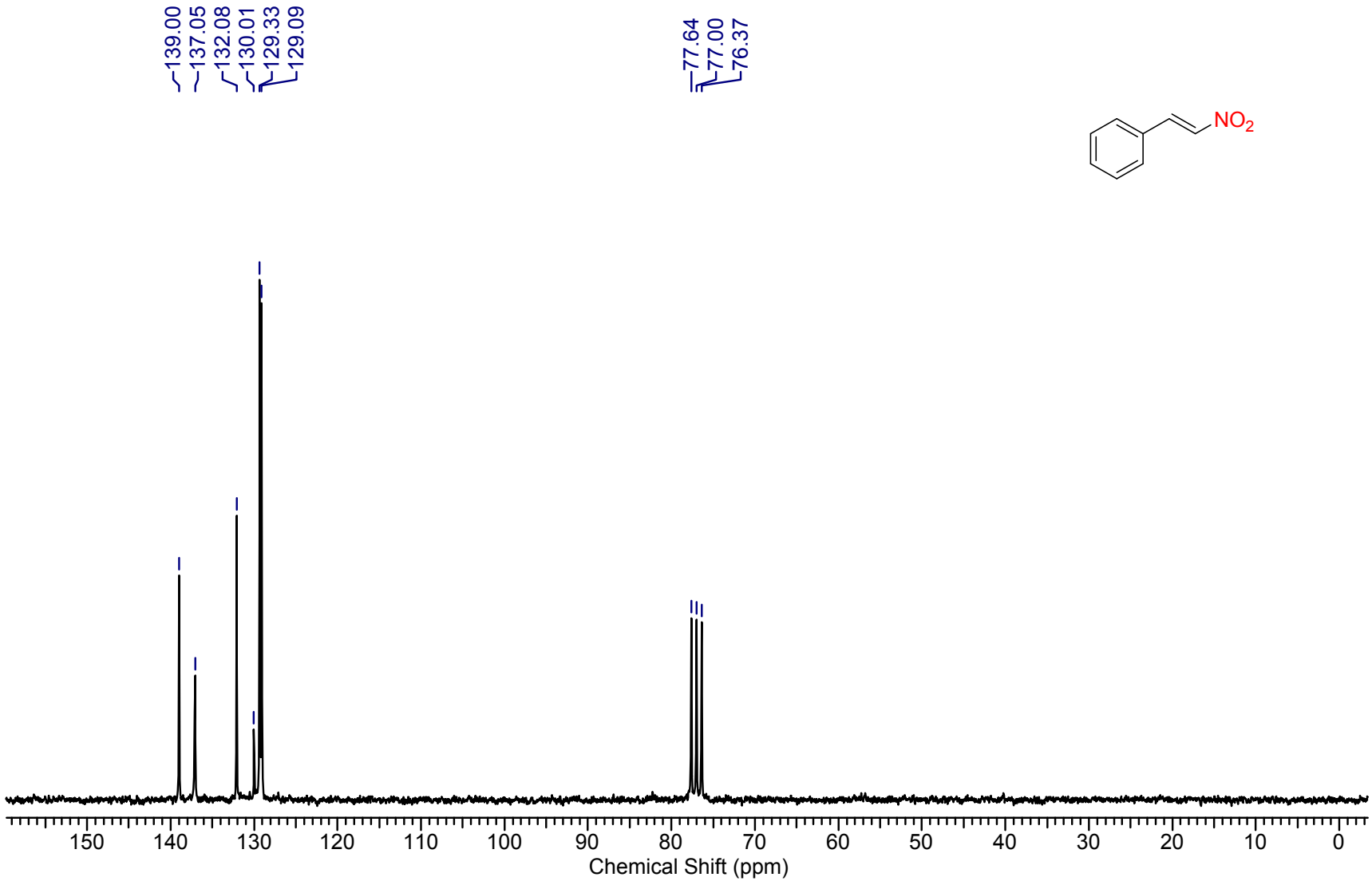


Figure S10b. ^{13}C NMR of **1d**

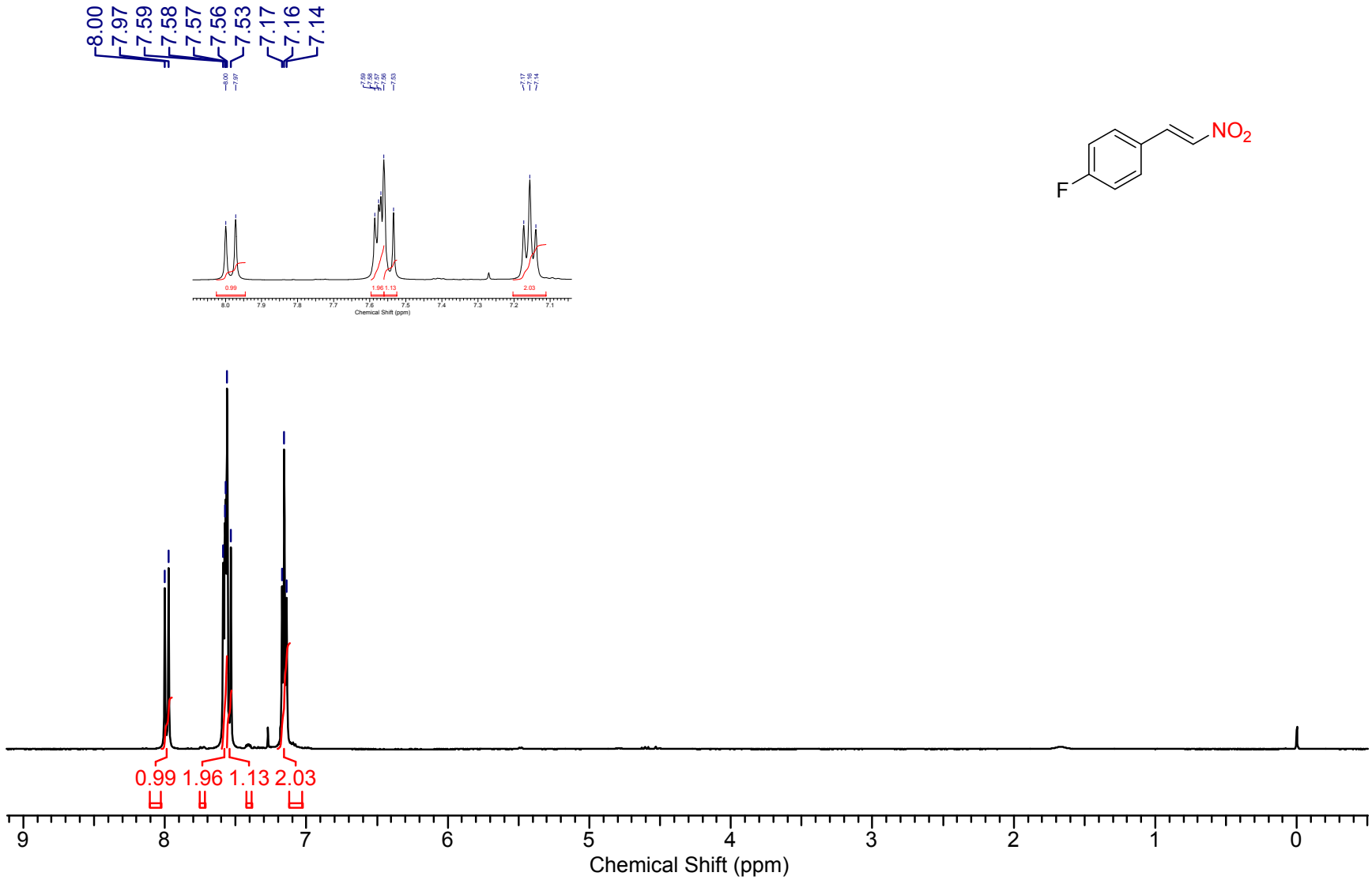


Figure S11a. ^{1}H NMR of **1e**

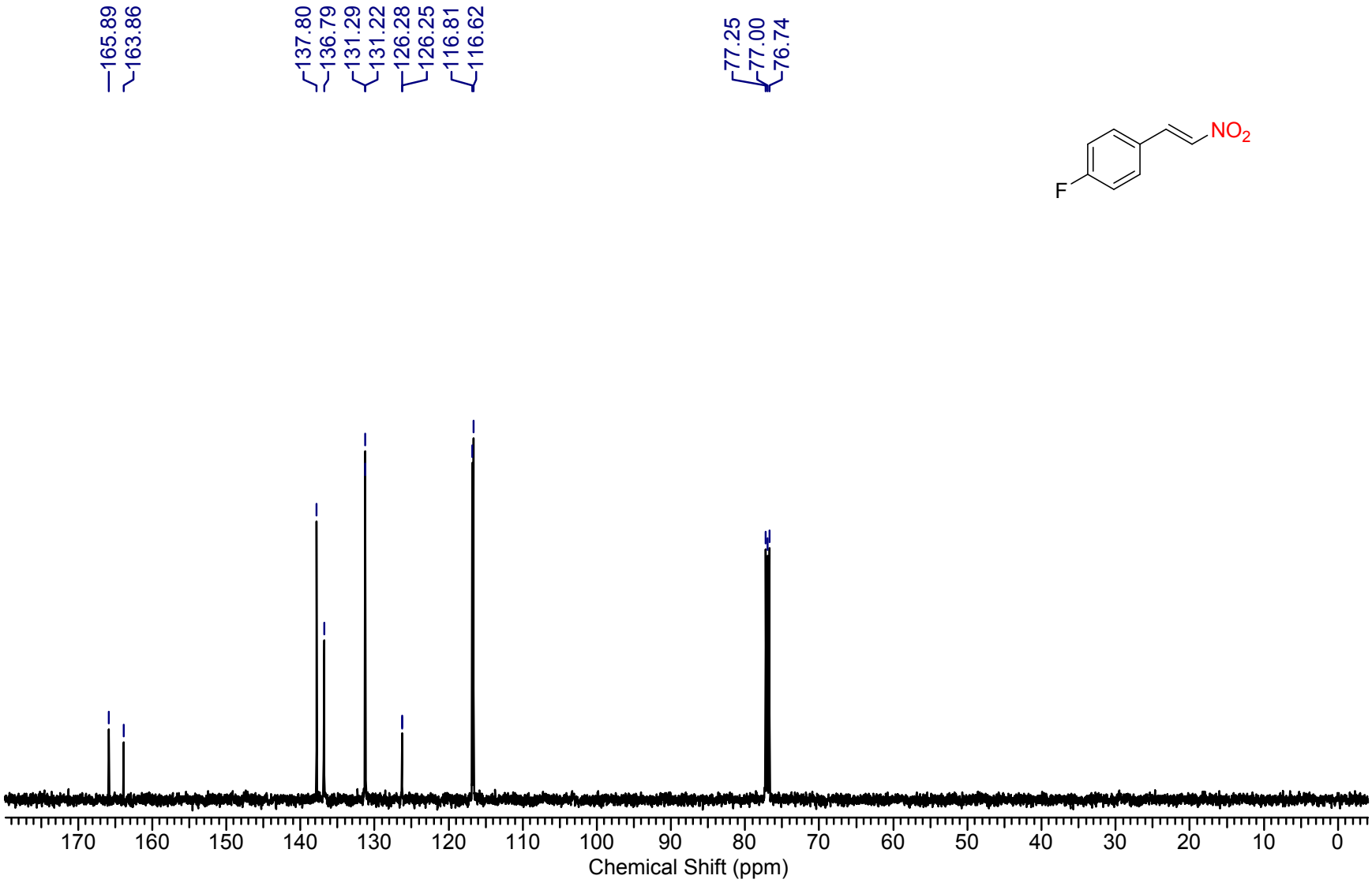


Figure S11b. ^{13}C NMR of **1e**

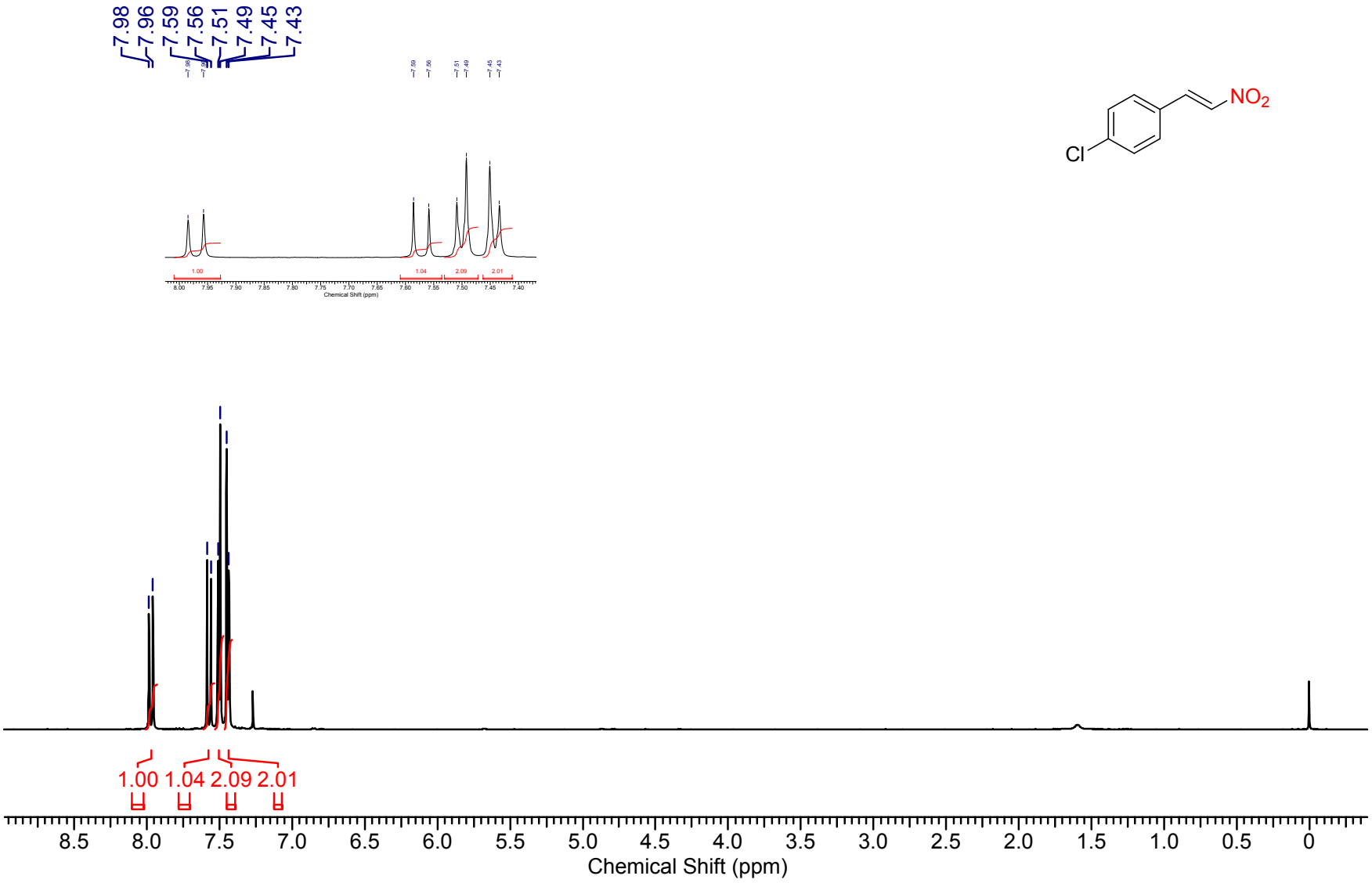


Figure S12a. ^{1}H NMR of **1f**

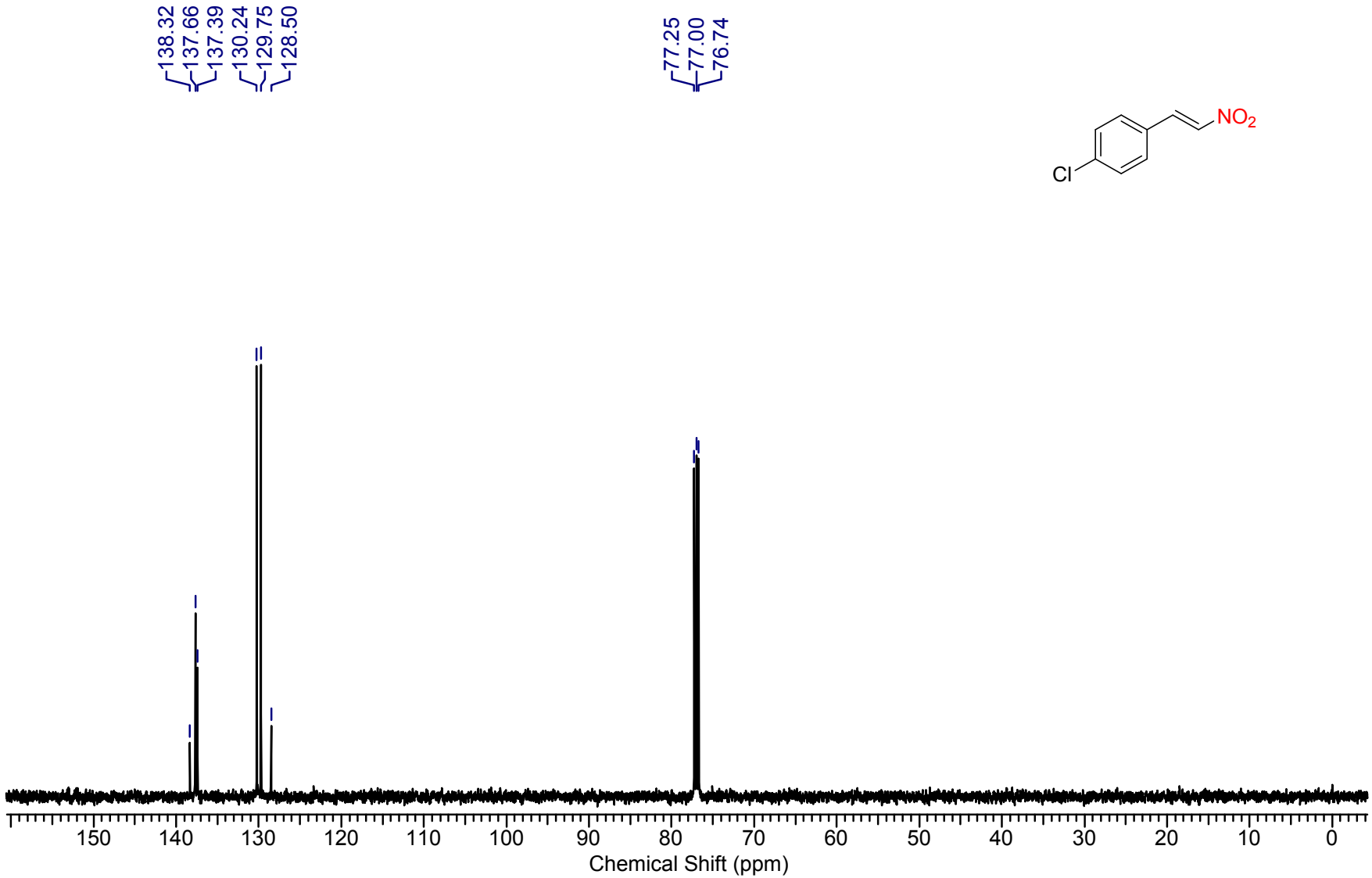


Figure S12b. ^{13}C NMR of **1f**

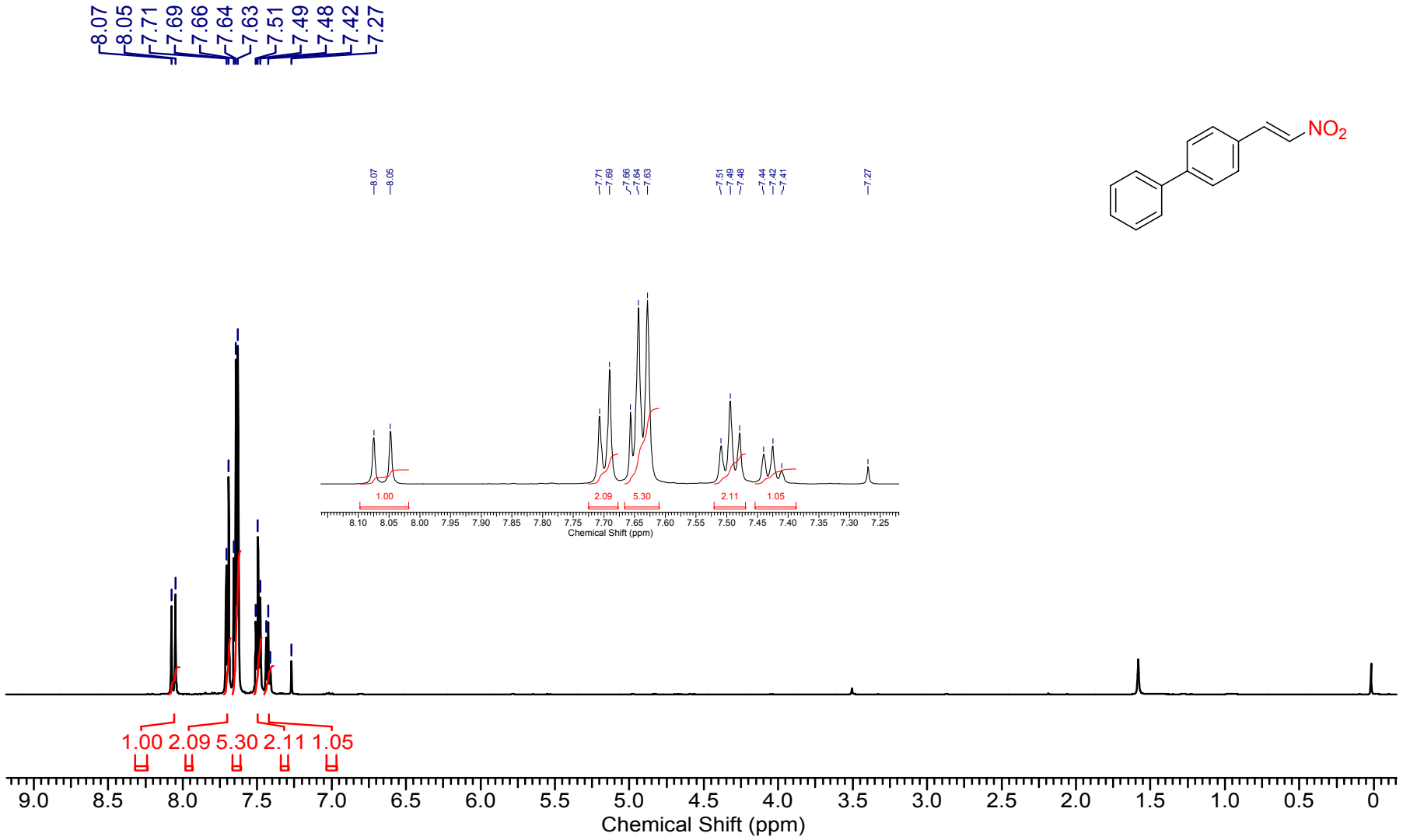


Figure S13a. ^{1}H NMR of **1g**

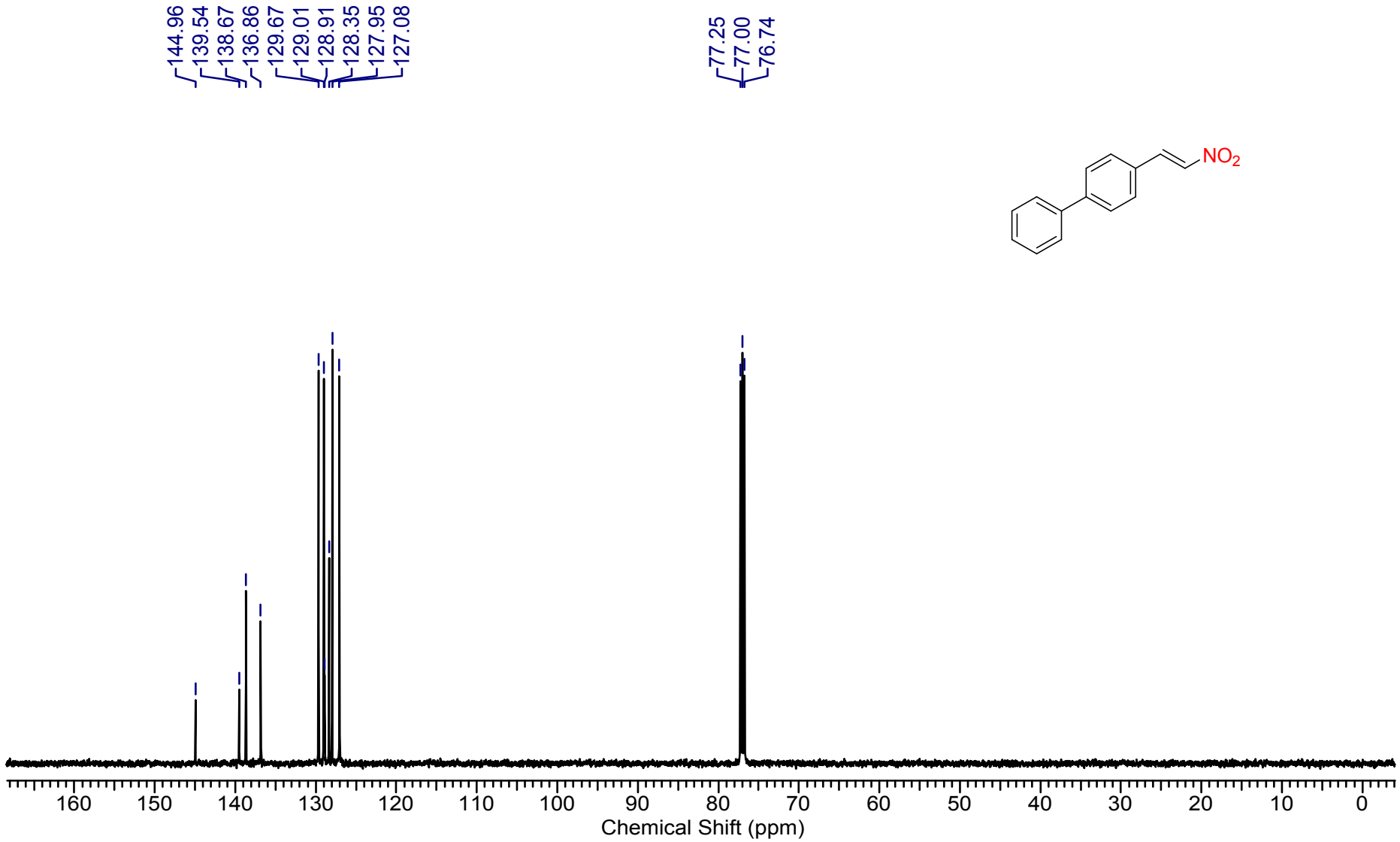


Figure S13b. ^{13}C NMR of **1g**

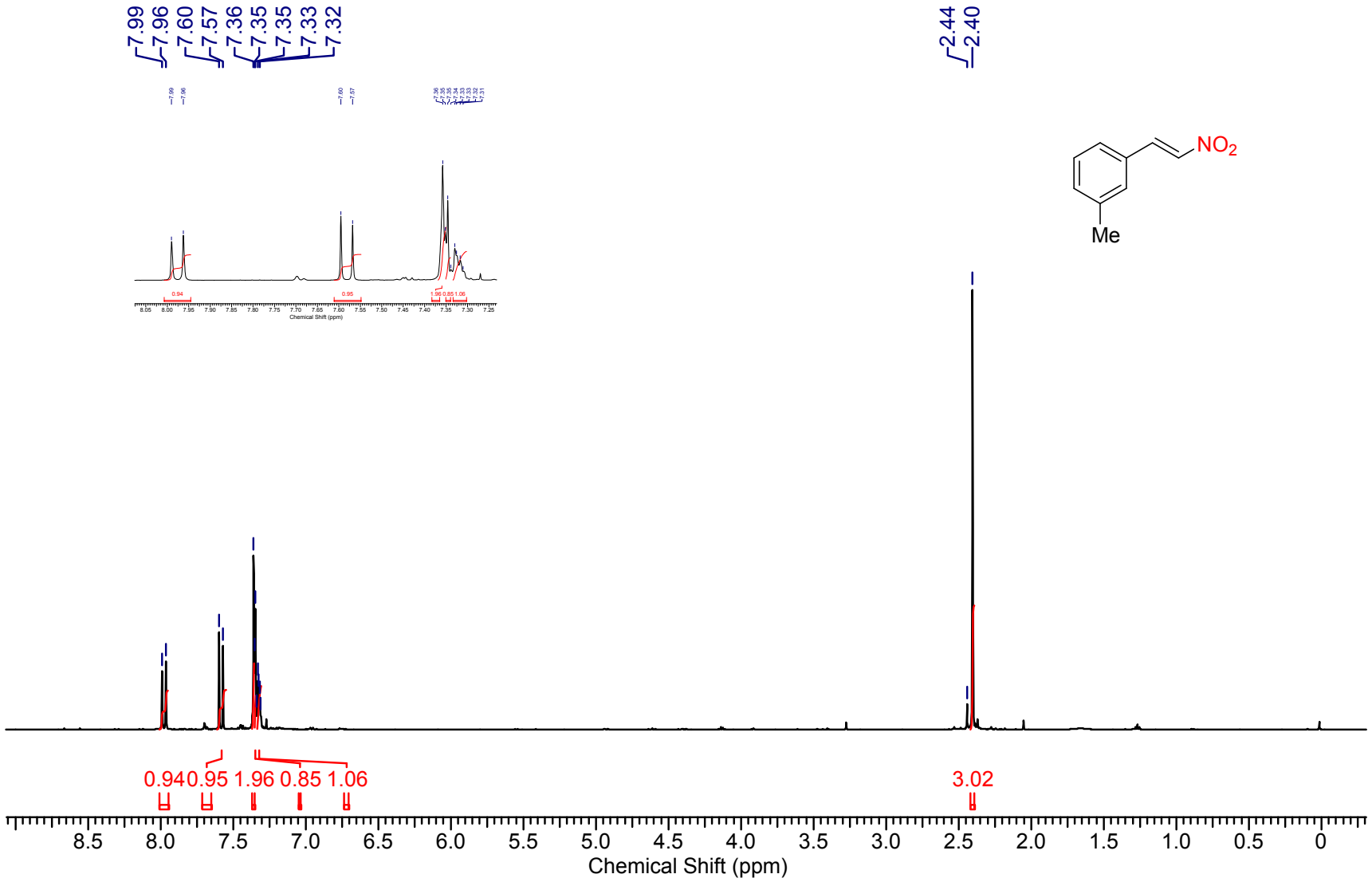


Figure S14a. ^{1}H NMR of **1i**

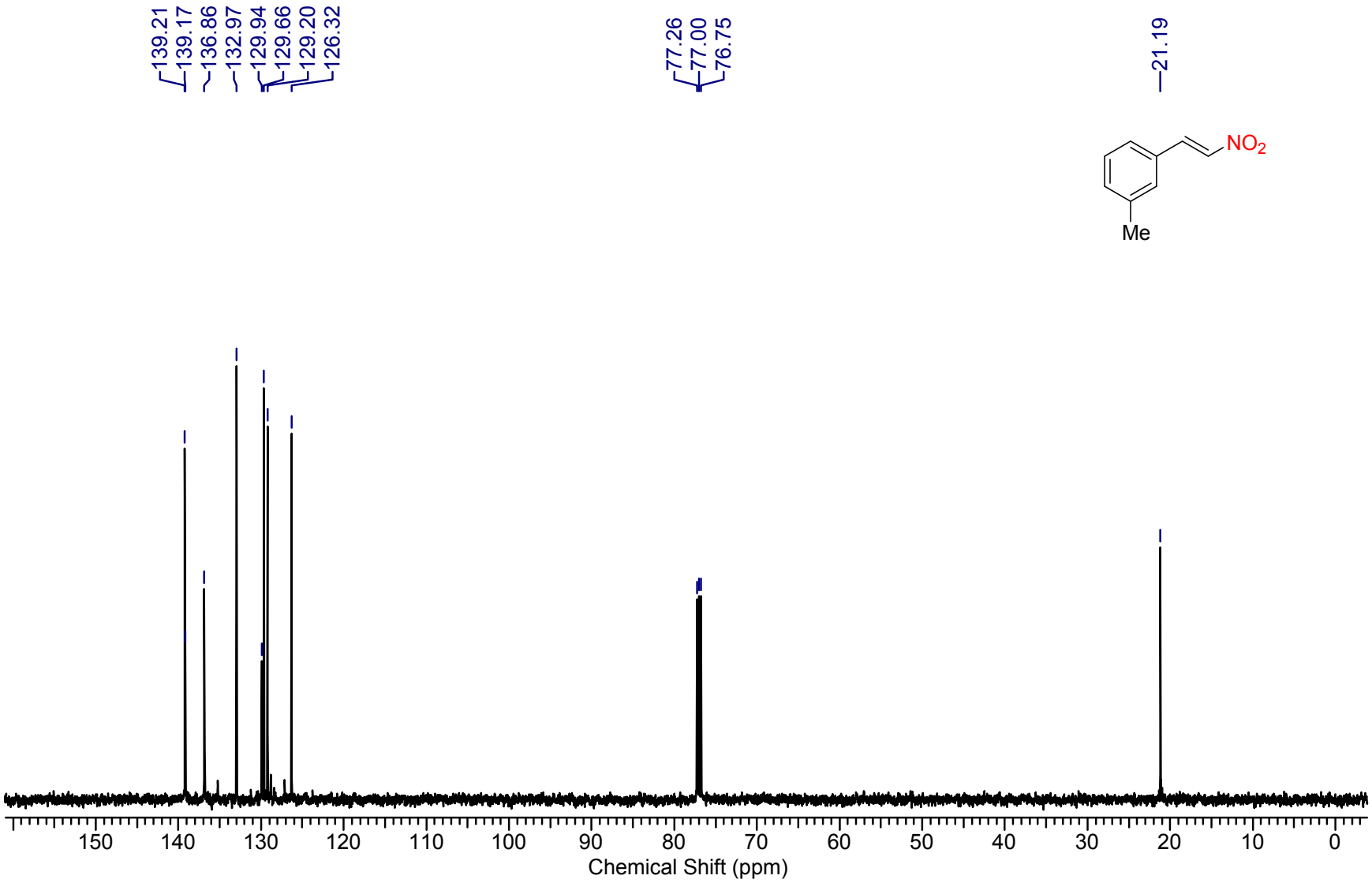


Figure S14b. ^{13}C NMR of **1i**

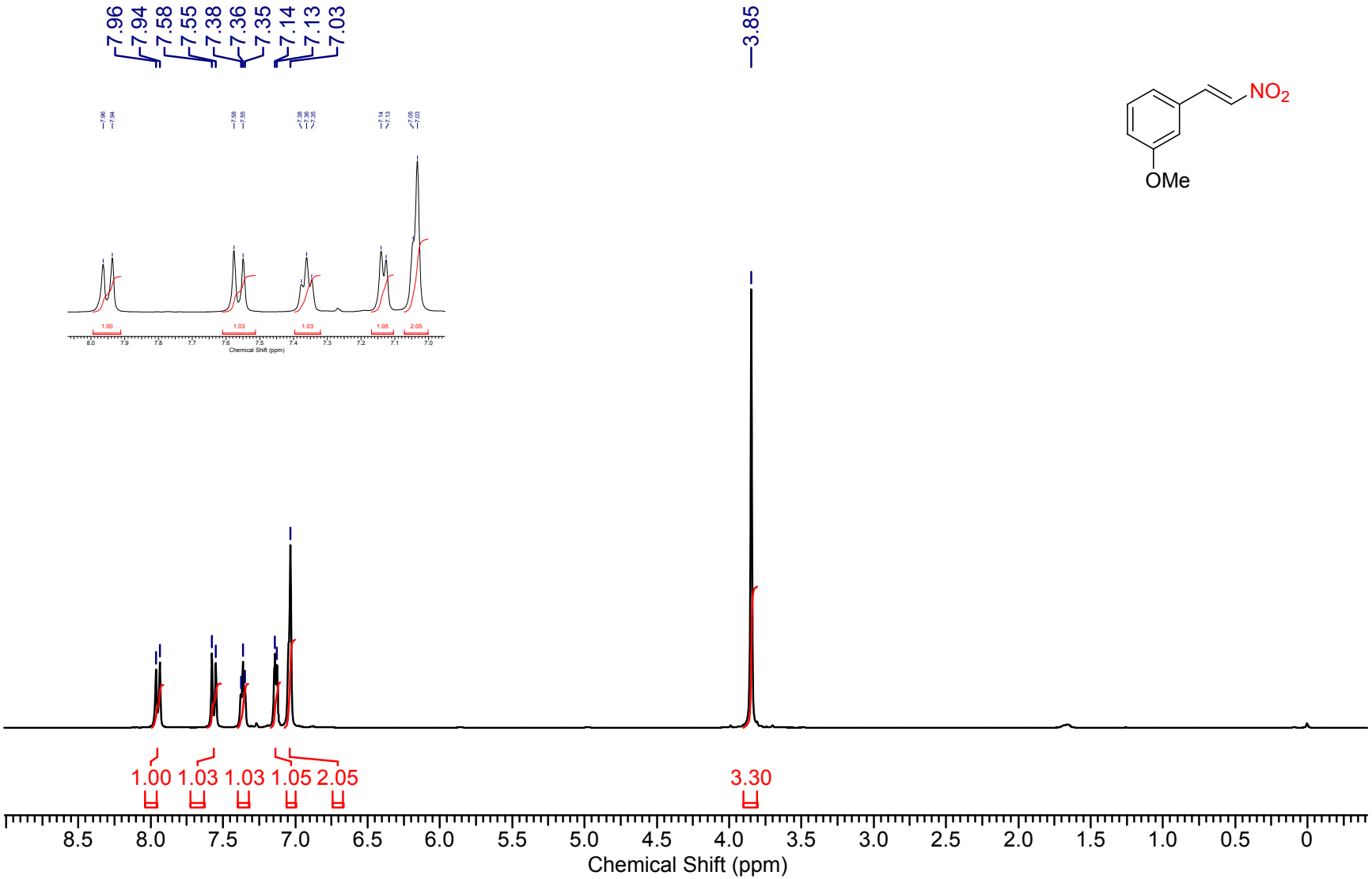


Figure S15a. ^{1}H NMR of **1j**

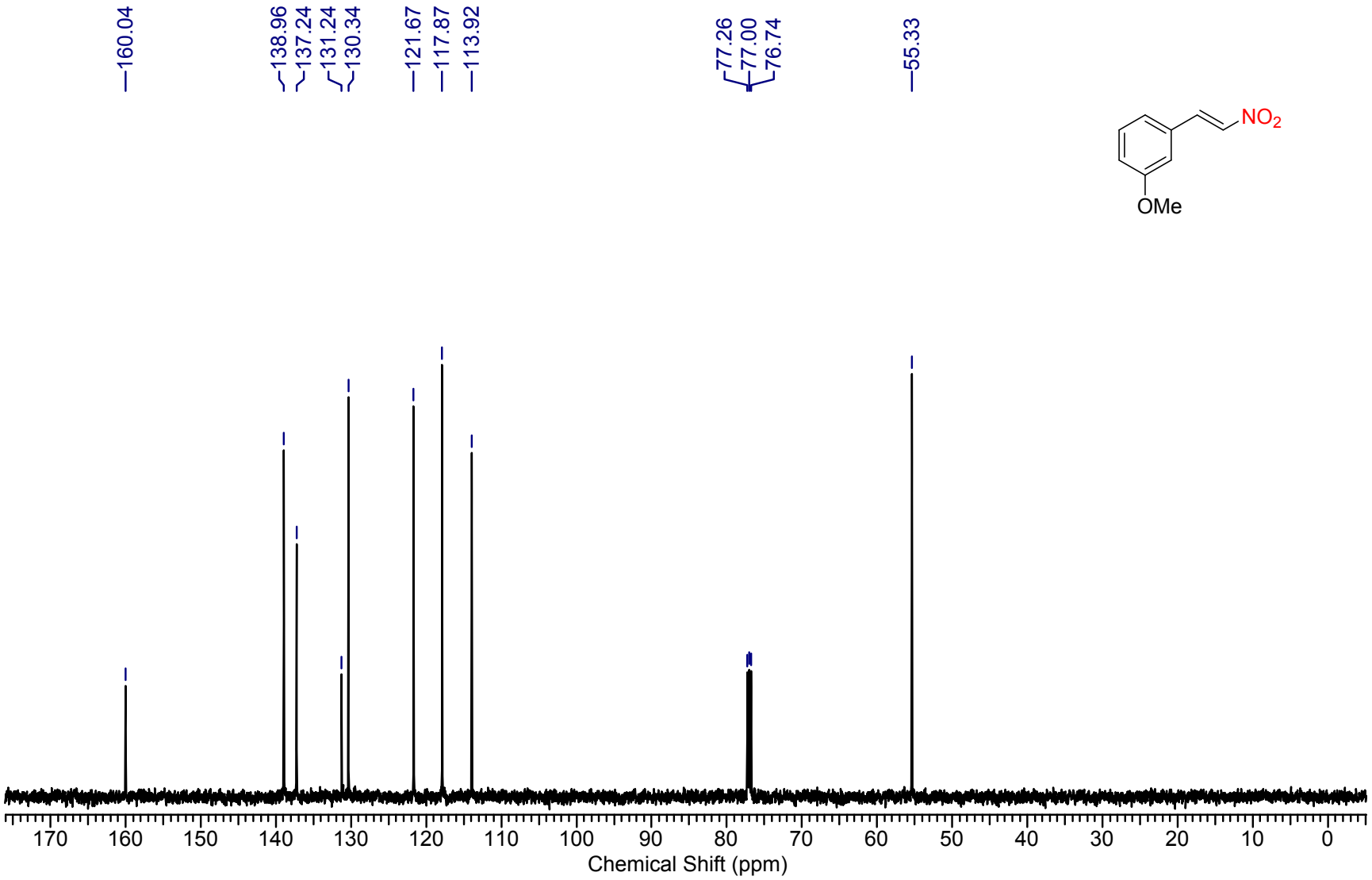


Figure S15b. ^{13}C NMR of **1j**

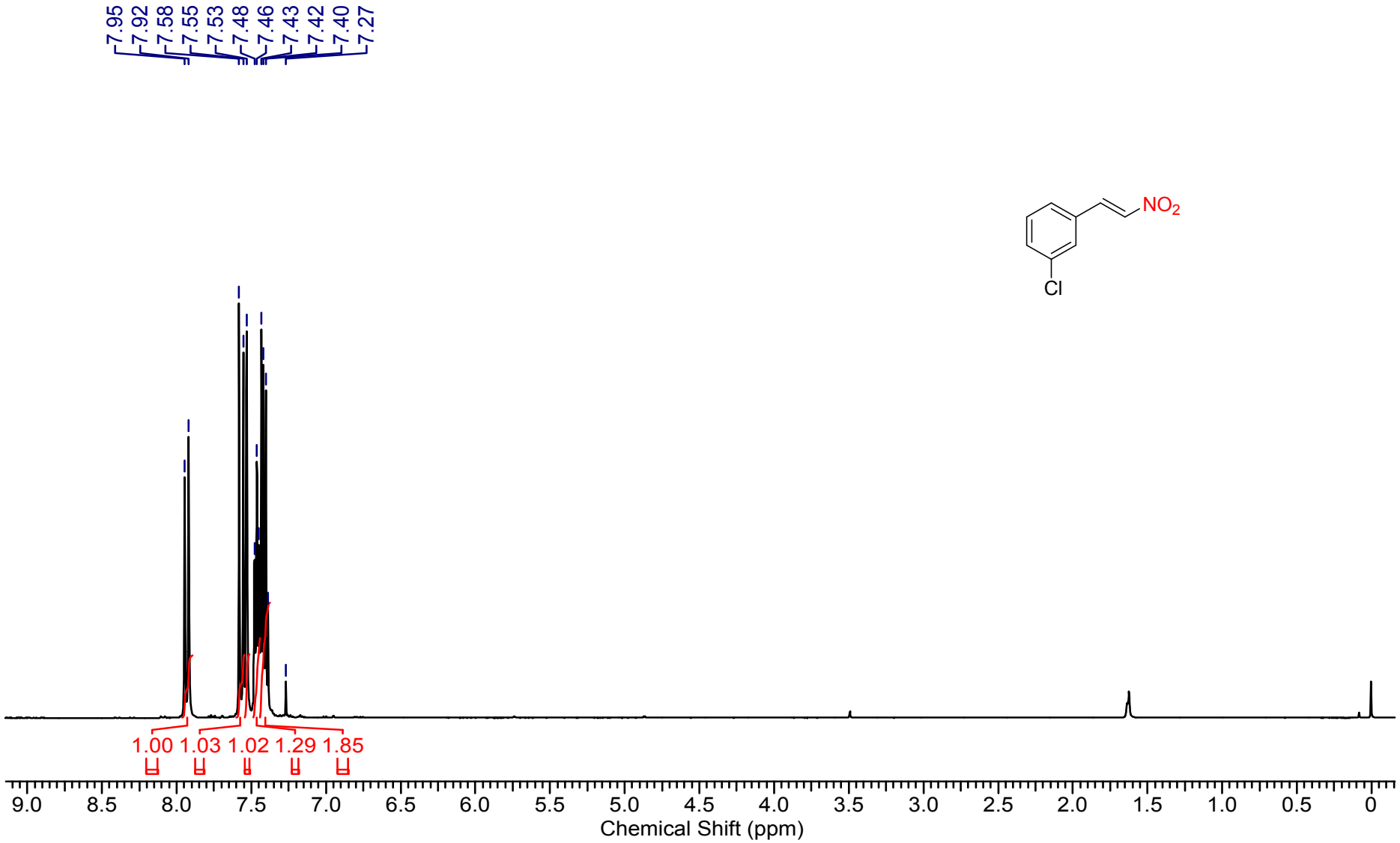


Figure S16a. ^{1}H NMR of **1k**

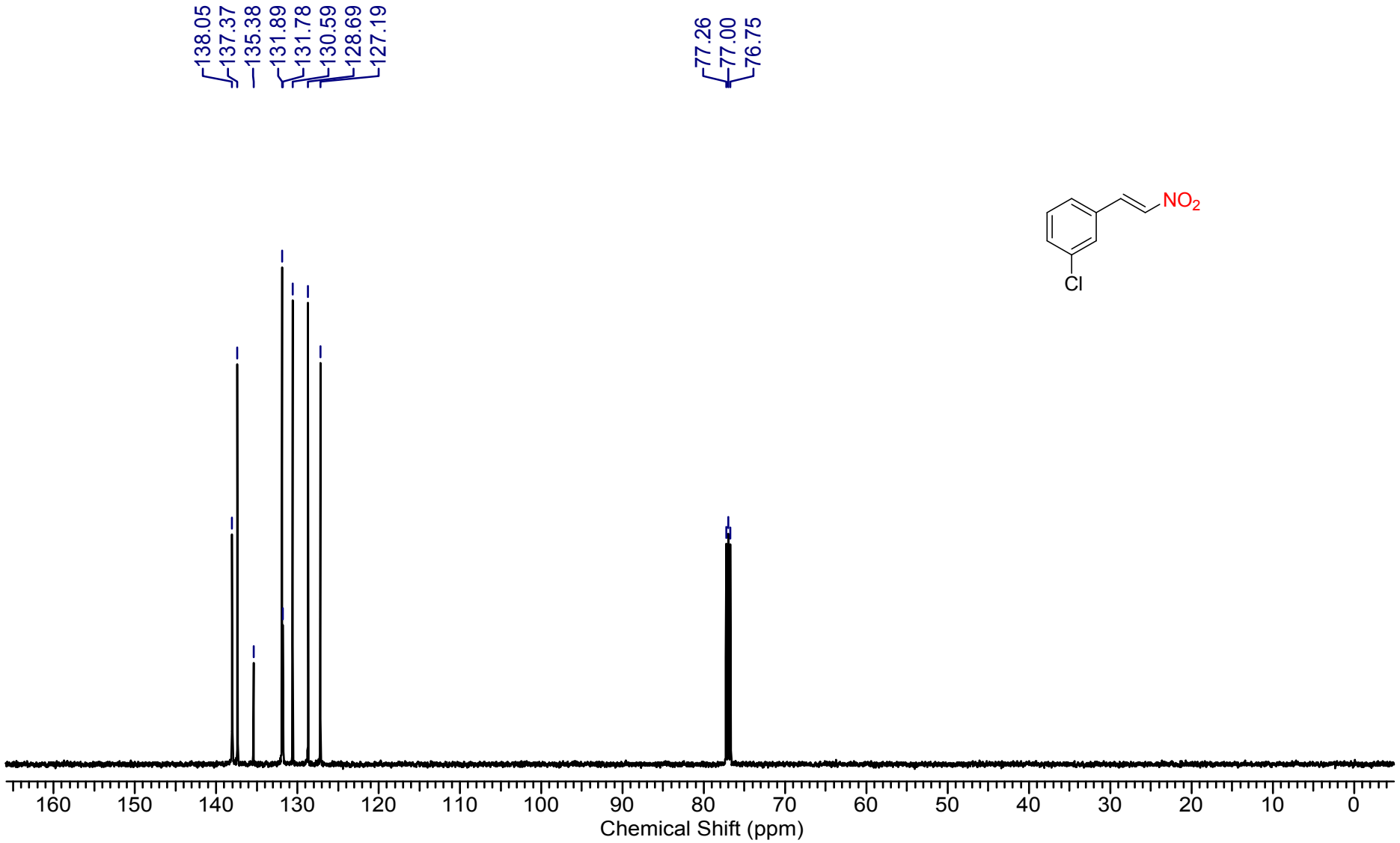


Figure S16b. ^{13}C NMR of **1k**

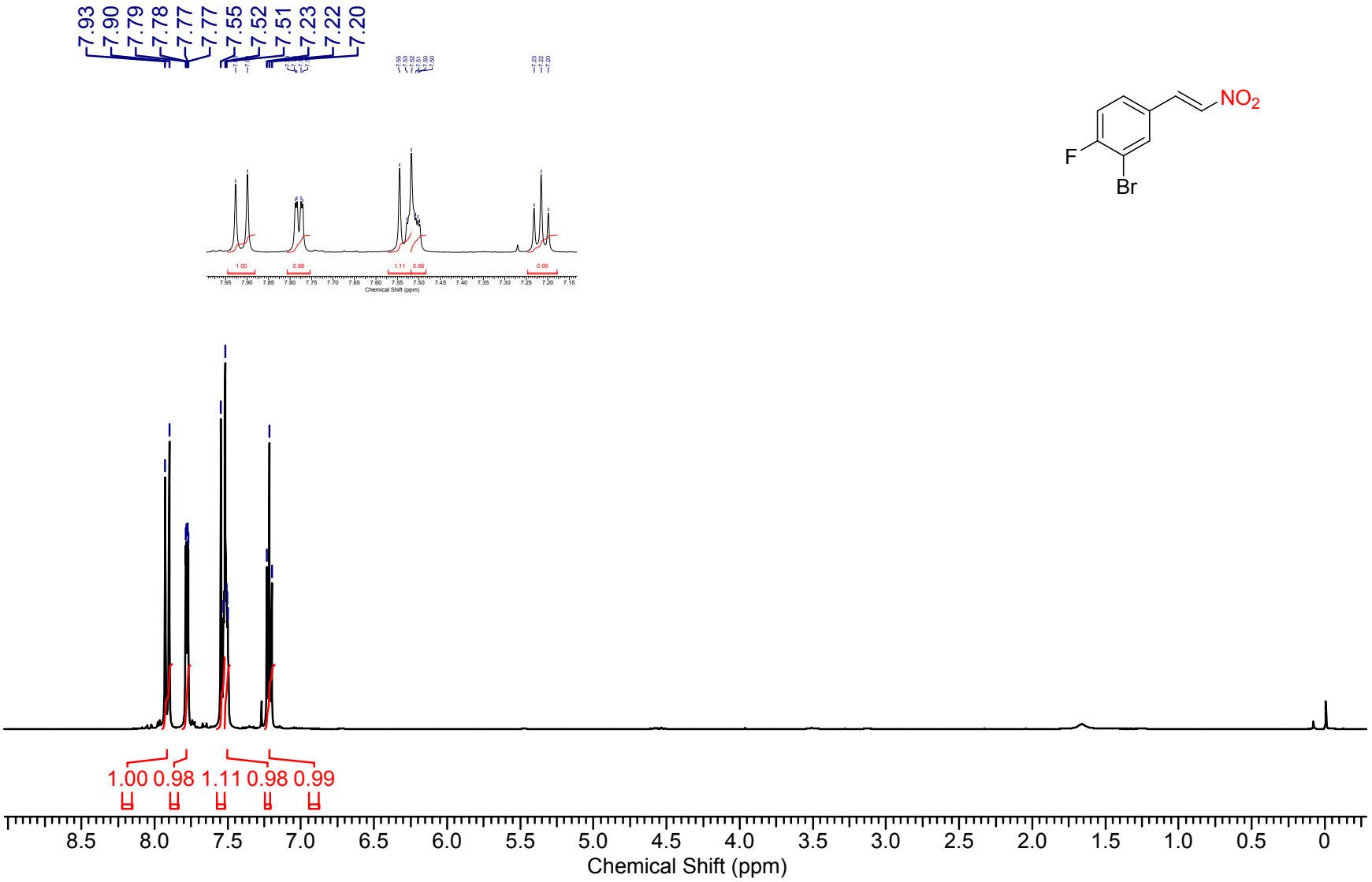


Figure S17a. ^{1}H NMR of **1l**

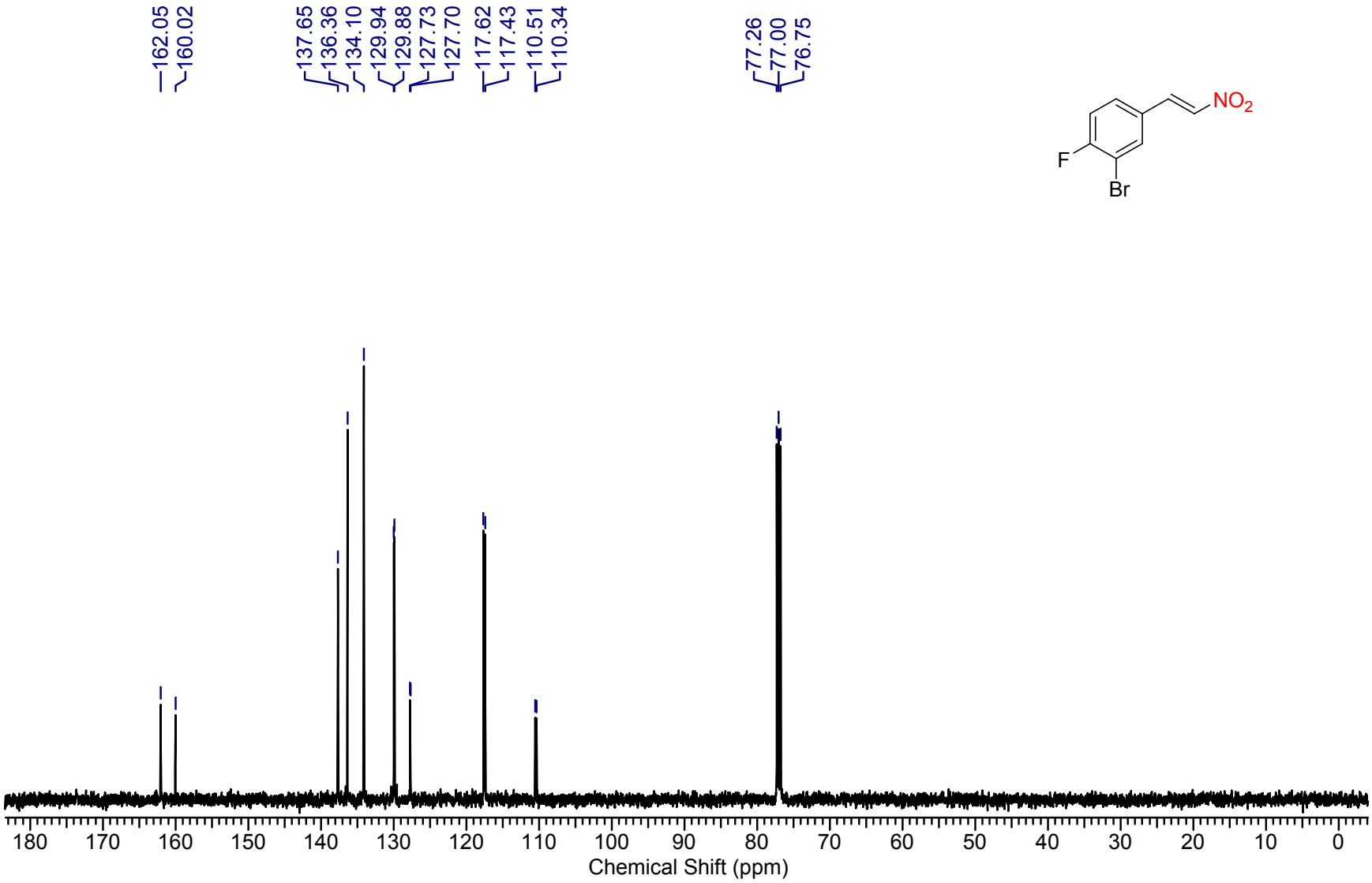


Figure S17b. ^{13}C NMR of **1l**

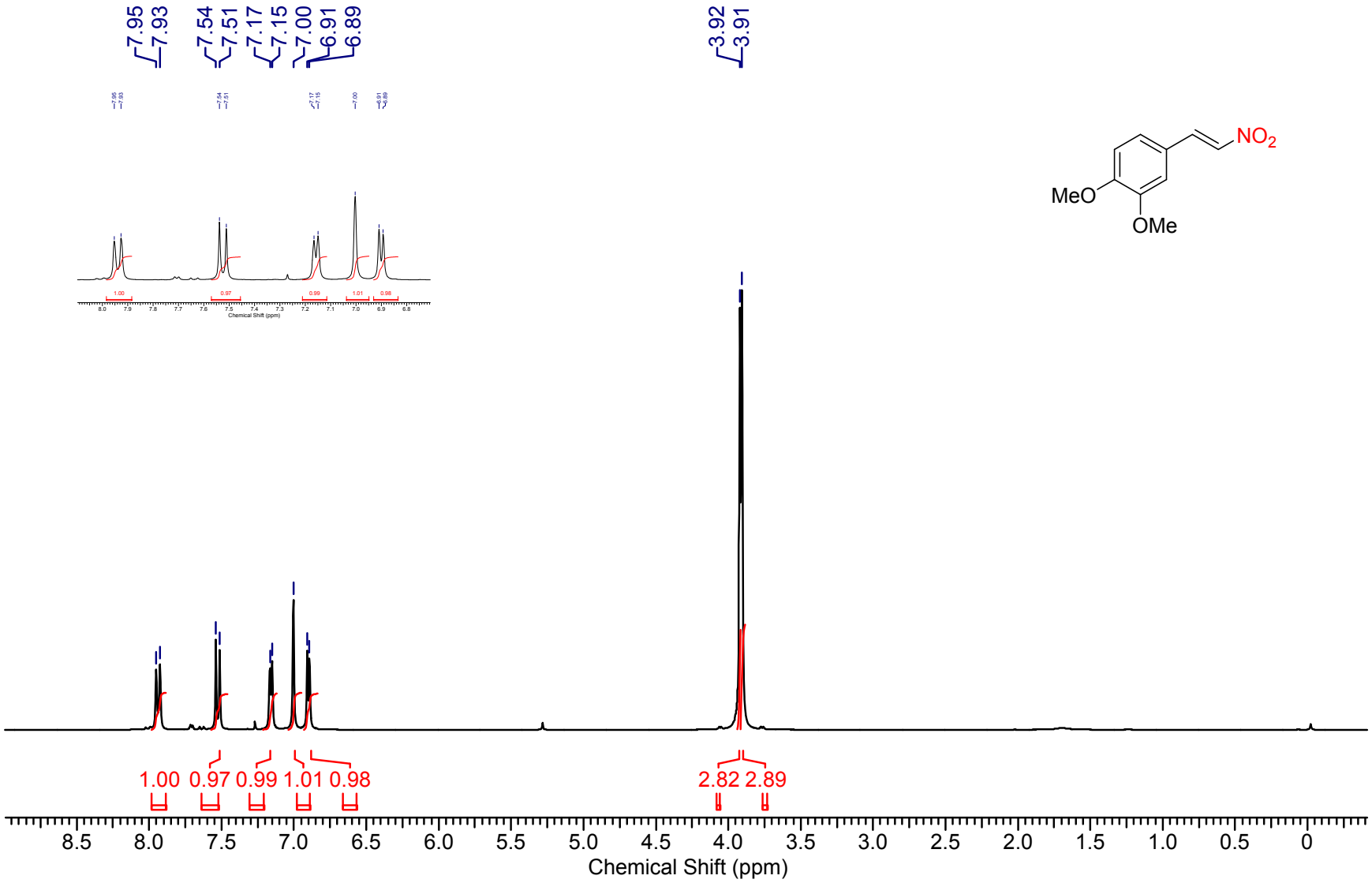


Figure S18a. ^{1}H NMR of **1m**

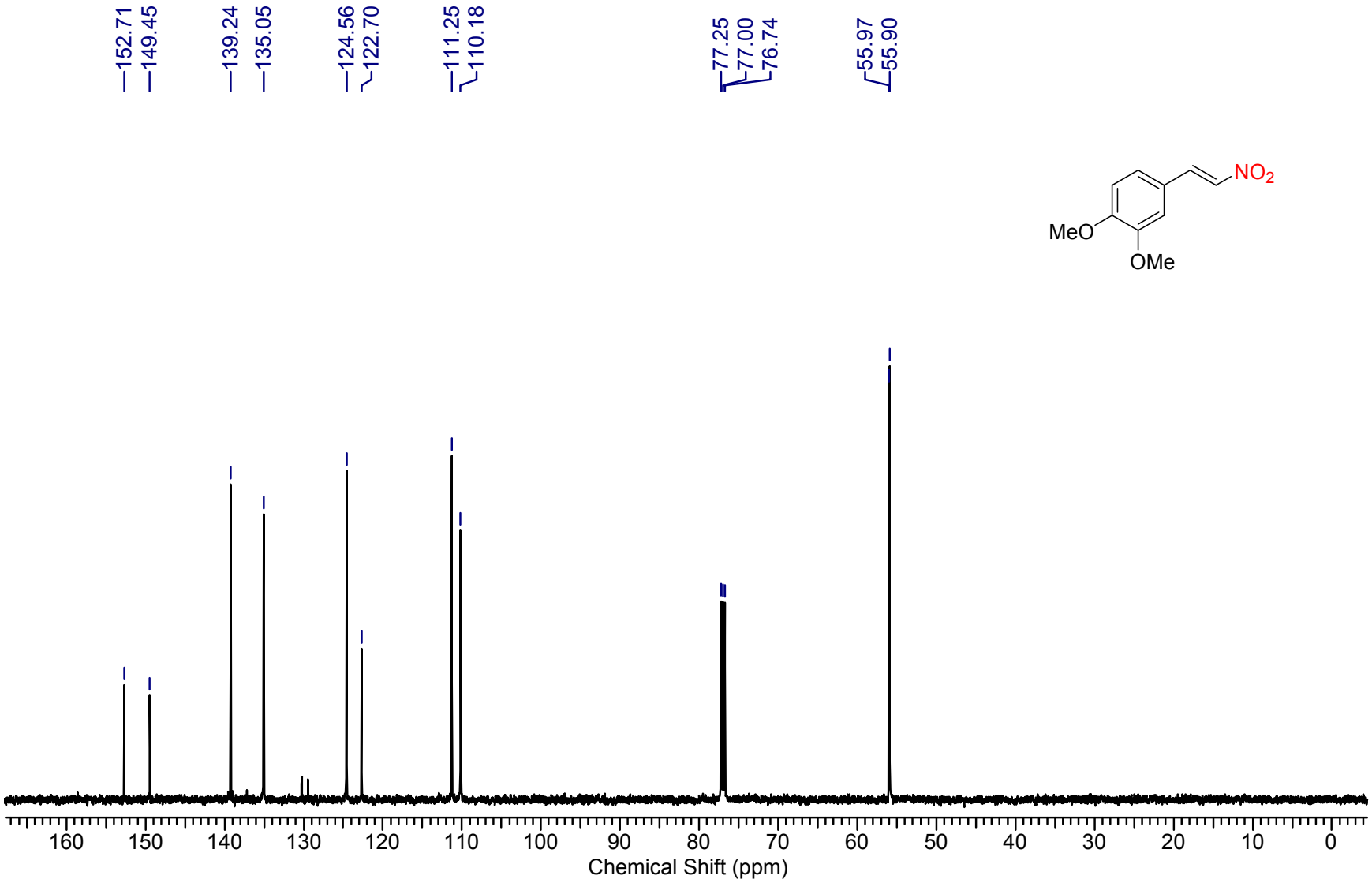


Figure S18b. ^{13}C NMR of **1m**

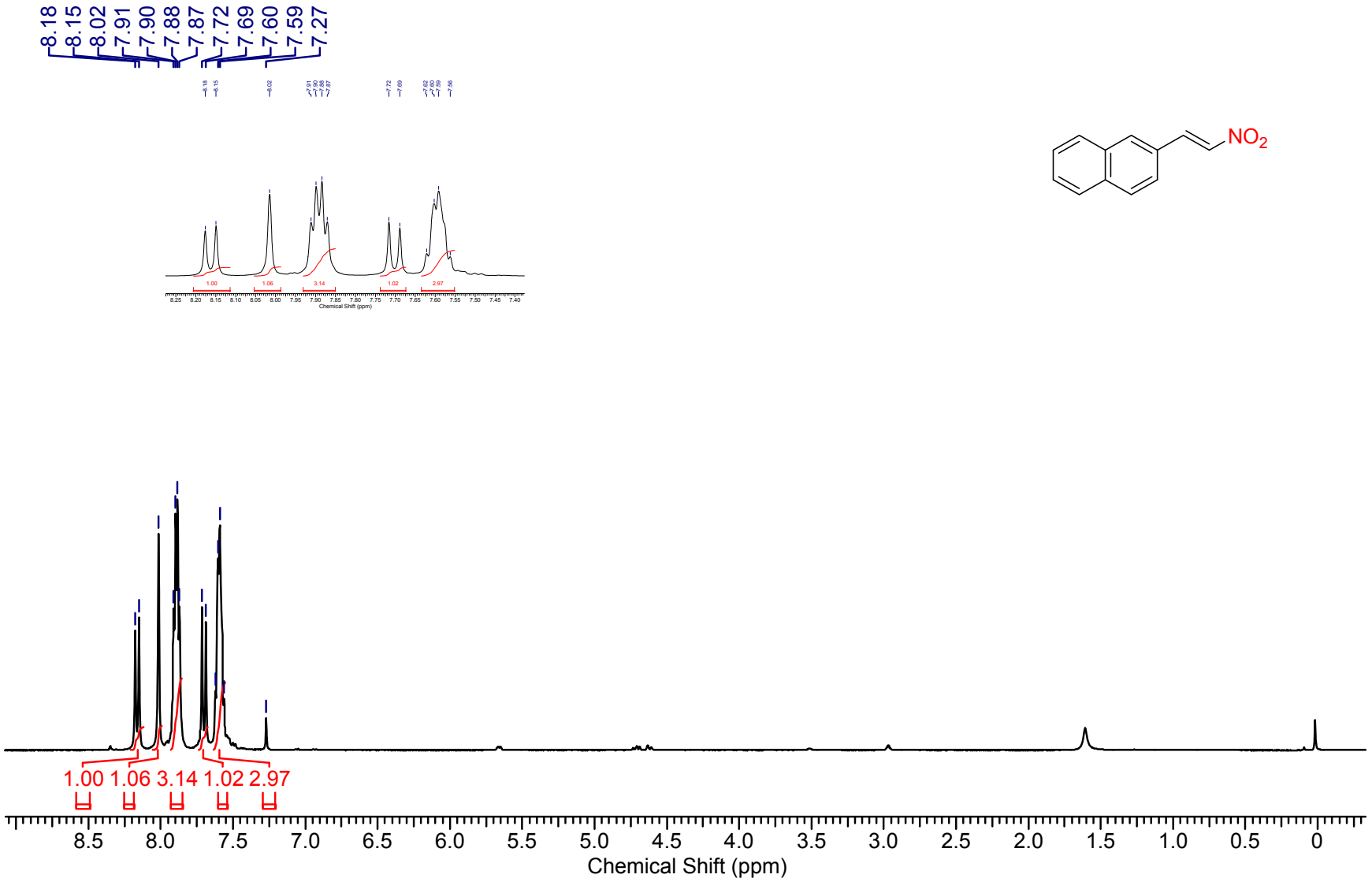


Figure S19a. ^{1}H NMR of **1n**

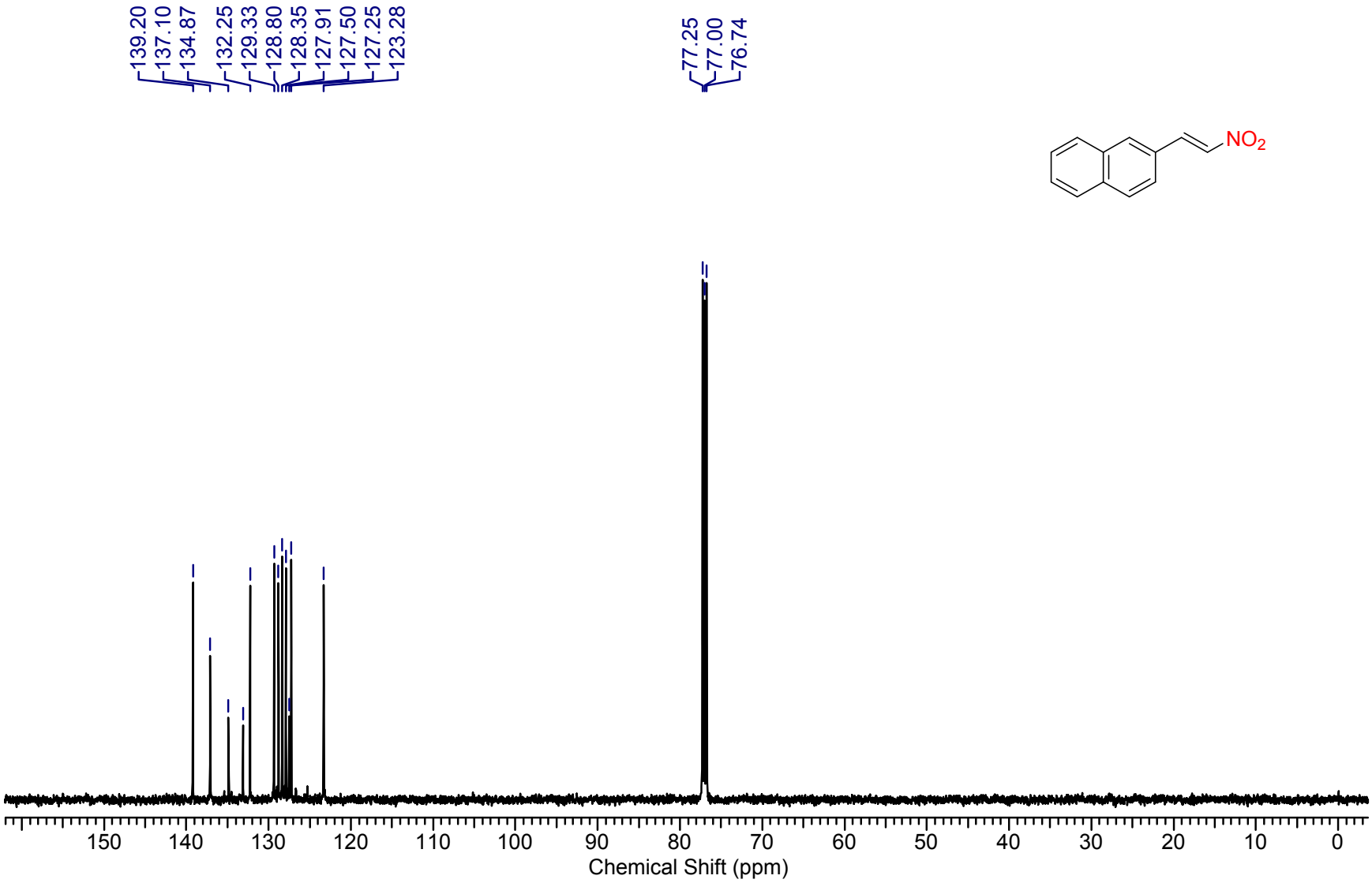


Figure S19b. ^{13}C NMR of **1n**

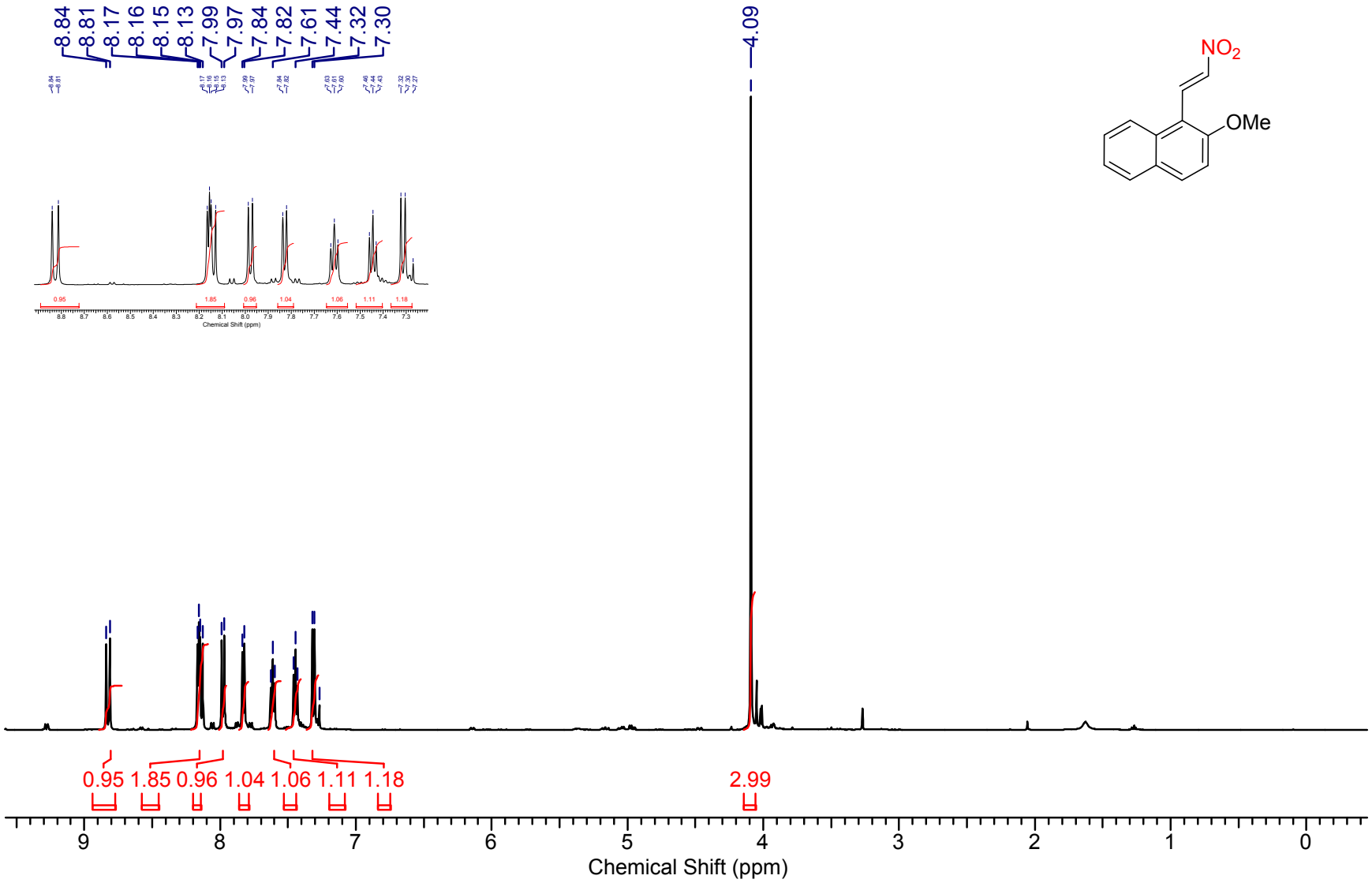


Figure S20a. ^{1}H NMR of **1o**

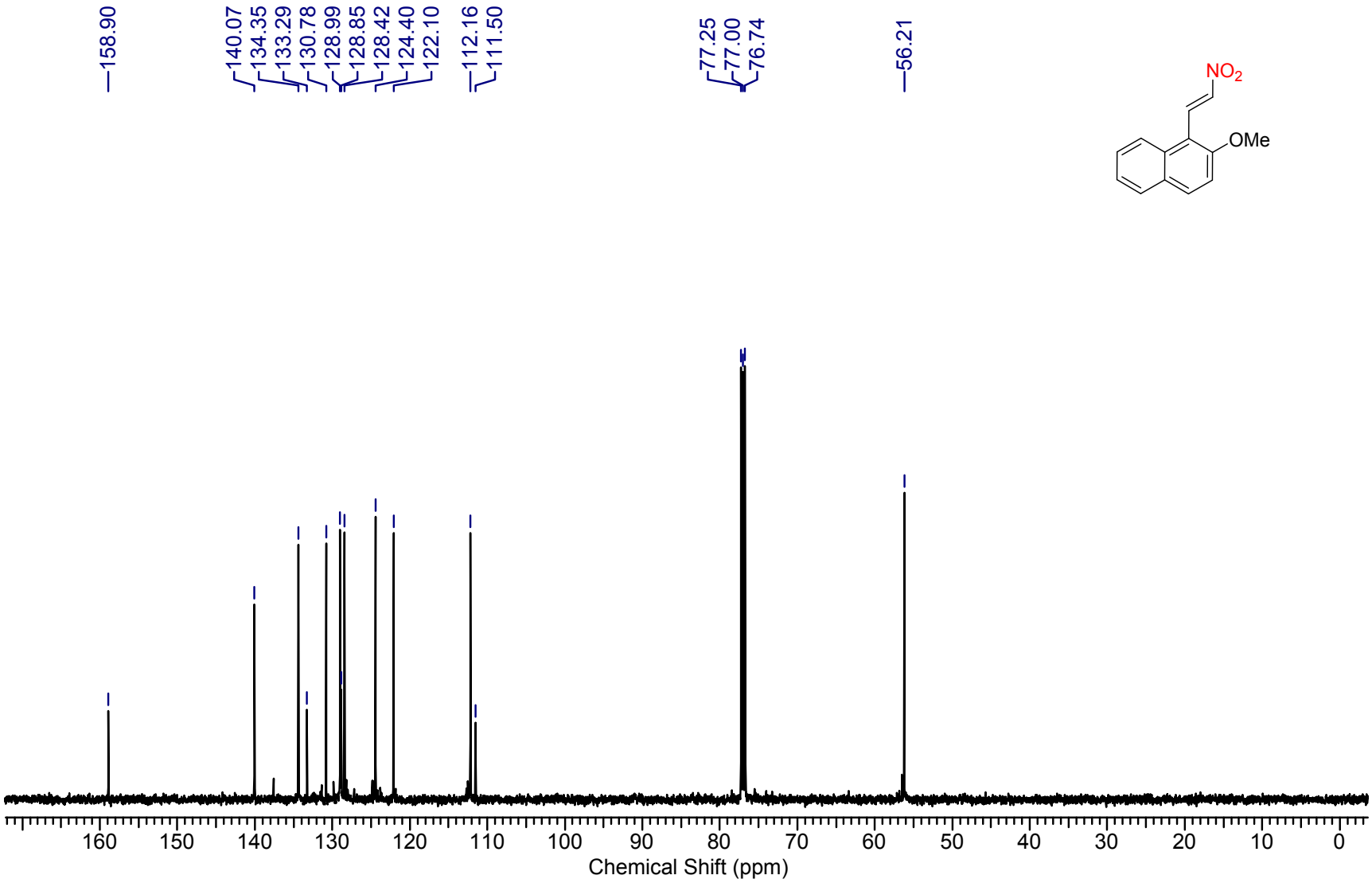


Figure S20b. ^{13}C NMR of **1o**

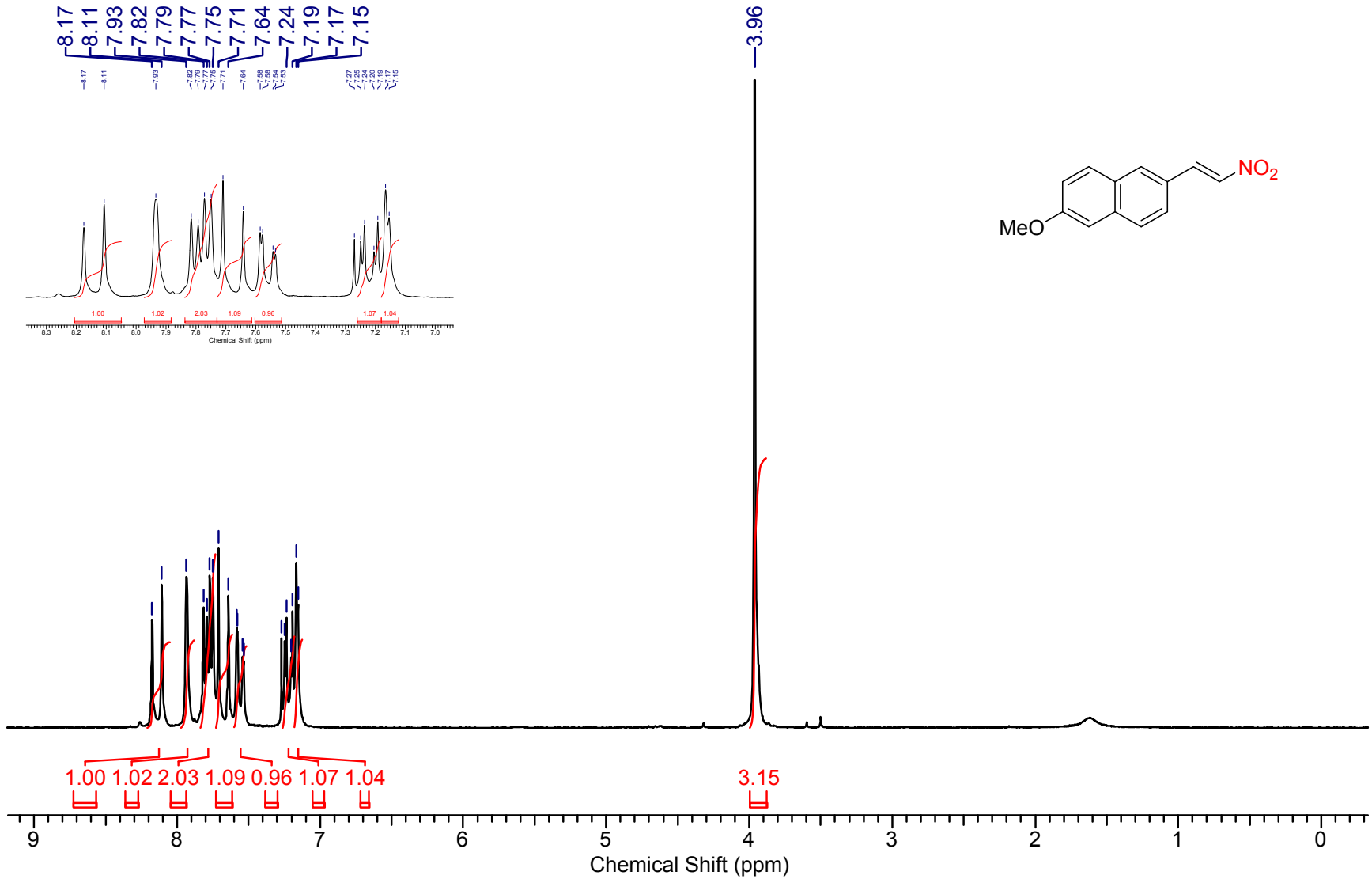


Figure S21a. ^{1}H NMR of **1p**

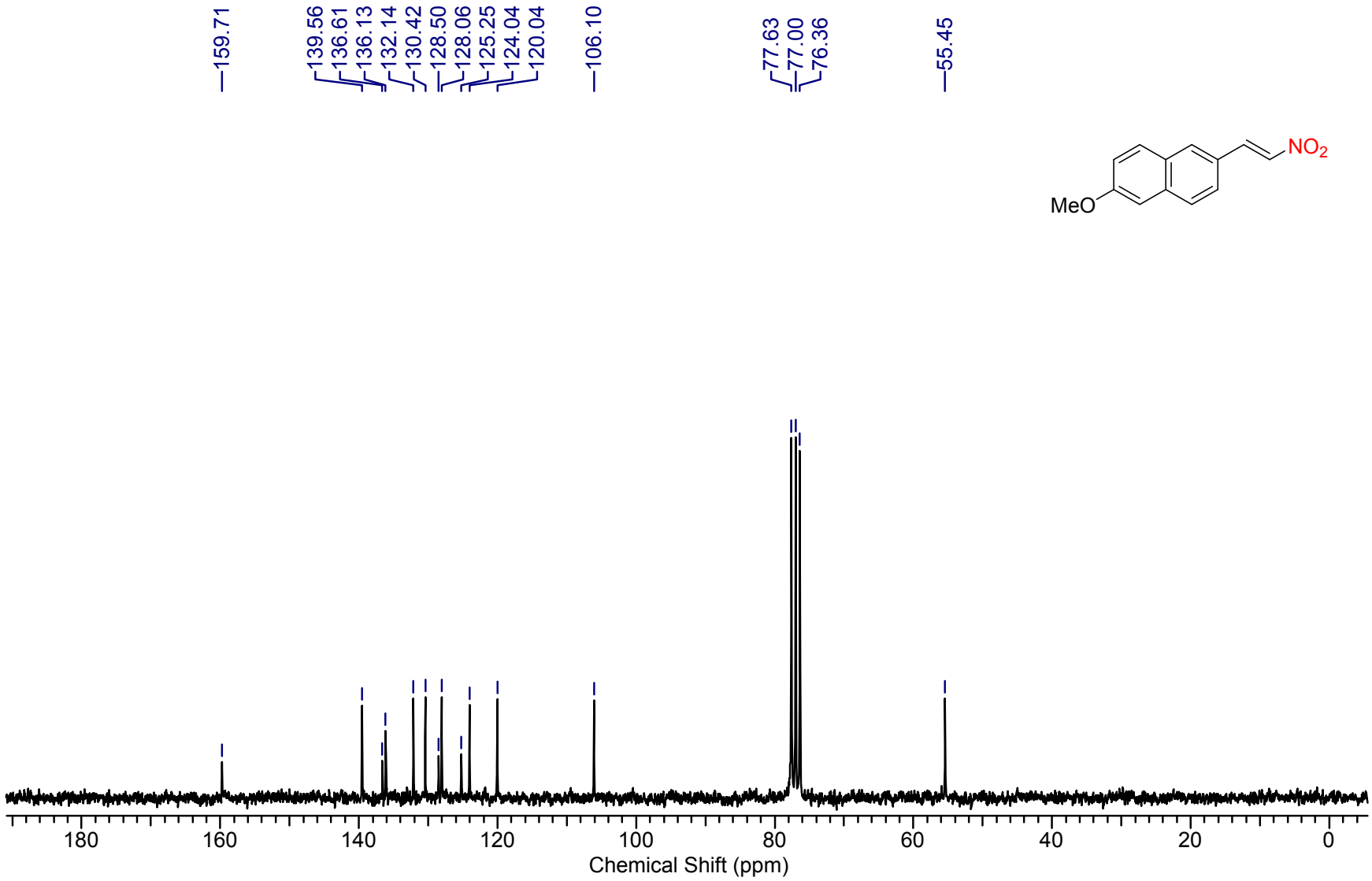


Figure S21b. ^{13}C NMR of **1p**

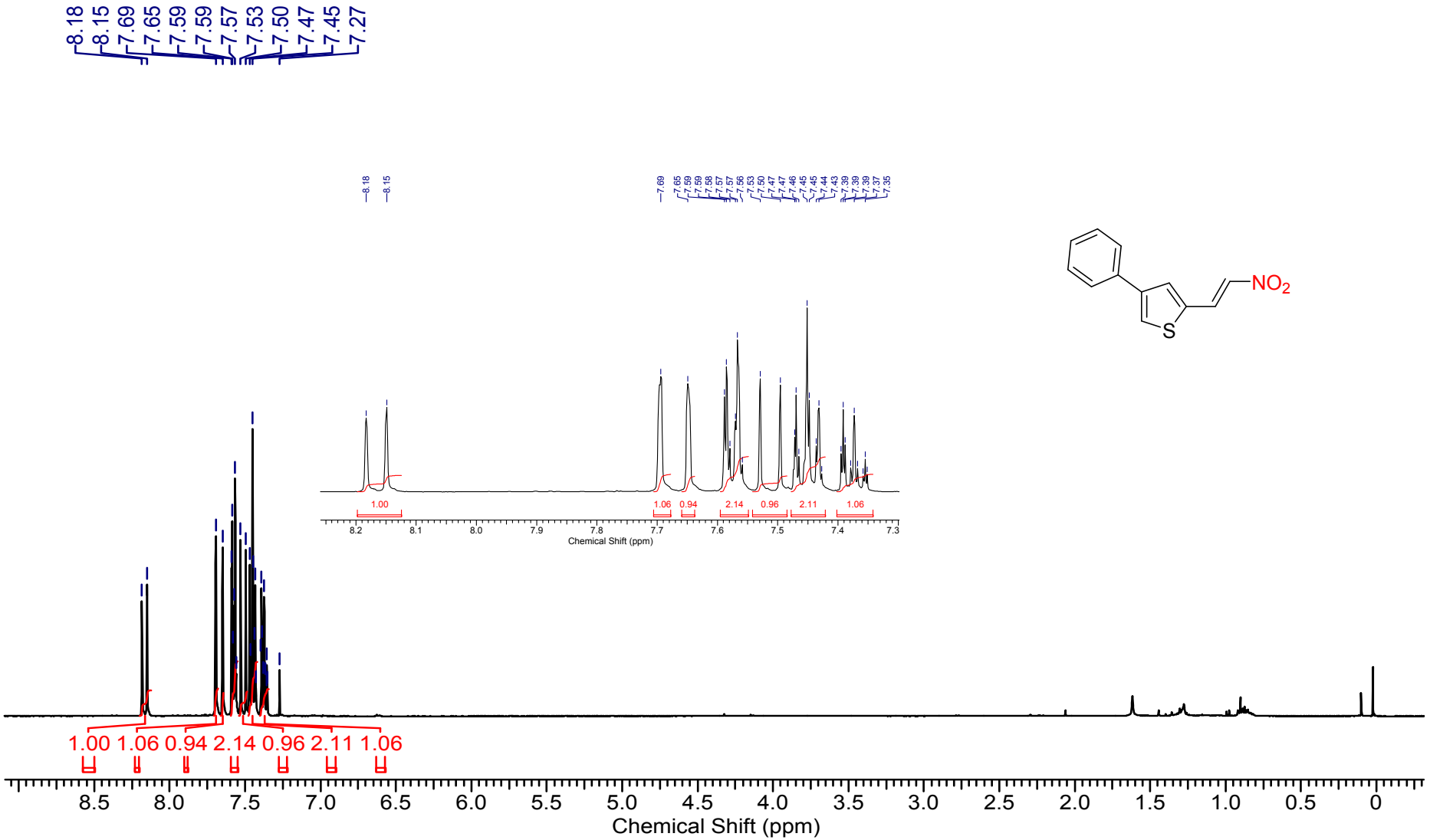


Figure S22a. ^{1}H NMR of **1r**

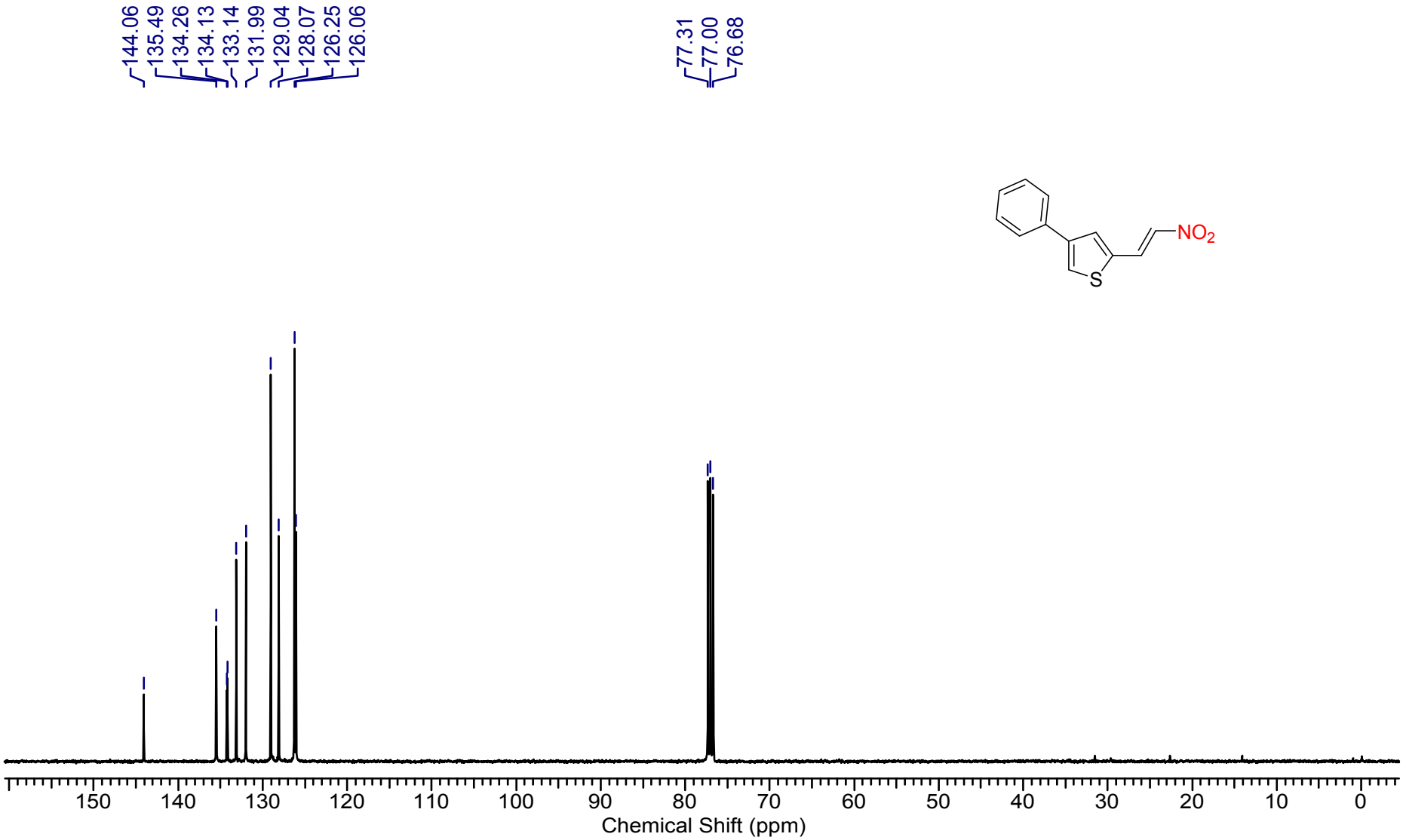


Figure S22b. ^{13}C NMR of **1r**

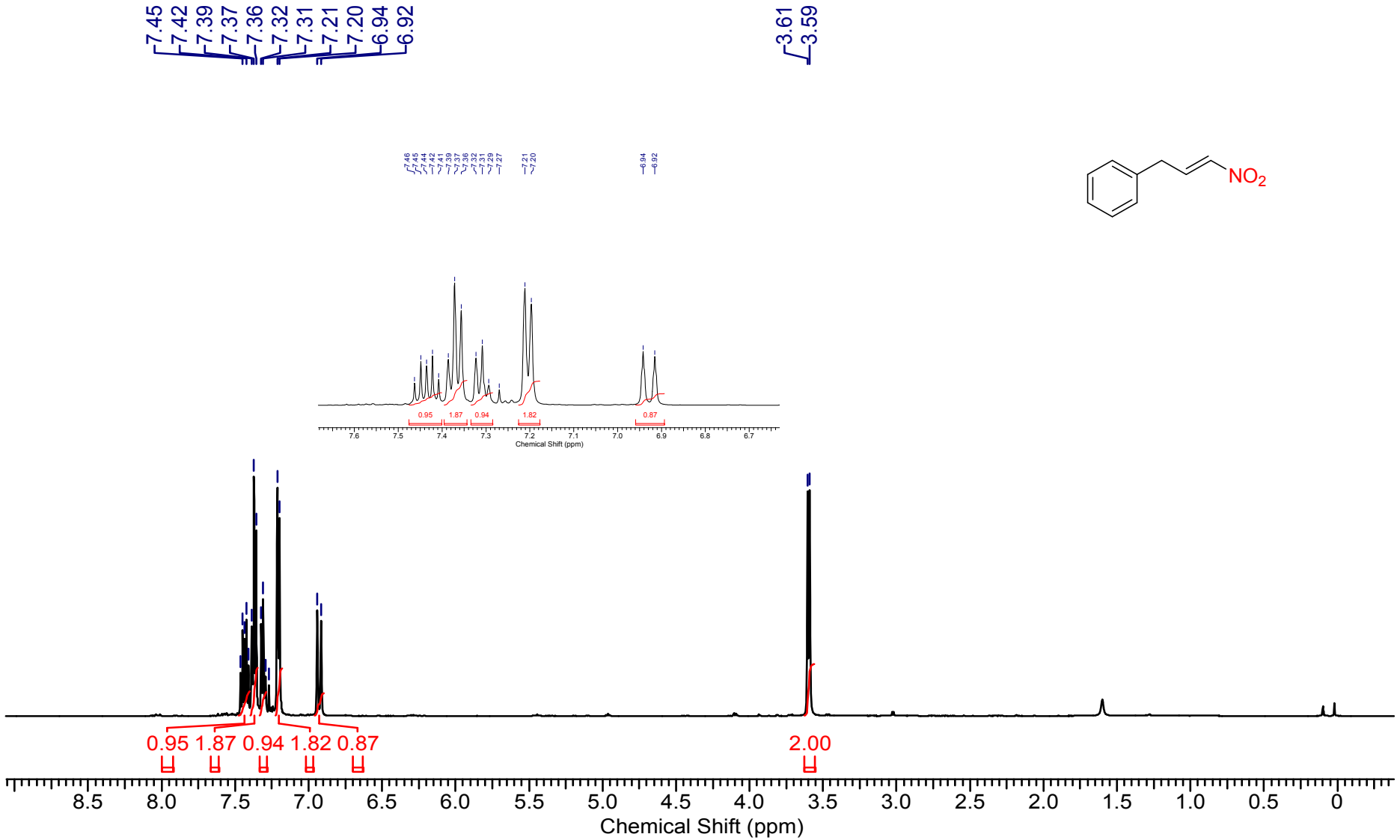


Figure S23a. ^{1}H NMR of **1s**

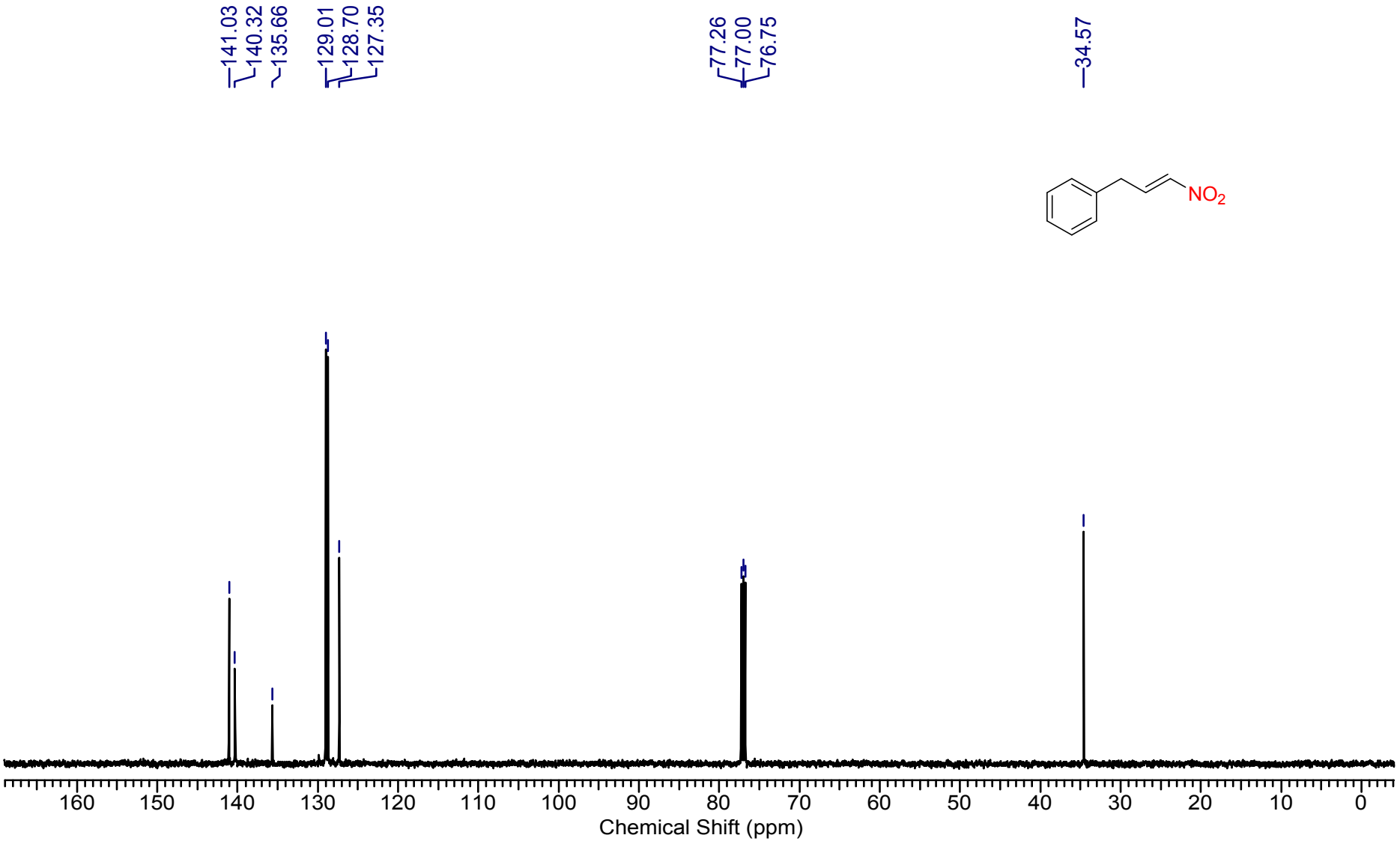


Figure S23b. ^{13}C NMR of **1s**

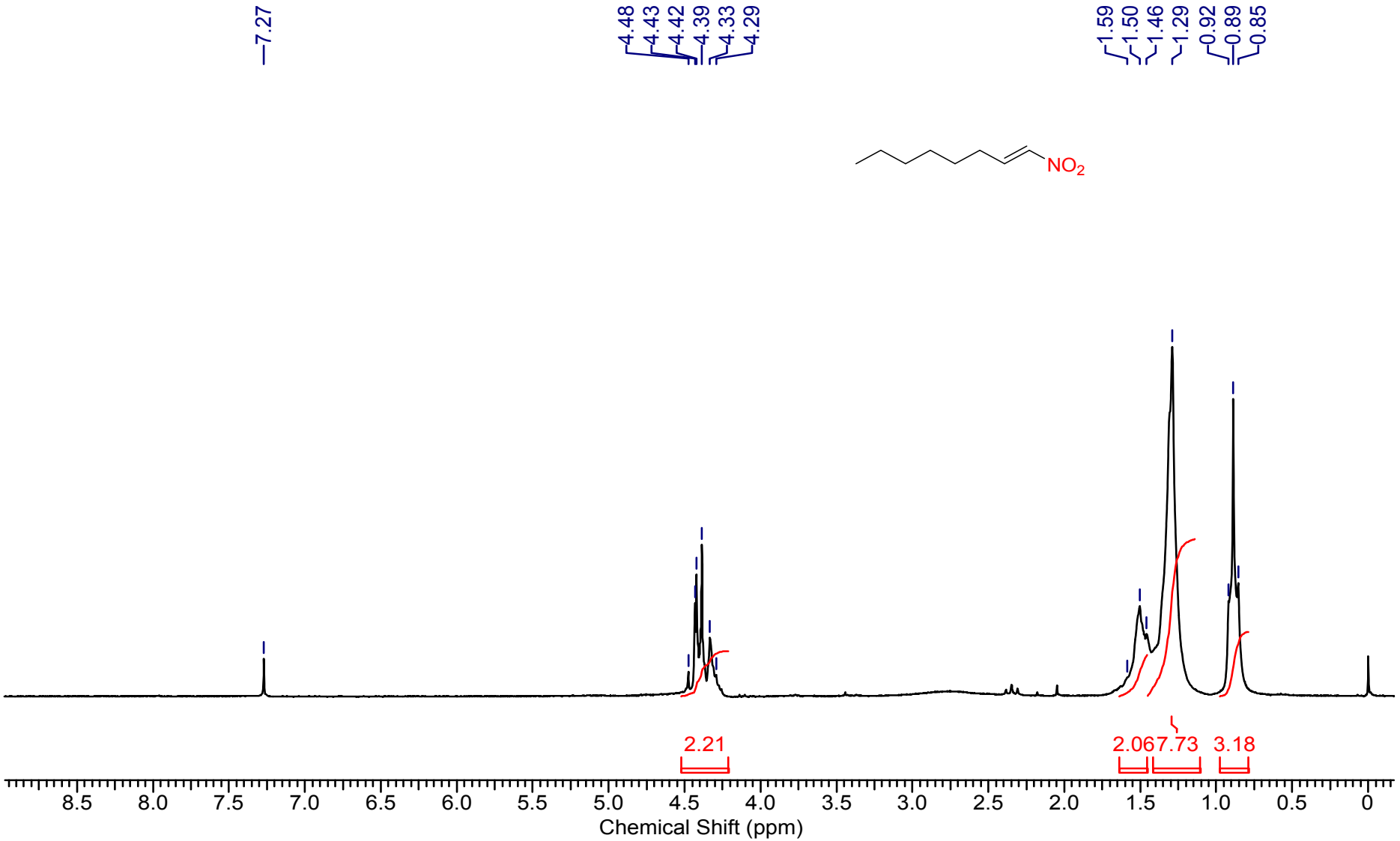


Figure S24a. ^{1}H NMR of **1t**

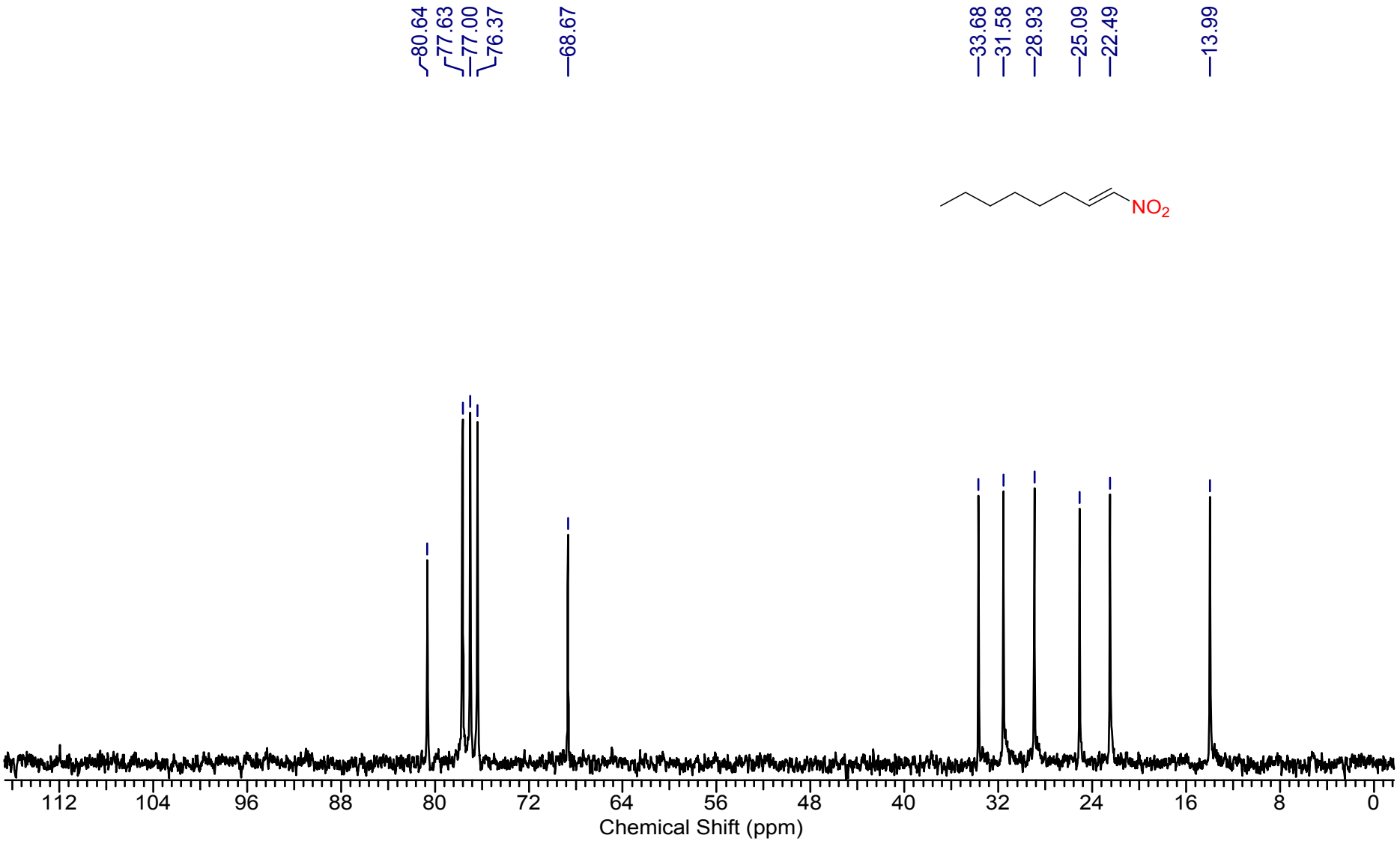


Figure S24b. ^{13}C NMR of **1t**

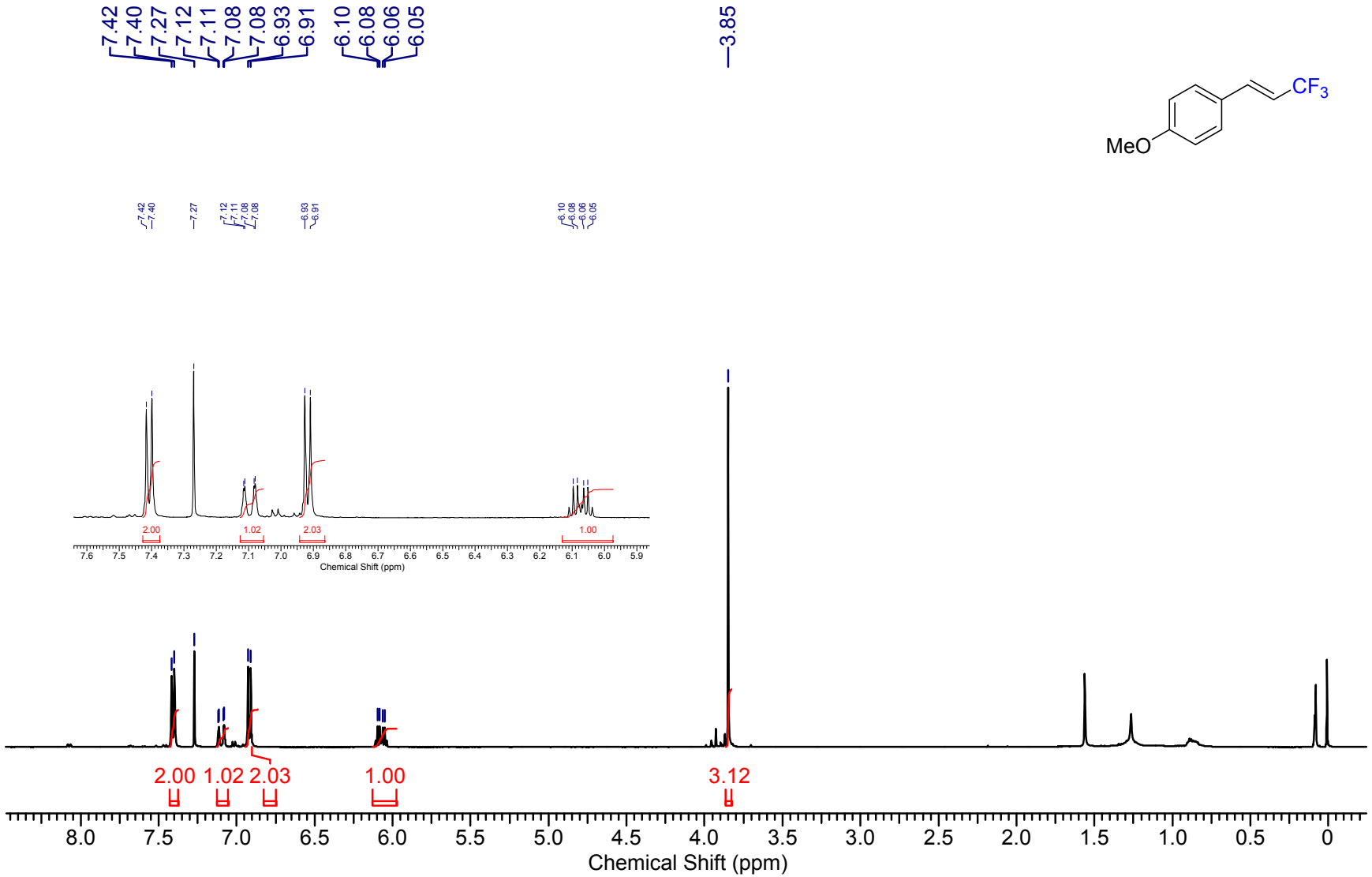


Figure S25a. ^{1}H NMR of **3a**

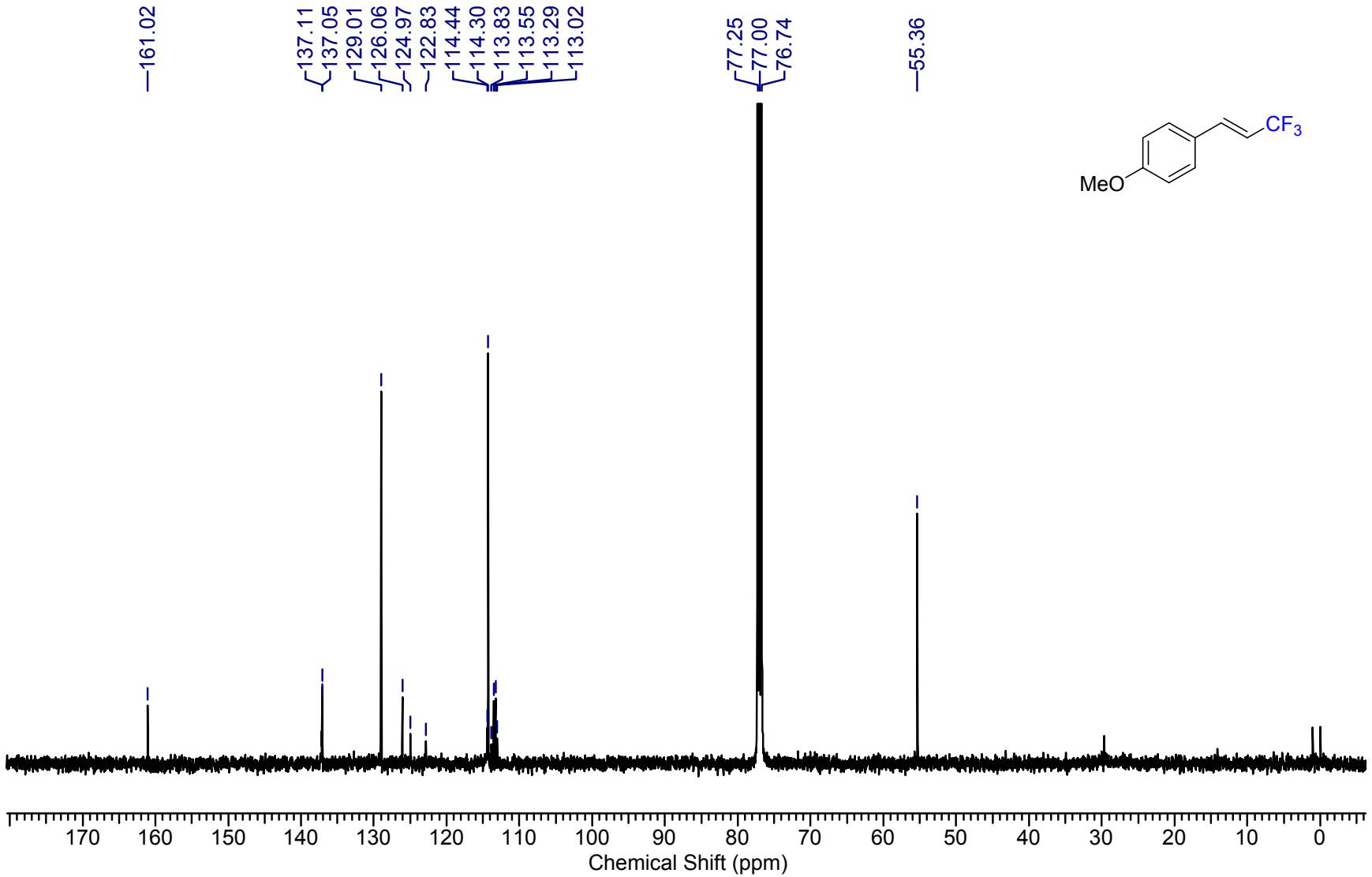


Figure S25b. ^{13}C NMR of **3a**

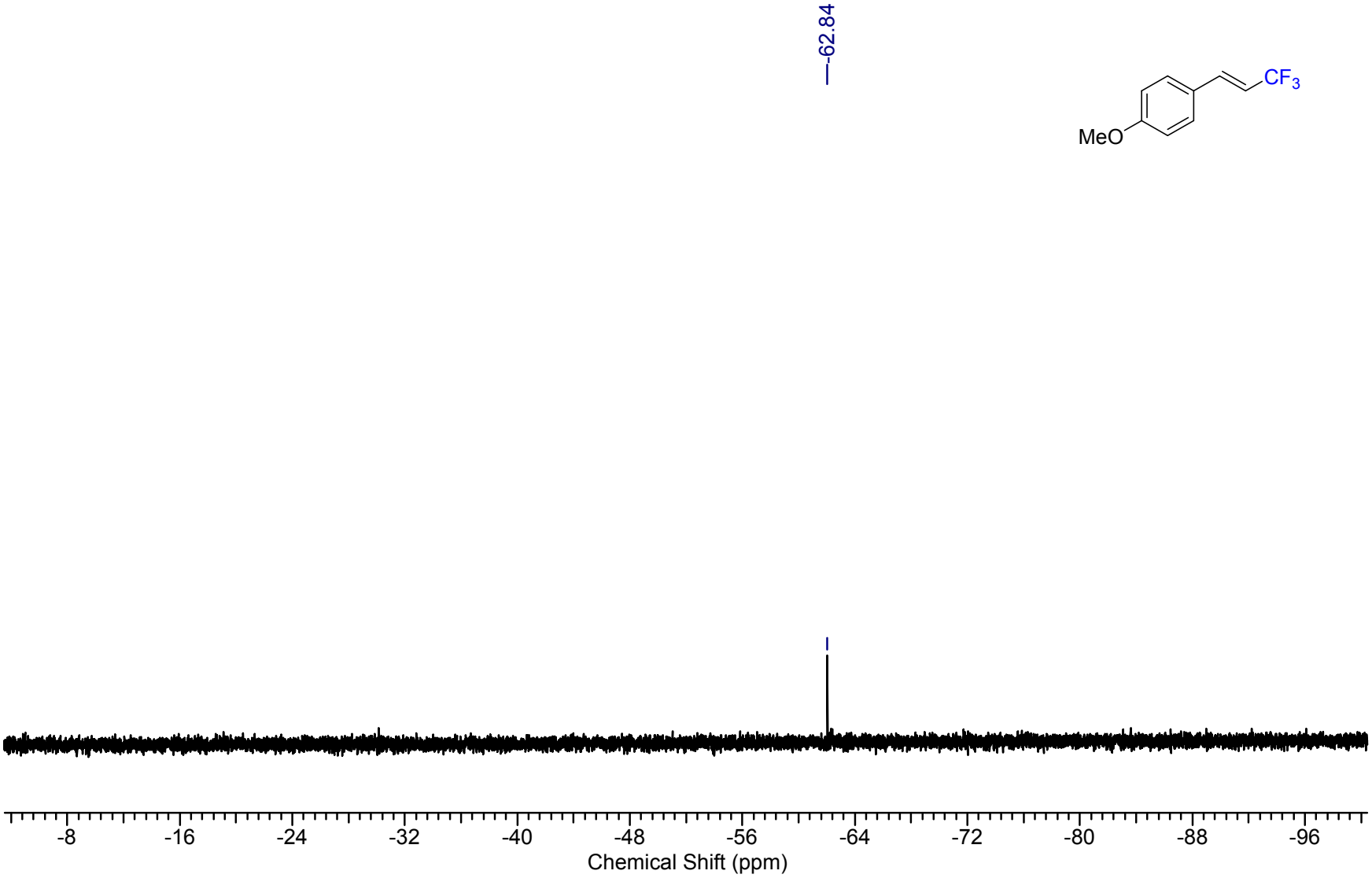


Figure S25c. ^{19}F NMR of **3a**

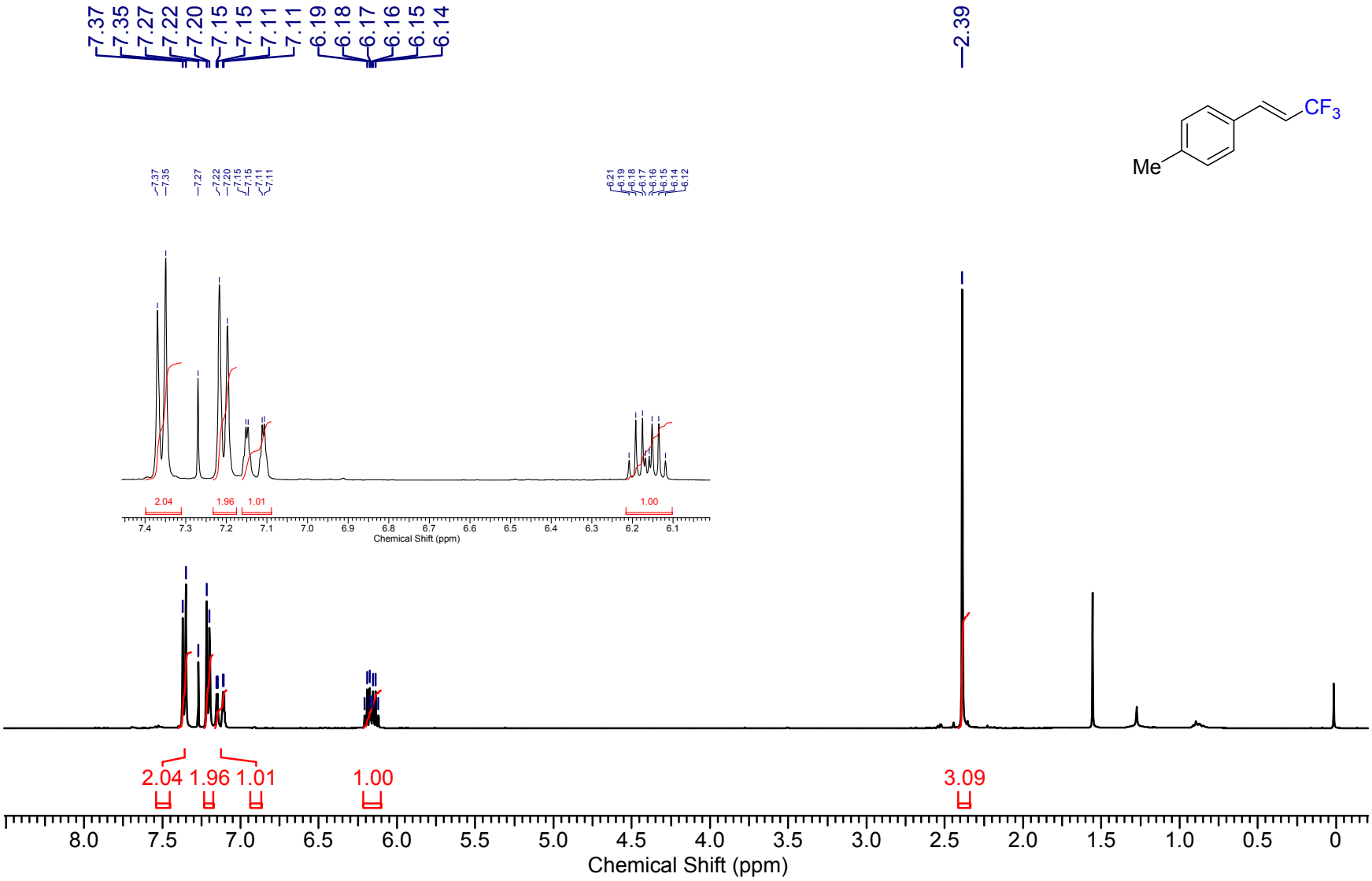


Figure S26a. ^{1}H NMR of **3b**

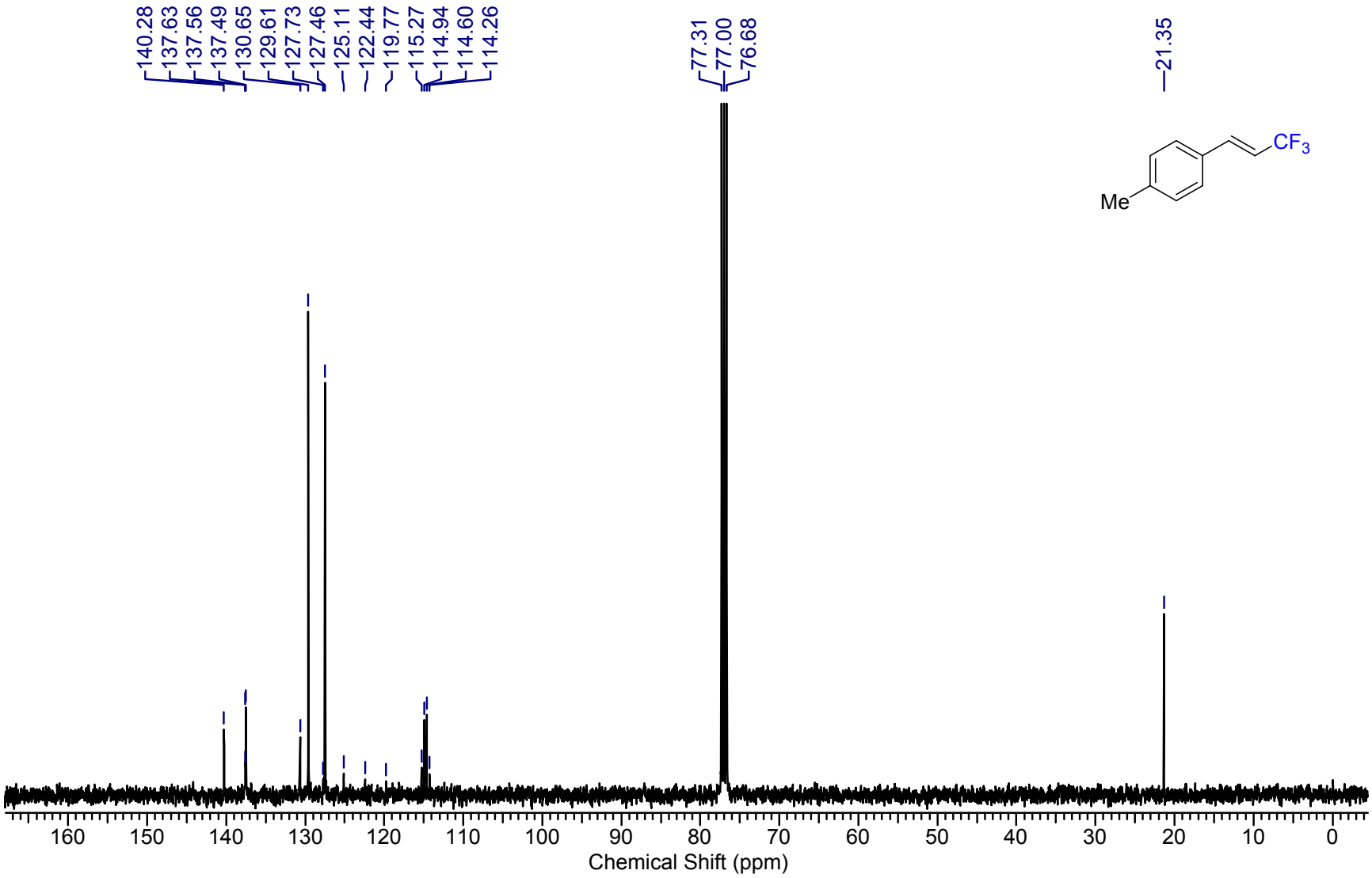


Figure S26b. ^{13}C NMR of **3b**

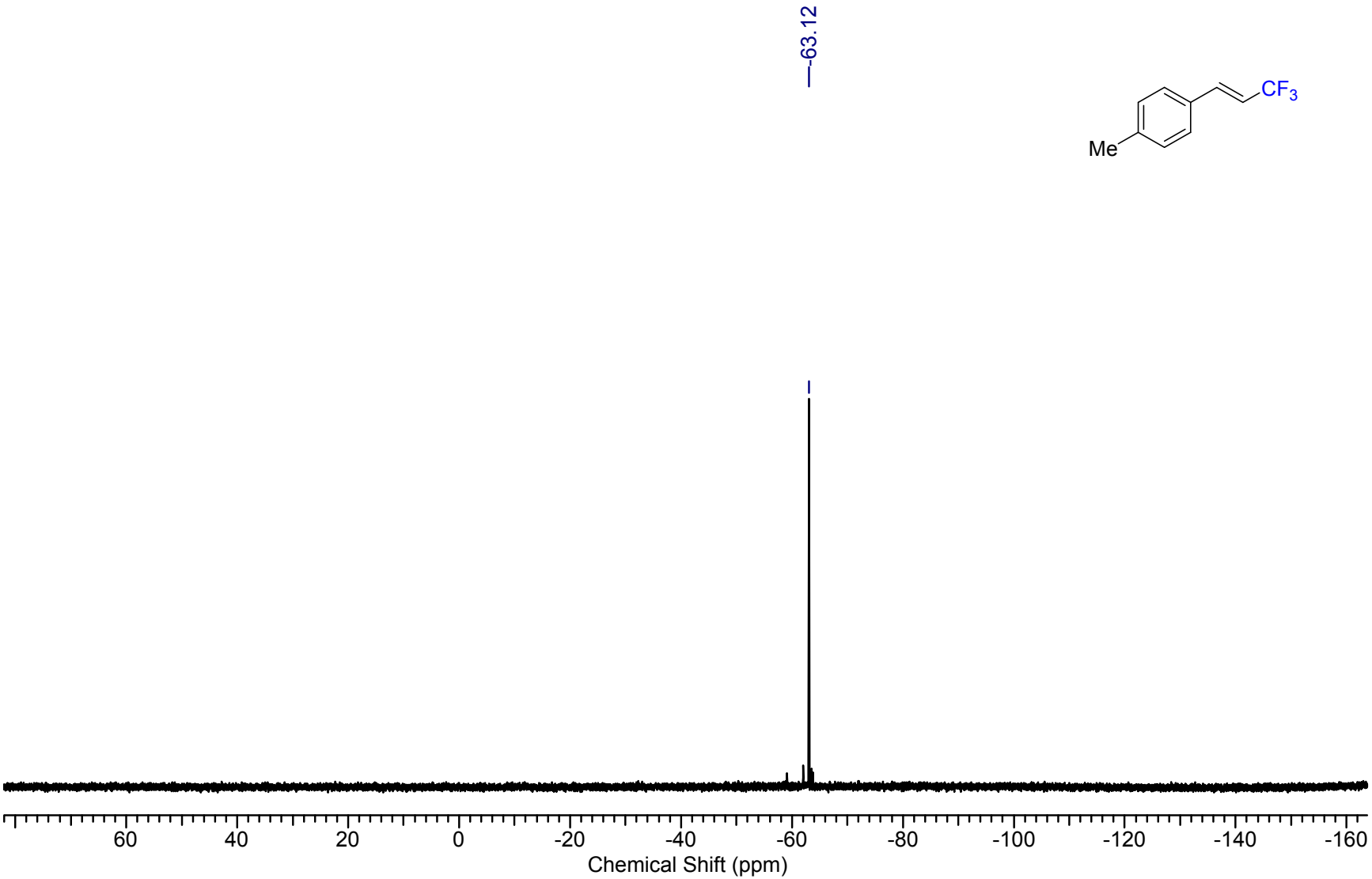


Figure S26c. ^{19}F NMR of **3b**

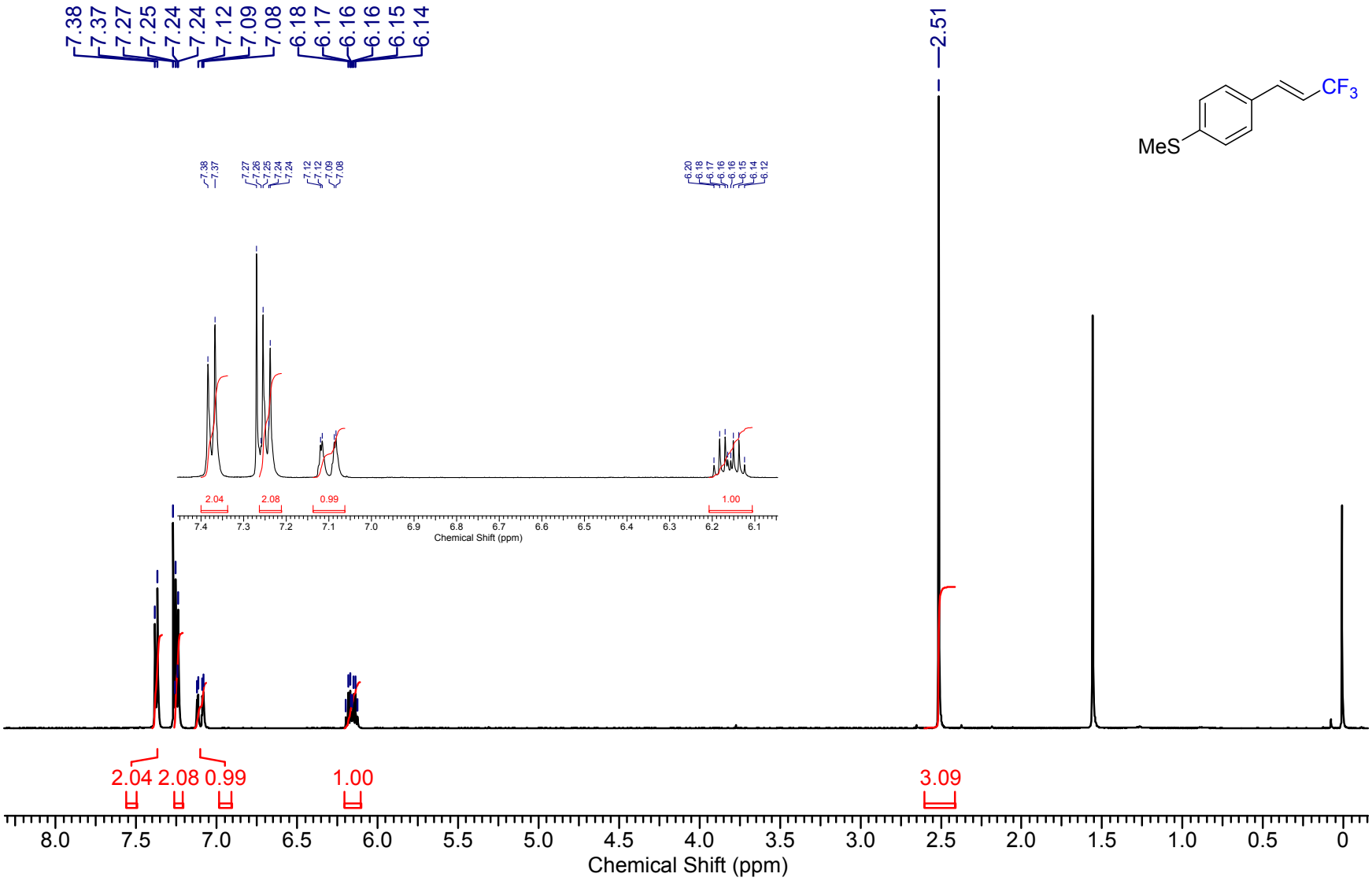


Figure S27a. ^{1}H NMR of **3c**

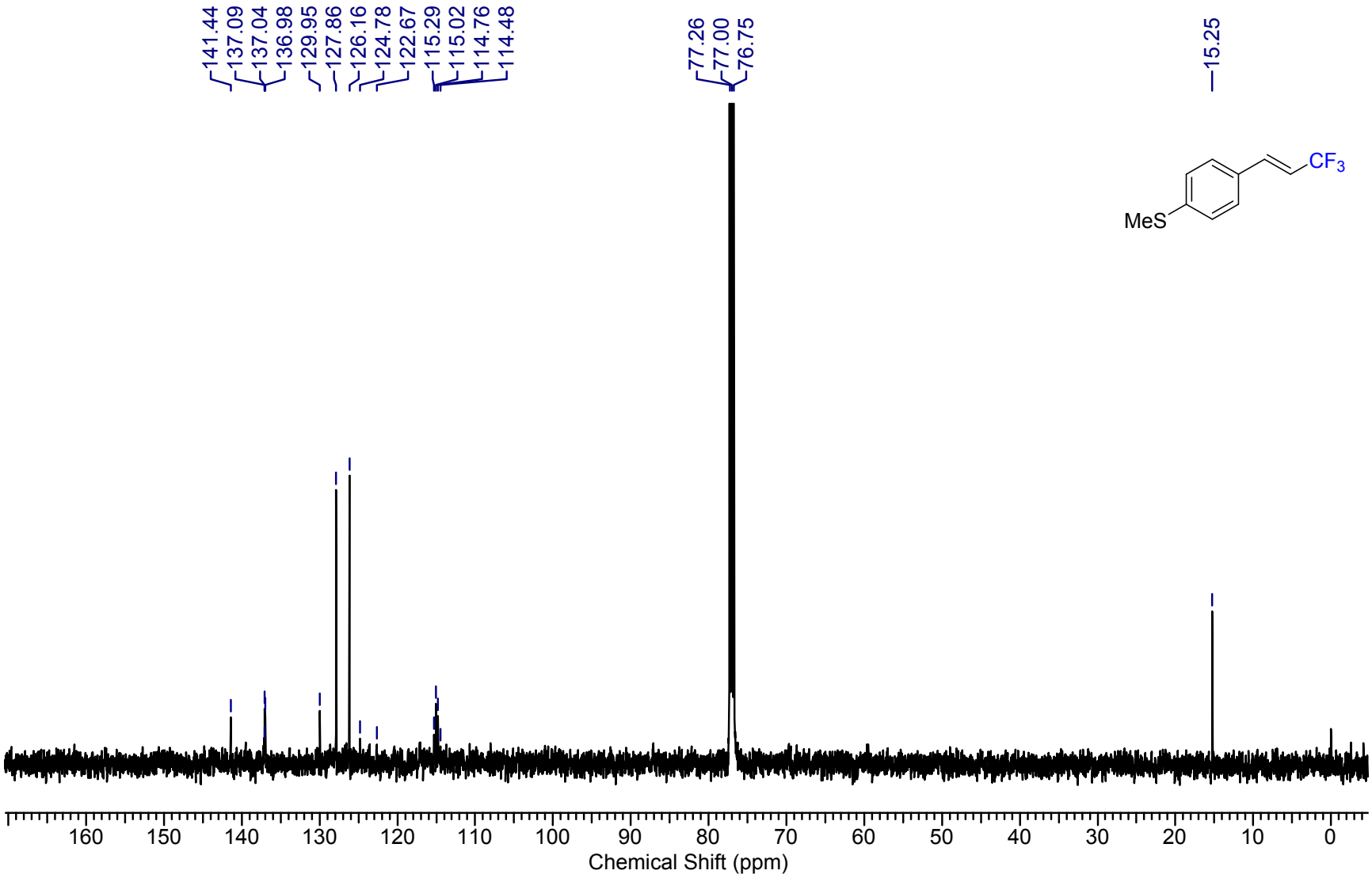


Figure S27b. ^{13}C NMR of **3c**

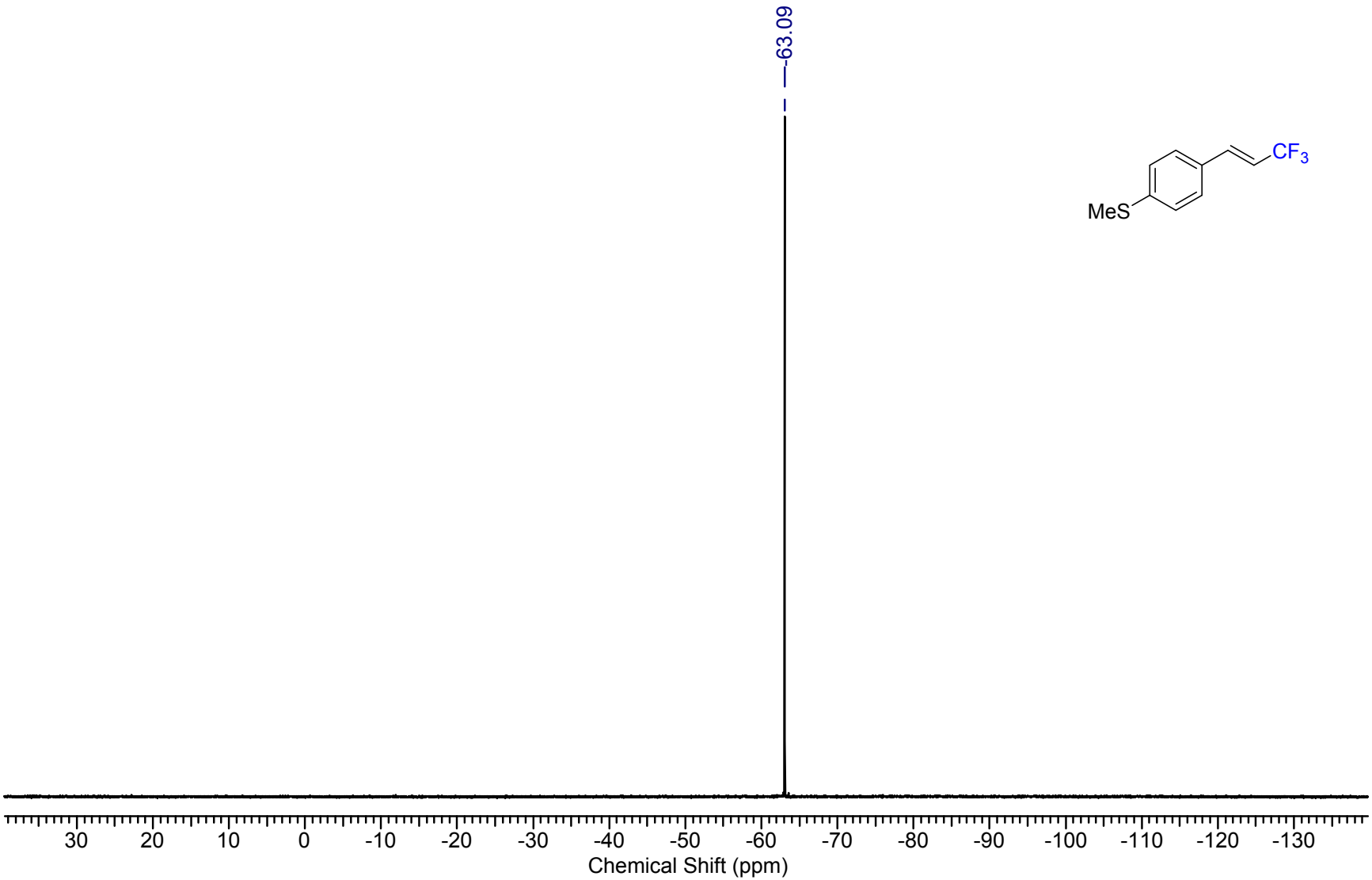


Figure S27c. ^{19}F NMR of **3c**

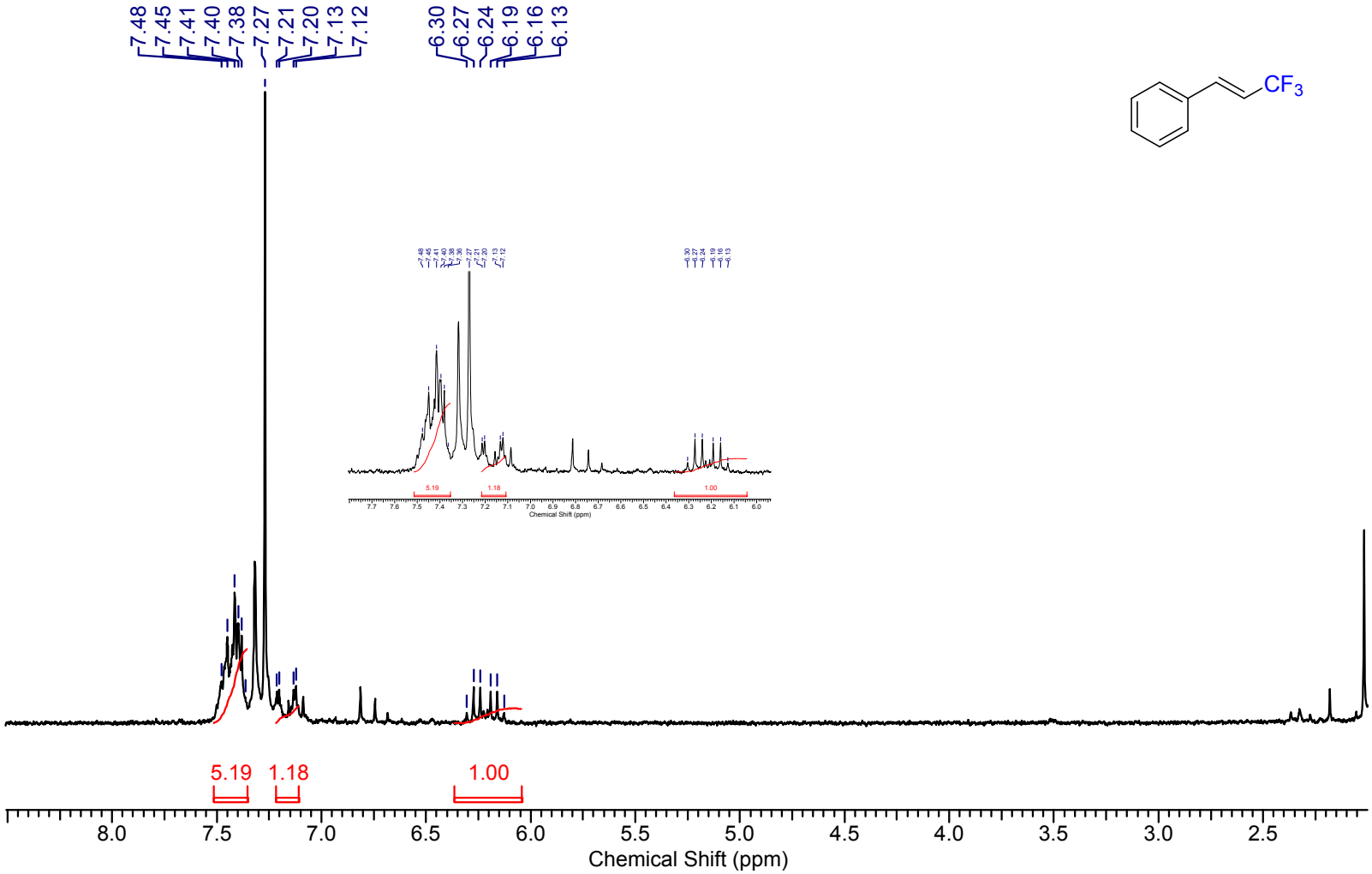


Figure S28a. ^{1}H NMR of **3d**

(In the chemical shift range of 1.5 to 0.8 ppm, impurity peaks from pet ether were observed)

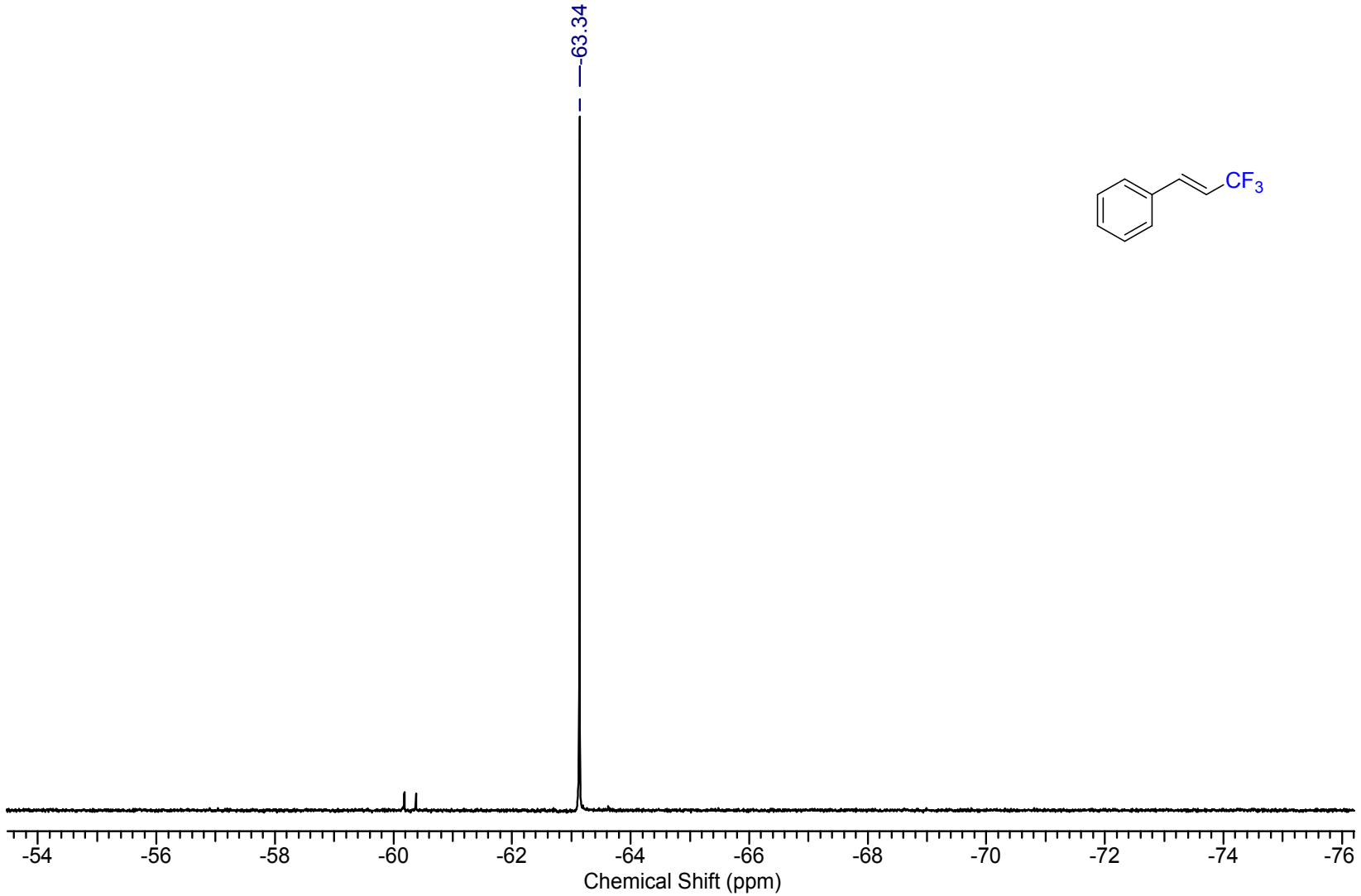


Figure S28b. ^{19}F NMR of **3d**

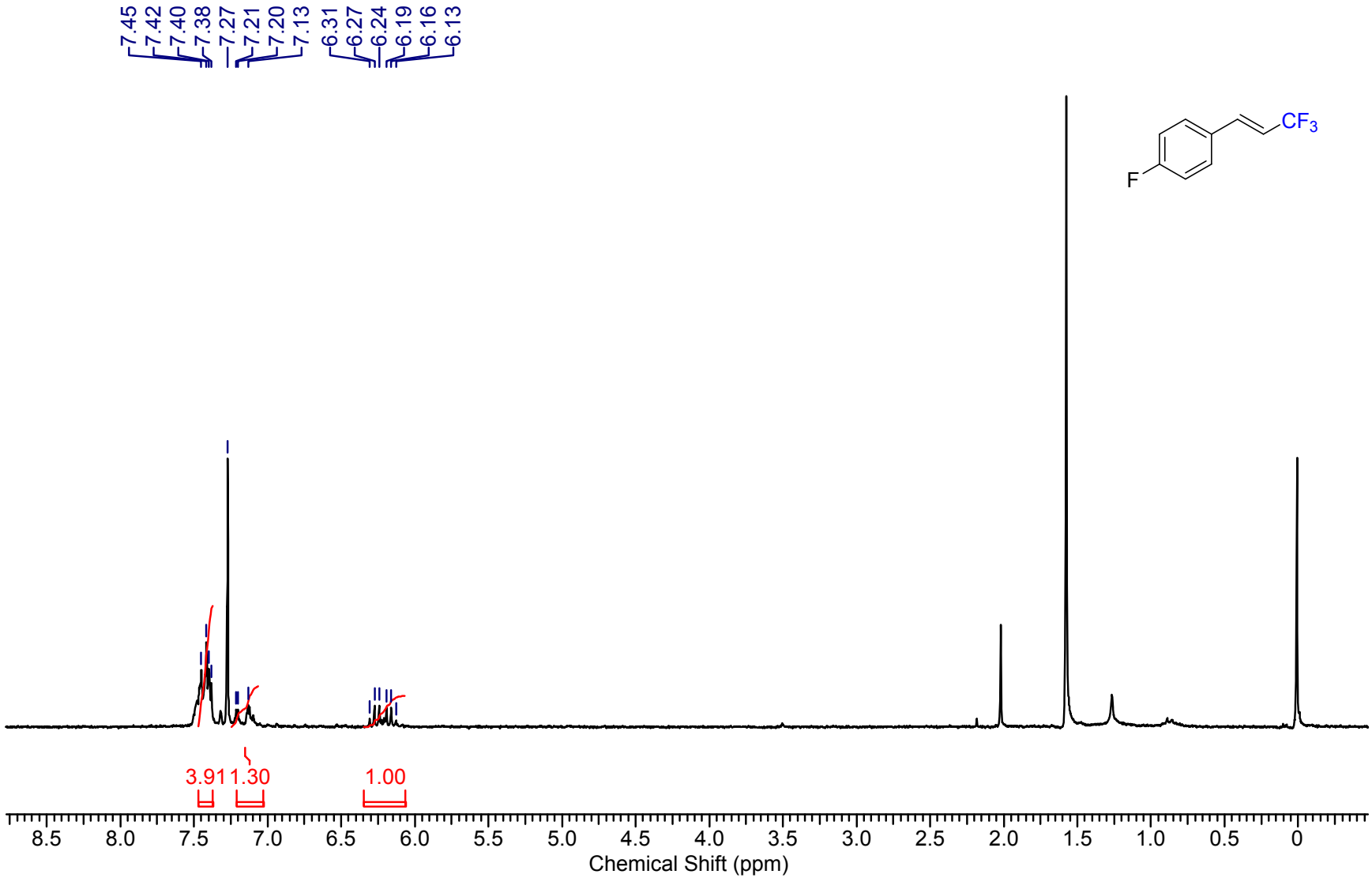


Figure S29a. ^{1}H NMR of **3e**

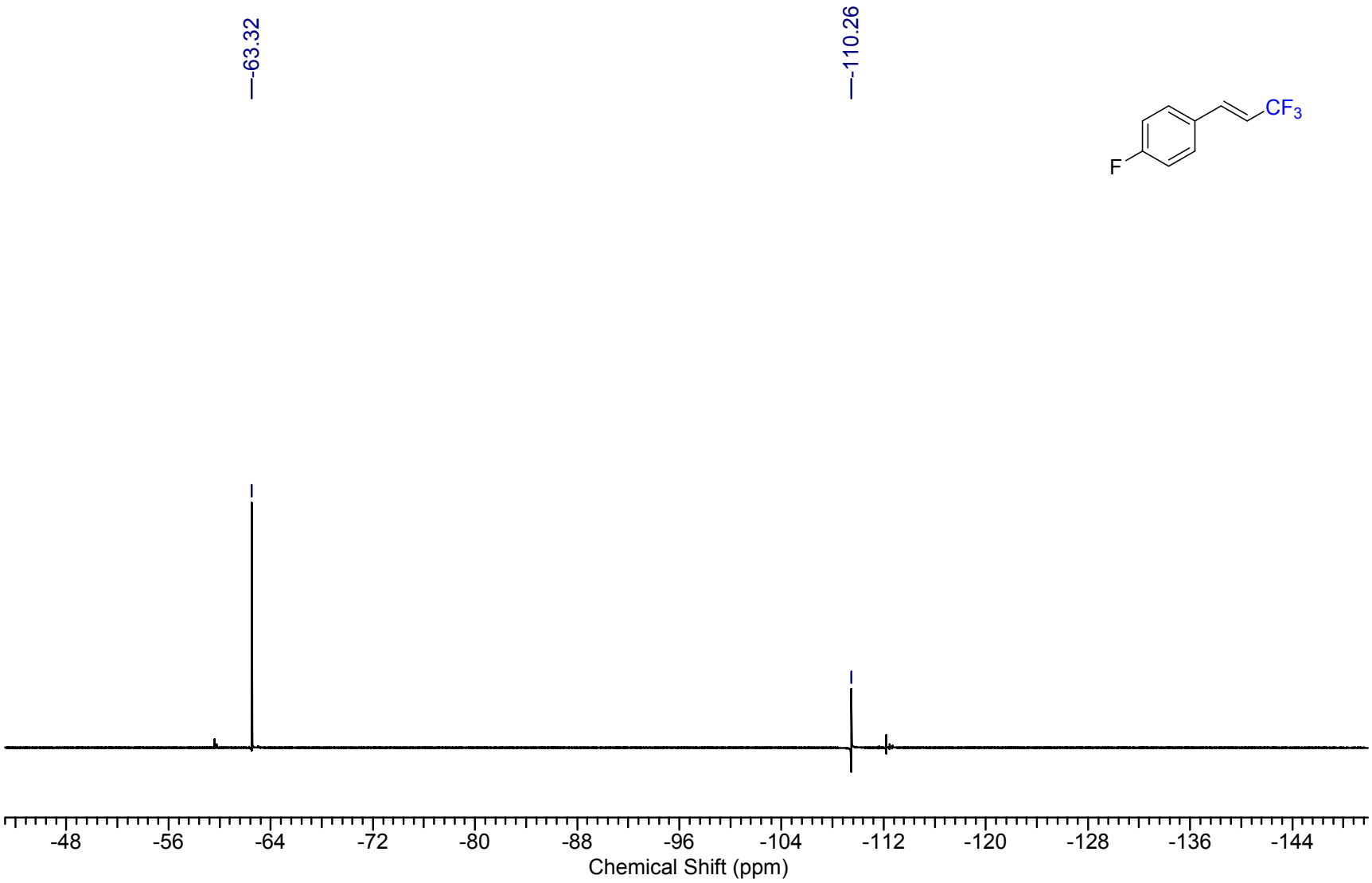


Figure S29b. ^{19}F NMR of **3e**

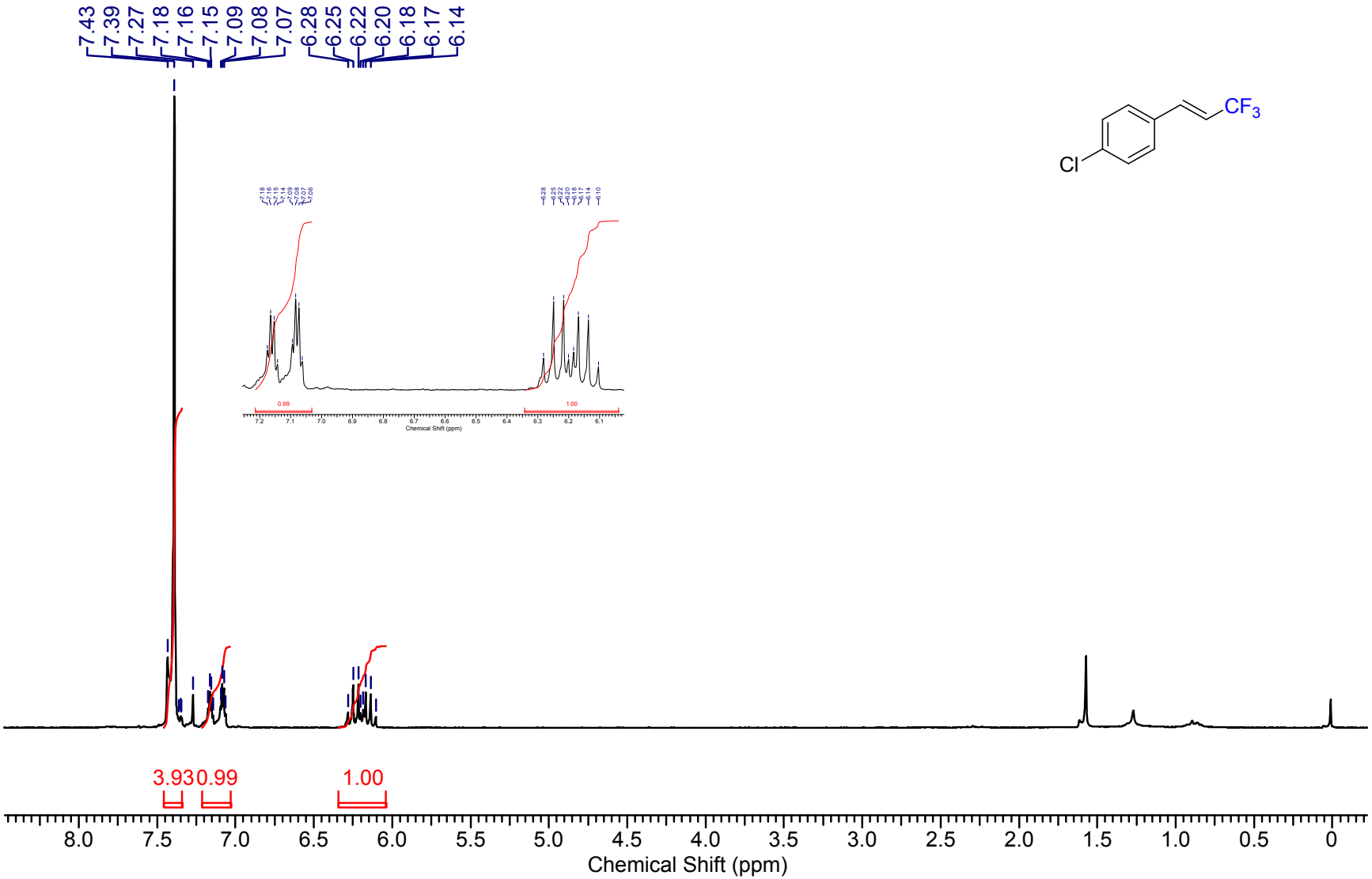


Figure S30a. ^{1}H NMR of **3f**

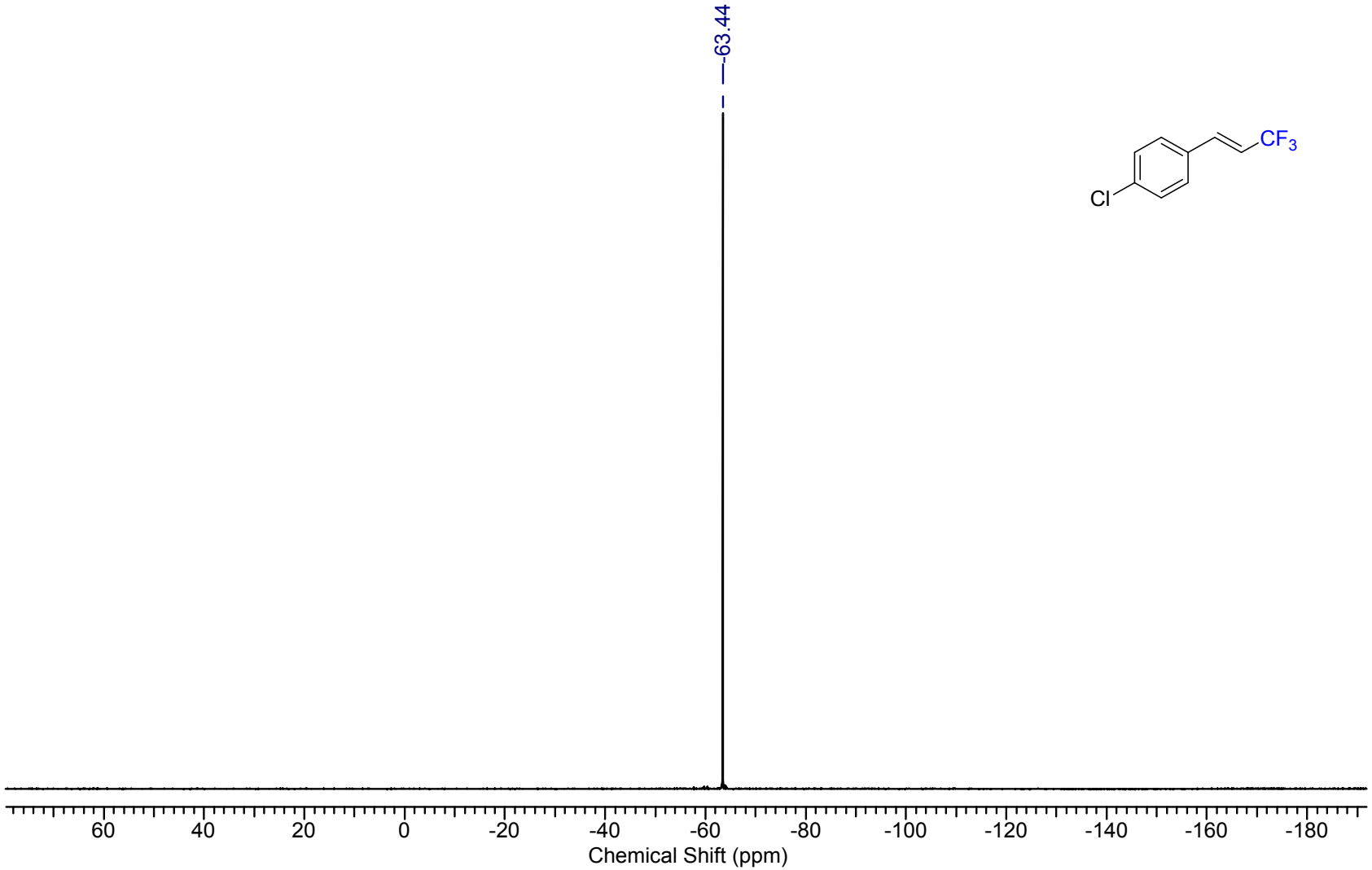


Figure S30b. ^{19}F NMR of **3f**

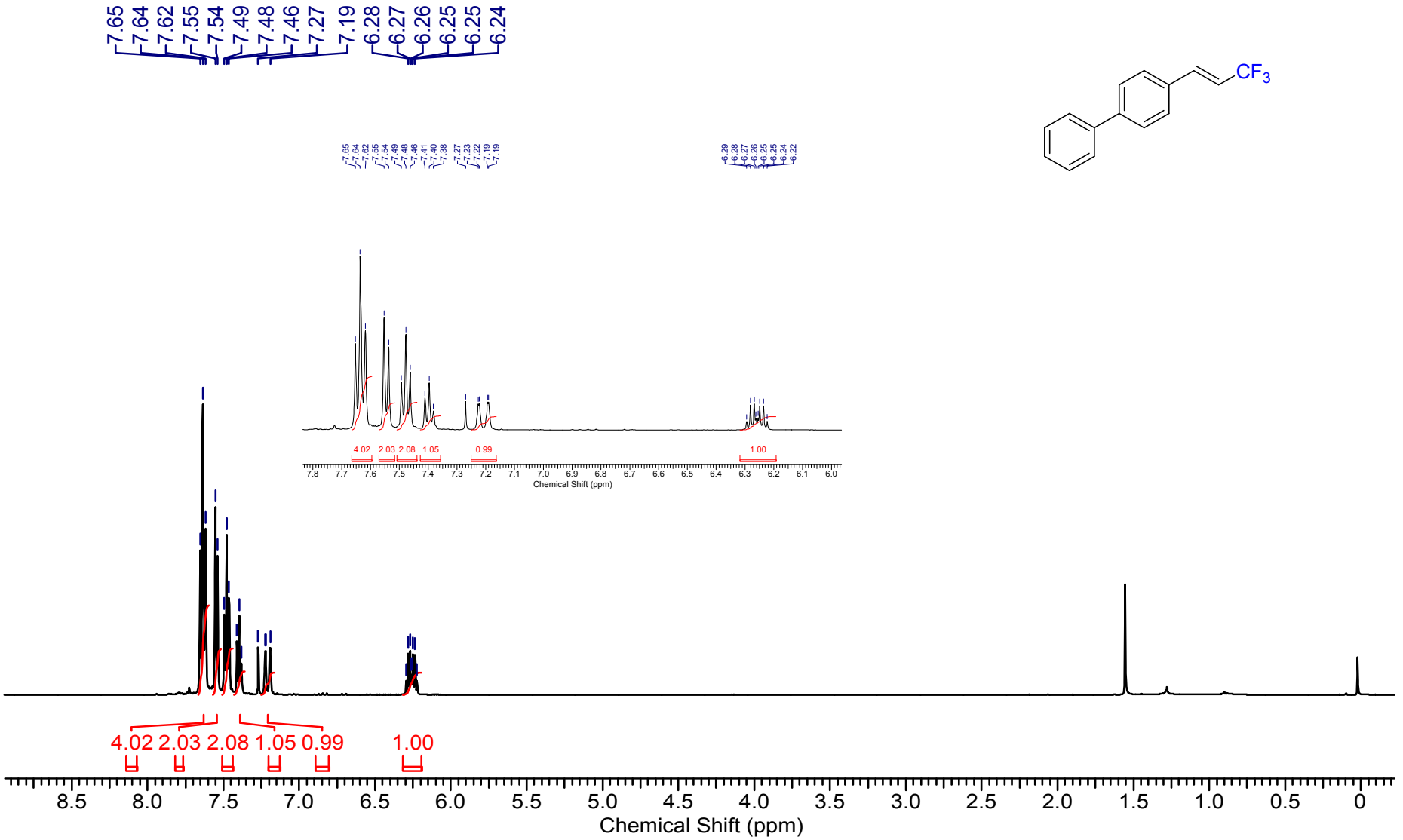


Figure S31a. ^{1}H NMR of **3g**

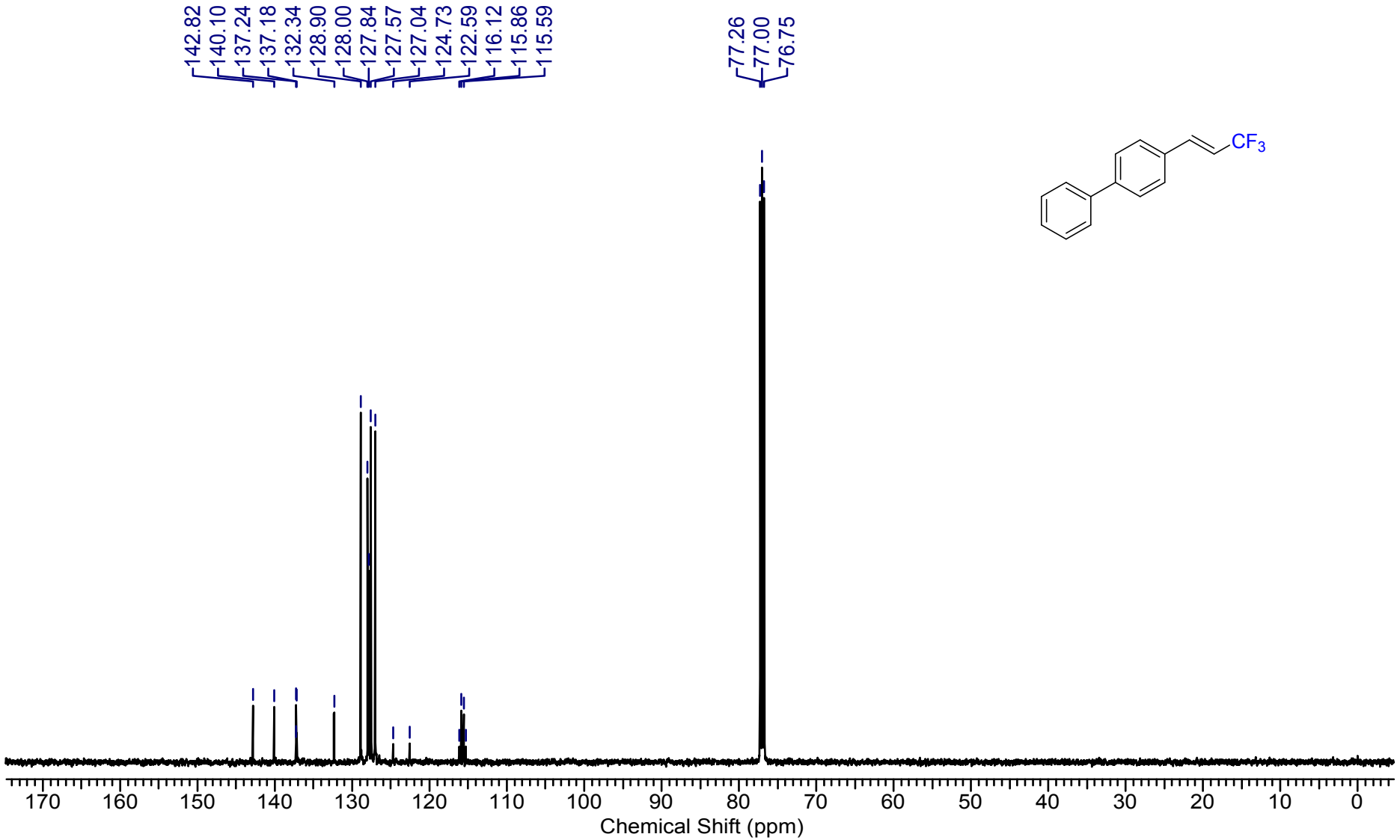


Figure S31b. ^{13}C NMR of **3g**

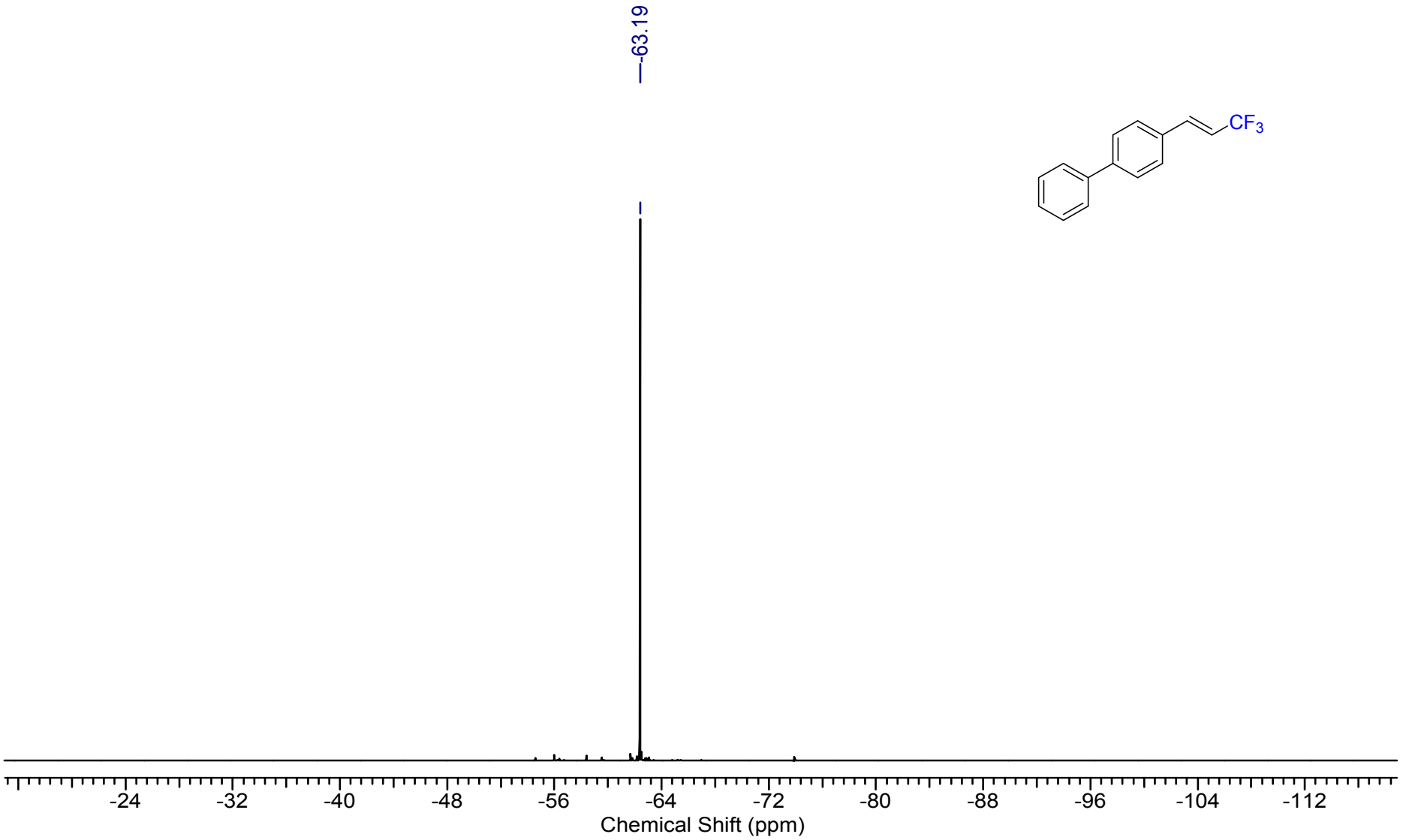


Figure S31C. ^{19}F NMR of **3g**

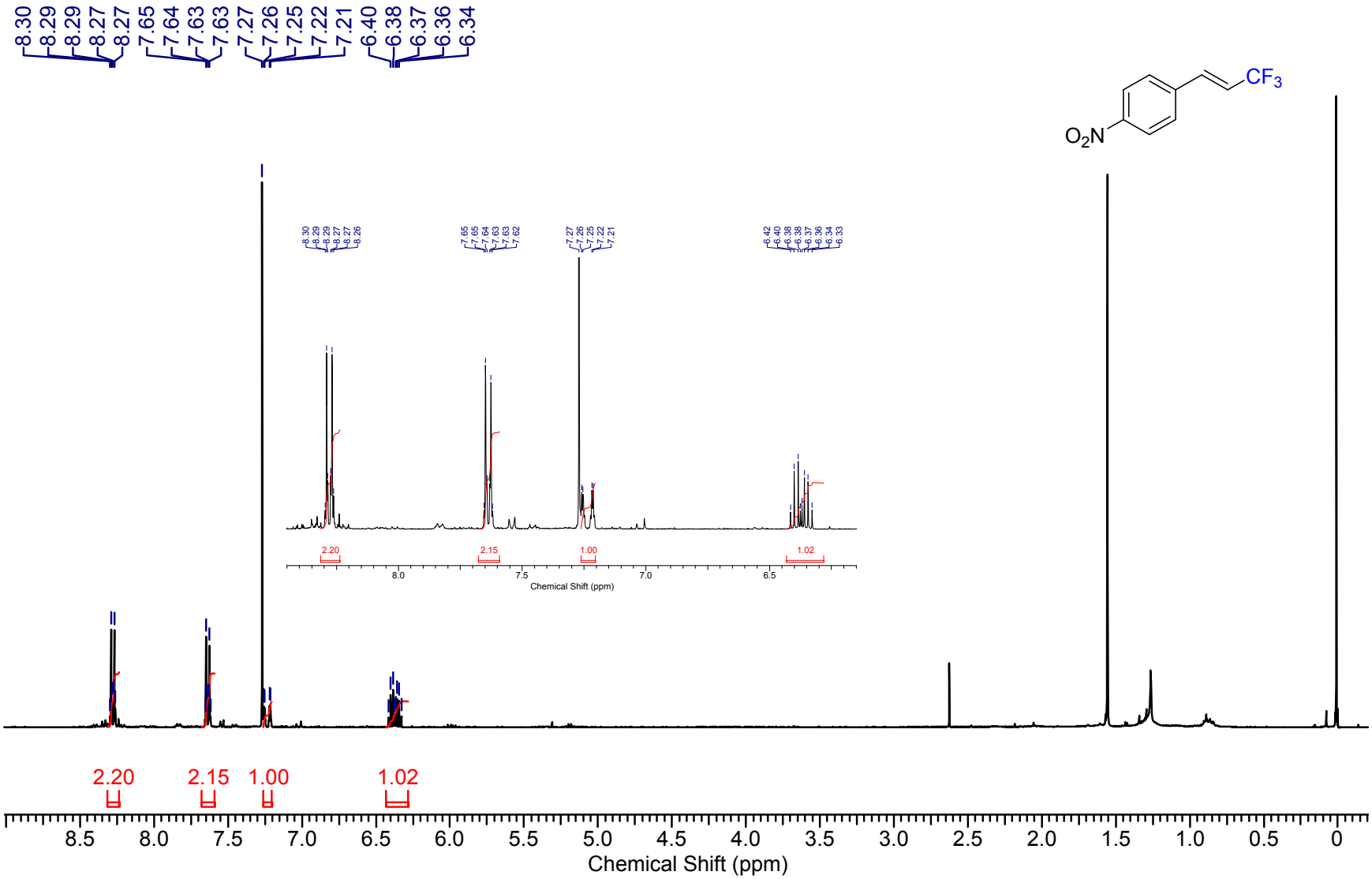


Figure S32a. ^{1}H NMR of **3h**

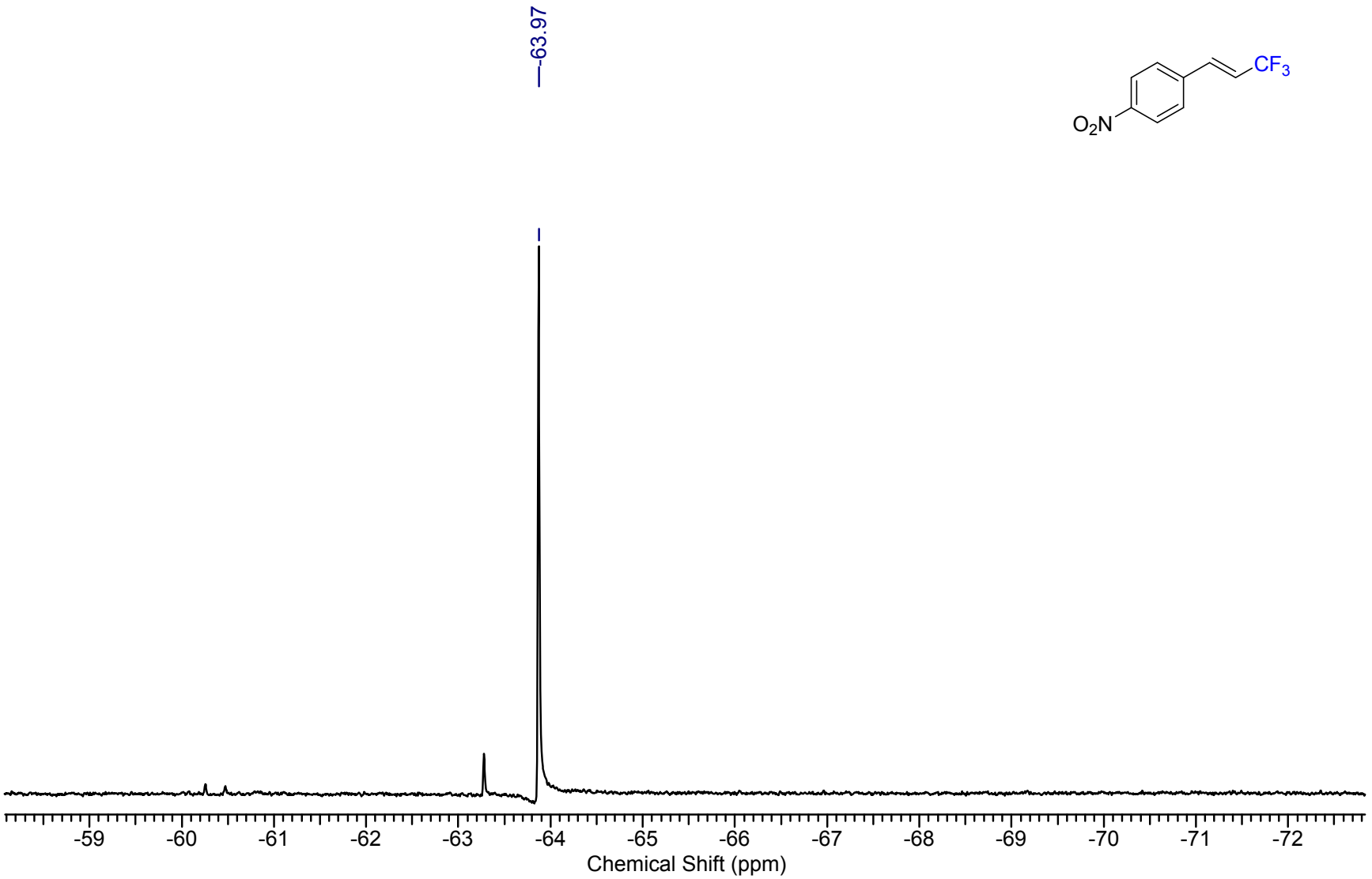


Figure S32b. ^{19}F NMR of **3h**

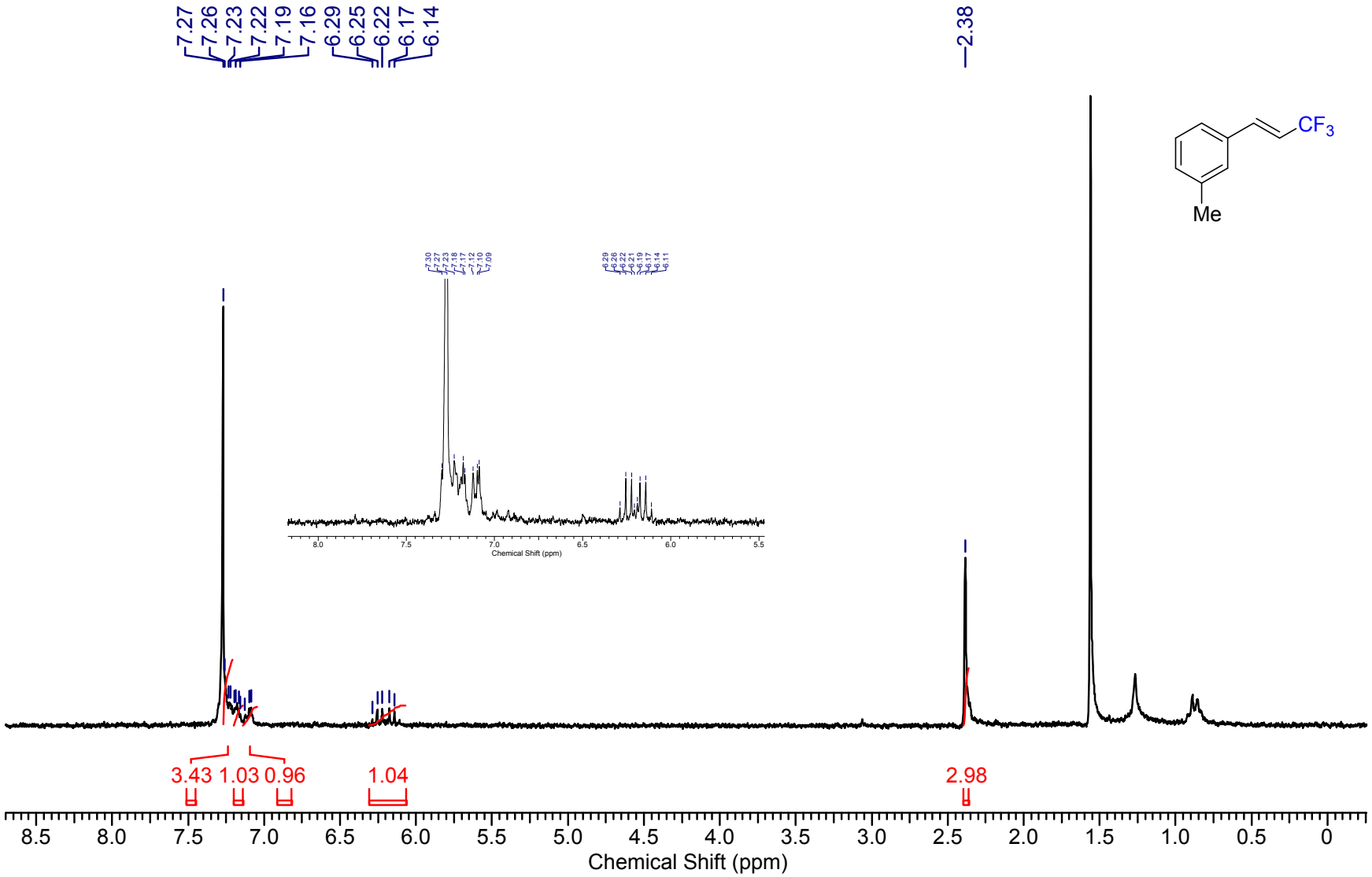


Figure S33a. ^{1}H NMR of **3i**

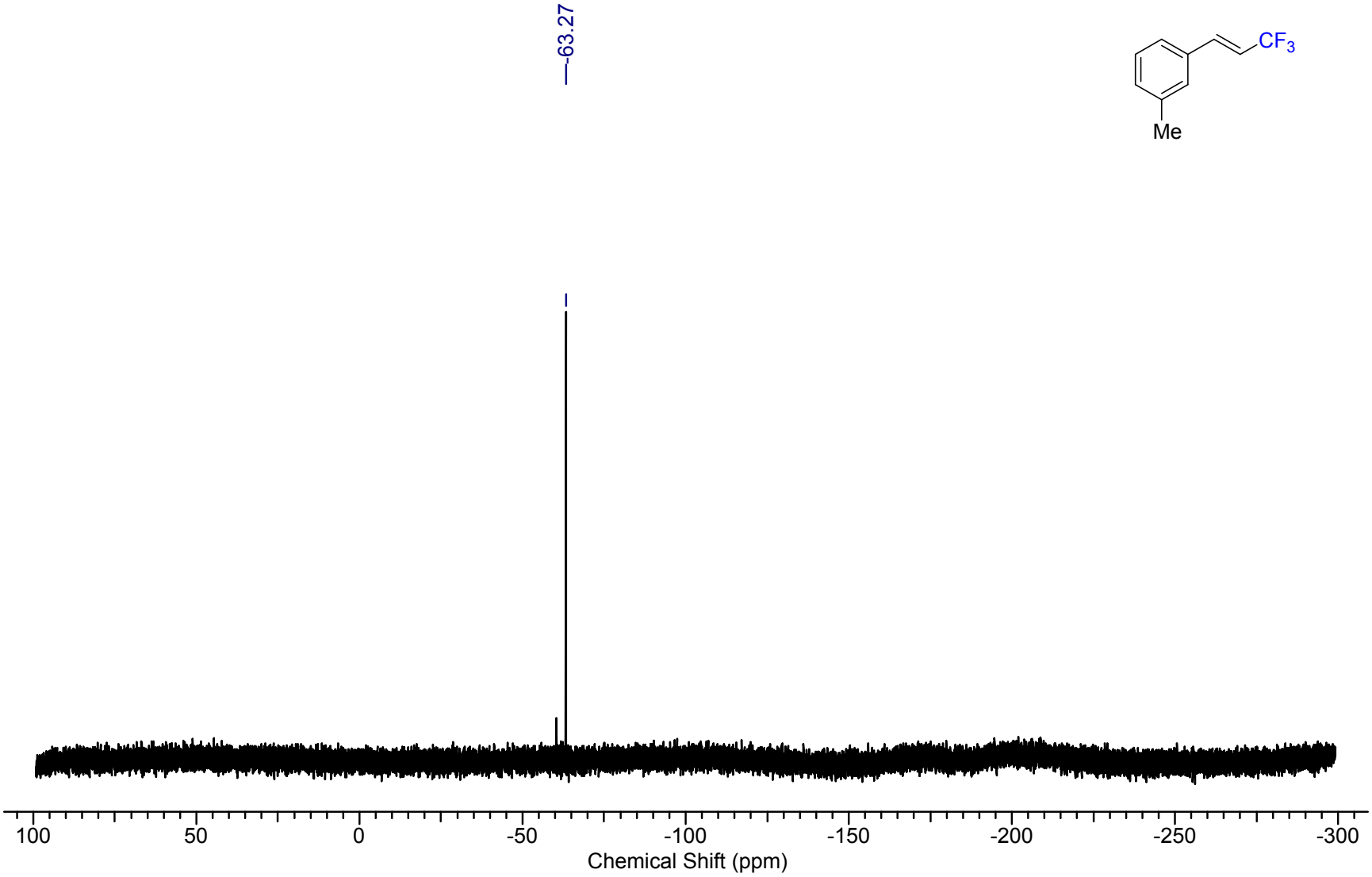


Figure S33b. ^{19}F NMR of **3i**

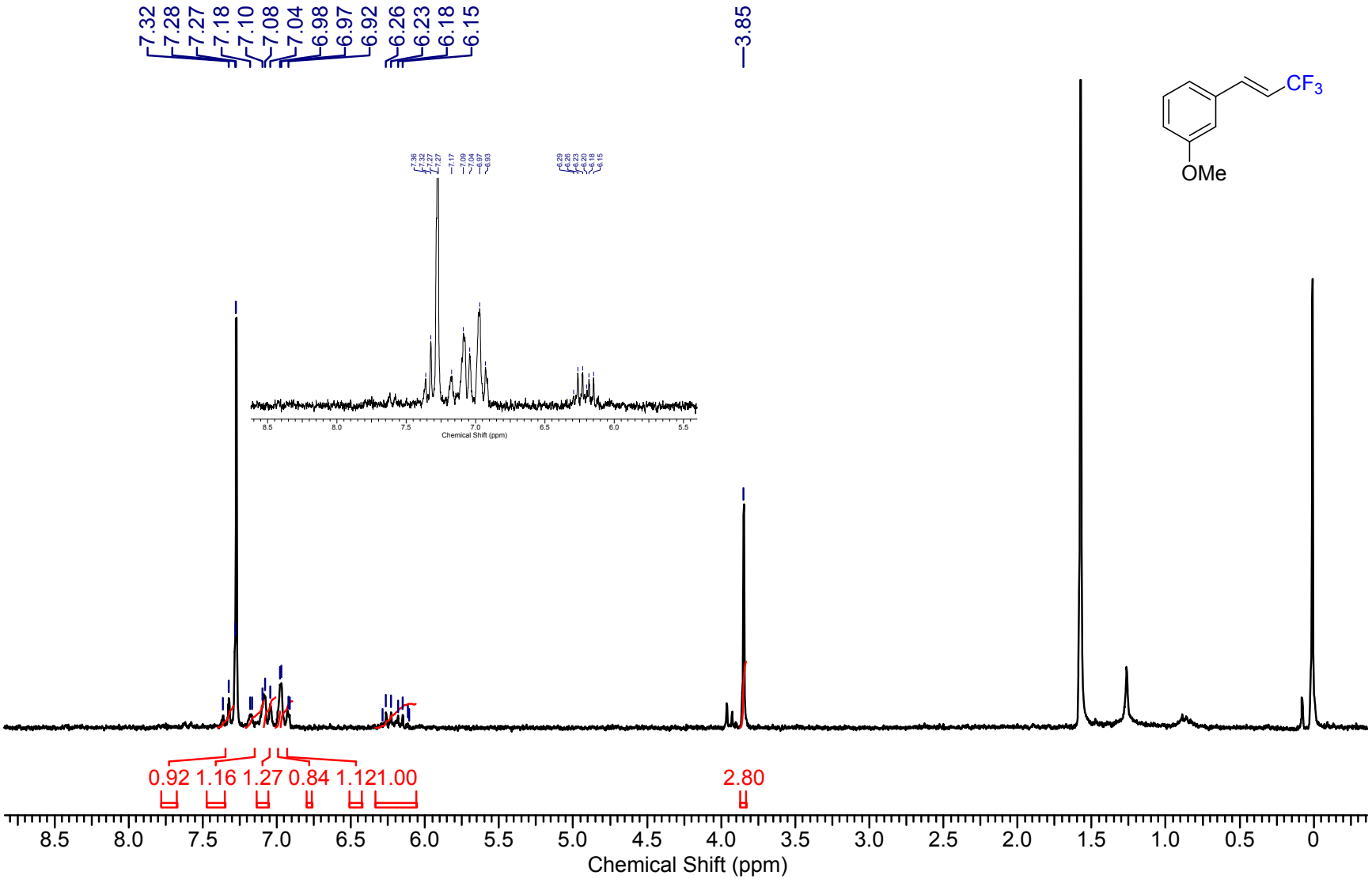


Figure S34a. ^{1}H NMR of **3j**

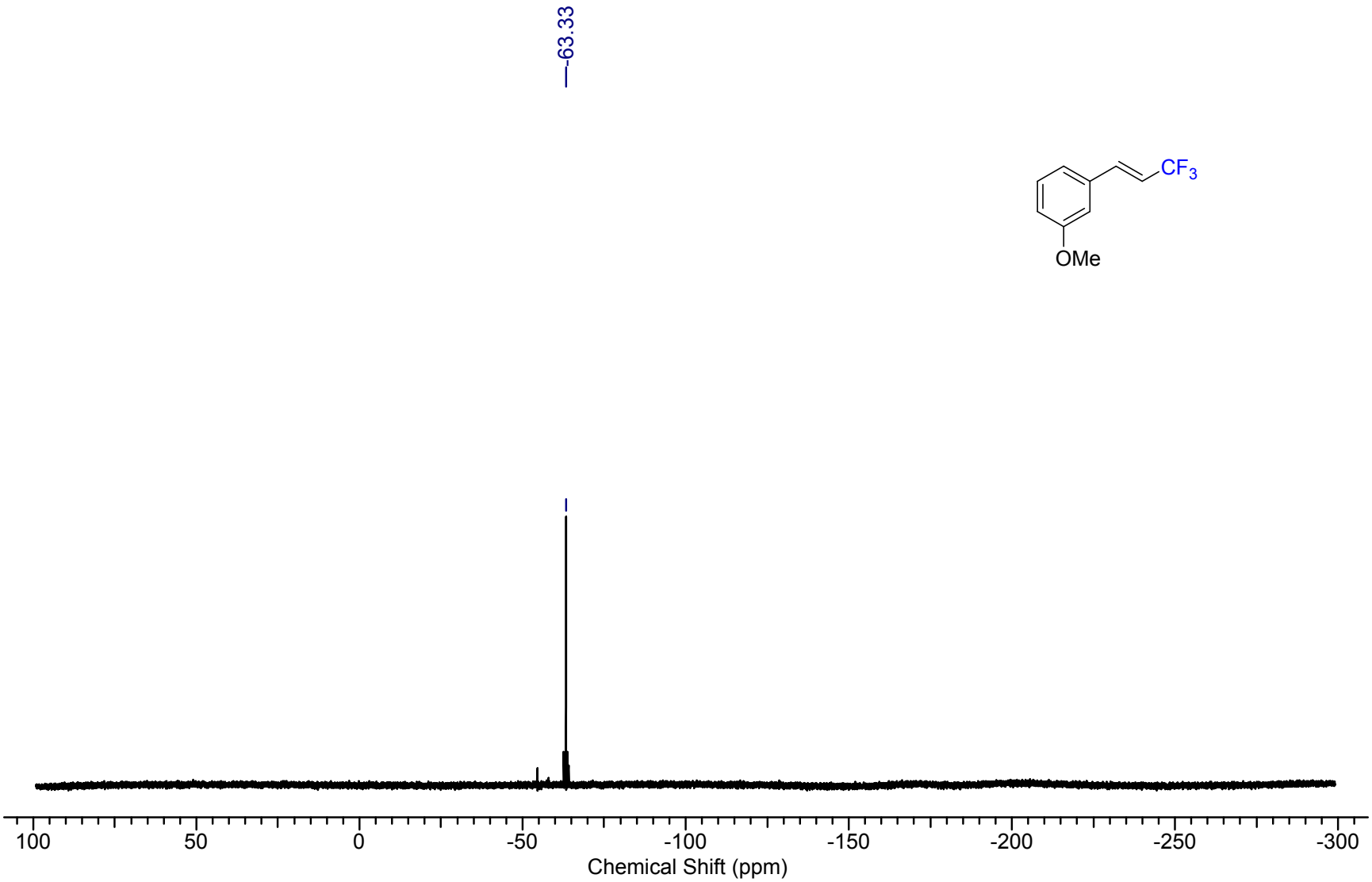


Figure S34b. ^{19}F NMR of **3j**

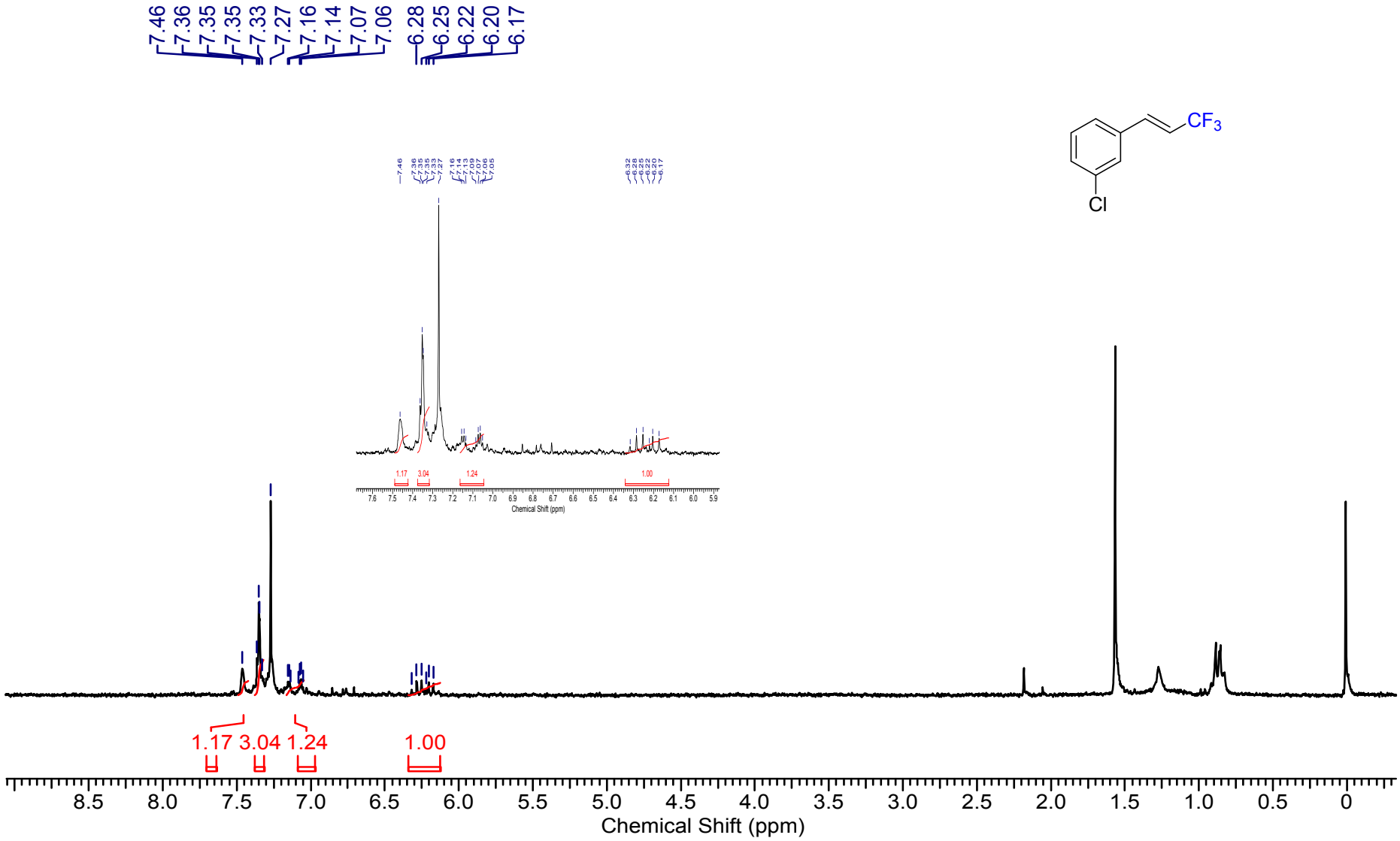


Figure S35a. ^{1}H NMR of **3k**

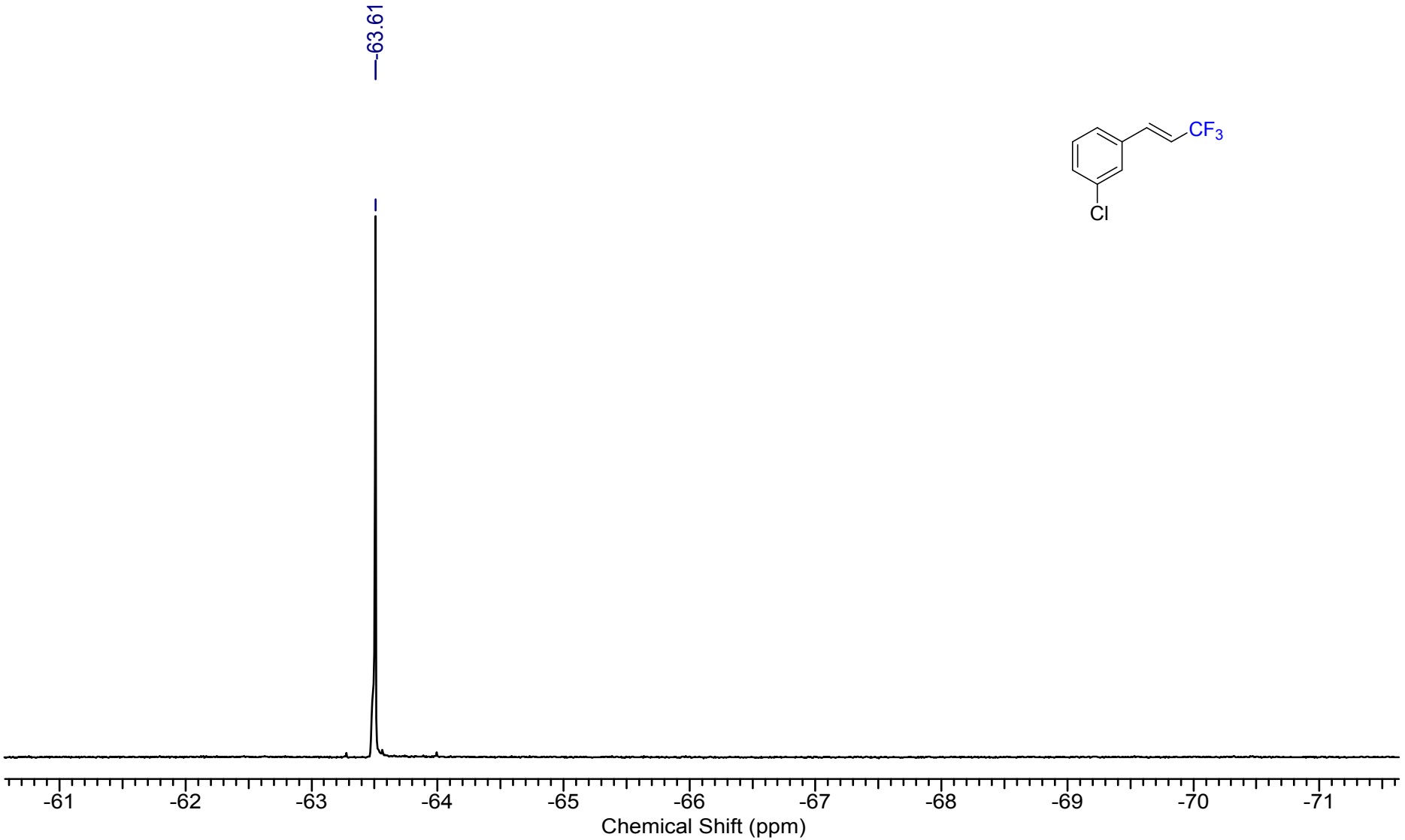


Figure S35b. ^{19}F NMR of **3k**

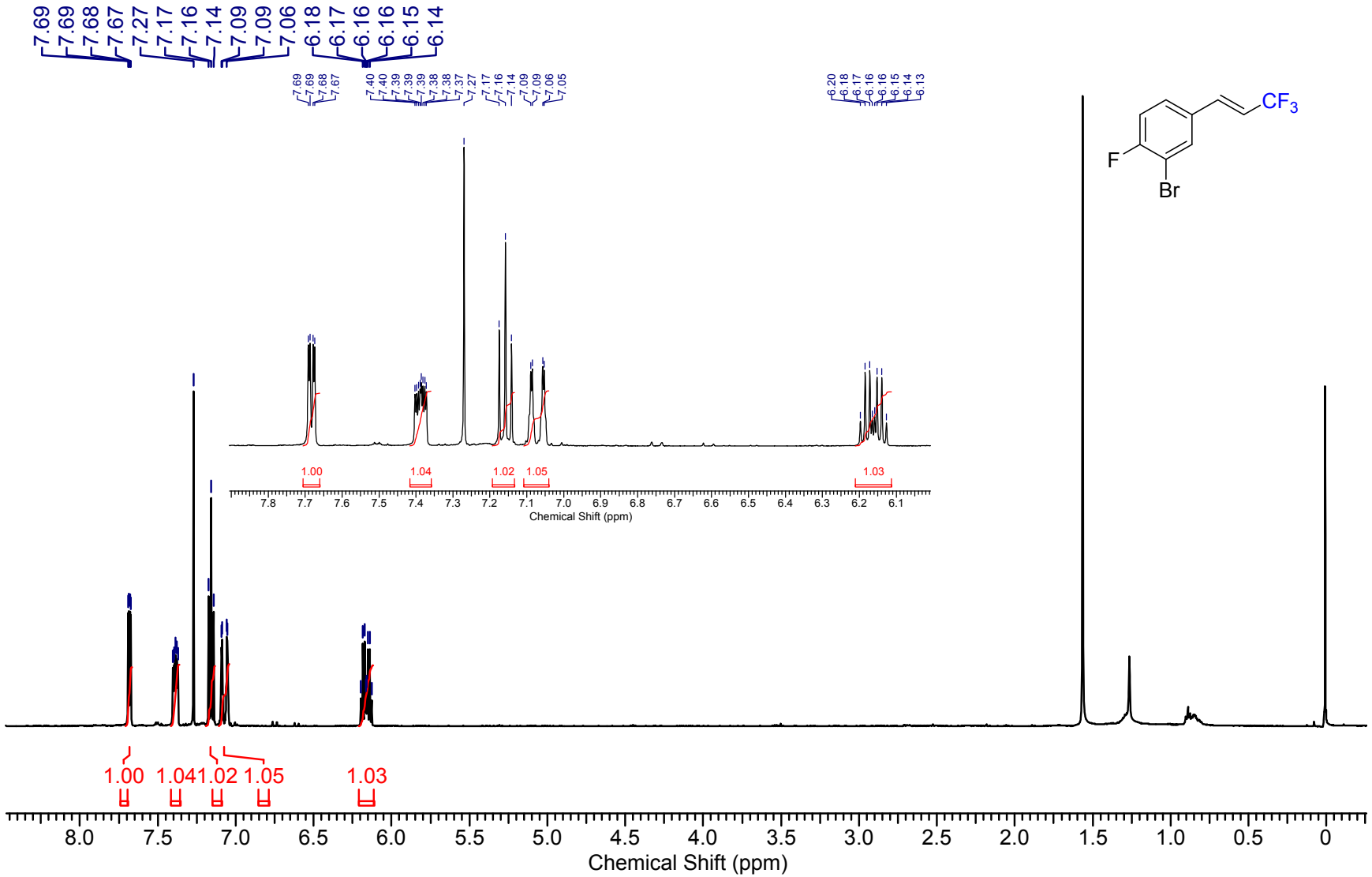


Figure S36a. ^{1}H NMR of **3l**

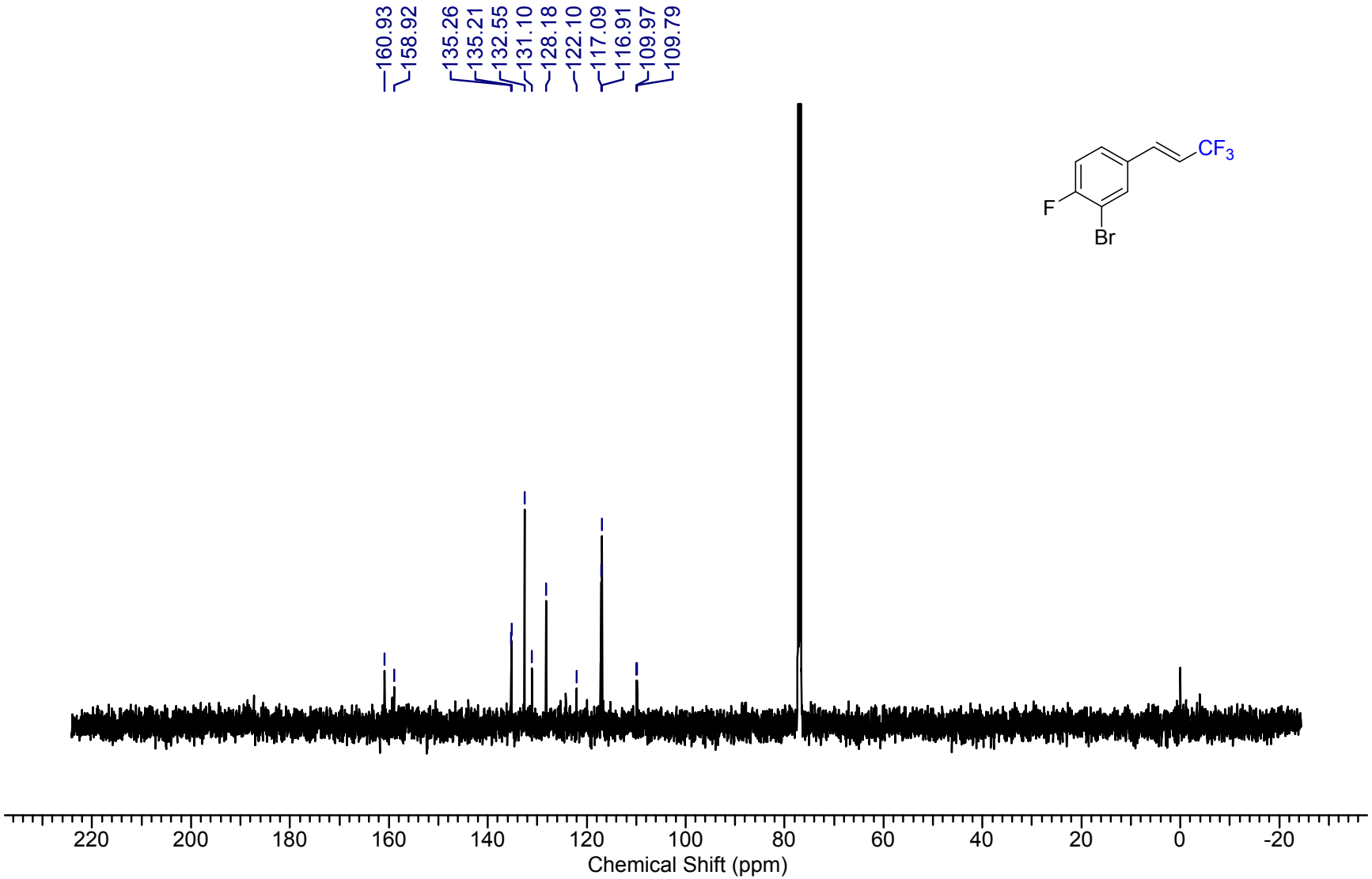


Figure S36b. ^{13}C NMR of **3l**

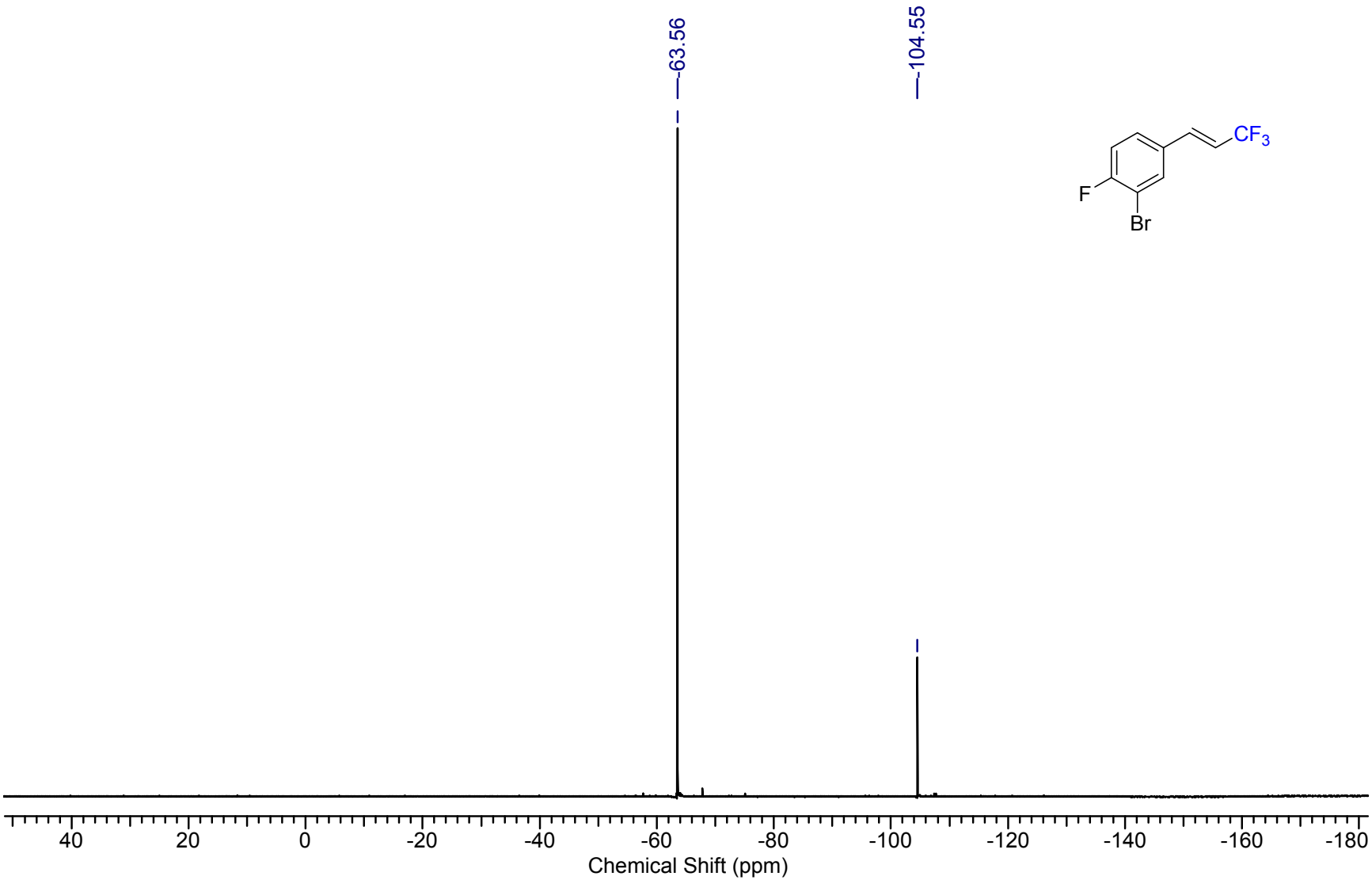


Figure S36c. ^{19}F NMR of **3l**

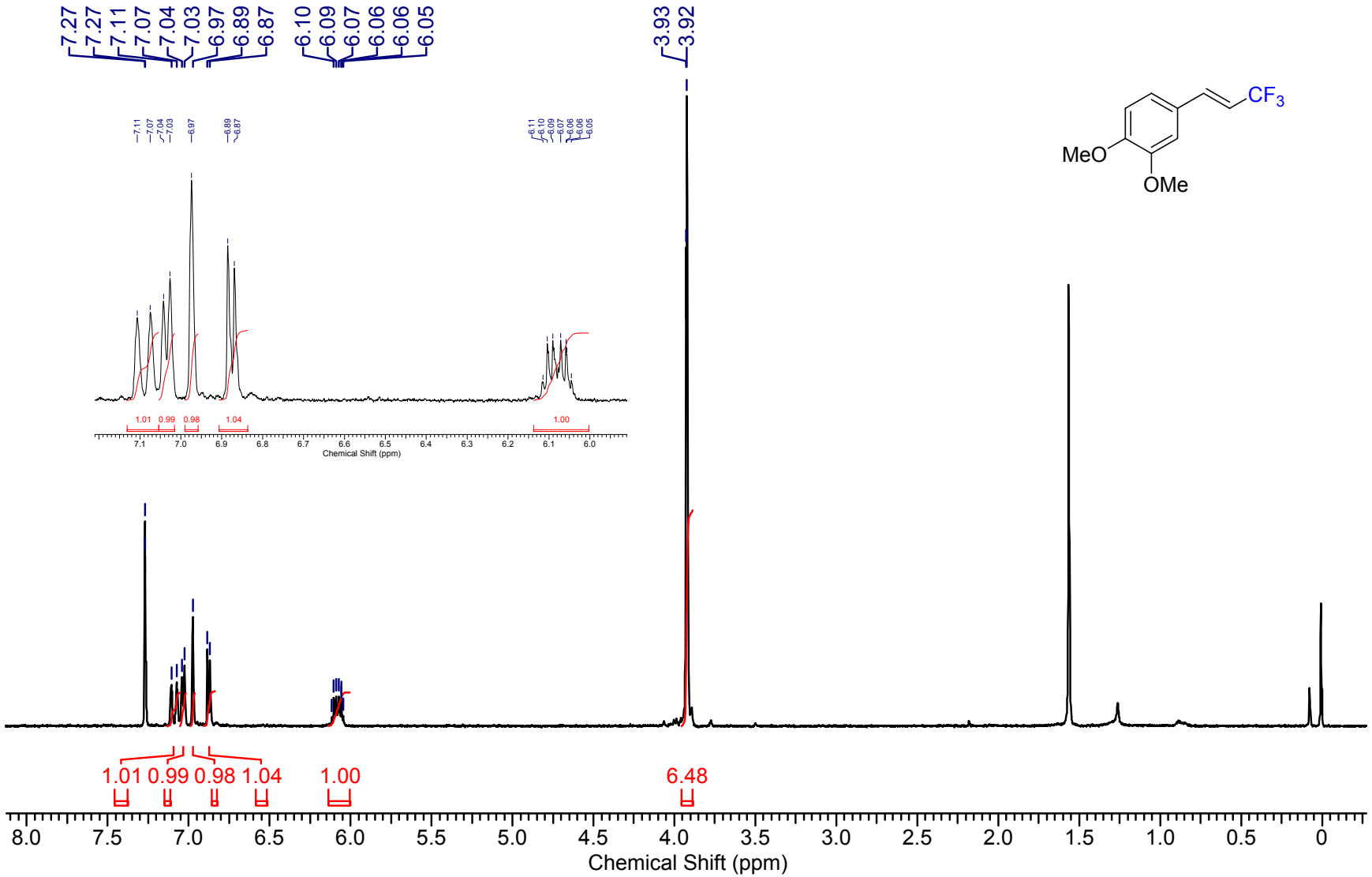


Figure S37a. ^{1}H NMR of **3m**

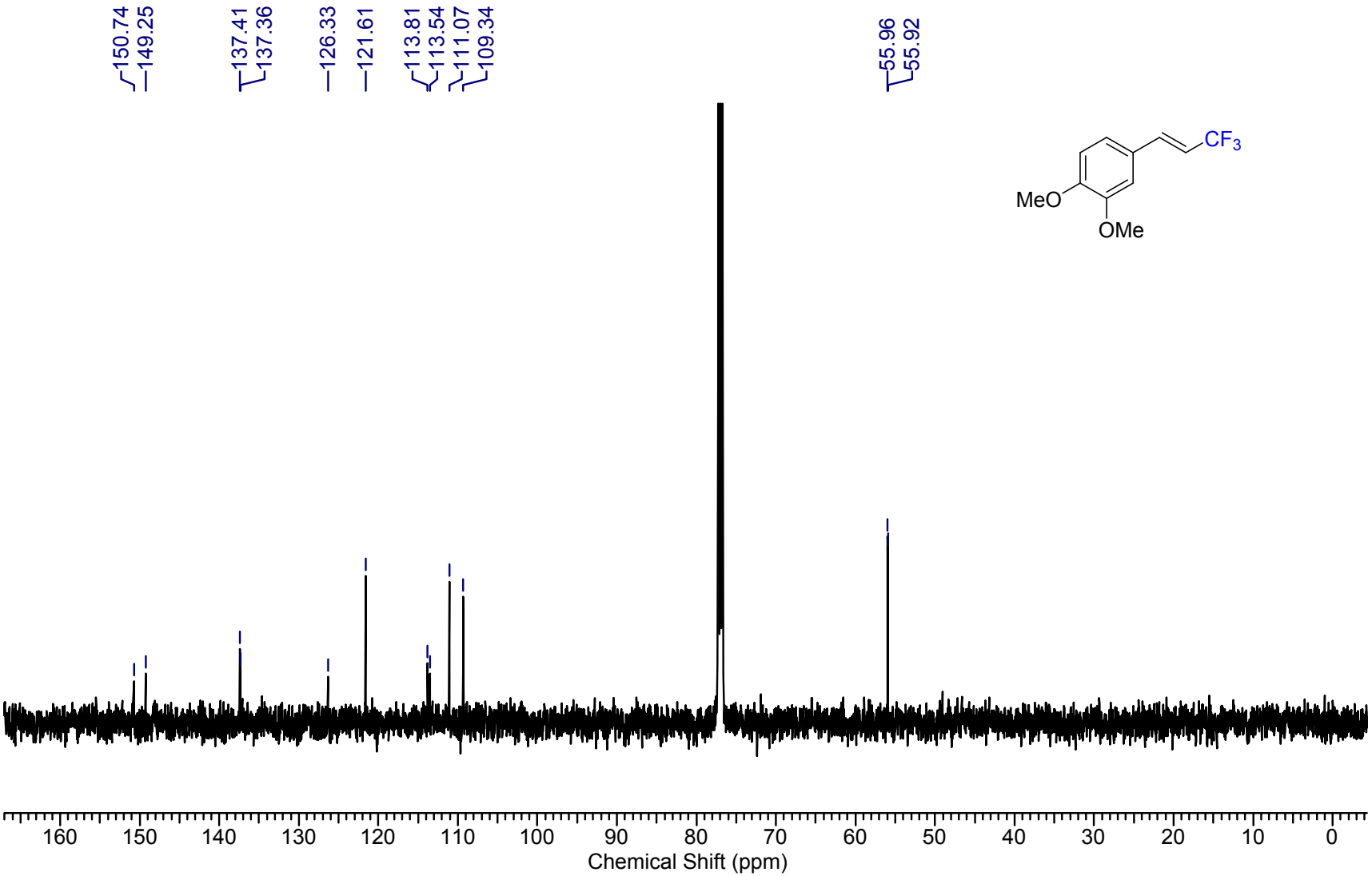


Figure S37b. ^{13}C NMR of **3m**

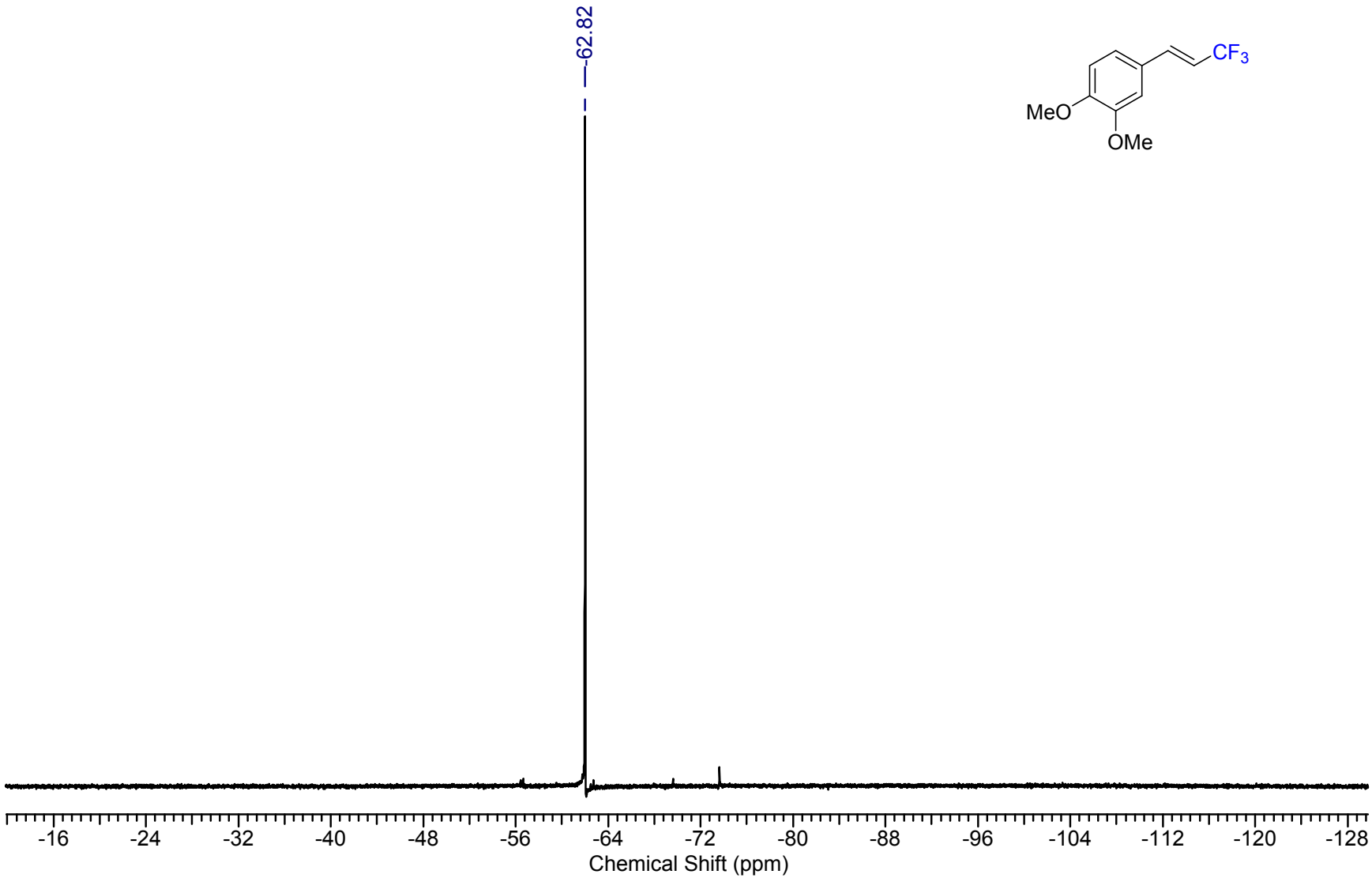


Figure S37c. ^{19}F NMR of **3m**

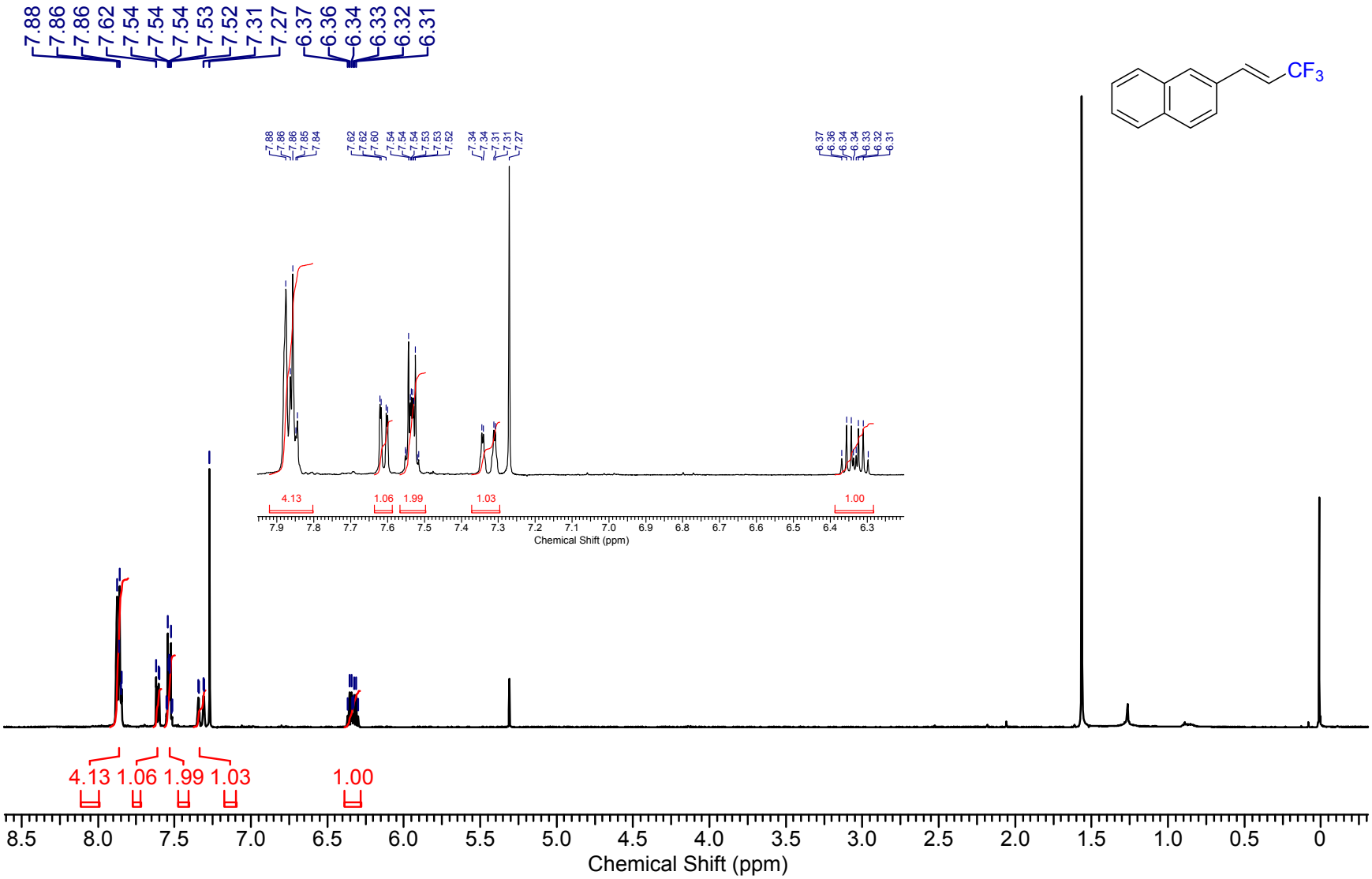


Figure S38a. ^{1}H NMR of **3n**

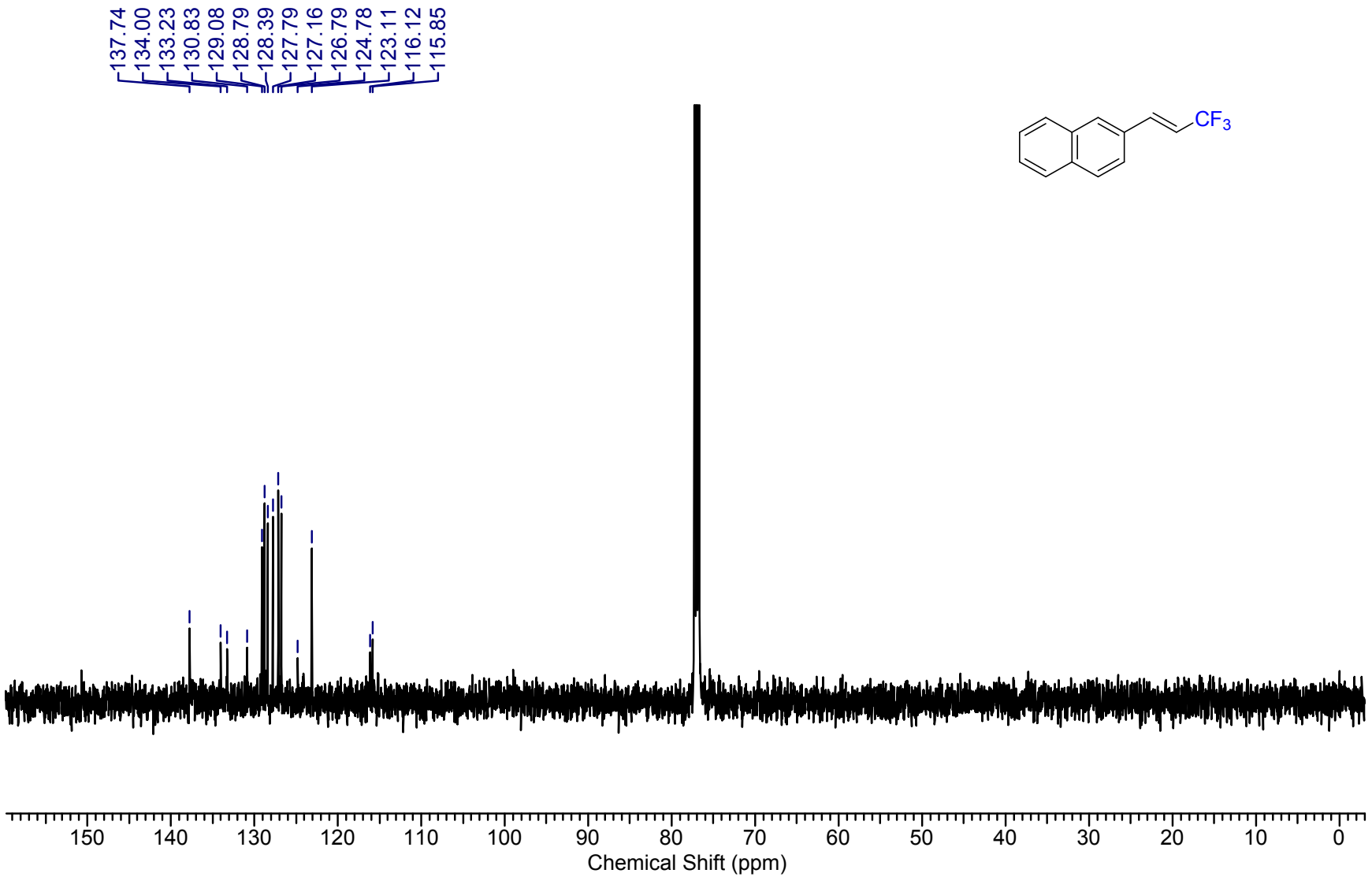


Figure S38b. ^{13}C NMR of **3n**

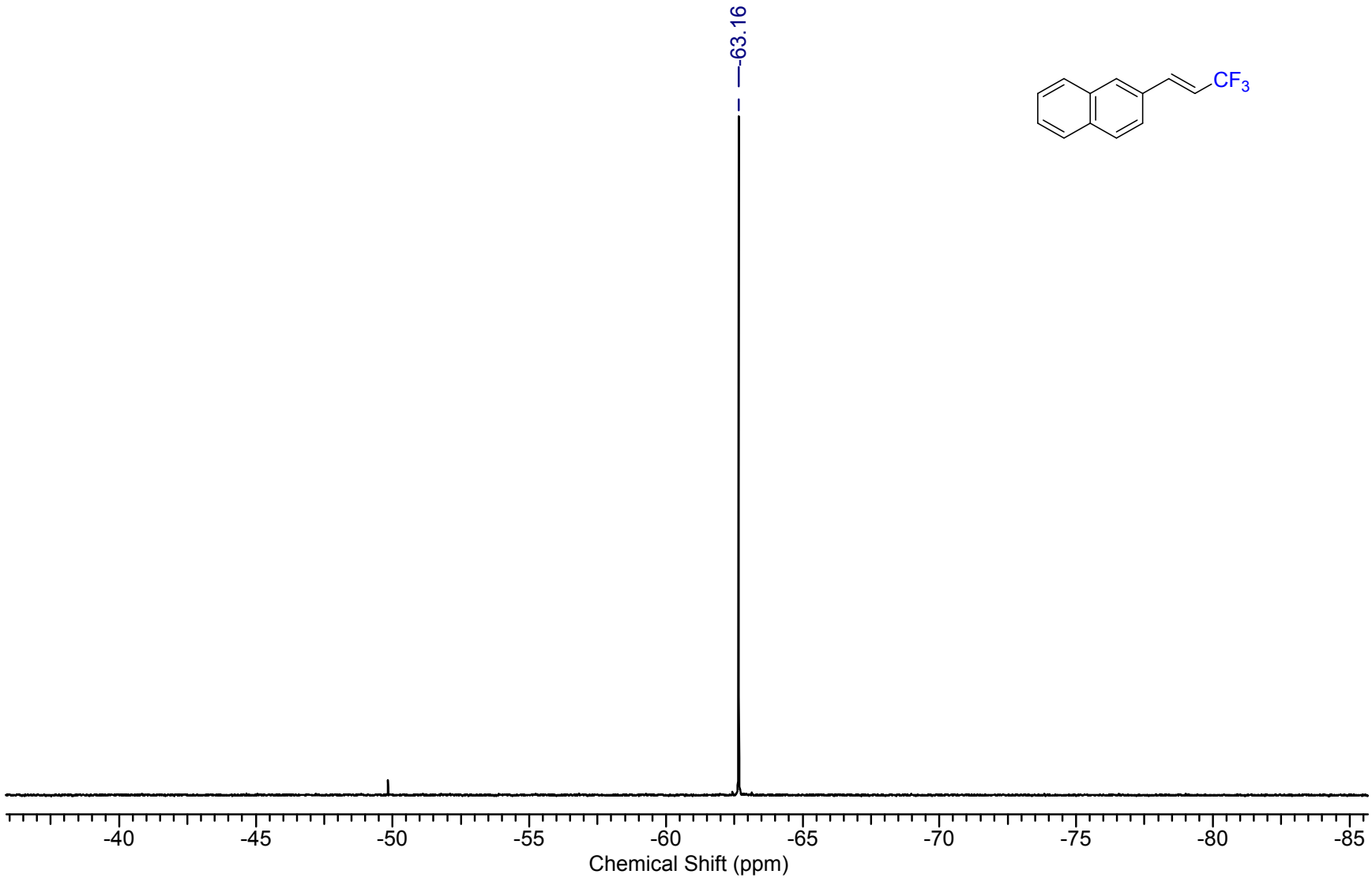


Figure S38c. ^{19}F NMR of **3n**

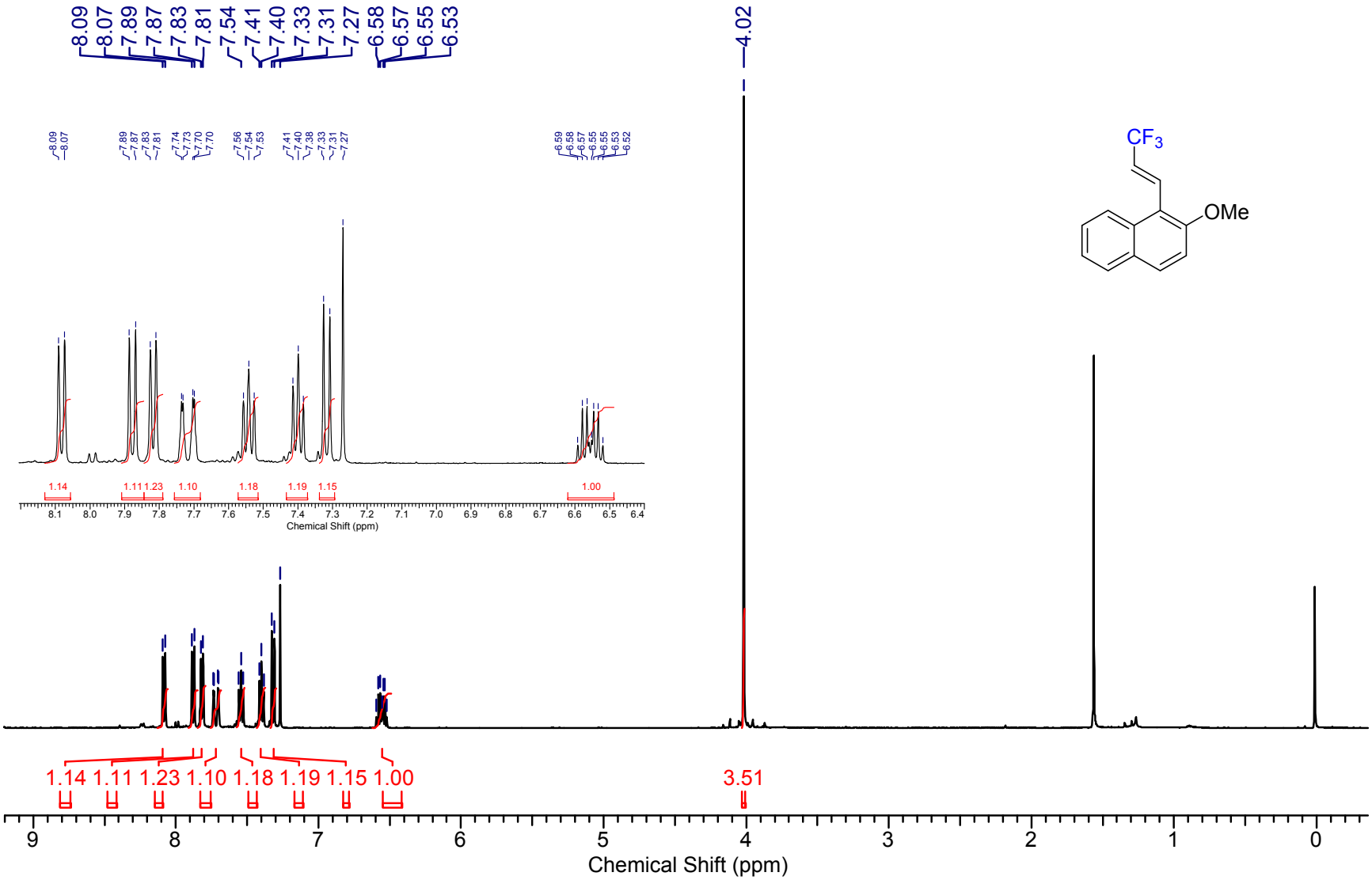


Figure S39a. ^{1}H NMR of **3o**

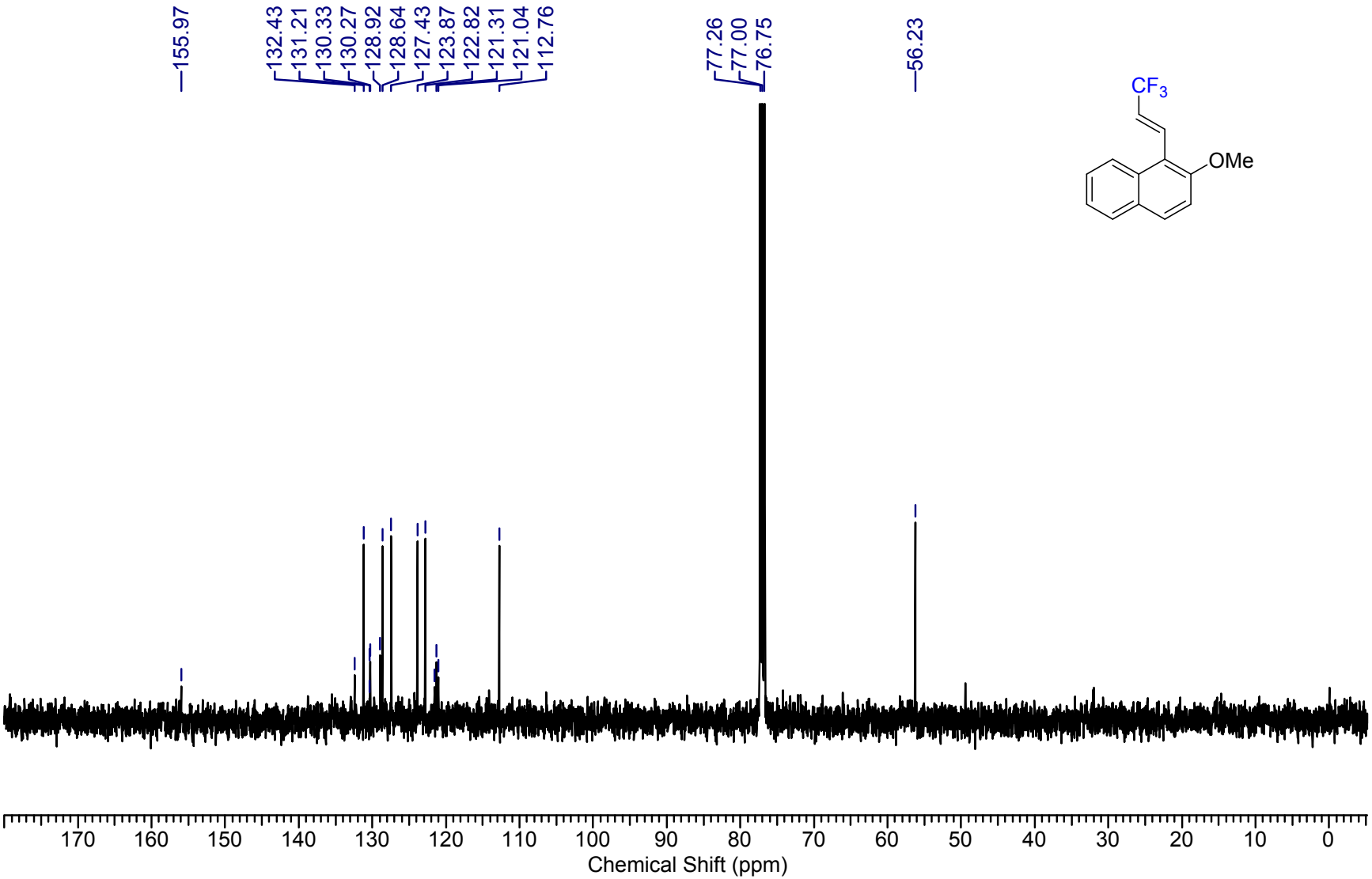


Figure S39b. ^{13}C NMR of **3o**

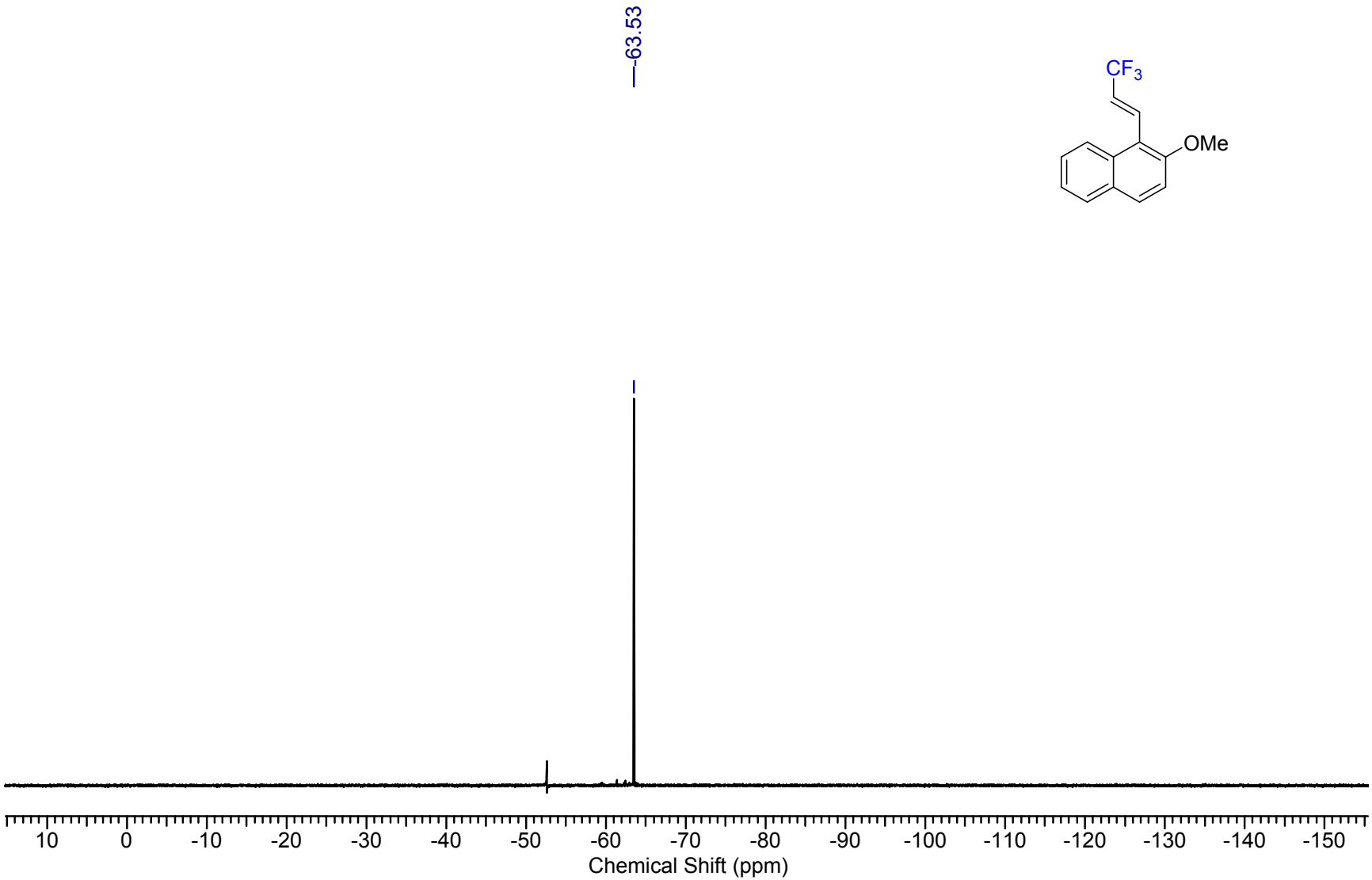


Figure S39c. ^{19}F NMR of **3o**

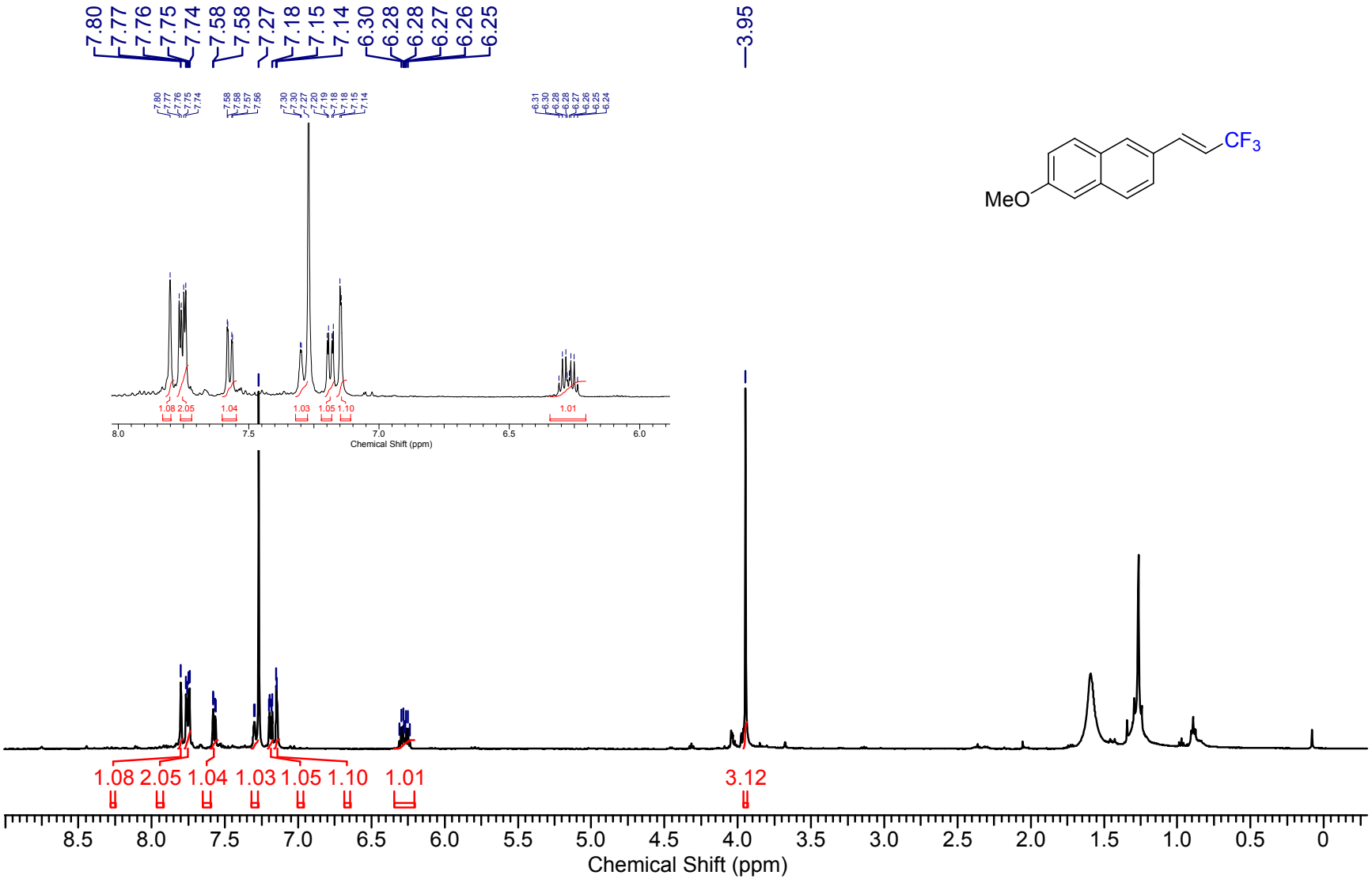


Figure S40a. ^{1}H NMR of **3p**

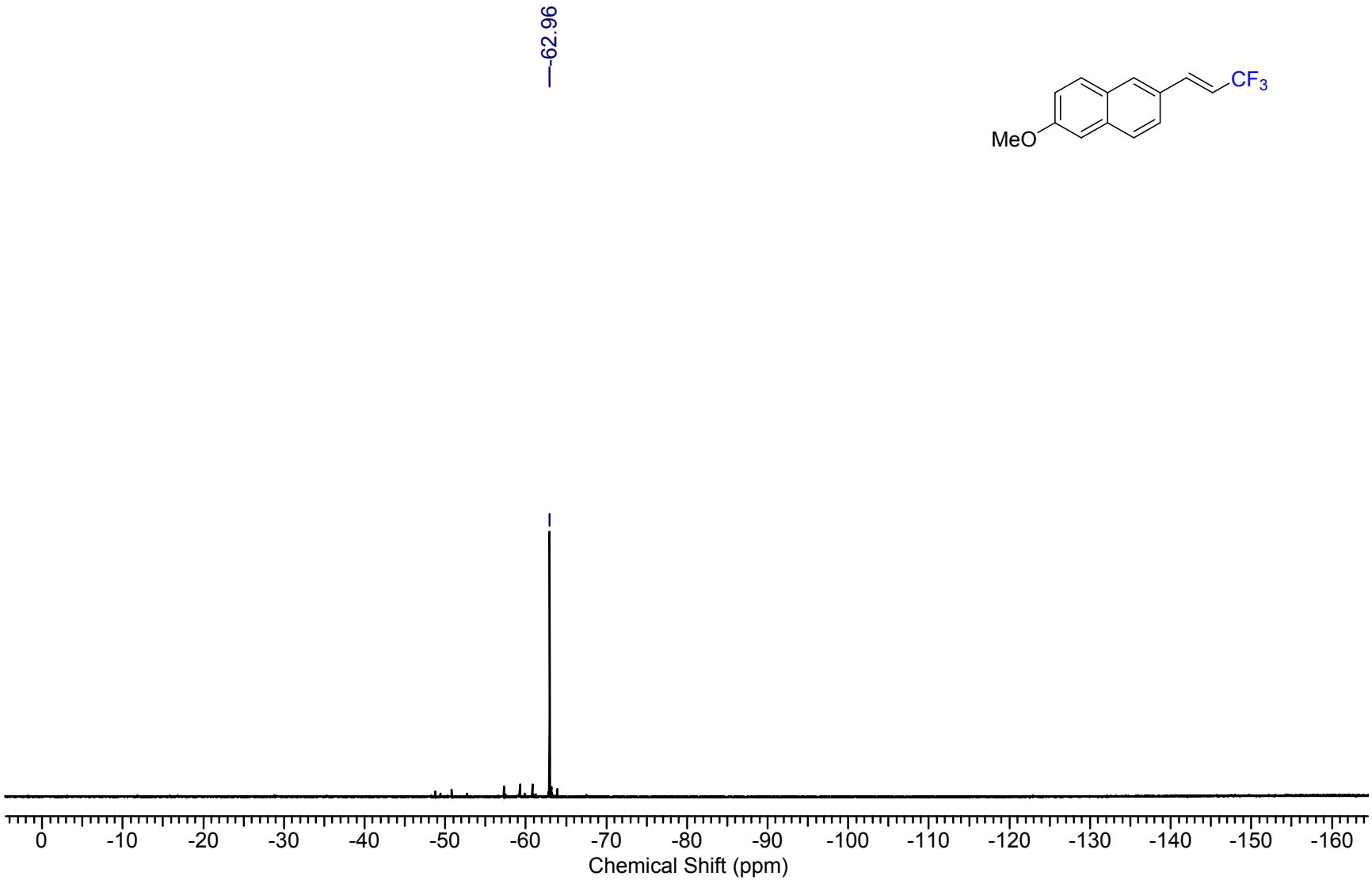


Figure S40b. ^{19}F NMR of **3p**

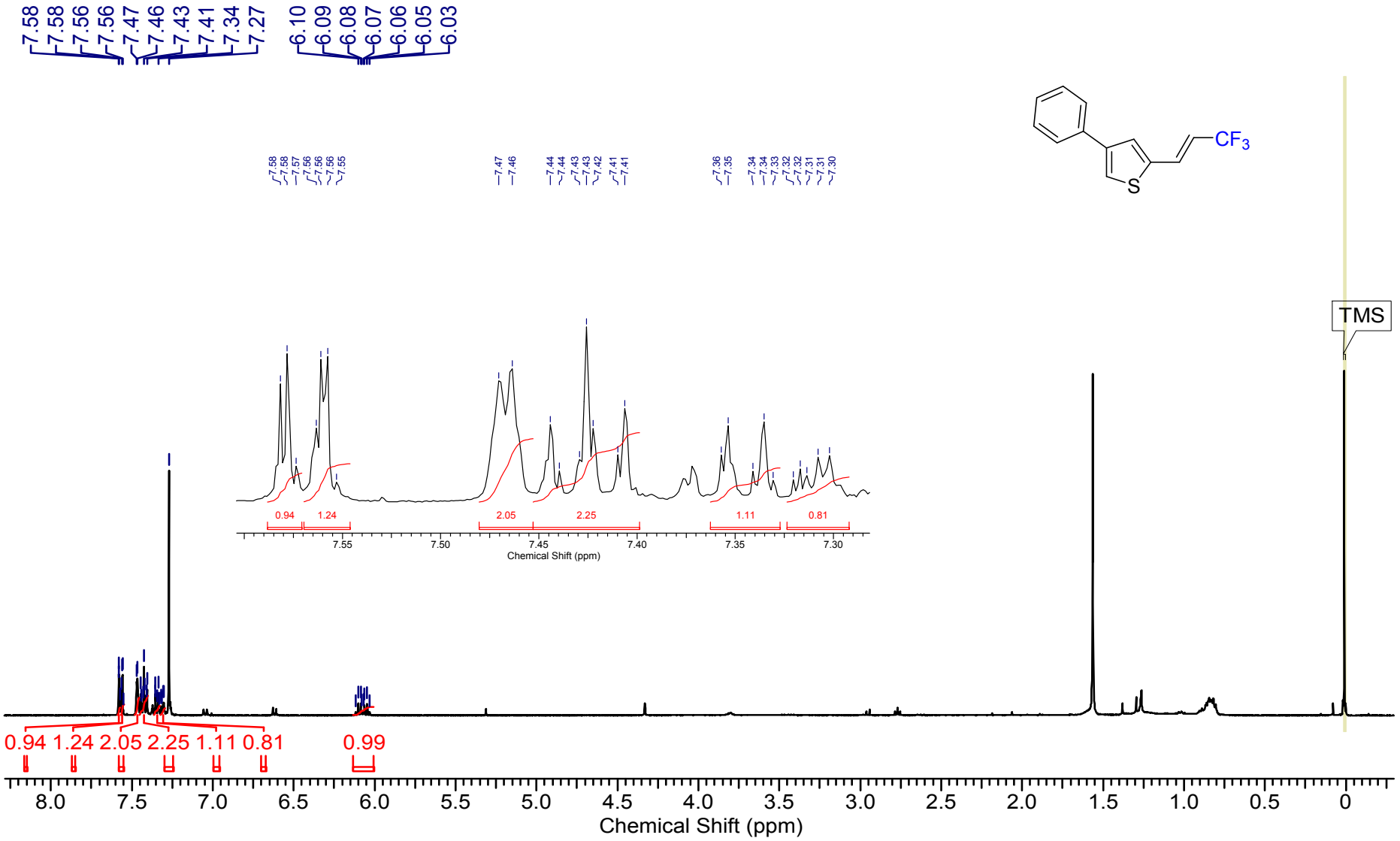


Figure S41a. ^{1}H NMR of **3r**

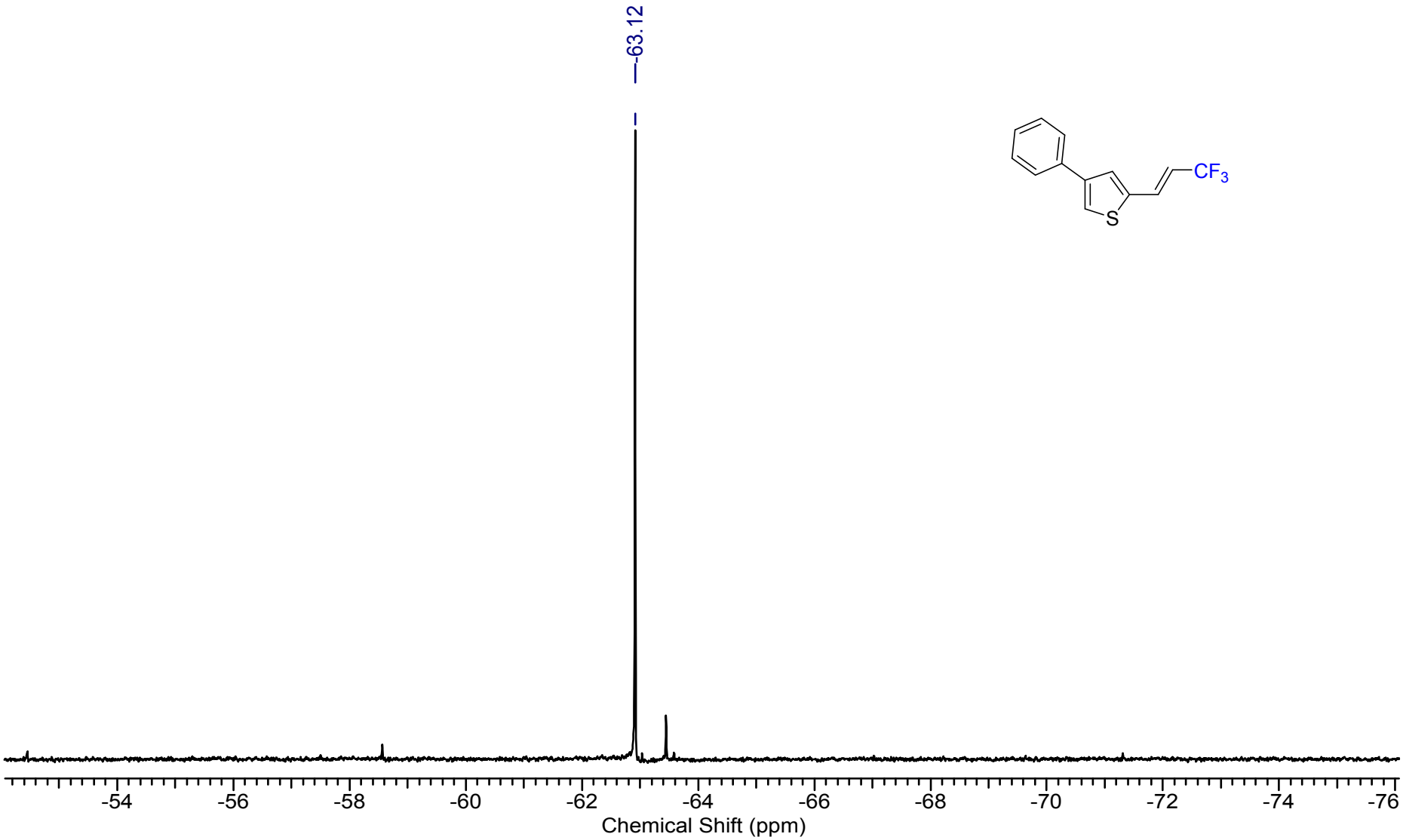


Figure S41b. ^{19}F NMR of **3r**